Correlating Ultrafast Dynamics, Liquid Crystalline Phases, and Ambipolar Transport in Fluorinated Benzothiadiazole Dyes

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A key challenge in the field of organic electronics is predicting how chemical structure at the molecular scale determines nature and dynamics of excited states, as well as the macroscopic optoelectronic properties in thin film. Here, the donor–acceptor dyes 4,7-bis[5-[4-(3-ethylheptyl)-2,3-difluorophenyl]-2-thienyl]-2,1,3-benzothiadiazole (2,3-FFPTB) and 4,7-bis[5-[4-(3-ethylheptyl)-2,6-difluorophenyl]-2-thienyl]-2,1,3-benzothiadiazole (2,6-FFPTB) are synthesized, which only differ in the position of one fluorine substitution. It is observed that this variation in chemical structure does not influence the energetic position of the molecular frontier orbitals or the ultrafast dynamics on the FFPTB backbone. However, it does result in differences at the macroscale, specifically regarding structural and electrical properties of the FFPTB films. Both FFPTB molecules form crystalline films at room temperature, whereas 2,3-FFPTB has two ordered smectic phases at elevated temperatures, and 2,6-FFPTB does not display any liquid crystalline phases. It is demonstrated that the altered location of the fluorine substitution allows to control the electrostatic potential along the molecular backbone without impacting molecular energetics or ultrafast dynamics. Such a design strategy succeeds in controlling molecular interactions in liquid crystalline phase, and it is shown that the associated molecular order, or rather disorder, can be exploited to achieve ambipolar transport in FFPTB films.

1. Introduction

A key requirement for enabling commercial applications of organic electronics is the rational design of high-performance organic semiconductors (OSCs) that can be easily processed with low-cost, large-throughput fabrication techniques. While high carrier mobilities are generally desirable, optoelectronic devices, such as organic light-emitting diodes[1] and organic photovoltaics,[2] specifically profit from ambipolar transport, i.e., balanced electron and hole transport. However, the majority of OSCs are predominantly unipolar, and demonstrate higher hole mobilities than electron mobilities.[3] Therefore, device fabrication typically requires the deposition of multiple unipolar OSCs to achieve the desired electrical properties, thereby complicating the fabrication protocols. Soluble small-molecule semiconductors that form crystalline films have the potential to combine the advantages of high chemical purity and superior (opto)electronic properties with good processability. However, crystalline organic films formed from soluble small molecules often display poor structural and thermal integrity, as well as lower carrier mobilities compared to nonsoluble small-molecule derivatives. In other words, processability generally comes at the expense of both reduced thermal and mechanical stability, as well as electrical transport.

In this study, we synthesized soluble small-molecule dyes that form crystalline films at room temperature, but...
demonstrate liquid crystalline (LC) phases at elevated temperatures. LC semiconductors have a broad application potential in the field of organic optoelectronics, due to the possibility to exploit molecular self-assembly in the LC phases and obtain highly ordered molecular films with preferential molecular alignment, spacing, and $\pi-\pi$ stacking in the direction of electrical transport.$^{[4,5,9]}$ Previous studies have shown that crystalline small-molecule films displaying LC phases at elevated temperature demonstrate increased film stability, lower densities of grain boundaries, and high carrier mobility.$^{[7,8]}$ Further, ambipolar transport has been reported for discotic semiconductors that form columns$^{[4,5,9]}$ with reduced intermolecular disorder.$^{[10,11]}$ By contrast, strategies to achieve ambipolar transport in non-LC OSCs tend to focus on device engineering related to reducing electronic trap states,$^{[12,13]}$ or tailoring the energetic position$^{[14]}$ and spatial distribution of the molecular frontier orbitals$^{[15–17]}$ with respect to transport layers and contact materials.$^{[18]}$ To date, most studies on LC OSCs have focused on transistor applications,$^{[7,19,20]}$ and there are few reports of LC OSCs in optoelectronic applications, such as light emission$^{[21]}$ and near-infrared absorption.$^{[22]}$ Recently, considerable potential has been demonstrated for the use of LC OSCs in photovoltaics to achieve thicker active layers without increasing recombination losses.$^{[22–26]}$ One reason that application of LC OSCs in optoelectronics is still limited may be related to the complex intermolecular interactions in LC films, as these impact intermolecular coupling, and in turn, the optical absorption and emission spectra of OSC films.$^{[8,27]}$

We combine the approach of utilizing the self-assembly properties of soluble small-molecule LC dyads with molecular design strategies from high performance optoelectronic OSCs, namely by combining a donor–acceptor molecular backbone with fluorine (F)-substitution. Donor–acceptor (DA) – or “push–pull” – molecules consist of a combination of alternating electron-deficient and electron-rich building blocks. This design strategy has been applied successfully to selectively tune the frontier molecular orbitals and optical bandgap, as well as improve carrier transport via preferential molecular packing in film.$^{[28]}$ The development of DA molecules has led to high carrier mobilities in organic field effect transistors$^{[3,28]}$ and record power conversion efficiencies in organic photovoltaics.$^{[29,30]}$

Substituting F for hydrogen lowers the energetic position of the molecular frontier orbitals$^{[31]}$ due to the strong electron withdrawing nature of F, resulting in improved chemical and thermal stability.$^{[12–36]}$ Further, F interactions with neighboring carbon, sulfur, and hydrogen atoms$^{[32]}$ promote increased molecular planarity$^{[37]}$ leading to face-on stacking, smaller intermolecular distances$^{[38]}$ and increased $\pi-\pi$ interactions$^{[39]}$ thereby increasing carrier mobility.$^{[8,35,40]}$ In this respect, fluorination of benzothiadiazole (BT),$^{[41]}$ the most widely employed acceptor building block for high performance DA semiconductors,$^{[42]}$ combines the advantages of DA design with the advantages of F-substitution. F-substitution offers a promising handle to control the molecular packing of DA molecules to increase carrier mobility, especially electron mobility,$^{[43]}$ and even to achieve balanced ambipolar transport in OSC films.$^{[43–45]}$

