

Spectroscopic investigations of light-emitting thin-film materials with intrinsic or induced supramolecular chirality

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Summary

In this cumulative doctoral thesis, polymer-based film blends with large circular dichroism (CD) and large circularly polarized luminescence (CPL) are investigated using advanced steady-state and time-resolved optical spectroscopy and microscopy methods to understand their structure and dynamics upon photoexcitation. These systems include polymer thin films consisting of intrinsically chiral polyfluorene derivatives, films with induced circular dichroism consisting of achiral polyfluorene derivatives and helicene-like chiral inducers as well as an organic host material which could be used together with these chiral polymer emitters.

First, a comprehensive picture of the photoinduced dynamics of the chiral helicene-like molecule (+)-/(-)-2,2'-dimethoxy-5,5',6,6'-tetrahydro-1,1'-bidibenzo-[*c,h*]acridine and its methylene-bridged analogue (+)-/(-)-bis-5,5',6,6'-tetrahydro-dibenzo[*c,h*]acridino[1,1',2,2'-*d,f*]-[1,3]dioxepine is obtained. After photoexcitation, the depopulation of the S₁ state is fast (< 50 ps) for both systems. The quantum yield for internal conversion (IC) is about 80%, resulting in the formation of hot ground state molecules (S₀*). Triplet formation via intersystem crossing (ISC) is responsible for the remaining 20%. The bridged system exhibits a reduced Stokes shift and a slightly slower S₁ decay. This effect is likely due to its more rigid structure. A characteristic excited-state absorption band at 575 nm is assigned to the T₁ state which decays on a time scale of more than 500 ps.

Very efficient chiral induction by these two additives is found in their blends with achiral poly-[(9,9-di-*n*-octylfluorenyl-2,7-diyl)-*alt*-(benzo-[2,1,3]thiadiazol-4,8-diyl)] (F8BT), reaching CD signals with peak signals of up to 9000 mdeg. The less rigid structure of the unbridged derivative might be responsible for the significantly better chiral induction, possibly because of better adaptation to the F8BT scaffold during the formation of the supramolecular structure. Using a newly developed setup for the detection of transient circularly polarized luminescence (TrCPL) with a time resolution of 28 ps, a static mechanism for the generation of the CPL is confirmed. When studying enantiomer mixtures of a given chiral additive as inducing agent for F8BT, it is found that the "sergeant and soldiers" concept and "majority rules" do not apply, as demonstrated by CD and CPL microscopy images of the different thin film blends.

In addition, cholesteric thin films of the intrinsically chiral polymer {9,9-bis[(3*S*)-3,7-dimethyloctyl]fluorenyl-2,7-diyl}-*alt*-benzo[2,1,3]thiadiazol-4,8-diyl} (c-PFBT) are produced which also reach large CD values of up to 10000 mdeg. These are characterized

in the UV–Vis range upon photoexcitation using a newly developed setup for broadband transient circular dichroism (TrCD) spectroscopy. The ultrafast chiral response of the c-PFBT copolymer thin film was of supramolecular origin. TrCD signals only monitor the recovery of the ground state S_0 without contributions from excited-state CD signals, which makes their interpretation easier than for the transient absorption (TA) response. The relaxation processes are assigned to mainly diffusive S_1 – S_1 singlet–singlet annihilation (SSA) and a minor channel for Förster resonance energy transfer (FRET). In addition, charge pair formation is observed with a total quantum yield of 15%.

The fluorescing polymer films may be applied as materials for OLEDs which emit circularly polarized light, so-called CP-OLEDs. Such devices require host materials for the transfer of electrical charges to the emitter. Understanding the photophysical processes in such a host material, namely 1,3-bis(*N*-carbazolyl)benzene (mCP), is therefore important. Thus, mCP is investigated in tetrahydrofuran (THF) solution and in poly(methyl methacrylate) (PMMA) film blends at different dopant concentrations. Time-correlated single photon counting (TCSPC) provides a monoexponential decay with lifetimes in the range of 6–7 ns for “isolated” mCP in solution and in the mCP:PMMA thin film with a mass ratio of 2:98. With increasing dopant concentration in the mCP:PMMA blends and also for the neat mCP thin film, the mCP emission is strongly quenched. Neat mCP films and films with high mCP content show three different bands, which are assigned to monomer, aggregate and excimer emission. At higher mCP concentration, an S_1 – S_0 homo-FRET mechanism becomes operative. This way, the excitation energy is transferred via other mCP molecules to an energetically lower trap site, which can be either an mCP aggregate or excimer. For the neat mCP thin film, the average relaxation lifetimes for the monomer, aggregate and excimer bands are 0.92, 3.84 and 7.22 ns respectively. Complementary transient absorption measurements show that at high initial exciton number densities, triplet formation, which has a quantum yield of 20% in THF, is outperformed by SSA.

Zusammenfassung

In dieser kumulativen Doktorarbeit werden Polymerfilme mit starkem Zirkulardichroismus (CD) und starker zirkular polarisierter Lumineszenz (CPL) mit Hilfe von fortschrittlichen stationären und zeitaufgelösten optischen Spektroskopie- und Mikroskopie-Verfahren untersucht, um ihre Struktur und Dynamik nach Photoanregung zu verstehen. Die untersuchten Systeme umfassen Polymerdünnschichten aus intrinsisch chiralen Polyfluoren-Derivaten, Filme mit induziertem Zirkulardichroismus basierend auf achiralen Polyfluoren-Derivaten und helicenartigen chiralen Additiven sowie ein organisches Wirtsmaterial, das zusammen mit diesen chiralen Polymer-Emittern verwendet werden kann.

Zunächst wird ein umfassendes Bild der photoinduzierten Dynamik des chiralen helicenartigen Moleküls (+)-/(-)-2,2'-Dimethoxy-5,5',6,6'-tetrahydro-1,1'-bidibenzo-[*c,h*]acridin und seines methylenverbrückten Analogons (+)-/(-)-Bis-5,5',6,6'-tetrahydro-dibenzo[*c,h*]acridino[1,1',2,2'-*d,f*]-[1,3]dioxepin erhalten. Nach der Photoanregung erfolgt die Entvölkerung des S_1 -Zustands in beiden Systemen schnell (< 50 ps). Die Quantenausbeute für die innere Konversion (IC) beträgt etwa 80%, was zur Bildung von Molekülen im angeregten Grundzustand (S_0^*) führt. Die Triplettbildung über Intersystem Crossing (ISC) ist für die verbleibenden 20% verantwortlich. Das überbrückte chirale Additiv zeigt eine geringere Stokes-Verschiebung und einen etwas langsameren S_1 -Abklingprozess. Dieser Effekt ist wahrscheinlich auf die starrere Struktur des verbrückten Derivats zurückzuführen. Eine charakteristische Absorptionsbande im angeregten Zustand bei 575 nm wird dem T_1 -Zustand zugeordnet. Dieser T_1 -Zustand zeigt einen Abfall auf Zeitskalen von mehr als 500 ps.

Eine sehr effiziente chirale Induktion durch diese beiden Additive wird in Dünnschichten von Mischungen mit achiralem Poly-[(9,9-di-*n*-oktylfluorenyl-2,7-diyl)-*alt*-(benzo-[2,1,3]thiadiazol-4,8-diyl)] (F8BT) beobachtet. Hierbei werden CD-Signale mit Spitzenwerten von bis zu 9000 mdeg erreicht. Die weniger starre Struktur des nichtverbrückten Derivats könnte für die deutlich bessere chirale Induktion verantwortlich sein, möglicherweise aufgrund einer besseren Anpassung an die F8BT-Umgebung während der Bildung der supramolekularen Struktur. Mithilfe eines neu entwickelten Aufbaus zur Detektion transienter zirkular polarisierter Lumineszenz (TrCPL) mit einer Zeitauflösung von 28 ps wird ein statischer Mechanismus für die CPL-Erzeugung bestätigt. Bei der Untersuchung von Enantiomergemischen eines bestimmten chiralen Additivs für F8BT wird festgestellt, dass das „Sergeant and

Soldiers“-Konzept und „Majority Rules“ nicht anwendbar sind, wie die CD- und CPL-Mikroskopie-Bilder der verschiedenen Dünnschichten zeigen.

Außerdem werden cholesterische Dünnschichten des intrinsisch chiralen Polymers {9,9-Bis[(3*S*)-3,7-dimethyloktyl]fluorenyl-2,7-diyl}-*alt*-benzo[2,1,3]thiadiazol-4,8-diyl} (c-PFBT) hergestellt, die ebenfalls hohe CD-Werte von bis zu 10000 mdeg erreichen. Diese werden im UV–Vis-Bereich nach Photoanregung mittels eines neu entwickelten Aufbaus für die breitbandige transiente Zirkulardichroismus-Spektroskopie (TrCD) charakterisiert. Die ultraschnelle chirale Antwort der c-PFBT-Copolymer-Dünnschicht ist supramolekularen Ursprungs. Die TrCD-Signale erfassen nur die Relaxation zurück in den Grundzustand S_0 ohne Beiträge von CD-Signalen aus dem angeregten Zustände, was die Interpretation der Signale im Vergleich zu transienten Absorptionsmessungen (TA) vereinfacht. Die Relaxationsprozesse werden hauptsächlich der diffusiven S_1 – S_1 -Singlet–Singlet-Annihilierung (SSA) und einem kleineren Kanal für den Förster-Resonanzenergietransfer (FRET) zugeschrieben. Außerdem wird Ladungspaarbildung mit einer Gesamtquantenausbeute von 15% beobachtet.

Fluoreszierende Polymerfilme können als Materialien für OLEDs eingesetzt werden, die zirkular polarisiertes Licht emittieren (sogenannte CP-OLEDs). Solche Bauelemente benötigen Wirtsmaterialien für den Ladungstransfer zum Emitter. Daher ist das Verständnis der photophysikalischen Prozesse in solchen Wirtsmaterialien, wie z.B. 1,3-Bis(*N*-carbazolyl)benzol (mCP), wichtig. mCP wird in Tetrahydrofuran (THF)-Lösungen und in Polymethylmethacrylat (PMMA)-Filmmischungen mit unterschiedlichen Dotierungskonzentrationen untersucht. Mittels zeitkorrelierter Einzelphotonenzählung (TCSPC) wird ein monoexponentieller Abfall mit Lebensdauern im Bereich von 6 bis 7 ns für „isoliertes“ mCP in Lösung und in der mCP:PMMA-Dünnschicht mit einem Massenverhältnis von 2:98 ermittelt. Mit steigendem Dotierungsanteil in den mCP:PMMA-Mischungen sowie in der reinen mCP-Dünnschicht ist die mCP-Emission dagegen viel schwächer. Reine mCP-Filme und Filme mit hohem mCP-Anteil zeigen drei unterschiedliche Banden, die Monomer-, Aggregat- und Excimer-Emissionen zugeordnet werden. Bei höherer mCP-Konzentration tritt ein S_1 – S_0 -Homo-FRET-Mechanismus auf. Dabei wird die Anregungsenergie letztendlich auf ein energetisch niedrigeres mCP-Aggregat oder Excimer übertragen. Ergänzende transiente Absorptionsmessungen zeigen, dass bei höheren Anregungsdichten die Triplettbildung, die in THF eine Quantenausbeute von 20% besitzt, durch den SSA-Prozess unterdrückt wird.

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1. Introduction

1.1 Chiral materials for organic light-emitting diodes (OLEDs)

Organic light-emitting diodes are one of the cornerstones of modern optoelectronic technology, enabling the development of thin and flexible electroluminescent displays. The emitting layers of these devices are based on organic semiconductor thin films and are nowadays found everywhere in our daily life, in smartphones, tablets or commercial presentation screens, replacing traditional backlit liquid-crystal displays (LCDs).^[1–3] In OLEDs, the emitting layer is only one of many other organic layers, including for instance transport and blocking layers for holes and electrons. Additional filter layers are commonly used to remove glare originating from ambient light. However, these antiglare layers reduce the intensity emitted from the OLED surface by approximately 50%. Therefore, if OLEDs emitting circularly polarized light (so-called CP-OLEDs) could be used instead, light of already the correct handedness would be transmitted through the antiglare filter, resulting in a much better energy efficiency of the device.^[4] Moreover, such materials, emitting circularly polarized light, are also promising for other optoelectronic applications, such as optical data storage,^[5–9] liquid-crystal lasers,^[10] photodetectors for circularly polarized light^[11] and polarization-sensitive markers for safety applications.^[12]

Chiral materials can emit circularly polarized luminescence (CPL), which is quantified as the difference in the emitted intensities for left-circularly polarized and right-circularly polarized light, I_{LCP} and I_{RCP} , respectively:^[9]

$$\text{CPL} = I_{\text{LCP}} - I_{\text{RCP}} \quad (1.1)$$

Normalization to the photoluminescence intensity for randomly polarized light I_{random} provides the dissymmetry factor g_{lum} , with a limiting value of -2 and $+2$:^[9]

$$g_{\text{lum}} = \frac{\text{CPL}}{I_{\text{random}}} = \frac{I_{\text{LCP}} - I_{\text{RCP}}}{0.5 \cdot (I_{\text{LCP}} + I_{\text{RCP}})} \quad (1.2)$$

At the same time, such chiral materials exhibit circular dichroism (CD), which is the difference in optical density (OD) for LCP and RCP light:^[9]

$$\text{CD} = \text{OD}_{\text{LCP}} - \text{OD}_{\text{RCP}} = \log_{10} \left(\frac{I_{\text{ref}}}{I_{\text{sample}}} \right)_{\text{LCP}} - \log_{10} \left(\frac{I_{\text{ref}}}{I_{\text{sample}}} \right)_{\text{RCP}} \quad (1.3)$$

Normalization to the optical density for randomly polarized light OD_{random} provides the dissymmetry factor g_{abs} , with limiting values of -2 and $+2$:^[9]

$$g_{\text{abs}} = \frac{CD}{OD_{\text{random}}} = \frac{OD_{\text{LCP}} - OD_{\text{RCP}}}{0.5 \cdot (OD_{\text{LCP}} + OD_{\text{RCP}})} \quad (1.4)$$

Isolated chiral molecules in general show only very weak CD activity (< 150 mdeg or less, with 32.982 mdeg corresponding to 1 mOD) and g_{abs} in the range of 10^{-3} – 10^{-4} also accompanied by a very weak CPL signal ($g_{\text{lum}} \approx 10^{-3}$ – 10^{-4}). Such systems are not of interest for future applications in CP-OLEDs and related systems. Therefore, in this thesis the focus lies on chiral systems with an exceptionally high CD (exceeding 10000 mdeg) and also CPL response, with dissymmetry factors of 0.1 and above. To achieve this, polymer structures with supramolecular chirality are required which are introduced in the following. These can be either composed of intrinsically chiral polymers (Chapter 1.2)^[13] or achiral polymers in which supramolecular chirality is induced by chiral additives (Chapter 1.3). For the latter case, in this thesis we explore a new class of helicene-like additives, which has been developed by the Guy group at the University of Lyon^[14] and are introduced together with other chiral additives in Chapter 1.4. Lastly, the application of such compounds in CP-OLEDs requires the combination with appropriate charge transport layers, and Chapter 1.5 provides a short overview of host materials for OLEDs.

1.2 Optically active polyfluorene derivatives

Polyfluorenes are conjugated phenylene-based polymers which possess attractive photophysical properties. The ability to generate efficient blue emission makes this class of materials attractive for applications in OLEDs^[15] and polymer-based lasers.^[16] The basic ladder-type structure of polyfluorene, in which every second phenyl ring of a polyphenylene is bridged, is shown in Figure 1.2.1. For these applications, the emission can be controlled and tuned through functionalization of the polyfluorene backbone or the addition of substituents. In the solid state, interactions between the molecules or polymer chains also affect the emission in terms of a red-shift caused by the formation of aggregates.^[17] Copolymerization with other monomer units provides access to an even wider spectral emission window, from blueish green (thiophene copolymers) through green (cyanostilbene copolymers) to yellow (bithiophene copolymers).^[18]

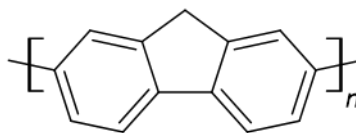


Figure 1.2.1. Chemical structure of polyfluorene.

In the melt, polyfluorene-based polymers exhibit complex morphological structures. A liquid crystalline phase can be aligned and quenched into the glassy state. This makes this material promising for optoelectronic applications requiring polarized electroluminescence. In 1997, Grell *et al.* presented polydioctylfluorene that forms a liquid-crystalline state at a transition temperature of 170 °C. By temperature-quenching on a rubbed polyimide substrate, liquid crystallinity was preserved in the glassy state, with high orientational ordering delivering polarized emission.^[19]

1.2.1 Optically active polyfluorenes with intrinsic chirality

An example of an intrinsically chiral copolymer is poly({9,9-bis[(3*S*)-3,7-dimethyloctyl]fluorenyl-2,7-diyl}-*alt*-{benzo[2,1,3]thiadiazol-4,8-diyl}), shortly c-PFBT (Fig. 1.2.2), which consists of a polyfluorene backbone bearing chiral (3*S*)-3,7-dimethyloctyl substituents. While these polymers show only very weak CD and CPL activity in the unannealed (pristine state), they exhibit an extraordinarily strong CD and CPL response after thermal annealing above the transition temperature to the chiral nematic phase.^[8,13,20] Such a strong chiroptical signal has been typically assigned to the formation of long-range supramolecular cholesteric arrangements.^[20] In contrast, Campbell, Fuchter and co-workers recently assigned this strong chiroptical response of c-PFBT to coupling of molecular magnetic and electric moments in the framework of a molecular picture of chirality.^[8] There is obviously considerable disagreement in the literature regarding the structural origin of the strong CD and CPL response of the copolymer films consisting of intrinsically chiral copolymers, and this issue is therefore addressed in detail by the paper in Chapter 4 of this thesis which confirms the supramolecular origin of the remarkably strong CD and CPL response of chiral c-PFBT films. Highly purified c-PFBT polymer for that study was kindly provided by Profs. Dong Hoon Choi and Min Ju Cho from Korea University.

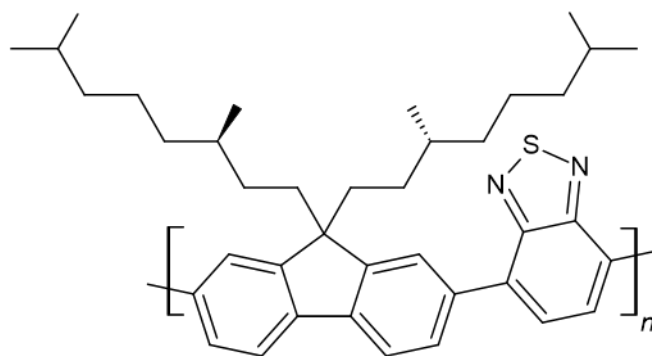


Figure 1.2.2. Chemical structure of the chiral polyfluorene derivative poly({9,9-bis[(3*S*)-3,7-dimethyloctyl]fluorenyl-2,7-diyl}-*alt*-benzo[2,1,3]thiadiazol-4,8-diyl}) or shortly c-PFBT.

1.2.2 Optically active polyfluorene derivatives with induced chirality

In Chapter 1.2.1, an intrinsic chiral copolymer system, which by itself induced large optical activity in supramolecular structures, was discussed. Alternatively, chiral additives can be used for chiral induction in intrinsically achiral polymers, to achieve the formation of chiral supramolecular arrangements. In the presence of such chiral additives, the achiral polymer chains will induce the formation of helical structures in the nematic phase, when the phase transition temperature is surpassed. For instance, the optical activity of such a polymer blend consisting of achiral poly-[(9,9-di-*n*-octylfluorenyl-2,7-diyl)-*alt*-(benzo-[2,1,3]thiadiazol-4,8-diyl)] (shortly, F8BT, chemical structure in Figure 1.2.3) with the chiral additive aza[6]helicene reaches signals of up to 16000 mdeg in the steady-state circular dichroism spectra. The sign of the CD response depends on the chirality of the dopant, leading to opposite signals for the different enantiomers.^[7,21]

In a recent study, chiral induction employing additives featuring axial chirality in F8BT polymer blends was investigated by Morgenroth et al. The authors used (*R*)-(+)-2,2'-dimethoxy-1,1'-binaphthalene and (*S*)-(-)-2,2'-dimethoxy-1,1'-binaphthalene as chiral additives and characterized the photoinduced dynamics of the resulting cholesteric thin-film polymer blends using transient circular dichroism (TrCD) spectroscopy. A chiral discrimination on ultrafast time scale for thin films of opposite helicity was successfully demonstrated. The combination of broadband transient absorption and TrCD experiments made the assignment of the polymer dynamics upon electronic excitation, quantification of the exciton relaxation and charge-pair formation channels possible.^[22] Yet, the chiral induction of the binaphthalene-based chiral additives was relatively weak, making it necessary to search for chiral inducers leading to a much higher CD and CPL response, as outlined in the following chapter.

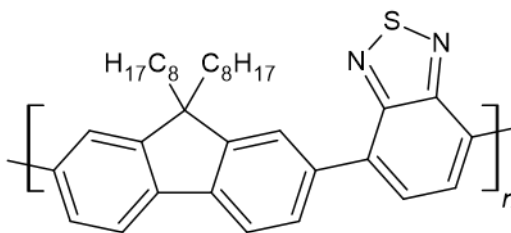


Figure 1.2.3. Chemical structure of poly-[(9,9-di-*n*-octylfluorenyl-2,7-diyl)-*alt*-(benzo-[2,1,3]thiadiazol-4,8-diyl)] (F8BT), the achiral copolymer which is combined with chiral additives.

1.2.3 Helicene-like compounds for chiral induction

Helicenes represent a particularly promising class of optically active additives.^[23] The synthesis of enantiopure helicenes is challenging, because of the complex synthesis pathways and the elaborate purification steps.^[23–25] Therefore, synthetically more easily accessible helicene-like alternatives have been investigated. For instance, Guy and co-workers have established a facile, large-scale synthesis route based on dibenzo[*c,h*]acridines which provides enantiopure helicene-like molecules with pronounced CPL activity.^[14,26]

Understanding the intrinsic photophysical properties of such helicene-like molecules in the condensed phase is critical for understanding their function in thin films and their behavior in optoelectronic devices, for instance when they are mixed into blends with achiral copolymers for applications in CP-OLEDs. Time-resolved laser-based pump-probe spectroscopies (Chapter 1.4) are powerful techniques to characterize the electronic and structural relaxation processes in the excited states of such helicene-like molecules. In this doctoral thesis, the photoinduced dynamics of thin films consisting of chiral 2,2'-dimethoxy-5,5',6,6'-tetrahydro-1,1'-bidibenzo[*c,h*]acridines and their methylene-bridged analogs were investigated (see the paper in Chapter 3). Chemical structures of the enantiomers, denoted as (+)-2, (–)-2 and (+)-3, (–)-3, are provided in Figures 1.2.4 and 1.2.5, respectively. The materials were synthesized, chemically characterized and kindly provided by the group of Dr. Laure Guy at the University of Lyon. They identified a fluorescence quantum yield for these systems of about 1%.^[14] The photoinduced processes in thin films consisting of the helicene-like molecules were investigated using broadband transient absorption covering the complete UV–vis–NIR range (260–1600 nm) from the femtosecond to the microsecond time range in combination with transient fluorescence investigations.

The high potential of helicenes as additives for induced circular dichroism (ICD) in achiral copolymers, such as F8BT, was recognized previously. For instance, a thin-film blend of aza[6]helicene and F8BT showed a large ICD of up to 20 000 mdeg as well as large dissymmetry parameters g_{abs} and g_{lum} for absorption and luminescence.^[7,21,27] The paper in Chapter 5 of this thesis will describe an application of the helicene-like chiral additives based on the dibenzo[*c,h*]acridine motif developed by the Guy group to induce a large supramolecular chiroptical response in F8BT.

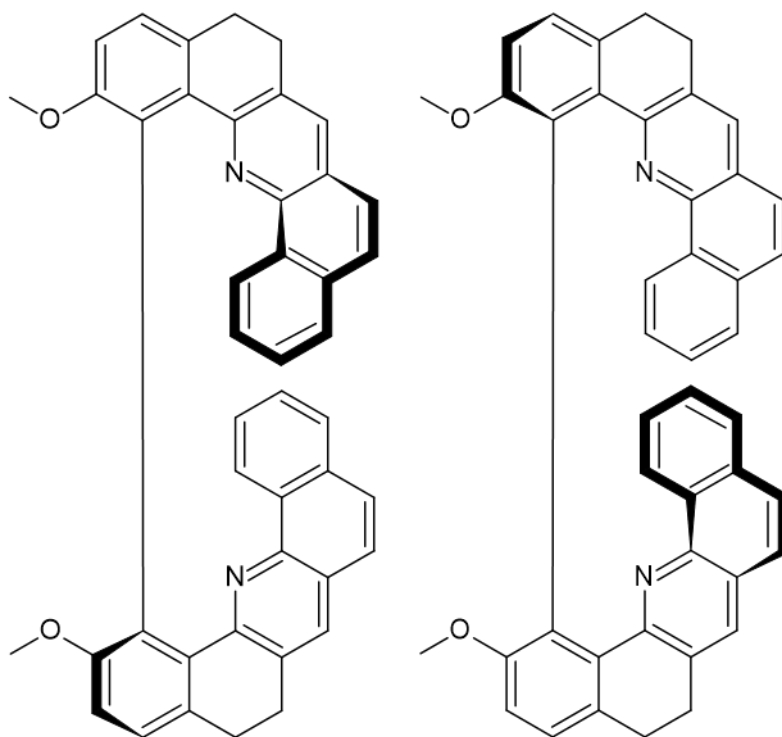


Figure 1.2.4. Chemical structures of the enantiopure 2,2'-dimethoxy-5,5',6,6'-tetrahydro-1,1'-bidibenzo[*c,h*]acridine (-)-2 (left) and (+)-2 (right).

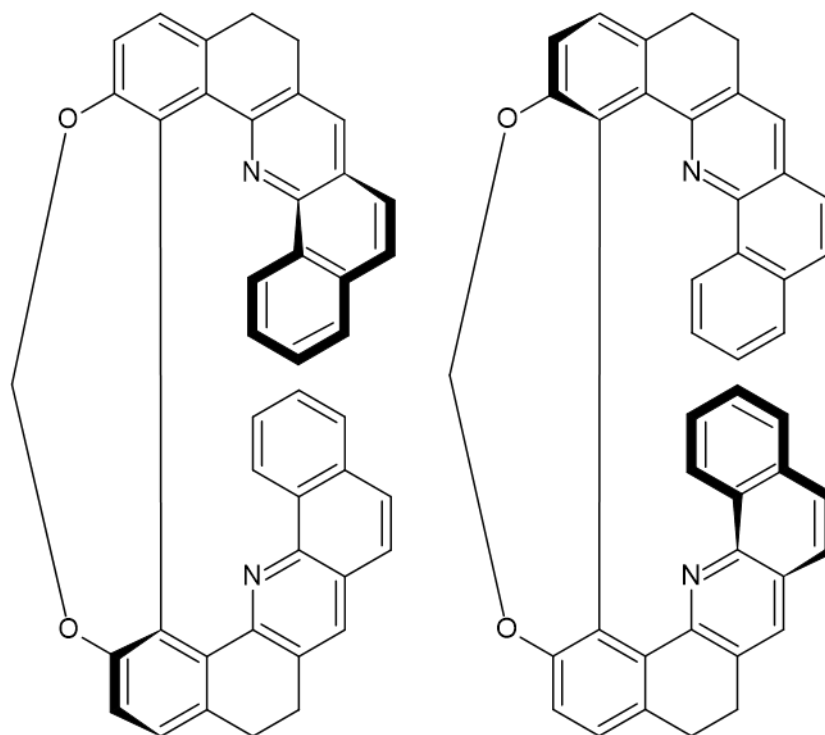


Figure 1.2.5. Chemical structures of the enantiopure bis-5,5',6,6'-tetrahydrodibenzo[*c,h*]acridino[1,1',2,2'-*d,f*]-[1,3]dioxepine (–)-3 (left) and (+)-3 (right).

1.3 Host materials for CP-OLED compounds

Aside from the emitter, another important constituent of any CP-OLED device is the host material. Important prerequisites for such a host material are a high triplet energy to prevent exciton back-transfer and suitable charge-transport properties combined with thermal and morphological stability.^[28] To this end, carbazole derivatives exhibit beneficial photophysical and electrical properties.^[29–34] The high-lying S_1 singlet and T_1 triplet states render these materials promising candidates for host materials in efficient blue-emitting OLEDs,^[35–37] since energy transfer from the triplet excited states of the light-emitting guest chromophore to the host molecules does not occur. A carefully selected doping level of the guest in the host material will lead to sufficient separation of the individual guest molecules. Therefore, processes like singlet–singlet annihilation (SSA) and triplet–triplet annihilation (TTA) between emitter molecules will be prevented, while the host provides appropriate charge transport with low energy barriers for electron- and hole-injection as well as energy transfer to the emitter.^[36,38–40] In this doctoral thesis, the carbazole derivative 1,3-bis(*N*-carbazolyl)benzene (mCP) is investigated using steady-state and time-resolved spectroscopic techniques. The chemical structure of the compound is shown in Figure 1.3.1. Although extensive photophysical data on mCP has

been reported in the literature, especially for its solid-state phase, these findings do not consistently match: For instance, while Forrest and co-workers found weak structured emission of T_1 with vibronic peaks at 430 and 460 nm that only emerged at a very low temperature of 10 K,^[41] Wu et al. and Tsuboi et al. reported a weak band with vibronic features at 410 and 440 nm in the phosphorescence spectrum of the T_1 state.^[29,30] Moreover, Kim and co-workers assigned the 0–0 peak of the T_1 emission at 455 nm which is at variance with the other reports.^[39] Since the energetic location of the triplet state of a host material plays an important role in an OLED device, the reason for such conflicting results should be clarified. This thesis therefore aims at a better understanding of the photophysical properties of mCP in solution and in thin films. mCP is investigated in the solvent tetrahydrofuran (THF), in thin film blends consisting of mCP and poly(methyl methacrylate) (PMMA) and also as a neat film. The characterization techniques used are steady-state absorption and emission spectroscopy, time-correlated single photon counting (TCSPC) and broadband UV–vis–NIR transient absorption spectroscopy. They are employed to disentangle the complex relaxation processes of the excited states of mCP after photoexcitation.

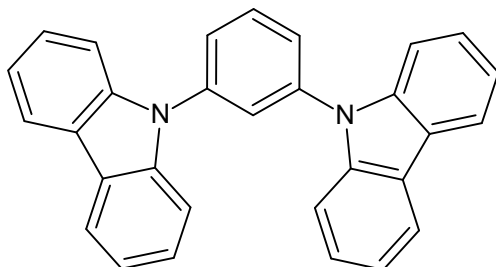


Figure 1.3.1. Chemical structure of 1,3-bis(*N*-carbazolyl)benzene (mCP).

1.4 Chiroptical spectroscopy and microscopy

Steady-state CD spectroscopy discriminates between molecular systems of different chirality and has been widely applied to chemical and biological systems.^[9,42–45] Time-resolved circular dichroism (TrCD) spectroscopy offers a powerful approach for investigating photoinduced changes in excited-state chirality on ultrashort time scales. However, so far this technique has only been implemented in a few laboratories, even more rarely in the context of spectrally broadband CD detection with femtosecond temporal resolution.^[46,47] This is likely due to complex issues regarding polarization management and the weak optical activity of many systems resulting in small transient

signals. For example, Fiebig and co-workers recorded the transient response of merocyanine nanorod aggregates with sub-picosecond time resolution over the spectral range of 360–550 nm using a Pockels cell for polarization switching.^[48] Oppermann et al. investigated an enantiopure ruthenium complex as well as a chiral synthetic thioamide-substituted dipeptide in the UV range of 250–370 nm with 500 fs time resolution with the polarization switching done by a photoelastic modulator.^[49,50] For polarization switching, Brixner and co-workers employed a setup to generate LCP and RCP light by an arrangement of mirrors and periscopes.^[51,52] The above techniques directly determine the transient CD signal as the difference in optical density for probing with LCP and RCP light ($\Delta CD = \Delta \Delta OD = \Delta OD_L - \Delta OD_R$). An alternative technique to extract ΔCD information of a system was reported by Cho and co-workers. The free induction decay of the optical activity was converted into a chiral response using self-heterodyned detection.^[53–55] Later on, the technique was applied by Hiramatsu and Nagata to enantiopure $[Ru(bpy)_3]^{2+}$,^[56] but more than this test setup has not yet been reported.

The current work describes an improved setup for TrCD spectroscopy which is based on switching the probe polarization by a Pockels-cell-based design employing a deuterated KDP crystal. This modification provides improved time resolution of down to 100 fs and an increase in intensity of the circularly polarized multifilament supercontinuum combined with a reduction of intensity fluctuations. To investigate different local domains of optically active thin films, local microscopic mapping using TrCD is presented as a proof-of-concept. The spatial resolution is 50 μm and limited by the pump-beam size. To further characterize local chiroptical properties of these films, steady-state CD and CPL microscopy imaging techniques are developed with a diffraction-limited spatial resolution of 500 nm. These setups collect wide-field absorption and emission images simultaneously, including spectra integrated over the entire field of view. Details regarding their implementation are provided in Chapter 2.4.5.

Regarding the time-resolved detection of CPL, there are different approaches reported in the literature, as summarized by Meskers.^[57] Dependent on the type of setup, they are limited to slower processes in the time range of 0.01–100 ms in the case of differential photon counting,^[58–60] or the time resolution has a coarse point-by-point spacing of about 200 ps in the case of time-correlated single photon-counting (TCSPC).^[61]

In this thesis, a newly developed TCSPC-based setup is employed to collect transient CPL signals. In this setup, the combination of a fast detector and a TCSPC board with

high temporal resolution leads to a very good signal-to-noise ratio with an instrument response function of 28 ps. The detailed setup is described in Chapter 2.4.4.

1.5 Aim of the work

The current thesis aims at a comprehensive spectroscopic understanding of the structure and dynamics of polymer-based systems with a large chiroptical response. This includes intrinsically chiral polymer thin films consisting of c-PFBT, films with induced circular dichroism consisting of achiral F8BT and helicene-like chiral inducers, and also host materials, specifically mCP, to be combined with chiral polymer and other chiral emitters in CP-OLEDs.

The first goal is to improve and extend an existing setup based on broadband transient absorption to investigate transient CD changes of chiral molecular systems with an ultrafast time resolution on the order of 100 fs. The realization of such a TrCD setup makes it possible to achieve another goal, a detailed characterization of the chiral dynamics of thin films consisting of the intrinsically chiral polymer c-PFBT. Together with complementary studies using CD and CPL microscopy, an understanding of the underlying physical reasons of the supramolecular CD response is sought.

Next, it is the aim to understand the supramolecular CD response in achiral polymer systems mixed with helicene-like chiral additives. To this end, the spectroscopy and photoinduced dynamics of these chiral inducers, such as (+)-2 and (–)-2, (+)-3 and (–)-3, need to be investigated and understood in detail. After that, these helicene-like chiral additives are combined with the achiral polymer F8BT, and these films are studied using TrCD spectroscopy and CD/CPL microscopy. Additional information regarding the supramolecular mechanism of CPL generation is sought by implementing a new setup for transient circularly polarized luminescence (TrCPL) with a superior time resolution reaching down to several ten picoseconds.

Finally, as one step toward the realization of CP-OLEDs, the carbazole-based host material mCP is investigated. Since the host material is another central component in an OLED device, the understanding of the detailed photophysical processes in mCP and related compounds is desirable, and mCP is therefore investigated here in detail.

2. Experimental methods

2.1 Pump-SuperContinuum-Probe (PSCP) spectroscopy

2.1.1 Overview of pump-probe laser spectroscopy

A pump-probe spectroscopy setup consists of at least two laser beams. One beam excites the sample into an excited state (pump beam) and the subsequent dynamic processes are monitored by a second beam (probe beam) after a well-defined time delay. The experimental quantities observed may be absorption, phase shift, birefringence, diffraction, fluorescence, photoelectrons or ions.^[62] Hence, some of the applications described require ultrashort or high-power pulses. The first functioning solid-state ruby laser was built in 1960 by Theodore Maiman, which opened up a huge field of applications.^[63] First attempts in 1967 using a Q-switched ruby laser investigated the excited singlet state absorption of coronene.^[64] The fundamental wavelength of 694.3 nm with a pulse length of about 30 ns was frequency-doubled using a non-linear monopotassium phosphate (KDP) crystal. The generated signal beam of 347 nm was used to pump the solution of coronene in acetonitrile. The red idler beam was focused into a gas cell, which generated a breakdown spark. Different gas media xenon, argon and oxygen delivered illumination times of 1 μ s, 200 and 30 ns, respectively. A single exposure spectrograph using Polaroid films was illuminated. The authors described early excited-state absorption features around 500 nm with a peak at 520 nm with an additional peak at 320 nm which had not been seen before.^[64,65] The time resolution, which is limited by the laser pulse duration, was increased by two orders of magnitude compared to other techniques like flash photolysis to that date with flash-lamp illumination durations of 20–50 μ s.^[66–68]

The technique was constantly improved over time with ongoing laser development and electrotechnical modifications.^[69] Nowadays, the time resolution in transient absorption can reach the region of several hundred attoseconds with further compression techniques of the fundamental laser beam.^[70] In the current thesis, different molecular systems were investigated by the Pump-Supercontinuum Probe setup (PSCP).^[71] Here, the probe pulse was generated by the conversion of a fundamental or second harmonic laser pulse into a spectrally broad multifilament supercontinuum. Transient absorption signals were observed over different wavelength windows depending on the fundamental beam used for the generation of the supercontinuum. While the near-infrared (NIR) setup used in this thesis covers a wavelength range from 780 to 1650 nm, the ultraviolet to

visible (UV–vis) setup spans the wavelength region 260 to 680 nm. In this work, the polarization state of the supercontinuum probe beam was further modulated to collect the transient circular dichroism response as the difference in absorption between left- and right-circularly polarized light.

2.1.2 Laser system

A titanium:sapphire (Ti:Sa) solid-state laser from Coherent Inc. (Libra USP-HE) delivers ultrashort pulses with a half-width of 50 fs at a fundamental wavelength of 800 nm, an operating frequency of 920 Hz and a power of 4 W. A schematic of the Libra laser system is shown in Figure 2.1.1.

Briefly, a Ti:Sa oscillator (Vitesse) delivers ultrashort (50 fs) seed pulses of the fundamental wavelength 800 nm with a repetition frequency of 80 MHz at 340 mW. In the next step, the pulses are stretched to ca. 500 ps by sending them eight times over a diffraction grating (G). The s-polarized pulse is then guided into the regenerative amplifier (RGA), by reflecting it off the titanium:sapphire laser gain medium (TS) inside a Z-folded cavity. Population inversion of the Ti:Sa medium is achieved by an AlGaAs laser diode-pumped Nd:YLF laser (Evolution), which operates at a repetition frequency of 920 Hz in Q-switch mode, based on an acousto-optic modulator (AOM). The laser delivers pulse durations of 150 ns with a total power of 20 W at a wavelength of 527 nm after second harmonic conversion in a nonlinear lithium triborate crystal (LBO). A single stretched pulse from the Ti:Sa oscillator is trapped in the RGA cavity by turning on the upper Pockels cell (PC, operating in quarter-wave ($\lambda/4$) mode) once the beam has passed it after reflection from the upper mirror. The single pulse inside the RGA, which is now p-polarized, passes through the amplifier cavity approximately 15 to 16 times. After optimum amplification has been reached, the lower Pockels cell is turned on (to quarter-wave mode) just before the pulse enters it. After the pulse has passed this Pockels cell a second time after reflection from the lower mirror, it has therefore s-polarization. This s-polarized pulse is then reflected off the thin-film polarizer (P) and guided via several mirrors and a periscope into the compressor stage. Here, the laser beam is recompressed

to its initial pulse length of approximately 50 fs, but the pulse energy is now amplified by about a factor of 10^6 .

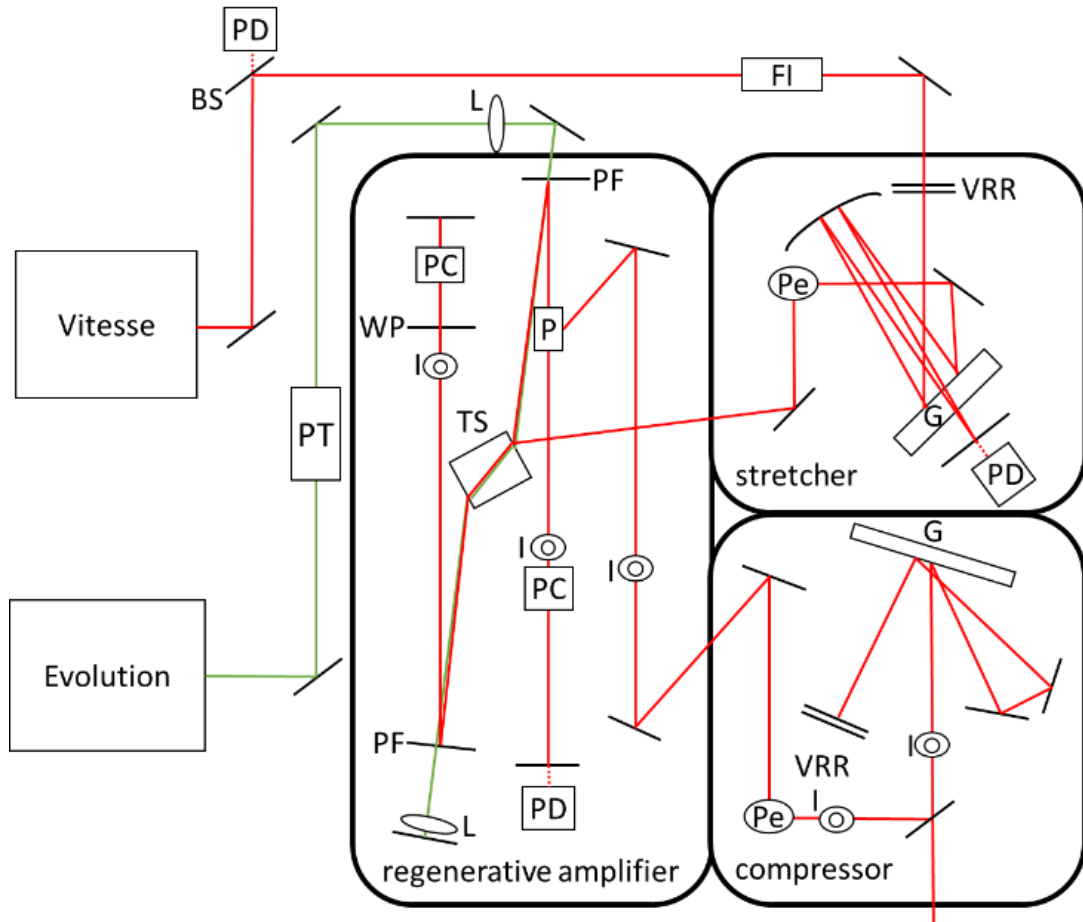


Figure 2.1.1 Schematic representation of the operating principle of Coherent's Ti:Sa laser system based on reference [1]. Pockels Cells PC, Lens L, Thin-Film Polarizer P, Laser gain medium titanium:sapphire TS, Beam Splitter BS, pump telescope PT, quarter-wave plate WP, Iris I, Grating G, Photo Diode PD, Faraday Isolator FI, Periscope Pe, vertical Retroreflector RR, pump through folding mirror PF.

2.1.3 Optical Parametric Amplifier

An optical parametric amplifier (OPA, Coherent OPerA-Solo) converts the fundamental beam of the regenerative Ti:Sa amplifier into a wavelength in the range of 240–2600 nm. A scheme of the system is shown in Figure 2.1.2, and its setup consists of three main sections.

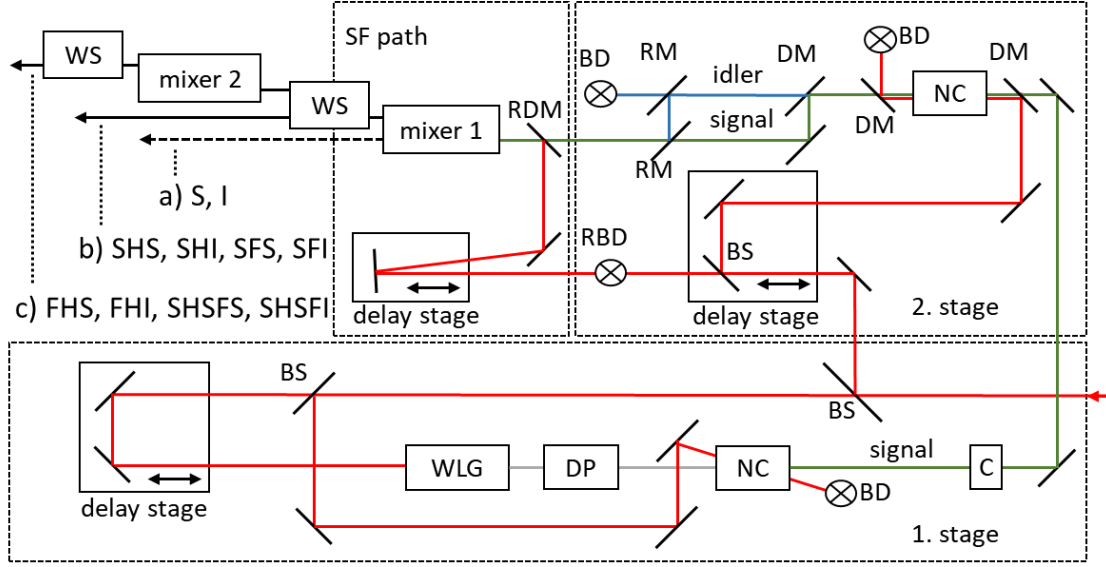


Figure 2.1.2 Schematic of the Coherent OPA system (OPeA-Solo). Components are beam splitter BS, white-light generator WLG, dispersive plate DP, nonlinear crystal NC, beam dump BD, compensator C, dichroic mirror DM, removable dichroic mirror RDM, removable beam dump RBD, removable mirror RM and wavelength separator WS. The output beam paths are a) Idler I and Signal S, b) second harmonic signal SHS, second harmonic idler SHI, sum frequency signal SFS and sum frequency idler SFI, and c) fourth harmonic signal FHS, fourth harmonic idler FHI, second harmonic sum frequency signal SHSFS and second harmonic sum frequency idler SHSFI. Note: Output path a) is unaffected by mixer 1.^[72]

In the first stage, the fundamental beam of 800 nm passes a beam splitter (BS) while 95% are reflected to the second stage. The transmitted beam is further separated into two paths. The first beam path travels through a delay stage and a white-light generator (WLG). The resulting white-light continuum is then stretched by a dispersive plate (DP) and hits a nonlinear crystal (NC). The second beam (800 nm) is crossed with a white light beam inside the nonlinear crystal in a noncollinear arrangement. Depending on the delay stage, the fundamental beam temporally overlaps with a certain spectral portion of the up-chirped white-light continuum. The selected wavelength (the so-called signal beam, for example 1200 nm) is subject to parametric amplification by the energy of the fundamental beam, with a residual energy appearing as a so-called idler beam (in this example 2400 nm) as follows:

$$\frac{1}{800 \text{ nm}} = \frac{1}{1200 \text{ nm}} + \frac{1}{2400 \text{ nm}} \quad (2.1)$$

The remaining fundamental beam and the idler beam are blocked geometrically. The signal beam is sent through a compensator (C), collimated and then directed into the second nonlinear crystal of the second stage. The remaining 95% of the fundamental beam from the first stage are directed via a tunable delay stage and a dichroic mirror (DM) into the nonlinear crystal, where the signal beam is amplified. Since the signal and

fundamental beams are collinear, the unconverted fundamental wavelength is filtered out by a subsequent dichroic mirror and a beam dump (BD). In addition, the generated idler beam can be used for further wavelength conversion. The signal and idler beams are separated by a dichroic mirror. The idler is blocked while the signal beam is reflected to a beta barium borate (BBO) crystal (mixer 1). Second harmonic generation (SHG) can be achieved in a BBO crystal, for example:

$$\frac{1}{1200 \text{ nm}} + \frac{1}{1200 \text{ nm}} = \frac{1}{600 \text{ nm}} \quad (2.2)$$

To generate the second harmonic, the BBO is aligned to the phase-matching angle by a computer-controlled rotation stage. By inserting the removable mirrors (RM), the idler beam is reflected into mixer 1, while the signal beam is blocked.

In the third stage, the fundamental beam passes through a delay stage and is directed into mixer 1 via a removable dichroic mirror (RDM). Either the signal or the idler beam can be converted by sum frequency generation (SFG). For example, the sum frequency of 800 nm and a signal beam of 1200 nm is obtained as follows:

$$\frac{1}{800 \text{ nm}} + \frac{1}{1200 \text{ nm}} = \frac{1}{480 \text{ nm}} \quad (2.3)$$

After wavelength conversion in mixer 1 and also mixer 2 (for generating for instance UV wavelengths down to 240 nm), the unconverted radiation is filtered out by respective wavelength separators (WS).^[72]

2.1.4 Optical setup: Broadband transient absorption

Broadband transient absorption (TA) spectra are obtained using the PSCP technique. A schematic representation of the setup is shown in Figure 2.1.3.

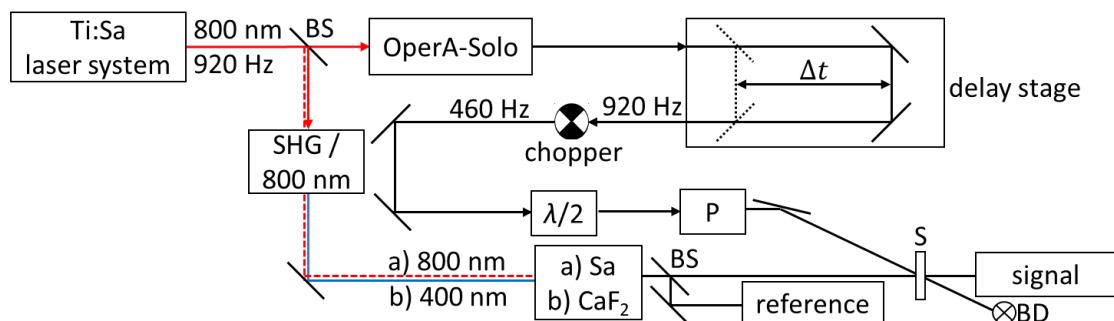


Figure 2.1.3 Schematics of the PSCP setup for transient absorption used in this thesis. For detection in the NIR, the fundamental beam of 800 nm generates a supercontinuum in a sapphire crystal (a) Sa). In the UV-vis setup the fundamental beam is frequency doubled to 400 nm. The supercontinuum is generated in a calcium fluoride crystal (b) CaF₂).

A broadband multifilament supercontinuum serves as the probe beam and is generated by focusing a seed laser pulse into an appropriate crystal. For the transient absorption setup in the UV–vis range, a laser pulse with a seed wavelength of 400 nm is focused into a 2 or 3 mm thick calcium fluoride crystal, generating the supercontinuum in the wavelength range of 260–680 nm. Another transient absorption setup for the near-infrared (NIR) covers wavelengths from 780 to 1650 nm by focusing a seed wavelength of 800 nm into a 2 mm thick sapphire crystal. To avoid damage from the high-power laser beam, the CaF_2 and sapphire crystals are continuously and randomly moved in a plane perpendicular to the beam axis during the experiment.

The resulting multifilament supercontinuum is strongly divergent, and is therefore imaged by a combination of several concave and convex aluminum-coated mirrors: Mirrors are used instead of lenses to avoid introducing additional up-chirp into the laser pulse. Moreover, the residual unconverted seed beam traverses the optical system with much less divergence than the supercontinuum beam and can therefore be blocked by a mechanical beam dump which is placed in front of the first concave mirror in the imaging setup. In addition, for the UV–vis PSCP setup we achieve a spectrally flat white light spectrum by sending the initially generated whitelight spectrum, through a methanol solution containing a mixture of dyes which absorb preferentially the remaining 400 nm seed wavelength of the probe beam. For this purpose, a home-made dye solution containing Coumarin 466, Coumarin 153 (both from Lambda Physik) and ATTO390 (ATTO-TEC) is applied which absorbs preferentially in the 400 nm range, but much less in the remaining UV and visible range, resulting in a flattening of the white light spectrum. The filter solution is continuously pumped from a reservoir through a flow cell to avoid burn-ins on the quartz cell windows by the focused supercontinuum pulses. The white light is then separated by a beam splitter. One beam is detected by a reference spectrograph. The other beam traverses the sample in a focal point (where it is overlapped with the pump beam, see below) and is detected by the signal spectrograph.

An appropriate wavelength is selected as the pump beam using the OPA system (OPerA-Solo) to excite the sample with pulse durations in the range of 50–80 fs. The output is guided to a motorized delay stage (Physik Instrumente, UV–vis experiment: M-531.5IM; NIR experiment: M-531.2S1). The variable difference in beam path length by passing the stage can reach up to 60 cm, which corresponds to a maximum time delay of 2 ns. A rotating slit disk (chopper) operating at a frequency of 460 Hz blocks every

second pump pulse. A combination of a half-wave plate ($\lambda/2$) and a polarizer (P) controls the power of the pump beam which is set at the magic angle (54.7°) with respect to the polarization of the probe beam. The pump beam is then focused at a small angle (about 11°) with respect to the probe beam at the same focal point into the sample (S). Typically, the pump beam diameter ($200\ \mu\text{m}$, as measured by a CCD camera) is slightly larger than the probe beam diameter ($50\ \mu\text{m}$), to prevent loss of the signal caused by slightly inappropriate adjustments of the delay stage and the spatially chirped supercontinuum beam. The sample cell is continuously and randomly moved in the focal plane (x - and y -axis) by two piezo micropositioning stages (Physik Instrumente, M664.164) to minimize any photochemical decomposition induced by the intense laser radiation.

The time-resolved difference in optical density $\Delta\text{OD}(t)$ measures the temporal variation of the population of transient species in the excited state at a given time t . The ground-state molecules are excited by an ultrashort pump pulse at the specific wavelength (λ_{pump}) at time $t = 0$. Subsequently, at a given delay time t , the two intensities of the broadband probe beam are measured at the signal spectrograph, once with the pump beam on ($I(t)$, chopper wheel open) and after that with the pump beam off ($I_0(t)$, chopper wheel closed). Each time, the supercontinuum is also recorded separately in the reference spectrograph to be able to correct for fluctuations in the white light shot-by-shot. Then one obtains the optical density (i.e. $\text{OD}(t) = \log_{10}(I_0(t)/I(t))$) over the wavelength range of the white light probe beam. The difference between the optical densities ($=\Delta\text{OD}(t)$) with pump pulse ($\text{OD}_{\text{wP}}(t)$) and without pump pulse ($\text{OD}_{\text{woP}}(t)$) then determines the $\Delta\text{OD}(t)$ signal at a specific time delay t between the pump and probe beams:

$$\Delta\text{OD}(t) = \text{OD}_{\text{wP}}(t) - \text{OD}_{\text{woP}}(t) = \log_{10}\left(\frac{I_0(t)}{I(t)}\right)_{\text{wP}} - \log_{10}\left(\frac{I_0(t)}{I(t)}\right)_{\text{woP}} \quad (2.4)$$

The probe and reference signals are detected using grating spectrometers with photodiode arrays having 512 pixels. The photodiode material is selected depending on its quantum efficiency in the wavelength region of interest. In the UV–vis measurements, silicon is employed, whereas in the NIR measurements indium gallium arsenide is used.

2.1.5 Optical setup: Broadband transient circular dichroism

The setup for broadband transient circular dichroism (TrCD) is an extension of the UV–vis PSCP setup for broadband transient absorption, in which the probe beam path is

modified. An overview of the TrCD setup, which is an extension and improvement of the original TrCD setup^[73], is shown in Figure 2.1.4.

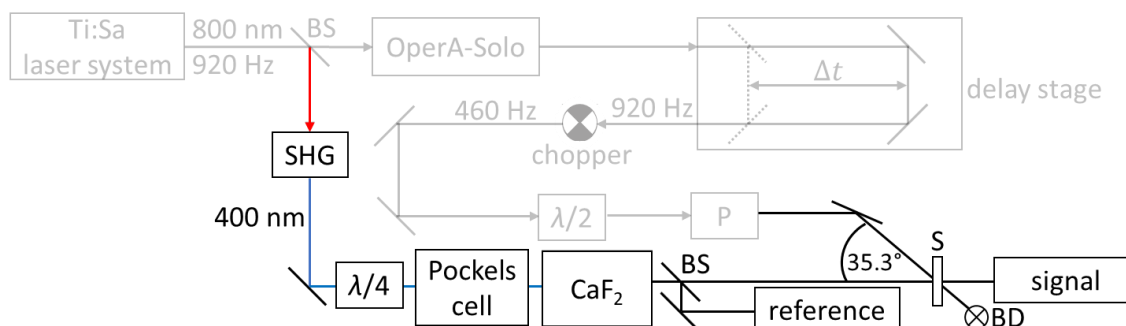


Figure 2.1.4 Overview of the modified PSCP setup for transient circular dichroism. The 400 nm seed beam in the probe path is left-circularly polarized by a quarter-wave plate ($\lambda/4$) and can be switched by a Pockels cell, which operates in half-wave mode ($\lambda/2$), to right-circularly polarized light. The pump beam hits the sample with an angle of 35.3° relative to the probe beam.

The fundamental wavelength of 800 nm is frequency-doubled to 400 nm by a BBO crystal. The pulse energy of the beam is about 20 μJ . The initially linearly polarized light is sent through a high precision quarter-wave plate (B. Halle Nachfl., $\lambda/4$ at 400 nm) resulting in left-handed circular (LCP) polarization. A Pockels cell using a potassium dideuterium phosphate (DKDP) crystal (Eksma MP1) operates in half-wave mode (ca. 2500 V). With the voltage off, the polarization stays LCP. However, with the voltage on, the handedness of the seed beam is converted from left- to right-circularly polarized (RCP). These seed pulses generate a broadband multifilament UV–vis supercontinuum in a 3 mm thick calcium fluoride crystal. Importantly, the resulting supercontinuum maintains the same polarization as the seed beam (i.e. either LCP or RCP). The probe beam is then separated with one beam guided to the reference spectrograph. The other beam is focused into the sample and detected by the signal spectrograph. The pump beam crosses the probe beam at an angle of 35.3° (the so-called “magic angle” of TrCD spectroscopy) and generates population in the excited state.^[73,74] In that way, quadrupole-field effects are excluded.^[75,76] The measured transient CD signal (ΔCD) is detected as a double difference signal in absorption with left- and right-circularly polarized probe beams (OD_{LCP} , OD_{RCP}):

$$\begin{aligned}
\Delta CD &= (OD_{LCP} - OD_{RCP})_{WP} - (OD_{LCP} - OD_{RCP})_{woP} \\
&= \left(\log_{10} \left(\frac{I_0}{I} \right)_{LCP} - \log_{10} \left(\frac{I_0}{I} \right)_{RCP} \right)_{WP} \\
&\quad - \left(\log_{10} \left(\frac{I_0}{I} \right)_{LCP} - \log_{10} \left(\frac{I_0}{I} \right)_{RCP} \right)_{woP}
\end{aligned} \tag{2.5}$$

2.1.6 Data acquisition

The analog signals from the photodiode arrays are read out and converted into digital signals by electronics (Hamamatsu or Entwicklungsbüro Stresing). The 920 Hz output of the Ti:Sa laser provides the master trigger for synchronization of the experiments. A measurement program (LabWindows, National Instruments) sets the position of the delay stage and reads out the electronics. A measurement typically consists of three measurement blocks with different time windows and time increments. A single datapoint is averaged over 1000 laser shots and each block is measured and averaged three times. The dark current of the photodiodes is measured beforehand with the laser beams blocked and subtracted from the signal.

It should be noted that the path of the movers for the white-light generating crystals (calcium fluoride or sapphire) follows a Lissajous curve to avoid local burn-ins in the crystals. Still, over extended operation times of weeks to months, “bad spots” in the crystals are unavoidable. When the seed beam passes such areas, the white light spectrum has a bad quality and is strongly distorted. Such events can be detected in the reference spectrometer. Therefore, before each measurement, the shape of the “clean undistorted” white light spectra is measured and the standard deviation of these “normal” spectra is determined. Then, during a measurement, spectra showing too large a deviation from this standard deviation are discarded, and the corresponding data point is remeasured until the deviation is in the required range.

2.1.7 Data treatment

2.1.7.1 Chirp correction

The self-phase modulation and group velocity dispersion of the supercontinuum beam cause a separation of the spectral components in time. This leads to a temporal mismatch in the different spectral components of the probe beam in a pump–probe experiment at any pump–probe delay. This effect is called “chirp” and needs to be corrected for.^[71]

Because of the normal dispersion of transparent materials, the refractive index $n(\lambda)$ for substances, such as quartz, glass, calcium fluoride, sapphire or organic solvents decays with increasing wavelength. Therefore, inside a given material, the short-wavelength components propagate at a lower velocity c ($= c_0/n(\lambda)$, where c_0 is the speed of light in vacuum) which results in a so-called “up-chirp” (lower frequencies come first and higher frequencies follow later). Therefore, e.g. when the supercontinuum beam passes the calcium fluoride crystal or the sample cell, the red components will travel faster than the blue components and will therefore “meet” the practically unchirped pump pulse at different times, see Figure 2.1.5 for an illustration of the process. The raw transient absorption and transient CD spectra therefore need to be chirp-corrected. A convenient way to achieve this is to use the coherent artifact of a sample. Because the white light crystal is thicker in the TrCD experiment (3 mm compared to 2 mm in the PSCP setup), the chirp is also larger and amounts to about 2 ps. The time window of the measurement block for short time scales in the UV–vis experiments therefore needs to be extended.

2.1.7.2 Preparation of the time-resolved spectra

The measured time-resolved spectra are post-processed using a program written in Matlab. First, the respective measurement blocks are averaged. Next, the transient absorption and transient CD signals frequently contain additional time-independent signals, such as a scattering signal at the pump beam wavelength and steady-state emission of the sample. These contributions are removed by subtracting a set of spectra averaged over a certain range of negative pump–probe delay times ($\Delta t < 0$). Afterwards, these spectra are subjected to the chirp correction explained in Chapter 2.1.7.1. A polynomial of typically third or fifth order is used to describe the wavelength-dependent chirp of the signal, and the spectra are subsequently resampled in time using this chirp-correction function. The exported data sets (HDF5 or ASCII format) of the corrected transient spectra are then further processed using different versions of OriginPro (2021–2025).

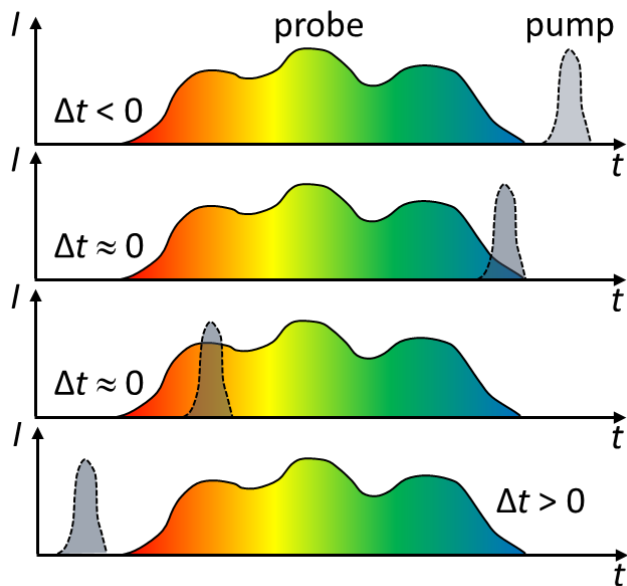


Figure 2.1.5 Scheme illustrating the generation of the chirp in PSCP and TrCD experiments. The longer-wavelength components of the probe beam travel faster than those at shorter wavelengths. At “negative” pump–probe delay times $\Delta t < 0$ (first panel), the probe beam arrives first and then the pump beam. With increasing time delay Δt , the pump beam will first overlap with the blue portion of the supercontinuum (second panel) and at even larger Δt with the red portion of the supercontinuum (third panel). The fourth panel illustrates the situation when all spectral components of the probe beam arrive much later than the pump beam. Therefore, a chirp correction of the PSCP and TrCD experiments is required, so that all spectral components are shifted to the same time zero.

2.2 Sample preparation

2.2.1 Pretreatment of the glass substrates

Borosilicate glass slides (Duran Wheaton Kimble) are cleaned using the following procedure. They are first washed with soapy distilled water, afterwards placed in beaker filled with technical acetone, and then treated for 30 min in an ultrasonic bath. The glass slides are then dried under a nitrogen stream (Messer, 4.6) and cut to a size of about 25×25 mm². Aside from the removal of hydrophilic and hydrophobic residues, any remaining contaminations are removed by ozone treatment in an UV irradiation chamber (Dinies ELG100S, 2 UVC lamps operating at 253.7 nm with 11W) for 15 min. The ozone treatment also improves the wettability of the glass substrates.