To date, most studies have focused on the impact of F-substitution on molecular morphology$^{[38]}$ and device performance.$^{[33,34,40,41,46]}$ However, the position of the F-substitution on the ultrafast distribution of electron density as well as vibronic dynamics on the BT molecular backbone has not yet been investigated. This is of crucial importance for the nature and evolution of excited states, as well as electron transfer processes that govern the performance of optoelectronic devices. For example, lasing thresholds and photoluminescence (PL) lifetimes of high-performance copolymers with BT acceptor units are governed by their precise site-specific molecular architecture.$^{[47]}$ Furthermore, polaron-pair formation yields and recombinination rates in conjugated DA polymers strongly depend on both the difference in the DA electron affinity as well as the DA arrangement.$^{[48]}$ In addition, the molecule’s environment influences energy and charge transfer between the D and A units.$^{[49]}$ In the light of these previous reports, it appears promising to utilize the precise location of the F-substitution as an additional knob for controlling excited-state lifetimes. Surprisingly, however, this molecular engineering avenue remains largely unexplored to date.

In the following section, we employ a combination of molecular design strategies which have not yet been widely adopted in the design of OSC for optoelectronics.$^{[40,50]}$ or applied for the development of ambipolar materials. Specifically, we synthesize soluble, F-substituted DAD dyes that consist of a central BT acceptor unit sandwiched by two thiophene acceptor units. The dyes form crystalline films at room temperature and LC phases at elevated temperatures. We then study how varying the position of one of the two F-substitutions influences the position of the frontier molecular orbitals, the distribution of electrostatic potential along the molecular backbone, and the emergence of LC phases in the OSC films. To investigate how the position of the F-substitution influences electronic and vibronic dynamics on the molecular backbone on ultrafast timescales, we then perform state-of-the-art ultrafast vibrational and electronic spectroscopy, specifically femtosecond stimulated Raman spectroscopy (FSRS), to the best of our knowledge for the first time on such compounds, as well as transient absorption (TA) spectroscopy. Finally, we compare these ultrafast studies with steady-state optical spectroscopy, theoretical modeling, structural studies, and electrical characterization. We show that variations in the position of the F-substitution on the dyes have little impact on properties and dynamics at the molecular scale; however, the resulting variations in intermolecular interactions and packing in the OSC film are stark, and these effects can be exploited to achieve ambipolar transport. Closing the gap between properties at the molecular scale, ultrafast dynamics, and steady-state optical and electrical properties in films is a crucial step toward new insights for dedicated molecular design.

2. Results

2.1. Molecular Structure and Liquid Crystalline Properties

We synthesized the F-substituted BT derivatives shown in Figure 1a, 4,7-bis[5-[4-(3-ethylheptyl)-2,3-difluorophenyl]-2-thienyl]-2,1,3-benzothiadiazole (2,3-FFPTB), and Figure 1b, 4,7-bis[5-[4-(3-ethylheptyl)-2,6-difluorophenyl]-2-thienyl]-2,1,3-benzothiadiazole (2,6-FFPTB). A double F-substitution was applied on the lateral
benzene rings on both molecules. For 2,3-FFPTB, the H was substituted for F at positions 2 and 3, while for 2,6-FFPTB, the F-substitution was performed at positions 2 and 6.

Figure 1c,d displays results from density functional theory (DFT) on the variation in electrostatic potential along the molecular backbone for 2,3-FFPTB and 2,6-FFPTB, respectively: in 2,3-FFPTB, the electrostatic potential on the lateral benzene rings at the location of the double F-substitution is increased (shown in red), and decreased correspondingly (shown in blue) opposite to the F-substitution. By contrast, the variation in the electrostatic potential along the 2,6-FFPTB backbone is less pronounced.

These differences in local electronic density of both LC dyes lead to stark differences in the molecular packing. Both dyes form crystalline films at room temperature and isotropic melts at temperatures above 130 °C (see Table S1 in the Supporting Information). But, 2,3-FFPTB demonstrates two LC smectic mesophases at slightly elevated temperatures (Crystalline → Smectic I at 103 °C, Smectic I → Smectic II at 116 °C, and Smectic II → Isotropic at 141 °C), while 2,6-FFPTB does not demonstrate any ordered LC mesophases (Crystalline → Isotropic at 131 °C). From the perspective of electronic applications, such soluble small molecules that form crystalline films at room temperature, but display LC properties at elevated temperatures, are interesting because they combine the advantages of good chemical purity, molecular self-assembly and self-healing, high carrier mobility, and excellent structural and thermal durability.

2.2. Optical Properties of FFPTB in Solution

For 2,3-FFPTB, Figure 2a depicts the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), computed at the DFT level of theory. The HOMO is highly delocalized over the FFPTB backbone, while the LUMO is localized on the central BT unit. As shown in Figure S17 (Supporting Information), 2,6-FFPTB features nearly identical spatial distributions and energetic positions of the HOMO and LUMO levels. The computed bandgap of 2.4 eV is the same for both molecules (within about 0.1 eV) and agrees well with the experimentally measured optical absorption and PL spectra shown in Figure 2b. Both molecules exhibit one visible (2.1–3.1 eV) and one UV (3.1–4.1 eV) absorption peak, and peaks are minimally redshifted in the 2,3-FFPTB spectra compared to the 2,6-FFPTB spectra. The PL spectra feature one broad band between 1.4 and 2.4 eV.