2.2.2 Spin-coating procedure and post-annealing of the thin films

The thin films are directly deposited on the pretreated glass slides in a nitrogen atmosphere with relative humidity < 1%. Precursor solutions of the materials to be investigated are prepared at typical polymer concentrations of 7.5 mg ml⁻¹. The solution is a mixture of chlorobenzene (Merck, > 99%) and chloroform (Merck, ≥ 99.8%) (1:9 by volume). The intrinsically chiral or achiral polymer is weighed in a vial, and the solution

is added with a micropipette (Carl Roth). In the case of chiral induction, the enantiopure chiral helicene-like additives are added to the polymer at the desired weight percentage. A different approach is carried out for the experiment with induced chirality in the polymer cholesteric phase with enantiomeric excess of the chiral additive. The enantiomeric excess (*ee*) describes the mass excess of one enantiopure isomer (m_1) to the other (m_2) and is defined as:

$$ee = \frac{|m_1 - m_2|}{m_1 + m_2} \quad (2.6)$$

Here, stock solutions are prepared, and appropriate volumes of the polymer and solutions of the chiral additive are mixed in a separate vial. The resulting precursor solutions are filtered through a 0.45 μm pore size PTFE filter prior to the spin-coating process. A scheme of the spin-coating technique and the post-annealing process is shown in Figure 2.2.1. The solutions are casted onto the glass slides while they are spinning on a chuck. The chuck rotates in either one or two separate steps with certain speeds and durations. A typical spin-coating condition for polymer thin films is a speed of 500 revolutions per minute (rpm) for 60 s. The film thickness can be varied easily by controlling the rotation speed during the spin-coating process. Depending on the spin coating parameters, film thicknesses in the range of about 100–400 nm are achieved. Even thicker films are produced by applying a “loading time” during which the solution stays on the not yet rotating substrate for a defined time interval. The thick films may exhibit a more inhomogeneous surface, because of uneven evaporation of the volatile solutions. The as-cast pristine thin films are placed on a hot plate for a certain time period, at a well-defined temperature in the range of 50–200 $^{\circ}\text{C}$ to investigate the impact of thermal treatment on the structure of the polymer thin film.

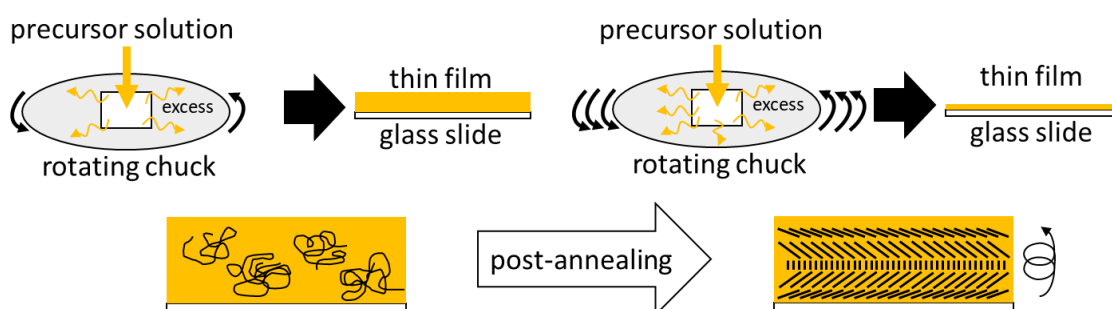


Figure 2.2.1 Schematic of the spin-coating and post-annealing procedure. The speed of the rotating chuck controls the thickness of the resulting polymer thin film. The post-annealing process leads to the evaporation of the remaining solvent and the formation of a supramolecular polymer structure, for instance a cholesteric (= chiral nematic) phase.

2.3 Material characterization

2.3.1 Differential scanning calorimetry

2.3.1.1 Preparation of aluminum crucibles

Aluminum crucibles (Netzsch, 25 μ l) were filled with the polymer F8BT or the mixture of the polymer and the chiral additive. The polymer powder appears to be susceptible to electrostatic charging. It is thus challenging to place appropriate amounts (about 10 mg) into the small crucible. Therefore, highly concentrated solutions in THF ($c = 12 \text{ mg ml}^{-1}$) are added dropwise to the crucible under a flow of nitrogen. The solution evaporates, and this step is repeated until the desired mass is reached. The pans are dried overnight in a nitrogen atmosphere with a humidity of less than 1%. A hole is then punched into the lid so that any overpressure is released from the crucible during heating. Finally, the crucible is pressed, and the exact mass is taken.

2.3.1.2 Differential scanning calorimetry measurements

The differential scanning calorimetry (DSC) curves were taken with the kind support of Dr. C. Pritzel (University of Siegen, Chemistry and Structure of Novel Materials) using a thermo-microbalance-based instrument for simultaneous TG-DSC measurements (Netzsch STA449 C Jupiter). The sample chamber is flushed with two nitrogen and one argon purge channel with a gas flow of 20 ml min^{-1} each. The reference is an empty aluminum crucible. Multiple heating and cooling segments are combined with a temperature difference rate of $10 \text{ }^{\circ}\text{C min}^{-1}$. The heating scans are as follows: The first segment goes up to a temperature of $80 \text{ }^{\circ}\text{C}$ to remove solvent. The next heating segments employ heating ranges from $30 \text{ }^{\circ}\text{C}$ to 170 , 320 and $330 \text{ }^{\circ}\text{C}$. The cooling segments are located between the heating segments, and the temperature goes down to $30 \text{ }^{\circ}\text{C}$ in each case.^[77]

2.3.2 Atomic force microscopy

Atomic force microscopy images are taken with a XE-100 instrument (PSIA). A silicon tip is used in non-contact mode. Thin-film thicknesses are determined from the height profile of a scratched surface. The scratches are imprinted using a fine-tipped stainless-steel tweezer. Multiple randomly selected points along the scratches are recorded. The images are adjusted linearly along the horizontal axis to correct for the tilt of the sample. Here, the surfaces of the glass substrate and the polymer surface appear as a lower and a

higher plateau, respectively. The lines along the vertical axis are averaged. The total film thickness is then determined by the height difference of the glass and sample surface.^[78]

2.4 Optical characterization

2.4.1 Steady-state absorption and photoluminescence

Steady-state absorption spectra of thin films and solutions are recorded with a double-beam spectrophotometer (Cary 5000, Varian) in transmission mode. Background correction is performed internally, and the spectral resolution is typically 0.5 nm. Spectra of the thin films are measured in a closed aluminum contact cell with a 2 mm thick quartz window (Suprasil I) and a Viton sealing ring. The cell is connected to a nitrogen purge line (Messer, 4.6) which flushes the cell continuously. Liquid samples are investigated in quartz cuvettes (Hellma) with path lengths of 1 mm or 10 mm. The reference for the measurements is either air, a quartz cuvette containing the same pure solvent or a clean glass sample mounted in an aluminum contact cell with a quartz window.

Steady-state photoluminescence spectra are recorded by a fluorescence spectrophotometer (Eclipse, Agilent). The data is typically collected with a step-size of 1 nm and a slit width of 5 nm of the excitation and emission monochromators. Thin film samples are placed in the excitation beam at an angle of $\theta = 45^\circ$ to avoid direct reflection of excitation light into the detector. Liquid samples are measured in 10 mm quartz cuvettes (Hellma) in a cuvette holder. The sensitivity of the detector and spectrograph depends on the wavelength. Therefore, a calibration curve is determined using reference dyes, such as Coumarin 466, Coumarin 153, DCM, Pyridin1 and Styryl 9M (all from Lambda Physik). Solutions of these dyes are prepared in ethanol (spectroscopic grade), and fluorescence spectra of these reference dyes are recorded. These are shown in Figure 2.4.1 (top panel).

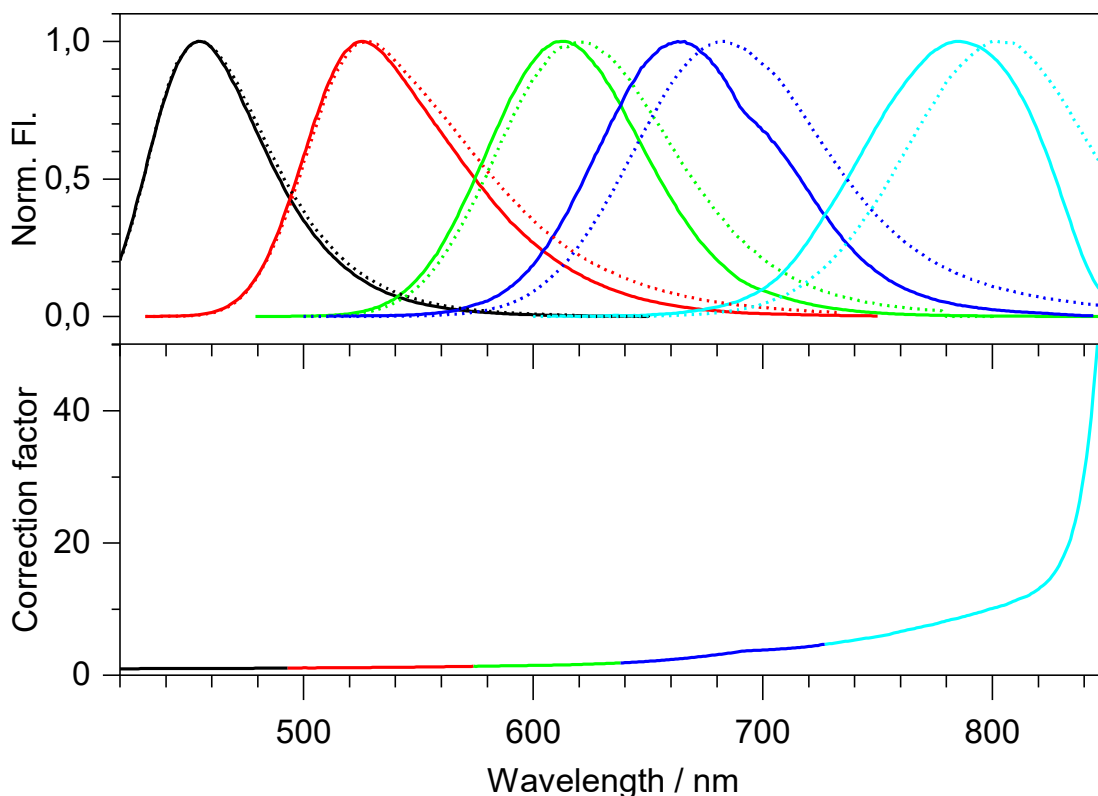


Figure 2.4.1. Steady-state fluorescence spectra of different dyes covering the wavelength region above 420 nm (top panel). The emission of each dye was recorded after excitation at the corresponding $0 \rightarrow 1$ transition. The dyes are Coumarin 466 (black), Coumarin 153 (red), DCM (green), Pyridin1 (blue) and Styryl 9M (light blue). The solid lines correspond to the experimental data, whereas the dotted lines are the respective data from reference.^[79] In the bottom panel, the resulting wavelength-dependent correction factor is shown in the same color code as the original data.

Emission spectra are obtained after excitation at the corresponding $S_0 \rightarrow S_1$ transition. A correction factor $C(\lambda)$ is calculated by comparison of the normalized measured fluorescence spectra $I_{\text{exp}}(\lambda)$ with reference spectra $I_{\text{lit}}(\lambda)$ taken from the literature.^[79]

$$C(\lambda) = \frac{I_{\text{lit}}(\lambda)}{I_{\text{exp}}(\lambda)} \quad (2.7)$$

Each spectrum is evaluated between the intersection points of the data sets, and the wavelength-dependent correction factor is determined.^[80] Each segment of the correction factor curve is then overlapped by appropriate scaling in the overlap regions.

2.4.2 Steady-state circular dichroism

A steady-state spectrometer (Chirascan, Applied Photophysics) is employed to collect the steady-state circular dichroism (CD) spectra. The spectral resolution is typically 1 nm at an acquisition time per point of 0.5 s. The monochromator bandwidth is either 1 nm or 0.1 nm. The detector voltage is set at “low” for CD signals above 4000 mdeg and at “high”

for the range 0–4000 mdeg. Prior to the measurement, a baseline is measured with a reference sample. Thin-film samples are cut to an appropriate size, mounted inside a home-made sample holder and placed into the cuvette compartment of the spectrometer perpendicular to the incoming probe beam.

Since February 2021 another instrument has been employed, which is based on a modification of the double-beam absorption spectrometer (Cary 5000, Varian). Circular dichroism spectra are obtained with a home-built add-on employing combinations of a polarizer and a quarter-wave plate for different spectral regions (Thorlabs WP25M-UB and AQWP05M-340 for 260–410 nm, Thorlabs LPVISE100-A and AQWP05M-580 for 400–700 nm). LCP and RCP light is generated by rotating the fast axis of the quarter-wave plate either +45 or –45 degrees with respect to the polarizer axis. Therefore, the transmission of the reference spectra (I_{ref}) and sample spectra (I_{sample}) are collected for LCP and RCP light without background correction. The wavelength-dependent CD spectra are calculated as:

$$\text{CD} = \text{OD}_{\text{LCP}} - \text{OD}_{\text{RCP}} = \log_{10} \left(\frac{I_{\text{ref}}}{I_{\text{sample}}} \right)_{\text{LCP}} - \log_{10} \left(\frac{I_{\text{ref}}}{I_{\text{sample}}} \right)_{\text{RCP}} \quad (2.8)$$

The spectral data from the two regions are combined and smoothed.^[74]

2.4.3 Circularly polarized luminescence

Circularly polarized luminescence (CPL) spectra are measured upon illumination at $\lambda = 365$ nm (full width at half maximum (FWHM) of 10 nm) of the thin film via a continuous-wave UV LED from Thorlabs (M365LP1). An UG 1 short pass filter (Schott) is placed in the excitation beam to narrow the spectral region of the excitation and remove parasitic emission of the LED at higher wavelengths. After illumination of the thin-film sample at an angle of $\theta = 45^\circ$, luminescence with either preferred LCP or RCP character is detected at an angle of 90° with a combination of a polarizer and a quarter-wave plate. The quarter-wave plate (Thorlabs AQWP05M-580) converts LCP or RCP portions of the emission to linear polarization, and a polarizer (Thorlabs LPVISE100-A) analyzes the intensity of the two linearly polarized components at an angle of +45 or –45 degrees with respect to the fast axis of the quarter-wave plate. The emission is focused into a fiber-optic cable with a diameter of 600 μm and guided through a 25 μm slit into a grating spectrograph (Avantes AvaSpec-Hero) containing a back-illuminated thermoelectrically cooled CCD array image sensor with 1024×58 pixels.^[74]

A calibration curve is determined using a NIST-traceable halogen light source from Avantes (Avalight-HAL-S-Mini2) operating in standard mode. The color temperature of the blackbody radiation is 2850 K. The irradiance spectrum of the calibration lamp is calculated based on Planck's law:

$$U(\nu, T) = \frac{8 \pi h \nu^3}{c^3} \frac{1}{\exp\left(\frac{h\nu}{kT}\right) - 1} \quad (2.9)$$

The calibration data file is stored in the AvaSoft software (Avantes) and relative irradiance data is internally corrected by the correction curve. The assignment of the individual pixels (P) to each wavelength ($\lambda(P)$) is provided by the instrument based on the following polynomial expression:

$$\lambda(P) = \text{Int} + X_1 P + X_2 P^2 + X_3 P^3 + X_4 P^4 \quad (2.10)$$

The parameters are intercept $\text{Int} = 2.943 \times 10^{16}$ and $X_1 = 7.844 \times 10^{13}$, $X_2 = -1.624 \times 10^9$, $X_3 = -7.566 \times 10^5$ and $X_4 = 0$.^[81] An example for the calibration procedure is shown in Figure 2.4.2.

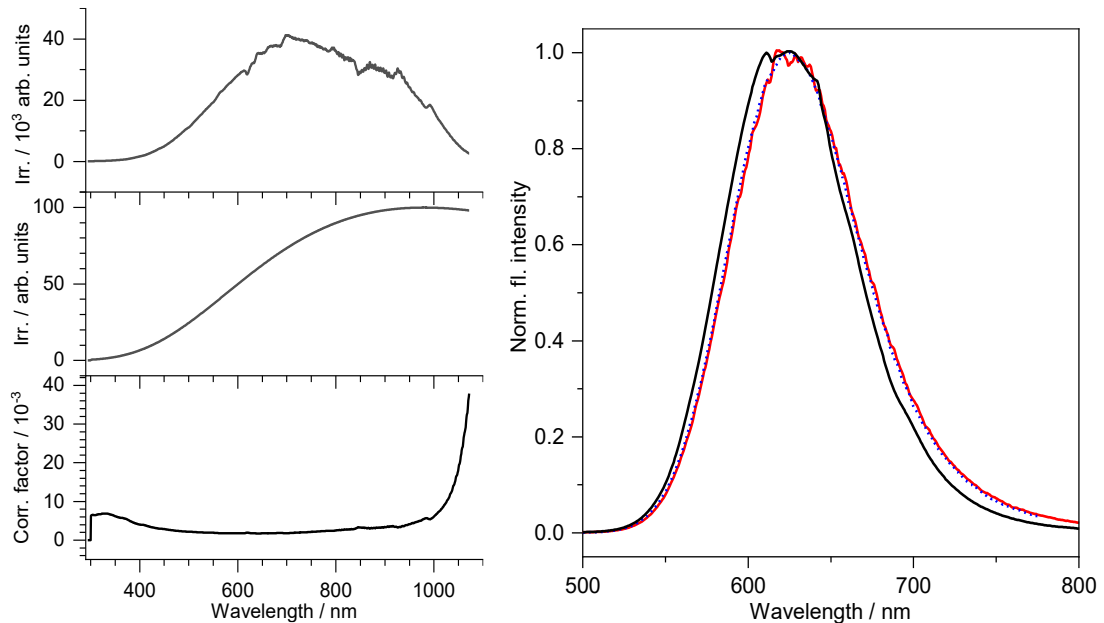


Figure 2.4.2 Calibration procedure of the Ava-Spec Hero spectrograph. Left: In the top panel, the raw irradiance spectrum of the calibration lamp Avalight-HAL-S-Mini2 is shown. The expected blackbody spectrum at a temperature of 2850 K is shown in the middle panel. The calculated wavelength-dependent correction factor is shown in the bottom panel. Right: An example for the correction of the emission spectrum of the dye DCM is given. The solid black line is the raw emission spectrum upon excitation at 365 nm. After applying the correction function, the result (solid red line) matches very well with the reported DCM calibration spectrum from reference^[79] (dotted blue line).

2.4.4 Time-correlated single photon counting

Time-correlated single photon counting (TCSPC) is performed with a spectrofluorimeter from Horiba Jobin-Yvon (TemPro) with 55 ps per channel time resolution.[J. Arden-Jacob, Phys. Chem. Chem. Phys., 2013] Thin-film samples are illuminated by a pulsed LED (Horiba Scientific NanoLED, 368 nm, FWHM of 12 nm, 1.1 ns pulse duration, 6.5 pJ per pulse; or 454 nm, FWHM 26 nm, 1.1 ns pulse duration, 3.2 pJ per pulse). The instrument response function (IRF) is measured with a scattering thin film of mesoporous TiO₂ deposited on a glass substrate. A 3 mm thick longpass filter (Schott GG395 or GG495) removes any unwanted scattering signal from the excitation beam. The intensity of the emission was adjusted by adding appropriate neutral density filters preventing saturation of the detector. The relative polarization of the excitation and the emission beam was at the magic angle (54.7°). Time constants and the respective amplitudes were determined by reconvolution of the data with the IRF.^[74,82]

An alternative setup to collect transient photoluminescence decays based on the TCSPC principle is also newly used in this thesis and is briefly described in the following. Here, photoexcitation is performed by a mode-locked titanium:sapphire femtosecond laser oscillator (Spectra-Physics Tsunami). The fundamental laser emission at 820 nm with a repetition frequency of 80 MHz and a pulse duration of 80 fs is frequency doubled to 410 nm. The power and polarization are adjusted by a combination of a Glan-Taylor polarizer (Karl Lambrecht, MGTYS10) and a half-wave plate (Alphas, PO-TWP-L2-25-UVIR). Depolarization of the laser beam is achieved by means of a Hanle depolarizer. The emission is collected at an angle of 90° with respect to the excitation beam through a wire-grid polarizer (Thorlabs WP25M-UB) at the magic-angle condition (54.7°). The light is collimated by a lens and sent through a bandpass filter with a center wavelength of 530 nm and FWHM of 10 nm (Thorlabs, FB530-10). Another lens refocuses the light onto a hybrid multialkali photodetector with a cathode diameter of 3 mm (Becker & Hickl, HPM-100-07). A TCSPC module (Becker & Hickl, SPC-130IN) is synchronized by the laser signal which is detected by a fast photodiode (Becker & Hickl, PHD-400-N-SET). Single-photon events are measured by the detector, with the TCSPC module operating in reversed start-stop configuration. Alternatively, a pulsed UV-LED (Becker & Hickl, UVL-FB-270) with 273 nm emission and 20 MHz repetition frequency is employed as the excitation source. It has a pulse width of 500 ps and its output is randomly polarized.

Time-resolved circularly polarized photoluminescence is collected with the addition of a quarter-wave plate (Thorlabs AQWP05M-580) in front of the polarizer in the

emission path, with its fast axis oriented at either +45 or −45 degrees with respect to the polarizer axis. The circularly polarized luminescence is detected by the difference of two separate measurements with identical data collecting times. An instrument response function is measured for a dilute suspension of colloidal silica nanoparticles (Merck, Ludox AM-40). The time constants and amplitudes are determined by tail fits of the photoluminescence decays using the FAST program (Edinburgh Instruments).

2.4.5 Optical light microscopy

2.4.5.1 Circular dichroism microscopy

Circular dichroism microscopy images of thin-film samples are taken with a modified inverted microscope (Olympus IX71). Light from a halogen lamp is sent through a broadband polarizer (Thorlabs LPVISE100-A), a quarter-wave plate (Thorlabs AQWP05M-580) and a condenser to generate either LCP or RCP light for sample illumination, depending on the angle of the fast-axis of the quarter-wave plate with respect to the polarizer axis. A microscope objective with 40 times magnification (Olympus LCPLFL, NA 0.60) collects the transmitted light, which is then guided through a bandpass filter with a center wavelength of 470 nm and an FWHM of 10 nm (Thorlabs FB470-10). The image is then refocused with a 1:1 matched achromatic doublet pair with equal focal lengths ($f_1 = f_2 = 100$ mm, Thorlabs MAP10100100-A). A non-polarizing beam splitter (Thorlabs CCM1-BS013/M) divides the signal into two parts in a 50:50 ratio. Simultaneously, a charge-coupled device (CCD) camera (PCO Sensicam QE) takes the images with a diffraction-limited resolution of about 500 nm, while the transmitted spectra are collected by a lens and guided through an optical quartz fiber with 600 μm core diameter to the grating spectrograph already mentioned above (Avantes AvaSpec-Hero). CD spectra are obtained by collecting the transmission of the sample and a glass reference for either +45° or −45° angle of the fast axis of the quarter wave-plate with respect to the polarizer axis (see eq. (2.8)).^[74]

2.4.5.2 Circularly polarized luminescence microscopy

CPL images of thin-film samples are recorded with the same microscope and detection setup as described in the previous chapter. Upon UV photoexcitation using a xenon lamp / monochromator combination (Till Photonics Polychrome 5000, 150 W, $\lambda_{\text{pump}} = 365$ nm, FWHM 14 nm), the emission of the sample is collected by the microscope objective. A

longpass filter (440 nm) removes any scattered emission of the excitation light source. LCP and RCP luminescence is analyzed by a combination of an achromatic broadband quarter-wave plate (Thorlabs AQWP05M-580) and a polarizer (Thorlabs LPVISE100-A) with either $+45^\circ$ or -45° angle of the fast axis of the quarter wave-plate with respect to the polarizer axis. The detection of the images and spectra over the entire field of view follows the same process of obtaining CD spectra and images as described in Chapter 2.4.5.1.^[74]

2.5 Chemicals

All chemicals are used as received. The compound c-PFBT was kindly provided by D. H. Choi and M. J. Cho from Korea University (Seoul, South Korea). The chiral helicene-like compounds 2,2'-dimethoxy-5,5',6,6'-tetrahydro-1,1'-bidibenzo-*[c,h]*acridine and the methylene bridged derivative bis-5,5',6,6'-tetrahydro-dibenzo-*[c,h]*acridino[1,1',2,2'-*d,f*]-[1,3]dioxepine were kindly provided by Dr. Laure Guy from the University of Lyon (France).

Table 2.5.1 Chemicals used in this work.

Chemical	Purity	Comments	Manufacturer / Provider
Acetone		technical grade	
Acetone	99.8%	p. a.	Fischer Scientific
Acetonitrile	>99.99%	Uvasol	Carl Roth
Atto390			Atto-TEC
Chlorobenzene	> 99%		Merck
Chlorobenzene	≥ 99.8%	anhydrous	Sigma-Aldrich
Chloroform	≥ 99.8%		Carl Roth
Coumarin 152A			Lambda Physik
Coumarin 153			Lambda Physik
Coumarin 466			Lambda Physik
c-PFBT		$M_n = 7.46$ kDa	Korea University
DCM			Lambda Physik
Ethanol	≥ 99.9%	p. a.	Merck
F8BT		$M_n \leq 25$ kDa, $M_w \leq 75$ kDa	Sigma-Aldrich
Ludox, SiO ₂		colloidal, 40 w% in water	Sigma-Aldrich
mCP	≥99.5%		Lumtec
Pyridin 1			Lambda Physik
Styryl9M			Lambda Physik
Tetrahydrofuran	≥ 99.9 %	Uvasol	Merck
Water		deionized	
(+)-2			University of Lyon
(-)-2			University of Lyon
(+)-3			University of Lyon
(-)-3			University of Lyon

c-PFBT: Poly({9,9-bis[(3*S*)-3,7-dimethyloctyl]fluorenyl-2,7-diyl}-*alt*-benzo[2,1,3]thiadiazol-4,8-diyl})

F8BT: Poly-[(9,9-di-*n*-octylfluorenyl-2,7-diyl)-*alt*-(benzo-[2,1,3]thiadiazol-4,8-diyl)]

mCP: 1,3-bis(*N*-carbazolyl)benzene

2: 2,2'-dimethoxy-5,5',6,6'-tetrahydro-1,1'-bidibenzo-*[c,h]*acridine

3: Bis-5,5',6,6'-tetrahydro-dibenzo-*[c,h]*acridino[1,1',2,2'-*d,f*]-[1,3]dioxepine

3. Ultrafast excited-state dynamics of thin films consisting of helicene-like molecules based on dibenzo[*c,h*]acridine

This chapter contains the publication:

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Ultrafast excited-state dynamics of thin films consisting of helicene-like molecules based on dibenzo[*c,h*]acridine

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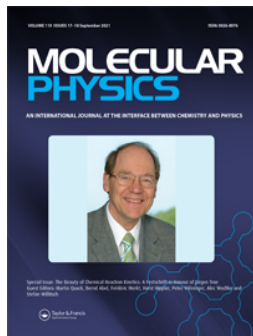
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The Electronic Supplementary Information is attached to the main article.

Statements for author contributions:

Marius Morgenroth (M.M.) is the first author of this publication and performed most of the experiments and manuscript preparation. He prepared all thin films and solutions containing the sample. The helicene-like molecules based on dibenzo[*c,h*]acridine were provided by L. Guy from the University of Lyon, France. M.M. characterized the films using steady-state absorption and luminescence spectroscopy. He performed all broadband transient absorption experiments in the Vis–NIR range for the thin films and solutions described in this publication. M.M. analyzed all pump–supercontinuum probe (PSCP) spectra for this manuscript. He performed the analysis of the recombination kinetics based on an approach implemented by K.O. and T.L. The PSCP setup and measurement program were significantly improved and expanded by M.S. All authors contributed to the manuscript. All authors discussed the results and provided detailed comments and suggestions for improvement, which were subsequently added.



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Ultrafast excited-state dynamics of thin films consisting of helicene-like molecules based on dibenzo[*c,h*]acridine

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ABSTRACT

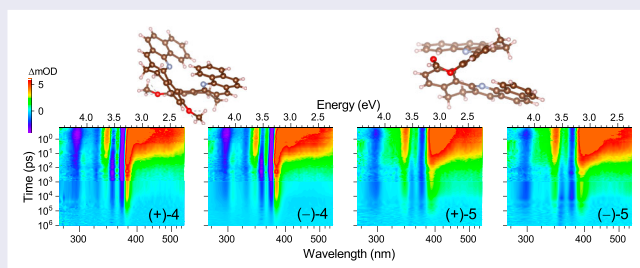
We investigated the excited-state dynamics of bridged and non-bridged chiral helicene-like bidibenzo[*c,h*]acridines deposited as a thin film. Broadband UV/VIS–NIR transient absorption spectroscopy from the femtosecond to the microsecond time-scale and transient fluorescence measurements were employed to understand the photoinduced processes in these organic thin-film layers. Photoexcitation at 370 nm populates the S_1 state, which has a lifetime of 15 and 36 ps for the non-bridged and bridged derivative, respectively. In both cases, the decay is governed by internal conversion (78% and 84%), whereas intersystem crossing represents only a smaller channel (21% and 15%), and the remaining 1% accounting for fluorescence. Fast repopulation of the S_0 state leads to the generation of hot ground state molecules (S_0^*), with characteristic finger-type transient absorption features. The T_1 state decays back to S_0 by intersystem crossing with a time constant of 775 and 5500 ps, respectively. Even at high excitation fluence, there are no indications for higher-order processes, such as singlet–singlet annihilation or Förster energy transfer. Photoexcitation also launches coherent acoustic phonons in these films, appearing as damped oscillations in the transient absorption kinetics on the red and blue edge of each S_0 absorption band, with a period of about 190 ps.

ARTICLE HISTORY

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KEYWORDS

Helicenes; laser spectroscopy; photophysics; chirality; thin films



1. Introduction

Helicenes [1] represent an important class of chiral molecules with potential applications in optoelectronic devices, such as OLEDs (organic light-emitting diodes) with circularly polarised emission [2–6]. Very often, fairly complex enantiopure synthesis pathways or elaborate purification steps are required [1,7,8], rendering it difficult to produce these compounds on a gram scale. However, recently the Guy group was able to establish a large-scale facile synthesis of enantiopure helicene-like molecules based on the dibenzo[*c,h*]acridine unit, which exhibit pronounced circularly polarised luminescence

(CPL) [9,10]. Chiral helicene derivatives have also shown considerable potential as additives for induced circular dichroism (ICD) [11–15], by inducing, for example, supramolecular chiral phases in achiral copolymer materials, such as poly[(9,9-dioctylfluorene-2,7-diyl)-co-(1,4-benzo-(2,10,3)-thiadiazole)] (F8BT). Giant ICD signals of up to 20,000 mdeg as well as large *g* factors for absorption and luminescence were obtained, for example, by adding chiral aza[6]helicene to F8BT [3,16,17].

When it comes to optoelectronic applications in organic thin films, a detailed knowledge of the intrinsic photophysical properties of the helicene-like molecules

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in the condensed phase is required. In addition, understanding the photophysics in this class of molecules is interesting by itself. Time-resolved laser-based pump–probe studies are particularly useful in this respect because they reveal electronic and/or structural relaxation processes in the excited state of these compounds.

Here, we investigate the photoinduced dynamics of chiral helicene-like molecules based on the dibenzo[*c,h*]acridine motif as thin films: two chiral 2,2'-dimethoxy-5,5',6,6'-tetrahydro-1,1'-bidibenzo[*c,h*]acridines denoted as (+)-4 and (–)-4, featuring a more flexible structure, and their corresponding, much more rigid, methylene-bridged analogues (+)-5 and (–)-5 (Figure 1), where the numbering of the structures refers to the notation of a previous paper from one of our groups [9]. There, a low fluorescence quantum yield of about 1% was identified for these systems [9]. In the current study, we aim at a detailed characterisation of the photoinduced processes in thin films of these helicene-like molecules using broadband transient absorption over the complete UV/VIS–NIR range (260–1600 nm) covering the femtosecond to the microsecond range in combination with transient fluorescence measurements.

2. Experimental methods

2.1. Preparation of chiral helicenes and thin films

The chiral helicene compounds were prepared as described previously [9]. Microscope glass slides (Duran Wheaton Kimble) were treated in soapy distilled water and afterwards in acetone in an ultrasonic bath for 30 min each. After drying with nitrogen, the glass slides were cut into dimensions appropriate for the spin coating apparatus. Subsequently, the slides were treated in a UV-C chamber (ELG100S, Dinies) for 15 min.

A 7.5 mg/mL precursor solution of each helicene compound was prepared in a mixture of chlorobenzene (> 99%, Merck) and chloroform (CHCl₃, ≥ 99.8%, Carl

Roth) at a ratio of 1:9 by volume. The solution was treated in an ultrasonic bath for 60 min and filtered through a polytetrafluoroethylene (PTFE) filter with 45 µm pore size using a syringe. The precursor solution was then spin-coated onto the glass slides at 500 rpm for 60 s in a nitrogen atmosphere with a humidity of less than 1% and subsequently annealed on a hot plate at 150°C for 15 min. We did not find any indication for thermal racemisation.

2.2. Steady-state optical spectroscopy

Steady-state absorption spectra of the thin films were recorded using a Varian Cary 5000 spectrophotometer using a slit width of 0.5 nm. Electronic circular dichroism (CD) spectra were measured using an Applied Photophysics Chirascan instrument. Steady-state photoluminescence and circularly polarised luminescence were recorded using a newly established setup: The unpolarised output of a continuous wave UV-LED (Thorlabs M365LP1, 365 nm centre wavelength), which was connected to a high-power LED driver (Thorlabs DC2200), was sent through a bandpass filter (Schott UG 1, 3 mm) to illuminate the thin film. Thin-film samples were mounted at an angle of 45° relative to the excitation light, with the substance side facing away from the detector. Fluorescence collected at a right angle first travelled through a zero-order achromatic broadband quarter-wave plate (Thorlabs AQWP05M-580, 350–850 nm) and a broadband polariser (Thorlabs LPVISE100-A). The fluorescence was then focused into a fibre-optic cable (UV/VIS–NIR, 600 µm diameter) attached to a spectrograph with a 1024 × 58 pixel back-illuminated and thermoelectrically cooled charge-coupled device (CCD) detector (Avantes AvaSpec-Hero, 25 µm slit width), which was (relatively) photometrically calibrated against a tungsten halogen reference lamp (Avantes Avalight-Hal-S-Mini2, blackbody radiation at 2850 K). CPL spectra were obtained by subtracting the emission spectra of two consecutive measurements (60 s integration time each) with the polariser axis set at either 0° or 90° and the fast axis of the quarter-wave plate fixed at 45°. Two measurement cycles were averaged for each compound. The whole setup was realised using a sturdy cage-mount system (Thorlabs) to minimise off-axis misalignment of the optical components [18].

2.3. Pump – supercontinuum probe (PSCP) spectroscopy

Ultrafast broadband transient absorption spectroscopy in the UV/VIS–NIR range (260–1600 nm) [19,20] was performed based on the pump – supercontinuum probe (PSCP) concept [21] at a repetition frequency of 920 Hz.

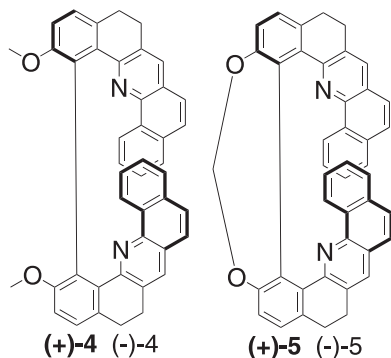


Figure 1. Molecular structures of the chiral helicene-like molecules 4 and 5.

For ultrafast experiments up to 1.5 ns with ca. 80 fs time resolution, the samples were excited at 460 nm using a wavelength of 370 or 355 nm. For measurements up to time scales of a few hundred microseconds with about 420 ps time resolution, excitation was performed at 355 nm by an electronically synchronised frequency-tripled Nd:YAG microlaser [22]. Thin films were mounted in a home-built contact cell [23] and constantly flushed by dry nitrogen. The samples were randomly moved over an area of $2 \times 2 \text{ mm}^2$ in the plane perpendicular to the probe laser beam using two linear piezo-driven translation stages. Transient spectra were modelled by global kinetic analysis [24,25] using the kinetic scheme discussed below. The shape of the species-associated spectra (SAS) was represented by a set of Gaussian functions with variable position, width and height. These were optimised during the fitting procedure, except for the known steady-state ground state absorption spectrum.

2.4. Time-correlated single-photon counting

Transient fluorescence decays of the helicene samples were recorded by time-correlated single-photon counting (TCSPC) using a Horiba Jobin-Yvon TemPro system (55 ps/channel) [26]. The thin films were photoexcited at 1 MHz repetition frequency using a UV-LED (Horiba Scientific NanoLED, 368 nm, full width at half maximum (FWHM) 12 nm, pulse duration 1.1 ns, $6.5 \text{ pJ pulse}^{-1}$). The instrument response function (IRF) was measured using a TiO_2 thin film. The stray light of the excitation beam was cut off by a longpass filter (Schott GG395, 3 mm thick). Time constants and amplitudes were obtained by a deconvolution procedure using the measured IRF.

3. Results and discussion

3.1. Steady-state absorption, circular dichroism and luminescence spectroscopy

Prior to discussing the time-resolved dynamics, we would like to provide an overview of the steady-state optical properties of these systems. The absorption and fluorescence spectra of the thin films for compounds (+)-4/(−)-4 and (+)-5/(−)-5 are displayed in Figures 2(a) and 3(a), respectively. Representative photographs of the highly transparent thin film samples with very low optical scattering are shown in the inset of the bottom panel. The $S_0 \rightarrow S_1$ absorption band of compound 4 (with predominantly $\pi-\pi^*$ HOMO–LUMO excitation [9]) shows a pronounced vibrational structure with fairly sharp peaks at 369 and 351 nm. These are assigned to the $0' \leftarrow 0$

and $1' \leftarrow 0$ transitions, with a spacing of 1390 cm^{-1} . The larger intensity of the $0' \leftarrow 0$ transition suggests a similar geometry of the ground and excited electronic states. The vibrational structure of the bridged compounds (+)-5 and (−)-5 is similar, however, the two vibronic peaks are substantially broadened and red-shifted (372 and 354 nm). Previous calculations using density functional theory (DFT) have shown that for the isolated non-bridged compound 4 up to three conformers exist at room temperature, whereas for the bridged compound 5 only a single conformer is preferred, which exhibits significant $\pi-\pi$ stacking, and consequently a smaller helical pitch and a longer effective conjugation length (which is responsible for the red shift) [9]. Compound 5 shows a significantly broadened vibronic structure, despite the smaller number of conformers, and a probably more regular, possibly columnar [27], arrangement in the film. We, therefore, suspect that the substantially larger π -stacking contributions in compounds (+)-5 and (−)-5 lead to more pronounced excitonic contributions to the spectrum, which could explain the increased spectral broadening [28]. The peak of the fluorescence spectrum is located at 433 nm for compound 4, resulting in a Stokes shift of 0.497 eV, the corresponding values for the bridged compound 5 are 427 nm and 0.431 eV, respectively. The smaller Stokes shift in the case of compound 5 is likely related to its more rigid structure.

Panels b and c of Figures 2 and 3 show the CD and CPL spectra as well as the corresponding g_{abs} and g_{lum} values of the two thin films. The dissymmetry factor g_{abs} for the absorbance is defined as

$$g_{\text{abs}} = \frac{2(A_{\text{LCP}} - A_{\text{RCP}})}{A_{\text{LCP}} + A_{\text{RCP}}} \quad (1)$$

Here, A_{LCP} and A_{RCP} are the decadic absorbances of the sample for left and right circularly polarised light, respectively. Correspondingly, the dissymmetry factor g_{lum} for the photoluminescence is given as

$$g_{\text{lum}} = \frac{2(I_{\text{PL,LCP}} - I_{\text{PL,RCP}})}{I_{\text{PL,LCP}} + I_{\text{PL,RCP}}} \quad (2)$$

In this case, $I_{\text{PL,LCP}}$ and $I_{\text{PL,RCP}}$ denote the intensities of the left and right circularly polarised photoluminescence, respectively (see Figures S1–S4 in the Supporting Online Material for the corresponding photoluminescence spectra). Despite the comparable peak absorbance, compounds (+)-5 and (−)-5 exhibit a substantially larger CD response close to the peak of the absorption band (absolute value 120 mdeg) with a substantial $|g_{\text{abs}}| > 10^{-2}$ in contrast to (+)-4 and (−)-4 (absolute value 17 mdeg, $|g_{\text{abs}}| = 10^{-3}$). The considerably weaker CD response of compound 4 was previously

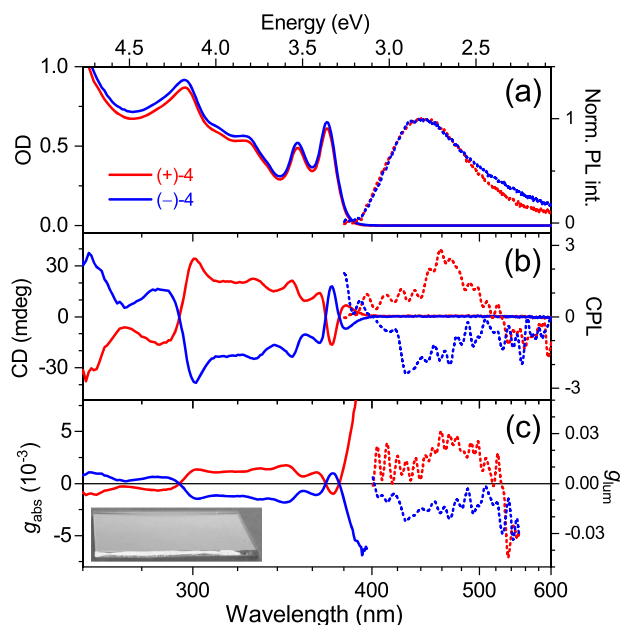


Figure 2. (a) Steady-state absorption (solid lines) and luminescence (dotted lines) spectra, (b) CD (solid lines) and CPL spectra (dashed lines), and (c) g_{abs} (solid lines) and g_{lum} (dashed lines) values for the compounds (+)-4 (red) and (-)-4 (blue). The inset in panel c shows a photograph of a thin film for compound (+)-4. The highly transparent and very low-scatter thin-film layer is only visible at oblique incidence due to its difference in reflectance compared with glass.

explained in terms of closely spaced transitions to different excited electronic states with CD contributions of opposite sign and different CD contributions of the different conformers [9]. It is important to note that, beside the slight red-shift also observed in the absorption spectrum, the measured CD response is similar to that in solution. This indicates that these two helicene-like molecules do not form extended supramolecular chiral arrangements, in contrast, for example, to cholesteric liquid crystals of optically active copolymers [29].

3.2. Time-resolved fluorescence experiments on the thin films

Figure 4 shows transient emission kinetics after excitation at 368 nm for thin films of the compounds (+)-4 and (-)-5 in panels a and b, respectively. The kinetics are dominated by an ultrafast decay component (< 70 ps (99.3%) for compound 4 and < 160 ps (94.5%) for compound 5), which are both within the time resolution of the TCSPC setup. Taking this result together with the known fluorescence quantum yield from solution (0.6% and 1.4%) [9], this already suggests that for both compounds the decay of S_1 must be dominated by ultrafast nonradiative processes. The question regarding the individual contributions of internal conversion (IC) and

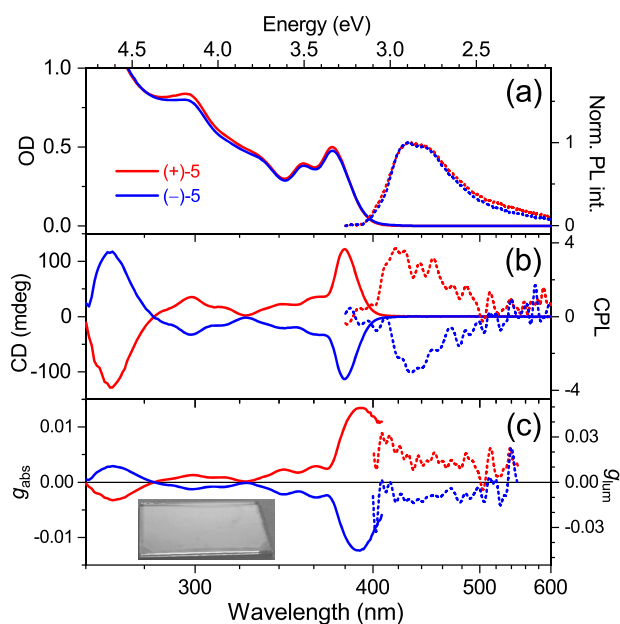


Figure 3. (a) Steady-state absorption (solid lines) and luminescence (dotted lines) spectra, (b) CD (solid lines) and CPL spectra (dashed lines), and (c) g_{abs} (solid lines) and g_{lum} (dashed lines) values for the compounds (+)-5 (red) and (-)-5 (blue). The inset in panel c shows a photograph of a thin film for compound (-)-5.

intersystem crossing (ISC) will be addressed below when the results of the broadband transient absorption results are discussed in detail. In the TCSPC transients, there are also two minor long-lived components with time constants of about 1.2 and 5.5 ns. The weak 1.2 ns component could be due to some slow reverse intersystem crossing (RISC) from T_1 back to S_1 , which would however require a small (on the order of $k_B T$) energy difference between T_1 and S_1 . Other possibilities could be the formation of an excimer species with low quantum yield or the presence of a small fluorescent impurity (below the detection limit of the NMR experiments). Currently, we cannot decide between these different options, because, for example, in the transient absorption experiments reported below such minority species will be totally overwhelmed by the spectral contributions of the transient main excited species (S_1 , T_1 and vibrationally hot ground state molecules S_0^*) of compounds 4 and 5.

3.3. Broadband transient absorption spectra and their global kinetic analysis

Transient absorption experiments were carried out from the femtosecond to the millisecond time scale to understand the photoinduced dynamics of these helicene-like compounds in detail. The transient absorption response

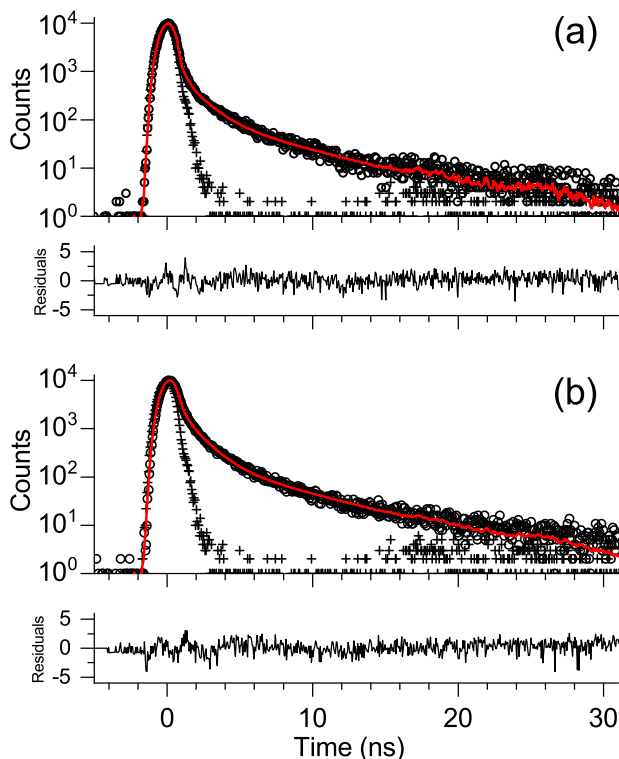


Figure 4. Time-resolved fluorescence decays (open circles) of (a) (+)-4 and (b) (–)-5 obtained from TCSPC measurements after photoexcitation at 368 nm. The red lines are triexponential fits convolved with the instrument response function (shown as crosses). Residuals of the fits are displayed in each case. Fit parameters are provided in Table 1.

for the respective enantiomeric pairs (+)-4 and (–)-4 as well as (+)-5 and (–)-5 provided (as expected) identical dynamics. Therefore, in the following, we will focus on the results for the (+)-enantiomers only. Transient UV/VIS–NIR spectra for the less rigid compound (+)-4 are shown in Figure 5, and the accompanying species-associated spectra (SAS) and spectral fits from the global kinetic analysis are presented in Figure 6. Time constants and quantum yields are summarised in Table 1. We modelled the data based on the following kinetic scheme with branching from the first excited singlet state (S_1) populating both the T_1 triplet state and the vibrationally hot ground electronic state S_0^* :

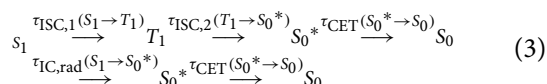


Figure 5(a) shows the early-time dynamics around zero time delay. We observe the build-up of a ground state bleach (GSB) feature below 390 nm, with characteristic peaks which resemble the inverted steady-state absorption spectrum (dashed blue line in panel d). Above 390 nm we find a very broad excited-state absorption

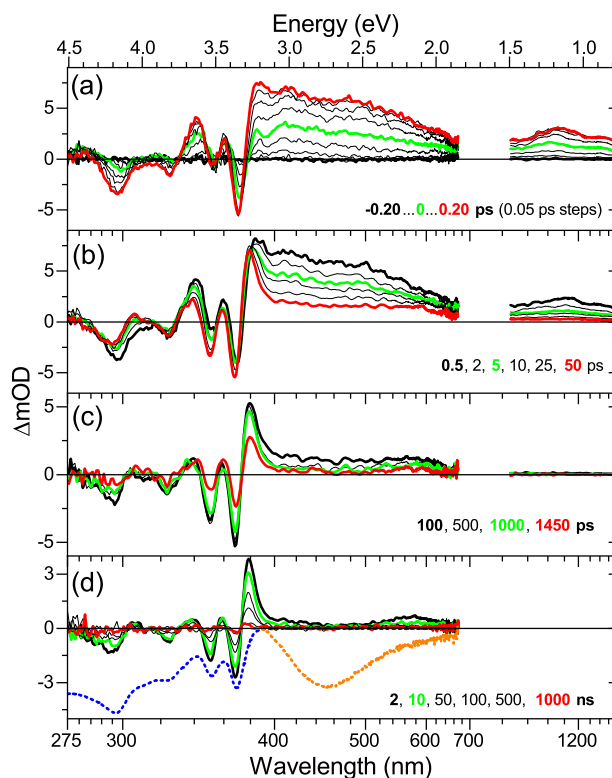


Figure 5. UV/VIS–NIR broadband transient absorption spectra of a thin film of compound (+)-4. (Panels a–c) Ultrafast time scale up to 1.45 ns after photoexcitation at 370 nm (80 fs time resolution), (d) Time scale up to 1 μ s after photoexcitation at 355 nm (420 ps time resolution). Spectra at selected delay times are highlighted by different colours. The inverted steady-state absorption spectrum and the steady-state stimulated emission spectrum are shown in panel d as a dashed blue and a dashed orange line, respectively. ΔmOD on the ordinate denotes the difference (divided by 10^{-3}) in optical density (OD), that is, the difference in absorbance, between the spectra obtained with and without the pump beam.

(ESA) band which extends into the NIR up to 1600 nm and also has positive spectral contributions in the UV region below 365 nm (green SAS in Figure 6(a)). It is assigned to the initially populated S_1 state. We do not see any indications for stimulated emission (SE) from S_1 , which would appear as a negative band with a peak around 440 nm (dashed orange line in panel d). This SE band is likely overwhelmed by the strong ESA contribution in this spectral region resulting in a net absorption.

In panel b, which contains the spectral development between 0.5 and 50 ps, we see the decay of the broad Vis–NIR S_1 ESA band accompanied by a corresponding decay of the UV GSB band in the range 295–310 nm. According to the global kinetic analysis, this decay with a time constant of 15 ps (consistent with the upper limit provided by the complementary TCSPC experiments) leads to the formation of two species: One of them shows a characteristic ‘finger structure’ in the

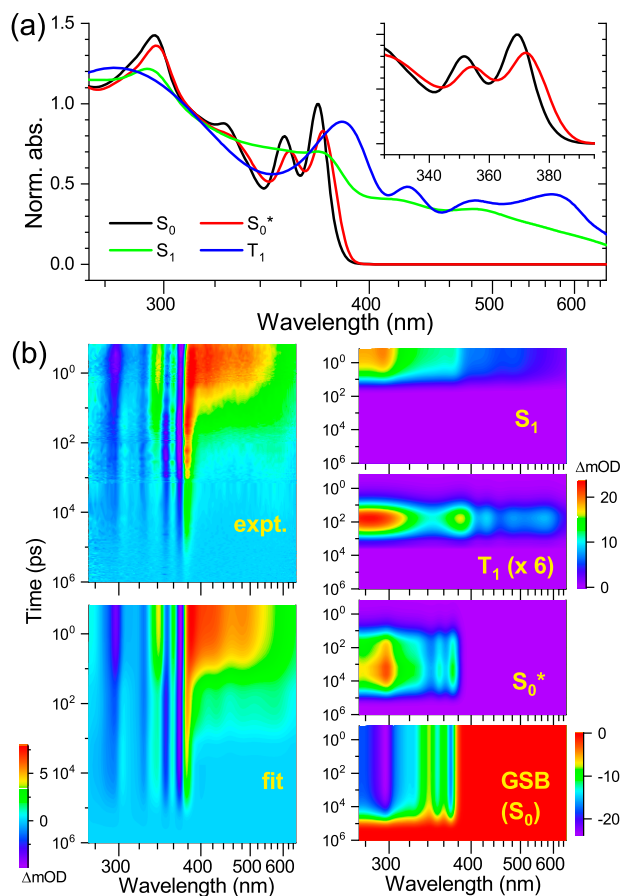


Figure 6. Global kinetic analysis for the UV/VIS transient broadband absorption spectra of the thin film of helicene-like compound (+)-4. (a) Species-associated spectra (SAS) from the global kinetic analysis for the species S_1 (green line), T_1 (blue line), S_0^* (vibrationally hot singlet state, red line) and S_0 (ground state absorption, black line), normalised at the longest-wavelength peak of the S_0 absorption spectrum. The inset highlights the difference between the S_0^* and S_0 species. (b) Left: Contour plots of the experimental transient absorption spectra (top) and the simulated transient absorption spectra based on the global kinetic analysis (bottom). Right: Contour plots highlighting the importance of different species in different time regimes. Note the logarithmic time axis.

range 330–400 nm. The pronounced absorption band at 379 nm is located on the red wing of the steady-state absorption spectrum, and two additional weaker absorption peaks remain at 339 and 359 nm, where the steady-state absorption has minima (dashed blue line in panel d). At the same time, the bleach peaks at 350 and 368 nm become even more pronounced. This spectral signature is a hallmark of vibrationally hot S_0^* molecules in the ground electronic state, as, for example, demonstrated for organic molecules in solution, such as azulene, anthracene and carotene derivatives [24,30–33]. It is also reflected in the results of the global kinetic analysis in Figure 6(a) (inset), where the hot S_0^* spectrum (red)

Table 1. Results of time-resolved fluorescence and broadband transient absorption experiments for the helicene-like compounds 4 and 5.

Quantity	Compound 4	Compound 5
TCSPC		
τ_1 (ps)	70 ^a	160 ^a
A_1 (%)	99.3	94.5
τ_2 (ns)	1.21	1.17
A_2 (%)	0.6	5.2
τ_3 (ns)	5.42	5.53
A_3 (%)	0.1	0.3
Transient absorption		
$\tau_{ISC,1}(S_1 \rightarrow T_1)$ (ps)	73	236
$\tau_{IC,rad}(S_1 \rightarrow S_0^*)$ (ps)	19	43
$\tau(S_{1,total})$ (ps)	15	36
$\Phi_{ISC,1}$ (%)	21	15
$\Phi_{IC} + \Phi_{rad}$ (%)	79	85
$\tau_{ISC,2}(T_1 \rightarrow S_0^*)$ (ps)	775	5500
$\tau_{CET}(S_0^* \rightarrow S_0)$ (ns)	65	56
$\Phi_{rad}(S_0^*)$ (%) ^b	0.6	1.4
$\tau_{rad}(S_1 \rightarrow S_0^*)$ (ns) ^b	2.5	2.6
$\Phi_{IC}(S_1 \rightarrow S_0^*)$ (%) ^b	78.4	83.6
$\tau_{IC}(S_1 \rightarrow S_0^*)$ (ps) ^b	19	44

^aValues represent upper limits to the true value (width of the IRF about 1.1 ns).

^bFluorescence quantum yields in solution from Ref. [9]. Quantum yields for fluorescence and IC as well as the radiative and IC lifetimes estimated based on these values.

is broader, has smaller minima than the ‘cold’ S_0 spectrum (black) and is also slightly red-shifted. These hot S_0^* molecules are directly formed by IC from the S_1 state. In addition, already in Figure 5(b) we see a long absorption pedestal extending up to 600 nm. This feature cannot be explained by the absorption of hot ground state molecules, because it is too far away from the S_0 absorption region. The only reasonable explanation for this band is the formation of the T_1 triplet state from S_1 , competing with the IC process (and also fluorescence, see below).

In Figure 5(c), covering the time range up to 1450 ps, a decay of all bands is observed, which is due to an overlap of beginning vibrational cooling of S_0^* and ISC from T_1 to S_0^* . By 1450 ps, the red spectrum exhibits a more clearly separated triplet absorption band with a peak at about 575 nm. To cover much longer time scales up to the millisecond range, additional experiments were carried out using excitation by an Nd:YAG microlaser at 355 nm (third harmonic), which was synchronised electronically with the supercontinuum probe beam of the femtosecond laser system. Representative transient spectra from 2 up to 1000 ns are displayed in Figure 5(d). One observes that the triplet band at 575 nm decays much faster than the vibrational ‘hot band’ at 379 nm. The resulting time constant for ISC is 775 ps, and the cooling of S_0^* is well described by a time constant of 65 ns. This very slow cooling process is interesting by itself because collisional energy transfer (CET) of highly vibrationally excited S_0^* molecules in organic solvents or supercritical fluids typically occurs on the picosecond to several ten picosecond

time scale [24,30–33]. However, here we have the special situation, that the bath surrounding the vibrationally hot helicene-like molecules consists of the same molecules, which are initially at room temperature. As a result, while the hot molecules lose their excess energy, they heat up other, chemically identical molecules. Therefore, the excess energy stays in the thin film layer and can only be dissipated by heat transfer (acoustic phonon relaxation) to the underlying glass substrate. The observed time scale on the order of several 10 ns is reasonable and consistent with, for example, slow acoustic phonon relaxation in thin films [22].

We note that the accuracy of the branching ratio between the T_1 and S_0^* channel from the global kinetic analysis is not particularly high, because a smaller (larger) branching ratio for triplet formation can be compensated to a certain extent by a larger (smaller) absorption coefficient of the triplet SAS. In the current case, we assumed that the absorption coefficient of the T_1 state above 400 nm should be similar to that of the S_1 state. This procedure is supported by the fact that allowed $S_1 \rightarrow S_n$ and $T_1 \rightarrow T_n$ transitions in the same molecule very often have similar oscillator strengths, see, for example, all-*trans* retinal [34] or the small organic hole-transport material H101 as example cases [25]. Therefore, we arrive at the blue triplet SAS in Figure 6(a). For instance, a reduction of the T_1 quantum yield from 21% (Table 1) to 10% would require an about twice as large absorption coefficient of the blue SAS in Figure 6(a), which would be already unrealistic from a photophysical standpoint. We, therefore, roughly estimate the error bars for the triplet quantum yield as $(21 \pm 10)\%$. Higher accuracy could be perhaps achieved using a separate triplet sensitisation experiment in solution employing, for example, benzophenone to determine the absolute absorption coefficient of T_1 [35]; however, this is also not trivial, because UV excitation of the triplet sensitizer will at the same time also excite the helicene-like molecule (with strong absorption in the same wavelength range), so the correlation between the GSB region and the triplet absorption in such an experiment might not be unique. Having estimated the triplet quantum yield as $\Phi_{ISC,1} = 21\%$, the combined quantum yield for IC and fluorescent radiative decay must be $\Phi_{IC,rad} = 79\%$. Using the independently measured quantum yield $\Phi_{rad} = 0.6\%$ from the experiments of Guy et al. [9], we arrive at a quantum yield for internal conversion of $\Phi_{IC,rad} = 78.6\%$ and a time constant for the radiative decay of $\tau_{rad} = 2.5$ ns.

A comparison of the experimental and optimised simulated spectra for compound (+)-4 is provided in Figure 6(b) as contour maps (left side), highlighting the very good fit to the data. Fits to selected kinetic traces including species contributions are provided in Figures

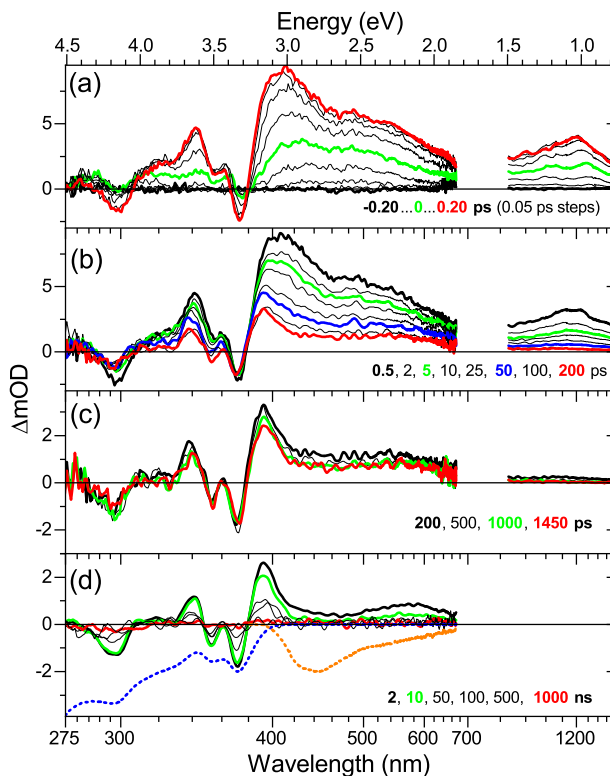


Figure 7. UV/VIS–NIR broadband transient absorption spectra of a thin film of compound (+)-5. (Panels a–c) Ultrafast time scale up to 1.45 ns after photoexcitation at 370 nm (80 fs time resolution), (d) Time scale up to 1 μ s after photoexcitation at 355 nm (420 ps time resolution). Spectra at selected delay times are highlighted by different colours. The inverted steady-state absorption spectrum and the steady-state stimulated emission spectrum are shown in panel d as a dashed blue and a dashed orange line, respectively. ΔmOD on the ordinate denotes the difference (divided by 10^{-3}) in optical density (OD), that is, the difference in absorbance, between the spectra obtained with and without the pump beam.

S5 and S6 of the Supporting Online Material. On the right side of Figure 6(b), we see four additional contour plots describing, on which time scales the individual species mainly contribute. We also clearly see that S_0^* and T_1 are populated in parallel from S_1 , and that ISC from T_1 is much faster than vibrational cooling of the S_0^* species.

A similar investigation was carried out for the more rigid compound (+)-5. Respective transient UV/VIS–NIR spectra are provided in Figure 7, and the SAS and fit results from the global kinetic analysis are compiled in Figure 8. The same kinetic scheme as for compound (+)-4 was employed, and the resulting time constants and quantum yields are summarised in Table 1. Fits to selected kinetic traces including species contributions can be found in the Supporting Online Material (Figures S7 and S8).

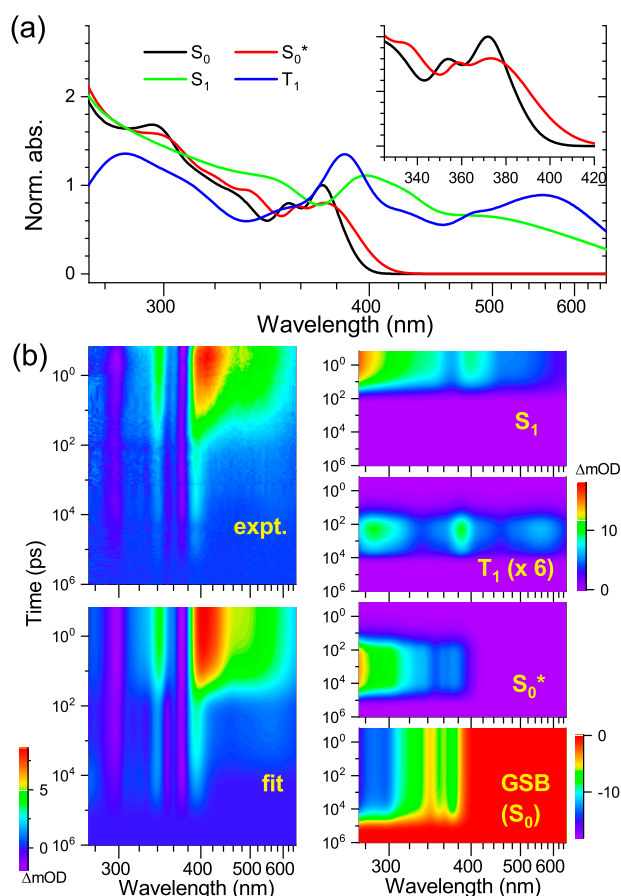


Figure 8. Global kinetic analysis for the UV/VIS transient broad-band absorption spectra of the thin film of helicene-like compound (+)-5. (a) Species-associated spectra (SAS) from the global kinetic analysis for the species S_1 (green line), T_1 (blue line), S_0^* (vibrationally hot singlet state, red line) and S_0 (ground state absorption, black line), normalised at the longest-wavelength peak of the S_0 absorption spectrum. The inset highlights the difference between the S_0^* and S_0 species. (b) Left: Contour plots of the experimental transient absorption spectra (top) and the simulated transient absorption spectra based on the global kinetic analysis (bottom). Right: Contour plots highlighting the importance of different species in different time regimes. Note the logarithmic time axis.

The evolution of the UV/VIS–NIR transient absorption spectra of compound (+)-5 in Figure 7(a–d) is quite similar to that of compound (+)-4, however with several distinct differences. First of all, the GSB features at 307 and 353 nm are much broader, consistent with the broader inverted steady-state absorption spectrum (dashed blue line in panel d). Moreover, the decay of the S_1 state (green SAS in Figure 8(a)) is much slower (36 instead of 15 ps), as can be directly seen upon the comparison of panel b in Figures 7 and 5. As for compound (+)-4, we clearly see the ‘finger structure’ below 420 nm, characteristic for S_0^* , and the separate T_1 absorption around 575 nm (blue SAS in Figure 8(a)). As a result

of the broader S_0 spectrum, the corresponding spectrum of S_0^* is also further broadened and red-shifted, as for compound (+)-4 (Figure 8(a), black and red lines, respectively). The quantum yield for triplet formation of 15% is comparable to that for compound (+)-4, with a similar estimated error limit of roughly $\pm 10\%$. Cooling of the S_0^* species by CET is again much slower (56 ns) than ISC from T_1 to S_0 . The contour plots in Figure 8(b) show the very good agreement of the global kinetic fit with the experimental transient spectra (left side) and the contributions of the different species are highlighted in the contour diagrams on the right. Comparing the relaxation of both compounds, the slightly slower S_1 decay of compound 5 is likely connected to its more rigid structure. If, for example, vibrational movement is required in finding a conical intersection for internal conversion to S_0^* , it can likely be reached faster in the more flexible compound 4.

We note that attempts to apply our recently implemented setup for transient circular dichroism (TrCD) spectroscopy [29] to these films have not been successful so far, because the transient signals of these films are probably below the current detection limit. Based on the maximum amplitude of the steady-state CD spectra (about 100 and 30 mdeg for compound 4 and 5, corresponding to 3 and 1 mOD, respectively), we would expect for a degree of excitation of 10% a peak signal of less than 0.3 mOD (0.1 mOD for compound 5), which is likely within the noise level of the current setup.

3.4. Fluence dependence of transient absorption spectra

To exclude any competing higher-order processes, such as singlet–singlet annihilation (SSA, via a diffusive bimolecular mechanism $S_1 + S_1 \rightarrow S_n + S_0$ [36] or non-radiative Förster energy transfer ($S_1 \rightarrow S_0$ accompanied by $S_1 \rightarrow S_n$) [37,38]), which may occur in thin films with closely packed molecules [15], we performed a systematic study of the fluence dependence of the transient absorption spectra for compound (+)-4. These processes should manifest themselves, for example, in a considerably accelerated decay at high pump fluence at early delay times, where because of the increasing initial concentration the distance between two S_1 species becomes smaller and smaller. One of the S_1 species involved in the process could then relax back to S_0 , thereby considerably accelerating the recovery of the ground electronic state, and the other species would be promoted to a higher S_n state [15]. In addition, distinct changes in the spectral shape could occur, arising, for example, from the S_n species formed as intermediates, or because new species are generated by consecutive reactions, such as charge-transfer

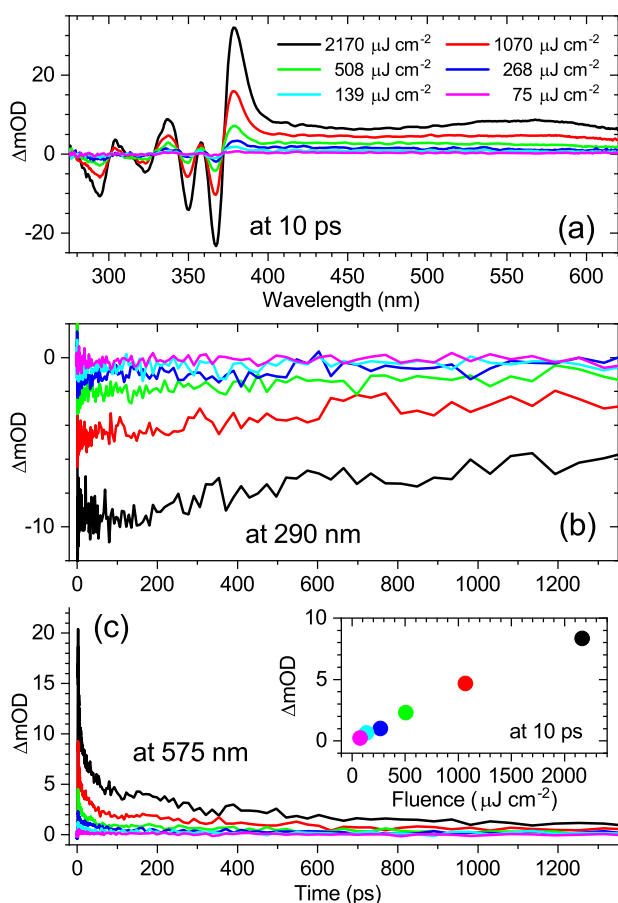


Figure 9. Fluence dependence of transient absorption signals for compound (+)-4. (a) Transient spectra at 10 ps for the fluences indicated. (b) and (c) Kinetics at 290 and 575 nm, respectively. The inset in (c) shows an example for the linearity at 10 ps.

or electron–hole pair states [15,39]. However, as demonstrated in Figure 9, the spectra and kinetics recorded for a change of pump fluence by a factor of 30 did not find any indications for such processes. This linearity is clearly observed in the representative transient spectra at 10 ps (panel a) and the kinetics at 290 and 575 nm (panels b and c, respectively). The inset in panel c shows the linearity at 10 ps and 575 nm. Only a slight levelling-off is observed at the highest fluence, which is likely due to a beginning saturation of one-photon excitation at the cost of increasingly important two-photon excitation processes.

The good linearity is likely due to the fact that we are dealing here with small molecular species, where hopping of the initial excitation to other neighbouring molecules (as, for example, required for the bimolecular SSA mechanism) has a much higher activation barrier than, for example, in conjugated copolymer chains, such as polyfluorene derivatives [15]. There, the initial excitation can be more easily delocalised along the polymer chain, and, therefore, an appropriate partner for the SSA or Förster processes is more easily found.

3.5. Coherent acoustic phonons propagating in the thin film

Upon closer inspection of the transient absorption kinetics, we recognised oscillatory features on the kinetics in specific regions of the steady-state absorption spectrum. This effect is highlighted in Figure 10 for a thin film of compound (+)-4. Figure 10(a) shows the steady-state absorption spectrum (black) and its first derivative (red). Particularly strong oscillations were observed in spectral ranges, where the first derivative has extrema, that is, at the point of steepest slope on the long-wavelength and short-wavelength wings of each absorption band. The corresponding kinetics after photoexcitation with 50 fs pulses at 355 nm at four representative wavelengths, as indicated by the coloured circles on the derivative in panel a, are shown in Figure 10(b). In each case, the kinetic traces were fitted by a sum of a biexponential function and a damped cosine function with a frequency of 5.24 GHz (corresponding to a vibrational period of 191 ps) and a damping time constant of 315 ps,

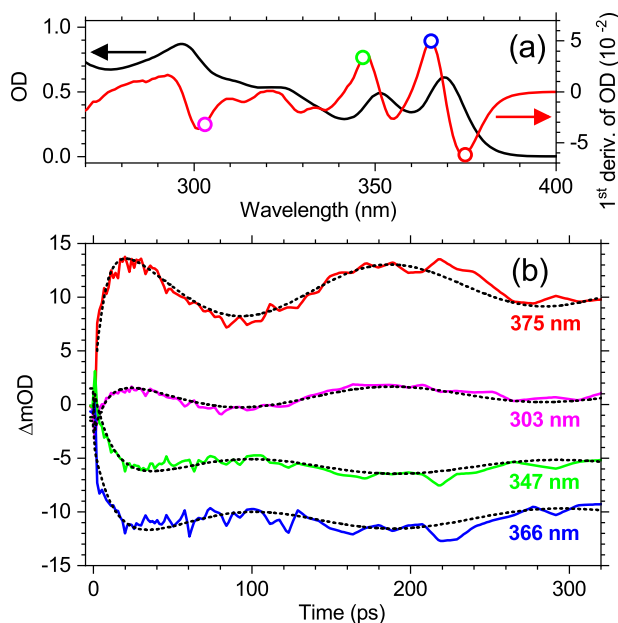


Figure 10. Coherent acoustic phonon dynamics of a thin film of compound (+)-4 after excitation at 355 nm. (a) Steady-state absorption spectrum (black line) and its first derivative (red line). Coloured open circles on the line of the first derivative indicate the positions of probe wavelengths of the kinetics shown in b. (b) Oscillatory kinetics at different probe wavelengths. Note the phase shift of π for the oscillations on the red wings (375 and 303 nm) relative to those on the blue wings (366 and 347 nm) of the absorption bands. Note that in each case 5–7 kinetics in an interval of 1.5–2.5 nm were averaged to arrive at a higher signal-to-noise ratio. Black dotted lines are best fits using a sum of a biexponential function and a damped cosine function with an acoustic phonon frequency of 5.24 GHz and a damping time constant of 315 ps.

as indicated by the black dotted lines. We observed a phase shift of π for the oscillations on the red wings (375 and 303 nm) relative to those on the blue wings (366 and 347 nm) of the absorption bands. This indicates a periodic spectral shift of all absorption bands, which gives rise to an increase of absorption on the red edge, whereas at the same time there is a concomitant decrease in absorption on the blue edge of each band.

The reason for the slow oscillations can be understood as follows: Excitation by the 355 nm pump pulse induces a longitudinal sound wave (strain pulse), which then propagates through the organic thin film and is reflected back and forth between the two interfaces, that is, organic film/air and organic film/glass [40]. This gives rise to a periodic change in the transient absorption signal [41,42]. The weak dampening of the oscillation occurs, because part of the wave propagates into the underlying substrate upon each pass, whereas reflection at the organic film/air interface is essentially lossless because of the large mismatch of the acoustic impedances [29]. The periodic shift of the absorption band likely arises from acoustic phonon emission due to the deformation potential [40] arising from the sudden changes in bond distance and electron distribution upon photoexcitation, effectively leading to a 'local pressure increase', which is responsible for the initial red-shift of each band. In addition, the aforementioned fast electronic relaxation processes of the helicene-like molecules, such as IC to S_0 , lead to a substantial local heating on a picosecond time scale. This gives rise to an expansion of the thin film, also generating an acoustic phonon [40,43], which modulates the transient absorption signal.

4. Conclusions

In the current study, we obtained a comprehensive picture of the photoinduced dynamics of two chiral helicene-like molecules based on the dibenzo[*c,h*]acridine motif. Upon photoexcitation to the S_1 state of the unbridged and bridged helicene-like compound, depopulation of the S_1 state is fast (< 50 ps), the main depopulation channel being IC leading to the production of hot ground state molecules (S_0^*), with about 80% quantum yield, whereas triplet formation is mainly responsible for the remaining 20%. Bridging of the two dibenzo[*c,h*]acridine units reduces the Stokes shift and slows down the S_1 decay slightly, which is likely the result of its more rigid structure. The T_1 state, with a characteristic band at 575 nm, decays on time scales longer than 500 ps.

With regard to potential applications of these molecules for chiral induction in copolymer host materials [3,15–17], in particular, for potential applications in

chiral OLED devices [3,4], the absence of visible absorption bands in these helicene-type molecules is certainly advantageous, as there will be no overlap with emission bands of the host material, even if a larger concentration of the chiral dopant would be required. Work along these lines is currently pursued in our laboratories.

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Disclosure statement

No potential conflict of interest was reported by the author(s).

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Supporting online material for

**Ultrafast excited-state dynamics of thin films
consisting of helicene-like molecules based on
dibenzo[*c,h*]acridine**

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1. Circularly polarised luminescence spectra

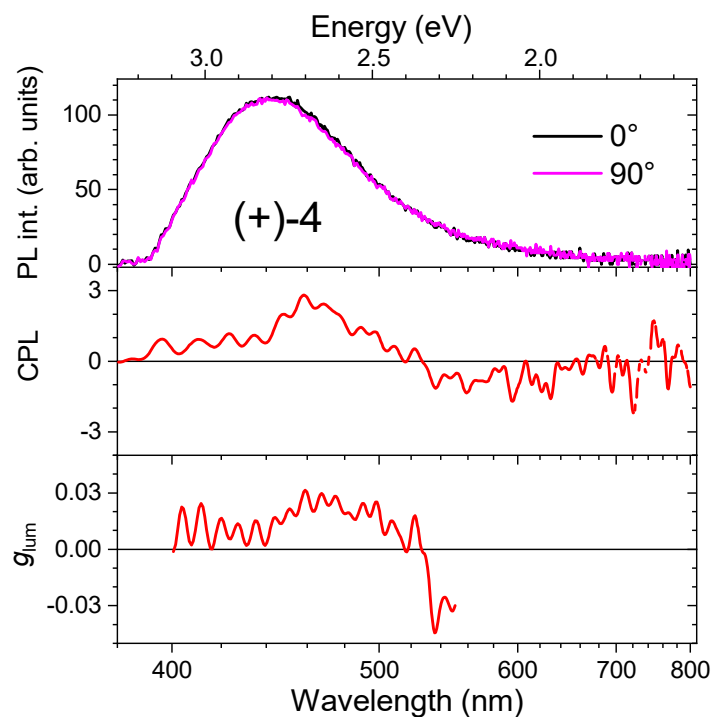


Figure S1. (a) Photoluminescence spectra at 0° and 90° polariser setting, (b) the resulting circularly polarised luminescence and (c) the corresponding g_{lum} for the helicene-like compound (+)-4.

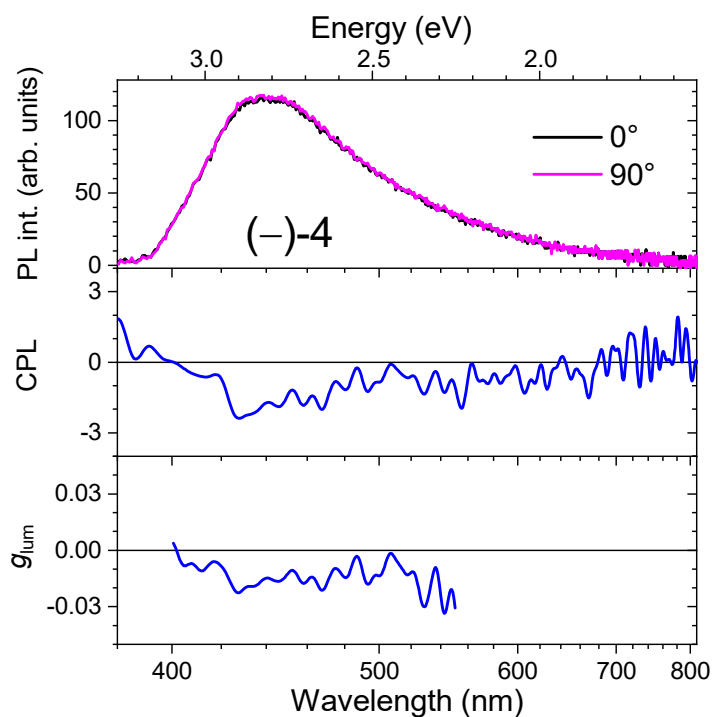


Figure S2. (a) Photoluminescence spectra at 0° and 90° polariser setting, (b) the resulting circularly polarised luminescence and (c) the corresponding g_{lum} for the helicene-like compound (-)-4.

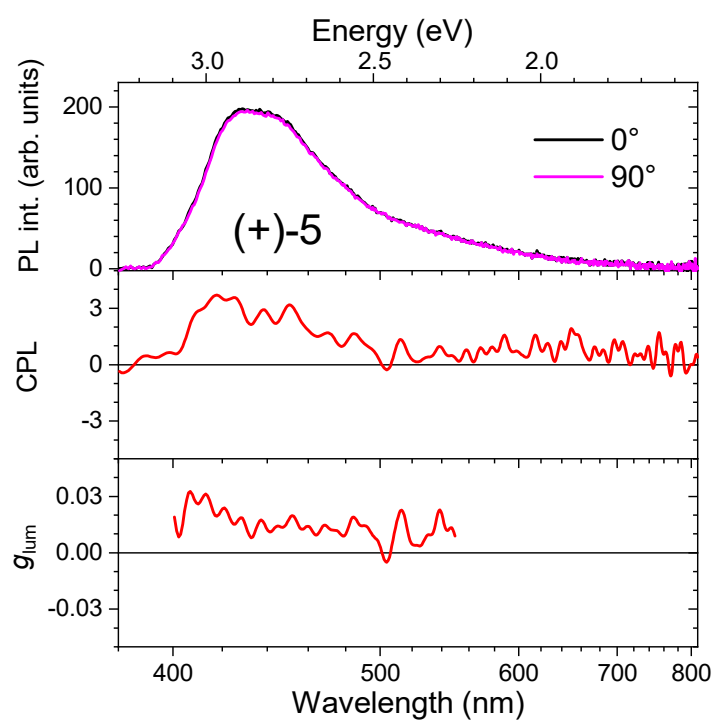


Figure S3. (a) Photoluminescence spectra at 0° and 90° polariser setting, (b) the resulting circularly polarised luminescence and (c) the corresponding g_{lum} for the helicene-like compound (+)-5.

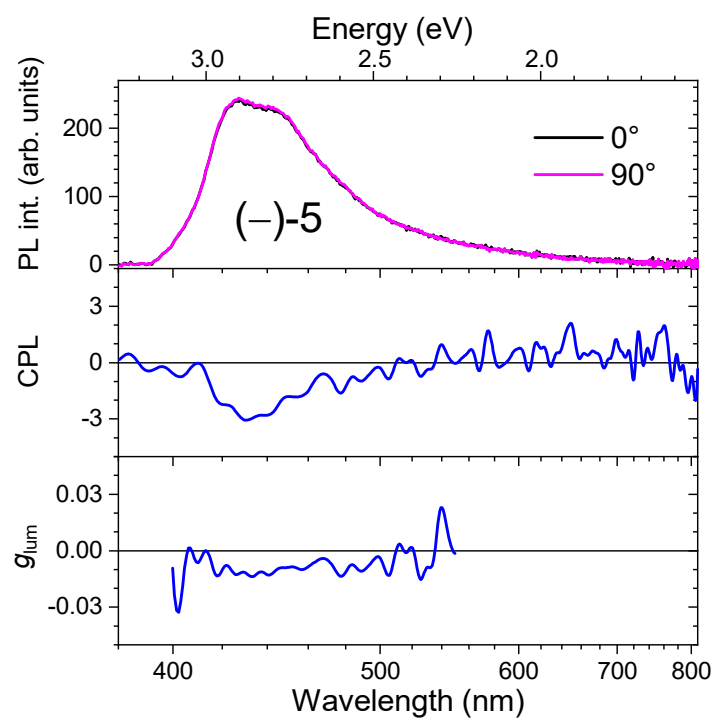


Figure S4. (a) Photoluminescence spectra at 0° and 90° polariser setting, (b) the resulting circularly polarised luminescence and (c) the corresponding g_{lum} for the helicene-like compound (-)-5.

2. Fits to the kinetics from the global analysis

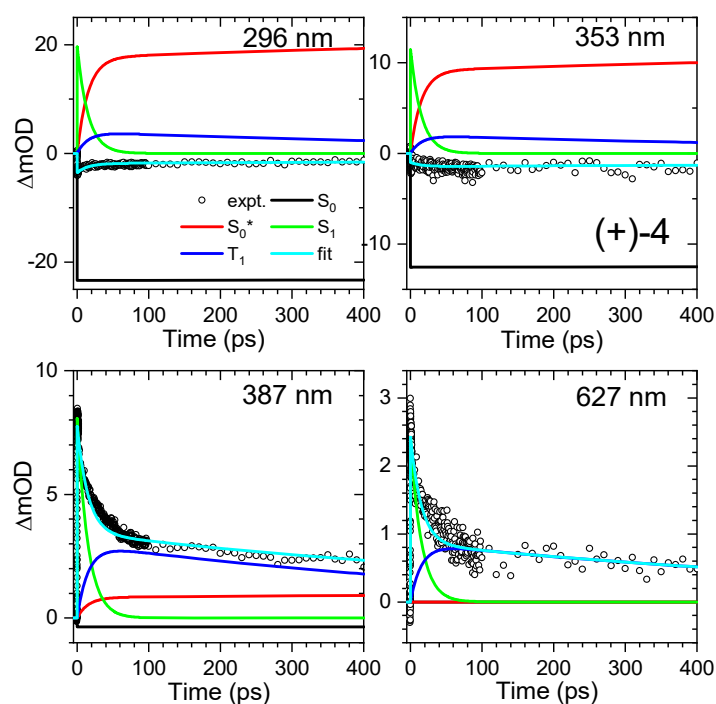


Figure S5. Fits to the experimental kinetics up to 400 ps from transient absorption experiments for compound (+)-4 at four representative probe wavelengths including species contributions.

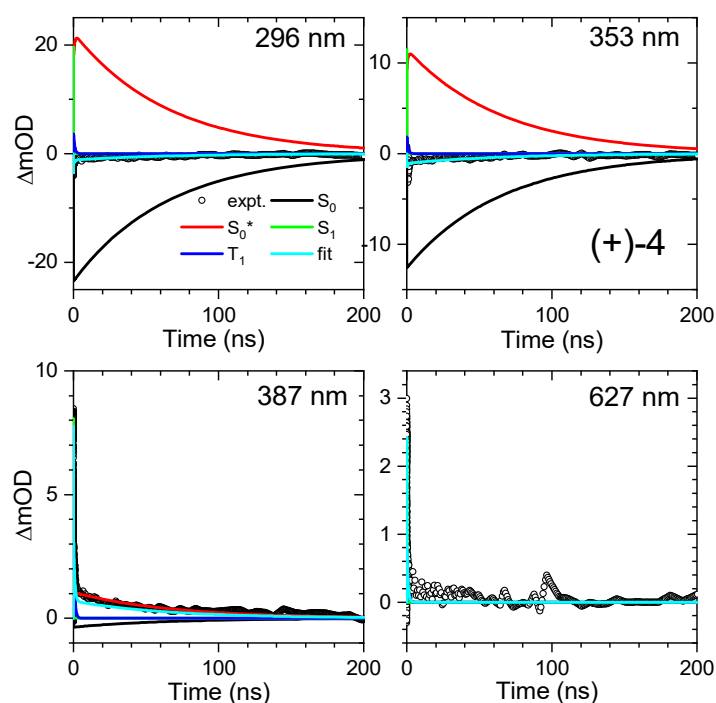


Figure S6. Fits to the experimental kinetics up to 200 ns from transient absorption experiments for compound (+)-4 at four representative probe wavelengths including species contributions.

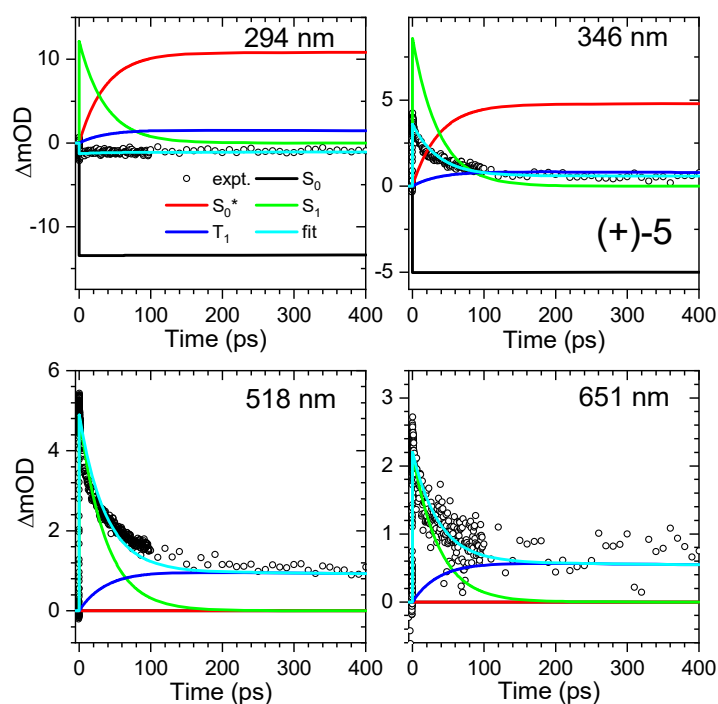


Figure S7. Fits to the experimental kinetics up to 400 ps from transient absorption experiments for compound (+)-5 at four representative probe wavelengths including species contributions.

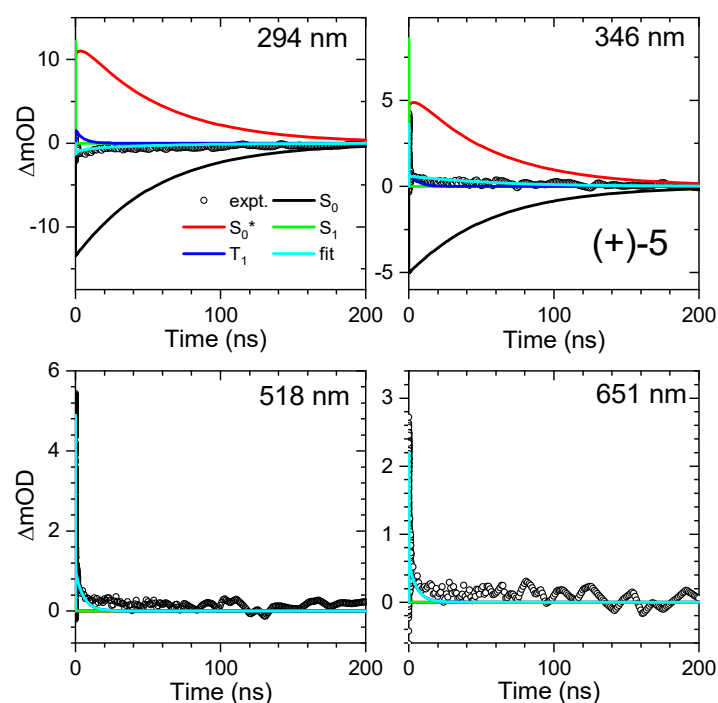


Figure S8. Fits to the experimental kinetics up to 200 ns from transient absorption experiments for compound (+)-5 at four representative probe wavelengths including species contributions.

4. Mapping the broadband circular dichroism of copolymer films with supramolecular chirality in time and space

This chapter contains the publication:

Morgenroth, M., Scholz, M., Cho, M. J., Choi, D. H., Oum, K. and Lenzer, T.

Mapping the broadband circular dichroism of copolymer films with supramolecular chirality in time and space

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Marius Morgenroth (M.M.) is the first author of this publication and performed most of the experiments and manuscript preparation. K.O. and T.L. conceived the project. M.M. prepared the thin film samples and performed the steady-state absorption experiments. M.M. and M.S. conducted the CD and CPL spectroscopy and microscopy experiments. K.O., T.L., and M.M. carried out the transient circular dichroism and transient absorption experiments and performed the data evaluation. M.S., K.O., and T.L. implemented the optical and electronic setups and the CD and CPL microscopy. M.J.C. and D.H.C. synthesized the copolymer samples. T.L., M.M. and K.O. analyzed the spectroscopic results and wrote the paper.

ARTICLE



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OPEN

Mapping the broadband circular dichroism of copolymer films with supramolecular chirality in time and space

Marius Morgenroth¹, Mirko Scholz¹, Min Ju Cho², Dong Hoon Choi², Kawon Oum¹ [✉] & Thomas Lenzer¹ [✉]

Measurements of the electronic circular dichroism (CD) are highly sensitive to the absolute configuration and conformation of chiral molecules and supramolecular assemblies and have therefore found widespread application in the chemical and biological sciences. Here, we demonstrate an approach to simultaneously follow changes in the CD and absorption response of photoexcited systems over the ultraviolet–visible spectral range with 100 fs time resolution. We apply the concept to chiral polyfluorene copolymer thin films and track their electronic relaxation in detail. The transient CD signal stems from the supramolecular response of the system and provides information regarding the recovery of the electronic ground state. This allows for a quantification of singlet–singlet annihilation and charge-pair formation processes. Spatial mapping of chiral domains on femtosecond time scales with a resolution of 50 μm and diffraction-limited steady-state imaging of the circular dichroism and the circularly polarised luminescence (CPL) of the films is demonstrated.

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Broadband electronic circular dichroism spectroscopy, measuring the difference in optical density (OD) between left-circularly polarised (LCP or shortly L) and right-circularly polarised (RCP or shortly R) light (i.e. $CD = OD_L - OD_R$), is a powerful method to discriminate between molecular systems of different chirality. These include compounds and assemblies which behave as image and mirror-image (enantiomers) and diastereomers bearing several chiral centres. Chemical chirality occurs from very small to very large length scales, ranging from small molecular systems, e.g. naturally occurring D-sugars and L-amino acids, up to supramolecular structures, such as DNA or cholesteric polymer assemblies. As a result, steady-state CD spectroscopy has been widely applied to chemical and biological systems for obtaining absolute structural information^{1–5}.

Time-resolved CD (TrCD) spectroscopy has a high potential to elucidate changes in chirality on ultrashort time scales^{6,7}. Yet, applications employing spectrally broadband CD detection covering the dynamics down to the femtosecond time-scale are still scarce, likely due to the small transient signal of many CD-active systems and nontrivial issues regarding polarisation management. Notable exceptions include the transient response recorded for merocyanine nanorod aggregates over the spectral range 360–550 nm with subpicosecond time resolution by Fiebig and co-workers⁸ and investigations in the UV range (250–370 nm) of an enantiopure ruthenium complex and a chiral synthetic thioamide-substituted dipeptide with 500 fs temporal resolution of Oppermann et al.^{9,10}. Whereas in the former case, polarisation switching was achieved by a Pockels cell, the latter approach employed a photoelastic modulator. As another method, polarisation mirroring was introduced by Brixner and co-workers. There, an LCP pulse and its RCP mirror image were generated using an arrangement of mirrors and periscopes^{11,12}. All of these approaches directly determine the transient CD signal as the difference in OD for probing with LCP and RCP light ($\Delta CD = \Delta OD = \Delta OD_L - \Delta OD_R$). Alternatively, ΔCD can be obtained using self-heterodyned detection, where the chiral response is extracted from the free induction decay of the optical activity. This technique was introduced by Cho and co-workers^{13–15} and later on applied by Hiramatsu and Nagata¹⁶ to enantiopure $[Ru(bpy)_3]^{2+}$ as a test case, but further experiments of this type have not yet been reported.

Chiral copolymer thin films, such as poly($\{9,9\text{-bis}[(3S)\text{-}3,7\text{-dimethyloctyl]fluorenyl\text{-}2,7\text{-diyl}\}\text{-alt}\text{-}\{benzo[2,1,3]thiadiazol\text{-}4,8\text{-diyl}\}$), shortly c-PFBT (Fig. 1a), are worthwhile targets for studies using TrCD and transient absorption (TA) methods. Such films are of considerable interest because they exhibit an extraordinarily strong CD response in the range of several degrees and also emit strong circularly polarised luminescence^{17–19}. This makes them attractive for applications such as colour-tuning devices or polymer-based OLEDs^{20–22}. The strong optical activity of these films is typically assigned to a long-range cholesteric (=chiral nematic) ordering¹⁷, yet this interpretation was very recently challenged by Campbell, Fuchter and co-workers, who assigned the origin of the strong chiroptical response of c-PFBT to the coupling of molecular magnetic and electric moments (i.e. single-molecule optical activity)^{19,23}.

In this work, we present an advanced setup for TrCD detection using a Pockels-cell-based polarisation-switching design employing a deuterated KDP crystal (replacing the previously used BBO^{24,25}). Consequently, the time resolution is improved to 100 fs, with the two decisive benefits of a substantial increase in the intensity of the circularly polarised multifilament supercontinuum over the spectral range covered (260–700 nm) and an accompanying reduction of its intensity fluctuations. Simultaneous detection of TrCD and TA signals ($\Delta OD = 0.5 \cdot [\Delta OD_L +$

$\Delta OD_R]$) from four consecutive probe laser shots (LCP and RCP, each with and without the pump beam) is demonstrated. We obtain TrCD and steady-state CD spectra for c-PFBT thin films which strongly support a supramolecular origin of the large CD response. In addition, TrCD mapping of such thin-film structures is important for understanding the dynamics in different chiral domains, and we demonstrate here a proof-of-concept implementation showing ultrafast CD mapping on the femtosecond time scale with a spatial resolution of 50 μm , as well as steady-state CD and CPL imaging with a diffraction-limited resolution of about 500 nm.

Results and discussion

Steady-state absorption, CD and CPL spectroscopy. The c-PFBT copolymer was deposited on borosilicate glass slides without an alignment layer and thermally annealed at 150 °C, resulting in yellow films (see photographs in Fig. 1a). Such films have multidomain cholesteric liquid crystalline order with the statistical orientation of the individual domains^{20,26}. Steady-state absorption spectra recorded with LCP and RCP light showed substantial differences (blue and red lines in the top panel of Fig. 1b), resulting in a strong CD response with OD values of up to -0.3 ($= -10,000$ mdeg) and a dissymmetry factor $g_{\text{abs}} = 2(OD_L - OD_R)/(OD_L + OD_R)$ approaching -0.5 (middle and bottom panels of Fig. 1b). In addition, the films displayed strongly polarised photoluminescence with a dissymmetry factor $g_{\text{lum}} = 2(I_L - I_R)/(I_L + I_R)$ of up to -0.4 (Fig. 1b, brown lines).

Importantly, the thin films showed virtually no changes in the CD response and the dissymmetry factor g_{abs} upon turning or flipping of the sample (Fig. 1c). Therefore, we conclude that there are no significant contributions resulting from a combination of linear anisotropies (i.e. linear dichroism and linear birefringence) in our sample in combination with any possible anisotropies in the spectroscopic setup. We also observed that the CD and g_{abs} values of c-PFBT increased considerably with film thickness, in agreement with previous observations of Abbel et al.¹⁷. This is demonstrated in Fig. 1d for three films with thicknesses d of 62 ± 5 , 106 ± 8 and 241 ± 16 nm (blue, red, and black lines, respectively).

Contactless laser-based determination of film thickness. The film thickness was determined in an all-optical, non-invasive fashion using laser-based picosecond ultrasonics^{27–29} from the TA traces of our ultrafast measurements. The TA kinetics of the polymer films exhibited pronounced damped oscillations at the edges of the ground-state absorption bands (see Fig. 1e) (pump wavelength 320 nm, probe wavelength range 470–510 nm). The oscillation in the absorption signal arises from a coherent acoustic phonon, which is induced by the pump laser pulse and propagates back and forth between the polymer–glass and polymer–nitrogen interface. The period of this oscillation is directly proportional to the thickness of the film ($d = \tau_a \cdot c_L/4$), where τ_a is the measured oscillation period of (100 ± 2) , (171 ± 3) and (388 ± 3) ps for the films investigated, and c_L is the longitudinal sound velocity of c-PFBT, which we previously determined as $(2490 \pm 150) \text{ m s}^{-1}$ ²⁹. The inset of Fig. 1e shows that the g_{abs} value is very small for the thinnest film and then strongly increases with the thickness (g_{abs} peak values of 0.028, 0.215, and 0.476, respectively). Such behaviour suggests a supramolecular (nonlocal) origin of the CD response in this thickness range^{17,20,26}. In contrast, single-molecule circular dichroism, where coupling between local electric and magnetic transition dipole moments is operative, should lead to a thickness-independent g_{abs} ^{17,19}.

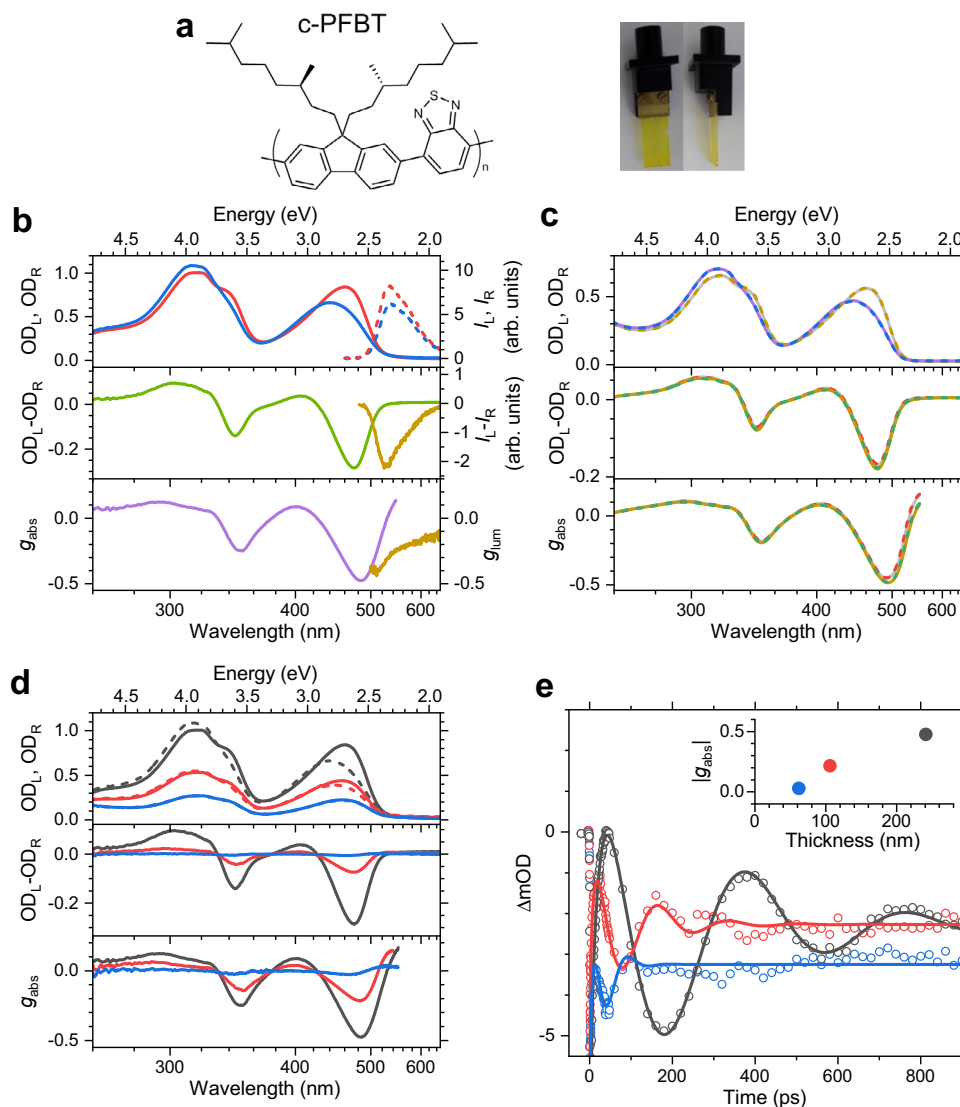


Fig. 1 Optical properties of the c-PFBT thin films. **a** Chemical structure of the c-PFBT copolymer and pictures of the thin film on glass. **b** Absorption spectra for left-circularly (blue solid line) and right-circularly polarised light (red solid line); emission spectra for left-circularly (blue dashed line) and right-circularly polarised light (red dashed line); CD spectrum (green line) and CPL spectrum (brown line); dissymmetry parameters g_{abs} (violet line) and g_{lum} (brown line). **c** Behaviour upon flipping and turning of the film: Absorption spectra for left-circularly polarised light (front side: grey solid line, backside: brown dashed line) and right-circularly polarised light (front side: violet solid line, backside: blue dashed line); CD spectra and g_{abs} (front side: grey solid line, front side turned by 180°: red dashed line, backside: brown solid line, backside turned by 180°: green dashed line). **d** Thickness-dependent absorbance (left-circularly polarised light: dashed lines, right-circularly polarised light: solid lines), as well as CD and g_{abs} for thin films with the thickness 62 nm (blue), 106 nm (red) and 241 nm (black). **e** Transient absorption signals averaged over the probe wavelength range 470–510 nm (open circles) showing oscillations due to a coherent acoustic phonon excited by the 320 nm pump laser pulse for thin films with the thickness 62 nm (blue), 106 nm (red) and 241 nm (black); solid lines represent the respective fits using a sum of a biexponential function and a damped cosine function; the inset shows the absolute peak value of g_{abs} as a function of film thickness, suggesting a supramolecular origin of the chiroptical response.

CD and CPL imaging with diffraction-limited resolution. To further characterise the chiroptical properties of the c-PFBT films, a microscopy setup for CD and CPL imaging was constructed. Several powerful setups for steady-state CD imaging have been established so far, starting from the early work of Maestre and Katz³⁰. These include circular dichroism imaging based on a wide-field microscope featuring illumination through a combination of an interference filter, a polariser and a tunable quarter-wave retarder³¹, scanning CD optical microscopy using a polariser and a photoelastic modulator³², CD microscopy with discretely modulated circular polarisation³³, as well as scanning UV–Vis circular dichroism experiments employing highly collimated synchrotron radiation^{34,35}. Our specific implementation

based on wide-field microscopy reaches a spatial resolution of ca. 500 nm and has the additional option to simultaneously record CD and CPL spectra integrated over the entire field of view. Representative results for different areas ($80 \times 60 \mu\text{m}^2$) of a c-PFBT film (thickness ca. 240 nm) are displayed in Fig. 2.

The CD image in panel a and the corresponding g_{abs} image in panel b (175,000 pixels each) was obtained at the peak of the CD spectrum using a 10 nm narrow bandpass filter with a centre wavelength of 470 nm. The graphs in panel c show the spectrally resolved data integrated over the complete field of view (OD for LCP and RCP light, CD and g_{abs} spectrum). The film area shows island-like structures and has a granular appearance, in agreement with microscope images obtained for a c-PFBT film between

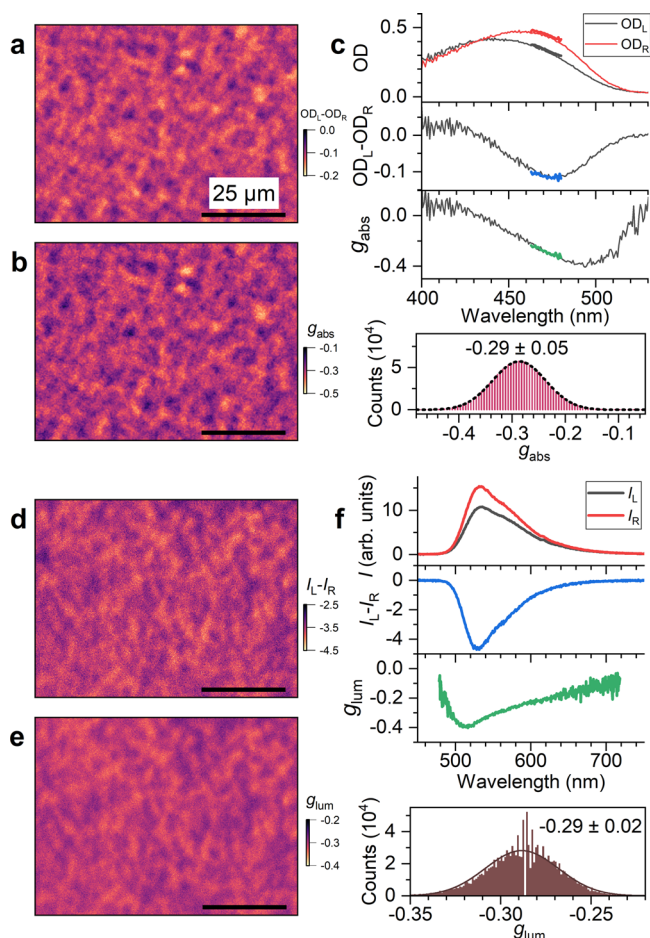


Fig. 2 CD and CPL imaging with diffraction-limited resolution of about 500 nm. **a** Microscope image ($80 \times 60 \mu\text{m}^2$) for the circular dichroism of a c-PFBT thin film. **b** Corresponding image for the dissymmetry factor g_{abs} . **c** Wavelength-dependent optical density for LCP (black) and RCP detection (red), the resulting CD signal and the g_{abs} spectrum (thin lines: full spectra, thick coloured lines: spectral region selected by the bandpass filter at 470 nm used for CD imaging) as well as the g_{abs} histogram with a Gaussian fit (dashed black line), all determined over the entire field of view ($210 \times 160 \mu\text{m}^2$). **d** Microscope image for the circularly polarised luminescence at another position on the same c-PFBT thin film. Excitation at 365 nm. **e** Corresponding image for the dissymmetry factor g_{lum} . **f** Wavelength-dependent photoluminescence spectrum for LCP (black) and RCP detection (red), the resulting CPL signal and the g_{lum} values for the c-PFBT emission band, as well as the g_{lum} histogram with a Gaussian fit (solid black line), all determined over the entire field of view. The length of the black scale bar in each image corresponds to 25 μm .

crossed polarisers from a previous study of Abbel et al.¹⁷, indicating a disordered multidomain liquid crystalline arrangement. The underlying structure was assigned recently to a long-range hierarchical arrangement of fibrils³⁶. The statistics over the entire field of view provides a histogram (bottom right), which is well described by a Gaussian distribution with $g_{\text{abs}} = -0.29 \pm 0.05$. For further illustration of the capabilities of diffraction-limited CD imaging, we provide additional images for other regions of the same film in Supplementary Note 1. We also checked the invariance of the CD images upon sample rotation and flipping, as illustrated in Supplementary Note 2, which proved that there are also no significant contributions on micrometre length scales resulting from a combination of linear dichroism and linear birefringence in our sample in combination with any possible

anisotropies of the CD microscopy setup. In addition, the structures revealed in the CD images are very similar to the structures observed using a conventional crossed-polariser arrangement (Supplementary Note 3).

Panels d and e contain the CPL and g_{lum} images for a different position on the same film obtained upon photoexcitation at 365 nm. The graphs in panel f show the spectrally resolved data integrated over the complete field of view (PL for LCP and RCP light, CPL and the g_{lum} spectrum, all in good agreement with the data shown in Fig. 1b). The appearance of the CPL and g_{lum} images is very similar to those obtained from CD imaging, i.e. they show the same island-type areas. Regions with larger absolute values of g_{lum} also show larger absolute values of g_{abs} . The statistics on the g_{lum} image provides a histogram, which can be again well described by a Gaussian distribution with $g_{\text{lum}} = -0.29 \pm 0.02$. The size of the structures seen both in the g_{abs} and g_{lum} images correlate well with the dimensions of fibre-type and aggregated spherulite arrangements reported by Di Nuzzo et al. and Lakhwani and co-workers for disordered multidomain films of c-PFBT^{20,36}.

To further highlight the capabilities of the method, we present in Fig. 3a–d CD imaging results for different areas ($80 \times 60 \mu\text{m}^2$) of another c-PFBT thin film. In this example, we intentionally selected four regions across the film (also in less homogeneous regions) where the CD images show pronounced differences. The shape of the CD spectra integrated over all regions is quite similar, with maximum OD amplitudes between -0.21 (-7000 mdeg) and -0.30 ($-10,000$ mdeg), as shown on the right side. The corresponding g_{abs} images are presented in panels e–h. The similar colours in panels e and h compared with the more disparate colours in a and d show that the stronger CD in panel a is due to the larger OD. Normalisation to the OD provides similar g_{abs} values in both cases, as shown in the histograms on the right side (-0.37 ± 0.02 vs. -0.36 ± 0.03). Still, the island-like structures observed in panel a are more extended than those in panel d, suggesting slight differences in the structure of both film regions.

Next, we compare panels a and b. The peak value of the CD spectrum in b is about 5% larger (-0.30 vs. -0.29 in OD). However, in this case, the difference in g_{abs} is 20% (-0.44 ± 0.03 vs. -0.37 ± 0.02), suggesting that the larger OD is not the main reason for the stronger circular dichroism in b. As the last pair, we compare panels c and d. The peak value of the CD spectrum in d is about 17% smaller (-0.21 vs. -0.25 in OD), yet g_{abs} are only smaller by about 8% (-0.36 ± 0.03 vs. -0.39 ± 0.05) showing that the difference in g_{abs} is only partly due to the different OD of the two regions. The most amazing difference is however the totally different appearance of the image in panel g. Here we find a mosaic structure, where micrometre-size regions with large absolute g_{abs} (yellow) are very close to micrometre-size regions with much smaller g_{abs} (violet). The distribution in panel g also has the largest width (-0.39 ± 0.05) and is skewed, with pronounced deviations from Gaussian behaviour. These four examples show the potential of diffraction-limited CD imaging to address differences in chiroptical properties with a high spatial resolution for systems, which macroscopically show quite similar averaged CD spectra. It could well be that the different appearance in less homogeneous regions points toward different aggregation pathways, as previously suggested for oligothiophene films^{34,35}. Still, the thin film regions in the centre of the substrate and at intermediate distances are very uniform and also microscopically homogeneous, with no clear indications for different aggregation pathways.

Ultrafast transient CD and TA experiments. Figure 4a displays typical results of the combined ultrafast TrCD/TA experiment, in

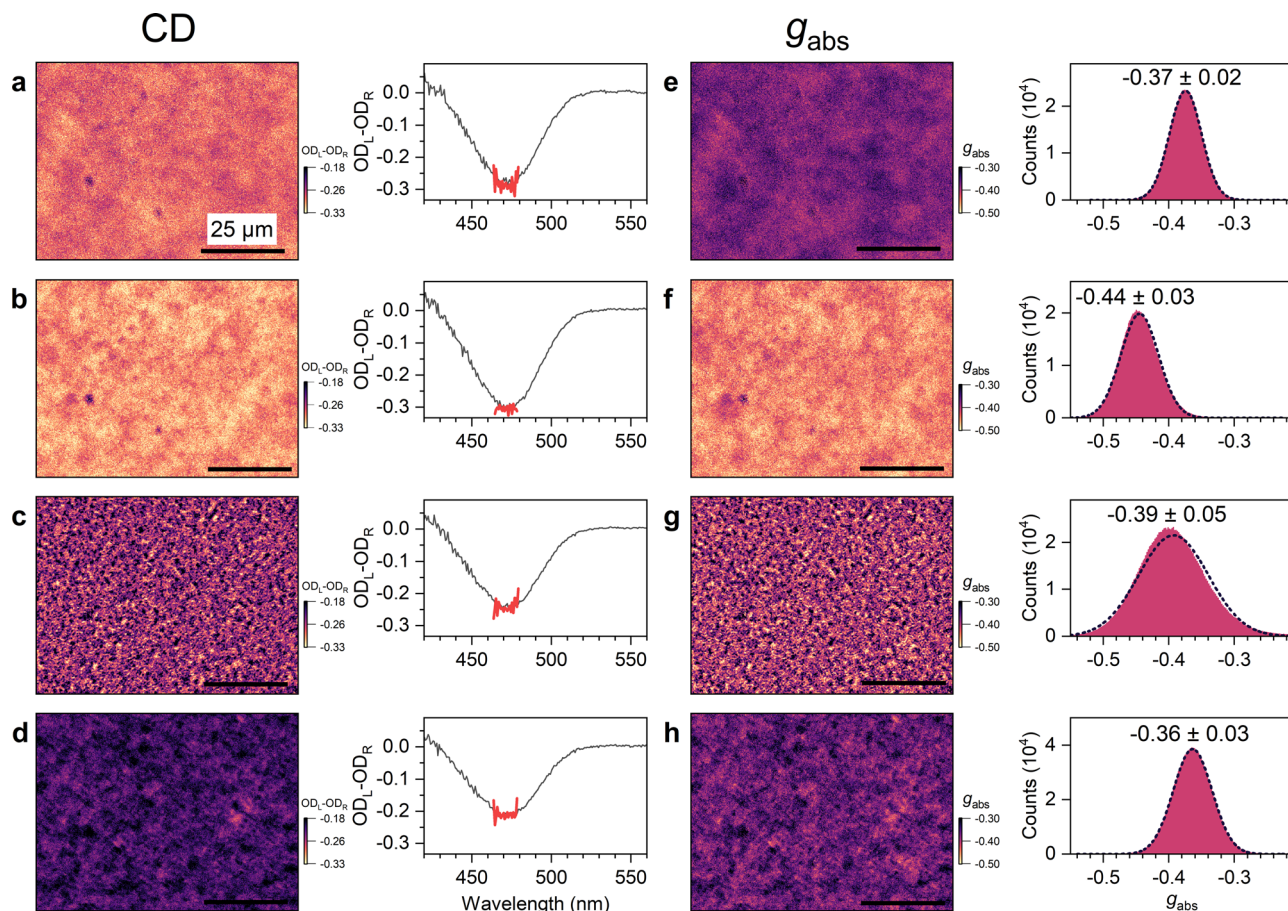


Fig. 3 CD imaging with diffraction-limited resolution for different regions of another c-PFBT thin film. **a–d** Microscope images ($80 \times 60 \mu\text{m}^2$) for the circular dichroism of the c-PFBT thin film at different positions. Plots on the right show the CD signals integrated over the entire field of view ($210 \times 160 \mu\text{m}^2$, thin black lines: full spectra, thick red lines: spectral region selected by the bandpass filter at 470 nm used for CD imaging). **e–h** Corresponding images for the dissymmetry factor g_{abs} , with histograms on the right including Gaussian fits as dashed black lines, determined over the entire field of view. The length of the black scale bar in each image indicates a distance of $25 \mu\text{m}$. Variations in counts in the g_{abs} distributions are due to the different bin sizes used.

which a 241 nm thin c-PFBT film was excited by 50 fs pump laser pulses at 320 nm. Here we focus on the TA and TrCD spectra at six representative time delays (see Supplementary Note 4 for contour plots of the complete data sets). TA spectra for probing with LCP and RCP light are shown as blue and red lines. At early times (0.2 ps in Fig. 4a), the TA spectra show pronounced ground state bleach (GSB) features centred at about 450 and 315 nm, as the pump beam initially promotes ground state (S_0) molecules to a higher excited singlet state S_x . These bands resemble the corresponding inverted steady-state absorption spectra for LCP and RCP probing (cf. Fig. 1b, top). Prominent excited state absorption (ESA) bands emerge at 620, 530 (shoulder), 365 and 284 nm. The differences in the TA spectra for LCP and RCP probing give rise to a pronounced TrCD difference signal, which is indicated by the green line. This giant TrCD signal closely resembles the inverted steady-state CD spectrum (Fig. 1b, middle). Remarkably, it does not show any clear sign of CD activity in the excited electronic state, see e.g. the region 360–380 nm, where the virtually silent TrCD signal is in marked contrast to the substantial ESA band of the TA spectrum. We take this important observation as a strong indication of the supramolecular nature of the CD response, as described in more detail below. The flat and weak, slightly negative TrCD signal above 520 nm, where c-PFBT does not have any ground-state absorption, is largely due to circular selective

scattering^{5,20,37,38}, and a similar weak feature is also observed in the ground-state CD spectrum.

The remaining panels in Fig. 4a show that at later times (0.5–980 ps) all bands in the TA and TrCD spectra decay. While the TrCD spectra exhibit essentially no changes in shape, the TA spectra for LCP and RCP probing show distinct differences. In the spectral range above 500 nm, the peak/shoulder structure at early times evolves into a flatter ESA band at later times (see the spectra at 100 and 980 ps). As will be discussed below in the kinetic analysis, the flat ESA band can be explained by the formation of a charge-pair state at early times.

Figure 4b contains spectra for different pump fluences, with initial exciton number densities $N_0(S_x)$ in the range 5.7×10^{17} – $1.2 \times 10^{19} \text{ cm}^{-3}$ at the fixed pump–probe delay time of 3 ps. In the two upper panels, the amplitude of the TA signals for probing with left-circularly and RCP light increases with increasing fluence below 500 nm. This is accompanied by a shift of the main GSB band from 455 to 445 nm. In contrast, above 500 nm there is a change in sign: At low pump fluence, there is a negative band below 580 nm, which we assign to stimulated emission from S_1 , whereas at high pump fluence there is absorption in the entire 500–650 nm range. As explained in more detail below, the latter effect is again consistent with the formation of a charge-pair state from S_1 by singlet–singlet

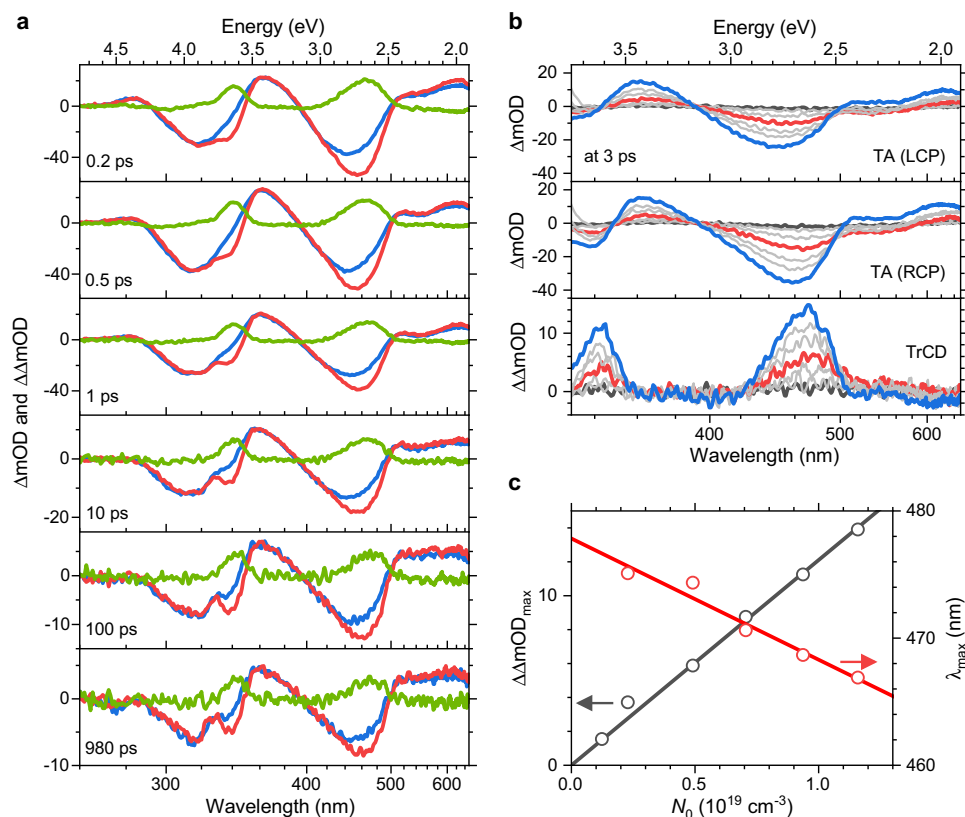


Fig. 4 Ultrafast transient circular dichroism and transient absorption spectra of a 241 nm thin c-PFBT thin film. **a** Spectra at six different delay times: transient absorption for probing with left-circularly polarised light (blue), right-circularly polarised light (red) and the resulting TrCD spectrum (green). **b** Fluence-dependent spectra at 3 ps for initial exciton number densities between 5.7×10^{17} (black) and $1.2 \times 10^{19} \text{ cm}^{-3}$ (blue); red line for $N_0 = 4.9 \times 10^{18} \text{ cm}^{-3}$; left-circularly polarised probe light (top), right-circularly polarised probe light (middle) and the resulting TrCD spectrum (bottom). **c** Correlation of the TrCD peak signal (black circles) and the peak position of the TrCD signal (red circles) with the initial exciton number density including a proportional (black) and a linear (red) fit.

annihilation (SSA). This process becomes faster at high pump fluence, and thus high initial exciton number densities in the polymer^{25,39}, as described by our kinetic modelling below. Therefore, under such high-fluence conditions, the S_1 population is already considerably depleted at 3 ps.

We are now coming to the corresponding fluence-dependent TrCD spectra, which are depicted in the bottom panel of Fig. 4b. The TrCD signal amplitude depends linearly on the pump fluence (Fig. 4c, black open circles and fit line). Interestingly, the main band of the TrCD spectrum at 475 nm also shows a fluence-dependent blue shift as observed for the TA spectra. This shift in wavelength is illustrated by the red open circles and the corresponding red fit line in Fig. 4c. We explain this as follows: At low pump fluence, the S_1 state gives rise to circularly polarised stimulated emission (CPSE), i.e. a difference in the induced S_1 emission for LCP and RCP probing. This process can be viewed as the analogue of CPL, which is however a spontaneous process. CPSE (as CPL) must have the same sign as the corresponding lowest-energy CD band, and as this transient CD bleach of c-PFBT has a positive sign, the CPSE response must also be positive. Indeed, such a CPSE feature is observed, e.g. in the red-coloured TrCD spectrum above 500 nm. This overlapping CPSE band will therefore lead to an apparent broadening of the band toward higher wavelengths at low pump fluence. At the same time, it compensates for the negative contribution above 500 nm, which is the only contribution in this spectral range at high pump fluence (cf. the blue TrCD spectrum above 500 nm in the bottom panel of Fig. 4b) and is due to circular selective scattering. At high pump fluence, CPSE at 3 ps will be largely absent because of fast

depletion of the S_1 state due to singlet–singlet annihilation, leading to an apparent blue-shift of the band in the TrCD spectrum²⁵. Note that the noise characteristics of the TA and TrCD signals (and thus also the CPSE contribution) are governed by laser noise, i.e. shot-to-shot fluctuations of the intensity and spatial profile of the laser pulses⁴⁰. In contrast, measurements of spontaneous CPL are limited by Poisson noise.

One central question is, why a clear CD bleach signal, as well as CPSE from the S_1 state, is observed, whereas one does not see any clear sign of excited-state CD bands in the TrCD spectra. We take this particular finding as a strong indication for the supramolecular origin of the TrCD response, as outlined in the following. Figure 5a shows an idealised sketch of a cholesteric helical arrangement consisting of five layers, each containing 25 c-PFBT units indicated as cylinders, with a side view of the planes on the left, and a view along the twist axis on the right. In the TrCD experiment, between 3% and 15% of the c-PFBT units are initially photoexcited, as can be easily estimated from the ratio of the initial bleach amplitude of the TA spectra and the steady-state absorbance of the sample.

In Fig. 5a we, therefore, choose an excitation level of 10% for an illustration, which is indicated by a statistical selection of 13 excited c-PFBT units in the five planes (excited: red, not excited: blue). One can well understand that photoexcitation makes about 10% of the S_0 chromophores inaccessible for the probe beam, which leads to the observed CD bleach feature in the TrCD spectra. In addition, the different electronic properties of the excited species will somewhat modify the in-plane and across-planes longer-range coupling between the electric and magnetic

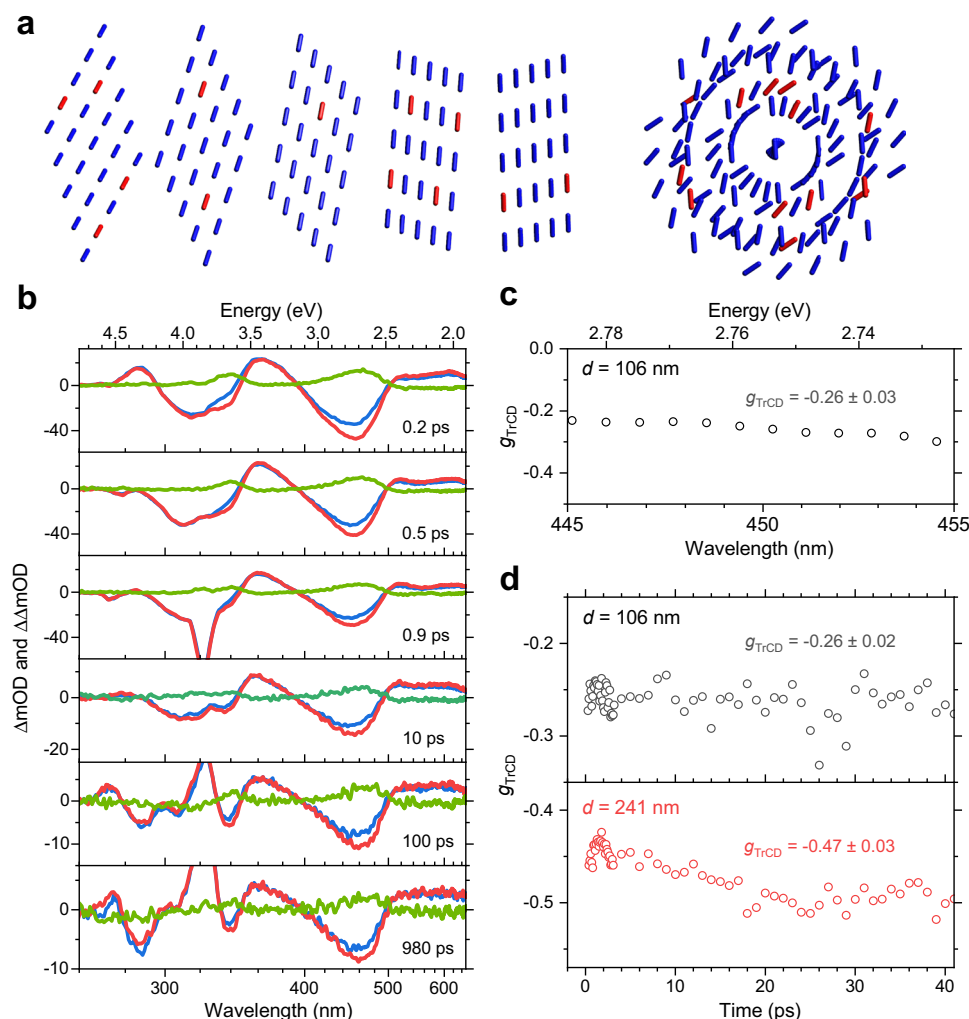


Fig. 5 Supramolecular origin of the ultrafast TrCD response of c-PFBT thin films. **a** Schematic representation of a cholesteric helical arrangement consisting of five layers with 25 c-PFBT units, where ground state c-PFBT units are shown as blue cylinders and excited state c-PFBT units are represented by red cylinders; left side: side view, right side: view along the twist axis. **b** Transient spectra for a 106 nm thin c-PFBT film at six different delay times: transient absorption for probing with left-circularly polarised light (blue), right-circularly polarised light (red) and the resulting TrCD spectrum (green). Note the about 50% smaller TrCD response compared with the 241 nm thin film (Fig. 4a) despite the comparable amplitude of the transient absorption signals. **c** Wavelength-dependence of the dissymmetry factor g_{TrCD} . **d** Time-dependence of the dissymmetry factor g_{TrCD} for a 106 nm thin film (top) and a 241 nm thin film (bottom).

transition dipole moments of c-PFBT in the S_0 state. However, this effect appears to be weak, as there is a close resemblance of the TrCD spectrum to the inverted steady-state CD spectrum. As already mentioned, CPL is also thought to be a long-range supramolecular effect, likely resulting from processes such as circular intensity differential scattering^{20,36} and linearly polarised luminescence of quasi-nematic layers with subsequent circular polarisation by the remaining film layer⁴¹. Therefore, the CPSE contribution in the TrCD spectra, i.e. directed S_1 emission induced by the probe beam of the TrCD experiment, should be based on similar effects as the CPL signal. In contrast, considering CD activity in the excited state, Fig. 5a suggests that efficient long-range coupling between the spatially widely distributed electronically excited c-PFBT units must be weak, both in-plane and across planes.