Figure 3a depicts the TA spectrum of 2,3-FFPTB in chloroform, after photoexcitation at 2.48 eV with a fluence of ≈3 × 10¹⁴ photons cm⁻² per pulse. The three predominant features are a quasi-instantaneous (<81 fs, instrument-response-limited) appearance of a negative absorption change in the visible (at about 2.1–2.9 eV) as well as a second negative band (at about 1.7–2.3 eV) on top of a broad positive background toward the red (from about 2.5 eV and extending down to about 1.2 eV, see also Figure 3b). We attribute these features to the ground-state bleach (GSB), stimulated emission (SE), and excited-state absorption (ESA) bands, respectively, based on the steady-state absorption and PL spectra shown in Figure 2b.

To capture the complete set of spectral and dynamic features, we fit the entire time- and wavelength-dependent TA data set of 2,3-FFPTB with the target-analysis scheme depicted in Figure 3b (see the Supporting Information for details of the fitting procedure). A minimum of five excited states were necessary to adequately describe the data, whereby a sequential evolution from state 1 to state 5 and subsequently to the ground state competes with recombination from states 2 and 4 to the ground state (GS). The corresponding evolution of the species...
associated difference spectra (SADS) is shown in Figure 3c, with fingerprints of the GSB, SE, and ESA bands in each of the five states.

In the rapid decay between states 1 and 2 (with a rate $k_{12} = 8.8 \text{ ps}^{-1}$), the GSB minimum rapidly shifts to the blue (from $\approx 2.45$ to $\approx 2.6 \text{ eV}$), the SE band shifts to the red (from $\approx 2.1$ to $\approx 2.0 \text{ eV}$) and partially quenches, while the ESA band acquires a strong and broad tail to the blue (overlapping with the SE band between $\approx 1.7$ and $2.3 \text{ eV}$). Typical processes on such ultrafast timescales in molecules may be due to i) internal conversion (from a higher-energy excited state $S_n$ to the lowest-energy singlet state $S_1$), ii) intersystem crossing (between the singlet state $S_1$ and triplet state $T_1$), iii) intramolecular vibrational relaxation, or iv) structural relaxations. However, we exclude i) internal conversion, due to the employed pump at the red edge of the $S_0 \rightarrow S_1$ (HOMO–LUMO) transition, and ii) significant contributions of intersystem crossing, due to the high PL quantum yield (QY). By contrast, iii) intramolecular vibrational relaxation may occur due to the (partial) charge-transfer character of the excited state with a HOMO delocalized along the molecule backbone and the LUMO localized on the BT acceptor unit (see Figure 2a). Such a partial charge-transfer character may also lead to iv) significant reorganization after photoexcitation, whereby the shifted equilibrium configuration of the excited state is reached via sub-picosecond structural relaxation via the solvent and via conformational changes of the molecule, including changes in planarity.[54]

A shift in the equilibrium configuration of ground and excited state is also fully consistent with the significant Stokes shift between steady-state absorption and PL of our molecules.

Figure 2. a) Computed HOMO and LUMO levels (shown for 2,3-FFPTB) at the DFT level of theory, and b) normalized absorption (thick lines) and photoluminescence (thin lines) spectra of 2,3-FFPTB (in red) and 2,6-FFPTB (in blue).

Figure 3. a) TA spectra of 2,3-FFPTB in chloroform, as a function of probe energy and time delay to a 2.48 eV (500 nm) pump pulse; TA changes (scaled by a factor 1000) are depicted as false colors; for reference, the steady-state absorption (dark gray line) and PL (light gray line) spectra are given in the top panel. A dashed white, gray, and black line serve as guide to the eye for the spectral shifts of GSB, SE, and ESA, respectively. b) Target analysis kinetic scheme illustrating the decay (and associated rate constants) of the initial excited state (1) via a series of excited states (2, 3, 4, and 5) back to the ground state. c) Species associated difference spectra (SADS) for excited states 1–5, with the same color coding as in subfigure (b). The spectral region of the pump is indicated with a gray bar. d–f) TA spectrum, kinetic scheme, and SADS, respectively, for 2,6-FFPTB.
(see Figure 2b) and other BT dyes[55] as well as the broad and featureless absorption and emission bands. Furthermore, our assignment of the observed spectral shifts to ultrafast vibrational relaxation is in line with blueshifted ESA bands during relaxation.[49,54] The initial GSB (redshifted with respect to the steady-state absorption band) and the initial SE (blueshifted with respect to the steady-state PL band) reflect a reduced Stokes shift and narrower bands immediately after photoexcitation. Hence, the (partial) charge-transfer state is not instantaneous and only reached after vibrational relaxation and structural reorganizations.

The subsequent excited-state evolution (with rates $k_{23} = 2.4 \, \text{ps}^{-1}$ and $k_{45} = 0.24 \, \text{ps}^{-1}$, respectively) yields continued spectral shifts and an ESA onset even further to the blue. We tentatively attribute these features to reorganizations involving the chloroform solvent, as the timescales are consistent with collision-induced and orientational polarizability relaxation in chloroform.[56] Competing with the transition $2 \rightarrow 3$, we identify an ultrafast nonradiative recombination channel (with a rate $k_{20} = 2.0 \, \text{ps}^{-1}$) back to the ground state, likely originating from partial dye aggregation. The remaining sequential processes (with rates $k_{34} = 1.3 \, \text{ns}^{-1}$ and $k_{59} = 0.11 \, \text{ns}^{-1}$) describe the radiative relaxation cascade back to the ground state on a timescale similar to related BT dyes.[55] Finally, we find that the inclusion of a slow recombination channel to the ground state (with a rate $k_{60} = 0.70 \, \text{ns}^{-1}$) further improves the fit, which may be ascribed to either rate heterogeneity and/or charge-transfer-mediated quenching via diffusive processes in the solvent.[57,58] It remains to be noted that both nonradiative rates ($k_{20}$ and $k_{59}$) do not represent intrinsic loss channels, as they can essentially be switched off via sufficient dilution, manifested in the high (92%) PL QY of dilute solutions, see Figure S16 in the Supporting Information.