Further support for the supramolecular origin of the TrCD signal is obtained from thickness-dependent TrCD measurements. Figure 5b contains the results for the 106 nm thin c-PFBT film at the same time delays as in Fig. 4a for the 241 nm thin film. Qualitatively, the TA and TrCD signals look the same for both

films, however importantly, the TrCD signal in Fig. 5b is by about a factor two smaller, although the initial TA bleach amplitude is almost the same as in Fig. 4a. To quantify this effect, we introduce the time-dependent dissymmetry factor g_{TrCD} . For that, we normalise the TrCD signal (i.e. $\Delta OD_L - \Delta OD_R$) to the TA signal for unpolarised light (which is $0.5 \cdot (\Delta OD_L + \Delta OD_R)$) resulting in $g_{TrCD} = 2(\Delta OD_L - \Delta OD_R) / (\Delta OD_L + \Delta OD_R)$. Figure 5c shows the wavelength-dependent g_{TrCD} averaged over the time interval 0.2–48 ps in the region of the main peak of the TrCD signal (445–455 nm). We obtain $g_{TrCD} = -0.26 \pm 0.03$ in good agreement with the steady-state value for g_{abs} in Fig. 1d (red line). The time dependence of g_{TrCD} is analysed in Fig. 5d. Interestingly, g_{TrCD} is largely time-independent, where the larger scatter at longer times is simply due to the substantially decreased signal amplitude of the TrCD signal. Corresponding measurements for the 241 nm thin film provide the value $g_{TrCD} = -0.47 \pm 0.03$, again in good agreement with the steady-state value g_{abs} (Fig. 1d, black line). The thickness-dependent g_{abs} and g_{TrCD} values, as well as the absence of CD activity in the excited state, provide strong arguments against a mechanism based on single-molecule

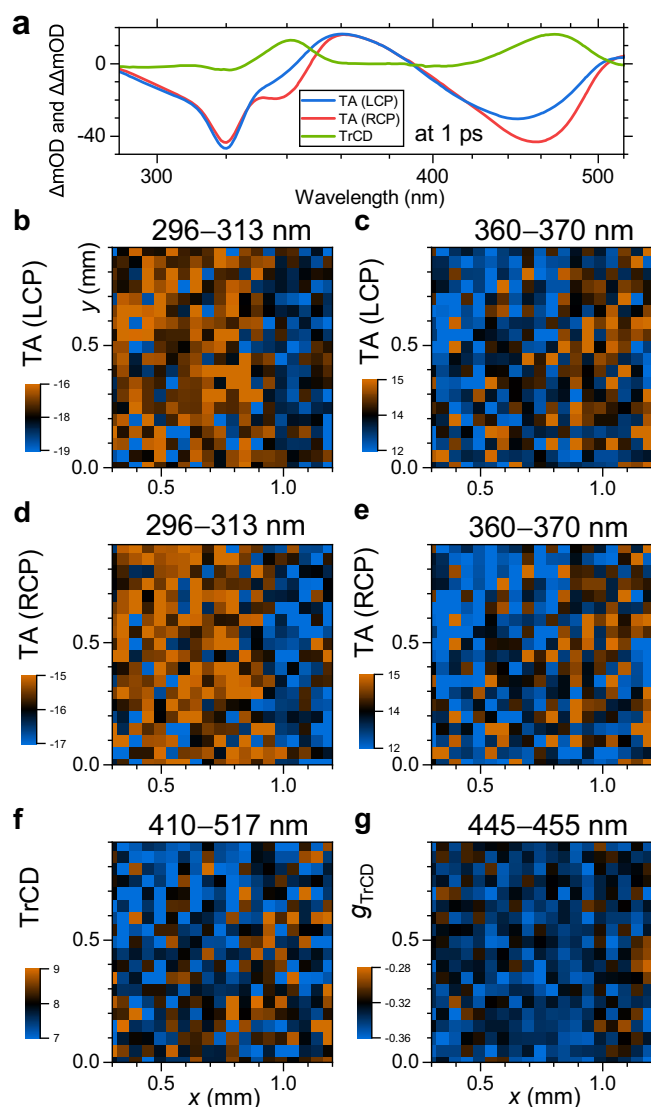


Fig. 6 Ultrafast transient absorption and circular dichroism mapping of a c-PFBT thin film at 1 ps. **a** Transient absorption spectra for probing with left-circularly polarised light (blue) and right-circularly polarised light (red), as well as the resulting TrCD spectrum (green), averaged over the complete map. **b** Transient absorption map for probing with left-circularly polarised light averaged over the wavelength range 296–313 nm. **c** Transient absorption map for probing with left-circularly polarised light (average: 360–370 nm). **d** Transient absorption map for probing with right-circularly polarised light (average: 296–313 nm). **e** Transient absorption map for probing with right-circularly polarised light (average: 360–370 nm). **f** Transient circular dichroism map (average: 410–517 nm). **g** Map for the dissymmetry factor g_{TrCD} (average: 445–455 nm).

circular dichroism, with coupling between local electric and magnetic transition dipole moments, which would predict thickness-independent gabs, g_{lum} ¹⁹ and also g_{TrCD} as well as pronounced CD activity in the electronically excited state. The TrCD signal for a given film thickness is still linearly dependent on the pump fluence, i.e. it scales with the number of initially excited polymer units (cf. Fig. 4b, c). The supramolecular nature of the transient chiral response manifests itself in terms of an additional constant scaling factor which increases the TrCD signal, which means it becomes much bigger for thicker films.

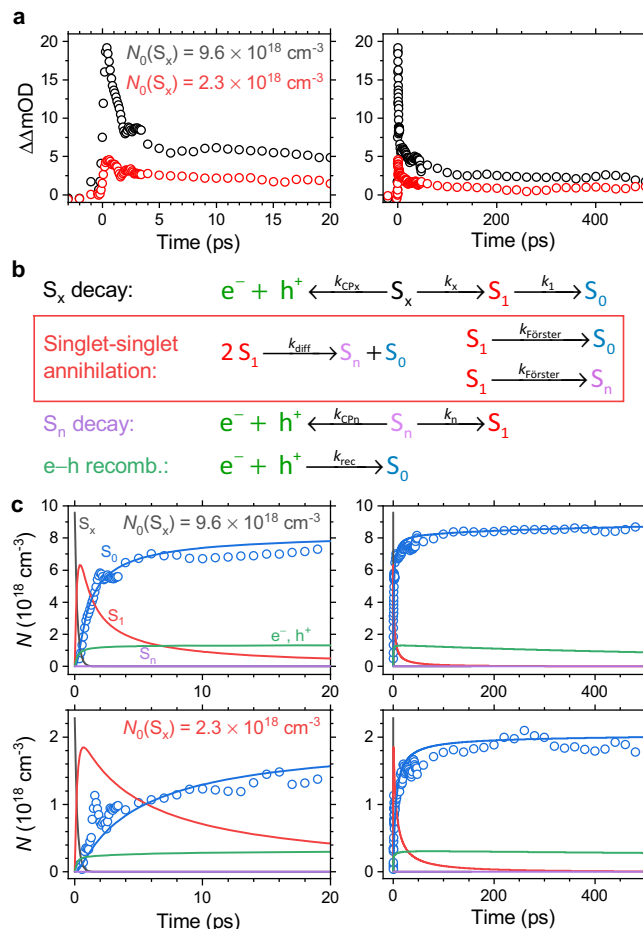


Fig. 7 Kinetic modelling of the TrCD kinetics of a 241 nm thin c-PFBT film. **a** TrCD decay kinetics (averaged over the TrCD peak region 460–470 nm) for the initial S_x exciton number densities $N_0(S_x) = 9.6 \times 10^{18} \text{ cm}^{-3}$ (black) and $2.3 \times 10^{18} \text{ cm}^{-3}$ (red). **b** Kinetic model for describing the population dynamics. **c** Results of the kinetic modelling for the initial S_x exciton number densities $9.6 \times 10^{18} \text{ cm}^{-3}$ (top) and $2.3 \times 10^{18} \text{ cm}^{-3}$ (bottom), with the dynamics on short time scales (up to 20 ps) on the left side and long time scales (up to 500 ps) on the right side. Blue circles: Recovery of S_0 population as experimentally determined in the TrCD measurements with corresponding blue fit lines obtained from the kinetic model; black, red, green and violet lines: number density of the S_x excitons, S_1 excitons, electron–hole pairs (e^- , h^+) and the S_n excitons, as obtained from the kinetic model.

Transient CD and transient absorption mapping. The high signal-to-noise ratio of the transient TA and TrCD signals also allows for a time-resolved point-by-point mapping of the c-PFBT thin film. The spatial resolution is defined by the probe beam diameter, which is currently 50 μm . Figure 6 shows an example of such a spatial mapping for an area of about 1 mm^2 area (roughly 400 points) at the time delay $t = 1$ ps. Panel a contains TA spectra for right- and left-circularly polarised probing and the resulting TrCD spectrum averaged over the complete area. Transient absorption maps for LCP and RCP probing are presented in panels b–e. These were averaged over two different wavelength intervals: 296–313 nm (GSB, panels b and d) and 360–370 nm (ESA, panels c and e). In both cases, blue colours correspond to smaller ΔOD values and brown colours to larger ones. All the maps for LCP and RCP probing agree very well. Note that the GSB and ESA maps appear inverted because of the opposite sign

of the signals in these wavelength ranges (cf. panel a). Variations across the maps are quite small, on the order of $\pm 10\%$.

The resulting TrCD map for the range 410–517 nm is depicted in panel f. It shows clear similarities to the LCP and RCP TA maps in panels c and e. This suggests that, for a given film thickness, there is a correlation between the amplitude of the TA and TrCD signals (larger values on the right side and smaller values on the left side of the map). When normalising the TrCD to the TA signal, i.e. plotting the map for the integrated (445–455 nm) dissymmetry parameter g_{TrCD} in panel g, the pattern largely disappears and one observes a more homogeneous distribution, with an average value of $g_{\text{TrCD}} = -0.33$. Time-resolved mapping with higher spatial resolution approaching the diffraction limit is planned for future studies.

Kinetic modelling of TrCD signals. We finally deal with the quantitative kinetic analysis of the ultrafast TrCD signals. Figure 7a shows the TrCD kinetics (averaged over the TrCD peak region 460–470 nm) after excitation at 320 nm for the two initial exciton number densities $N_0(S_x) = 9.6 \times 10^{18} \text{ cm}^{-3}$ (black) and $2.3 \times 10^{18} \text{ cm}^{-3}$ (red), respectively. It is evident that the dynamics do not follow a single exponential decay, and that it becomes much faster at larger values of $N_0(S_x)$, with a pronounced ultrafast decay component. This indicates that there must be higher-order processes besides simple intramolecular S_1 decay. The transients also show a long-lived component, which does not decay up the maximum delay time of 1500 ps covered in the current experiments. Very importantly, the TrCD kinetics of c-PFBT below 520 nm are only sensitive to the S_0 ground state population and do not show contributions from excited-state species. Thus, the two TrCD signals exclusively reflect the recovery of the S_0 population, in contrast to transient absorption experiments, where the signal typically arises from a combination of contributions from several species with different absorption coefficients. Also, the TrCD signal is linearly dependent on the S_0 concentration for a given film thickness (cf. Fig. 4b, c). The supramolecular nature of the TrCD response becomes evident for different film thicknesses, where thicker films show much larger TrCD signals, which however still increase linearly with the S_0 concentration.

To describe the TrCD kinetics, we employed the kinetic model shown in Fig. 7b, which is further supported by fluence-dependent transient absorption experiments at the pump wavelengths 320 and 450 nm (see Supplementary Note 5). Photoexcitation at 320 nm populates a higher excited singlet exciton state denoted as S_x , which decays both by internal conversion to S_1 (rate constant $k_x = \tau_x^{-1}$) and by the formation of a long-lived charge-pair state (CP, i.e. electron and hole ($e^- + h^+$), rate constant $k_{\text{CPx}} = \tau_{\text{CPx}}^{-1}$). The total lifetime of the S_x state $\tau_{x,\text{total}} = (k_x + k_{\text{CPx}})^{-1}$ was determined as 206 fs from ultrafast transient absorption experiments (see Supplementary Note 5), which also clearly showed the long-lived absorption of the CP state. The S_1 exciton state decays to S_0 . For the lifetime of the S_1 excitons ($\tau_1 = k_1^{-1}$) a value of 235 ps was determined from separate transient fluorescence measurements (Supplementary Note 6).

Next, we address possible channels which are responsible for the fast decay of the kinetics in the subpicosecond to picosecond range. These are the two singlet–singlet annihilations (SSA) processes shown in the red box in Fig. 7b. One is the diffusive encounter of two S_1 excitons producing a higher excited S_n exciton and an S_0 ground state species with the rate constant k_{diff} . The other channel is Förster resonance energy transfer (FRET)^{42,43}, for which the decay of an S_1 exciton to S_0 simultaneously leads to excitation of a nearby S_1 exciton to a higher excited S_n state via a nonradiative dipole–dipole coupling mechanism. Both steps in the Förster process occur with the

distance-dependent first-order rate constant $k_{\text{Förster}}$. The resulting S_n species decay either by internal conversion to S_1 (rate constant $k_n = \tau_n^{-1}$) or by the formation of a CP state ($k_{\text{CPn}} = \tau_{\text{CPn}}^{-1}$). The electrons and holes produced by CP formation eventually recombine to repopulate the S_0 ground state (rate constant k_{rec}).

This kinetic model was implemented using the programme package Tenua 2.1⁴⁴, and details of the implementation are provided in Supplementary Note 7. The numerical solution provided an optimum fit, which is displayed in Fig. 7c. The resulting kinetic parameters are summarised in Supplementary Note 8. The TrCD signals at high (top panels) and low (bottom panels) laser fluence are displayed in terms of the absolute exciton number densities. As already pointed out above, the TrCD kinetics below 520 nm only monitor the S_0 ground state population and do not show contributions from excited states. Therefore, the experimentally measured values (blue circles) directly reflect the number density of S_0 , which in this case makes the modelling procedure of the TrCD response much easier than for a transient absorption signal. An extensive kinetic analysis of the TrCD kinetics showed that the fast recovery of S_0 population at early times (left panels) is predominantly due to diffusive S_1 – S_1 exciton annihilation (S_1 exciton number density shown as red lines), whereas FRET has only a minor contribution. For the lower initial exciton density, the rise of the S_0 population significantly slows down because of the second-order character of the diffusive process. For further illustration, simulations for the limiting cases (pure diffusive and pure FRET behaviour) are provided in Supplementary Note 9. Lastly, the TrCD experiments provide clear information on the efficiency of charge-pair formation for the highly excited S_x and S_n exciton states of c-PFBT. Taking the rate constants from the best fit, we obtain a yield of 9% for CP formation from the initially excited S_x state and about 6% for the same process in the S_n state accessed by the SSA processes, resulting in a total CP yield of 15%.

In summary, these broadband transient circular dichroism experiments in the UV–Vis range show that the ultrafast electronic response of chiral cholesteric c-PFBT copolymer thin films is of supramolecular origin. The TrCD signal of c-PFBT exclusively tracks population changes in the S_0 ground state (in contrast to the simultaneously recorded transient absorption) and allows for a particularly simple interpretation of the TrCD kinetics and the electronic relaxation processes in the film. Spatial mapping of the TrCD response allows quantifying local variations of the transient chiral response of these films and therefore complements steady-state CD and CPL imaging approaches.

Methods

Preparation of c-PFBT thin films. Intrinsically chiral PFBT (c-PFBT) copolymer with a number average molar weight (M_n) of 7.46 kg mol^{-1} and polydispersity (PDI) of 2.44 was prepared via Suzuki polycondensation from 2,7-bis(pinacoyl-9,9-bis((S)-3,7-dimethyloctyl)fluorene boronic ester, 3,6-dibromothiadiazoole and 2-pinacoyl-9,9-bis((S)-3,7-dimethyloctyl)fluorene boronic ester and then purified afterwards^{17,18}. A solution of c-PFBT in a chlorobenzene:chloroform mixture (1:9 by volume, concentration 7.5 mg ml^{-1}) was spin-coated on thoroughly cleaned 1 mm-thick borosilicate glass slides. The film thickness was controlled by adjustment of the spin-coating conditions using an optional preloading time of 30 s and rotation speeds in the range 500–4000 rpm. The films were then annealed in a nitrogen atmosphere at 150°C for 15 min. The thickness of the polymer films was determined in a contactless fashion by picosecond ultrasonics^{27,28} as $d = 0.25 \cdot \tau_a \cdot c_l$, where τ_a is the measured coherent acoustic phonon oscillation period (obtained from the ultrafast transient absorption kinetics averaged over the wavelength range 470–510 nm) and c_l is the known longitudinal sound velocity of c-PFBT (2490 m s^{-1})²⁹.

Steady-state optical spectroscopy. Steady-state absorption spectra of the thin films were measured using a Varian Cary 5000 spectrophotometer (slit width 0.5 nm). CD spectra were recorded on the same instrument using a home-built add-on employing polariser–achromatic quarter-wave plate combinations (Thorlabs WP25M-UB and AQWP05M-340 for the wavelength range 260–410 nm, Thorlabs LPVISE100-A and AQWP05M-580 for the spectral

region 400–700 nm). The CD spectrum was then obtained by taking the difference of two measurements, with the fast axis of the quarter-wave plate adjusted to either +45° or –45° with respect to the axis of the polariser. Steady-state PL and CPL spectra of the complete thin film samples were obtained as follows: The thin film was illuminated by light from a filtered (Schott UG 1, 3 nm) continuous-wave UV LED (Thorlabs M365LP1, 365 nm, FWHM 10 nm). Fluorescence emitted at right angle passed through a zero-order achromatic broadband quarter-wave plate and a broadband polariser (same combination as for the steady-state CD experiments) and was then focused into a fibre-optic cable connected to a spectrograph with a back-illuminated thermoelectrically cooled CCD detector (Avantes AvaSpec-Hero). CPL spectra were obtained by subtracting the emission spectra of two consecutive measurements with the polariser axis set at either 0° or 90° and the fast axis of the quarter-wave plate fixed at 45°.

Steady-state circular dichroism microscopy. CD microscopy images were recorded on an inverted microscope (Olympus IX71). Illumination of the c-PFBT sample was performed by a halogen lamp using a modified condenser setup featuring an additional polariser (Thorlabs LPVISE100-A) and an achromatic broadband quarter-wave plate (Thorlabs AQWP05M-580). The transmitted light was collected by a microscope objective (Olympus LCPLFL, 40×, NA 0.60) and sent through a bandpass filter (Thorlabs FB470-10, 470 nm centre wavelength, FWHM 10 nm). It then passed a 1:1 matched achromatic doublet pair ($f_1 = f_2 = 100$ mm, Thorlabs MAP10100100-A) and was divided by a non-polarising 50:50 beam splitter (Thorlabs CCM1-BS013/M). One part was detected by a CCD camera (PCO Sensicam QE) to obtain images with a diffraction-limited resolution of about 500 nm. The other part was focused by a quartz lens into an optical quartz fibre (600 µm core diameter) connected to a spectrograph, which was equipped with a back-illuminated thermoelectrically cooled CCD detector (Avantes AvaSpec-Hero) to record the intensity integrated over the entire field of view. Measurements for the light intensity of the c-PFBT sample (I) and a reference glass slide (I_0) were recorded with the fast axis of the quarter-wave plate set at either +45° or –45° with respect to the polariser axis. For comparison, conventional crossed-polariser images were obtained by removing the quarter-wave plate and introducing another polariser (Thorlabs LPVISE100-A) instead of the bandpass filter.

Steady-state circularly polarised luminescence microscopy. For CPL microscopy, the light at 365 nm (FWHM 14 nm) emitted from a 150 W xenon lamp/monochromator combination (Till Photonics Polychrome 5000) was coupled into the same inverted microscope by a quartz fibre to excite the c-PFBT sample through the microscope objective. The luminescence passed through a long-pass filter (440 nm) and an achromatic broadband quarter-wave plate (Thorlabs AQWP05M-580). The beam was then divided by a non-polarising 50:50 beam splitter (Thorlabs CCM1-BS013/M). One part passed through a polariser (Thorlabs LPVISE100-A) and was detected by the CCD camera to obtain PL images (diffraction-limited resolution ca. 500 nm). The other part of the PL passed through another polariser (Thorlabs LPVISE100-A) and was then detected by the same lens/fibre/spectrograph combination already mentioned above, to record spectra integrated over the entire field of view. CPL images and CPL spectra were obtained from two measurements, in which the fast axis of the quarter-wave plate was set at either +45° or –45° with respect to the polariser axis. The CPL images were more blurred and had less contrast than the CD images, likely because of the longer integration time (2 s vs. 1–10 ms, resulting in a larger influence of mechanical vibrations of the setup) and isotropic fluorescence scattered and reflected at domain boundaries of the film.

Ultrafast broadband transient circular dichroism spectroscopy. The transient circular dichroism experiment is based on amplified titanium:sapphire laser system running at 920 Hz (Coherent Libra USP-HE, 800 nm). The linear polarisation of the second harmonic pulses (400 nm, 50 fs pulse length, ca. 20 µJ pulse^{–1}) was converted into left-circular polarisation by means of a high-precision quarter-wave plate (B. Halle Nachfl.). The circularly polarised beam then traversed a DKDP Pockels cell (Eksma MP1), replacing the BBO-based Pockels cell used in an older design^{24,25}. Switching from left-circular to right-circular polarisation was achieved by applying a pulsed half-wave voltage of 2500 V. The circularly polarised 400 nm seed pulses were focused into a translating CaF₂ plate (thickness 3 mm), generating a broadband multifilament UV–Vis supercontinuum (260–700 nm), which was then separated into a signal and a reference beam by means of a broadband beam splitter. At the thin film sample, the circularly polarised signal beam (beam diameter 50 µm) was crossed by the linearly polarised output of an optical parametric amplifier (Coherent OPerA Solo, pumped by the same titanium:sapphire laser system), generating 50 fs pump pulses at 320 or 450 nm (beam diameter 200 µm). The pump pulses were time-delayed by a motorised translation stage and mechanically chopped at half of the probe beam repetition frequency. To exclude any unwanted contributions of quadrupole-field interactions to the TrCD signal, the magic angle of 35.3° between the propagation directions of the pump and probe beams was employed^{45,46}. Complementary experiments at a pump–probe crossing angle of 11°, i.e. for a nearly collinear arrangement typically used in transient absorption experiments, were almost identical and therefore suggest that contributions from quadrupole-field interactions for the c-PFBT sample are negligible. The signal and reference beams were sent into two separate spectrographs

where they were imaged onto 512-element silicon photodiode arrays, with the reference measurement allowing for a shot-to-shot correction of the supercontinuum fluctuations. The resulting transient circular dichroism signal $\Delta CD = \Delta OD_L - \Delta OD_R$ was obtained from four consecutive laser shots (LCP and RCP, each with and without the pump beam) and averaged 3000 times for a given delay time. The time-resolution of the setup was ca. 100 fs. The typical measurement time to acquire a complete spectral data set (ΔOD_L , ΔOD_R and ΔOD) for 300 different delay times with the S/N ratio shown in Fig. 4a was about 60 min for the c-PFBT copolymer thin films studied here. Initial exciton number densities were determined from the measured laser fluence, obtained by a calibrated photodiode (Thorlabs S120VC) and a CCD-camera-based beam profiler (Visulux) using the known absorbance and thickness of the thin films.

Ultrafast broadband transient absorption spectroscopy. Additional transient absorption measurements were recorded with the setup mentioned above, however with the first quarter-wave plate and Pockels cell removed and the linearly polarised pump and probe beams crossing at an angle of about 11° at the sample with the polarisation planes of both beams set at the magic angle of 54.7° to guarantee anisotropy-free detection. For both the transient absorption and transient circular dichroism measurements, the c-PFBT thin film was kept inside an aluminium cell under a constant flow of dry nitrogen. This cell was mounted on two piezo stages (minimum step size 0.1 µm) for random movement within a quadratic plane (2 × 2 mm²), which was normal to the propagation direction of the probe beam. For spatial mapping, a quadratic area of the thin film sample was probed in a random fashion (1 mm², 20 × 20 = 400 points with 50 µm step size in each direction).

Time-correlated single-photon counting (TCSPC). Transient fluorescence decays of the c-PFBT thin films were collected using TCSPC on a Horiba Jobin-Yvon TemPro system with 55 ps/channel⁴⁷. Photoexcitation was performed at 1 MHz repetition frequency using a pulsed LED (Horiba Scientific NanoLED, 454 nm, FWHM 26 nm, pulse duration 1.1 ns, 3.2 pJ pulse^{–1}). Stray light of the excitation beam was removed by means of a long-pass filter (Schott GG495, thickness 3 mm). The response function of the setup was determined using a TiO₂ thin film sample. A deconvolution procedure was applied to extract the time constants and amplitudes from a biexponential fit.

Kinetic analysis of transient circular dichroism data. The kinetic scheme provided in Fig. 7b was implemented and numerically solved using the programme Tenua 2.1⁴⁴. The rate constants in the mechanism were varied to arrive at an optimal description of the TrCD decay kinetics.

Data availability

The data that support the findings of this study are available from the corresponding authors upon request.

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Author contributions

K.O. and T.L. conceived the project. M.M. prepared the thin film samples and performed the steady-state absorption experiments. M.M. and M.S. conducted the CD and CPL spectroscopy and microscopy experiments. K.O., T.L., and M.M. carried out the transient circular dichroism and transient absorption experiments and performed the data evaluation. M.S., K.O., and T.L. implemented the optical and electronic setups and the CD and CPL microscopy. M.J.C. and D.H.C. synthesised the copolymer samples. T.L., M.M. and K.O. analysed the spectroscopic results and wrote the paper.

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Competing interests

The authors declare no competing interests.

Additional information

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Supplementary Information for

Mapping the broadband circular dichroism of copolymer films with supramolecular chirality in time and space

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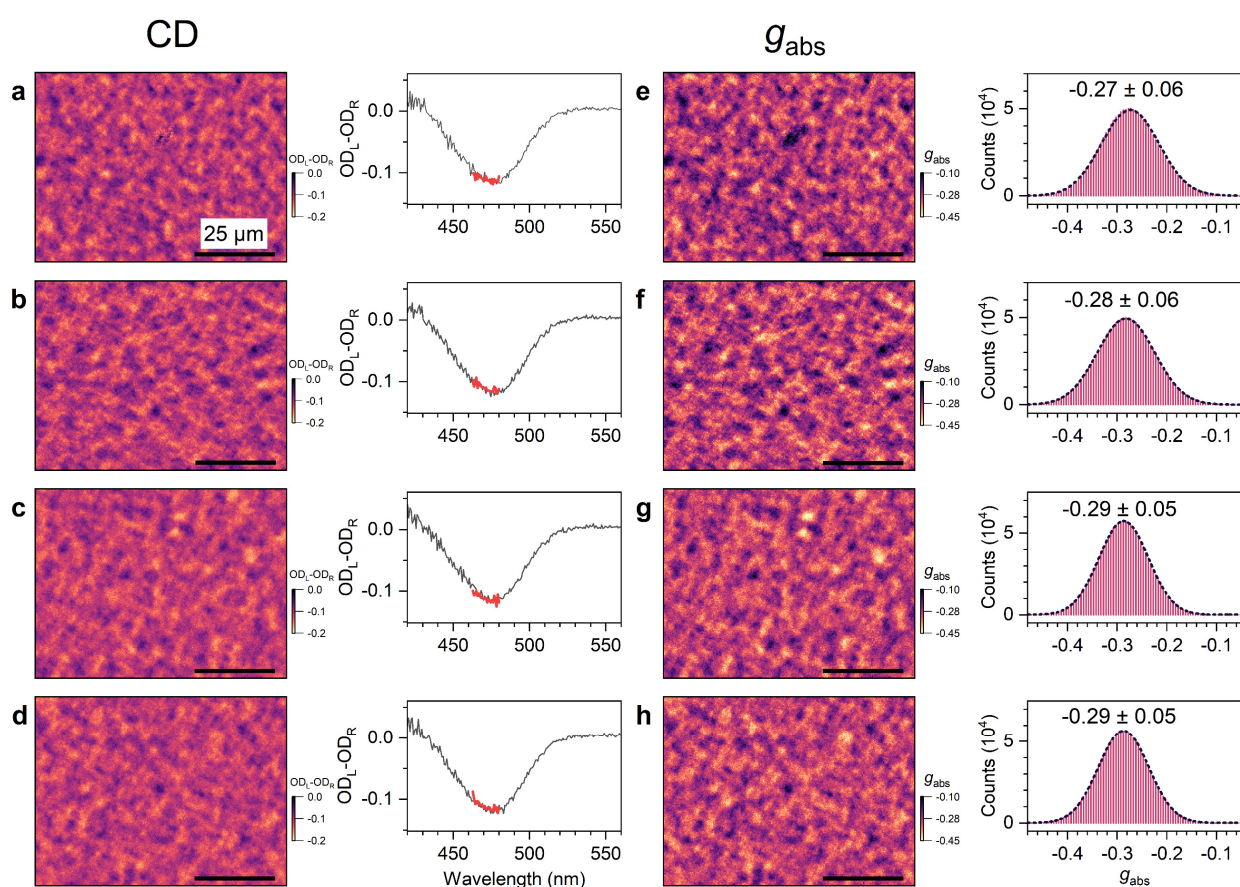
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Supplementary Note 1.

CD imaging of c-PFBT thin films with diffraction-limited resolution

Supplementary Fig. 1 shows CD imaging results for four different areas ($80 \times 60 \mu\text{m}^2$) of the c-PFBT thin film investigated in Fig. 2 of the main manuscript. The CD images in panels a-d look very similar, as do the corresponding CD spectra integrated over the entire field of view ($210 \times 160 \mu\text{m}^2$) on the right side. The corresponding g_{abs} images are presented in panels e-h. The four regions have a very similar appearance, suggesting a good uniformity of the c-PFBT thin film over larger length scales. This is confirmed by the g_{abs} statistics on the right side of panels e-h, where the g_{abs} distributions are very similar and perfectly described by Gaussian functions with large average g_{abs} values of -0.28 ± 0.06 . Note that the images in panels c and g correspond to the representative regions selected in panels a and b of Fig. 2 in the main manuscript, respectively.

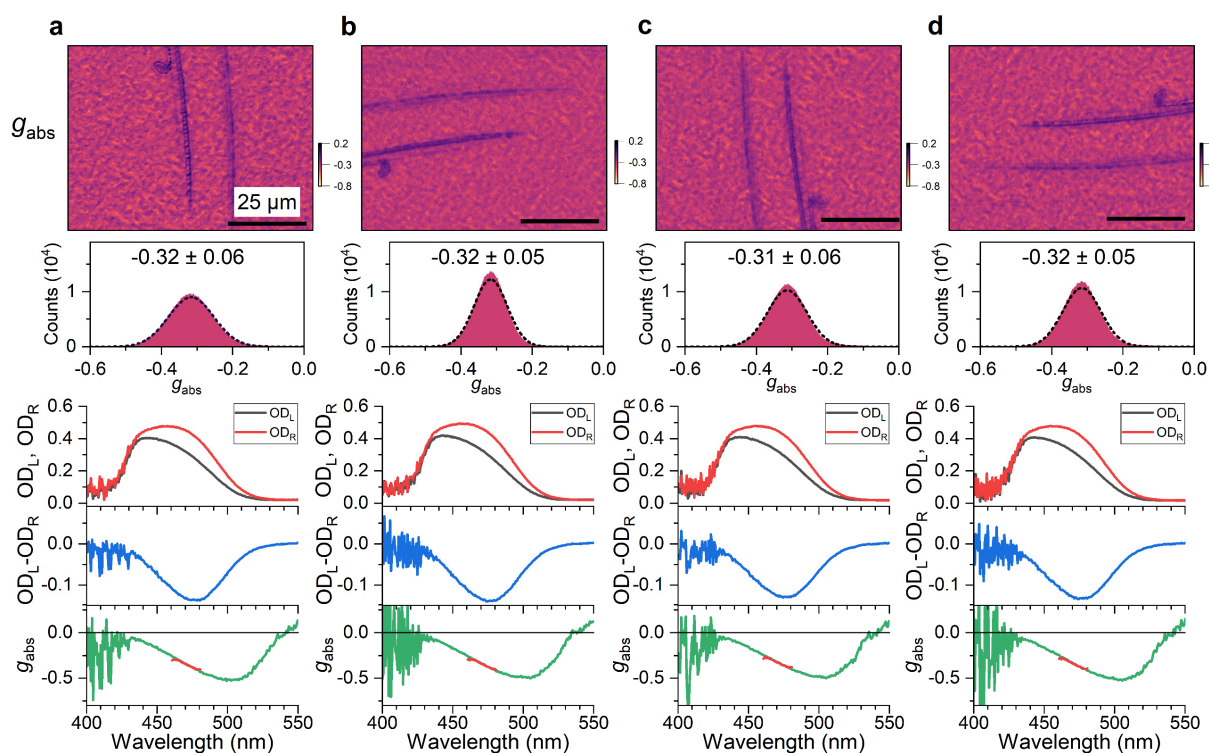


Supplementary Fig. 1 CD imaging with diffraction-limited resolution for different regions of the c-PFBT thin film analysed in Fig. 2 (main manuscript). a-d Microscope images ($80 \times 60 \mu\text{m}^2$) for the circular dichroism of the c-PFBT thin film at different positions. Plots on the right show the CD signals integrated over the entire field of view ($210 \times 160 \mu\text{m}^2$, thin black lines: full spectra, thick red lines: spectral region selected by the band pass filter ($470 \pm 10 \text{ nm}$) used for CD imaging). e-h Corresponding images for the dissymmetry factor g_{abs} , with histograms on the right including Gaussian fits as dashed black lines, determined over the entire field of view. The length of the black scale bar in each image indicates a distance of $25 \mu\text{m}$. The images in panels c and g correspond to the panels a and b of Fig. 2 in the main manuscript, respectively.

Supplementary Note 2.

Invariance of CD images under sample rotation and flipping

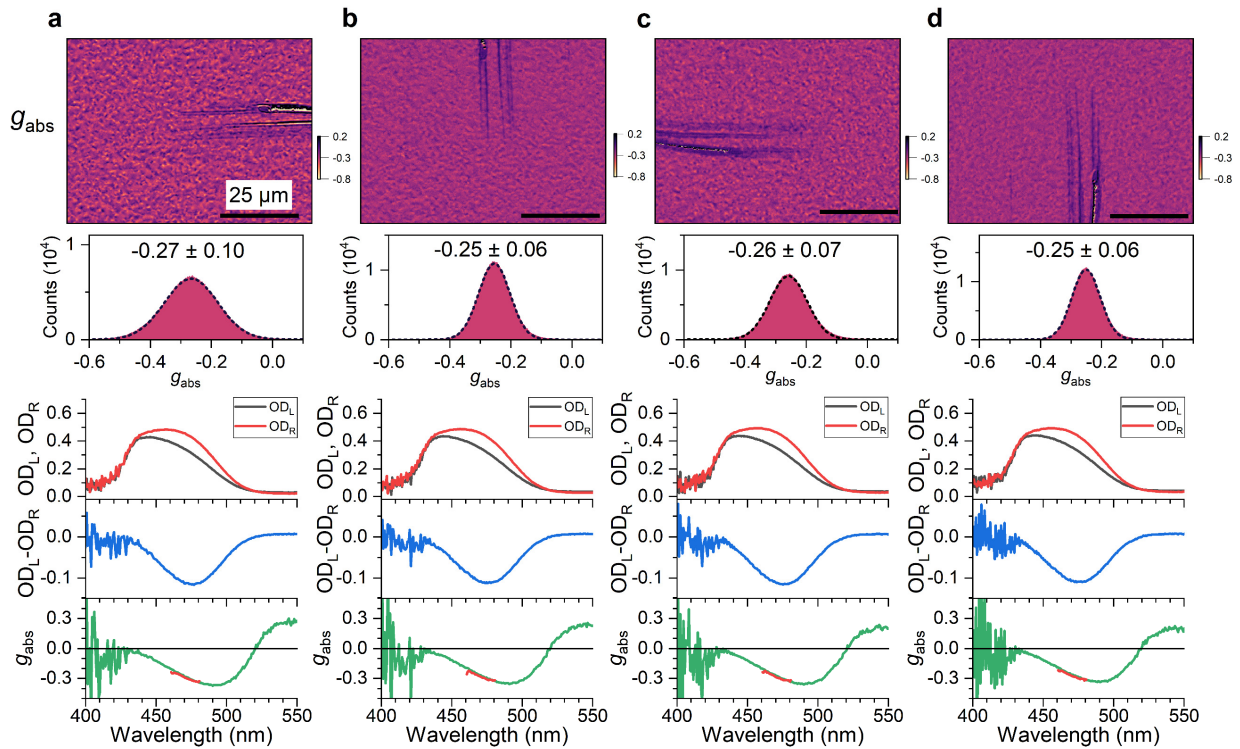
Figure 1c in the main manuscript already showed that the thin films exhibit virtually no changes in the CD response and the dissymmetry factor g_{abs} upon turning or flipping of the thin film samples on a several millimetre length scale. Here, we additionally demonstrate that this also holds over the micrometre length scale observed in the CD images. An example is shown in Supplementary Fig. 2 for the same film used in Fig. 1c of the main manuscript. We intentionally picked a scratched area, which makes the 90° stepwise rotation in anticlockwise direction easily visible. The scratches also provide a convenient reference for comparing individual features in the images. As one can clearly see, the images are indeed invariant under rotation, with an average g_{abs} value of -0.32 . The area-integrated spectra for OD_L , OD_R , $\text{OD}_L - \text{OD}_R$ and g_{abs} are also virtually identical. Therefore, we can also exclude contributions on the micrometre scale resulting from a combination of linear dichroism and linear birefringence in our sample in combination with any possible anisotropies of the CD microscopy setup. As a nice side information further illustrating the power of CD imaging, we can see that in the region of the scratches there is strongly reduced CD activity (blueish colours), which indicates that the film in the scratched regions must be either very thin (low CD activity) or even completely missing.



Supplementary Fig. 2 Invariance of a CD image under anticlockwise rotation of the film sample.

a Microscope image ($80 \times 60 \mu\text{m}^2$) for the dissymmetry parameter g_{abs} of a 240 nm thick c-PFBT thin film (top) with a histogram of g_{abs} values (middle) including a Gaussian fit (dashed black line), determined over the entire field of view, and spectra integrated over the entire field of view ($210 \times 160 \mu\text{m}^2$, bottom) showing the optical density for left- and right-circularly polarised light (OD_L (black line), OD_R (red line)), the CD spectrum (blue line) and the g_{abs} spectrum (green line), with the thick red line indicating the spectral region selected by the band pass filter ($470 \pm 10 \text{ nm}$) used for CD imaging. **b-d** Same as in panel a, but sample manually rotated anticlockwise in 90° steps. The length of the black scale bar in each CD image indicates a distance of 25 μm .

We also repeated the same measurements after flipping the sample. Here we needed to search for a different scratched spot, and the results are shown in Supplementary Fig. 3. Again, the images are virtually invariant under 90° anticlockwise rotation. The average g_{abs} value of this different region is slightly lower (-0.26) but still very close to the value for the region shown in Supplementary Fig. 2. Also here, we can exclude contributions on the micrometre scale resulting from a combination of linear dichroism and linear birefringence in our sample in combination with any possible anisotropies of the CD microscopy setup.

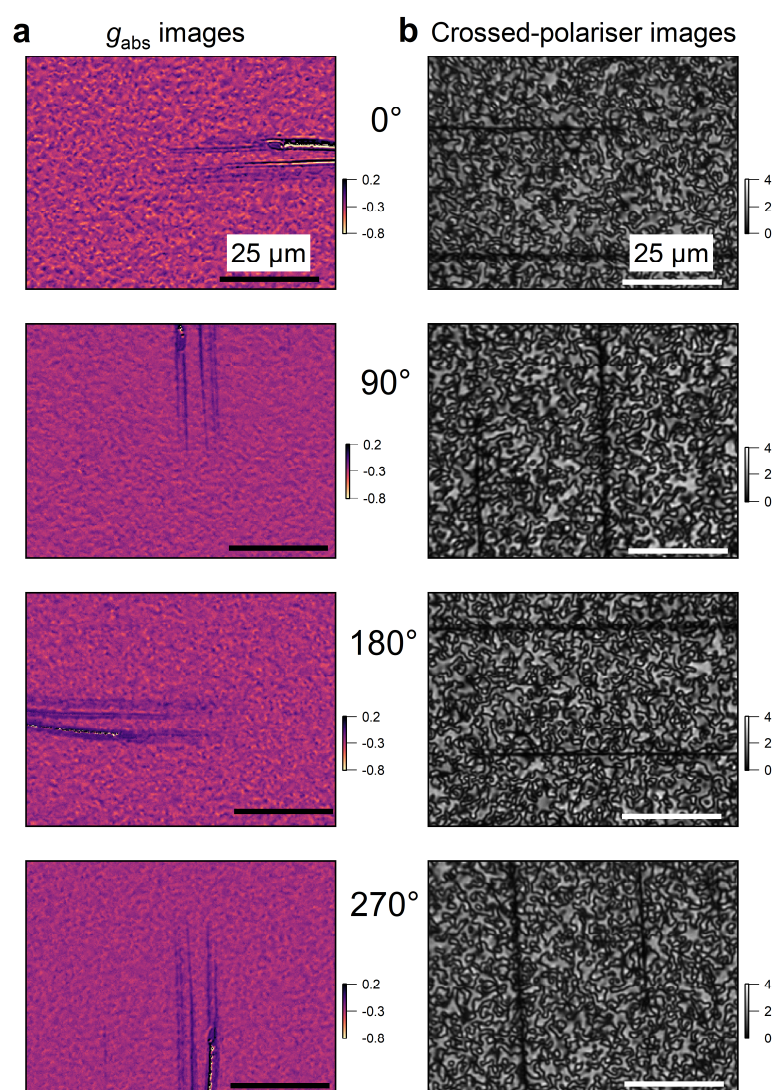


Supplementary Fig. 3 Invariance of the CD image under anticlockwise rotation after flipping the same sample used in Supplementary Fig. 2. a-d Microscope images for g_{abs} , g_{abs} distributions and absorption, CD and g_{abs} spectra, obtained using the same procedure as in Supplementary Fig. 2, employing subsequent 90° anticlockwise rotation steps.

Supplementary Note 3.

Comparison of CD images and crossed-polariser images

Supplementary Fig. 4 shows a comparison of images of a c-PFBT thin film for the dissymmetry parameter g_{abs} (panels in a, same as in Supplementary Fig. 3a-d) and images for another region of the same film using a conventional crossed-polariser arrangement (panels in b). In both cases, the images were rotated anticlockwise in 90° steps. The crossed-polariser images show very similar island-type structures which lead to changes in the polarisation of the linearly polarised illumination beam. The distinct black lines of the scratches suggest that the c-PFBT film in these regions is either very thin or missing, so that no change in polarisation takes place.

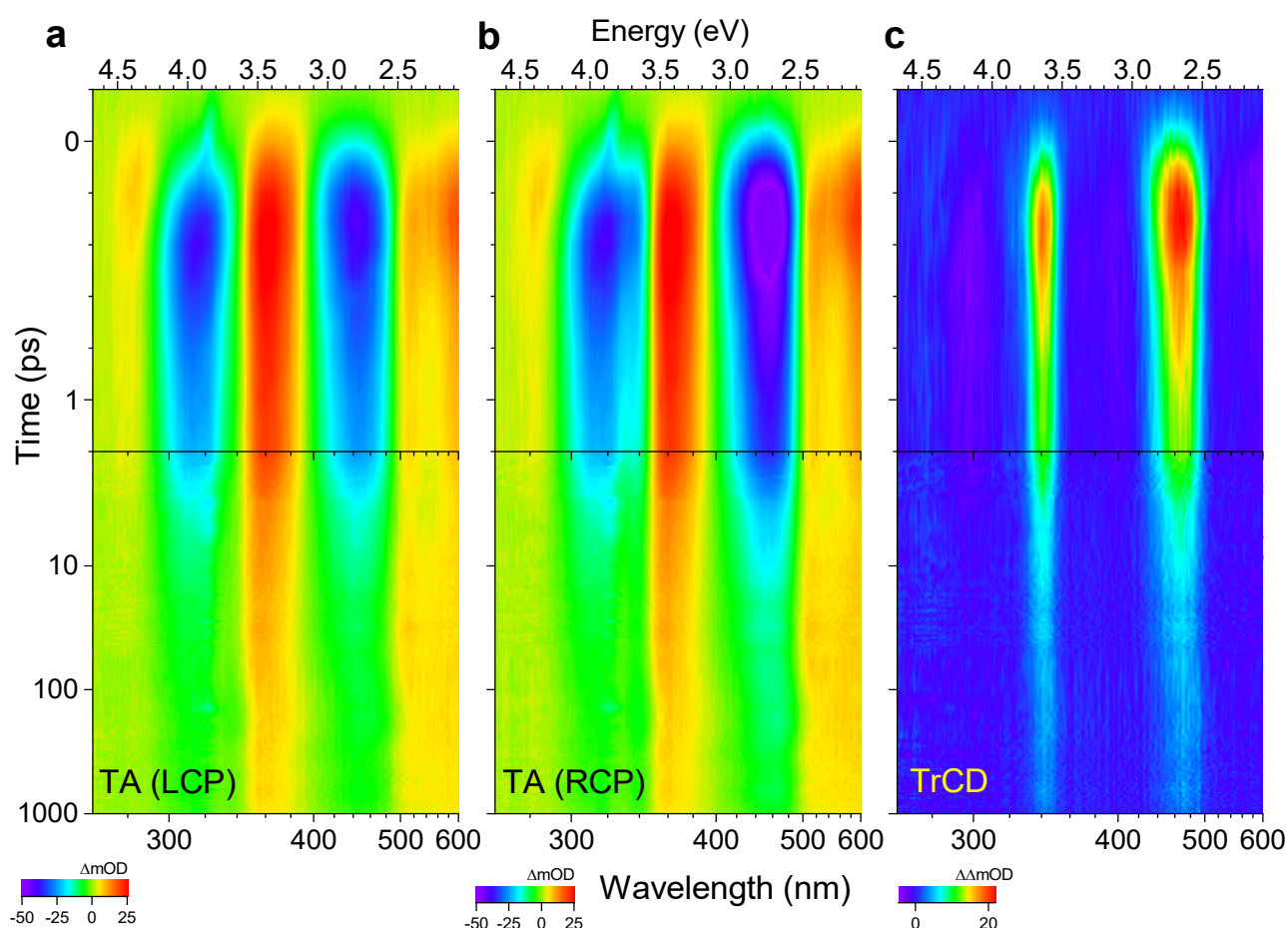


Supplementary Fig. 4 Comparison of CD images and crossed-polariser images obtained for anticlockwise rotation of a c-PFBT thin film sample. **a** Same microscope images ($80 \times 60 \mu\text{m}^2$) for the dissymmetry parameter g_{abs} of a 240 nm thick c-PFBT thin film as shown in Supplementary Fig. 3 manually rotated in steps of 90° (from top to bottom). **b** Same as in panel a, but for another region of the same film located between crossed polarisers. The length of the black and white scale bars in each of the images indicates a distance of 25 μm .

Supplementary Note 4.

Contour diagrams of transient CD and absorption experiments

Supplementary Fig. 5 shows the complete data set of the transient absorption spectra for left-circularly and right-circularly polarized probing (panels a and b) and the resulting transient circular dichroism spectra (panel c) for the 241 nm thin c-PFBT film as contour plots. The sample was excited at 320 nm. Spectra for selected delay times from this data set were already provided in Fig. 4a of the main manuscript. It is clearly visible that the bleach regions (blue) around 340 and 455 nm of the transient absorption spectra for RCP probing (panel b) are more negative than for LCP probing (panel a). This is the reason for the positive features (red) in the TrCD contour plot (panel c), which is the difference between the contour plots in panels a and b. The TrCD spectra closely resemble the inverted steady-state CD spectrum. Weak circularly polarised stimulated emission is visible in panel c as a feature of violet colour above 520 nm.

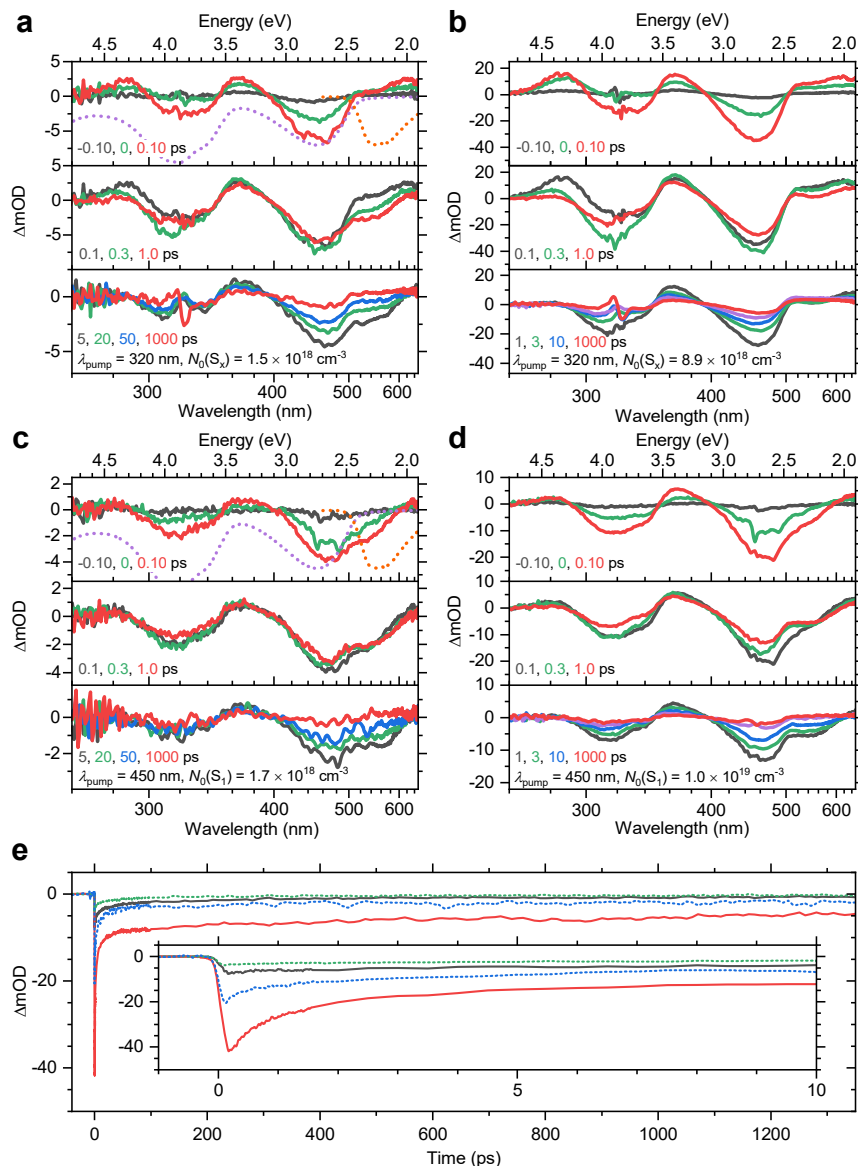


Supplementary Fig. 5 Contour diagrams of ultrafast transient absorption and transient circular dichroism spectra of a 241 nm thin c-PFBT film after excitation at 320 nm. **a** Transient absorption for probing with left-circularly polarised light. **b** Transient absorption for probing with right-circularly polarised light. **c** Transient circular dichroism (difference of the contour diagrams shown in panels a and b). Note the logarithmic time axis.

Supplementary Note 5.

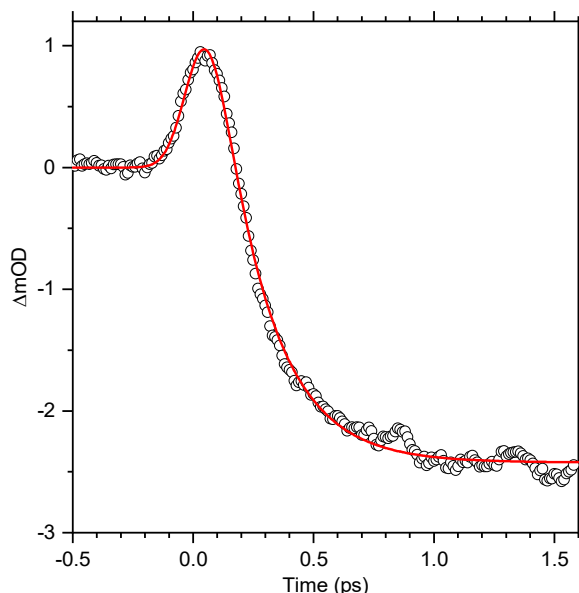
Additional UV–Vis broadband transient absorption experiments

Supplementary Fig. 6 shows ultrafast broadband transient absorption experiments for a 157 nm thin c-PFBT film at the pump wavelengths 320 nm (S_x excitation, panels a and b) and 450 nm (S_1 excitation, panels c and d). In each case, experiments were carried out at low and high initial exciton number densities: for 320 nm excitation $N_0(S_x) = 1.5 \times 10^{18}$ and $8.9 \times 10^{18} \text{ cm}^{-3}$, and for 320 nm excitation $N_0(S_1) = 1.7 \times 10^{18}$ and $1.0 \times 10^{19} \text{ cm}^{-3}$.



Supplementary Fig. 6 Ultrafast broadband transient absorption experiments for a 157 nm thin c-PFBT film. **a** Pump wavelength: 320 nm, $N_0(S_x) = 1.5 \times 10^{18} \text{ cm}^{-3}$. **b** Pump wavelength: 320 nm, $N_0(S_x) = 8.9 \times 10^{18} \text{ cm}^{-3}$. **c** Pump wavelength: 450 nm, $N_0(S_1) = 1.7 \times 10^{18} \text{ cm}^{-3}$. **d** Pump wavelength: 450 nm, $N_0(S_1) = 1.0 \times 10^{19} \text{ cm}^{-3}$. Dotted violet and orange lines in panels a and c are the inverted steady-state absorption and the S_1 stimulated emission spectrum, respectively. **e** Kinetics averaged over the wavelength range 460–470 nm for 320 nm excitation (black solid line: $N_0(S_x) = 1.5 \times 10^{18} \text{ cm}^{-3}$, red solid line: $N_0(S_x) = 8.9 \times 10^{18} \text{ cm}^{-3}$) and 450 nm excitation (green dashed line: $N_0(S_1) = 1.7 \times 10^{18} \text{ cm}^{-3}$, blue dashed line: $N_0(S_1) = 1.0 \times 10^{19} \text{ cm}^{-3}$), with a magnification for short times in the inset.

We focus here on additional spectroscopic information of central importance for the kinetic modelling procedure. First of all, we compare the different spectral evolution for excitation at 320 and 450 nm. Around zero time-delay, the transient absorption spectra for 320 nm excitation (panel a) show a bleach feature, which has the same shape as the inverted steady-state absorption spectrum (dotted violet line). In contrast, for 450 nm excitation (panel c) the transient spectra clearly show also a stimulated emission feature above 500 nm, which comes from the S_1 exciton state. For excitation at 320 nm (panel a), this S_1 stimulated feature is initially missing and only builds up at later times, see the spectra at 0.1, 0.3 and 1 ps. We therefore assign this process to internal conversion from the S_x state to the S_1 state. The kinetic fit in the wavelength range 525–570 nm (Supplementary Fig. 7) provides the lifetime of the S_x state as $\tau_{x,\text{total}} = 206$ fs. As shown in the kinetic modelling (main manuscript), the corresponding rate constant $k_{x,\text{total}} = \tau_{x,\text{total}}^{-1} = 4.85 \times 10^{12} \text{ s}^{-1}$ is the sum of the rate constant k_x for internal conversion from S_1 to S_x and the rate constant k_{CPx} for charge-pair formation (i.e. generation of an electron–hole pair). This value was employed as an important constraint in the kinetic modelling procedure and leads to an accurate value of the S_1 –CP branching ratio. The long-lived absorption of the CP state is clearly visible in the transient absorption spectra above 600 nm (cf. the red spectra at 1000 ps in panels a–d).



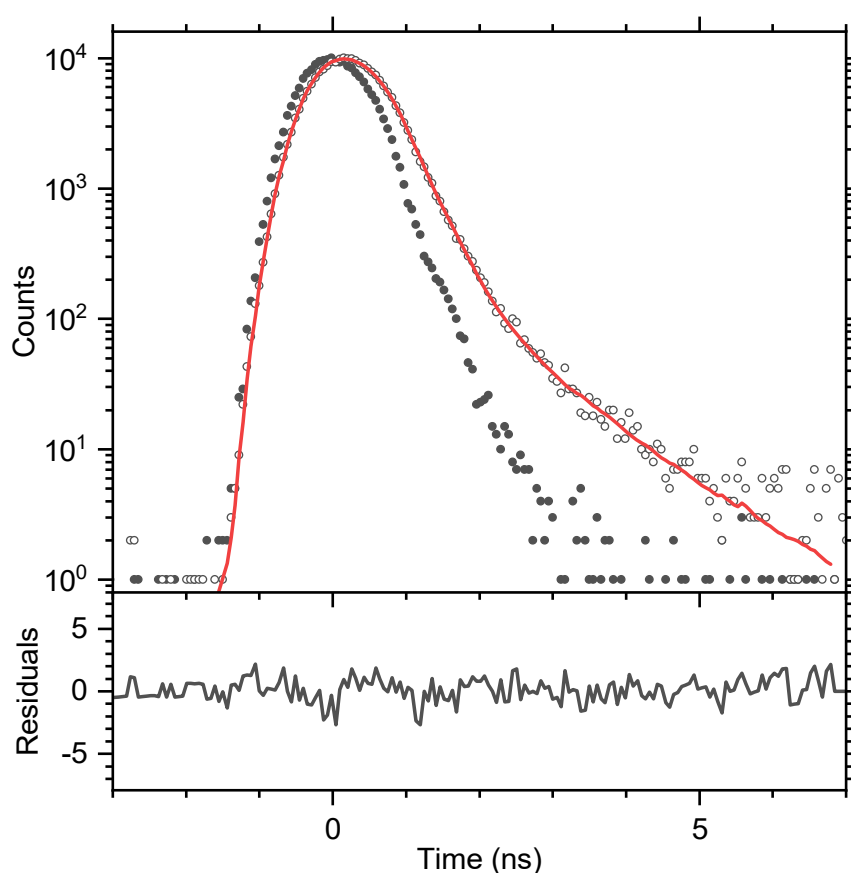
Supplementary Fig. 7 Kinetics for the decay of the S_x exciton state of c-PFBT. Open circles: Kinetics after excitation at 320 nm (averaged over the wavelength range 525–570 nm, $N_0(S_x) = 1.5 \times 10^{18} \text{ cm}^{-3}$). Solid red line: Kinetic fit (convolution with the cross correlation of 75 fs) employing a monoexponential decay and a constant negative offset. The fit provides the S_x lifetime $\tau_{x,\text{total}} = 206$ fs.

For both excitation wavelengths, a higher initial exciton number density N_0 leads to a drastic acceleration of the decay of the bleach region, that means an accelerated recovery of the ground state S_0 due to higher-order processes. This is highlighted by the four kinetic traces shown in Supplementary Fig. 6e. This dependence on N_0 is consistent with the TrCD kinetics (Fig. 7a, main manuscript). However, interpretation of the TrCD kinetics is much easier, because it is only sensitive to the S_0 population dynamics. In contrast, for the transient absorption kinetics it is more difficult to disentangle the overlapping spectral contributions of the S_x , S_1 , CP and S_0 species.

Supplementary Note 6.

Transient fluorescence experiments

Supplementary Fig. 8 shows the fluorescence decay curve of the S_1 exciton state of a c-PFBT thin film after excitation by a pulsed LED at 454 nm detected using time-correlated single photon counting (TCSPC). These measurements are at very low fluence, with an estimated initial S_1 exciton number density $N_0(S_1) = 2 \times 10^9 \text{ cm}^{-3}$. This value is 9–10 orders of magnitude smaller than in the transient absorption and transient circular dichroism experiments. At such a low N_0 value, singlet–singlet annihilation processes can be completely neglected. The observed decay is therefore due to the intrinsic lifetime of the S_1 excitons. The fitting procedure provides the time constant $\tau_1 = 235 \text{ ps}$. The fit also shows a second, minor time constant $\tau_2 = 1070 \text{ ps}$ ($A_2 = 0.9\%$), which could be due to a very small amount of a fluorescing impurity in the polymer which is not detectable in the transient circular dichroism and transient absorption experiments.



Supplementary Fig. 8 Fluorescence decay of the S_1 exciton state of a c-PFBT thin film after photoexcitation at 454 nm measured by TCSPC. Open circles: Fluorescence decay. Solid circles: Instrument response function (IRF). The red line is a biexponential fit obtained from deconvolution, with the time constants (amplitudes) $\tau_1 = 235 \text{ ps}$ ($A_1 = 99.1\%$) and $\tau_2 = 1070 \text{ ps}$ ($A_2 = 0.9\%$). Note the semilogarithmic representation. Fit residuals are provided in the bottom panel. An appropriate longpass filter (Schott GG495) was employed to cut off stray light from the excitation source.

Supplementary Note 7.

Kinetic model

To describe the relaxation processes of c-PFBT after photoexcitation, we employ the kinetic model introduced in Fig. 7b of the main manuscript, which is based on the one used by us previously for describing the photoinduced dynamics of the copolymer F8BT¹. The mechanism is summarised and explained in the following in more detail:



Step S1 describes the unimolecular relaxation of the initially excited c-PFBT species to S_0 . This decay starts from the S_1 singlet exciton state for the pump wavelength 450 nm (rate constant $k_1 = \tau_1^{-1}$, where τ_1 is the corresponding lifetime of 235 ps, cf. Supplementary Fig. 8) or a higher excited singlet exciton state denoted as S_x (rate constant $k_x = \tau_x^{-1}$, for excitation at 320 nm into a higher singlet absorption band), which then decays via S_1 to S_0 . As discussed in our previous publication on F8BT¹, only higher electronic states, denoted as S_x , are capable of directly dissociating into a charge pair state (CP, electron (e^-) and hole (h^+)) as indicated by step S2 in the mechanism (rate constant $k_{CPx} = \tau_{CPx}^{-1}$).

Still, there are clear spectral hallmarks for the formation of the CP state upon population of S_1 , as indicated by the transient absorption feature above 600 nm (Supplementary Fig. 6), and the pronounced dependence of the kinetics of the S_0 recovery on the initial exciton number density $N(S_1)$. Thus, there must be higher-order processes populating a higher-energy exciton state S_n from S_1 . These are singlet–singlet annihilation (SSA) channels, which are efficient at high exciton number densities, but less important at low exciton number densities. There are two competing SSA processes: One is the diffusive bimolecular SSA channel (step S3), in which two S_1 exciton species diffuse along the polymer chains with a diffusion constant D and then react, once they reach the critical contact distance R_c . This leads to the formation of a high-energy S_n exciton state and an S_0 ground state. The corresponding rate constant $k_{diff} (= \tau_{diff}^{-1})$ is²:

$$k_{diff} = 4\pi D R_c \quad (S8)$$

SSA between two S_1 excitons may also occur via nonradiative Förster resonance energy transfer (FRET)^{3,4}. This requires overlap of the emission band of the S_1 donor and the ESA band of the S_1 acceptor⁵. The loss of S_1 species via FRET is of first order (step S4a, with the rate constant $k_{Förster} =$

$\tau_{\text{Förster}}^{-1}$) and leads to simultaneous excitation of the S_1 acceptor, which is also of first order (step S4b, again with the rate constant $k_{\text{Förster}} = \tau_{\text{Förster}}^{-1}$). The total rate of S_1 loss due to FRET is therefore:

$$\frac{dN(S_1)}{dt} = -2k_{\text{Förster}} \cdot N(S_1) \quad (\text{S9})$$

The rate constant $k_{\text{Förster}}$ displays a characteristic R^{-6} dependence on the donor–acceptor distance R , where τ_1 is the radiative S_1 lifetime of the donor and R_0 is the distance, at which there is equal probability for the radiative decay and the FRET process^{3,4}:

$$k_{\text{Förster}} = \frac{1}{\tau_1} \left(\frac{R_0}{R} \right)^6 \quad (\text{S10})$$

Therefore, close S_1 pairs react much faster than more distant pairs. Because the S_1 exciton number density $N(S_1)$ decreases during relaxation, at later times only more distant pairs with smaller $k_{\text{Förster}}$ values remain. This makes the Förster process intrinsically time-dependent, and the average rate constant $\langle k_{\text{Förster}} \rangle$ for the S_1 ensemble decreases steadily over time. In a kinetic mechanism, one would like to get rid of this R dependence and retain only the dependence on the exciton number density $N(S_1)$. Therefore, similar to earlier treatments^{1,5}, we use the relation between the S_1 exciton number density and the average exciton radius $\langle r \rangle$ (or, equivalently, the corresponding exciton distance $\langle R \rangle = 2 \cdot \langle r \rangle$):

$$N(S_1) = \left(\frac{4}{3} \pi \langle r \rangle^3 \right)^{-1} = \left(\frac{1}{6} \pi \langle R \rangle^3 \right)^{-1} \quad (\text{S11})$$

Rearranging Eq. S11 for $\langle R \rangle$ and substituting it into Eq. S10 provides (rewritten as an ensemble average)

$$\langle k_{\text{Förster}} \rangle = \frac{1}{\tau_1} \left(\frac{R_0}{\langle R \rangle} \right)^6 = \frac{\pi^2 R_0^6}{36 \tau_1} N(S_1)^2 \quad (\text{S12})$$

Reformulating Eq. S9 as an ensemble average and combining it with Eq. S12 leads to

$$\frac{dN(S_1)}{dt} = -2 \langle k_{\text{Förster}} \rangle N(S_1) = -\frac{\pi^2 R_0^6}{18 \tau_1} N(S_1)^3 = -k_{\text{FRET}} N(S_1)^3 \quad (\text{S13})$$

As a result, the rate of the S_1 exciton loss is proportional to $N(S_1)^3$, resulting in an apparent third-order behaviour with the rate constant k_{FRET} . For the sake of an easier treatment, we therefore replace the Förster-type SSA processes S4a and S4b in the kinetic scheme by the equivalent steps S14a and S14b:



We need to use two third-order steps with the same rate constant k_F to correctly account for the stoichiometry of the FRET process. For the decay of S_1 we obtain from steps S14a and S14b

$$\frac{dN(S_1)}{dt} = -6k_F N(S_1)^3 \quad (\text{S15})$$

with the third-order rate constant $k_F = k_{\text{FRET}}/6$.

To obtain the corresponding Förster radius R_0 , we use a connection between $\langle k_{\text{Förster}} \rangle$ (first order, Eq. S10) and $k_{\text{FRET}} = 6 k_F$ (Eqs. S13 and S15) by comparing the respective half-lives. The third-order half-life $t_{1/2,3.o.}$ obtained from Eq. S15 is:

$$t_{1/2,3.o.} = \frac{1}{4k_F N(S_1)^2} \quad (S16)$$

Correspondingly, we obtain from the first-order expression in Eq. S13

$$t_{1/2,1.o.} = \frac{\ln(2)}{2\langle k_{\text{Förster}} \rangle} \quad (S17)$$

Next, we use Eqs. S12, S16 and S17 to arrive at an expression for the Förster radius R_0 (under the assumption that the two half-lives should be the same):

$$R_0 = \sqrt[6]{\frac{\langle k_{\text{Förster}} \rangle 36 \tau_1}{\pi^2 N(S_1)^2}} = \sqrt[6]{\frac{\ln(2) 18 \tau_1}{t_{1/2,1.o.} \pi^2 N(S_1)^2}} = \sqrt[6]{\frac{k_F \ln(2) 72 \tau_1}{\pi^2}} \quad (S18)$$

Equation S18 was employed to convert the third-order rate constant k_F (obtained from the kinetic modelling) into the corresponding R_0 value.

The remaining steps in the kinetic mechanism deal with the fate of the excited species S_n resulting from the SSA processes. The S_n exciton state either decays back to S_1 with $k_n = \tau_n^{-1}$ (step S5), or produces a charge pair (electron–hole pair, step S6) with $k_{\text{CPn}} = \tau_{\text{CPn}}^{-1}$. Recombination of the charge pair occurs on much longer time scales ($k_{\text{rec}} = \tau_{\text{rec}}^{-1}$), as indicated by step S7.

Supplementary Note 8.

Summary of optimised fit parameters for the TrCD kinetics

Supplementary Table 1 summarises the kinetic fit parameters employed for the optimised kinetic simulations of Fig. 7c in the main manuscript. Note that the dominant SSA process is the diffusive channel and that Förster resonance energy transfer plays a minor role and leads only to a small improvement of the fit.

Supplementary Table 1 Summary of parameters obtained from the kinetic analysis of the fluence-dependent measurements of c-PFBT upon photoexcitation at 320 nm.

Physical quantity (unit)	Value	Physical quantity (unit)	Value
$N_{0,\text{high}}(S_x) \text{ (cm}^{-3}\text{)}$	9.60×10^{18}		
$N_{0,\text{low}}(S_x) \text{ (cm}^{-3}\text{)}$	2.29×10^{18}		
$k_x(S_x \rightarrow S_1) \text{ (s}^{-1}\text{)}$	4.40×10^{12}	$\tau_x \text{ (fs)}$	227
$k_{\text{CPx}}(S_x \rightarrow e^- + h^+) \text{ (s}^{-1}\text{)}$	4.50×10^{11}	$\tau_{\text{CPx}} \text{ (ps)}$	2.22
$k_{x,\text{total}} = k_x + k_{\text{CPx}} \text{ (s}^{-1}\text{)}$	4.85×10^{12}	$\tau_{x,\text{total}} \text{ (fs)}$	206
		$\Phi_{\text{CPx}} \text{ (\%)}$	9.3
$k_1(S_1 \rightarrow S_0) \text{ (s}^{-1}\text{)}$	4.26×10^9	$\tau_1 \text{ (ps)}$	235
$k_F(3 S_1 \rightarrow S_n + 2 S_0) \text{ (cm}^6 \text{ s}^{-1}\text{)}$	2.00×10^{-27}		
$k_F(3 S_1 \rightarrow 2 S_n + S_0) \text{ (cm}^6 \text{ s}^{-1}\text{)}$	2.00×10^{-27}		
$k_{\text{FRET}} \text{ (cm}^6 \text{ s}^{-1}\text{)}$	1.20×10^{-26}		
$\langle k_{\text{Förster}} \rangle (S_1 \rightarrow S_0) \text{ (s}^{-1}\text{)}^a$	$1.63 \times 10^{13} (N_{0,\text{high}})$	$R_0 \text{ (nm)}^b$	11.6
	$9.26 \times 10^{11} (N_{0,\text{low}})$		
$k_{\text{diff}}(2 S_1 \rightarrow S_n + S_0) \text{ (cm}^3 \text{ s}^{-1}\text{)}$	8.00×10^{-8}		
$k_n(S_n \rightarrow S_1) \text{ (s}^{-1}\text{)}$	3.8×10^{14}	$\tau_n \text{ (fs)}$	3
$k_{\text{CPn}}(S_n \rightarrow e^- + h^+) \text{ (s}^{-1}\text{)}$	2.3×10^{13}	$\tau_{\text{CPn}} \text{ (fs)}$	40
$k_{n,\text{total}} = k_n + k_{\text{CPn}} \text{ (s}^{-1}\text{)}$	4.0×10^{14}	$\tau_{n,\text{total}} \text{ (fs)}$	3
		$\Phi_{\text{CPn}} \text{ (\%)}$	6
$k_{\text{rec}}(e^- + h^+ \rightarrow S_0) \text{ (cm}^3 \text{ s}^{-1}\text{)}$	7.9×10^{-10}		

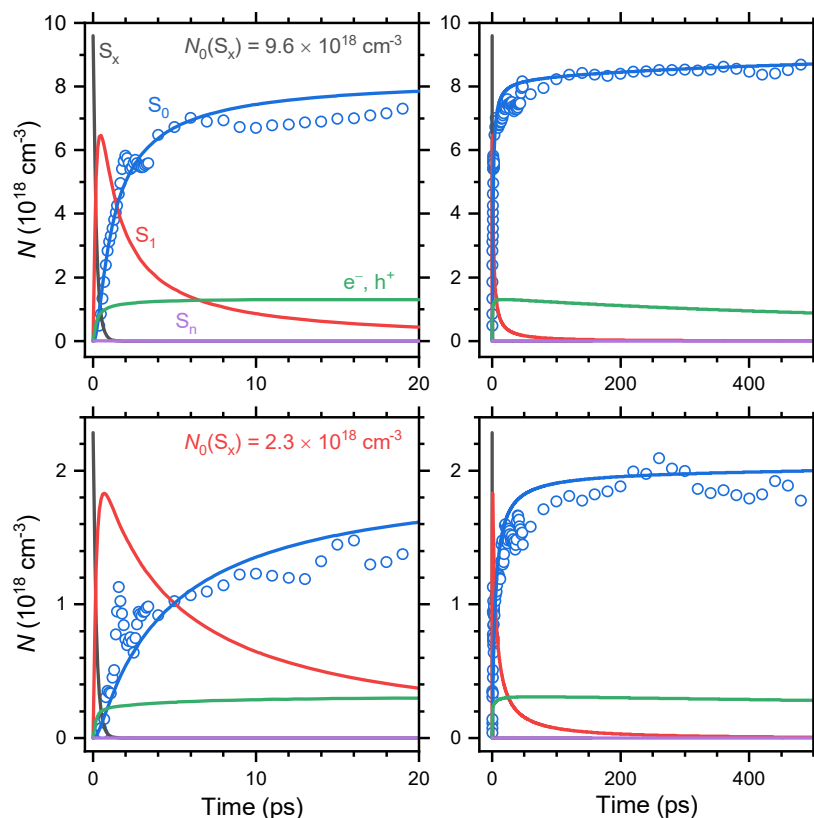
^a From Eq. S12.

^b From Eq. S18.

Supplementary Note 9.

Kinetic simulations for two limiting cases

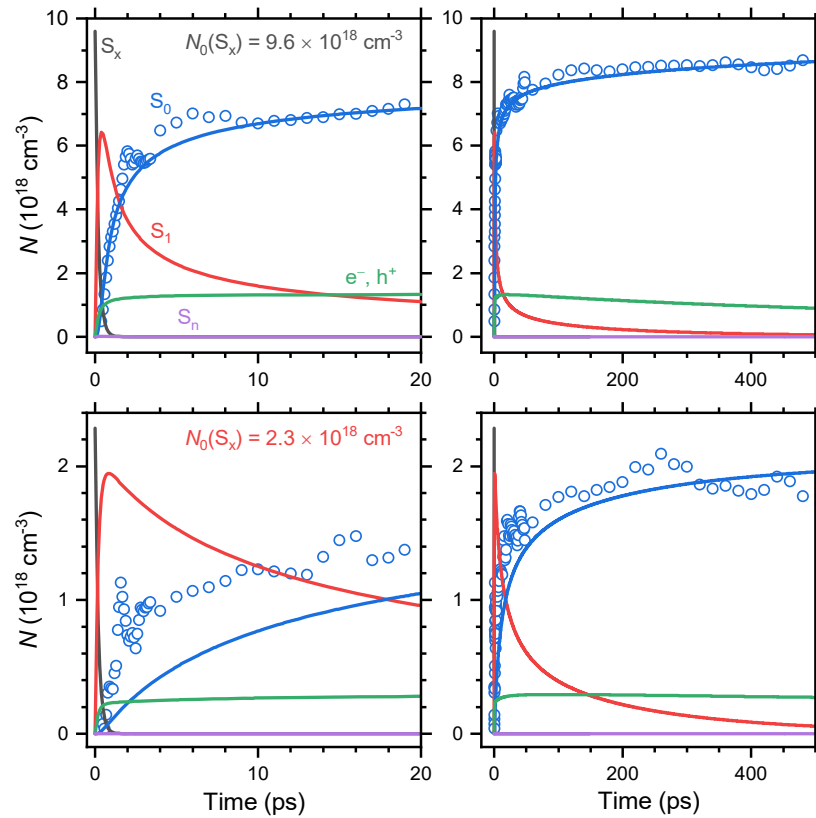
To address the relative importance of the different singlet–singlet annihilation processes in S_1 , i.e. bimolecular diffusive and FRET, we provide here two instructive results from the kinetic modelling. Supplementary Fig. 9 shows the result, which is obtained when there is only the diffusive SSA process (with optimised rate constant $k_{\text{diff}} = 1.0 \times 10^{-7} \text{ cm}^3 \text{ s}^{-1}$ and no FRET ($k_F = 0$)). The fit curves for high and low initial exciton number densities $N_0(S_x)$ are almost as good as in Fig. 7c of the main manuscript, only at longer times they are slightly too fast.



Supplementary Fig. 9 Results of the kinetic modelling with only bimolecular diffusive singlet–singlet annihilation. The model employed the same parameters as in Supplementary Table 1, with the following two exceptions: $k_{\text{diff}} = 1.0 \times 10^{-7} \text{ cm}^3 \text{ s}^{-1}$ and $k_F(3 S_1 \rightarrow S_n + 2 S_0) = k_F(3 S_1 \rightarrow 2 S_n + S_0) = 0$. Initial S_x exciton number densities $9.6 \times 10^{18} \text{ cm}^{-3}$ (top) and $2.3 \times 10^{18} \text{ cm}^{-3}$ (bottom). The dynamics on short time scales (up to 20 ps) are shown on the left side and long time scales (up to 500 ps) on the right side. Blue circles: Recovery of S_0 population as experimentally determined in the TrCD measurements with corresponding blue fit lines obtained from the kinetic model; black, red, green and violet lines: number density of the S_x excitons, S_1 excitons, electron-hole pairs (e^- , h^+) and the S_n excitons, as obtained from the kinetic model.

As a comparison, Supplementary Fig. 10 shows results for the other limiting case. Here, the diffusive SSA process was switched off ($k_{\text{diff}} = 0$) and the rate constant for Förster resonance energy transfer was adjusted. Importantly, it is only possible to match the rise for one of the initial exciton number density conditions. In the current example we did this for $N_0(S_x) = 9.6 \times 10^{18} \text{ cm}^{-3}$ (top) using $k_F = 6.0 \times 10^{-27} \text{ cm}^6 \text{ s}^{-1}$. This provides a very good match, however the simulation for the lower exciton number density $N_0(S_x) = 2.3 \times 10^{18} \text{ cm}^{-3}$ (bottom) rises too slowly. This can be easily understood as

follows: The FRET process shows an apparent third-order behaviour (cf. Eq. S13) for which the half-life of the S_1 decay is proportional to $N(S_1)^{-2}$ (cf. Eq. S16). In contrast, for the second-order diffusive mechanism the half-life is proportional to $N(S_1)^{-1}$. Therefore, if the diffusive SSA process is able to match both kinetics at high and low $N_0(S_x)$ (and correspondingly $N(S_1)$) already quite well, the third-order FRET process must become much too slow with decreasing $N(S_1)$, because of the larger and larger half-life due to the inverse square dependence on $N(S_1)$. These two limiting cases from the kinetic modelling therefore clearly show that the diffusive SSA process must be the dominant process which is responsible for the observed dependence of the TrCD kinetics on the exciton number density. Adding a small contribution of the Förster mechanism slows down the kinetics somewhat at longer times, which results in the slightly better fit presented in the main manuscript (Fig. 7c).



Supplementary Fig. 10 Results of the kinetic modelling with Förster resonance energy transfer (FRET) as the only singlet-singlet annihilation process. The model employed the same parameters as in Supplementary Table 1, with the following two exceptions: $k_{\text{diff}} = 0$ and $k_F(3 S_1 \rightarrow S_n + 2 S_0) = k_F(3 S_1 \rightarrow 2 S_n + S_0) = 6.0 \times 10^{-27} \text{ cm}^6 \text{ s}^{-1}$. Initial S_x exciton number densities $9.6 \times 10^{18} \text{ cm}^{-3}$ (top) and $2.3 \times 10^{18} \text{ cm}^{-3}$ (bottom). The dynamics on short time scales (up to 20 ps) are shown on the left side and long time scales (up to 500 ps) on the right side. Blue circles: Recovery of S_0 population as experimentally determined in the TrCD measurements with corresponding blue fit lines obtained from the kinetic model; black, red, green and violet lines: number density of the S_x excitons, S_1 excitons, electron-hole pairs (e^- , h^+) and the S_n excitons, as obtained from the kinetic model.

A larger number of parameters enters the kinetic model (Supplementary Table 1), so we would like to finally comment on the uniqueness of the fit and possible concerns regarding overfitting the TrCD data. We note that the majority of parameters is either determined independently (and therefore can be kept fixed) or is very well defined, as summarised by the following points:

- 1) Because the TrCD kinetics is only sensitive to the concentration of the S_0 population (a single species), there are no ambiguities regarding relative contributions of different overlapping CD-active species with different species-associated CD values. The TrCD kinetics can be therefore taken as a direct measure of the time-dependent change of the S_0 number density.
- 2) We employed three different initial exciton number densities. In addition to the two initial number densities $N_{0,low}(S_x)$ and $N_{0,high}(S_x)$ in the TrCD experiments, there is also the condition of very low number density covered by the TCSPC experiment (Supplementary Fig. 8) which directly provides the rate constant k_1 for the decay of the S_1 state (in the absence of singlet–singlet annihilation processes), see step S1. k_1 is therefore fixed.
- 3) The initial exciton number densities of the TrCD experiments and the TCSPC experiment were independently determined and are therefore also fixed.
- 4) In addition, the transient absorption kinetics in Supplementary Fig. 7 provides the total rate constant $k_{x,total}$ for the decay of the initially populated S_x state, which decays via two parallel channels. This value poses a strict limit on the sum of the two rate constants for the formation of the S_1 state (k_x) and the formation of the charge pair state (k_{CPx}), i.e. $k_{x,total} = k_x + k_{CPx}$.
- 5) The ratio of the rate constants k_x and k_{CPx} (steps S1 and S2) and the ratio of the rate constants k_n and k_{CPn} (steps S5 and S6) are also well defined by the experimentally observed yield for the long-lived CP state, which can be directly determined from the incomplete recovery of the TrCD kinetics. Only 85% of the S_0 population is recovered at about 500 ps, see Supplementary Figs. 9 and 10 (top right panel, blue line), so only 15% of the initially excited c-PFBT population ends up in the CP state (green line). The rate constant $k_{x,total}$ was measured independently. Therefore, k_x and k_{CPx} are well defined, with $k_x \gg k_{CPx}$. k_n and k_{CPn} are also well defined: Because the total yield of the CP state is only 15%, k_n must be considerably larger than k_{CPn} . In addition, the sum $k_{n,total} = k_n + k_{CPn}$ must be large, because the singlet–singlet annihilation processes would otherwise be too slow, and it would not be possible to fit the fast rise of the TrCD signal at early times.
- 6) As demonstrated by the systematic parameter variations in Supplementary Figs. 9 and 10, the dependence of the S_0 recovery on the different initial exciton number densities is governed by the competition of bimolecular diffusive SSA (step S3) and FRET (steps S14a and S14b), which leads to accurate values for the SSA rate constants k_{diff} and k_F .
- 7) The final electron–hole recombination step S7 has only a very weak influence on time scales up to 500 ps, as shown by the green lines in Supplementary Figs. 9 and 10 (right panels), and therefore the value for k_{rec} should only be taken as a rough estimate.

We therefore conclude that all parameters entering the kinetic model are well defined and provide detailed kinetic information regarding the individual processes involved.

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5. Spatiotemporal Mapping of Efficient Chiral Induction by Helicene-Type Additives in Copolymer Thin Films

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Statement for author contributions:

Marius Morgenroth (M.M.) is the first author of this publication and performed most of the experiments and manuscript preparation. K.O. and T.L. conceived the project. The helicene-like molecules based on dibenzo[*c,h*]acridine were provided by L. Guy from the University of Lyon, France. M.M. prepared the thin film samples and performed the steady-state absorption experiments. M.M. conducted the CD and CPL spectroscopy and microscopy experiments. K.O., T.L., and M.M. carried out the transient circular dichroism and transient absorption experiments and performed the data evaluation. M.S., K.O., and T.L. implemented the optical and electronic setups and the CD and CPL microscopy. T.L., M.M. and K.O. analyzed the spectroscopic results and wrote the paper.

Circular Dichroism

Spatiotemporal Mapping of Efficient Chiral Induction by Helicene-Type Additives in Copolymer Thin Films

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Abstract: We observed efficient induction of chirality in polyfluorene copolymer thin films by mixing with helicene-type chiral additives based on the dibenzo-[c,h]acridine motif. Images obtained from circular dichroism (CD) and circularly polarized luminescence (CPL) microscopy provide information about the chiral arrangements in the thin films with diffraction-limited resolution. The CD signal shows a characteristic dependence on the film thickness, which supports a supramolecular origin of the strong chiral response of the copolymer. In particular, we demonstrate the discrimination between films of opposite chirality based on their ultrafast transient chiral response through the use of femtosecond broadband CD spectroscopy and a newly developed setup for transient CPL spectroscopy with 28 ps time resolution. A systematic variation of the enantiomeric excess of the chiral additive shows that the “Sergeants and Soldiers” concept and “Majority Rules” are not obeyed.

Introduction

Supramolecular copolymer thin films exhibiting a strong chiral response are of considerable interest for diverse optoelectronic and photonic applications, such as OLEDs with circularly polarized luminescence (CPL),^[1–5] liquid-crystal lasers,^[6] photodetectors,^[7] and polarization-dependent security features.^[8] In principle, there are two approaches to obtain such chiral copolymer systems. One of them uses intrinsically chiral polymers forming supramolecular chiral structures after annealing at temper-

atures above the transition to the chiral nematic phase.^[9,10] Alternatively, enantiopure organic molecules can be mixed into an intrinsically achiral polymer, leading to induced chirality after annealing of the polymer-additive blend. Regarding the latter case, helicenes have proved themselves as efficient chiral additives,^[3,11,12] yet the large-scale synthesis of enantiopure helicenes remains a difficult task.^[13,14] Recently, the Guy group succeeded in the facile preparation of enantiopure helicene-like molecules on a gram scale.^[15,16] These molecules feature dibenzo[c,h]acridine units and exhibit quite weak CD and CPL activity. Here, we show that these helicene-type molecules however act as highly efficient chiral additives and demonstrate this for the achiral copolymer poly-[(9,9-di-*n*-octylfluorenyl-2,7-diyl)-*alt*-(benzo-[2,1,3]thiadiazol-4,8-diyl)], shortly F8BT (**1**). Specifically, we used 2,2'-dimethoxy-5,5',6,6'-tetrahydro-1,1'-bidibenzo-[c,h]acridine **2** and its methylene-bridged analog **3** (Figure 1).^[15] The photophysics of the pure compounds **2** and **3** has been investigated in detail previously.^[15,17]

We address open questions regarding the origin of the large induced chiral response in such films by employing steady-state CD and CPL microscopy with diffraction-limited resolution.^[18] CD microscopy also provides a clear picture of the influence of film thickness and the impact of enantiomeric excess of the chiral helicene-type additive on the chiral properties. In addition, the dynamic response of these unique copolymer films is investigated on femtosecond time-scales using transient broadband circular dichroism (TrCD) spectroscopy^[18,19] and a newly developed setup for transient circularly polarized luminescence (TrCPL) measurements enabling picosecond time-resolution. Together with the results from steady-state CD and CPL microscopy,

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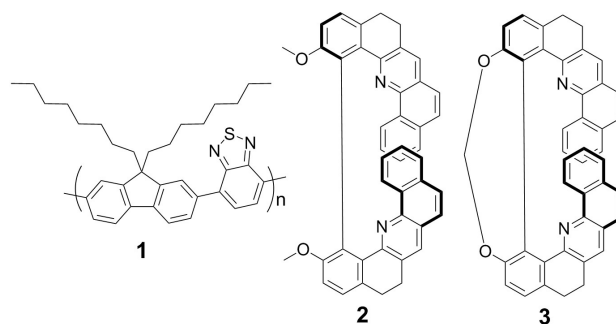


Figure 1. Chemical structures of the achiral F8BT copolymer **1** and the unbridged and bridged helicene-type chiral additives **2** and **3**, respectively (shown are the (+)-enantiomers).

these experiments support a supramolecular origin of the strong chirality in these systems.

Results and Discussion

CD and CPL Microscopy of Chiral Thin Films

Thin films were prepared by spin-coating solutions of the copolymer **1** and the chiral additives **2** or **3** in a mixture of chlorobenzene and chloroform onto glass slides. Subsequent annealing at 150 °C provided yellow films with a thickness in the range 100–360 nm, depending on the spin-coating conditions. Details about the film preparation process and experimental procedures are provided in the Supporting Information (Note 1).

The films were investigated using our very recently developed setup for CD microscopy.^[18] Representative data for F8BT films containing the chiral helicene-type additives (+)-**2**, (–)-**2**, (+)-**3** and (–)-**3** are displayed in Figure 2a–d. The upper panels show CD microscope images of the dissymmetry factor g_{abs} , which is defined as the CD signal normalized to the optical density for unpolarized light [Eq. (1)]:

$$g_{\text{abs}} = \frac{\text{CD}}{\text{OD}_{\text{unpolarized}}} = \frac{\text{OD}_{\text{L}} - \text{OD}_{\text{R}}}{0.5(\text{OD}_{\text{L}} + \text{OD}_{\text{R}})} \quad (1)$$

Here, OD_{L} and OD_{R} are the optical densities for the absorption of left circularly polarized (L or LCP) and right circularly polarized (R or RCP) light, respectively. Microscope images with a diffraction-limited resolution of ca. 400 nm were recorded using a bandpass filter with a center wavelength of 470 nm (FWHM 10 nm), which is located close to the peak of the CD spectrum. As shown by the blue and red colors in Figure 2a and b, the unbridged helicene-type chiral molecules (+)-**2** and (–)-**2** lead to strong chiral induction of opposite sign, reaching g_{abs} values of –0.32 and 0.33, respectively. The microscope images show island-like granular structures of micrometer dimensions, consistent with a statistical orientation of the individual copolymer domains.^[1,20] Comparable textures are also observed in the crossed-polarizer images provided in the Supporting Information (Note 2). In addition, the appearance is very similar to that of thin films formed from intrinsically chiral polyfluorene copolymers, such as c-PFBT.^[18] An analysis of the complete images, containing about 175 000 data points, finds that the g_{abs} distributions can be well described by a

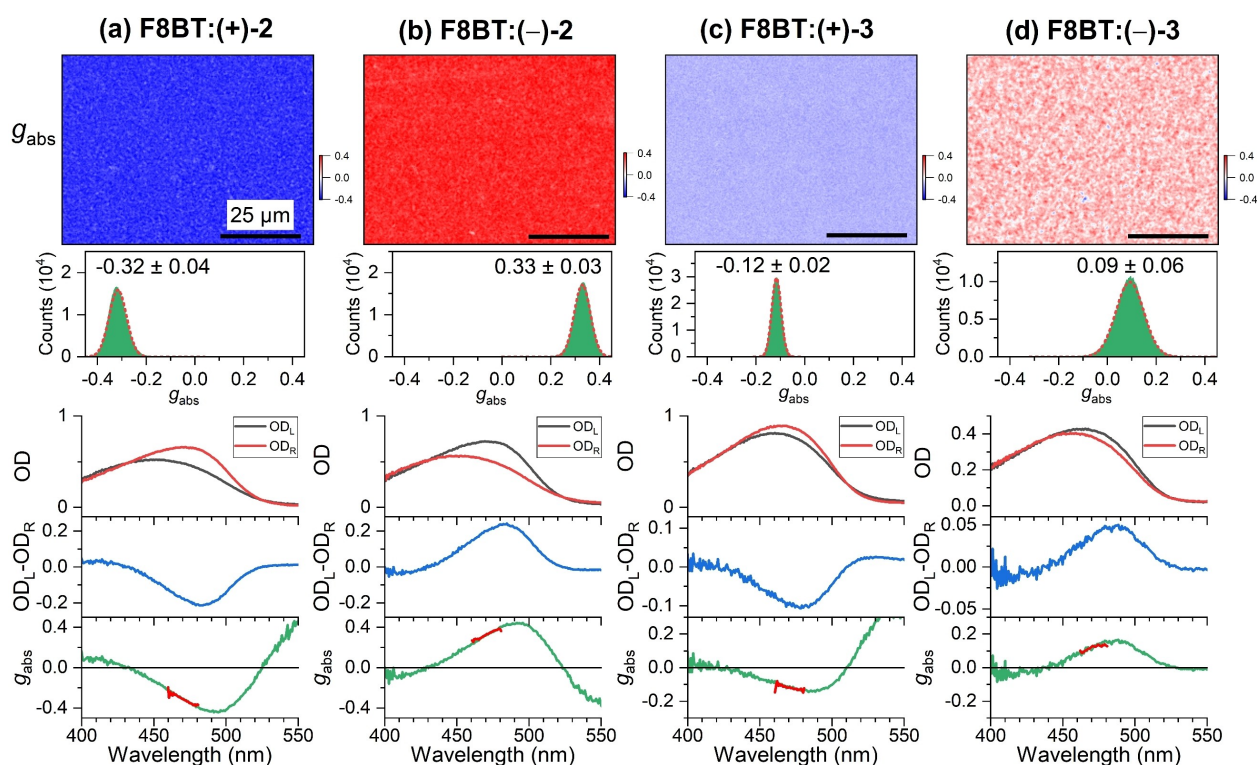


Figure 2. CD microscopy for blends of the achiral polymer F8BT (**1**) and the two enantiomers of the helicene-type molecules **2** and **3**. a) Microscope image ($80 \times 60 \mu\text{m}^2$) showing the dissymmetry parameter g_{abs} of an F8BT:(+)-**2** thin film (top) with the distribution of g_{abs} values (middle) including a Gaussian fit (dashed red line), determined over the entire field of view, and corresponding spectra integrated over the entire field of view ($210 \times 160 \mu\text{m}^2$, three panels at the bottom) displaying the optical density for left- and right-circularly polarized light (OD_{L} (black line), OD_{R} (red line)), the CD spectrum ($\text{OD}_{\text{L}} - \text{OD}_{\text{R}}$, blue line) and the g_{abs} spectrum (green line), with the thick red line indicating the spectral region selected by the bandpass filter (470 nm, FWHM 10 nm) used for CD imaging. b)–d) Same as in panel a, but for F8BT:(–)-**2**, F8BT:(+)-**3** and F8BT:(–)-**3** thin films. The black scale bar in each CD image corresponds to a distance of 25 μm . In each case, 33 wt% of the helicene-type additive was employed. The values for the film thickness in panels a–d were ca. 200 nm, ca. 250 nm, 202 nm and 156 nm, respectively.

Gaussian function (green areas and dashed red lines). The absorption spectra for LCP and RCP light (black and red, integrated over the complete field of view) show pronounced differences in the region of the $S_0 \rightarrow S_1$ absorption band of F8BT resulting in large CD values of -0.21 and 0.24 , corresponding to -7000 and 7900 mdeg, respectively ($1 \text{ OD} = 32982 \text{ mdeg}$), and peak g_{abs} values of -0.44 and 0.44 at 495 nm . These values rival those for helicene additives, such as 1-aza[6]helicene.^[3,11,21]

We note that annealing of the blends is absolutely required to obtain a strong chiral response, whereas pristine blends are CD-silent (Supporting Information, Note 3). The annealed samples also did not exhibit any changes in the CD response and the dissymmetry factor g_{abs} upon rotation of the thin film down to the few hundred nanometer length scale. Contributions resulting from a combination of linear dichroism and linear birefringence in combination with any possible anisotropies of the CD microscopy setup can be therefore safely excluded (Supporting Information, Note 4). An additional investigation using differential scanning calorimetry (DSC) of pure F8BT and F8BT:(+)-2 thin films with 33 wt % of the chiral additive demonstrated that addition of (+)-2 barely changed the transition temperature to the chiral supramolecular phase (Supporting Information, Note 5).

Chiral induction in achiral F8BT by the bridged helicene-type molecules (+)-3 and (-)-3 leads to qualitatively similar results (Figure 2c,d). The images show the same type of island-like granular structures, yet, the chiral induction is weaker, as shown by the pale blue and red colors. The image analysis provides distributions, which can be well modeled by Gaussian functions with $g_{\text{abs}} = -0.12 \pm 0.02$ and 0.09 ± 0.06 , respectively. The absorption spectra, integrated over the complete field of view, also show the clear but smaller difference between illumination with LCP and RCP light. We obtain peak CD values of -0.11 and 0.05 , corresponding to -3500 and 1600 mdeg, respectively, with peak g_{abs} values at 485 nm of -0.14 and 0.16 , respectively.

Complementary information is provided by measuring the circularly polarized luminescence of these films using our recently introduced setup for CPL microscopy.^[18] Here, one can define a corresponding dissymmetry factor g_{lum} for CPL [Eq. (2)],

$$g_{\text{lum}} = \frac{\text{CPL}}{I_{\text{unpolarized}}} = \frac{I_{\text{L}} - I_{\text{R}}}{0.5(I_{\text{L}} + I_{\text{R}})} \quad (2)$$

where I_{L} and I_{R} are the luminescence intensities for LCP and RCP light, respectively. CPL images for blends of F8BT with the unbridged helicene-type chiral molecules (+)-2 and (-)-2 are provided in Figure 3a and b. A strong chiral induction of opposite sign is clearly indicated by the blue and red colors, and the image analysis provides distributions with $g_{\text{lum}} = -0.32 \pm 0.02$ and 0.22 ± 0.02 , respectively. The difference of 30 % in the g_{lum} values could arise from slightly different annealing temperatures, as previously observed by Wade et al.^[12] The structures in the CPL images have a very similar island-like granular appearance as the CD images,

but are more blurred, most likely due to reflection and scattering of the isotropic luminescence from polymer domain boundaries as well as the influence of minuscule vibrations of the microscopy setup during the fluorescence integration time of several seconds.

The corresponding luminescence spectra of the F8BT:2 blends for LCP and RCP illumination (black and red lines, integrated over the complete field of view) show pronounced differences in intensity for the region of the $S_1 \rightarrow S_0$ emission band of F8BT. This is reflected in the strong CPL spectra of opposite sign. We obtain peak g_{lum} values at 570 nm of -0.42 and 0.27 , respectively.

CPL microscopy images for the F8BT:3 blends are presented in Figure 3c and d. The analysis of the pale blue and pale red images provides distributions for the dissymmetry factor with $g_{\text{lum}} = -0.12 \pm 0.02$ and 0.16 ± 0.02 , respectively. Differences in the LCP and RCP emission and the CPL spectra are clearly smaller than for the F8BT:2 blends (black, red and blue lines). Peak g_{lum} values at 560 nm are -0.11 and 0.16 . We finally would like to emphasize that there are no contributions of the chiral additives to the spectral features in Figures 2 and 3, because their absorption, emission, CD and CPL spectra are located at shorter wavelengths, as independently determined in our previous study of pure (+)-2, (-)-2, (+)-3 and (-)-3 thin films. The g_{abs} and g_{lum} values of these compounds both as molecules in solution and as thin films are quite small (about 10^{-2} or below). Films of the pure additive therefore do not support chiral supramolecular structures.^[15,17]

Ultrafast Transient CD Spectroscopy and Microscopy of F8BT Blends with the Helicene-Type Additives (+)-2 and (-)-2

In TrCD spectroscopy, an ultrashort laser pulse ($\lambda = 320 \text{ nm}$) promotes chiral molecules to an electronically excited state, and subsequently the sample is probed alternately by LCP and RCP broadband laser pulses covering the UV/Vis range ($260\text{--}600 \text{ nm}$). The TrCD signal is thus obtained as [Eq. (3)],

$$\begin{aligned} \Delta\text{CD}(t) &= \Delta\text{AOD}(t) = \text{AOD}_{\text{L}}(t) - \text{AOD}_{\text{R}}(t) \\ &= \text{OD}_{\text{L,wp}} - \text{OD}_{\text{L,wop}} - \text{OD}_{\text{R,wp}} + \text{OD}_{\text{R,wop}} \end{aligned} \quad (3)$$

where “wp” means with pump beam and “wop” without pump beam. The experiment simultaneously provides information regarding the transient circular dichroism and transient absorption of the sample with a time resolution of about 100 fs. The transient absorption signal for unpolarized probing is obtained as [Eq. (4)].

$$\text{AOD}_{\text{unpolarized}}(t) = 0.5(\text{AOD}_{\text{L}}(t) + \text{AOD}_{\text{R}}(t)) \quad (4)$$

Details of the TrCD setup are provided in the Supporting Information (Note 1). In the following, we focus on the TrCD results for F8BT blends with the helicene-type molecules (+)-2 and (-)-2 because of their superior chirality-inducing properties. In the contour plot for F8BT:(+)-2 (Figure 4a), the transient absorption spectra for LCP

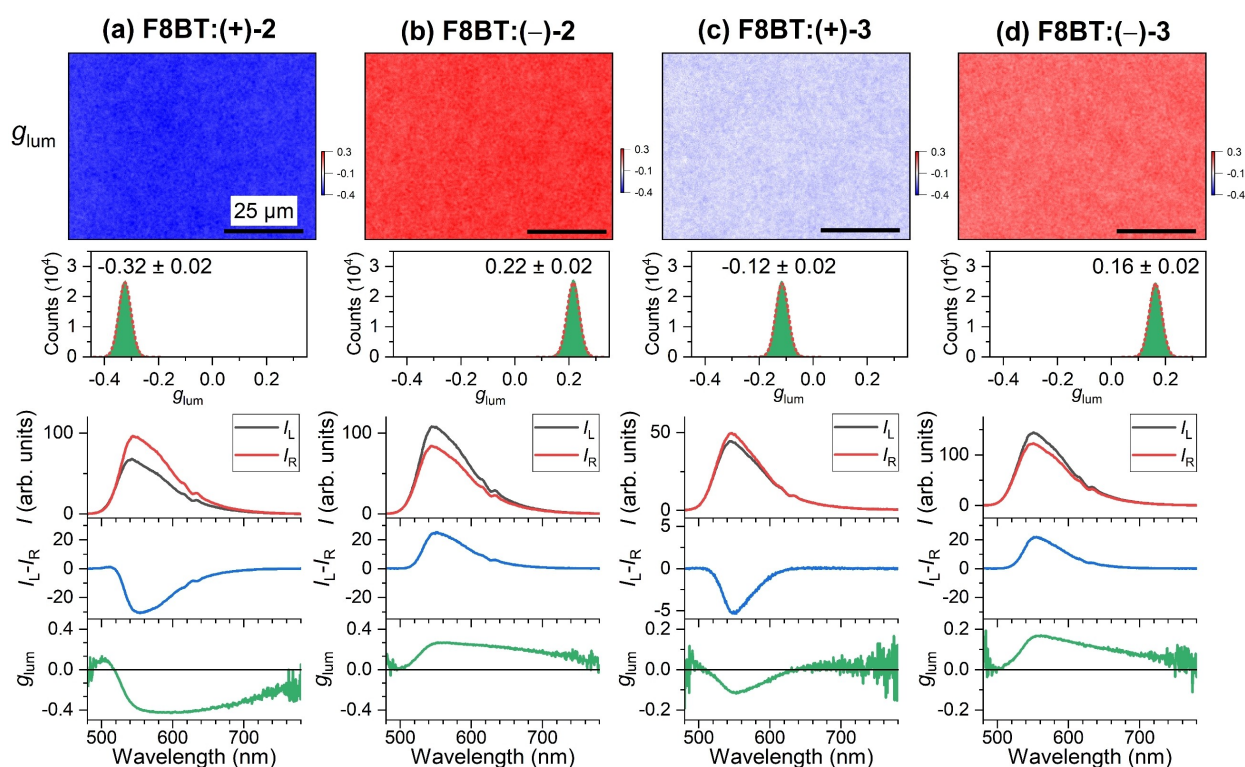


Figure 3. CPL microscopy for blends of the achiral polymer F8BT (**1**) and the two enantiomers of the helicene-type molecules **2** and **3**. a) Microscope image ($80 \times 60 \mu\text{m}^2$) showing the dissymmetry parameter g_{lum} of an F8BT:(+)-**2** thin film (top) measured using a bandpass filter with a center wavelength of 560 nm (FWHM 10 nm), with the distribution of g_{lum} values (middle) including a Gaussian fit (dashed red line), determined over the entire field of view, and corresponding spectra integrated over the entire field of view ($210 \times 160 \mu\text{m}^2$, three panels at the bottom) displaying the luminescence intensity for left- and right-circularly polarized light (I_L (black line), I_R (red line)), the CPL spectrum ($I_L - I_R$, blue line) and the g_{lum} spectrum (green line). b)–d) Same as in panel a, but for F8BT:(-)-**2**, F8BT:(+)-**3** and F8BT:(-)-**3** thin films. The black scale bar in each CPL image corresponds to a distance of 25 μm . In each case, 33 wt% of the helicene-type additive was employed. The values for the film thickness in panels (a)–(d) were 198 nm, 251 nm, 150 nm and ca. 150 nm, respectively.

and RCP detection exhibit distinct blue-violet colored ground state bleach (GSB) features at 320 and 465 nm and pronounced yellow-orange excited state absorption bands at 380 and 550 nm, which clearly belong to F8BT.^[22] We note that the GSB feature for RCP detection at 465 nm is much stronger than for LCP detection, and there is also an additional blueish sideband at 340 nm, only observed for RCP detection. The contour plot for the TrCD measurement, which corresponds to the difference of the contour plots for LCP and RCP detection, therefore, shows two positive CD features at 345 and 480 nm (orange) which must belong to the supramolecular F8BT assembly. They coincide with the position of the main peaks of the steady-state CD spectrum of the chiral F8BT blend. The TrCD spectrum therefore looks like an inverted steady-state CD spectrum, without indications for excited-state CD activity (cf. Figure 4c). Its absence is consistent with a supramolecular origin of the CD signal: For a fractional excitation of about 10% F8BT units (given by the ratio of the transient absorption bleach and the steady-state absorbance of the sample), the excited-state polymer species are too far apart to establish any efficient in-plane or across-planes couplings between the excited-state chromophores.^[18] What is there-

fore observed is just a bleach of the ground-state CD spectrum of the F8BT film.

If the picture above is correct, we should observe a mirror-image like behavior in the TrCD spectra of F8BT:(-)-**2**. This is indeed the case, as demonstrated by the contour plot of Figure 4b. Now, the GSB feature for LCP detection at 465 nm is more extended than for RCP detection, and there is a broader blueish sideband at 340 nm for LCP detection. As a result, the TrCD spectrum has negative features at 345 and 480 nm, at the same position, but of opposite sign than for F8BT:(+)-**2** (cf. the TrCD spectra at 1 ps shown in Figure 4c). Transient CD spectroscopy is therefore able to distinguish between the two different chiral supramolecular assemblies on ultrafast time scales.

Representative kinetic traces averaged over the low-wavelength band of the TrCD bleach region (340–350 nm) are shown for F8BT:(+)-**2** and F8BT:(-)-**2** in Figure 4d. Both signals exhibit a fast decay over the first few picoseconds, which is governed by singlet-singlet annihilation. The residual signal (15% at 1000 ps) is due to a long-lived charge-pair state. Detailed results from a modeling of the TrCD kinetics are provided in the Supporting Information (Note 6).

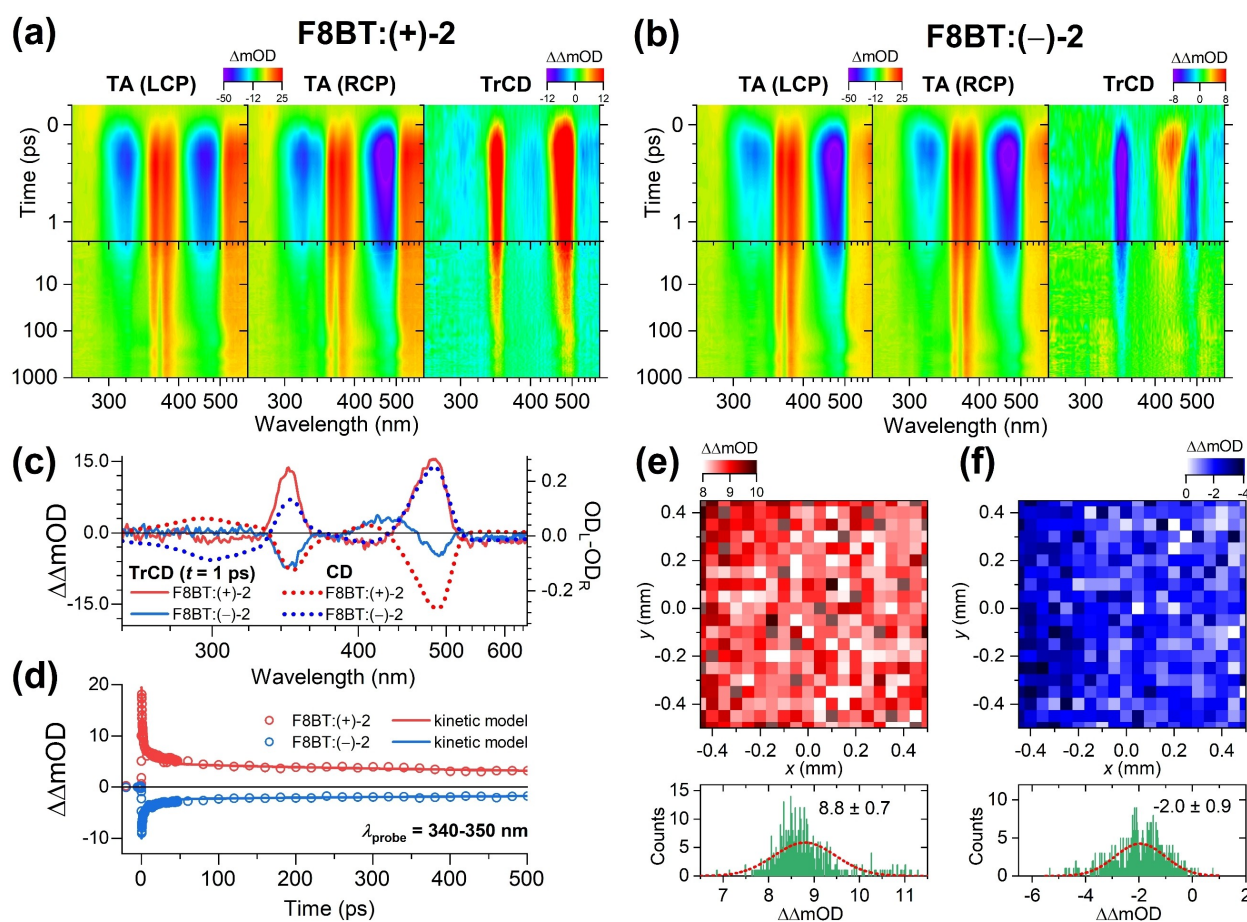


Figure 4. Ultrafast transient absorption and transient circular dichroism spectroscopy and microscopy of F8BT:(+)-2 and F8BT:(-)-2 thin films. a) Left: Transient absorption of F8BT:(+)-2 for probing with left-circularly polarized light, middle: Transient absorption for probing with right-circularly polarized light, right: Transient circular dichroism (difference of the contour diagrams for TA (LCP) and TA (RCP)). b) Same as in a, but for F8BT:(-)-2. c) Comparison of TrCD spectra at 1 ps (solid lines) and steady-state CD spectra (dotted lines) for F8BT:(+)-2 (red) and F8BT:(-)-2 (blue). d) Experimentally measured kinetics (open circles) averaged over the probe wavelength range 340–350 nm including fits from a kinetic model (solid lines) for F8BT:(+)-2 (red) and F8BT:(-)-2 (blue). e) Top: Ultrafast transient circular dichroism map of F8BT:(+)-2 at 1 ps (average: 425–525 nm). Bottom: Histogram of TrCD values from the transient CD map (green) including a Gaussian fit (red dashed line). f) Same as in (e), but for F8BT:(-)-2. Note the logarithmic time axis in the contour plots of panels (a) and (b).

The TrCD setup also enables spatial point-by-point mapping of the thin films, with the 50 μm spatial resolution of the TrCD probe beam. This is demonstrated for the F8BT:(+)-2 and F8BT:(-)-2 thin films in panels e and f of Figure 4, respectively. The maps are recorded for a delay time of 1 ps and are averaged over the spectral region 425–525 nm. Again, there is a clear chiral discrimination of the two samples, with positive $\Delta\Delta\text{OD}$ values in the case of F8BT:(+)-2 (red areas), and negative $\Delta\Delta\text{OD}$ in the case of F8BT:(-)-2 (blue areas). From the statistics of the map ($20 \times 20 = 400$ points) we obtain ΔCD values of 8.8 ± 0.7 and -2.0 ± 0.9 mOD from a Gaussian fit to the histograms, as shown in the lower half of panels e and f.

Transient Circularly Polarized Luminescence Spectroscopy with Picosecond Time Resolution

Chirality-sensitive ultrafast spectroscopic methods are valuable tools for monitoring transient electronic and structural changes of optically active molecules and supramolecular structures. Beside ultrafast transient CD spectroscopy, time-resolved CPL approaches have been frequently utilized, as summarized very recently by Meskers.^[23] These include high-sensitivity setups employing differential photon counting techniques, which are however limited to slower processes in the time range 0.01–100 ms.^[24–26] TCSPC-based approaches so far have reached sub-nanosecond time-resolution with a fairly coarse point-by-point spacing of about 200 ps.^[27]

Here, we present results from a new instrument for transient CPL spectroscopy based on TCSPC with picosecond time-resolution. We employed excitation at 410 nm ($S_0 \rightarrow S_1$ transition of F8BT) by the second harmonic of an

80 MHz titanium:sapphire femtosecond laser oscillator and detection of the TrCPL signal by a fast hybrid photo-multiplier detector in combination with a high-resolution TCSPC electronics, resulting in an instrument response function of 28 ps. Single photon counting provides a very good signal-to-noise ratio, because high photon count rates up to 10 MHz can be harnessed with state-of-the-art photon-counting electronics and combined with extended photon accumulation times. In the current experiments for thin films with a strong chiral response, peak counts up to 2×10^5 (channel width: 3 ps) were sufficient to arrive at a clean TrCPL signal.

Figure 5 contains our results for the chiral F8BT:(+)-2 and F8BT:(-)-2 thin films in comparison with an F8BT thin film without chiral additive. A bandpass filter centered at the emission wavelength 530 nm (10 nm FWHM) was employed. Panels a and b show the decays for the F8BT:(+)-2 film (blue circles) for LCP and RCP emission,

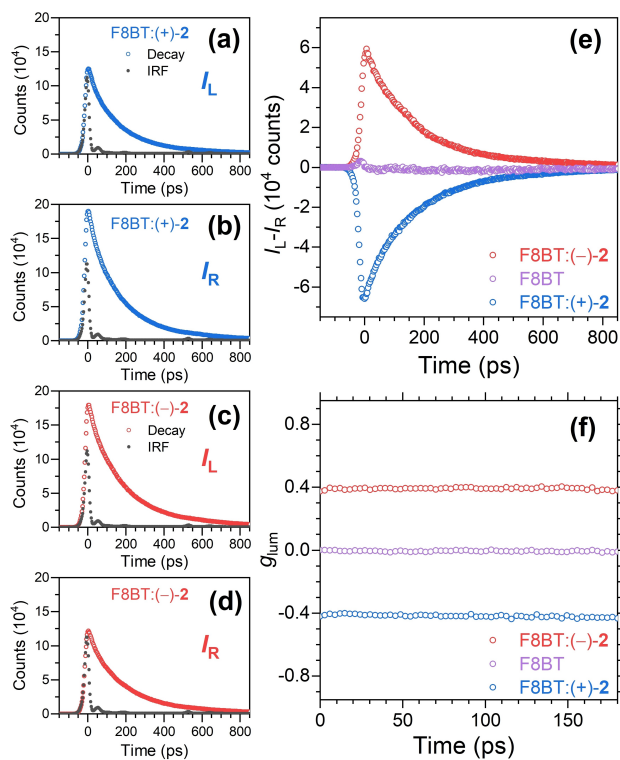


Figure 5. Time-resolved CPL spectroscopy with picosecond time resolution for F8BT:(+)-2, F8BT:(-)-2 and F8BT thin films using a bandpass filter at 530 nm. a) Transient photoluminescence intensity I_L at left circular polarization for the F8BT:(+)-2 film (open blue circles) and laser scattering signal I_L obtained from a colloidal SiO_2 nanoparticle suspension (solid black circles) providing the instrument response function of the setup. b) Same as in panel a, but showing the photoluminescence intensities I_R for right circular polarization. c) and d) Same as in panels a and b, but for the F8BT:(-)-2 thin film and the same nanoparticle suspension. e) Resulting transient CPL signal $I_L - I_R$ for the F8BT:(+)-2 thin film (blue circles) and the F8BT:(-)-2 thin film (red circles). Also shown is the transient CPL signal of an achiral F8BT thin film (without chiral additive, violet circles). f) Resulting time resolved g_{lum} signal for the F8BT:(+)-2 (blue circles), F8BT:(-)-2 (red circles) and F8BT thin films (violet circles).

respectively. The solid black circles indicate the scattering signal from a dispersion of achiral silica nanoparticles, showing the sharp detector response (with a small after-pulse) and an FWHM of 28 ps. We note that the much larger peak intensity of the I_R transient for the thin film already indicates a substantial negative transient CPL and g_{lum} signal. In contrast, I_L and I_R for the scattering solution are identical. Panels c and d of Figure 5 display the corresponding results for the F8BT:(-)-2 film (red circles), including the same scattering signal as in panels a and b (black circles). Here, the intensity of the I_L transient of the film is much larger, indicating a positive CPL and g_{lum} .

The resulting transient CPL signals for the two thin films, with peak signals of about 60000 counts, are depicted in panel e. The kinetics resemble mirror images. For comparison, we also include the response of the achiral F8BT thin film (violet circles), which essentially shows no CPL signal and only a small undulation around time zero. Panel f contains the resulting time-resolved g_{lum} signal. For the achiral F8BT sample g_{lum} is zero, whereas we observe essentially time-independent values of -0.41 and 0.37 in the case of the chiral F8BT:(+)-2 and F8BT:(-)-2 thin films, respectively. We find very similar results in complementary TrCPL experiments using excitation at 273 nm by a UV-LED (Supporting Information, Note 7).

The result is consistent with a supramolecular origin of CPL. The strong CPL signal likely arises from circular intensity differential scattering^[1,28] or from a mechanism where initially linearly polarized luminescence emitted from a quasi-nematic layer is circularly polarized by passing the remaining film layer,^[29] or it could be a combination of both. The transient CPL signals in panel e are therefore solely due to the electronic decay of population from the S_1 exciton state. They do not reflect any structural changes in the excited state.

Thickness-Dependent Chirality of F8BT Films with Helicene-Type Additives

Further insight regarding the origin of the very large CD signals of the F8BT:(+)-2 and F8BT:(-)-2 thin films can be gained from studying the thickness dependence of the chiral response.^[9,12,18] Results for three F8BT:(+)-2 films of different thickness (each with 33 wt % of the chiral additive) are shown in Figure 6a–c, and additional examples are provided in the Supporting Information (Note 8). The thickness of the three films was determined in situ by picosecond ultrasonics^[18,30–32] using the transient absorption kinetics [determined via Eq. (4)] averaged over the wavelength range 490–520 nm. Characteristic oscillations appear in the transient absorption signals (Figure 6d), which arise from a coherent acoustic phonon propagating back and forth between the two interfaces of the film. The oscillation period τ_a of the acoustic phonon was obtained from a fit by a sum of a biexponential and a damped cosine term providing values of (166 ± 1) , (256 ± 2) and (573 ± 3) ps. The thickness d of the films was then determined via^[33] [Eq. (5)],

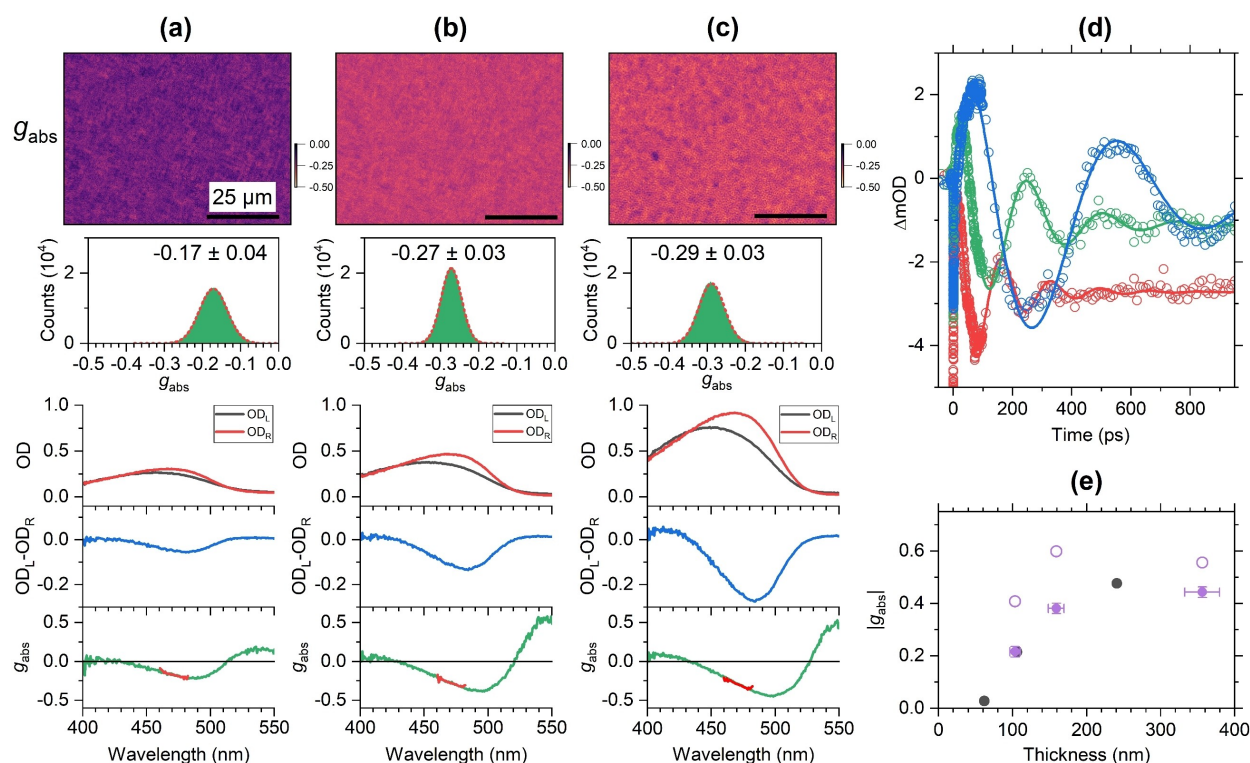


Figure 6. Thickness-dependent chirality of F8BT:(+)-2 thin films. a) Microscope image ($80 \times 60 \mu\text{m}^2$) for the dissymmetry parameter g_{abs} of a film with the thickness $d = 103 \text{ nm}$ (top) and a corresponding histogram of g_{abs} values (green) including a Gaussian fit (dashed red line), determined over the entire field of view, and spectra integrated over the entire field of view ($210 \times 160 \mu\text{m}^2$, bottom) showing the optical density for left- and right-circularly polarized light (OD_L (black), OD_R (red)), the CD spectrum (blue) and the g_{abs} spectrum (green), with the thick red line indicating the spectral region selected by the bandpass filter (center wavelength 470 nm) employed for CD imaging. b) and c) Same as in panel a, but for films with the thicknesses $d = 159$ and 356 nm . The length of the black scale bar in each CD image corresponds to $25 \mu\text{m}$. d) Oscillatory transient absorption kinetics ($\lambda_{\text{pump}} = 320 \text{ nm}$) averaged over the probe wavelength interval $490\text{--}520 \text{ nm}$ (open circles) indicating the propagation of a coherent acoustic phonon in films with a thickness of 103 nm (red), 159 nm (green) and 356 nm (blue); solid lines are fits based on a sum of a biexponential term and a damped cosine term. e) absolute value of the peak of g_{abs} as a function of the film thickness d , as indicated by the violet solid circles (including error bars), open violet circles are results from the approximate reflectivity correction described in the text; corresponding g_{abs} values for three intrinsically chiral c-PFBT films (data from ref. [18]) are shown as black circles for the sake of a better comparison.

$$d = 0.25\tau_{\text{a}}c_{\text{L}} \quad (5)$$

where c_{L} is the longitudinal sound velocity of the F8BT:(+)-2 thin film. Here, we use a value of $(2490 \pm 150) \text{ ms}^{-1}$, which we previously obtained from the closely related polyfluorene copolymer c-PFBT.^[32] This way, we arrive at thicknesses of 103 , 159 and 356 nm for the three films.

The microscope image of the thinnest film (panel a), recorded by a bandpass filter with the center wavelength 470 nm (FWHM 10 nm) located close to the peak of the CD spectrum, shows a granular structure. The histogram of g_{abs} values is well described by a Gaussian distribution with $g_{\text{abs}} = -0.17 \pm 0.04$. Spectra integrated over the complete field of view, shown in the lower half of panel a, provide peak CD and g_{abs} values of -0.054 (-1800 mdeg) and -0.21 , respectively.

Upon increasing the layer thickness to 159 nm (panel b), the average optical activity increases substantially, as indicated by the pronounced color change of the image from violet to orange, resulting in a Gaussian distribution with $g_{\text{abs}} = -0.27 \pm 0.03$. The spectra provide peak values of

-0.133 (-4400 mdeg) and -0.38 for the CD response and g_{abs} , respectively. A further substantial increase of the layer thickness to 356 nm (panel c) leads to a slighter increase of g_{abs} (-0.29 ± 0.03), as indicated by the brighter orange color of the image. The peak values of the CD response and g_{abs} are -0.276 (-9100 mdeg) and -0.44 , respectively.

In the case of molecular chirality, g_{abs} should be independent of thickness.^[20] However, the correlation in Figure 6e indicates a clear increase of $|g_{\text{abs}}|$ up to a thickness of ca. 150 nm and a leveling-off above (violet solid circles). This is consistent with experiments for supramolecular structures of the chiral copolymer c-PFBT, also included in Figure 6e (black circles).^[18]

A similar thickness dependence was found previously by Lakhwani and Meskers for thermally annealed poly-[9,9-bis((3S)-3,7-dimethyloctyl)-2,7-fluorene] films.^[20] This result also suggests that the large induced CD signal of these F8BT:(+)-2 films arises from supramolecular chirality.

We note that considering reflection losses at the interfaces will increase the values for g_{abs} , but will not significantly change the trend in the thickness dependence of g_{abs} . Here, we consider an approximate correction method

proposed by Schulz et al.,^[34] which is valid for a free-standing slab of material and will lead to an overestimation of g_{abs} . Applying their correction, we obtain the violet open circles in Figure 6e. While all g_{abs} values increase, the difference Δg_{abs} between the first two points remains almost the same. A short description of the model is provided in the Supporting Information (Note 9).

Influence of the Amount of the Chiral Additive and its Enantiomeric Excess

Additional CD experiments accompanied by atomic force microscopy (AFM) measurements were performed, in which the amount of the chiral additive (+)-**2** was varied systematically (Supporting Information, Note 10). The surface morphology recorded by AFM shows aggregated structures of less than 1 μm size which may be correlated with CD-active regions of similar size found in the CD microscope images.

In the field of induced chirality, the issue of enantiomeric excess has been frequently discussed in terms of the “Sergeant and Soldiers” principle and “Majority Rules” concepts.^[35–39] For instance, previous studies dealing with the aggregation of intrinsically chiral polythiophenes into a supramolecular structure in the poor solvent *n*-decanol found a nonlinear relation between the g_{abs} value and the percent enantiomeric excess. Already for 20 % monomer enantiomeric excess, about 90 % of the maximum g_{abs} value was reached.^[37] Similar results were reported for chiral polyisocyanates.^[35,36] In such systems, chiral amplification is induced by a small enantiomeric excess of “chiral sergeants” who control the (supramolecular) chirality of a large amount of “achiral soldiers”. Here, we investigate if these concepts are still valid when mixtures of the helicene-type additives (+)-**2** and (–)-**2** with different percent enantiomeric excess are present in the F8BT thin film.

Figure 7 shows the results of such a systematic study. A total of 33 wt % was kept for the sum of the two enantiomers, which is the same as for the optimized conditions using only a single enantiomer, such as in Figure 2. The enantiomeric excess was varied systematically between 20 % ee of (+)-**2** and 20 % ee of (–)-**2**, as indicated in panels a–e. We focus first on the spectra integrated over the whole field of view shown in the lower half of each panel. Even for the extreme cases with 20 % ee of (+)-**2** and (–)-**2**, only weak chiral induction is observed, with absolute peak values of 0.04 (1300 mdeg) for the CD signal and 0.10 for g_{abs} . For 10 % ee, this drops sharply to 0.01 (300 mdeg) and 0.03 for the CD and g_{abs} values, respectively. As expected, the racemic mixture shows no CD response. These findings are clearly not compatible with the “Sergeant and Soldiers” and “Majority Rules” principles, which would predict substantial preferred chiral induction already at 20 % ee.

Next, we focus on the g_{abs} images at the top of panels a–e. Here, we observe granular structures similar to those in Figure 2, however now with domains of roughly 600–900 nm diameter with positive and negative g_{abs} side-by-side, either equally distributed (racemic mixture) or dominated by the

chiral additive in excess (20 % ee). It therefore appears as if there is a homogeneous distribution of regions with different g_{abs} over small length scales according to the individual contributions of the respective chiral additives rather than a “The winner takes it all” situation as in the “Sergeant and Soldiers” and “Majority Rules” concepts.

Conclusion

The current investigation clearly demonstrates that helicene-type additives based on the dibenzo[*c,h*]acridine motif indeed act as very efficient chiral additives for polyfluorene copolymers, such as F8BT (**1**). Interestingly, the unbridged chiral additive **2** exhibits significantly better chiral induction properties than additive **3**, which structurally differs only by one additional methylene bridge. Perhaps the less rigid structure of **2** is responsible for its better adaptation to the F8BT environment during the formation of the supramolecular chiral phase.

The supramolecular origin of the large chiral optical response, detected in absorption and luminescence, both steady-state and time-resolved, is underpinned by several experimental findings. The nonlinear increase of the dissymmetry parameter g_{abs} with film thickness is not compatible with a molecular picture of chirality, which would predict g_{abs} values which are independent of thickness. Furthermore, the ultrafast CD experiments only find transient spectral features of the copolymer’s electronic ground state and no clear indications for transient excited-state chirality. The latter is probably due to the weak coupling between the widely spaced excited-state chromophores in the film, again pointing toward a supramolecular origin of the transient CD signal. Furthermore, measurements using a newly developed setup for picosecond transient CPL spectroscopy reveal a time-independent dissymmetry parameter g_{lum} , which is compatible with a static mechanism for the generation of CPL: Circular polarization could be imprinted on the initially emitted photons by either circular selective scattering or a change in polarization upon passing the residual supramolecular chiral film structure. Taken together, all of these findings are also compatible with the picture emerging for supramolecular chiral assemblies consisting of intrinsically chiral polymer chains.^[18]

In the course of the current investigations it has also become more and more apparent that CD and CPL microscopy techniques with diffraction-limited resolution are indispensable tools for understanding the chiral organization of such supramolecular assemblies. This is, for instance, underlined by the experiments dealing with the impact of the enantiomeric excess of the chiral additive on the chiral response. These measurements do not find clear indications for a “Sergeants and Soldiers” concept or “Majority Rules” underlying chiral structure formation in polyfluorene copolymer thin films. Likewise, TrCPL spectroscopy with picosecond time resolution, as presented in this study, is a welcome addition to the chiroptical toolbox and has considerable potential for the investigation of systems with much weaker chirality.