The TA spectra of 2,6-FFPTB can be modeled with a kinetic scheme (see Figure 3e) identical to the one for 2,3-FFPTB (see Figure 3b), with a slightly faster initial relaxation ($k_{12} = 14 \, \text{ps}^{-1}$ and $k_{23} = 2.7 \, \text{ps}^{-1}$, respectively) and a slightly slower first recombination channel ($k_{34} = 1.7 \, \text{ps}^{-1}$). Importantly, the similarity of the ultrafast excited-state dynamics as well as an identical near-degeneracy in PL QY in 2,6-FFPTB and 2,3-FFPTB (see Figure S15 in the Supporting Information) establishes that differences in F-substitution location do not significantly alter the ultrafast optical properties.

2.3. Vibrational Response of FFPTB in Solution

Reports on the vibrational spectra of F-substituted BT[34] and benzodithiophene[59] derivatives have shown that F, which is more electronegative and massive than H, influences local molecular bond length as well as molecular torsion. To test this, we performed FSRS on the FFPTB derivatives. This variant of ultrafast vibrational spectroscopy may i) verify our assignments from the TA data, and ii) probe differences in the nuclear dynamics and vibronic couplings as a function of F-substitution. The background and details to the FSRS experiment can be found in the Supporting Information along with the theoretically calculated and experimentally measured spontaneous Raman spectra of the FFPTB derivatives. Briefly, a first laser pulse photoexcites the LC dyes at 3.1 eV; subsequently, two additional laser pulses probe changes to the stimulated Raman spectrum, as a function of time delay after the photoexcitation. The bottom panel in Figure 4b shows the ground-state stimulated Raman spectra of 2,3-FFPTB (gray solid line) and 2,6-FFPTB (gray dashed line), and Figure S10 (Supporting Information) shows the full transient stimulated Raman spectrum data set for both LC dyes.

To extract the underlying spectral and kinetic signatures, we fit the FSRS data sets in Figure S11 (Supporting Information) with a global analysis scheme using a sequential decay model with four components (see Figure 4a). We note that the 4-component FSRS model is essentially identical to the 5-component target analysis scheme employed for the TA data (see Figure 3b,e), except for lumping the two sub-picosecond TA components into one sub-picosecond FSRS component. The latter was motivated by the slightly longer instrument response function (IRF) of the FSRS experiment (200 fs in FSRS vs 81 fs in TA), which precluded resolution of the fastest ($\approx 10 \, \text{ps}^{-1}$) component. For both FFPTB dyes, Figure 4b displays the ground-state Raman spectrum (bottom panel) as well as the FSRS fit (top panel), with the first, second, third, and fourth spectral components depicted by black, red, blue, and green

![Figure 4](image-url) Global analysis of FSR spectra. a) Sequential scheme with four components; IRF denotes the instrument response function. b) Top panel: fitted FSR spectra of 2,3-FFPTB (solid lines) and 2,6-FFPTB (dotted lines) with the first, second, third, and fourth spectral components depicted by black, red, blue, and green lines, respectively; for clarity, the FSR components are vertically stacked; the corresponding decay rates for 2,3-FFPTB and 2,6-FFPTB are shown to the left and right, respectively. Modes assigned to the BT donor and acceptor moieties as well as the benzene ring are indicated by tags. Bottom panel: ground-state (GS) Raman gain spectra of 2,3-FFPTB (gray solid line) and 2,6-FFPTB (gray dotted lines).
lines, respectively. The initial decay rates are quasi-identical for 2,6-FFPBT and 2,3-FFPBT ($k_{12} = 1.9$ ps$^{-1}$ and $k_{13} = 0.21$ ps$^{-1}$ in both cases). At later times, the decay is slightly slower in 2,6-FFPBT ($k_{14} = 4.2$ ns$^{-1}$ and $\tau_0 = 0.43$ ns$^{-1}$, respectively) compared to 2,3-FFPBT ($k_{14} = 6.1$ ns$^{-1}$ and $k_{0} = 0.51$ ns$^{-1}$, respectively).

For the 2,3-FFPTB dye, all spectral components (1–4) present a small bleach of the ground-state Raman spectrum in the probed spectral region (i.e., between ~1300 and 1800 cm$^{-1}$), possibly due to a slight photoinduced reduction of the scattering cross-section. Furthermore, for the spectral components 2–4, modes shared between donor and benzene ring (at about 1450 and 1500 cm$^{-1}$) exhibit a blue shift, while a new broad peak appears in between the modes associated to the acceptor (at about 1550 cm$^{-1}$) and benzene ring (at about 1635 cm$^{-1}$). For component 1, i.e., before vibrational relaxation and structural rearrangements, more complicated spectra are observed involving changes also in relative peak intensities. In summary, the excited-state Raman spectra at later times (>1 ps) are similar to the ground spectra, yet modes involving donor and acceptor moieties are slightly shifted, consistent with photoinduced formation of a charge-transfer state.

The ultrafast Raman spectra of 2,6-FFPTB reproduce the excited-state dynamics of the 2,3-FFPTB dye. A minor difference is found at ~1640 cm$^{-1}$ where only 2,6-FFPTB exhibits a bleach. Since this band is attributed to a C–C ring stretch vibration involving the C atom bound to F, this suggests that the excited-state charge distribution reduces the Raman scattering cross-section in 2,6-FFPTB (with F-substituted at either side of the benzene ring) but not in 2,3-FFPTB (with both F-substituted at the same side).

We conclude that the difference in position of the F-substitution on 2,3-FFPTB versus 2,6-FFPTB does not result in any significant differences in the optical properties of the molecules. First, 2,3-FFPTB demonstrates a slightly smaller (by 0.01 eV) optical bandgap than 2,6-FFPTB, as evidenced by the experimental absorption and emission spectra (Figure 2b), in line with the same small differences in the computed HOMO–LUMO gaps (Figure S17, Supporting Information). The spontaneous ground-state Raman spectra indicate that changing the position of the F-substitution changes the symmetry of Raman modes associated with the benzene ring, leading to a change in peak intensity. But we do not observe signatures in the spectra that indicate any differences in molecular conformation or planarity between 2,3-FFPTB and 2,6-FFPTB samples. Second, the analysis of the ultrafast TA and FSRS data yield quasi-identical spectral signatures in both dyes with only slight variation in the kinetics. Taken together, our data suggest that the differences in F-substitution do not substantially affect the steady-state optical properties, the ultrafast dynamics of optically excited states, or the vibronic coupling. This is an important result for material design, as F-substitution is generally an interesting strategy toward selectively tuning the energetics of the frontier molecular orbitals, improving molecular stability, and controlling molecular packing in film. The F-substitution should, therefore, not result in undesired changes in the optical properties, such as shifting of the absorption/emission maxima, or a decrease in the PL QY.

By contrast, in a film environment, electronic coupling between molecular neighbors is associated with gas-to-crystal shifts, resulting in changes in the optical properties (see also Figure S16 in the Supporting Information). These shifts are determined by the molecular packing in a film. In the next section, we show how, despite very comparable optical properties of the FFPTB molecules, the LC properties, specifically the ordered LC phases at elevated temperatures, of 2,3-FFPTB can be exploited to tune electrical transport, and achieve balanced electron and hole transport in FFPTB films.

### 2.4. Crystal Structure and Molecular Packing in FFPTB Films

The unit cells and lattice parameters of the two FFPTB derivatives were determined from X-ray diffraction (XRD) measurements on single crystals. While 2,3-FFPTB forms a triclinic cell with two molecules per unit cell (volume of 2042.1 Å$^3$), 2,6-FFPTB forms a monoclinic unit cell with four molecules per unit cell (volume of 4151.9 Å$^3$). The structures of the unit cells, as well as the lattice parameters are included in Figure S2 (Supporting Information). From the unit cells of the FFPTB crystals, we were able to calculate the charge-transfer integrals between the nearest neighbor molecules. Figure 5 shows the nearest molecular neighbors in the a) 2,3-FFPTB and the b) 2,6-FFPTB unit cells, respectively.

According to Marcus theory, the rate of electron transfer $k_{et}$ between the molecular pair A and B is given as

$$k_{et} = \frac{2\pi}{\hbar} |J|^2 \frac{1}{\sqrt{4\pi\lambda k T}} \exp\left[-\frac{\lambda}{4kT}\right]$$

where $\lambda$ is the reorganization energy, $J$ is the charge-transfer integral of the pair A and B, $\hbar$ is the Planck’s constant, $k$ is the Boltzmann constant, and $T$ is the temperature. Based on this approach, we calculated the values of $J$ for the molecular pairs in Figure 5 for hole ($J_h$) and electron ($J_e$) transfer, and these values are summarized in Table 1.

The rod-like nature of the FFPTB molecule, as well as the anisotropic stacking in film, results in differences in the values of $J$ between adjacent molecules. Recent theoretical studies have highlighted the importance of considering the 3D distribution of $J$ values between all molecular neighbors (not just in the direction of transport) to achieve high mobility values in OSC solids. This suggests that even slight modifications to intermolecular coupling in the film induced by annealing in LC mesophases may have a large impact on carrier mobility in such anisotropic films.

From a comparison of the XRD patterns taken from FFPTB single crystals and XRD patterns taken from FFPTB spin cast films, we conclude that crystallites in 2,3-FFPTB films orient with the c-axis perpendicular to the substrate (Figure S3, Supporting Information), while crystallites in 2,6-FFPTB films oriented with the a-axis perpendicular to the substrate (Figure S4, Supporting Information). To investigate the influence of thermal annealing in LC mesophases on molecular packing in FFPTB films, we performed in situ XRD measurements during a heating and cooling cycle, see the Supporting Information. Figure 6 shows the peak position ($2\theta$) and the full width at half maximum (FWHM) of the (001) peak extracted from the XRD patterns during heating (red) and subsequently cooling (blue).
the a) 2,3-FFPTB and b) 2,6-FFPTB films. The arrows indicate the scan direction of the heating and cooling cycles, while the dashed lines in Figure 6a indicate the Crystalline $\rightarrow$ Smectic I and the Smectic I $\rightarrow$ Smectic II transitions extracted from differential scanning calorimetry and on a polarization microscope with a hot stage. Both the 2,3-FFPTB and 2,6-FFPTB samples were heated up to 160 °C and subsequently cooled, i.e., both were measured at temperatures above the transition to the isotropic melt.

For the 2,3-FFPTB films, we observe thermal hysteresis in the 2$\theta$ peak position during the heating–cooling cycle, in particular at the temperatures correlated with the transitions through the smectic phases. Before heating, the XRD pattern from the as-spun film reveals a well-defined diffraction peak at 2$\theta = 3.4 \pm 0.1$, corresponding to a lattice constant of about 26 Å. During heating, the peak position shifts to lower 2$\theta$ values (i.e., the lattice constant increases). The increase in lattice constant with temperature is minimal until the film is heated above 116 °C (Smectic I $\rightarrow$ Smectic II transition). At 130 °C, 2$\theta = 2.8 \pm 0.1$ and the lattice constant is about 32 Å. Above 130 °C, no diffraction peaks are found in the pattern (Smectic II $\rightarrow$ Isotropic transition). During cooling, the 2$\theta$ values remain relatively constant with decreasing temperature until the temperature is below the Smectic I $\rightarrow$ Crystalline transition. During

| Pair 1 | Pair 2 | Pair 3 |
|-------|-------|-------|
| 2,3-FFPTB | | |
| $J_+ [\text{meV}]$ | 107 | 107 | 5 |
| $J_- [\text{meV}]$ | 36 | 96 | 20 |
| 2,6-FFPTB | | |
| $J_+ [\text{meV}]$ | 62 | 76 | 9 |
| $J_- [\text{meV}]$ | 41 | 70 | 19 |

Figure 5. The three nearest molecular neighbor pairs in the a) 2,3-FFPTB and b) 2,6-FFPTB unit cells.