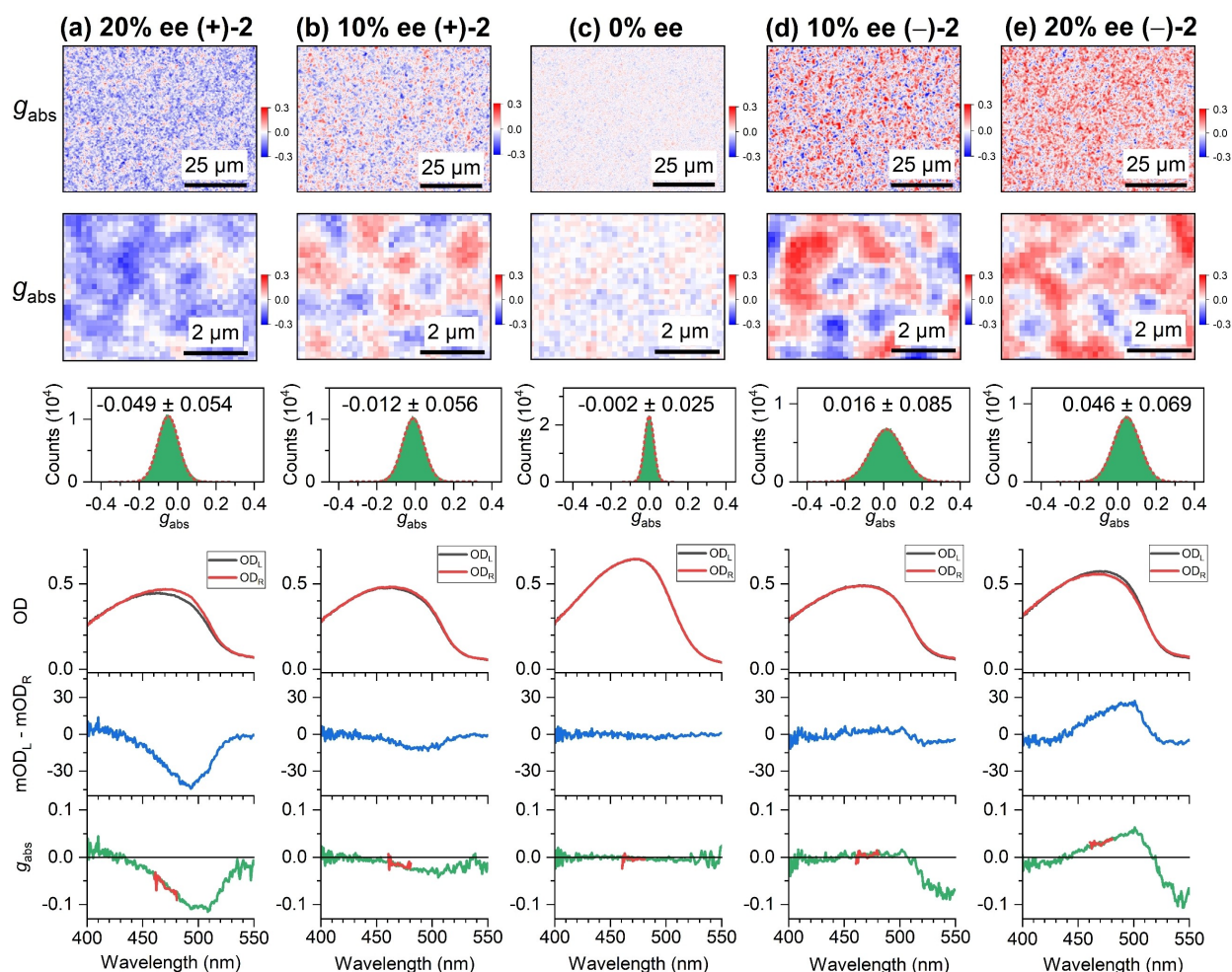


Figure 7. Chirality of F8BT thin films with different percent enantiomeric excess of the helicene-type compounds (+)-**2** and (–)-**2**. a) Microscope image ($80 \times 60 \mu\text{m}^2$) including a zoom-in of a representative region for the dissymmetry parameter g_{abs} of a film with 20% ee of (+)-**2** (top) with a histogram of g_{abs} values (green) including a Gaussian fit (dashed red line), determined over the entire field of view, and spectra integrated over the entire field of view ($210 \times 160 \mu\text{m}^2$, bottom) showing the optical density for left- and right-circularly polarized light (OD_L (black), OD_R (red)), the CD spectrum (blue) and the g_{abs} spectrum (green), with the thick red line indicating the spectral region selected by the bandpass filter (center wavelength 470 nm) employed for CD imaging. b)–e) Same as in panel a, but for films with 10% ee of (+)-**2**, 0% ee (racemic), 10% ee of (–)-**2** and 20% ee of (–)-**2**. The length of the black scale bars in the CD images corresponds to 25 μm or 2 μm . The values for the film thickness in panels (a)–(e) were 221 nm, 236 nm, 316 nm, 234 nm and 275 nm, respectively.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding authors upon reasonable request.

Keywords: Circular Dichroism • Circularly Polarized Luminescence • Supramolecular Chirality • Thin Films • Ultrafast Spectroscopy

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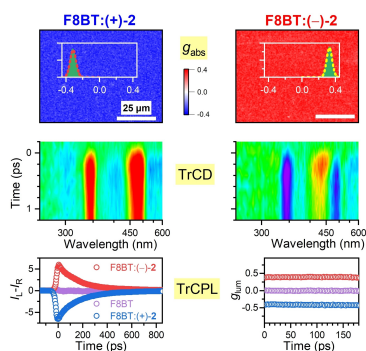
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Research Articles

Circular Dichroism

M. Morgenroth, M. Scholz, L. Guy,
K. Oum,* T. Lenzer* — e202203075

Spatiotemporal Mapping of Efficient Chiral
Induction by Helicene-Type Additives in
Copolymer Thin Films



A special class of helicene-type additives, which are straightforward to synthesize in large amounts, induce strong chirality in polyfluorene copolymer thin films. Advanced chirality-sensitive microscopy techniques and ultrafast time-resolved spectroscopic methods based on transient circular dichroism and transient circularly polarized luminescence reveal the supramolecular origin of the chiroptical properties.



Supporting Information

Spatiotemporal Mapping of Efficient Chiral Induction by Helicene-Type Additives in Copolymer Thin Films

M. Morgenroth, M. Scholz, L. Guy, K. Oum, T. Lenzner**

Supporting Information

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Supporting Note 1. Experimental Details

1.1 Preparation of Glass Slides for Spin-Coating

Microscope glass slides (Duran Wheaton Kimble) were treated in soapy distilled water and afterwards in acetone in an ultrasonic bath for 30 minutes each. After drying with nitrogen, the glass slides were cut into pieces to fit the chuck of the spin coater. The slides were treated in a UV chamber (Dinies ELG100S, 2 UV-C lamps with 253.7 nm emission, 11 W each) for 15 minutes.

1.2 Preparation of Thin Films

The chiral helicene compound 2,2'-dimethoxy-5,5',6,6'-tetrahydro-1,1'-bidibenzo[*c,h*]acridine **2** and its methylene-bridged analog **3** were prepared as described previously.^[1] A mixture of poly-[(9,9-di-*n*-octylfluorenyl-2,7-diyl)-*alt*-(benzo[2,1,3]thiadiazol-4,8-diyl)], shortly F8BT or **1**, (Merck, $M_n \leq 25000 \text{ g mol}^{-1}$) and one of the enantiopure helicene-type compounds was dissolved in a solution of chlorobenzene (Merck, > 99%) and chloroform (Merck, $\geq 99.8\%$) in a ratio of 1:9 by volume. For some experiments, the compounds were also dissolved in toluene. The concentrations of F8BT and the chiral additive (CA) were 7.50 mg mL^{-1} and 3.75 mg mL^{-1} (i.e. $m_{\text{CA}}/(m_{\text{CA}}+m_{\text{F8BT}}) = 33 \text{ wt\%}$ of the CA), providing the highest CD values. For systematic studies, other weight percentages were also tested. The solution was treated in an ultrasonic bath for 60 minutes and filtered through a $0.45 \mu\text{m}$ PTFE filter using a syringe. The precursor solution was then spin-coated onto the glass slides (without alignment layer) at 500 rpm for 60 s in a nitrogen atmosphere (humidity: < 1%) and subsequently annealed on a hot plate at 150°C for 15 minutes.

1.3 Preparation of Thin Films with Different Enantiomeric Excess Ratios

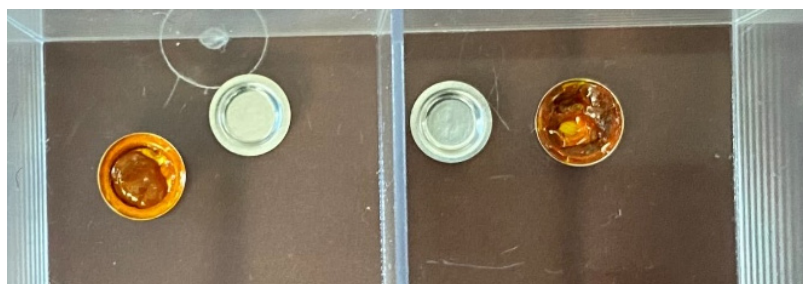
Precursor solutions of the copolymer and the chiral additive (+)-**2** and (–)-**2** were prepared for different enantiomeric excess (ee) ratios using concentrations of 7.50 mg mL^{-1} for F8BT and 3.75 mg mL^{-1} for compound **2**. They were spin-coated and heat-treated as described above. Concentrated stock solutions of F8BT and the enantiopure additives were prepared in a mixture of chlorobenzene and chloroform (1:9 v:v) and treated by ultrasound for 60 minutes. The volumes required were gaged by a microliter pipette, mixed and then filtered through a $0.45 \mu\text{m}$ PTFE filter using a syringe. Values for the percent enantiomeric excess of the chiral helicenes were 20%, 10% and 0% (racemic mixture). Concentrations and volumes are summarized in Supporting Table 1.1.

Supporting Table 1.1. Concentrations and volumes for solutions of F8BT and the (+)-2** and (–)-**2** enantiomers used for preparing blends with different percent enantiomeric excess of the chiral additive.** A total volume of 0.4 mL precursor solution was sufficient for spin-coating two thin films.

		%ee				
		20 for (–)- 2	10 for (–)- 2	0 (racemic)	10 for (+)- 2	20 for (+)- 2
$c \text{ (mg mL}^{-1}\text{)}$	F8BT (1)	12	12	12	12	12
$c \text{ (mg mL}^{-1}\text{)}$	(+)- 2	10	10	10	10	10
$c \text{ (mg mL}^{-1}\text{)}$	(–)- 2	10	10	10	10	10
$V \text{ (mL)}$	F8BT (1)	0.25	0.25	0.25	0.25	0.25
$V \text{ (mL)}$	(+)- 2	0.06	0.07	0.08	0.08	0.09
$V \text{ (mL)}$	(–)- 2	0.09	0.08	0.08	0.07	0.06
$V_{\text{total}} \text{ (mL)}$	Mixture	0.40	0.40	0.40	0.40	0.40
$c_{\text{total}} \text{ (mg mL}^{-1}\text{)}$	F8BT (1)	7.50	7.50	7.50	7.50	7.50
$c_{\text{total}} \text{ (mg mL}^{-1}\text{)}$	(+)- 2	1.50	1.69	1.88	2.06	2.25
$c_{\text{total}} \text{ (mg mL}^{-1}\text{)}$	(–)- 2	2.25	2.06	1.88	1.69	1.50

1.4 Differential Scanning Calorimetry (DSC)

F8BT and an F8BT:(+)-**2** mixture (with 33 wt% of the chiral additive) were each dissolved in THF. The concentration of F8BT and the mixture were 12 mg mL⁻¹ and the solutions were treated in an ultrasonic bath for 60 minutes. Afterwards, the solutions were filtered through 0.45 µm PTFE filters with a syringe. The solutions were dripped step-by-step into aluminum crucibles (Netzsch, 25 µL) and dried under a flow of nitrogen. The procedure was repeated until a mass of about 10 mg was reached. The pans were then further dried in a nitrogen atmosphere with less than 1% humidity for about 12 hours. Prior to the measurement, small holes were pierced into the lid, then the crucible and the lid (Supporting Figure 1.1) were pressed together and the exact mass was measured.



Supporting Figure 1.1. Image of the aluminum crucibles containing the samples. Left side: F8BT:(+)-**2** (33 wt% chiral additive). Right side: pure F8BT.

DSC data were collected using a thermo-microbalance-based simultaneous TG-DSC instrument (Netzsch STA 449 C Jupiter). An empty aluminum crucible served as a reference. Two independent nitrogen gas flows (20 ml min⁻¹ each) and an additional argon gas flow (20 ml min⁻¹) were employed for purging. Multiple temperature segments were traversed and are summarized in Supporting Table 1.2. A fixed heating rate of 10 °C min⁻¹ was used for the heating and cooling segments. The first segment went up to a temperature of 80 °C to evaporate residual THF. After cooling down to about 30 °C, the next segment went up to a temperature of 170 °C. According to Donley et al., the glass transition temperature of F8BT samples with different molecular weights ($M_n = 9\text{--}255$ kg mol⁻¹) is in the range 135–140 °C.^[2] A temperature of 170 °C should therefore provide a well resolved signal for the glass transition and a non-destructive first scan for the F8BT:(+)-**2** blend, as we observed beginning decomposition of the chiral additive above 200 °C. After cooling down to 30 °C, two heating cycles to 320 and 330 °C, respectively, were carried out, each one followed by cooling to 30 °C.

Supporting Table 1.2. Temperature program of the DSC measurements.

Segment	T_{initial} (°C)	T_{final} (°C)	Heating rate (°C min ⁻¹)
1	25	80	10
2	80	30	10
3	30	170	10
4	170	30	10
5	30	320	10
6	320	30	10
7	30	330	10
8	330	30	10

1.5 Atomic Force Microscopy (AFM)

Images of the topography of annealed F8BT and F8BT:(+)-**2** thin films (with 9, 17 and 33 wt% of the chiral additive) were taken with an atomic force microscope (PSIA XE-100) in non-contact mode using a cantilever with a silicon tip. The resolution was 512 times 512 pixel for an area of $6 \times 6 \mu\text{m}^2$, with a scan rate of 0.5 Hz. The AFM images were evaluated using the software package Gwyddion^[3] (version 2.61) and visualization was carried out using OriginPro2022 (OriginLab Corporation). Forward and backward scans were averaged and afterwards background corrected.

1.6 Steady-State Absorption Spectroscopy and Microscopy

A Varian Cary 5000 spectrophotometer was employed to measure steady-state absorption spectra of macroscopic ($5 \times 5 \text{ mm}^2$) thin film areas using a slit width of 0.5 nm. CD spectra were recorded on the same spectrometer by adding a home-built assembly featuring polarizer – achromatic quarter-wave plate combinations covering the UV–Vis range, as described previously.^[4] For systematic measurements of the chiral response for different weight ratios of the copolymer and the chiral additive, we also used an Applied Photophysics Chirscan instrument, which was kindly provided by the Ihmels group (Organic Chemistry 2, University of Siegen). Circular dichroism, circularly polarized luminescence and crossed-polarizer microscopy experiments of the thin film samples were performed on a recently established setup, which is built around a modified Olympus IX71 inverted microscope, providing images with a diffraction-limited resolution of about 400 nm as well as CD and CPL spectra integrated over the entire field of view.^[4]

1.7 Ultrafast Broadband Transient Circular Dichroism and Absorption Spectroscopy

Transient circular dichroism and transient absorption spectra were recorded on a setup based on an amplified titanium:sapphire laser system (Coherent Libra USP-HE), as described previously.^[4] The thin film samples, which were kept inside an aluminum cell under a constant flow of dry nitrogen, were excited at 320 nm and probed by broadband multifilament UV–Vis supercontinuum pulses (260–700 nm), which were either alternately left and right circularly polarized (TrCD experiments) or linearly polarized (transient absorption measurements). The kinetic analysis of the TrCD data was performed using the program Tenua 2.1.^[5] The rate constants in the mechanism were varied to arrive at an optimal description of the TrCD kinetics.

The thickness of the polymer films was determined from the transient absorption kinetics using picosecond ultrasonics^[6,7] assuming that the longitudinal sound velocity of the thin films is equal to that of the previously investigated closely related copolymer c-PFBT ($v_L = 2490 \text{ m s}^{-1}$).^[8] Error bars for the thickness were determined from an error propagation analysis considering the known uncertainty of v_L ^[8] and the uncertainty of the period of the coherent acoustic phonon oscillation obtained from the fit.

1.8 Time-Correlated Single Photon Counting

A new setup for time-correlated single photon counting (TCSPC) was constructed to record transient photoluminescence decays. The samples were photoexcited by the second harmonic (410 nm) of a mode-locked titanium:sapphire oscillator (Spectra-Physics Tsunami, pulse duration 80 fs, 80 MHz repetition frequency). Tuning of the polarization and the laser pulse energy was achieved by the combination of a Glan-Taylor polarizer (Karl Lambrecht, MGTYS10) and a tunable zero-order half-wave phase retardation plate (Alphas, PO-TWP-L2-25-UVIR). The photoluminescence of the samples was collected at an angle of 90° by a quartz lens, sent through a bandpass filter (Thorlabs,

FB530-10, center wavelength 530 nm, FWHM 10 nm), and then refocused by another quartz lens onto a hybrid multialkali photodetector with a cathode diameter of 3 mm (Becker & Hickl, HPM-100-07). The signal pulses from the detector and the synchronization pulses of the laser (recorded by a fast photodiode, Becker & Hickl, PHD-400-N-SET) were fed into the inputs of a TCSPC module (Becker & Hickl, SPC-130IN) which was operated in reversed start-stop configuration.

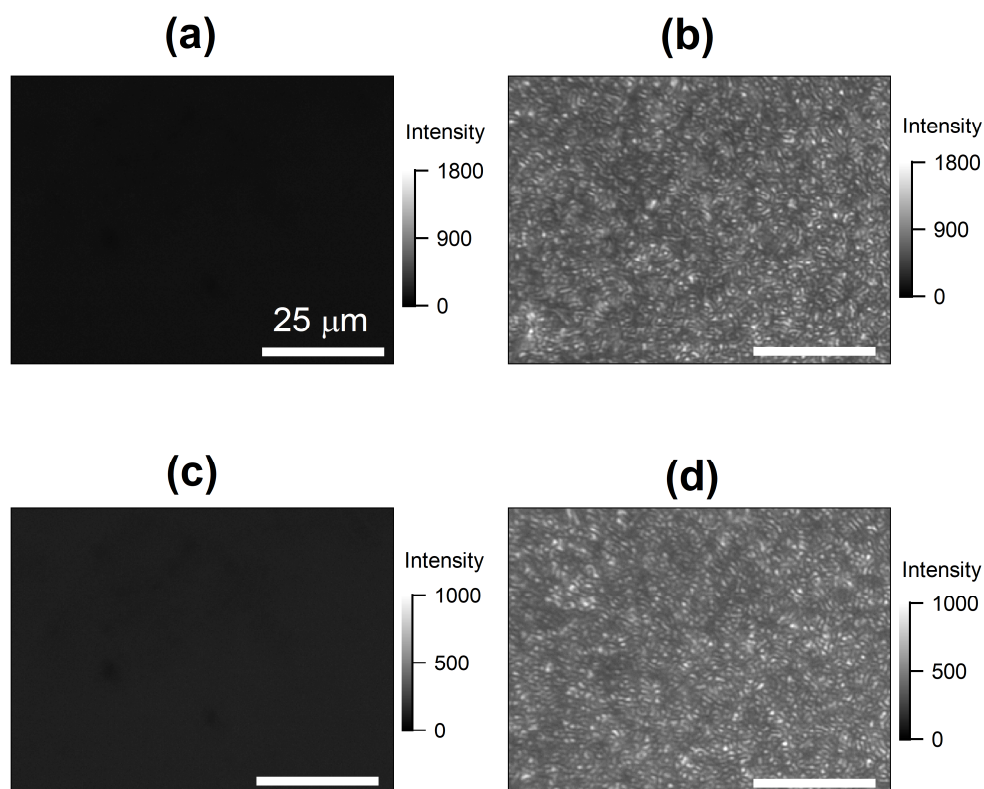
For lifetime measurements, the samples were excited by vertically polarized laser light (0°) and the photoluminescence was recorded at the magic angle (54.7°) employing a wire-grid polarizer (Thorlabs WP25M-UB) in the photoluminescence detection path. For time-resolved CPL measurements, the 410 nm laser pulses were sent through a Hanle depolarizer to scramble the polarization prior to excitation. In the detection path, an achromatic broadband quarter-wave plate (Thorlabs AQWP05M-580) was inserted between the collecting lens and the polarizer. CPL kinetics were obtained by subtracting the decays of two consecutive TCSPC measurements (recorded for identical collection times) with the polarizer axis fixed at 0° and the fast axis of the quarter-wave plate set at either $+45^\circ$ or -45° with respect to the polarizer axis. An instrument response function (IRF) of 28 ps was determined from the laser scattering signal of a diluted suspension of colloidal silica nanoparticles (Merck, Ludox AM-40). The time constants and amplitudes of the thin-film photoluminescence decays were obtained from tail fits employing the FAST program (Edinburgh Instruments).

Additional TCSPC experiments with lower time-resolution were carried out using a pulsed UV-LED (Becker & Hickl, UVL-FB-270, 273 nm, 20 MHz repetition frequency) as the excitation source. For lifetime measurements, the output of the LED was vertically polarized (0°) by means of a wire-grid polarizer (Thorlabs WP25M-UB). For time-resolved CPL measurements, the samples were excited directly by the unpolarized output pulses of the LED. For these experiments, the time resolution was limited by the LED pulse width of 500 ps.

Supporting Note 2.

Crossed-Polarizer Images of F8BT:(+)-2 Thin Films

In Supporting Figure 2.1 we present crossed-polarizer images of different F8BT:(+)-2 thin films. The upper row contains images of a pristine film (panel a) and an annealed (150 °C) film (panel b) spin-coated from a chlorobenzene:chloroform mixture. The lower row shows similar images, but for films spin-coated from toluene. The black images in panels a and c indicate that the pristine (as-deposited) films do not turn the initially linear polarization of the light. This is consistent with the presence of only weak molecular optical activity due to the embedded chiral helicene-type additive. In contrast, the crossed-polarizer images of the annealed films in panels b and d show characteristic granular textures, which are consistent with the structures observed in the CD and CPL images (cf. Figures 2, 3, 6 and 7 in the main manuscript). The strong optical activity of the annealed films indicates the formation of a chiral supramolecular arrangement.

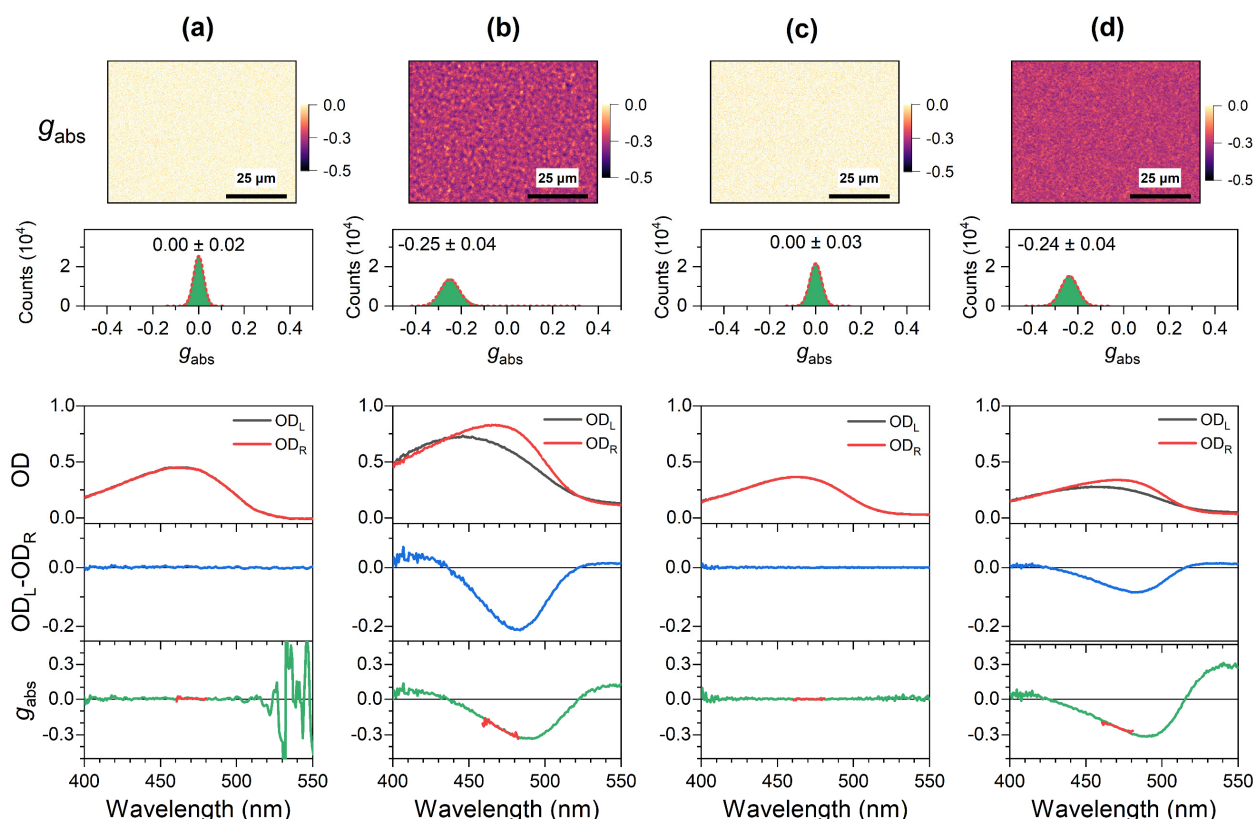


Supporting Figure 2.1. Crossed-polarizer images for F8BT:(+)-2 thin films. a) Pristine thin film spin-coated from a mixture of chlorobenzene and chloroform. b) Annealed thin film originally spin-coated from a mixture of chlorobenzene and chloroform. c) Pristine thin film spin-coated from toluene. d) Annealed thin film originally spin-coated from toluene. Blends were deposited employing 33 wt% of the chiral additive. Images for a/b and c/d were recorded for identical conditions. The white scale bar in each image corresponds to a distance of 25 μm .

Supporting Note 3.

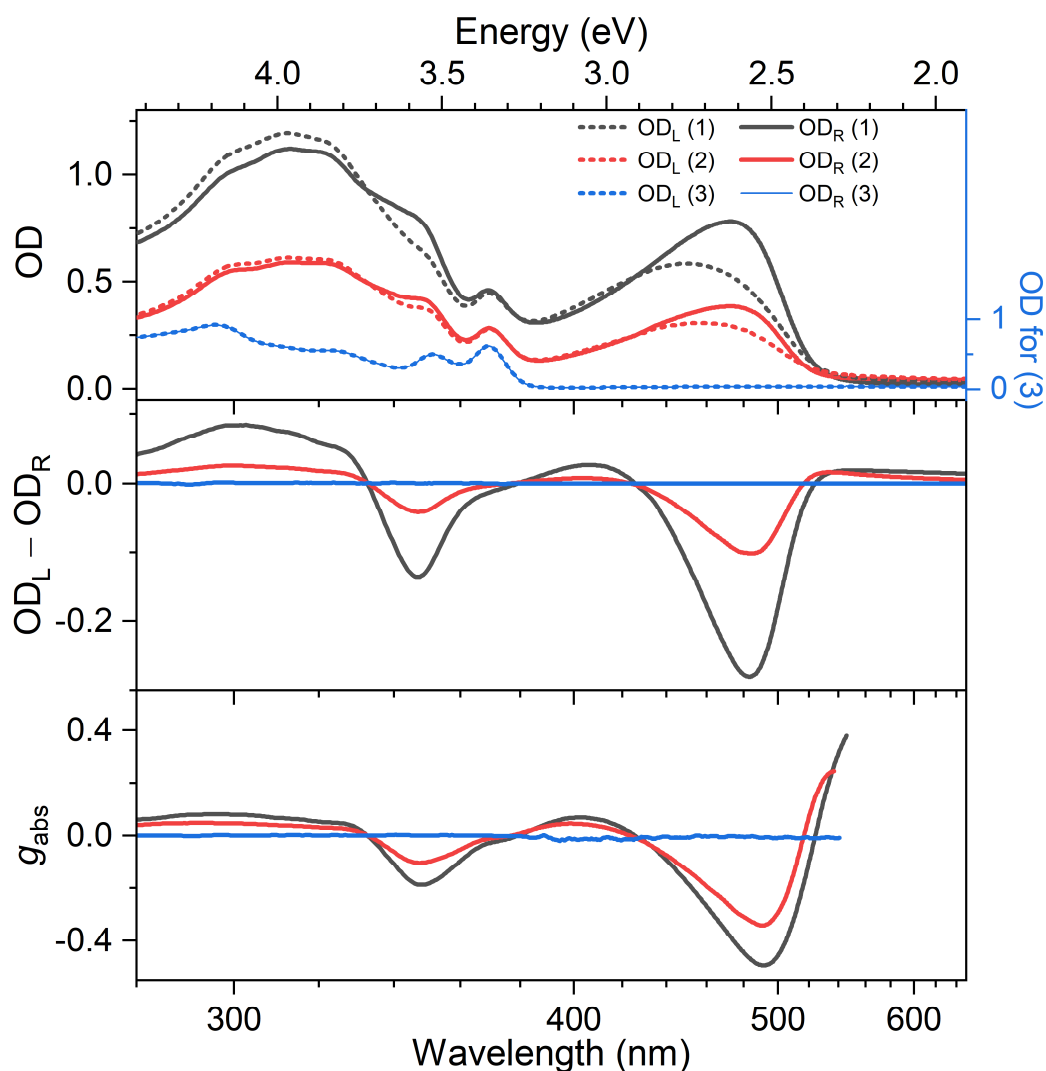
Chiral Response of Pristine and Annealed F8BT:(+)-2 Thin Films

In Supporting Figure 3.1 we present CD microscope images and spectra of F8BT:(+)-2 thin films spin-coated from a chlorobenzene:chloroform mixture (1:9 v:v) in pristine form (panel a) and after annealing at 150 °C (panel b). Panels c and d show corresponding data, but for these thin films the spin-coating was performed from toluene. The images and spectra of the pristine films in panels a and c show no CD response, whereas the annealed films in panels c and d exhibit pronounced CD activity.



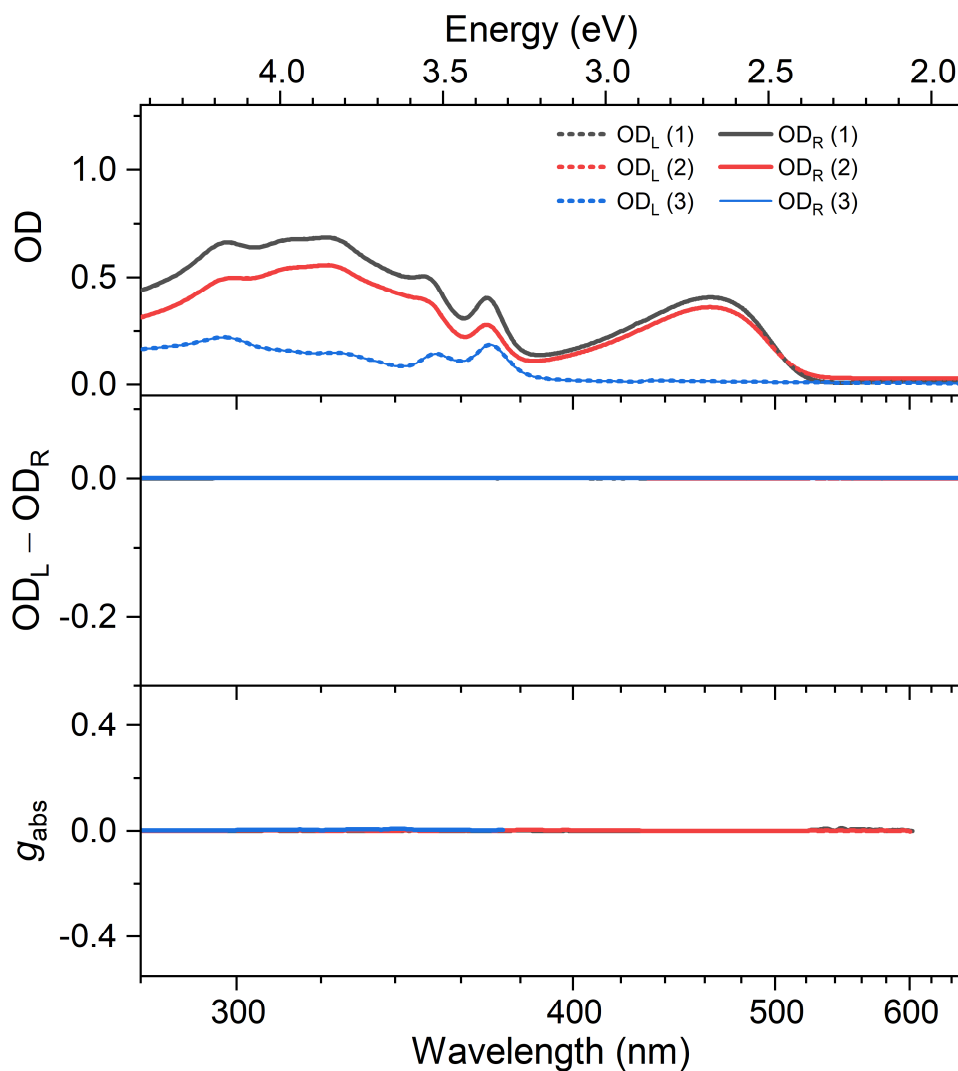
Supporting Figure 3.1. CD microscopy of pristine and annealed F8BT:(+)-2 thin films spin-coated from different solvents. a) Microscope image ($80 \times 60 \mu\text{m}^2$) showing the dissymmetry parameter g_{abs} of a pristine F8BT:(+)-2 thin film spin-coated from a chlorobenzene:chloroform mixture (top) with the distribution of g_{abs} values (middle) including a Gaussian fit (dashed red line), determined over the entire field of view, and corresponding spectra integrated over the entire field of view ($210 \times 160 \mu\text{m}^2$, three panels at the bottom) displaying the optical density for left- and right-circularly polarized light (OD_L (black line), OD_R (red line)), the CD spectrum ($\text{OD}_L - \text{OD}_R$, blue line) and the g_{abs} spectrum (green line), with the thick red line indicating the spectral region selected by the bandpass filter (470 nm, FWHM 10 nm) used for CD imaging. b-d) Same as in panel a, but for an annealed F8BT:(+)-2 thin film spin-coated from a chlorobenzene:chloroform mixture, a pristine F8BT:(+)-2 thin film spin-coated from toluene, and an annealed F8BT:(+)-2 thin film spin-coated from toluene, respectively. The scale bar in each CD image corresponds to a distance of 25 μm . In each case, 33 wt% of the helicene-type additive was employed.

Supporting Figure 3.2 shows bulk steady-state absorption spectra (top) for LCP and RCP probing (dashed and solid lines, respectively), CD spectra (middle) and g_{abs} spectra (bottom) for annealed thin films of F8BT:(+)-**2** thin films spin-coated from a chlorobenzene:chloroform mixture (1:9 v:v, black lines) or from toluene (red lines), and also for a thin film of the pure helicene-type additive (+)-**2** (blue lines). After deposition, all films were annealed at 150 °C. The F8BT:(+)-**2** blends exhibit a strong chiral response. The large CD values arise from supramolecular chirality. In contrast, on the same OD scale, the thin film of the pure helicene-type additive (+)-**2** does not show any appreciable optical activity, which suggests molecular chirality, i.e. the thin film of the chiral additive does not form a chiral supramolecular arrangement.



Supporting Figure 3.2. Steady-state optical spectra for annealed F8BT:(+)-2** thin films spin-coated from a chlorobenzene:chloroform mixture (black, 1) or toluene (red, 2) and for an annealed thin film of pure compound (+)-**2** (blue, 3). Top) Absorption spectra for LCP (dashed lines) and RCP detection (solid lines). Middle) CD spectra. Bottom) g_{abs} spectra. Blends were deposited employing 33 wt% of the chiral additive.**

In Supporting Figure 3.3, we provide spectra for the pristine (= as deposited) thin films for comparison. In this case, the thin films of the blends do not show CD activity. Formation of a chiral supramolecular arrangement therefore requires annealing of the blends above the transition temperature.

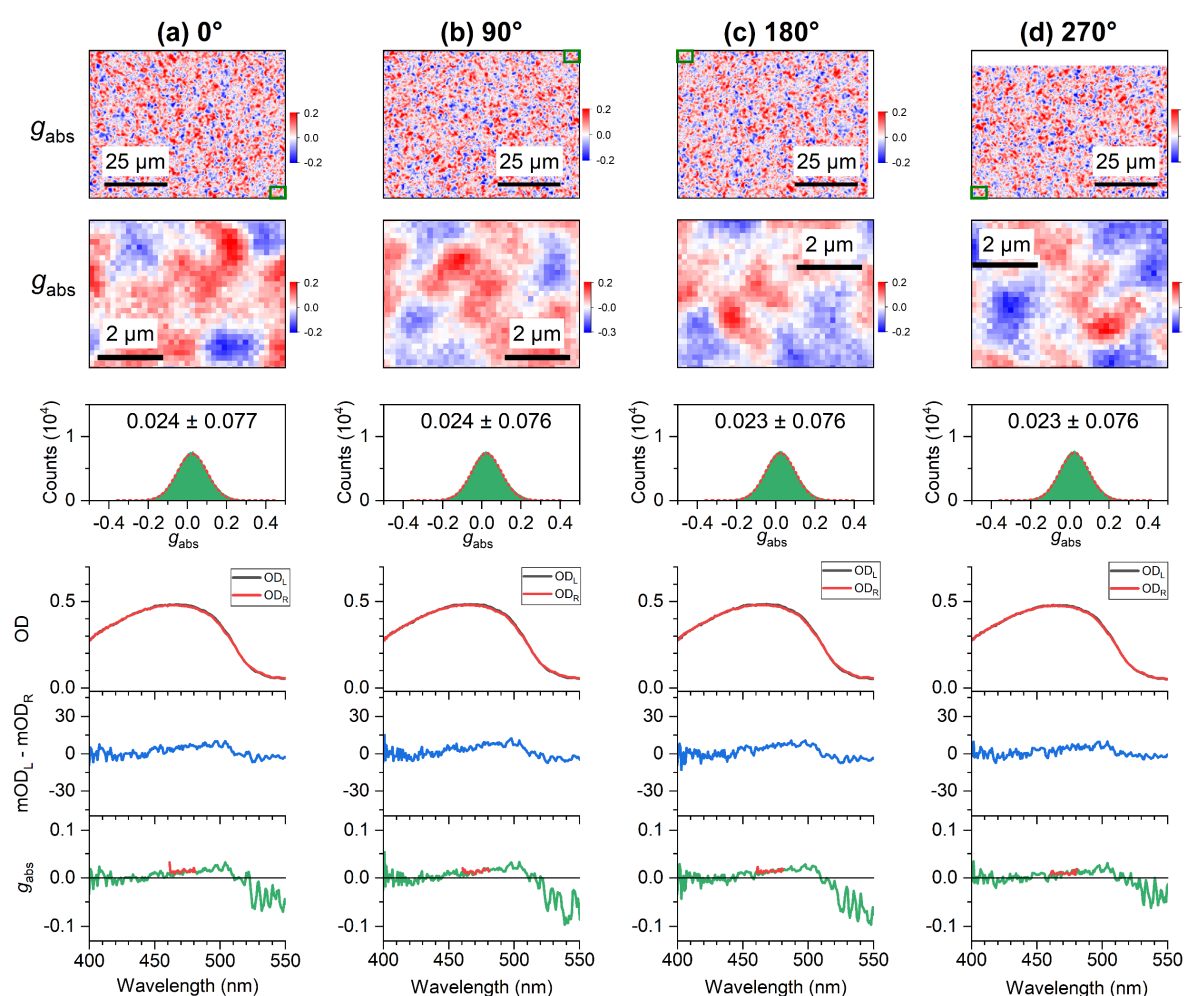


Supporting Figure 3.3. Same as in Supporting Figure 3.2, but for the pristine (as deposited) films.

Supporting Note 4.

Invariance of CD Signals of F8BT:2 Thin Films Under Sample Rotation

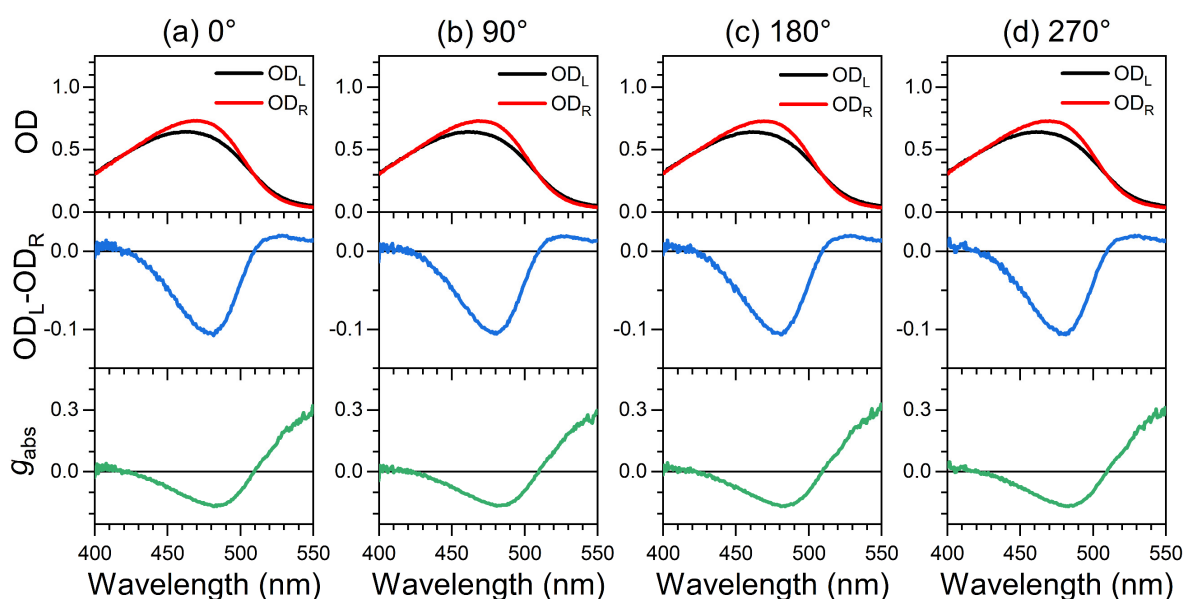
Supporting Figure 4.1 shows CD microscope images and spectra of an F8BT film containing 33 wt% of an enantiomer mixture of the helicene-type chiral additive **2**, with 10% enantiomeric excess of (–)-**2**. Under these conditions, small domains of opposite chirality with high g_{abs} contrast can be easily distinguished in the CD microscope, as indicated by the small red and blue regions appearing side-by-side in the overview microscope images in the top row of the figure. This property makes such films ideal candidates to check the invariance of the chiral response upon sample rotation, even for very small regions with length scales on the order of the diffraction limit.



Supporting Figure 4.1. Invariance of CD microscope images under rotation for an F8BT:2 thin film with 10% enantiomeric excess of the helicene-type compound (–)-2**.** a) Microscope image ($80 \times 60 \mu\text{m}^2$, top row) including a zoom-in of a representative region (second row, indicated by the small rectangular region in the top row) for the dissymmetry parameter g_{abs} , with a histogram of g_{abs} values (green) including a Gaussian fit (dashed red line), determined over the entire field of view (third row), and spectra (bottom row) integrated over the entire field of view ($210 \times 160 \mu\text{m}^2$) showing the optical density for left- and right-circularly polarized light (OD_L (black), OD_R (red)), the CD spectrum (blue) and the g_{abs} spectrum (green), with the thick red line indicating the spectral region selected by the bandpass filter (470 nm, FWHM 10 nm) employed for CD imaging. b-d) same as in panel a, but for a rotation of the sample by 90° , 180° and 270° , respectively.

In the second row, we zoom into a specific region of the film (indicated by a rectangle in each of the images in the first row). The selected part of the image features a prominent horseshoe-shaped red region of positive g_{abs} . One camera pixel in each of these images represents a CD measurement for a $160 \times 160 \text{ nm}^2$ area, and the estimated optical resolution is 400 nm (Abbe diffraction limit, with a numerical aperture of the 40x objective of 0.60 and a center wavelength of the bandpass filter of $\lambda = 470 \text{ nm}$). Upon rotation of the sample in 90° steps, one can nicely follow the corresponding rotation of the horseshoe-shaped region. Most importantly, there are no changes in the sign and amplitude of the CD response of this region. Therefore, we conclude that contributions resulting from a combination of linear dichroism (LD) and linear birefringence (LB) in combination with any possible anisotropies of the CD microscopy setup can be safely excluded for length scales down to 400 nm. The finding is confirmed by the OD_L , OD_R , CD and g_{abs} spectra in the bottom row, which all yield results which are invariant upon rotation.

In addition, Supporting Figure 4.2 shows area-integrated spectra for OD_L , OD_R , $\text{OD}_L - \text{OD}_R$ and g_{abs} of an arbitrary area of an F8BT:(+)-2 thin film obtained using the CD microscope setup. There are virtually no changes in the CD response and the dissymmetry factor g_{abs} upon turning the thin film sample, meaning that the response of the samples is invariant under rotation. Thus, we can again exclude contributions resulting from a combination of LD and LB effects in our sample in combination with any possible anisotropies of the CD microscope optics. We previously observed very similar behavior for thin films of the intrinsically chiral copolymer c-PFBT. Such a behavior is a hallmark of multidomain supramolecular liquid crystalline order with statistical orientation of the individual domains.^[9,10] There, it was also shown that such samples do not change their CD response when the sample is flipped.

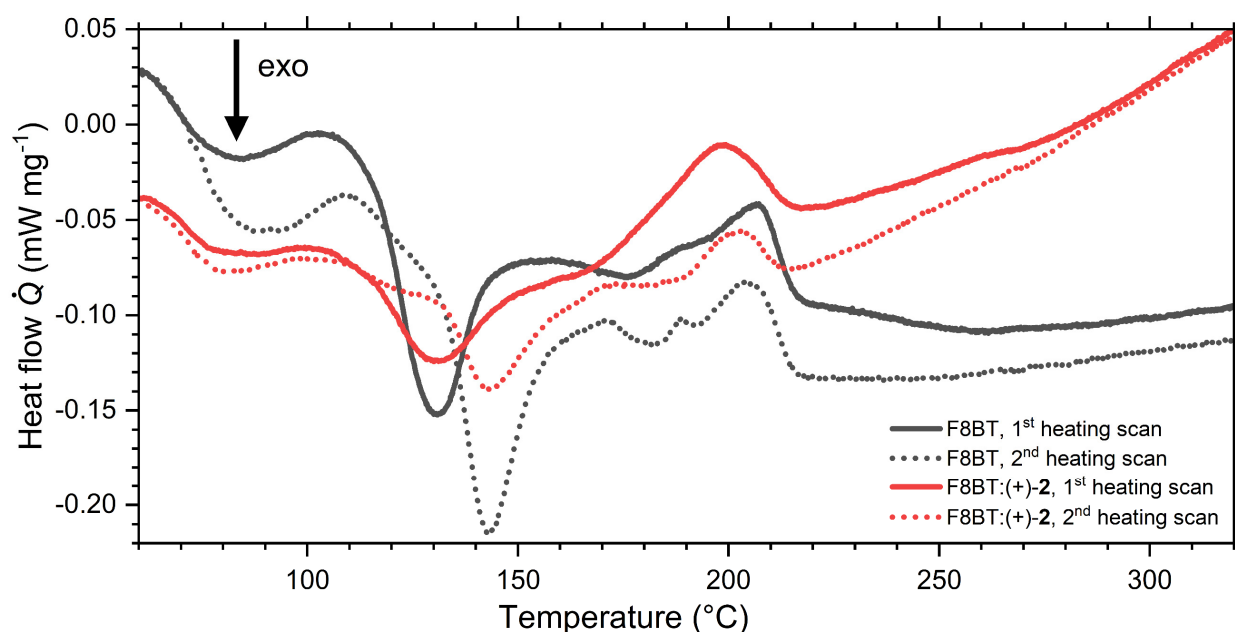


Supporting Figure 4.2. CD microscope spectra of an F8BT:(+)-2 thin film (33 wt% of the chiral additive) integrated over the entire field of view ($210 \times 160 \mu\text{m}^2$) displaying the optical density for left- and right-circularly polarized light (OD_L (black line), OD_R (red line)), the CD spectrum ($\text{OD}_L - \text{OD}_R$, blue line) and the g_{abs} spectrum (green line). Spectra were recorded for the same film area by 90° stepwise rotation in anticlockwise direction. a) 0° . b) 90° . c) 180° . d) 270° .

Supporting Note 5.

DSC Measurements for Pure F8BT and an F8BT:(+)-2 Blend

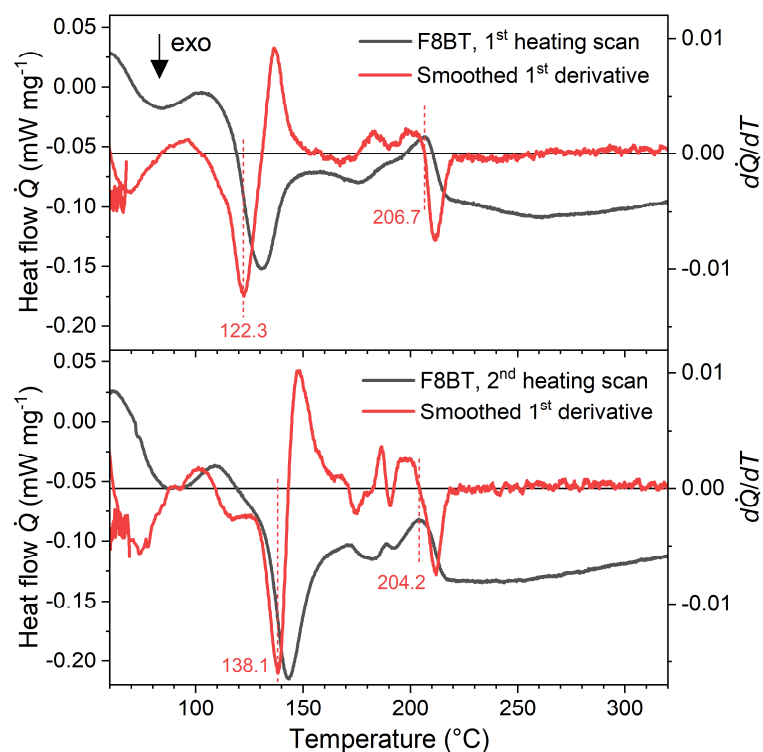
In Supporting Figure 5.1, we show the heat flow $\dot{Q}$ measured in the DSC experiments as a function of temperature for pure F8BT (black) and the F8BT:(+)-2 blend with 33 wt% of the chiral additive. Two heating runs for the temperature ranges 30–320 °C and 30–330 °C are shown as solid and dotted lines, respectively.



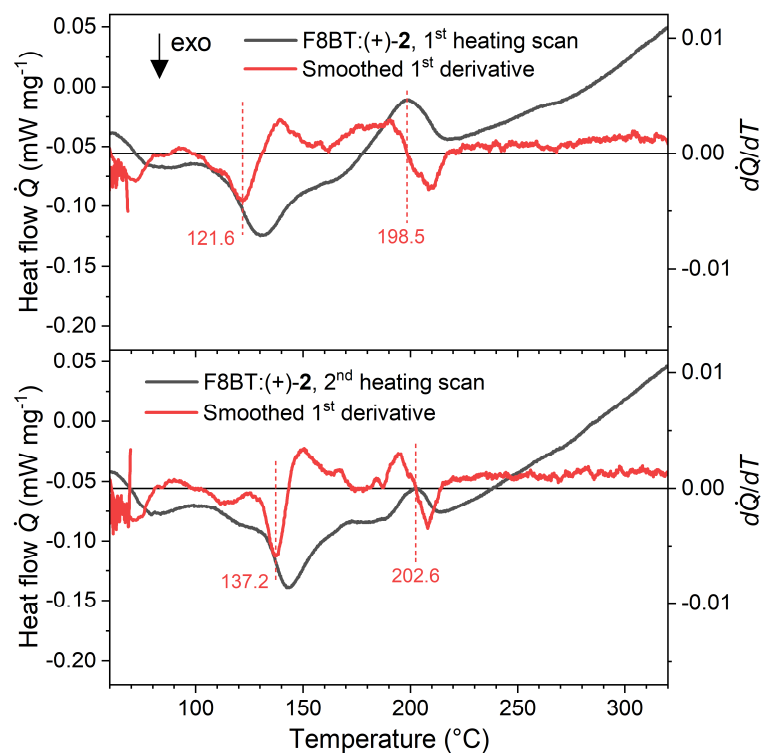
Supporting Figure 5.1. Comparison of the temperature-dependent heat flows for two heating scans of F8BT and F8BT:(+)-2. Solid lines: first heating scans, dotted lines: second heating scans, black: pure F8BT, red: F8BT:(+)-2 blend with 33 wt% of the helicene-type chiral additive.

A further analysis was performed using the smoothed first derivative of the heat flow. Results for F8BT and the F8BT:(+)-2 blend are shown in Supporting Figures 5.2 and 5.3, respectively. We start with the discussion of the first heating scan (top panels). An exothermic peak at 130 °C in the heat flow curve was attributed to the crystallization step from an amorphous glassy state to a nematic phase or rubbery state.^[2] A Gaussian peak analysis provided a minimum in the first derivative at 122.3 and 121.6 °C for pure F8BT and the F8BT:(+)-2 blend, respectively, which corresponds to the inflection point of the heat flow. It was therefore assigned to the glass transition temperature T_g . Most importantly, addition of the chiral helicene-type compound practically does not change the glass transition temperature of the polyfluorene copolymer. The melting range is indicated by the last local maximum in the heat flow curve. The zero crossing of the first derivative provides a melting temperature T_m of 206.7 and 198.5 °C for pure F8BT and the F8BT:(+)-2 blend, respectively.

A similar analysis was performed for the second heating scan (bottom panels). Here, we obtained values of $T_g = 138.1$ (137.2) °C and $T_m = 204.2$ (202.6) °C for pure F8BT (the F8BT:(+)-2 blend). We note that the T_g values for the second heating scan agree well with the range 135–140 °C reported by Donley et al.^[2] However, for a direct comparison of F8BT and the F8BT:(+)-2 blend, the first heating scan is probably more reliable, as we noted some decomposition of the helicene-type additive starting at about 200 °C.



Supporting Figure 5.2. Analysis of transition temperatures for the first (top) and second (bottom) heating scan of F8BT from Supporting Figure 5.1. Black lines: temperature-dependent heat flow. Red lines: Smoothed first derivative.



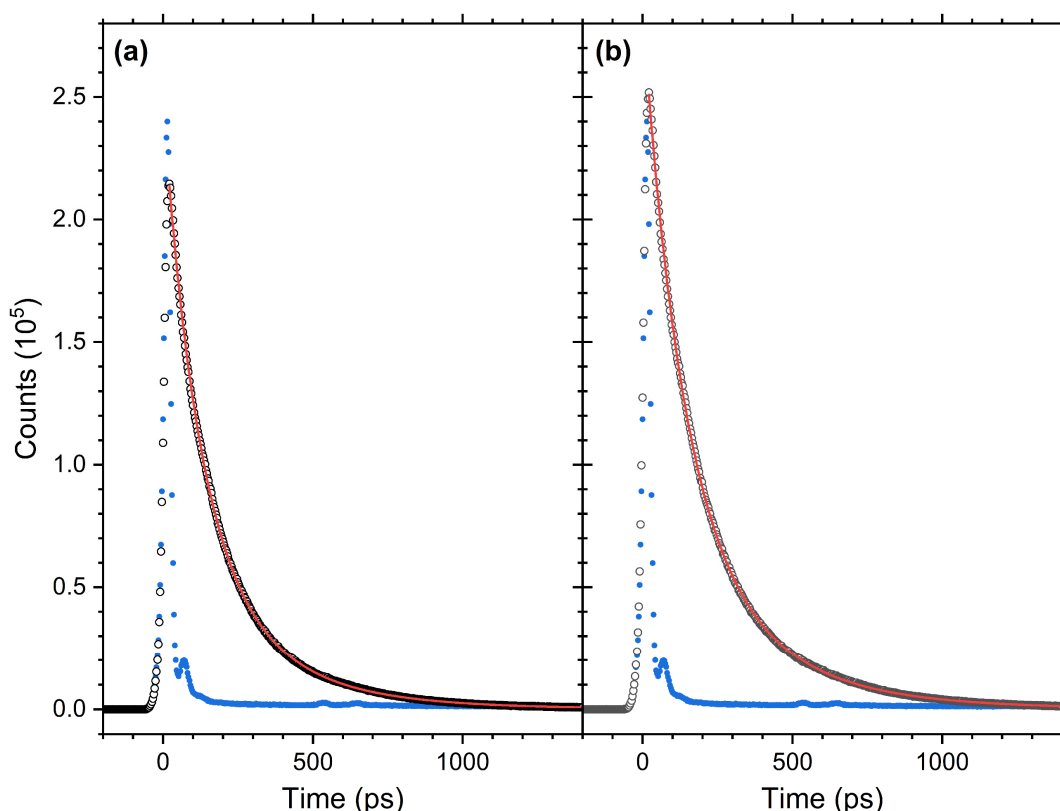
Supporting Figure 5.3. Same as in Supporting Figure 5.2, but for the F8BT:(+)-2 blend.

Supporting Note 6.

Ultrafast Electronic Relaxation of F8BT:(+)-2 and F8BT:(-)-2 Blends

Here, we discuss the dynamic processes underlying the TrCD signals in more detail. Representative kinetic traces averaged over the low-wavelength band of the TrCD bleach region (340–350 nm) of F8BT:(+)-2 and F8BT:(-)-2 were already presented in Figure 4d of the main manuscript. Both kinetic traces exhibit a fast decay over the first few picoseconds, which then slows down considerably, reaching a residual signal of about 15% at 1000 ps. These dynamics are directly correlated with the recovery of S_0 population, because the supramolecular TrCD response does not contain clear CD contributions from F8BT excited states.^[4]

Importantly, the fast decay of the TrCD signal at early times is not compatible with the intrinsic lifetime of the S_1 exciton state. We determined this independently using time-correlated single photon counting (TCSPC) at very low S_1 exciton densities ($N(S_1) < 1 \times 10^{10} \text{ cm}^{-3}$), where processes involving two S_1 singlet excitons cannot occur because of the large exciton–exciton distance. Supporting Figure 6.1 shows such TCSPC curves recorded at magic angle after photoexcitation by femtosecond pulses at 410 nm for F8BT:(+)-2 and F8BT:(-)-2 thin films in panels a and b, respectively. The vertically polarized 410 nm pulses exclusively excite the F8BT copolymer, because the helicene-type chiral additive absorbs only below 390 nm (cf. Supporting Figure 10.1). Photons are detected at the magic angle (54.7°), and the time resolution of the setup is about 28 ps.



Supporting Figure 6.1. Time-resolved fluorescence experiments for the S_1 exciton state of F8BT in F8BT:(+)-2 and F8BT:(-)-2 thin films after photoexcitation at 410 nm. a) Kinetics of the F8BT:(+)-2 thin film (open black circles) including a triexponential tail fit (red line) and the instrument response function (solid blue circles) recorded using a diluted colloidal SiO_2 nanoparticle solution. b) Same as in panel a, but for an F8BT:(-)-2 thin film.

The decay of the photoluminescence intensity is well described by a triexponential function:

$$I(t) = \sum_{i=1}^3 A_i \exp(-t / \tau_i) \quad (\text{S6.1})$$

The lifetimes τ_i and corresponding percentage amplitudes A_i were extracted from tail fits and are reported in Supporting Table 6.1. We also include fractional contributions to the photoluminescence intensity f_i (with $i = 1, 2$ or 3) which are defined as

$$f_i = \frac{A_i \cdot \tau_i}{\sum_{j=1}^3 A_j \cdot \tau_j} \quad (\text{S6.2})$$

and the average lifetime $\langle \tau \rangle$, which is calculated as

$$\langle \tau \rangle = \frac{\sum_{j=1}^3 A_j \cdot \tau_j^2}{\sum_{j=1}^3 A_j \cdot \tau_j} \quad (\text{S6.3})$$

The multiexponential character of the decay is not unexpected, because individual F8BT chromophores in blends with the helicene-type additive experience quite different environments with varying contributions of F8BT–F8BT and F8BT–**2** interactions. The photoluminescence decays are dominated by two time constants: 119 and 286 ps for F8BT:(+)-**2** and 132 and 304 ps for F8BT:(–)-**2**. The 10–20 ps difference between the two films probably arises from slight variations in the film preparation conditions. The amplitude ratio is roughly 2:1 and the two components together amount to more than 99% of the total amplitude. The third time constant of about 1200 ps has only a contribution of 0.5% and could arise from a very small amount of a luminescing impurity in the polymer. The resulting average lifetimes obtained from eq. (S6.3) are 233 and 253 ps for the two different films. Note that this time scale is much slower than the initial decays observed in Figure 4d of the main manuscript, which are on the order of a few picoseconds.

Supporting Table 6.1. Kinetic parameters extracted from triexponential tail fits to the kinetics of the F8BT:(+)-2** and F8BT:(–)-**2** thin films shown in Supporting Figure 6.1.** Error bars for the time constants are based on a support plane analysis and are reported for a confidence interval of 95%.

	τ_i (ps)	A_i (%)	f_i (%)	$\langle \tau \rangle$ (ps)
F8BT:(+)-2				
Component 1	119 ± 2	69.3	47.7	233
Component 2	286 ± 4	30.3	49.6	
Component 3	1240 ± 60	0.4	2.7	
F8BT:(-)-2				
Component 1	132 ± 2	66.2	44.8	253
Component 2	304 ± 5	33.3	52.3	
Component 3	1204 ± 60	0.5	2.9	

A more elaborate kinetic description is therefore required to describe the kinetics in Figure 4d of the main manuscript for the blends consisting of F8BT and the helicene-type chiral additives (+)-**2**

and (–)-**2**. We utilize a simplified version of the kinetic model introduced recently for the relaxation of c-PFBT thin films:^[4]



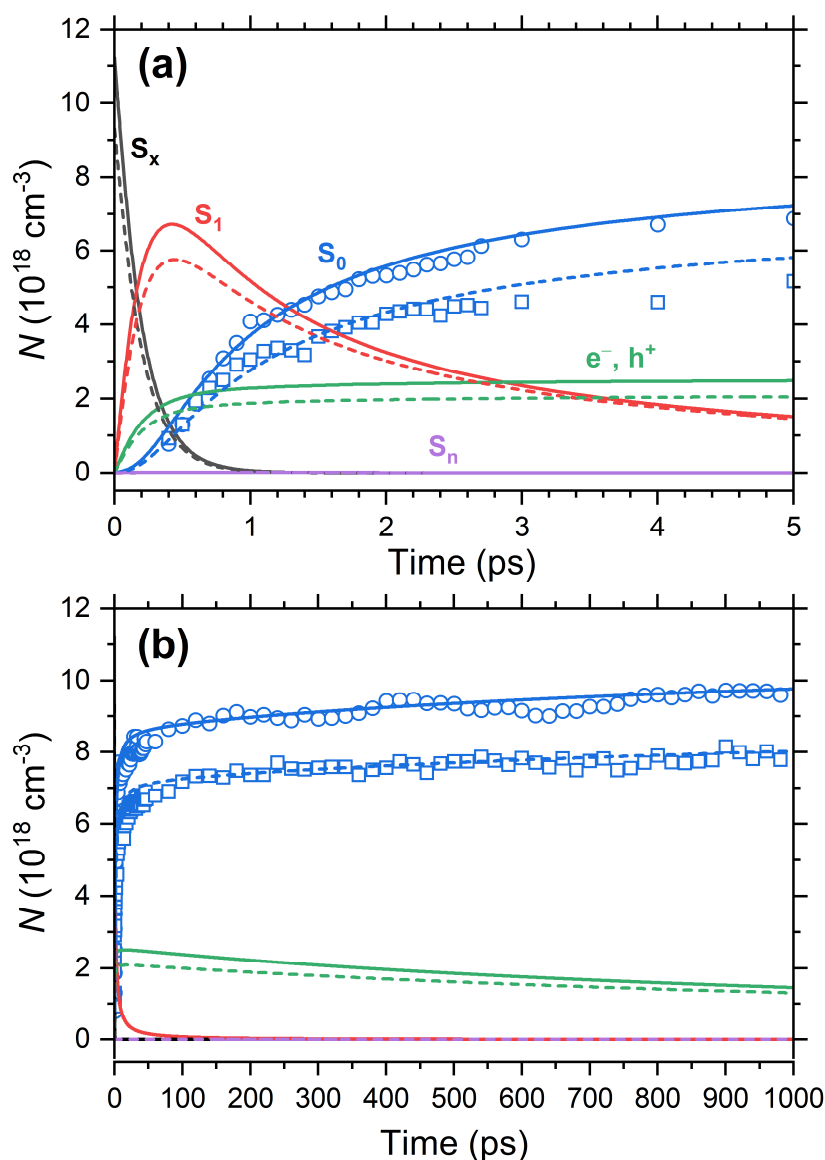
In the following, we briefly summarize the key steps of the model:^[4] Initially, a higher-lying singlet exciton state, denoted as S_x , is excited by the pump wavelength 320 nm. It decays with the rate constant $k_x = \tau_x^{-1}$ to S_1 singlet excitons, which relax further to S_0 with the rate constant $k_1 = \tau_1^{-1}$ (step S6.4). We associate τ_1 with the average lifetime $\langle \tau \rangle$ determined from the TCSPC measurements and use an averaged value of 243 ps for the F8BT copolymer in both films (cf. Supporting Table 6.1). As discussed previously, the S_x state can also directly dissociate into a charge pair state (CP, electron (e^-) plus hole (h^+)) according to step S6.5 (rate constant $k_{CPx} = \tau_{CPx}^{-1}$).^[4,11]

Beside unimolecular singlet exciton relaxation, there are also singlet–singlet annihilation (SSA) channels, which are only efficient at high exciton number densities. One possibility is diffusive bimolecular SSA according to step S6.6. Here, two S_1 excitons diffuse along an F8BT chain and then react, once they reach a critical distance. This leads to the formation of a high-energy exciton species S_n and an S_0 ground state. Alternatively, SSA between two S_1 excitons may also take place by nonradiative Förster resonance energy transfer (FRET).^[12,13] However, our previous study on c-PFBT showed that this is only a negligible channel.^[4] Therefore, for the simple model applied here, the FRET process is not included. The excited species S_n can either decay to S_1 ($k_n = \tau_n^{-1}$, step S6.7) or produce a charge pair via step S6.8 with $k_{CPn} = \tau_{CPn}^{-1}$. Bimolecular recombination of the charge pair occurs on longer time scales ($k_{rec} = \tau_{rec}^{-1}$) and is described by step S6.9.