Figure 6. Peak position (2$\theta$) and FWHM extracted from in situ XRD patterns of a) 2,3-FFPTB and b) 2,6-FFPTB while heating (red symbols) and subsequently cooling (blue symbols) the films. The arrows indicate the direction of the heating–cooling cycle.
heating, the FWHM of the peak decreases with temperature. Interestingly, the FWHM values are slightly higher during the cooling leg than the heating leg of the cycle. However, the start and end values of the full heating–cooling cycle (at 25 °C) are almost identical for both 2θ position and FWHM.

2,6-FFPTB films also demonstrate a decrease in the peak position (2θ = 4.6 ± 0.1 at 25 °C to 2θ = 4.5 ± 0.1 at 120 °C corresponding to an increase in lattice spacing from about 19.3 to 19.8 Å) during heating, although we note that the change is considerably less than that observed in the 2,3-FFPTB sample. Further, in contrast to the 2,3-FFPTB sample, the 2θ peak position shows negligible hysteresis during the heating–cooling cycle, while the FWHM of the peak decreases during heating, and does not recover during cooling. As a result, the FWHM is considerably lower at the end of the measurement.

The decrease in lattice spacing indicates a decrease in the distance between the nearest neighbors, i.e., an increase in the transfer integral values. Peak narrowing, on the other hand, is correlated with decreased disorder effects such as crystal defects and lattice strain. The hysteresis observed in the XRD data from the 2,3-FFPTB sample in the temperature range of the Smectic I and Smectic II phases therefore indicate local variations in molecular packing. Donor–acceptor dyes such as FFPTB are characterized by a nonhomogeneous distribution of electron density along the molecular backbone (Figure 2a). Therefore, such changes in the nearest neighbor coupling may be expected to have a dramatic impact on the optical and electrical properties of the OSC film. These effects must be considered for smart design of LC OSC molecules and reproducible fabrication of the OSC films for optoelectronic applications.

2.5. Optical and Electrical Properties of Annealed FFPTB Films

Annealing of LC OSC films has been reported to increase the carrier mobility of the OSC films at room temperature, as molecular ordering in LC phases persists when the OSC films are cooled back to room temperature.[7,8,61,62] Indeed, we observe that the grain size of the crystalline domains increases in annealed FFPTB films, as demonstrated by the polarized optical microscopy images (Supporting Information). In addition to increased grain size, annealing can also induce microscopic changes in molecular ordering (as observed in the in situ XRD measurements in Figure 6). To this end, we next studied the structural, optical, and electrical properties of annealed FFPTB films.

We note that all films were measured at room temperature in the crystalline phase; in brackets, we indicate the LC phase that corresponds to the annealing temperature. Specifically, we prepared the as-spun 2,3-FFPTB films (Crystalline), and 2,3-FFPTB films annealed at 80 °C (Crystalline), 105 °C (Smectic I), 120 °C (Smectic II), and 160 °C (Isotropic), and the as-spun 2,6-FFPTB films (Crystalline), and 2,6-FFPTB films annealed at 120 °C (Crystalline) and 160 °C (Isotropic).

Figure 7a shows the normalized XRD patterns of the as-spun 2,3-FFPTB (dashed), and 2,3-FFPTB films annealed at 80 °C (red), 105 °C (blue), 120 °C (green), and 160 °C (wine). The XRD pattern of the as-spun film demonstrates a prominent peak at 2θ = 3.33°, consistent with the (001) reflex. The peak position depends on the annealing conditions and shifts from 2θ = 3.36° (80 °C), to 2θ = 3.39° (105 °C), to 2θ = 3.42° (120 °C). This corresponds to a slight decrease in lattice spacing from 26.5 Å (as-spun) to 25.8 Å (annealed at 120 °C), 2,3-FFPTB films annealed at 160 °C, on the other hand, show a diffraction peak at 2θ = 3.39 Å, corresponding to an increase in lattice spacing (26.1 Å). The FWHM of the XRD peak is found to be the lowest in 2,3-FFPTB films annealed at 160 °C (0.063), and the highest in 2,3-FFPTB films annealed at 120 °C (0.080). This indicates that 2,3-FFPTB films annealed in the crystalline (80 °C) phase or isotropic melt (160 °C) yield more ordered crystalline domains than films cooled from the smectic phases (105, 120 °C). The annealing-induced broadening and shifting of the diffraction peaks observed in films annealed in the smectic phases is consistent with increased local structural disorder, resulting in lattice strain in the FFPTB crystal.[8] However, films cooled from the smectic phases yield smaller lattice distances, consistent with increased coupling between molecular neighbors in the films.

Figure 7b shows the normalized XRD patterns of 2,6-FFPTB films as-spun (black), annealed at 120 °C (green) and 160 °C (wine). The XRD pattern taken from the as-spun film yields a prominent peak at 2θ = 4.58 (lattice spacing of 19.25 Å) from the (100) reflex. The 2,6-FFPTB film annealed at 120 °C yields an XRD pattern with prominent and narrow peaks. According
to these results, annealing at the Crystalline → Isotropic transition (160 °C) yields the most crystalline 2,6-FFPTB films. In contrast to the 2,3-FFPTB films, annealing the 2,6-FFPTB films results in narrowing of the XRD peaks, but no significant shifting, which is consistent with increased order.

The full XRD patterns for FFPTB can be found in Figures S3 and S4 (Supporting Information). Lower intensity peaks at higher 2θ values are observed in all the FFPTB samples, specifically peaks at 2θ = 23.5°, corresponding to a lattice spacing of d = 3.6 Å. These lattice spacings are consistent with π–π stacking distances. We note that these peaks follow the same trends with annealing as described above. In the case of 2,3-FFPTB films, a peak is observed at around 2θ = 23.5° (d = 3.8 Å) that exhibits broadening and shifting upon annealing. Similarly, in the case of 2,6-FFPTB films, a peak is observed at 2θ ≈ 23.1°. However, in this case, we observe that the peaks narrow with increasing annealing temperature.

Figure 7c,d shows the normalized optical absorption spectra of the same 2,3-FFPTB and 2,6-FFPTB films, respectively. Interestingly, despite differences between both dyes, thermal annealing does not significantly influence the spectral shape. The absorption spectra of 2,3-FFPTB films appear to be blueshifted compared to the absorption of 2,6-FFPTB films. A closer examination of the absorption spectra, however, reveals three features that contribute to the overall absorption (centered around 2.25, 2.5, and 2.6 eV), previously attributed to a combination of vibronic progressions and spatial variations in short-range and long-range order within a film. These three absorption features differ in both films only in the relative intensities, and not in their spectral position. The fact that annealing the FFPTB films does not result in significant changes in the shape or intensity of the absorption spectra is an interesting result for producing LC OSC films with reproducible optical properties.

The carrier mobility was extracted from current–voltage measurements on single carrier diodes (Figures S12 and S13, Supporting Information). In contrast to the optical properties, the carrier mobility of the FFPTB films (Figure 8) varies by several orders of magnitudes upon thermal annealing. In Figure 8a,b, we compare the FWHM of the XRD data from Figure 7 (blue squares) and the hole (μh, black circles) and electron (μe, red stars) mobility values for the 2,3-FFPTB and 2,6-FFPTB films, respectively.

In the case of 2,3-FFPTB, annealing in the smectic phase induces an increase in the FWHM of the XRD peak as compare to films maintained at room temperature, which we attribute to increased local structural disorder in the former film. For 2,6-FFPTB, by contrast, annealing leads to more crystalline order and narrowing of the XRD peak.

We first consider the 2,3-FFPTB films. Interestingly, increased local structural disorder (increase in FWHM) in the films annealed in the smectic phase is correlated with ambipolar transport in these films, μh = μe. This ambipolar transport regime is reached by disparate annealing trends for μh and μe respectively: while μh monotonously increases with increased annealing temperature, μe follows a less obvious trend with annealing conditions. Overall, the values of μh follow a similar trend as the FWHM of the XRD peak, indicating that reduced local disorder improves hole transport. The hole mobility is three orders of magnitude higher in films annealed in the isotropic melt at 160 °C ((2.3 ± 0.3) × 10−4 cm2 V−1 s−1) compared to the as-spun films ((4.7 ± 0.3) × 10−7 cm2 V−1 s−1). Annealing in the crystalline and smectic phases only leads to moderate improvements in μh. On the other hand, μe is the highest in films displaying the highest values of FWHM of the XRD peak (annealed in the smectic phases), i.e., the most local disorder: μe increases by two orders of magnitude when the 2,3-FFPTB film is annealed in the Smectic I phase at 105 °C ((1.6 ± 0.2) × 10−5 cm2 V−1 s−1) compared to 2,3-FFPTB annealed in the crystalline phase at 80 °C ((3.3 ± 0.3) × 10−7 cm2 V−1 s−1). Annealing the 2,3-FFPTB at higher temperatures, i.e., in the Smectic II and Isotropic phases, does not further increase μe. Ambipolar transport, i.e., μe = μh, is achieved upon annealing in the Smectic II phase at 120 °C with μe = (1.8 ± 0.2) × 10−5 cm2 V−1 s−1 and μh = (9.5 ± 0.9) × 10−6 cm2 V−1 s−1, respectively.
By contrast, 2,6-FFPT is predominantly a unipolar hole transporter. The hole mobilities are higher than in 2,3-FFPTB and also increase over two orders of magnitude with annealing, from \((5.1 \pm 0.3) \times 10^{-6} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1} \) (as-spun) to \((6.1 \pm 0.3) \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1} \) (annealed at 160 °C). However, annealing only has a very modest influence on the \(\mu_h\) values, which are consistently 100–100 times lower than the \(\mu_e\) values. The \(\mu_h\) values in 2,6-FFPTB films are also lower than those observed in 2,3-FFPTB films for the same annealing temperature.

We note that these mobility values are consistent with reports from the literature on other F-substituted small-molecule dyes;\(^{40,50}\) however, reports of ambipolar dyes are rare.\(^{[1]}\) We rationalize the tunability of the mobility in the FFPTB films by considering the heterogeneous distribution of electron density along the FFPTB backbone. While the HOMO is delocalized over the molecular backbone, the LUMO is localized on the central BT acceptor unit. This means that hole transport is more robust against local structural defects in the FFPTB crystal than electron transport. By exploiting increased intermolecular interactions in the LC phase, small shifts in the position of molecular neighbors can have a large impact on electron transfer rates, and therefore carrier mobility.\(^{[65]}\) These results are consistent with the shifts and broadening in peaks at \(2\theta = 23.5^\circ\) (3.8 Å) with annealing in the XRD patterns of 2,3-FFPTB films (Figure S3, Supporting Information), that may be related to changes in \(\pi-\pi\) stacking that promote electron mobility. By contrast, narrowing of the peaks at \(2\theta = 23.1^\circ\) in 2,6-FFPTB (Figure S4, Supporting Information) indicates increased ordering, and increased hole mobility. These results show that with dedicated molecular design, such as F-substitution on donor–acceptor moieties, carrier transport can be tuned via molecular packing phenomena, while the optical properties of the molecule and film remain unchanged.