Contributions of the chiral additive to the spectral dynamics can be neglected, because the spectral CD signatures of films of these helicene-type molecules are distinctly different and much weaker than those of chiral F8BT arrangements.^[14] However, the electronic interactions between the chiral additive and F8BT in addition to the F8BT–F8BT interactions might influence the relaxation time constants of F8BT. In addition, the overlap of the two absorption bands at the pump wavelength of 320 nm needs to be considered, because a fraction of the photons will be absorbed by the chiral additive and will not be available for the photoexcitation of F8BT. This can be evaluated by separating the steady-state absorption spectra of the blends into absorption contributions of the chiral additive and F8BT, leading to an effective absorbance of F8BT at 320 nm. Examples for this procedure are shown in Supporting Figure 10.1. The effective absorbance enters the determination of the initial F8BT exciton number densities, which were $1.12 \times 10^{19} \text{ cm}^{-3}$ for F8BT:(+)-**2** and $9.32 \times 10^{18} \text{ cm}^{-3}$ for F8BT:(–)-**2**.

In Supporting Figure 6.2, the TrCD signals at short times (panel a) and long times (panel b) are displayed in terms of the absolute exciton number densities. The TrCD kinetics monitor the recovery of the S_0 ground state population and do not show contributions from electronically excited states.

The experimental data for F8BT:(+)-**2** (open blue circles) and F8BT:(-)-**2** (open blue squares) therefore directly reflect the number density of F8BT in S_0 . The kinetic model given by steps S6.4–S6.9 was implemented using the program package Tenua 2.1.^[5] The kinetic parameters were optimized to simultaneously fit the TrCD kinetics of both films. Compared with the fits for the previously investigated c-PFBT system,^[4] the rate constant k_{CPx} had to be increased to account for the larger quantum yield for CP formation from S_x . The rate constant k_{rec} for CP recombination was slightly reduced to describe the saturation behavior of the kinetic traces at long times better.



Supporting Figure 6.2. Kinetic modeling of the TrCD kinetics of F8BT:(+)-2** and F8BT:(-)-**2** thin films.** a) Results of the kinetic modeling for short time scales (up to 5 ps). Blue open circles and blue open squares: Recovery of S_0 population for the initial S_x exciton number densities $1.12 \times 10^{19} \text{ cm}^{-3}$ (F8BT:(+)-**2**) and $9.32 \times 10^{18} \text{ cm}^{-3}$ (F8BT:(-)-**2**), respectively, as experimentally determined by the TrCD measurements with corresponding solid and dashed blue fit lines obtained from the kinetic model; solid and dashed black, red, green and violet lines: number density of the S_x excitons, S_1 excitons, electron–hole pairs (e^- , h^+) and the S_n excitons, as obtained from the kinetic model. b) Same as in panel a, but for longer time scales up to 1 ns.

The kinetic model describes the changes in the S_0 population very well, both on short and long time scales, as shown by the solid blue lines (F8BT:(+)-2) and the dashed blue lines (F8BT:(-)-2). The fast recovery at early times (panel a) is predominantly due to diffusive S_1 - S_1 exciton annihilation, where the S_1 exciton number densities are shown as solid and dashed red lines. The TrCD kinetics also provide information regarding the efficiency of CP formation from the highly excited S_x and S_n exciton states of F8BT. Taking the results from the best fit, we obtain a yield of 19% for charge pair formation from S_x and about 6% for the same process in the S_n state. The total yield of charge pair formation is therefore 25% and thus slightly larger than the 15% previously found in the case of c-PFBT thin films. Supporting Table 6.2 summarizes the parameters obtained from the optimized fit.

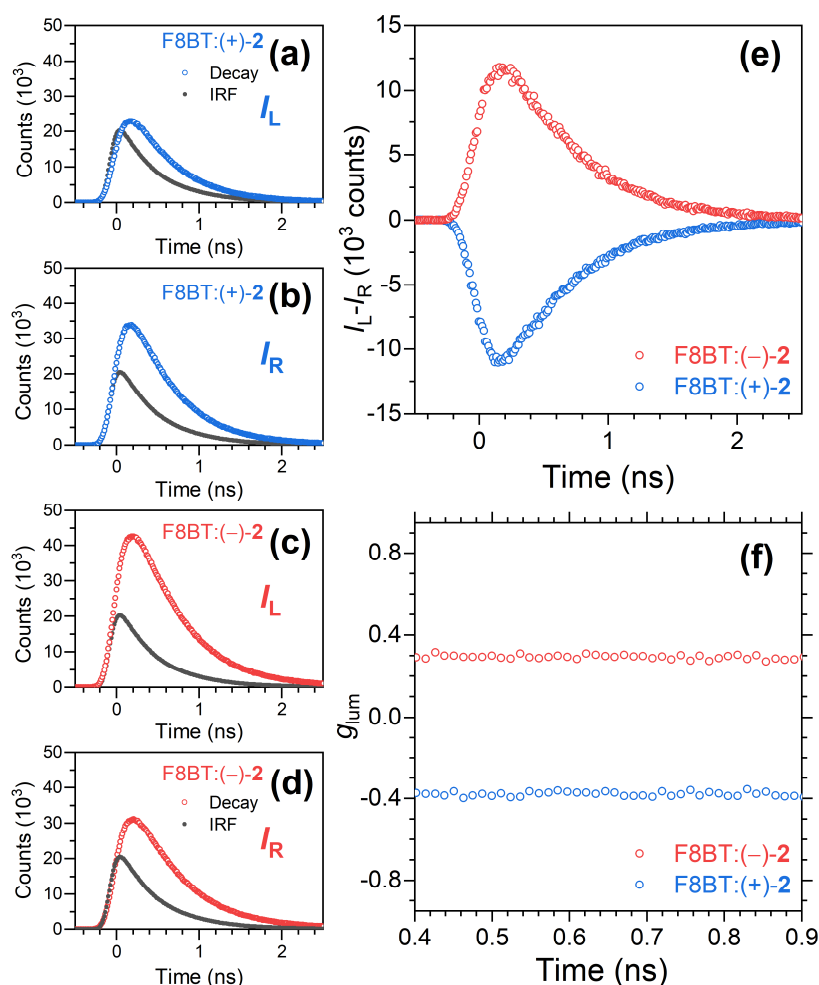
Supporting Table 6.2. Summary of parameters obtained from the kinetic analysis of the TrCD experiments for F8BT:(+)-2 and F8BT:(-)-2 upon photoexcitation at 320 nm.

Physical quantity (unit)	Value	Physical quantity (unit)	Value
$N_{0,\text{F8BT}:(+)-2}(S_x) \text{ (cm}^{-3}\text{)}$	1.12×10^{19}		
$N_{0,\text{F8BT}:(-)-2}(S_x) \text{ (cm}^{-3}\text{)}$	9.32×10^{18}		
$k_x(S_x \rightarrow S_1) \text{ (s}^{-1}\text{)}$	4.40×10^{12}	$\tau_x \text{ (fs)}$	227
$k_{\text{CPx}}(S_x \rightarrow e^- + h^+) \text{ (s}^{-1}\text{)}$	1.00×10^{12}	$\tau_{\text{CPx}} \text{ (ps)}$	2.22
$k_{x,\text{total}} = k_x + k_{\text{CPx}} \text{ (s}^{-1}\text{)}$	5.40×10^{12}	$\tau_{x,\text{total}} \text{ (fs)}$	185
		$\Phi_{\text{CPx}} \text{ (%)}$	19
$k_1(S_1 \rightarrow S_0) \text{ (s}^{-1}\text{)}$	4.12×10^9	$\tau_1 \text{ (ps)}$	243
$k_{\text{diff}}(2 S_1 \rightarrow S_n + S_0) \text{ (cm}^3 \text{ s}^{-1}\text{)}$	1.10×10^{-7}		
$k_n(S_n \rightarrow S_1) \text{ (s}^{-1}\text{)}$	3.8×10^{14}	$\tau_n \text{ (fs)}$	3
$k_{\text{CPn}}(S_n \rightarrow e^- + h^+) \text{ (s}^{-1}\text{)}$	2.3×10^{13}	$\tau_{\text{CPn}} \text{ (fs)}$	40
$k_{n,\text{total}} = k_n + k_{\text{CPn}} \text{ (s}^{-1}\text{)}$	4.0×10^{14}	$\tau_{n,\text{total}} \text{ (fs)}$	3
		$\Phi_{\text{CPn}} \text{ (%)}$	6
$k_{\text{rec}}(e^- + h^+ \rightarrow S_0) \text{ (cm}^3 \text{ s}^{-1}\text{)}$	3.0×10^{-10}		

Supporting Note 7.

Transient CPL Measurements Employing Excitation by a UV-LED

Supporting Figure 7.1 shows additional TrCPL experiments employing UV excitation at 273 nm by an unpolarized LED pulsed at 20 MHz. Here, the time resolution is much lower because of the longer LED pulse (FWHM 500 ps). Photoexcitation at 273 nm populates a higher singlet exciton state, which relaxes back to the luminescing S_1 exciton state on sub-picosecond time scales (cf. step (S6.4)). The results are consistent with those shown in Figure 5 of the main manuscript employing femtosecond laser excitation at 410 nm: We find a negative TrCPL signal for F8BT:(+)-2 and a positive TrCPL signal for F8BT:(-)-2, (panel e) resulting in time-independent g_{lum} values of 0.30 and -0.38 , respectively (panel f). The slight difference in g_{lum} values in the case of the F8BT:(-)-2 thin film (cf. Figure 5f in the main manuscript) is likely due to different sample areas illuminated.



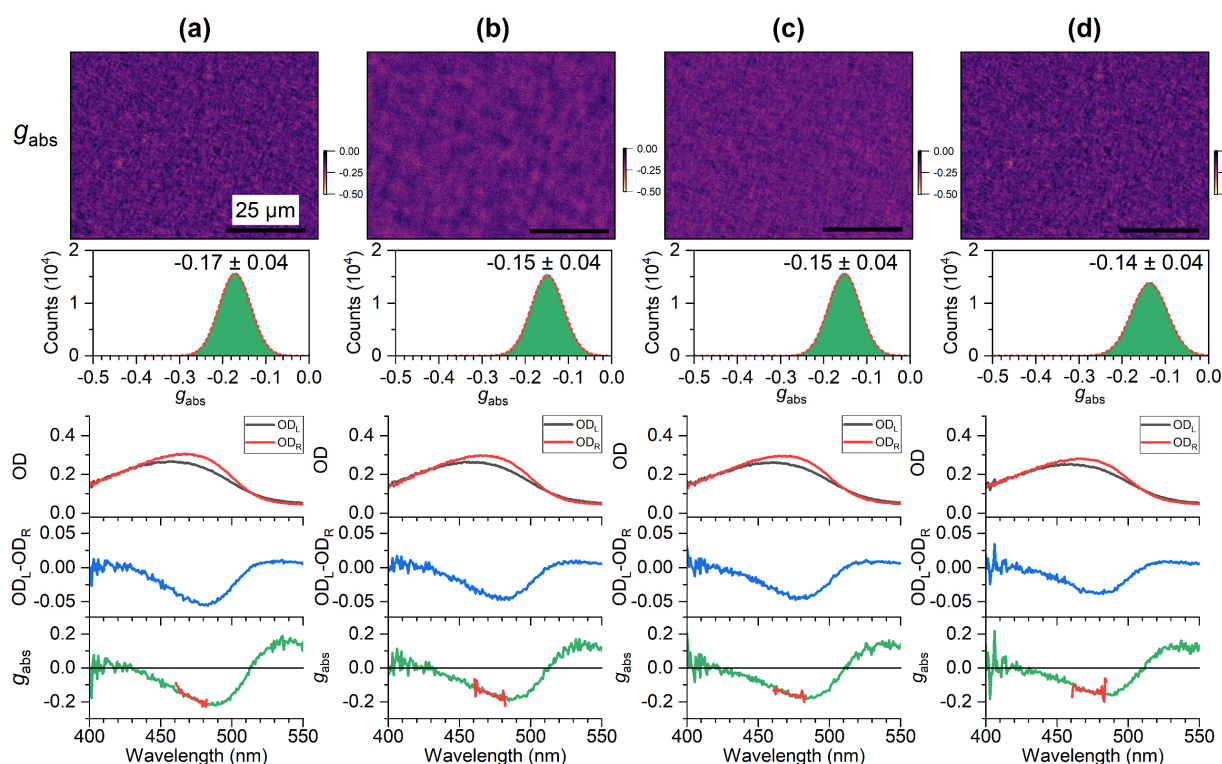
Supporting Figure 7.1. Time-resolved CPL spectroscopy for F8BT:(+)-2 and F8BT:(-)-2 thin films using a UV-LED for excitation ($\lambda = 273$ nm) and a bandpass filter at 530 nm for detection. a) Transient photoluminescence intensity I_L at left circular polarization for the F8BT:(+)-2 film (open blue circles) and laser scattering signal I_L obtained from a colloidal SiO₂ nanoparticle suspension (solid black circles) providing the IRF of the setup. b) Same as in panel a, but showing the photoluminescence intensities I_R for right circular polarization. c) and d) Same as in panels a and b, but for the F8BT:(-)-2 thin film and the same nanoparticle suspension. e) Resulting TrCPL signal $I_L - I_R$ for the F8BT:(+)-2 thin film (blue circles) and the F8BT:(-)-2 thin film (red circles). f) Resulting time-resolved g_{lum} signal for the F8BT:(+)-2 (blue circles) and F8BT:(-)-2 (red circles) thin films.

Supporting Note 8.

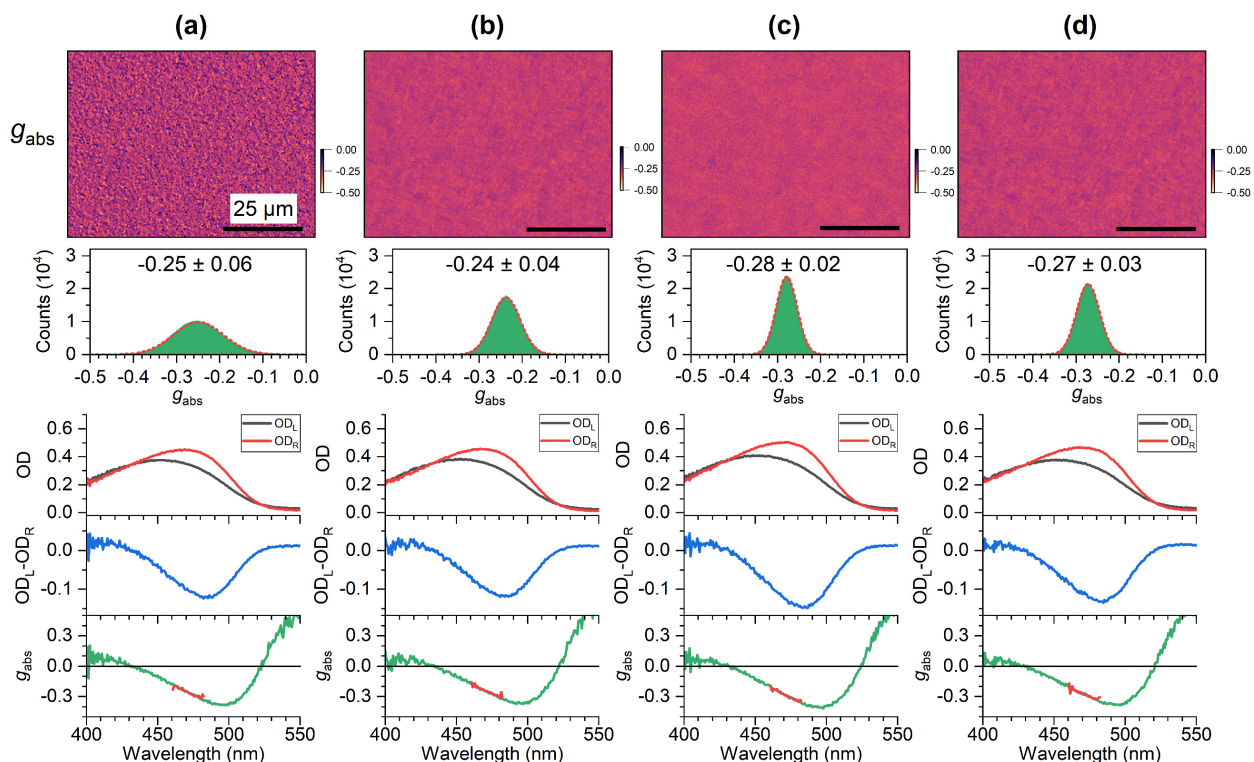
Dependence of CD Signals on Film Thickness

Supporting Figures 8.1–8.3 show additional microscopy data for the dependence of the circular dichroism on film thickness. The experiments were performed on the same three films already discussed in the main manuscript (Figure 6) and serve to illustrate the spot-to-spot variation of the optical properties for the individual samples. In general, the average g_{abs} values agree very well for all samples, so the overall changes in the chiral response are minor. We used the variation of the g_{abs} values for the different film regions to estimate error bars in Figure 6e of the main manuscript.

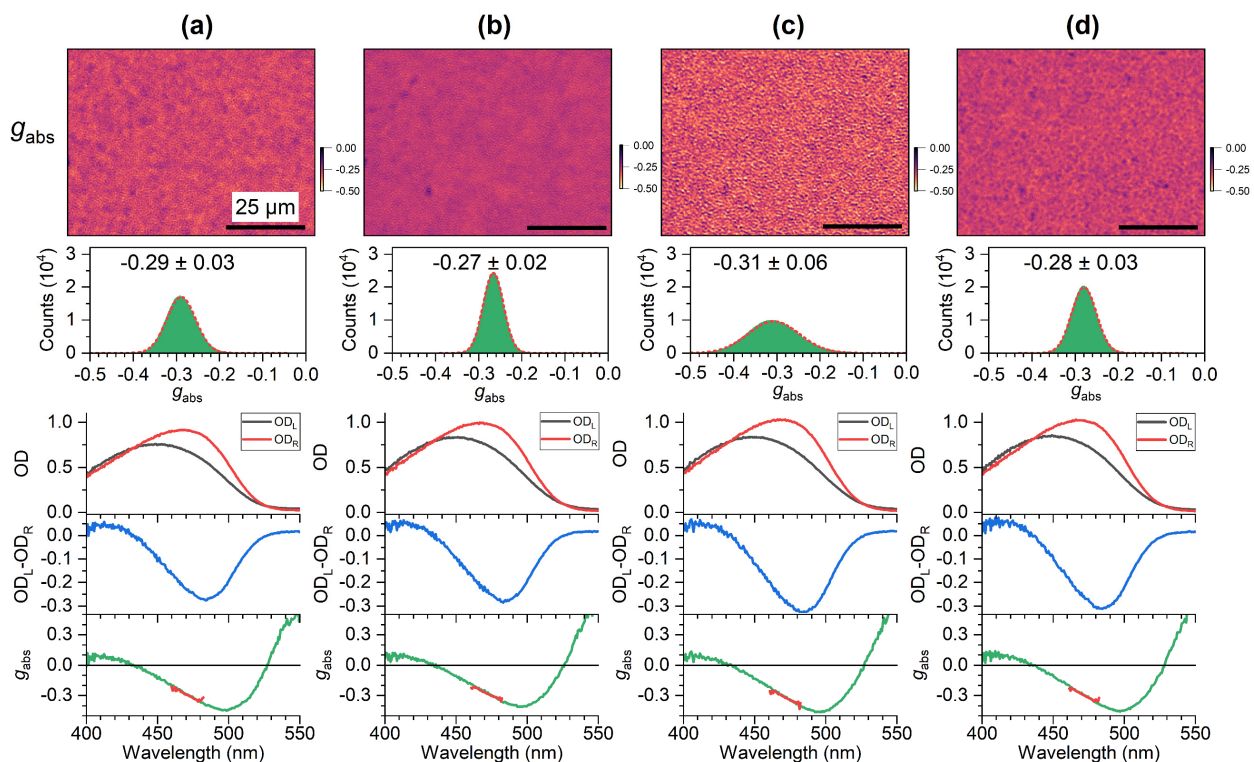
In some regions of the films, however, there is a distinct increase of the width of the g_{abs} distributions, most prominently visible in Supporting Figures 8.2a and 8.3c. There are considerable variations in g_{abs} , as indicated by the fine mosaic structure, where bright and dark spots with sub-micrometer spacing indicate substantial changes in the dissymmetry factor on small length scales, whereas for other films this distribution is more uniform. We are currently performing systematic studies to identify the reason for these differences, which could for instance originate from local variations of the annealing temperature across the film area during film preparation.



Supporting Figure 8.1. CD microscopy of a 103 nm thick F8BT:(+)-2 film. a) Microscope image ($80 \times 60 \mu\text{m}^2$) for the dissymmetry parameter g_{abs} (top) with a histogram of g_{abs} values (green) including a Gaussian fit (dashed red line), determined over the entire field of view, and spectra integrated over the entire field of view ($210 \times 160 \mu\text{m}^2$, lower half) displaying the absorption spectra for left- and right-circularly polarized light (OD_L (black line), OD_R (red line)), the CD spectrum (blue line) and the g_{abs} spectrum (green line; the thick red line indicates the spectral region selected by the bandpass filter used for CD imaging with a center wavelength of 470 nm). b-d) Same as in panel a, but at three other arbitrarily selected positions on the same film. The length of the black scale bar in each CD image corresponds to a distance of 25 μm .



Supporting Figure 8.2. CD microscopy of a 159 nm thick F8BT:(+)-2 film. a-d) Microscope images for g_{abs} , g_{abs} distributions as well as absorption, CD and g_{abs} spectra, obtained using the same procedure and the same color coding as in Supporting Figure 8.1.



Supporting Figure 8.3. CD microscopy of a 356 nm thick F8BT:(+)-2 film. a-d) Microscope images for g_{abs} , g_{abs} distributions as well as absorption, CD and g_{abs} spectra, obtained using the same procedure and the same color coding as in Supporting Figure 8.1.

Supporting Note 9.

Reflectivity Correction for the Dissymmetry Parameter g_{abs}

Schulz et al. presented a formula to approximately account for reflection losses at thin films.^[15] Their expression is derived from Stenzel's equation 7.9a for normal incidence on a thick slab neglecting interference effects and multiple reflections.^[16] Following Schulz et al., the expression for the experimentally measured absorbance is

$$A^{\text{exp}} = -\log_{10} (1-R)^2 + \frac{\alpha}{\ln(10)} d \quad (\text{S9.1})$$

Here, α is the absorption coefficient (base e), d is the film thickness and R is the reflectivity obtained from Fresnel's formula for normal incidence

$$R = \left(\frac{n_2 - n_1}{n_2 + n_1} \right)^2 \quad (\text{S9.2})$$

where n_1 is the refractive index of medium 1 and n_2 is the refractive index of medium 2. Thus, the corrected absorbance can be expressed as

$$A^{\text{corr}} = \frac{\alpha}{\ln(10)} d = A^{\text{exp}} + \log_{10} (1-R)^2 \quad (\text{S9.3})$$

Consequently, the corrected dissymmetry factor is obtained as:

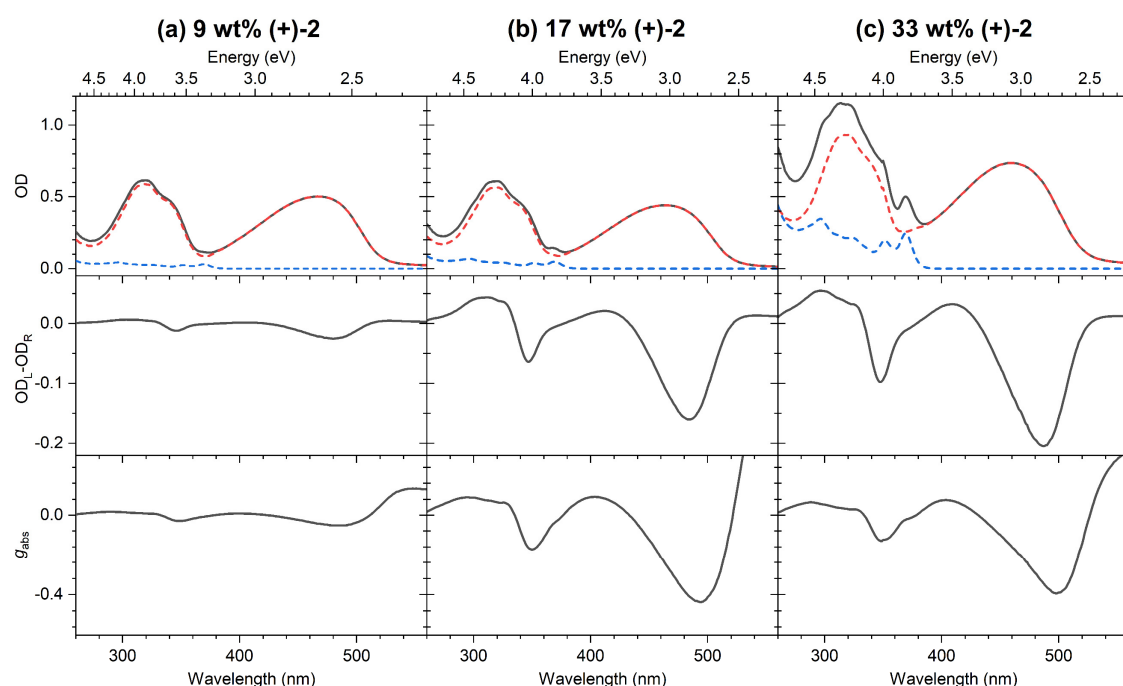
$$g_{\text{abs}}^{\text{corr}} = \frac{A_{\text{L}} - A_{\text{R}}}{A^{\text{corr}}} = \frac{A_{\text{L}} - A_{\text{R}}}{A^{\text{exp}} + \log_{10} (1-R)^2} \quad (\text{S9.4})$$

Note that their expression is for a free-standing slab of material, which is not the experimental situation in our case. Because of the substantial difference in the refractive indices ($n_1 \approx 2.15$ at the peak of the g_{abs} spectrum of F8BT,^[17] $n_2 \approx 1.0$ for air) the correction based on eq. (S9.4) will considerably overestimate the real correction, as it considers two interfaces of the copolymer thin film with air, whereas in our case we have the interfaces air–copolymer, copolymer–glass and glass–air. In any case, we obtain a value of -0.124 for the logarithmic correction term. As an example, for the three data points of the measurements dealing with the thickness dependence (violet solid circles in Figure 6e of the main manuscript), the corrected (uncorrected) absolute g_{abs} values for the three films are then, in increasing order of thickness: 0.408 (0.216), 0.598 (0.381) and 0.556 (0.443). Even after the correction, the g_{abs} value of the thinnest film is therefore substantially smaller than the g_{abs} values of the thicker films.

Supporting Note 10.

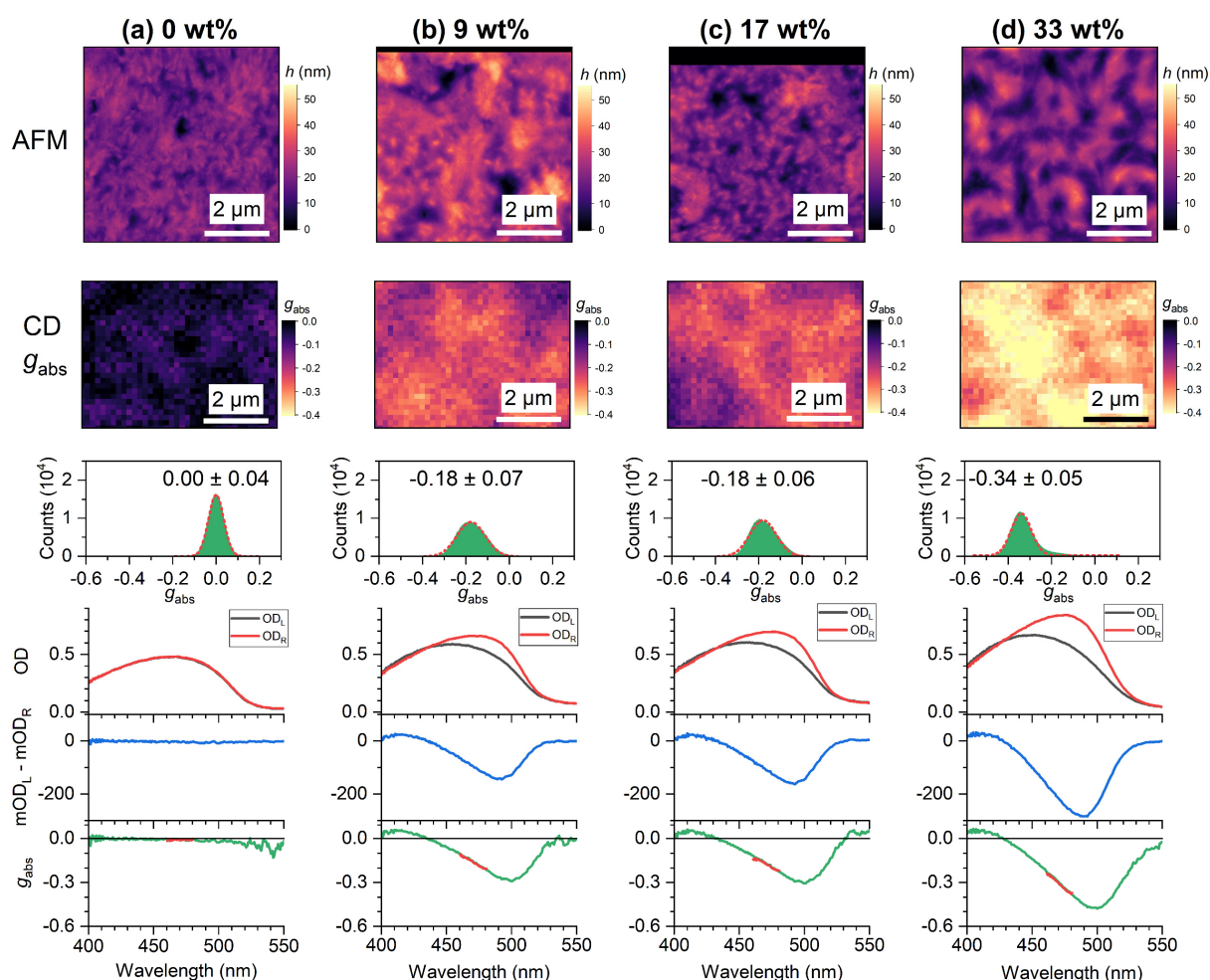
CD and AFM Experiments for Different F8BT:(+)-2 Blends

Supporting Figure 10.1 displays results from a systematic study of the chiral induction in the polyfluorene copolymer F8BT as a function of the weight percentage of the chiral additive (+)-2 using identical spin-coating and annealing conditions. The steady-state CD spectrometer (Applied Photophysics Chirascan) used in this experiment was kindly made available by H. Ihmels (Organic Chemistry 2, University of Siegen). Employing 9 wt% of the additive (panel a) results in a peak CD signal of -0.025 (-830 mdeg) and a peak g_{abs} value of -0.05 . An increase of the chiral response is observed when 17 wt% of (+)-2 are used (panel b). Here, we obtain a peak CD value of -0.161 (-5300 mdeg) and peak g_{abs} value of -0.43 . Using 33 wt% of the chiral additive leads to a further increase of the CD signal to -0.203 (-6700 mdeg), whereas the peak g_{abs} value is similar (-0.39). The results show that already 17% of the helicene-type compound (+)-2 are sufficient to induce a substantial chiral response. The experiment also gives a good impression, how F8BT and the chiral additive contribute to the steady-state absorption spectrum of the blend (red and blue dashed lines in the top panels of Supporting Figure 10.1). To estimate the absorption contributions of (+)-2 and F8BT in the blend, a scaled spectrum of a pure thin film of (+)-2 (blue dashed line), which we measured previously,^[14] was subtracted from the spectrum of the blend (black solid line), so that the characteristic peak of (+)-2 at 369 nm disappeared in the resulting F8BT spectrum (red dashed line). Measurements of the absorption spectrum of pure F8BT show a smooth minimum in this wavelength range.



Supporting Figure 10.1. Chiral induction in the copolymer F8BT as a function of the weight percent of the chiral helicene-type additive (+)-2. a) For 9 wt% of (+)-2: Top panel: Steady-state absorption spectrum of F8BT:(+)-2 (black solid line), scaled steady-state absorption spectrum of a pure (+)-2 thin film (blue dashed line) and the difference between these two spectra (red dashed line), which should approximate the pure F8BT absorption in the blend; middle panel: CD spectrum, bottom panel: g_{abs} spectrum. b) and c) Same as in a, but for 17 wt% (+)-2 and 33 wt% (+)-2, respectively. The values for the film thickness in panels a, b and c are 141, 120 and 235 nm, as measured by coherent acoustic phonon spectroscopy.

In addition, we carried out AFM and CD microscopy experiments for annealed pure F8BT and also F8BT:(+)-**2** thin films with varying amount of the chiral additive (9, 17 and 33 wt%) to check for a possible correlation between the surface morphology and the local CD activity of the thin films. The results are shown in Supporting Figure 10.2. The AFM images (top row) of the thin film surfaces show extended structures which could correspond to larger areas of fibrillar aggregates reported previously by Lakhwani and Meskers.^[10] For the thin film with 33 wt% of the chiral additive, these structures appear to be more curved and elongated, with higher and lower regions being connected over longer distances. Values for the mean roughness S_a (RMS roughness S_q) were 3.02 (3.86), 5.88 (7.68), 4.54 (5.71) and 5.58 (6.76) nm for F8BT thin films with 0, 9, 17 and 33 wt% of the chiral additive, respectively. Thus, the roughness of the blends does not depend systematically on the amount of the chiral helicene-type additive in the film.



Supporting Figure 10.2. Comparison of atomic force microscopy and CD microscopy images for F8BT:(+)-2** films with different amounts of chiral additive.** a) 0 wt% of the chiral additive (+)-**2**: AFM image with ca. 12 nm lateral resolution (top row), microscope image for the dissymmetry parameter g_{abs} with about 400 nm optical resolution (second row), histogram of g_{abs} values (green) with a Gaussian fit (dashed red line), determined over the entire field of view (third row), and spectra (bottom row) integrated over the entire field of view ($210 \times 160 \mu\text{m}^2$) showing the optical density for left- and right-circularly polarized light (OD_L (black), OD_R (red)), the CD spectrum (blue) and the g_{abs} spectrum (green), with the thick red line indicating the spectral region selected by the bandpass filter (470 nm, FWHM 10 nm) employed for CD imaging. b-d) same as in panel a, but for thin films with 9, 17 and 33 wt% of the chiral additive, respectively.

In contrast to the AFM images, which are sensitive to the surface morphology, the CD images monitor the chiral optical response of the complete film in transmission. The CD microscope provides a diffraction-limited resolution of ca. 400 nm, whereas the AFM images shown here have a lateral resolution of about 12 nm. The CD microscopy images are therefore considerably more blurred than the AFM images. Taking this blurring into account, the larger structures observed by AFM and CD microscopy appear to be quite similar. The size of these larger domains is in the range 600–900 nm, similar to those seen in Supporting Figure S4.1.

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6. Understanding Excited-State Relaxation in 1,3-Bis-(*N*-carbazolyl)benzene, a Host Material for Organic Light-Emitting Diodes

This chapter contains the publication:

Morgenroth, M., Lenzer, T. and Oum, K.

Understanding Excited-State Relaxation in 1,3-Bis-(*N*-carbazolyl)benzene, a Host Material for Organic Light-Emitting Diodes

J. Phys. Chem. C, **127**, 4582 (2023).

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Statement for author contributions:

Marius Morgenroth (M.M.) is the first author of this publication and performed most of the experiments and manuscript preparation. K.O. and T.L. conceived the project. M.M. prepared the thin film samples and performed the steady-state absorption experiments and microscopy experiments for characterization of the thin films containing the host materials. M.M. conducted the transient absorption experiments. K.O., T.L., and M.M. performed the data evaluation. K.O., and T.L. implemented the optical and electronic setups for the transient absorption spectroscopy. M.M., T.L. and K.O. analyzed the spectroscopic results and wrote the paper.

Understanding Excited-State Relaxation in 1,3-Bis(*N*-carbazolyl)benzene, a Host Material for Organic Light-Emitting Diodes

Marius Morgenroth, Thomas Lenzer,* and Kawon Oum*



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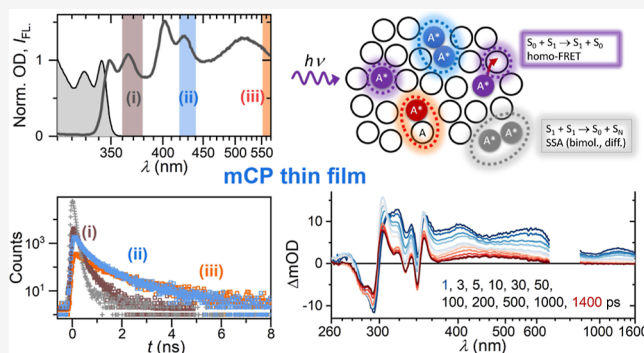


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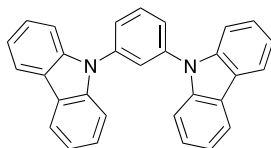
ABSTRACT: We present a detailed spectroscopic study of 1,3-bis(*N*-carbazolyl)benzene (mCP), a prototypical host material for blue emitters in organic light-emitting diodes, using time-resolved emission and ultrafast transient absorption spectroscopy. Upon photoexcitation, mCP dissolved in tetrahydrofuran and mCP dispersed at low number density in poly(methyl methacrylate) (PMMA) films show a monoexponential emission decay in the range 6–7 ns. Transient absorption experiments detect the formation of the T_1 triplet state from S_1 with a quantum yield of ca. 20%, a band maximum at 450 nm, and a lifetime on the microsecond time scale. The strong spectral overlap of S_1 stimulated emission and S_1 excited state absorption suggests that S_1 – S_1 singlet–singlet annihilation (SSA) based on Förster resonance energy transfer (FRET) should be feasible at high mCP concentrations in mCP:PMMA and neat mCP films. At these concentrations, the intensity of the mCP emission is strongly quenched and the spectra show a dramatic change exhibiting monomer, aggregate, and excimer emission bands. The small Stokes shift and thus the good overlap of the absorption and emission spectra of mCP open up the possibility for efficient diffusive S_1 singlet hopping in neat mCP films by means of a multi-step homo-FRET mechanism involving S_1 and the respective S_0 nearest neighbor. Fluence-dependent transient absorption measurements find pronounced S_1 – S_1 SSA. Kinetic modeling suggests a bimolecular diffusive SSA mechanism with a rate constant k_{diff} of $1.40 \times 10^{-8} \text{ cm}^3 \text{ s}^{-1}$. In contrast, modeling based on direct S_1 – S_1 FRET results in an unrealistically large Förster radius of 17 nm. These experiments therefore suggest that mCP molecules in S_1 efficiently diffuse through the mCP film by multi-step homo-FRET and annihilate upon approaching a critical distance to another mCP molecule in S_1 . Finally, we find clear spectral evidence for vibrationally hot mCP molecules (S_1^*) in the transient absorption spectra of neat mCP thin films, which cool down on a time scale from nanoseconds to microseconds.



1. INTRODUCTION

Carbazole derivatives, such as 1,3-bis(*N*-carbazolyl)benzene (shortly mCP, Scheme 1), are widely used as host materials for

Scheme 1. Chemical Structure of mCP



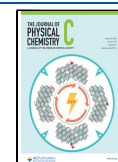
organic light-emitting diodes (OLEDs) because of their beneficial photophysical and electrical properties.^{1–6} They have high-lying S_1 singlet and T_1 triplet states, which is particularly important for realizing efficient blue-emitting OLEDs.^{7–9} This way, triplet excited states of the light-emitting guest chromophores cannot be quenched by triplet energy

transfer to the host molecules. In addition, by using an appropriate doping level of the guest, excited-state annihilation processes can be minimized as the emitters are separated far enough inside the host matrix so that processes such as singlet–singlet annihilation (SSA) and triplet–triplet annihilation (TTA) between the emitter molecules can be avoided. In addition, the host ensures appropriate transport of charges by providing low energy barriers for the injection of electrons and holes and, very importantly, efficient energy transfer to the emitter.^{8,10–12}

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Despite their importance for OLED applications, the photophysics and ultrafast spectroscopy of these host materials are severely underexplored and have not kept pace with the enormous developments in the field. Previous studies mostly focused on steady-state absorption and emission spectroscopy at different temperatures as well as time-resolved fluorescence with a time resolution in the several tens of picoseconds range. Even for the steady-state spectroscopy results, there are often conflicting reports: for instance, in the case of mCP thin films, Forrest and co-workers did not observe any emission of the T_1 triplet state of mCP at room temperature and only detected very weak structured emission of T_1 with vibronic peaks at 430 and 460 nm at a very low temperature of 10 K using gated detection starting from 1 μ s.¹³ In contrast, Wu et al. and Tsuboi et al. assigned a weak band with peaks at 410 and 440 nm in the long-wavelength tail of the emission spectrum to phosphorescence of the T_1 state.^{1,2} More recently, Kim and co-workers reported the 0–0 peak of the T_1 emission for a mCP thin film at 455 nm.¹¹ As the energetic location of the triplet state is relevant to OLED operation, such contradictory findings should be clarified. The detailed dynamic photo-physical processes of these compounds after photoexcitation and their time scales are largely unknown as well, especially in thin films, although these are important properties for their application in OLED systems. For instance, SSA and TTA processes between mCP molecules will compete with the desired energy transfer to the guest chromophore intended to be used as a blue emitter. Understanding the time scale of the SSA processes is also highly relevant to modeling efficiency roll-off effects in OLEDs, i.e., a decrease in efficiency with increasing current density, when operating at high brightness levels.¹⁴ Here, we therefore provide a detailed steady-state and time-resolved spectroscopic study of mCP in the solvent tetrahydrofuran (THF), in neat mCP thin films and in thin film blends consisting of mCP and poly(methyl methacrylate) (PMMA) with a wide variation of the mCP:PMMA ratio. We employ time-correlated single-photon counting (TCSPC) and broadband UV–vis–NIR transient absorption experiments to elucidate the complex relaxation processes of mCP in the excited state after photoexcitation, for instance, to determine the complete T_1 absorption spectrum and the time scale of the SSA processes.

2. EXPERIMENTAL SECTION

2.1. Sample Preparation. For steady-state and time-resolved absorption as well as fluorescence measurements, mCP (Lumtec, $\geq 99.5\%$) was dissolved in THF (Merck, Uvasol, $\geq 99.9\%$) at appropriate concentrations. The solutions were saturated with nitrogen by bubbling them for 15 min. Thin films of neat mCP and mCP:PMMA blends were deposited on fused silica substrates (Tempotec, RW25-25-1UV, JGS1), which were thoroughly cleaned using acetonitrile (Merck, Uvasol, $\geq 99.9\%$) and then subjected to ozone treatment for 15 min in a UV-C chamber (Dinies ELG100S) prior to use.

PMMA (Alfa Aesar) was dissolved in THF (5 mg mL⁻¹) in a tube shaker for 5 h, and mCP was dissolved in THF (5 mg mL⁻¹) and treated in an ultrasonic bath for 30 min. The solutions were mixed in appropriate amounts to match the desired mCP:PMMA ratio. The precursor solutions (typically 200 μ L per sample) were dropped onto the fused silica substrates using glass pipettes. The spin-coating conditions were 60 s at 500 rpm, and thicker blends, required for optical

measurements with low mCP content, were prepared with 30 s loading time. The coated slides were then dried for 10 min at 23 °C under a nitrogen atmosphere to evaporate the solvent.

2.2. Steady-State Absorption and Fluorescence Experiments. Steady-state absorption spectra of mCP dissolved in THF, neat mCP thin films, and the mCP:PMMA blends were recorded using a Varian Cary 5000 spectrophotometer with a slit width of 0.5 nm. Emission spectra were measured using an Agilent Cary Eclipse spectrometer with excitation and emission slit widths of 5 nm. The emission spectra were corrected by a calibration function considering the wavelength-dependent sensitivity of the instrument.

2.3. Ultrafast Transient Absorption Spectroscopy. Ultrafast broadband transient absorption spectroscopy was carried out on two setups based on an amplified titanium:sapphire laser system (Coherent Libra USP-HE), which covers the UV–vis (260–700 nm) and NIR spectral ranges (850–1630 nm) with a time-resolution of ca. 80 fs.^{15,16} mCP dissolved in THF, neat mCP thin films, and the mCP:PMMA blends were excited at 290 nm by an optical parametric amplifier (Coherent OPerA Solo). For pump–probe experiments up to several microseconds, the samples were excited by the fourth harmonic of a Q-switched Nd:YAG microlaser (Standa-Q1TH, 266 nm), which was electronically synchronized with the amplifier system.¹⁷ The time resolution of these measurements was 420 ps. The fluence of the pump laser beam was adjusted by a combination of a half-wave plate and a polarizer with the help of a calibrated photodiode (Thorlabs S120VC) and a beam profiler (Visulux). The measurements for mCP in THF were performed in quartz cuvettes (Hellma, Suprasil I) with a path length of 1 mm, and the thin films of neat mCP and mCP:PMMA deposited on the fused silica substrates were mounted inside a custom-made nitrogen-flushed aluminum holder.¹⁸ The cuvette and thin-film holder were constantly moved by an x – y piezo stage, sampling an area of 2×2 mm².

2.4. Time-Resolved Fluorescence Experiments. The setup for TCSPC has been described in detail previously.¹⁹ Briefly, the samples were excited by a pulsed UV-LED (Becker & Hickl, UVL-FB-270, 273 nm, 20 or 1 MHz repetition frequency). The output of the LED was vertically polarized (0°) by means of a wire-grid polarizer (Thorlabs WP25M-UB), and the emission was measured at an angle of 90° employing another wire-grid polarizer (Thorlabs WP25M-UB, set at the magic angle of 54.7°) and appropriate bandpass filters (Thorlabs, FWHM 10 nm). Photons were detected by a hybrid multialkali photodetector (Becker & Hickl, HPM-100-07) connected to a TCSPC module (Becker & Hickl, SPC-130IN) operating in a reversed start–stop configuration. The instrument response function (IRF) was determined from the LED scattering signal either using a diluted suspension of colloidal silica nanoparticles (Merck, Ludox AM-40) or a UV-grade fused silica diffuser (Thorlabs DGUV10-120 or DGUV10-1500). The time resolution was limited by the LED pulse width of 500 ps. The time constants and amplitudes of the emission signals were obtained from reconvolution using the FAST program (Edinburgh Instruments).

2.5. Atomic Force Microscopy. The thickness of the mCP thin films was recorded using an atomic force microscope (PSIA XE-100) in the non-contact mode using a cantilever with a silicon tip. The resolution was 1024 times 64 pixel for an area of 50×3.12 μ m², with a scan rate of 0.2 Hz. The atomic force microscopy (AFM) traces were evaluated using XEI

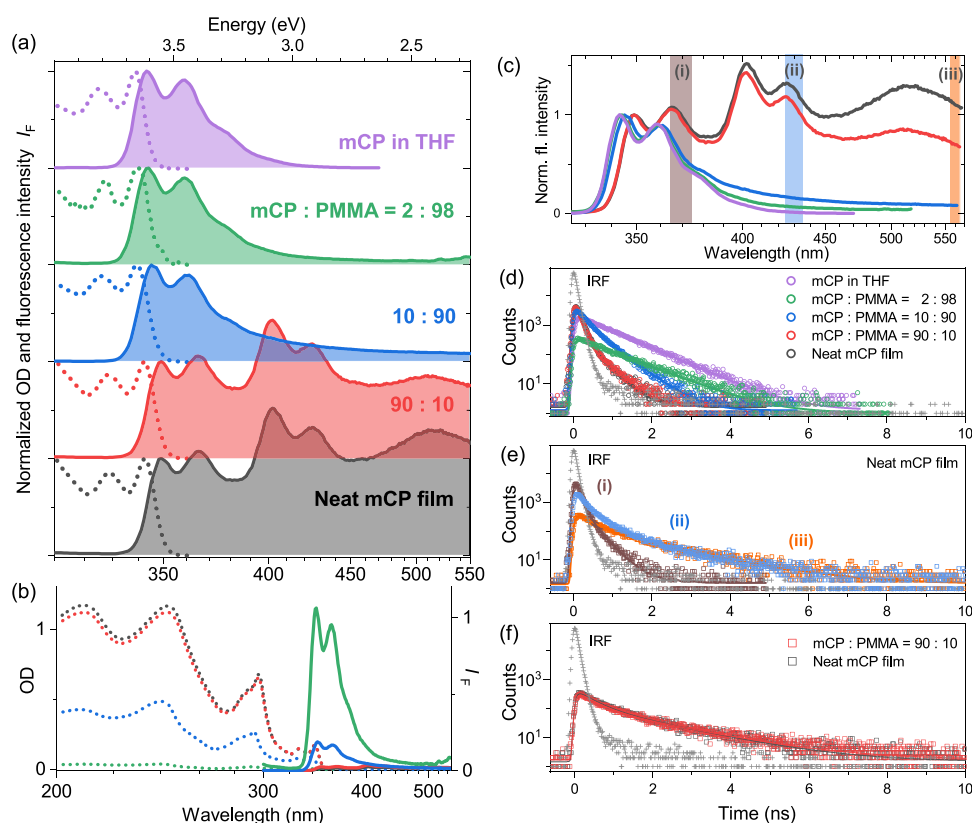


Figure 1. (a) Normalized steady-state absorption and fluorescence spectra ($\lambda_{\text{exc}} = 290$ nm), shown as dotted lines and solid lines with shading, respectively, for mCP dissolved in THF, mCP:PMMA blends with weight ratios of 2:98, 10:90, and 90:10, and a neat mCP thin film (from top to bottom), (b) thin-film spectra with the same color coding as that in panel (a), but compared on an absolute scale (absorption spectra shown down to 200 nm), and (c) superimposed normalized steady-state fluorescence spectra from panel (a) [the same color coding as that in panels (a,b)] including colored areas indicating the wavelength ranges of the bandpass filters employed for the TCSPC experiments: center wavelengths of (i) 370, (ii) 430, and (iii) 560 nm (FWHM in each case is 10 nm). (d) TCSPC data (symbols) recorded at 1 MHz repetition frequency with excitation at 273 nm for mCP in THF, the three different mCP:PMMA blends, and the neat mCP film obtained using the 370 nm bandpass filter [the same color coding as that in panels (a–c)]. Fit lines obtained from reconvolution using mono- or biexponential fit functions. (e) TCSPC data recorded at 1 MHz for the neat mCP film (symbols) and the kinetic fits (lines) are compared for the spectral regions (i) 370 nm (brown range), (ii) 430 nm (sky blue range), and (iii) 560 nm (orange range). (f) Same as in panel (e), but obtained with the 560 nm bandpass filter. In panels (d–f), the IRF is shown as black crosses.

(Version 4.3.4, Park Systems), and visualization was carried out using OriginPro2022b (OriginLab Corporation). After performing a background correction, the scan lines were averaged and the thickness was determined from the difference between the lower and upper plateaus.

3. RESULTS AND DISCUSSION

3.1. Steady-State Absorption and Emission of mCP in THF and Thin Films. Figure 1a shows steady-state absorption and fluorescence spectra of mCP in different solvation environments as dotted lines and solid lines with shaded areas, respectively. Characteristic spectral properties are summarized in Table S1 of the Supporting Information. In THF (violet), the lowest-energy absorption peak of the $S_0 \rightarrow S_1$ absorption band of mCP is located at 338 nm. The mirror-image-like structured fluorescence spectrum has a very small Stokes shift (52 meV, 418 cm^{-1}), which suggests that only small geometry changes occur upon photoexcitation to the S_1 state. The absorption and emission spectra of the PMMA film with the smallest mCP fraction (mCP:PMMA 2:98, green) look similar to those in THF. They are red-shifted by ca. 1 nm, exhibit a comparable but somewhat smaller Stokes shift (44 meV, 355 cm^{-1}), and have a slightly increased intensity in the

long-wavelength tail of the emission. A further increase of the mCP content leads to a further shift of the spectra (mCP:PMMA ratio 10:90, blue). Importantly, this is accompanied by a distinct relative increase in intensity of the long-wavelength tail of the fluorescence compared with the main emission band. At a high mCP content (mCP:PMMA 90:10, red) and for the neat mCP thin film (gray), the emission spectra change drastically, while the corresponding absorption spectra only show a slight red shift.

The emission spectra of the mCP-rich films can be roughly divided into at least three regions: The first one is an emission band in the range 340–380 nm with two distinct peaks, which is also observed for mCP in THF and is therefore present regardless of the fact, if the mCP molecules are isolated in solution or aggregated in films. We therefore assign this feature to mCP monomer emission. Only for the mCP:PMMA film with a high mCP amount (90:10) and the neat mCP film, there is a second structured emission band in the range 380–450 nm with two peaks at 402 and 425 nm, and an additional third band above 450 nm, which is broad and unstructured with a peak at about 515 nm.

The third, most red-shifted band can be safely assigned to mCP excimer emission as it resembles the excimer bands of

carbazole-containing cellulose derivatives²⁰ and carbazophanes.²¹ In contrast, the structured emission of the second band is incompatible with an excimer as the latter has a repulsive ground state and thus shows a broad emission. Instead, such bands were previously assigned to triplet emission.^{1,2} Nevertheless, the average lifetime (τ) of 7.2 ns for the emission band of the neat mCP thin film, which we obtained from the time-resolved fluorescence experiments reported below, is incompatible with a triplet state either. Also, the fluorescence excitation spectra detected in this band ($\lambda_{\text{det}} = 400$ nm) and in the long-wavelength band ($\lambda_{\text{det}} = 530$ nm) are broadened compared with the one recorded in the monomer band ($\lambda_{\text{det}} = 370$ nm), cf. Figure S1 (Supporting Information). This is likely a signature of chromophore preassociation (i.e., ground-state aggregates).²² Similar structured emission bands, which were red-shifted by about 0.3–0.5 eV with respect to the monomer emission, were previously observed for films of certain aggregate-forming BODIPY dyes and were assigned to *J*-coupled dimers.²³ These species also showed an increased vibronic peak spacing compared with the monomer, and a similar effect is found here for mCP (0.148 eV for the monomer vs. 0.165 eV for the aggregate). In addition, a spectral decomposition of the mCP thin film emission spectrum (Figure S2, Supporting Information) indicated an enhancement of the 0–0/0–1 emission peak ratio, also compatible with the formation of *J*-aggregates with small delocalization.^{23,24} Therefore, we assigned this structured red-shifted mCP emission band to a *J*-coupled dimer-type structure. In addition, we found that the intensity ratio of the excimer and monomer emission bands was dependent on the excitation wavelength, with more pronounced emission for the long-wavelength excimer band for shorter excitation wavelengths (Figure S3, Supporting Information), thus favoring the formation of this excimer relative to the *J*-coupled dimer species at higher initial excitation energies of mCP. We note that structured emission tails were previously found for mCP:polystyrene thin films (with 1 wt % mCP) and neat mCP thin films, which were produced via thermal vacuum deposition.^{1,2} Nevertheless, in contrast to our films here, the intensity of this excimer emission was weaker than that of the monomer emission. As we produced our films by spin-coating, we suspect that spin-coated thin films have stacking motifs different from those of films obtained via thermal vacuum deposition.

Furthermore, we note that the total emission yield decreased dramatically with increasing mCP content, as shown in Figure 1b. This is even more interesting considering the fact that the absorption of films with high mCP content is of course much larger than in an mCP:PMMA blend with a ratio of, e.g., 2:98. This indicates that the mCP monomer emission is strongly quenched upon reducing the mCP–mCP distance and that the aggregate and excimer emission bands are also very weak.

3.2. Time-Resolved Fluorescence Experiments. To understand the physical mechanisms underlying this complex fluorescence behavior in more detail, the lifetime of the emission bands in the different films was investigated using transient fluorescence experiments based on the TCSPC method. Figure 1c compares normalized emission spectra of mCP in the different solvation environments, with the spectral detection ranges for the mCP monomer (370 nm), aggregate (430 nm), and excimer bands (560 nm) indicated by the brown, sky blue, and orange regions, respectively. Figure 1d shows a comparison of the emission dynamics for the different

samples in the monomer emission band recorded at 1 MHz repetition frequency with 126 ps channel width. Lifetimes for these experiments and also complementary results at 20 MHz repetition frequency with 12.2 ps channel width are summarized in Table S2 of the Supporting Information. In THF (violet), a purely monoexponential decay of 5.97 ns is observed, which represents the lifetime of isolated mCP molecules in S_1 and compares favorably with the lifetime of 5.3 ns of mCP in toluene reported previously.²⁵ The decay of the film with the mCP:PMMA ratio of 2:98 (green) looks quite similar. Nevertheless, the measurements with higher time resolution (Table S2, Supporting Information) find two decay components ($\tau_1 = 7.21$ ns with $A_1 = 78.3\%$ and $\tau_2 = 1.24$ ns with $A_2 = 21.7\%$), resulting in an average relaxation time ($\langle\tau\rangle$) of 6.94 ns. This already indicates the growing influence of mCP–mCP interactions, even at quite low mCP number densities. With increasing mCP content in the PMMA host, the decay becomes faster, with average relaxation times of 2.64 ns for an mCP:PMMA ratio of 10:90 and ca. 0.8–0.9 ns for an mCP content of 90% and more. The proximity of the mCP molecules enables the formation of the aggregate and excimer species by only slight rearrangements of the local geometry. In addition, closer inspection of Figure 1a shows that the very small Stokes shift of mCP leads to a substantial overlap of the $S_0 \rightarrow S_1$ absorption and the $S_1 \rightarrow S_0$ emission bands. It is therefore likely that at higher mCP content, mCP(S_1)–mCP(S_0) Förster resonance energy transfer (FRET) is operative. Due to this homo-FRET process ($S_1 \rightarrow S_0$ accompanied by $S_0 \rightarrow S_1$) involving identical chromophores, the initial excitation efficiently migrates through the mCP film and can also, e.g., reach a site for aggregate or excimer formation. There, the excitation is trapped because the emission spectra of these species have no overlap with the absorption spectrum of mCP.

A comparison of the emission decays in the monomer, aggregate, and excimer emission bands of the neat mCP film is shown in Figure 1e, and a comparison for the neat mCP film and an mCP:PMMA film (90:10) in the excimer emission band is shown in Figure 1f. Fit parameters are included in Tables S3 and S4 of the Supporting Information. For the neat mCP film, we find an average relaxation time of 0.92 ns for the monomer, 3.84 ns for the aggregate, and 7.22 ns for the excimer. As the excimer band shows both a long lifetime and a weak emission, this points toward a small radiative rate constant of the excimer species. Regarding the mCP aggregates, previous studies on BODIPY films (which have a very small Stokes shift of the monomer emission, similar to mCP) suggest that the fluorescence quantum yield for such aggregate species is high.²³ Therefore, we conclude that only a small number of aggregate sites are available in the mCP thin film. We once more stress that the probability for being trapped at an excimer site appears to increase substantially with initial excitation energy. This was indicated by separate steady-state fluorescence experiments for an mCP thin film performed at different excitation wavelengths, which showed a pronounced increase in the amplitude of the excimer emission with increasing initial excess energy (Figure S3, Supporting Information). We also note that we were not able to detect a delayed or slowed-down increase of the aggregate and excimer emission, presumably because our time resolution in the TCSPC experiments was limited to about 500 ps.

3.3. Transient Absorption Spectroscopy of mCP in THF and Thin Films. To obtain further insights into the

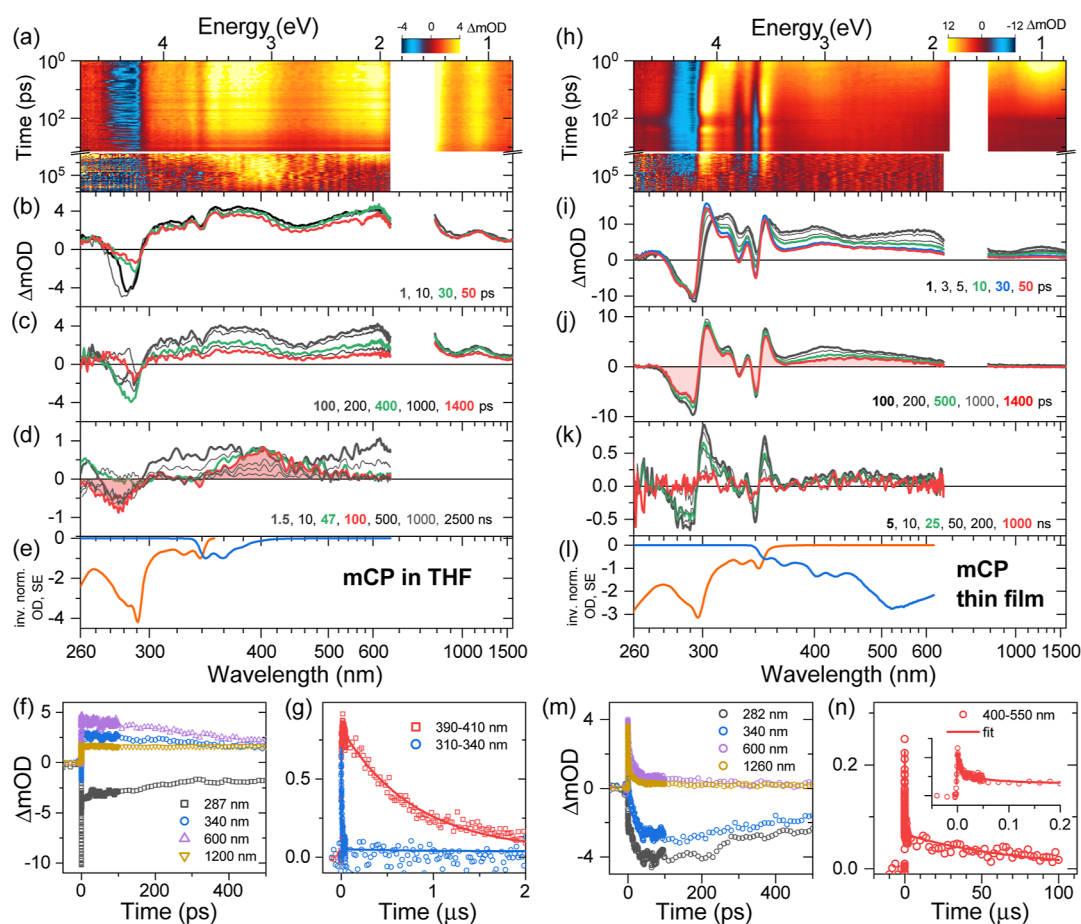


Figure 2. (a) Contour plot of transient absorption (TA) spectra of mCP in THF upon photoexcitation at 290 nm (femtosecond TA) and at 266 nm (nanosecond TA). Note the logarithmic time scale. (b–d) Transient absorption spectra at different delay times, as indicated by the colors. The transient spectrum at 100 ns, which represents the GSB and the ESA of the T_1 state, is filled with red color. (e) Inverted normalized steady-state absorption (red) and stimulated emission (blue). (f) Kinetics at 287 nm (GSB, black), 340 nm (blue), 600 nm (violet) (mostly S_1 ESA), and 1200 nm (brown) from femtosecond TA. (g) Kinetics of the S_1 region (blue, averaged over the range 310–340 nm) and of the T_1 region (red, averaged over the range 390–410 nm) upon nanosecond photoexcitation. (h–n) Corresponding plots for a neat mCP thin film.

dynamics of mCP after photoexcitation, UV–vis–NIR broadband transient absorption experiments covering the wavelength range 260–1600 nm range were carried out on femtosecond to nanosecond time scales. Results for mCP dissolved in THF and deposited as a neat thin film on quartz are shown in Figure 2. Panel a of Figure 2 shows a contour plot of the transient absorption experiments for mCP dissolved in nitrogen-saturated THF after excitation at 290 nm. Selected transient absorption spectra are provided in panels b–d. At early times (panel b), we observe the formation of a ground state bleach (GSB) around 280 nm and a broad excited state absorption (ESA) band spanning the entire UV–vis–NIR range, which is assigned to the $S_1 \rightarrow S_n$ transition. On top of this broad ESA band, several spectral dips are found, which are due to superimposed GSB and stimulated emission (SE) contributions: a characteristic minimum at 340 nm, which agrees with the overlapping 0–0 transitions in the inverted steady-state absorption spectrum and the $S_1 \rightarrow S_0$ stimulated emission spectrum (cf. panel e), and two weaker features corresponding to the respective 0–1 transition in the absorption and stimulated emission spectra at 325 and 359 nm. Up to 1400 ps, all bands appear to decay uniformly. However, panel d shows that a broad long-lived ESA band with a peak at 400 nm remains on much longer time scales. We assign this band to the

T_1 triplet state, and it is accompanied by a residual GSB feature below 345 nm, cf. the red-filled spectrum at 100 ns. Because of the broad overlapping ESA band, only an approximate quantum yield $\Phi(T_1)$ for triplet formation through intersystem crossing (ISC) from S_1 can be estimated, and based on the ratio of the GSB features at 340 nm at around 0.5 ps and at 100 ns, we arrive at a value of $(20 \pm 5)\%$. The $T_1 \rightarrow T_n$ absorption band finally decays on the nanosecond to microsecond time scale.

Panel f shows kinetic traces for time delays up to 500 ps, which clearly indicates the partial decay of the S_1 ESA band (340, 600, and 1200 nm) and the partial recovery of the GSB feature at 287 nm. Panel g highlights the kinetics on long time scales. The blue trace (averaged over the wavelength range 310–340 nm) is strongly dominated by S_1 dynamics (cf. the spectrum at 100 ps in panel d), and the fast spike-like decay is consistent with the S_1 lifetime of 6 ns extracted from the aforementioned TCSPC experiments. The red trace (averaged over the wavelength range 390–410 nm) is completely governed by the slow T_1 decay. A biexponential fit provides two time constants: the initial fast drop is due to the S_1 decay forming the T_1 state via ISC [$\tau(S_1) = 6$ ns, $A(S_1) = 14\%$], and the dominant slow decay arises from ISC/phosphorescence, leading to a triplet lifetime $\tau(T_1)$ of 790 ns [$A(T_1) = 86\%$].

Having characterized the dynamics of isolated mCP molecules in THF, we now turn to the dynamics in the neat mCP thin film. The excitation wavelength was 290 nm. Contour plots, transient absorption spectra, and the inverted steady-state absorption and SE spectra are provided in panels h–l of Figure 2. In contrast to that of THF, the decay dynamics of the film is considerably more complex as the proximity of the mCP molecules opens up additional intermolecular relaxation channels. Upon inspection of the decay dynamics shown from 1 to 50 ps (panel i), we identify a broad absorption band above 380 nm, which is due to $S_1 \rightarrow S_n$ ESA. This band decays much faster than in THF [cf. panel (b)], with substantial contributions within the first 5 ps. As we discuss in more detail below, this fast decay is due to SSA of two mCP molecules in the S_1 state, producing a higher excited S_n state (which repopulates S_1 by internal conversion) and an mCP molecule in S_0 . This fast decay of S_1 and the fast recovery of the S_0 population are clearly indicated by the early time portion in the kinetics at 282, 340, 600, and 1260 nm shown in panel m.

Looking at the spectral dynamics below 360 nm, we find a very different spectral relaxation behavior compared with that of THF. While at first sight, the positions of several negative going bands quite closely coincide with peaks of the steady-state absorption spectrum, the bands in the transient absorption spectrum are much sharper (cf. panels i and l). In addition, we find a new absorption band at 350 nm, which is only slightly red-shifted with respect to the $S_0 \rightarrow S_1$ (0–0) transition of the steady-state absorption spectrum. Another new absorption band is seen at 303 nm, also just to the red of the strong absorption band in the steady-state spectrum at 297 K. The sharp bleach bands and the extra absorption features are hallmarks of vibrationally “hot” mCP molecules in the ground electronic state (S_0^*), as shown previously for organic molecules in solution and in neat thin films.^{26–29} An example comparing a hot absorption spectrum with the steady-state spectrum at 297 K is shown in Figure S4 (Supporting Information). In the present case, these spectral features are long-lived and decay on the nanosecond to microsecond time scale (panel k). The energy transferred from an originally photoexcited mCP molecule heats up adjacent mCP molecules in S_0 , which are initially at a temperature of 297 K. Therefore, the deposited photon energy is converted into excess heat and then redistributed inside the mCP film. Eventually, this excess energy will be dissipated to the quartz substrate by heat transfer, but this happens on a slow time scale of hundred nanoseconds to microseconds (for a more detailed discussion, see Section 4 of the Supporting Information). Figure 3 shows the decays of three representative kinetics at 303, 340, and 348 nm, all of them located in the S_0^* spectral region. They can be fitted by a sum of three exponential functions with the time constants $\tau_1 = 2$ ns, $\tau_2 = 100$ ns, and $\tau_3 = 1000$ ns, highlighting that the complex cooling processes in the mCP film are stretched out over several orders of magnitude in time.

In addition, we find a weak broad absorption band with a peak at 450 nm (cf. the red spectrum at 1400 ps in panel j). This band decays very slowly, with a time constant of 66 μ s (panel n), and thus much slower than the T_1 absorption band in THF. It is also shifted by about 0.4 eV toward lower energies so that it does probably not arise from the same T_1 triplet state but more likely originates from a charge pair ($S_0^{\bullet+}$ and $S_0^{\bullet-}$), as discussed in more detail below.

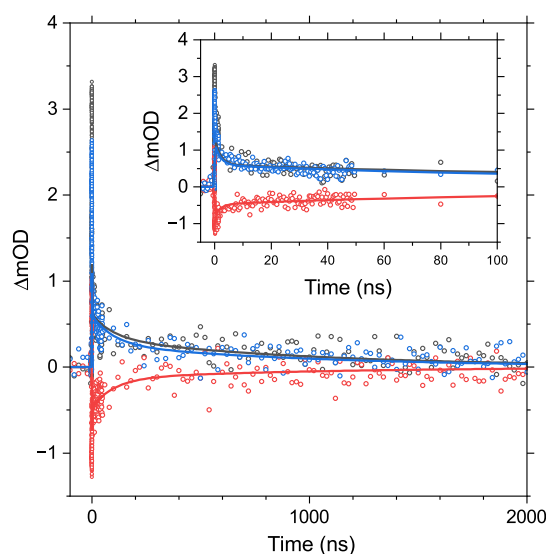


Figure 3. Decay kinetics of highly vibrationally excited mCP in the spectral region of the hot ground electronic state (S_0^*) for a neat mCP thin film recorded at 303 nm (black), 340 nm (red), and 348 nm (blue) up to 2000 ns. The correspondingly colored lines are triexponential fits with common time constants of $\tau_1 = 2$ ns, $\tau_2 = 100$ ns, and $\tau_3 = 1000$ ns. The inset shows a magnification up to 100 ns.

At this point, it is worthwhile to draw a comparison with the transient absorption spectra of a mCP:PMMA film (10:90) shown in Figure 4. In contrast to the neat mCP film, the contour plot and the transient spectra in panels a and b closely

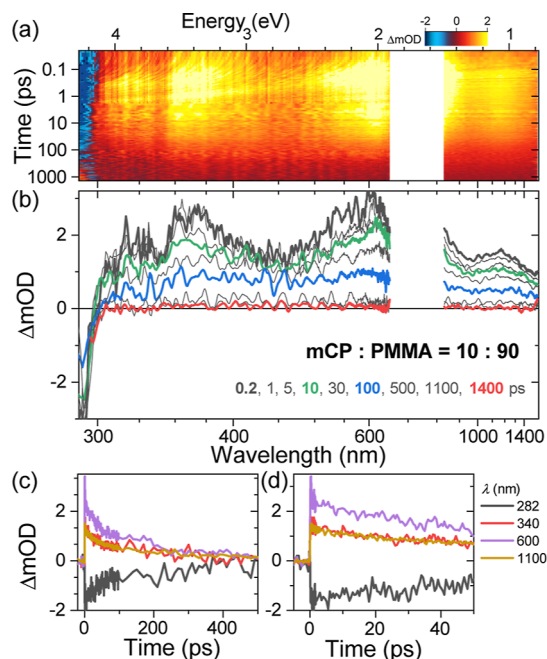


Figure 4. (a) Contour plot of ultrafast transient absorption spectra of an mCP:PMMA blend (10:90) upon photoexcitation at 290 nm. Note the logarithmic time axis. (b) Transient absorption spectra at different delay times in the range 0.2–1400 ps, with representative spectra indicated by thick colored lines. (c) Kinetics at 282 nm (GSB, black), 340 nm (red), 600 nm (violet), and 1100 nm (brown) shown up to 500 ps. (d) Same as in panel (c), but showing the dynamics at early times up to 50 ps.

resemble the spectral features in THF (Figure 2a,b). For instance, the broad S_1 ESA band has a characteristic minimum at 340 nm, which arises from the overlapping 0–0 transitions in the inverted steady-state absorption spectrum and the $S_1 \rightarrow S_0$ stimulated emission spectrum.

We do not see any clear spectral features associated with vibrationally hot mCP molecules because the excess energy is mainly transferred to the PMMA host matrix, which is in large excess and spectrally “silent”. Still, the kinetics in panels c and d already indicate a faster decay compared with mCP in THF, showing that even at this quite low mCP concentration, SSA processes between mCP molecules in the S_1 state are non-negligible.

3.4. Fluence-Dependent Transient Absorption Measurements and Their Kinetic Modeling for Neat mCP Thin Films. As already mentioned, the kinetics in panel m of Figure 2 clearly show the influence of SSA processes in terms of a fast decay of the traces at early times. The kinetics of these higher-order processes will be therefore very sensitive to the initial singlet number density. Therefore, transient absorption experiments at three different pump laser fluences were performed and afterward subjected to a detailed kinetic analysis. Panels a and b of Figure 5 show representative kinetics at 340 nm up to 100 ps and up to 1500 ps, respectively, with initial exciton number densities $N(S_x)$ of 3.15×10^{18} (blue circles), 6.30×10^{18} (red circles), and $1.19 \times 10^{19} \text{ cm}^{-3}$ (black circles), corresponding to fluences of 0.73, 1.46, and 2.77 mJ cm^{-2} (50 fs pulse length). These number densities were determined from accurate measurements of the laser fluence using the optical density and thickness of the film. The latter was determined from AFM experiments, which provided a value of 253 nm (panel c). We also note that we observed oscillations in the kinetics with a period of about 150 ps, which were particularly strong at the $S_0 \rightarrow S_1$ absorption edge. Panel d shows an example of a kinetic trace averaged over the wavelength range 345–355 nm. As demonstrated previously, such an oscillation originates from a coherent acoustic phonon induced by the pump beam, which propagates back and forth between the film/quartz and the film/nitrogen interface.^{19,26,30–33} Based on the known thickness measured by AFM, we were able to extract the longitudinal sound velocity c_L of the mCP film from the measured oscillation period, which was determined to be 6800 m s^{-1} .

In the following, we outline the kinetic model for describing the relaxation processes monitored by the kinetics in panels a and b. The probe wavelength 340 nm is located in a region, where one expects absorption contributions of the electronically excited singlet states as well as the hot ground state S_0^* . The initial positive spike in each signal comes from the ESA of the S_1 state. Decay of S_1 leads to the formation of the S_0^* state, resulting in a negative signal. We note that similar decays are observed in the S_1 ESA band, e.g., at 400 nm (Supporting Information, Figure S5). The resulting vibrationally hot molecules then cool down to form “cold” S_0 molecules, resulting in the final decay. A scheme of the different pathways for excited-state relaxation is provided in Figure 6. The specific kinetic model derived from this scheme is summarized by eqs 1–11 and explained in more detail below

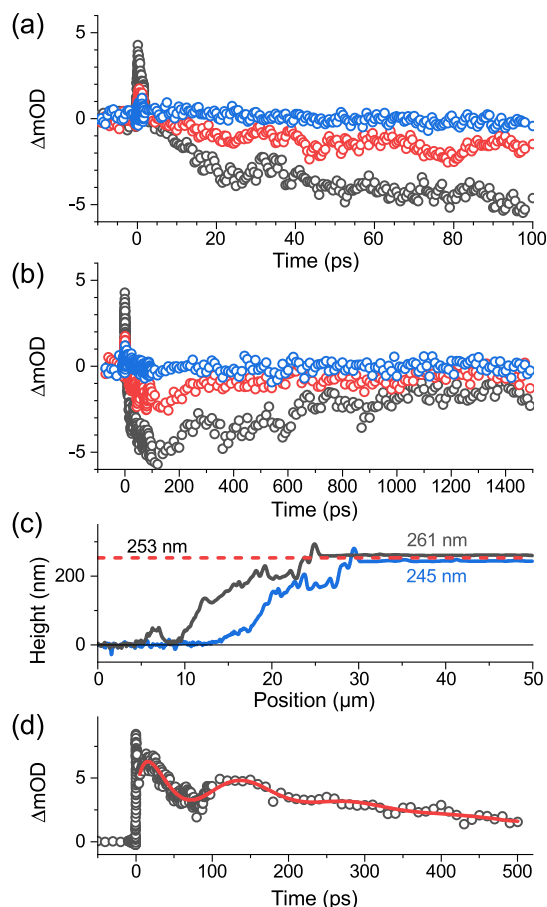


Figure 5. (a) Transient absorption kinetics of a neat mCP thin film up to delay times of 100 ps detected at a probe wavelength of 340 nm after photoexcitation at 290 nm. (b) Same as in panel (a), but shown up to 1500 ps. Initial exciton number densities $N(S_x)$: 3.15×10^{18} (blue circles), 6.30×10^{18} (red circles), and $1.19 \times 10^{19} \text{ cm}^{-3}$ (black circles). (c) Two AFM measurements for the mCP thin film providing a film thickness of 253 nm. (d) Oscillatory kinetics averaged over the spectral range 345–355 nm originating from a coherent acoustic phonon propagating in the film.

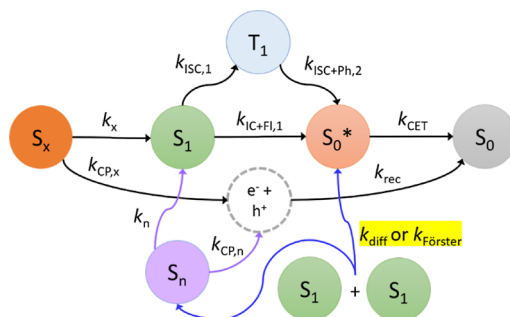


Figure 6. Overview of the different pathways for the relaxation of mCP in the excited state. Details regarding the kinetic modeling are provided in the text.





Photoexcitation at 290 nm prepares the mCP molecule in a higher excited singlet state S_x . Because we did not observe any pronounced spectral changes within the first picosecond, the lifetime of this state must be very short, presumably on the sub-100 fs time scale, producing the S_1 state by internal conversion (IC) with the rate constant k_x (eq 1). We also assume that the highly excited S_x state in the organic thin film can split into a charge pair (electron and hole, eq. 2, e.g., located on individual mCP molecules as an $S_0^{\bullet-}$ radical anion and an $S_0^{\bullet+}$ radical cation), as discussed previously for molecular OLED compounds, hole transport materials, and polymer thin films.^{19,33–35} The time constant for this process is $k_{\text{CP},x}$.

The S_1 state formed by IC from S_x can take several parallel channels: mCP may decay by IC and fluorescence to the vibrationally hot ground state S_0^* with the rate constant $k_{\text{IC+Fl},1}$, cf. eq 3, or alternatively to the T_1 state by ISC via eq 4 with the rate constant $k_{\text{ISC},1}$. Afterward, the T_1 state decays to S_0^* either by ISC or phosphorescence (eq 5, rate constant $k_{\text{IC+Ph},2}$). These are the only options for “isolated” mCP molecules in a solvent (such as THF) or widely distributed mCP molecules in an inert film (such as the example mCP:PMMA 2:98 in Figure 1a), where the S_1 number density is low. At larger S_1 number densities, such as in neat mCP films, higher-order SSA processes need to be considered. One channel is the bimolecular diffusive SSA of two S_1 species, forming a higher excited S_n singlet state and an S_0^* ground state species with the rate constant k_{diff} , i.e., eq 6 in the kinetic scheme. In this case, the diffusive transport of the S_1 excitation occurs by a hopping process, i.e., repeated homo-FRET between S_1 and its respective nearest S_0 neighbor, which is supported by the favorable overlap of the absorption and emission spectra (Figure 1a). This statistical migration process does not lead to any net population change in S_1 and S_0 but eventually brings two S_1 excitons into a critical contact distance. At this short distance, SSA takes place by homo-FRET of the two mCP molecules in S_1 , as explained below. The overall SSA process in eq 6 is of second-order because the diffusive hopping of the two S_1 excitations is rate-determining.

Alternatively, we consider direct SSA by homo-FRET of two mCP molecules in S_1 , i.e., $S_1 \rightarrow S_n$ accompanied by $S_1 \rightarrow S_0^*$, mediated by a nonradiative dipole–dipole coupling mechanism (without prior diffusion), so that one of the electronic excitations is “destroyed”



Here, the rate constant $k_{\text{Förster}}$ depends on the distance R of the two interacting S_1 molecules and will thus change over time during the relaxation^{36,37}

$$k_{\text{Förster}} = \frac{1}{\tau_1} \left(\frac{R_0}{R} \right)^6 \quad (13)$$

This expression shows a characteristic R^{-6} dependence on the donor–acceptor distance R , with τ_1 being the total S_1 lifetime of the donor in the absence of energy transfer. R_0 is the distance, where there is equal probability for the FRET process and the intramolecular decay of S_1 . To make this direct S_1 – S_1 FRET process tractable within a standard kinetic mechanism with time-independent rate constants, the alternative formulation based on eqs 7a and 7b was deduced previously instead of eqs 12a and 12b.^{33,38} There, it was shown that S_1 – S_1 FRET can be described as an apparent third-order process. The two separate eqs 7a and 7b are required to correctly account for the overall stoichiometry of the S_1 – S_1 FRET process, leading to the apparent third-order rate constant $k_{\text{FRET}} = 6 k_F$.³³ Such an S_1 – S_1 FRET process should be feasible because the S_1 emission spectrum overlaps with strong S_1 ESA, as demonstrated in the transient absorption spectra of Figure 2b.

Second-order diffusive and third-order FRET-type SSA processes produce a higher energy S_n state, which should behave similar to the initially prepared S_x state. Therefore, it can either decay to the S_1 state by IC with the rate constant k_n , cf. eq 8, or form a charge pair with the rate constant $k_{\text{CP},n}$ via eq 9. The vibrationally excited S_0^* molecules are deactivated by collisional energy transfer (CET) with adjacent mCP molecules to cold S_0 species (eq 10, rate constant k_{CET}). The appropriateness of such a simple first-order description of CET is shown in the Supporting Information (Figure S6). Finally, the electrons and holes of the charge pair states recombine on much longer time scales (eq 11, rate constant k_{rec}). We do not consider singlet fission³⁹ because the T_1 state of mCP is located at more than half of the energy of the S_1 state. Also, TTA is not relevant here because the time scale for the formation of the T_1 state is way too slow to accumulate any appreciable T_1 number density in the transient absorption experiments. In addition, we do not include contributions from the excimer and aggregate species observed in the steady-state and transient fluorescence spectra (Figure 1). In the transient absorption experiments, we do not see indications for such species with a lifetime in the several nanosecond range (Tables S3 and S4, Supporting Information), only bands which decay on the microsecond time scale (Figure 2n).

In the following, we will turn to the modeling of the kinetic traces in panels a and b of Figure 5, which was performed using the program Tenua.⁴⁰ First, the absorbance was converted into a time-dependent S_0^* number density. At the probe wavelength of 340 nm, we detect the formation of S_0^* from S_1 , which corresponds to the initial fast formation of the negative signal in panel a, and the subsequent cooling of S_0^* to S_0 , which is the much slower decay in panel b. Therefore, the peak in each kinetics near $t = 0$ was taken as an initial value of zero for the S_0^* number density. The kinetics were then inverted, and the amplitudes were scaled by the known initial number densities for the three different pump laser fluence conditions. The resulting time-dependent number densities of the S_0^*

population are displayed in Figure 7a–c for the time ranges of up to 50, 300, and 1500 ps, respectively. This conversion of the

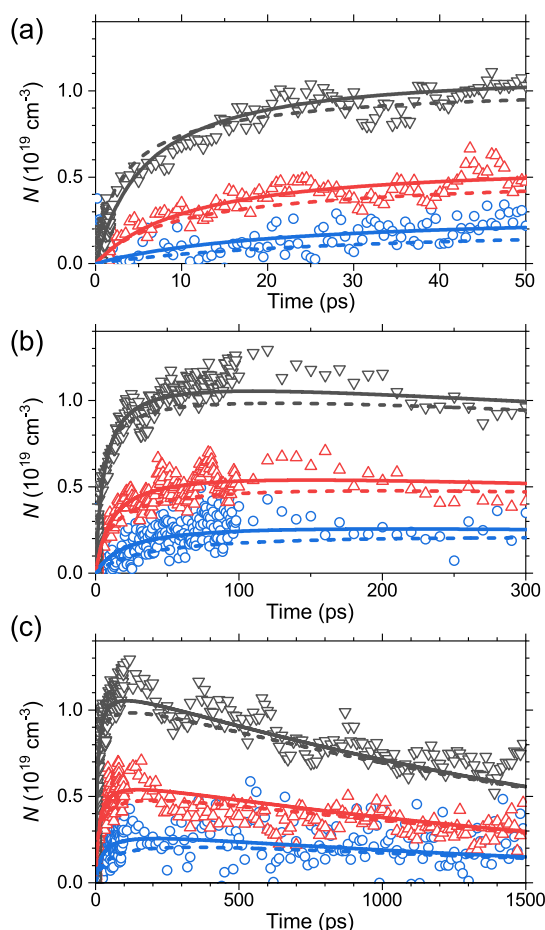


Figure 7. Kinetic modeling of the S_0^* number density N for the three different initial S_x number densities of 3.15×10^{18} (blue), 6.30×10^{18} (red), and $1.19 \times 10^{19} \text{ cm}^{-3}$ (black). Solid lines are for the kinetic model with diffusive SSA, and dashed lines are for the model with SSA based on direct S_1 – S_1 homo-FRET. (a) Time range up to 50 ps. (b) Time range up to 300 ps. (c) Time range up to 1500 ps.

transient absorption into a transient S_0^* number density profile is allowed because at the probe wavelength of 340 nm, the differences in absorption coefficients $\epsilon(S_1) - \epsilon(S_0)$ and $\epsilon(S_0) - \epsilon(S_0^*)$ are essentially the same. One can see this in the kinetic transient of Figure 5a: there the maximum positive amplitude (maximum S_1 population) and maximum negative amplitude (maximum S_0^* population, S_1 population practically fully depleted) are essentially identical. This means that the kinetic transient at 340 nm directly tracks the conversion of population from S_1 to S_0^* , or, in other words, the increase of S_0^* number density starting from a value of zero. The subsequent decay monitors the cooling process, i.e., the conversion of S_0^* into S_0 .

As it turned out, successful modeling of the initial fast increase up to 100 ps was exclusively dependent on the correct choice of the type and the rate constant of the S_1 – S_1 annihilation process. To determine the mechanism of SSA, we simulated two limiting cases: the solid lines are the results for purely diffusive SSA with the rate constant $k_{\text{diff}} = 1.40 \times 10^{-8} \text{ cm}^3 \text{ s}^{-1}$, whereas the dashed lines are the results of a simulation using only FRET with a rate constant $k_F = 8.00 \times$

$10^{-28} \text{ cm}^6 \text{ s}^{-1}$. The diffusive model provides a much better description of the experimental signals across the complete time range. The initial rise is slightly flatter and the curve saturates more slowly than for the simulation based on S_1 – S_1 FRET (cf. panel a), which is a result of the bimolecular compared with the apparent third-order mechanism. In addition, the diffusive model nicely follows all of the three curves for different pump laser fluences. Our result for k_{diff} is larger but still compares very well to the value $3.4 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ found for the related material 4'-bis(9-carbazolyl)-2,2'-biphenyl (CBP) by Ruseckas et al. using time-resolved fluorescence.⁴¹

In contrast, if the early-time behavior of the black curve for highest N_0 is modeled using S_1 – S_1 homo-FRET only (panel a), the experimental data at longer times for all three initial number densities are consistently underestimated. Importantly, an unrealistically large value for the Förster radius R_0 of 17 nm is required to fit the data, which is far outside the range expected for efficient S_1 – S_1 homo-FRET. There, typical values in the range of about 6 nm are expected for smaller organic molecular systems.⁴² The final decay of the three curves stems from the vibrational relaxation of the vibrationally hot mCP molecules and occurs on much slower time scales. By 1500 ps, the decay has not yet finished (see Figure 7c), and the visible range of the kinetics is well described by a rate constant k_{CET} of $5 \times 10^8 \text{ s}^{-1}$ ($\tau_{\text{CET}} = 2 \text{ ns}$, cf. also Figure 3).

We note that the kinetic model described by eqs 1–11 involves several other processes with their accompanying rate constants beside the SSA processes (eqs 6, 7a, and 7b). We would therefore like to provide a few comments regarding the accuracy of the fitted rate constants: The ratio of the rate constants k_x and $k_{\text{CP}x}$ (eqs 1 and 2) and the ratio of the rate constants k_n and $k_{\text{CP}n}$ (eqs 8 and 9) are directly linked to the yield for the formation of the long-lived CP state. An accurate value for this yield is difficult to estimate because at long delay times, the bleach feature below 380 nm (cf., e.g., Figure 2j at 1400 ps) is not a real population bleach but mainly reflects the difference absorption spectrum of S_0^* and S_0 molecules. The weak absorption band of the CP state with a peak at 450 nm suggests that the value is in the few percent range. This is for instance smaller than in copolymer systems, where this yield is in the range 15–25%.^{19,33,38} The total rate constants $k_{x,\text{total}} = \tau_{x,\text{total}}^{-1}$ of S_x and $k_{n,\text{total}} = \tau_{n,\text{total}}^{-1}$ of S_n are still well-defined (and also k_x and k_n). The generation of S_1 species must be ultrafast ($\tau_{x,\text{total}}$ and $\tau_{n,\text{total}}$ less than 100 fs) as both of them are relevant to correctly fit the steep rise of the kinetics in Figure 7a, which indicates the fast decay of S_1 population due to SSA.

The unimolecular decay channels of S_1 and T_1 (eqs 3–5) have fixed time constants in the nanosecond range, as determined from the TCSPC experiments in combination with the triplet yield for mCP in THF (obtained from transient absorption), which is assumed to be similar in the mCP film. The total S_1 lifetime in the absence of SSA processes is 6 ns for “isolated” mCP in THF and 6.7 ns for the mCP:PMMA 2:98 blend (cf. Table S2, Supporting Information), with an estimated quantum yield of about 20% for T_1 formation (see above). They are therefore way too slow to compete with the SSA processes at the singlet exciton number densities present in the transient absorption experiments. The lifetime of the T_1 state was fixed at the value for mCP in THF. Finally, the recombination of the charge pairs (eq 11) is very slow (66 μs), as seen in the fit provided in Figure 2n, and therefore also does not have an impact on the modeling shown in Figure 7.

A summary of the kinetic fit parameters is provided in the Supporting Information (Table S5). In addition, fit results using the same fit parameters are provided for another probe wavelength (318 nm) in the Supporting Information (Figure S7). The fits are as good as for the wavelength 340 nm, which shows the reliability of the fitting approach.

4. CONCLUSIONS

In this contribution, we were able to provide a comprehensive picture of the excited state dynamics of mCP, an important organic host material for blue emitters in OLEDs. The transient fluorescence experiments covered an excitation regime corresponding to very low number densities of the S_1 excited singlet state. Under these conditions, the influence of S_1 – S_1 annihilation can be excluded. Experiments for mCP in THF solution and in mCP:PMMA films with a very small mCP content showed a monoexponential kinetics with a mCP monomer lifetime in the range 6–7 ns. PMMA films with high mCP content and neat mCP thin films exhibited strongly quenched mCP emission featuring three different bands, assigned to monomer, aggregate, and excimer emission. mCP molecules in the S_1 state can migrate through the film via an S_1 – S_0 homo-FRET mechanism ($S_1 + S_0 \rightarrow S_0 + S_1$)^{42,43} and can emit monomer fluorescence “on the way” or be eventually trapped either at an aggregate or an excimer site. The homo-FRET mechanism is also supported by the small Stokes shift and the consequently good overlap of the mCP absorption and emission spectra.

In contrast, the UV–vis–NIR transient absorption experiments for the mCP thin film probed the dynamics for high number densities of the S_1 singlet state. Here, SSA was clearly detected ($S_1 + S_1 \rightarrow S_0 + S_n$), and the experiments favored a bimolecular diffusive mechanism. In contrast, modeling with a direct S_1 – S_1 homo-FRET mechanism resulted in an unrealistically large Förster radius. We therefore suggest that the S_1 excitation migrates through the neat mCP thin film by the aforementioned site-to-site hopping mechanism as there is always a very close mCP partner in S_0 for the excitation transfer. Annihilation takes place, once two mCP molecules in the S_1 state are within a critical contact distance.

The ultrafast transient absorption experiments for mCP in THF also provided clear evidence for the formation of the T_1 triplet state with a quantum yield of about 20%. The triplet state was spectrally characterized and has a microsecond lifetime in nitrogen-saturated THF. In the transient absorption experiments for the mCP thin film, the triplet yield is small because SSA outcompetes triplet formation. For the initial S_x exciton number densities of 1.19×10^{19} , 6.30×10^{18} , and $3.15 \times 10^{18} \text{ cm}^{-3}$ studied here, we obtain a triplet yield of 0.3, 0.5, and 1.0%, respectively. For very low initial S_x exciton number densities (e.g., TCSPC conditions), the T_1 excitons are very far apart, and there is no efficient migration process available for the T_1 species in the film. Thus, ISC and/or phosphorescence will prevail. Although the T_1 state has a long lifetime, the contribution of TTA will be therefore minor, when one initially uses photoexcitation. Looking at the spectra of Figure 2d and e, there is a substantial overlap between the T_1 absorption and the S_1 stimulated emission bands. Under electrical excitation in an OLED (T_1 : S_1 ratio 3:1 due to spin statistics), at high S_1 and T_1 exciton number densities, singlet–triplet annihilation between S_1 and T_1 ($S_1 + T_1 \rightarrow S_0 + T_n$) in addition to TTA should be feasible. These processes are also relevant to the roll-off characteristics of OLED devices.¹⁴

There are still several open questions, which will be worthwhile exploring in future investigations: here, we deliberately investigated thin films produced by spin-coating as this wet-chemical method has gained increased popularity in OLED fabrication because of the easier and cheaper manufacturing process compared with thermal vacuum deposition.^{5,8} In a future study, it will be interesting to see if there are relevant differences regarding the time-resolved spectroscopy of films prepared by spin-coating and thermal evaporation in vacuum, for instance with respect to the time constants of the SSA processes. In addition, transient absorption studies of representative blue emitters doped into mCP films will be of interest to follow processes, such as hetero-FRET between mCP and the blue emitter, in real time.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpcc.2c07440>.

Absorption, fluorescence, and fluorescence excitation spectra, time-resolved fluorescence experiments, spectrum of vibrationally hot mCP molecules at 1400 ps, slow vibrational cooling in mCP thin films, kinetics of mCP at the probe wavelengths of 340 and 400 nm, modeling of collisional energy transfer in mCP thin films, kinetic analysis of transient absorption data, and results of kinetic modeling at the probe wavelength of 318 nm (PDF)

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Notes

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Understanding Excited-State Relaxation in 1,3-Bis(*N*-carbazolyl)benzene, a Host Material for Organic Light-Emitting Diodes

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1. Absorption, Fluorescence, and Fluorescence Excitation Spectra

Table S1 summarizes characteristic spectral parameters of the “monomer species” in the absorption and fluorescence spectra of mCP in THF and in thin films. In general, the spectral shift induced by the different solvation environments as well as the Stokes shift are small.

Table S1. Peak positions of the 0–0 transition for the “monomer transition” in the absorption and fluorescence spectra of mCP in different environments including Stokes shifts.

Sample	$\lambda_{\text{abs}}^{0-0}$ (nm)	$\lambda_{\text{fl}}^{0-0}$ (nm)	ΔE_{Stokes} (meV)	$\Delta \tilde{\nu}_{\text{Stokes}}$ (cm ⁻¹)
mCP in THF	338.4	343.2	52	418
mCP:PMMA 2:98	339.4	343.6	44	355
mCP:PMMA 10:90	339.1	345.5	67	541
mCP:PMMA 90:10	342.1	349.0	72	583
mCP:PMMA 98:2	342.3	349.0	70	565
mCP thin film	342.5	349.5	72	583

Figure S1 shows fluorescence excitation spectra at different detection wavelengths for a neat mCP thin film. The spectra detected at the wavelengths 400 nm (red line) and 530 nm (blue line) are much broader than the spectrum recorded in the “monomer band” at 370 nm (black line). This is clearly visible in the region of the $S_0 \rightarrow S_1$ absorption band in the range 320–340 nm. This broadening of the fluorescence excitation spectrum is characteristic for excimer formation.¹

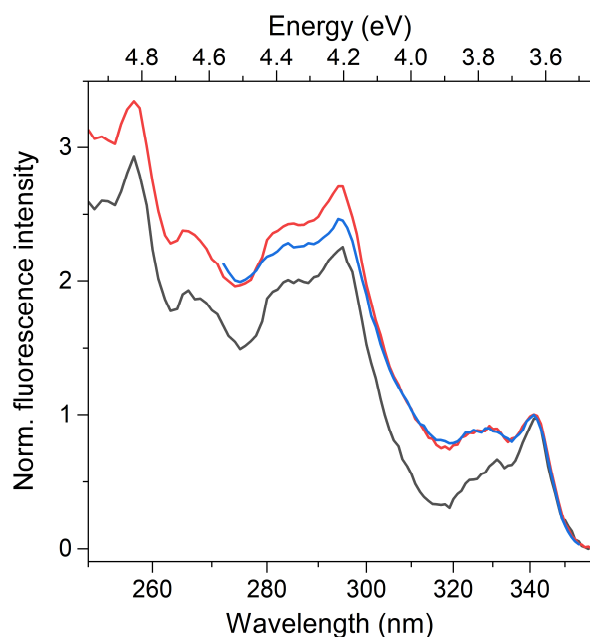


Figure S1. Fluorescence excitation spectra for a neat mCP thin film produced by spin-coating on quartz detected at 370 nm (black), 400 nm (red) and 530 nm (blue). All spectra were normalized at 341 nm.

Figure S2 shows an attempt to extract fluorescence spectra of individual electronic species from the emission spectrum of an mCP thin film (green solid line). Upon visual inspection, the spectrum can be roughly divided into two structured emission bands and at least one broad emission band. As discussed in the main manuscript, the double-peak band around 350 nm is assigned to monomer emission, the double-peak band around 420 nm is likely an aggregate emission (possibly a J-coupled dimer), and the broad band with a maximum around 520 nm arises from excimer emission. An approximate spectrum for the combined aggregate and excimer contributions was obtained by subtracting the emission spectrum of the mCP:PMMA blend (2:98, cf. Figure 1a in the main manuscript), which should be a good representation of mCP monomer emission in films. The spatial separation of the mCP molecules in such films is sufficiently large, so that mCP–mCP interactions are only weak. Because of the slightly different “solvation environment” of mCP molecules in PMMA and in neat mCP films, which leads to a different red-shift of the emission, the mCP:PMMA emission spectrum was slightly shifted toward larger wavelengths so that the rising edge of both emission spectra coincide. Subtraction of this “monomer” spectrum leads to the blue spectrum in Figure S2, which should be a good representation of the combined aggregate/excimer emission. Note that the residual weak “bumps” in the 350–380 nm region are likely due to the simplified subtraction procedure. The blue spectrum was fitted by a sum of Gaussian functions (red solid thin line). The three broad bands (cyan dashed lines) describe the unstructured excimer emission, whereas the two narrow bands (red dashed lines) represent the vibronic structure of the aggregate emission. Note that the 0–0/0–1 emission band ratio in the aggregate is slightly larger compared with the ratio of the monomer emission, which suggests weak electronic delocalization.^{2,3}

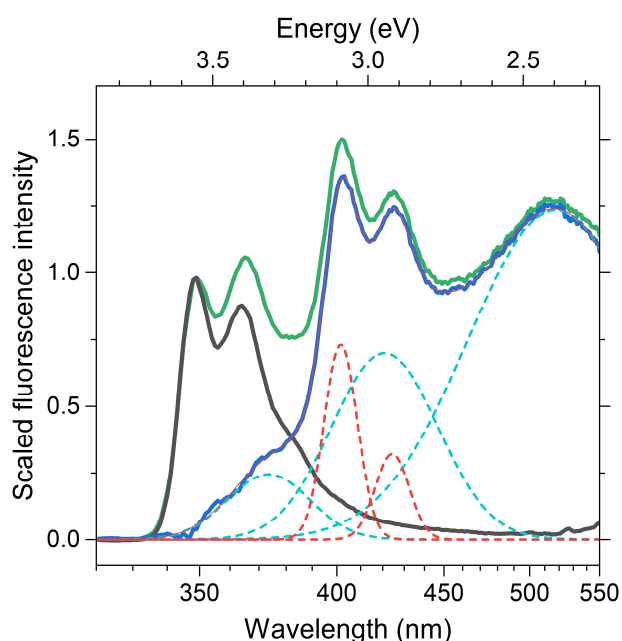


Figure S2. Estimating spectral contributions of different electronic species to the emission of a neat mCP thin film (green solid line). (Black solid line) Emission spectrum of an mCP:PMMA (2:98) thin film (shifted on the wavelength axis to match the rise of the emission spectrum of the neat mCP film), which should be a good approximation of the emission spectrum of mCP monomers. (Blue solid line) Difference of the green and the black spectrum representing an approximate emission spectrum due to combined mCP excimer and mCP aggregate contributions in the mCP thin film. (Red solid thin line) Fit of the blue spectrum to a sum of Gaussian functions with individual contributions assigned to excimer emission (cyan dashed lines, broad bands) and aggregate emission (red dashed lines, narrow bands). The excitation wavelength for both films was 290 nm.

In addition, Figure S3 shows the absorption spectrum (optical density, OD) of a neat mCP thin film (green line) together with the fluorescence spectra obtained when exciting the film at 270 nm (black line), 290 nm (red line) and 340 nm (blue line). Note that the intensity of the excimer band above 450 nm increases relative to the aggregate emission band at about 420 nm and also relative to the intensity of the monomer band at about 360 nm when shorter excitation wavelengths are employed. It therefore appears, as if there is an excitation energy dependent competition between the formation of the different emitting species. Obviously, excimer formation is progressively favored when the initial excitation energy is raised. We speculate that at higher excess energies, the homo-FRET-based hopping mechanism is able to explore a larger distance around the initial excitation, so that the probability for finding an excimer site is increasing.

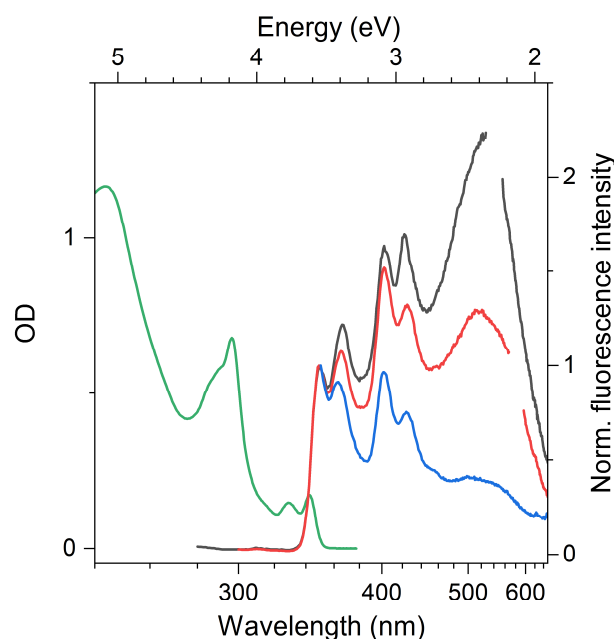


Figure S3. Absorption spectrum (green line) and fluorescence spectra detected after excitation at 270 nm (black line), 290 nm (red line) and 340 nm (blue line) for a neat mCP thin film spin-coated on quartz. The spectral regions in the fluorescence spectra around 540 and 580 nm for excitation at 270 nm and 290 nm, respectively, are not shown, because they exhibit considerable contributions of the excitation light arising from second-order diffraction of the grating-based emission spectrograph. All fluorescence spectra were normalized at 349 nm.

2. Time-Resolved Fluorescence Experiments

Time-resolved fluorescence measurements based on the TCSPC method were carried out for mCP dissolved in THF, for mCP:PMMA blends and for a neat mCP thin film. The samples were excited by a pulsed UV-LED operating at 273 nm either with a 1 MHz or 20 MHz repetition frequency. Different bandpass filters were employed to selectively detect the decay in the monomer band, the aggregate band and the excimer band, as discussed in the main manuscript.

The decay of the fluorescence intensity was described by a sum of exponential functions with up to three terms:

$$I(t) = \sum_{i=1}^3 A_i \exp(-t / \tau_i) \quad (\text{S2.1})$$

The lifetimes τ_i and associated percentage amplitudes A_i were extracted using a reconvolution procedure based on an instrument response function retrieved either from a Ludox solution or a fused silica diffuser. We obtained the “amplitude-weighted lifetime” τ_{aw} as

$$\tau_{\text{aw}} = \sum_{j=1}^3 A_j \cdot \tau_j \quad (\text{S2.2})$$

and the average lifetime $\langle \tau \rangle$ as

$$\langle \tau \rangle = \frac{\sum_{j=1}^3 A_j \cdot \tau_j^2}{\sum_{j=1}^3 A_j \cdot \tau_j} \quad (\text{S2.3})$$

The fit parameters are summarized in Tables S2-S4. Note that the experiments at 20 MHz (12.2 ps channel width) in several cases identify two faster components, which in the lower-resolution 1 MHz experiments (126 ps channel width) appear as a single component. The fast component in the measurements at 1 MHz therefore effectively represents an average of the two components measured in the TCSPC experiments with higher time resolution.

Table S2. Results for the TCSPC experiments at 1 MHz and 20 MHz repetition frequency ($\lambda_{\text{exc}} = 273 \text{ nm}$) for detection in the monomer emission band of mCP using a bandpass filter centered at 370 nm with an FWHM of 10 nm.

Rep. freq. (MHz)	Sample	τ_1 (ns)	τ_2 (ns)	τ_3 (ns)	A_1 (%)	A_2 (%)	A_3 (%)	τ_{aw} (ns)	$\langle \tau \rangle$ (ns)
1	mCP in THF	5.99	---	---	100.0	---	---	5.99	5.99
	mCP:PMMA 2:98	6.68	---	---	100.0	---	---	6.68	6.68
	mCP:PMMA 10:90	1.45	3.51	---	66.0	34.0	---	2.15	2.60
	mCP:PMMA 90:10	0.65	2.55	---	93.4	6.6	---	0.78	1.06
	mCP:PMMA 98:2	0.69	2.41	---	93.2	6.8	---	0.80	1.04
	mCP thin film	0.69	2.44	---	93.5	6.5	---	0.80	1.03
20	mCP in THF	5.97	---	---	100.0	---	---	5.97	5.97
	mCP:PMMA 2:98	7.21	1.24	---	78.3	21.7	---	5.91	6.94
	mCP:PMMA 10:90	0.44	1.48	3.51	9.4	56.3	34.3	2.08	2.64
	mCP:PMMA 90:10	0.40	1.46	4.05	92.8	6.3	0.9	0.50	0.86
	mCP:PMMA 98:2	0.36	0.76	3.05	74.6	23.5	1.9	0.50	0.80
	mCP thin film	0.40	1.33	3.88	92.1	7.0	0.9	0.50	0.82

Table S3. Results for the TCSPC experiments for another neat mCP thin film at 1 MHz and 20 MHz repetition frequency ($\lambda_{\text{exc}} = 273$ nm) for detection in the monomer (370 nm), aggregate (430 nm) and excimer emission bands (560 nm) of mCP using respective bandpass filters.

Rep. freq. (MHz)	λ_{max} of bandpass filter (nm)	τ_1 (ns)	τ_2 (ns)	τ_3 (ns)	A_1 (%)	A_2 (%)	A_3 (%)	τ_{aw} (ns)	$\langle \tau \rangle$ (ns)
1	370	0.39	1.82	---	88.9	11.1	---	0.55	0.92
	430	1.84	8.29	---	90.9	9.1	---	2.42	3.84
	560	2.85	11.3	---	78.6	21.4	---	4.65	7.22
20	370	0.21	0.91	2.55	83.5	14.3	2.2	0.36	0.83

Table S4. Results for the TCSPC experiments at 1 MHz and 20 MHz repetition frequency ($\lambda_{\text{exc}} = 273$ nm) for detection in the excimer emission band of mCP using a bandpass filter centered at 560 nm with an FWHM of 10 nm.

Rep. freq. (MHz)	Sample	τ_1 (ns)	τ_2 (ns)	τ_3 (ns)	A_1 (%)	A_2 (%)	A_3 (%)	τ_{aw} (ns)	$\langle \tau \rangle$ (ns)
1	mCP:PMMA 90:10	3.26	12.7	---	71.4	28.6	---	5.95	8.98
	mCP:PMMA 98:2	3.45	12.2	---	71.4	28.6	---	5.94	8.55
	mCP thin film	3.18	11.8	---	66.7	33.3	---	6.06	8.80
20	mCP:PMMA 90:10	2.51	8.57	12.66	57.9	34.2	7.9	5.38	7.69
	mCP:PMMA 98:2	2.49	9.26	---	58.3	41.7	---	5.31	7.41
	mCP thin film	2.56	8.88	11.82	59.5	35.7	4.8	5.26	7.36

3. Spectrum of Vibrationally Hot mCP Molecules at 1400 ps

Figure S4 compares the S_0 ground state spectrum of an mCP thin film at 297 K (red solid line) with the spectrum of the same sample 1400 ps after excitation with a laser pulse at 290 nm (blue dashed line). This spectrum was obtained by adding the transient absorption spectrum at 1400 ps (black solid line, taken from Figure 2j of the main manuscript) to the S_0 spectrum. For the “hot” spectrum, one can clearly observe a slight rise of the absorption on the red edge of the $S_0 \rightarrow S_1$ absorption band and a slight decrease of the absorption at the maximum. These changes are characteristic for vibrationally hot mCP molecules, and very similar spectra were observed for other vibrationally hot organic molecules, such as azulene.⁴

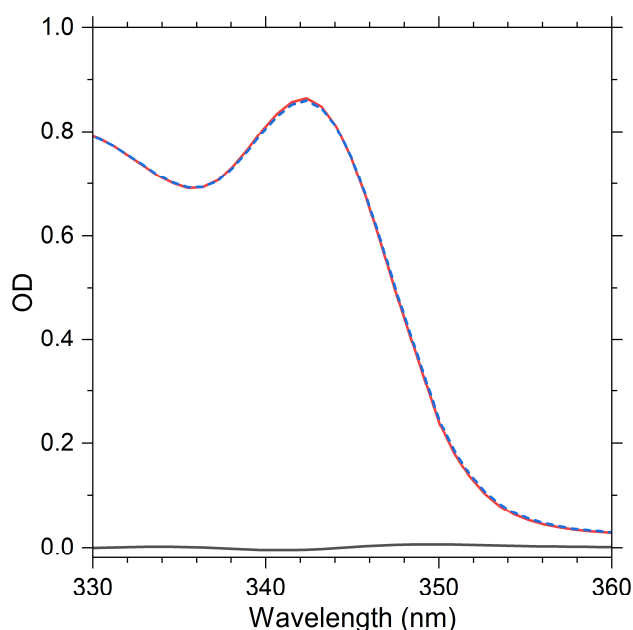


Figure S4. Comparison of the S_0 ground state spectrum of an mCP thin film at 297 K (red solid line) with the spectrum of the same sample 1400 ps after excitation with a laser pulse at 290 nm (blue dashed line). The black line is the measured transient absorption spectrum at 1400 ps.

4. Slow Vibrational Cooling in mCP Thin Films

Vibrationally hot organic molecules (S_0^*) diluted in an organic solvent or at low concentration in a host matrix, such as PMMA, relax quickly with typical time constants τ_{CET} in the range from picoseconds to several ten picoseconds.⁴ In this respect, the apparently very slow cooling process of vibrationally hot mCP molecules in a neat mCP film (Figure 2h-l, main manuscript) deserves further discussion. The effect is quite easy to understand and is explained in the following. The central point is that the vibrational energy of an initially hot mCP molecule (here denoted as S_0^{***}) is transferred to other originally vibrationally cold (room temperature) mCP S_0 molecules. In a simplified way, the process can be written as:



In this simple example, the vibrational energy is transferred to a single cold mCP molecule. In a crystal environment, the energy will of course spread over several adjacent S_0 mCP molecules. We define the measured absorbance as

$$A_{S_0^{\text{hot}}}(t) = \varepsilon_{S_0^{\text{hot}}}(t) c_{S_0^{\text{hot}}}(t) d \quad (\text{S4.2})$$

where “hot” is the collective notation for all sorts of vibrationally excited mCP molecules (in eq. (S4.1) S_0^{***} , S_0^{**} and S_0^*). Looking at eq. (S4.1), it is easily seen that, while the “hot band” absorption coefficients (e.g. at 348 nm in Figure 2j, main manuscript) of S_0^{**} and S_0^* are definitely smaller than that of S_0^{***} , the concentration of hot mCP molecules is now doubled. In the experiment, we monitor the product of absorption coefficient and concentration, and the precise change of the absorbance then depends on the difference in absorbance of the species on the right and left side of eq. (S4.1). This change will be quite small, or in other words, the excess energy is merely redistributed among the mCP molecules. Energy loss of the mCP film can only occur by heat transfer across the interface to the “optically silent” quartz substrate and only to a very small extent to the nitrogen atmosphere above the sample (with very small heat capacity).

The situation is very different for mCP diluted in PMMA (cf. Figure 4, main manuscript). Here, the energy is not transferred to mCP, but to an adjacent cold PMMA unit:



with the decisive difference that the concentration of hot mCP stays constant (but its hot band absorption coefficient is reduced). Therefore, the absorption decay of mCP will be much faster. PMMA^* is spectrally silent and does not contribute to the measured absorption spectrum. As for the neat mCP film, energy loss of the mCP:PMMA blend will occur by heat transfer across the interface to the “optically silent” quartz substrate and only to a very small extent to the nitrogen atmosphere above the sample.

5. Kinetics of mCP at the Probe Wavelengths 340 nm and 400 nm

Figure S5 shows a comparison of the transient absorption kinetics recorded at 340 nm (black solid line) and 400 nm (red solid line). The decay of both kinetic traces at early times is essentially identical, which can be demonstrated by scaling and shifting the 340 nm kinetics, providing the black dotted line. This decay monitors the loss of S_1 population, which is dominated by singlet–singlet annihilation. The probe wavelength 340 nm was used in the kinetic modeling procedure to provide a faithful representation of the loss of S_1 population. The negative signal formed upon S_1 decay arises from vibrationally hot molecules (S_0^*), which at this probe wavelength have a smaller absorption coefficient than cold ground state molecules (S_0). The residual absorption of the kinetics at 400 nm presumably arises from absorption of a charge pair state. It cannot be due to S_0 or S_0^* absorption, because it is located at a much longer wavelength than the absorption band of the electronic ground state of mCP, which starts rising below 360 nm.

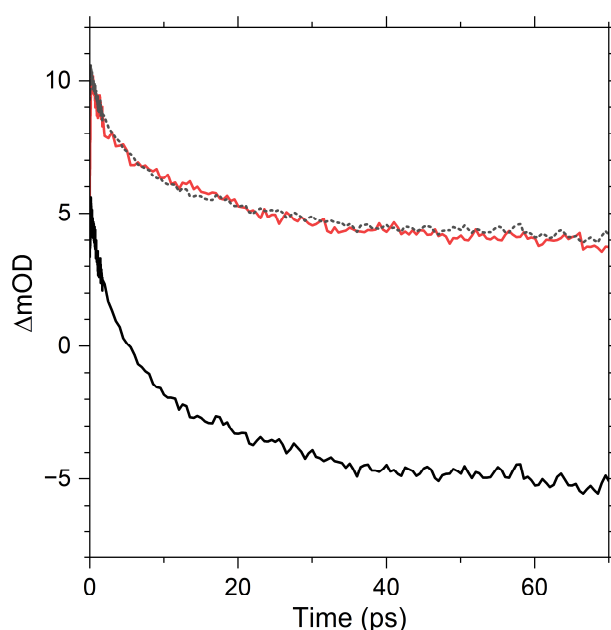


Figure S5. Kinetics of an mCP thin film excited at 290 nm and probed at 340 nm (black solid line) or 400 nm (red solid line). To obtain the black dotted line, the absorbance of the transient at 340 nm was scaled and shifted ($\Delta mOD(340 \text{ nm, scaled}) = 0.6 \cdot \Delta mOD(340 \text{ nm}) + 7.25$) to superimpose it with the transient at 400 nm.

6. Modeling of Collisional Energy Transfer in mCP Thin Films

In the kinetic mechanism of the main manuscript, collisional energy transfer is described by a simple first-order decay of a vibrationally hot S_0^* species to vibrationally cold S_0 molecules, cf. eq. (10) (main manuscript). Here, we describe why such an approach is of sufficient accuracy. Figure S6 shows kinetic traces in the region of the S_0 ground state absorption of an mCP film. The film was excited at 290 nm and probed at 340 nm (violet line) or 348 nm (red line, red edge of the steady-state absorption of mCP). When inverting, rescaling and overlaying the violet transient at 340 nm, one obtains the blue line, which shows a slow decay, which is practically identical to the one of the transient at 348 nm. This slow decay of the transients describes the cooling dynamics from S_0^* to S_0 . Therefore, for the kinetic fit of the vibrational cooling of S_0^* it is irrelevant, which probe wavelength we choose, and we therefore selected 340 nm. Also, for this cooling process in the neat mCP film (fitted time constant 2 ns), S_1 SE and ESA do not play a role, as there is basically no S_1 population left after 50 ps at the initial exciton number densities employed in the transient absorption experiments. This means that only S_0^* contributes to the kinetics (only 2% of the excitons are converted into long-lived charge pair states and the T_1 population is also small). We note that the superimposed damped oscillation in the kinetics is due to a coherent acoustic phonon propagating through the mCP thin film, as explained in the main manuscript.

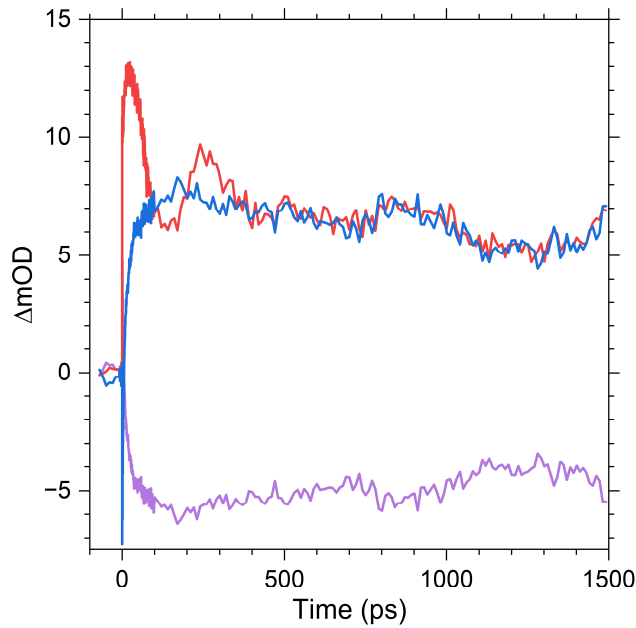


Figure S6. Kinetic traces of an mCP thin film excited at 290 nm and probed at 340 nm (violet line) or 348 nm (red line). The blue line is the inverted and scaled kinetics at 340 nm.

In a kinetic model, the time-dependent absorption $A_i(t)$ of a species i is typically described as:

$$A_i(t) = \varepsilon_i c_i(t) d \quad (\text{S6.1})$$

where ε_i is the *time-independent* absorption coefficient of the species, $c_i(t)$ is its time-dependent concentration and d is the constant path length of the sample. Spectra of vibrationally hot molecules depend on the temperature, and thus on the average internal energy $\langle E \rangle$ of the molecules in the electronic ground state. Therefore, the description for S_0^* is more complicated:

$$A_{S_0^*}(t) = \varepsilon_{S_0^*}(t) c_{S_0^*}(t) d \quad (\text{S6.2})$$

i.e. the absorption coefficient of S_0^* molecules is also *time-dependent*, because during the cooling process both the average energy and the absorption coefficient change. One way to tackle this problem is to introduce kinetic species with time-dependent spectra. We previously demonstrated such a procedure for derivatives of β -carotene in organic solvents.^{5,6} However, for the current modeling, a much simpler approach can be used. As discussed in detail by Schwarzer et al. for the vibrational deactivation of azulene, the S_0^* absorption coefficient on the red edge of the absorption band to a good approximation depends linearly on energy:⁴

$$\varepsilon(t) = a + b \langle E \rangle \quad (\text{S6.3})$$

Here, a and b are fit constants. Furthermore, for organic molecules, average energies transferred per collision, $\langle \Delta E \rangle$, typically show a linear dependence on the average energy $\langle E \rangle$.^{4,7} This leads to an exponential decay of the average internal energy of the mCP molecules:

$$\langle E(t) \rangle = \langle E(t=0) \rangle \exp\left(-\frac{t}{\tau_{\text{CET}}}\right) \quad (\text{S6.4})$$

Therefore, the slow decay which is observed in our transient absorption kinetics at 340 and 348 nm (Figure S6), directly reflects the change of the internal energy of mCP with time, and the first-order rate constant $k_{\text{CET}} = \tau_{\text{CET}}^{-1}$ provides direct information regarding the loss of average internal energy.

7. Kinetic Analysis of Transient Absorption Data

Table S5 contains the parameters extracted from the kinetic analysis of the transient absorption experiments, as discussed in the main manuscript.

Table S5. Summary of parameters employed in the kinetic analysis of the fluence-dependent experiments for the neat mCP thin film upon photoexcitation at 290 nm.

Physical quantity (unit)	Value	Physical quantity (unit)	Value
$N_{0,\text{high}}(S_x) \text{ (cm}^{-3}\text{)}$	1.19×10^{19}		
$N_{0,\text{medium}}(S_x) \text{ (cm}^{-3}\text{)}$	6.30×10^{18}		
$N_{0,\text{low}}(S_x) \text{ (cm}^{-3}\text{)}$	3.15×10^{18}		
$k_x(S_x \rightarrow S_1) \text{ (s}^{-1}\text{)}$	4.95×10^{13}	$\tau_x \text{ (fs)}$	20
$k_{\text{CPx}}(S_x \rightarrow e^- + h^+) \text{ (s}^{-1}\text{)}$	5.00×10^{11}	$\tau_{\text{CPx}} \text{ (ps)}$	2.0
$k_{x,\text{total}} = k_x + k_{\text{CPx}} \text{ (s}^{-1}\text{)}$	5.00×10^{13}	$\tau_{x,\text{total}} \text{ (fs)}$	20
		$\Phi_{\text{CPx}} \text{ (%)}$	1
$k_{\text{IC+Fl},1}(S_1 \rightarrow S_0^*, S_1 \rightarrow S_0^* + h\nu) \text{ (s}^{-1}\text{)}$	1.33×10^8	$\tau_{\text{IC+Fl},1} \text{ (ns)}$	7.5
$k_{\text{ISC},1}(S_1 \rightarrow T_1) \text{ (s}^{-1}\text{)}$	3.33×10^7	$\tau_{\text{ISC},1} \text{ (ns)}$	30
$k_{1,\text{total}} = k_{\text{IC+Fl},1} + k_{\text{ISC},1} \text{ (s}^{-1}\text{)}$	1.67×10^8	$\tau_1 \text{ (ns)}$	6.0
		$\Phi_{\text{ISC},1} \text{ (%)}$	20
$k_{\text{ISC+Ph},2}(T_1 \rightarrow S_0^*) \text{ (s}^{-1}\text{)}$	1.27×10^6	$\tau_{\text{ISC+Ph},2} \text{ (ns)}$	790
$k_F(3 S_1 \rightarrow S_n + 2 S_0^*) \text{ (cm}^6 \text{ s}^{-1}\text{)}$	8.00×10^{-28}		
$k_F(3 S_1 \rightarrow 2 S_n + S_0^*) \text{ (cm}^6 \text{ s}^{-1}\text{)}$	8.00×10^{-28}		
$k_{\text{FRET}} \text{ (cm}^6 \text{ s}^{-1}\text{)}$	4.80×10^{-27}		
$\langle k_{\text{Förster}} \rangle (S_1 \rightarrow S_0^*) \text{ (s}^{-1}\text{)}^a$	$1.01 \times 10^{13} (N_{0,\text{high}})$	$R_0 \text{ (nm)}^b$	17.0
	$2.82 \times 10^{12} (N_{0,\text{medium}})$		
	$7.05 \times 10^{11} (N_{0,\text{low}})$		
$k_{\text{diff}}(2 S_1 \rightarrow S_n + S_0^*) \text{ (cm}^3 \text{ s}^{-1}\text{)}$	1.40×10^{-8}		
$k_n(S_n \rightarrow S_1) \text{ (s}^{-1}\text{)}$	4.95×10^{13}	$\tau_n \text{ (fs)}$	20
$k_{\text{CPn}}(S_n \rightarrow e^- + h^+) \text{ (s}^{-1}\text{)}$	5.00×10^{11}	$\tau_{\text{CPn}} \text{ (ps)}$	2.0
$k_{n,\text{total}} = k_n + k_{\text{CPn}} \text{ (s}^{-1}\text{)}$	5.00×10^{13}	$\tau_{n,\text{total}} \text{ (fs)}$	20
		$\Phi_{\text{CPn}} \text{ (%)}$	1
$k_{\text{CET}}(S_0^* \rightarrow S_0) \text{ (s}^{-1}\text{)}$	5.0×10^8	$\tau_{\text{CET}} \text{ (ns)}$	2
$k_{\text{rec}}(e^- + h^+ \rightarrow S_0) \text{ (cm}^3 \text{ s}^{-1}\text{)}$	3.3×10^{-14}		

^a See eq. (S12) in the Supporting Information of ref. 8.

^b Based on eq. (S18) from the Supporting Information of ref. 8.

8. Results of Kinetic Modeling at the Probe Wavelength 318 nm

Figure S7 shows additional kinetic modeling results at the probe wavelength 318 nm for three different pump laser fluences using the parameters from Table S5, which were also used for the fits at the probe wavelength 340 nm (Figure 7, main manuscript). At the probe wavelength 318 nm, the kinetics at early times represents the sum of the decay of S_1 ESA (mainly due to singlet–singlet annihilation) and the concomitant formation of absorption of the hot vibrational ground state S_0^* resulting from the SSA process. The slow decay on longer time scales is due to vibrational cooling of S_0^* . As for the probe wavelength 340 nm, the model provides a very good description of the three transients.

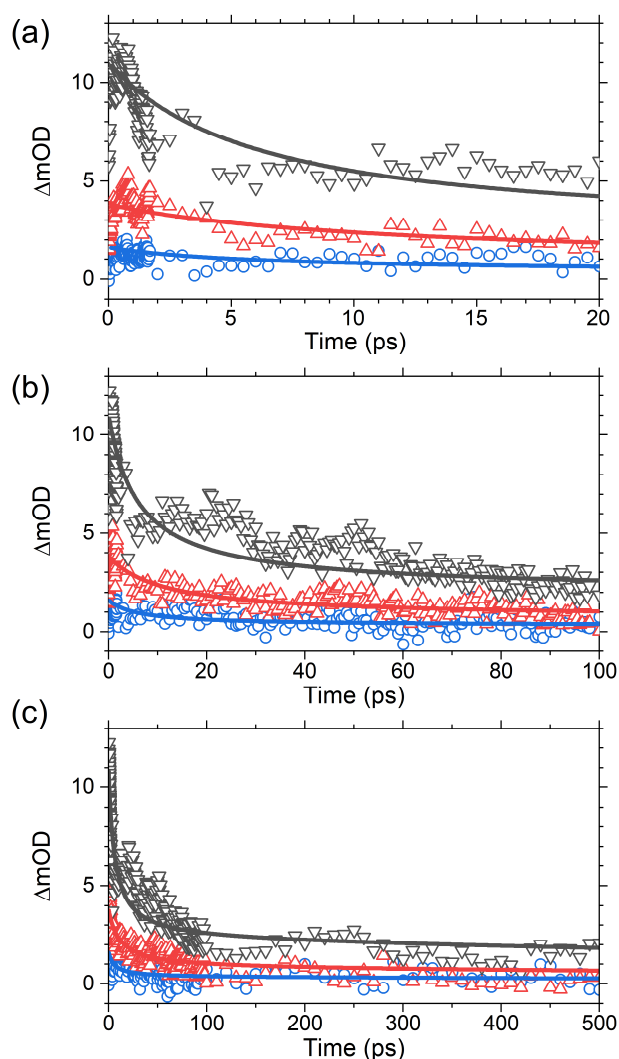


Figure S7. Kinetic modeling of fluence-dependent transient absorption signals at the probe wavelength 318 nm for the three different initial S_x number densities 3.15×10^{18} (blue), 6.30×10^{18} (red) and $1.19 \times 10^{19} \text{ cm}^{-3}$ (black). The lines represent fits based on the kinetic model with diffusive singlet–singlet annihilation, which provides the best description at the probe wavelength 340 nm (cf. Figure 7, main manuscript). (a) Time range up to 20 ps. (b) Time range up to 100 ps. (c) Time range up to 500 ps. Pump wavelength: 290 nm.

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Scientific contributions

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Contribution to scientific conferences

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