3. Summary

We investigated the influence of a minor molecular modification, i.e., 2,3 versus 2,6 F-substitution in FFPTB donor–acceptor dyes, on several key material properties of general importance in organic semiconductor devices, namely optical absorption and emission, ultrafast excited-state dynamics, ultrafast vibronic response, intermolecular packing, and electron and hole mobilities.

With DFT calculations and absorption measurements in solution, we demonstrate that the variation in the position of the F-substitution does not influence the energetic position or spatial distribution of the HOMO and LUMO levels. Likewise, TA and FSRS spectroscopy, the latter being the first time employed for such a material, reveal no appreciable differences between the ultrafast electronic and vibrational dynamics on the 2,3-FFPTB and 2,6-FFPTB backbones. The insensitivity of the steady-state and ultrafast electronic and vibrational response to F-substitution is an important insight for molecular design, as this indicates the potential to apply dedicated chemical substitution to improve chemical stability and film formation properties, without impacting the optical properties.

In contrast to the electronic and vibrational properties, film formation and charge transport are highly tunable via the location of the F-substitution due to altered electrostatics along the FFPTB backbone. Both 2,3-FFPTB and 2,6-FFPTB molecules form crystalline phases at room temperature, but the 2,3-F-substitution leads to larger differences in the electrostatic potential along the FFPTB backbone, resulting in complex intermolecular interactions and the emergence of liquid crystalline phases at elevated temperatures. By contrast, the 2,6-F-substitution does not demonstrate any liquid crystalline phases. In situ and steady-state XRD measurements reveal an increase in the density of structural defects in the 2,3-FFPTB films when annealed in the Smectic I and Smectic II phases. These defects are attributed to variations in intermolecular distances, that in turn result in variations in spacing and coupling between molecular neighbors. Interestingly, this is also correlated with an increase in electron mobility in the 2,3-FFPTB films, resulting in ambipolar transport in the films when annealed at temperatures corresponding to the Smectic I → Smectic II transition.

We attribute the possibility to independently tune the hole and electron mobilities in 2,3-FFPTB films to the donor–acceptor structure of the molecule, which results in the heterogeneous distribution of electron and hole wavefunctions, in this case, the delocalization of the HOMO along the molecule and the localization of the LUMO on the central BT unit. F-substituted molecules are known to pack in tight, brick-wall motifs with small intermolecular distances. The hole transport is therefore robust against structural defects, while electron mobility may be increased in the case of increased BT interactions between neighboring molecules. By contrast, annealing 2,6-FFPTB does increase crystal grain size and reduce structural defects in the FFPTB film. However, 2,6-FFPT remains predominantly a hole-transporting material, independent of the annealing conditions. Annealing the 2,6-FFPTB samples results in a comparable increase in both hole and electron mobilities, with hole mobility values remaining consistently higher than electron mobility values. These results demonstrate that electrical transport is ultimately determined by intermolecular packing and interactions in OCS films.

In conclusion, we have shown that the precise location of F-substitution represents an interesting design strategy for soluble small-molecule dyes that form crystalline films at room temperature, but display liquid crystalline phases at elevated temperature. Specifically, thermal annealing at various liquid crystalline phases allows to fabricate films of well-controlled morphology, intermolecular interactions, and charge transport properties, without compromising optical properties. Using a broad set of steady-state and ultrafast experimental methods as well as DFT calculations, we rationalize the dissimilar effect of F-substitution on structure and charge transport on the one side, and electronic and vibrational properties on the other side: F-substitution strongly alters electrostatics along the molecular backbone, thereby affecting structure and charge transport, ultimately enabling ambipolar transport of electrons and holes, while it hardly alters the spatial location and energies of frontier molecular orbitals, explaining the insensitivity of the optical and vibrational responses. Our design strategy, accounting for electrostatics and energetics in FFPTB upon F-substitution dyes, is translatable to similar material systems in organic optoelectronics and, hence, will help enable the design and fabrication.
of highly ordered organic films with predictable optoelectronic response and good thermal and structural integrity.

4. Experimental Section

Preparation of FFPTB Thin Films: Class substrates (for optical and XRD measurements) and glass coated with indium tin oxide (ITO) (for electrical measurements) were used. The ITO substrates were patterned and etched in hydrochloric acid before cleaning steps. All substrates were cleaned before use in detergent and rinsed with deionized water, then subsequently cleaned for 10 min in acetone, 2-propanol, deionized water, and ethanol using an ultrasonic bath. Thereafter, the substrates were dried under nitrogen flow, and treated for 15 min with an oxygen plasma. The substrates were then brought into a nitrogen filled glove box.

Preparations of the FFPTB solutions and films were performed in an inert nitrogen atmosphere. Solutions were prepared by dissolving 20 mg of FFPTB in 1 mL of chloroform (CHCl$_3$) and then left to stir overnight. The films were formed by spin coating the solution onto precleaned substrates. Layer thicknesses ranged between 170 and 230 nm and were measured with a Veeco DEKTAK 6M, Stylus Profiler equipped with a camera.

Preparation of FFPTB Diodes: Hole-only diodes were prepared with the following architectures: ITO/poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT-PSS)/FFPTB/MoO$_3$/Ag. For the hole-only devices, PEDOT-PSS was spun on the cleaned ITO substrates at 3500 rpm for 30 s (spin coater model WS-650M7-23NPPB) and baked at 140 °C for 10 min in an oven.

Electron-only diodes were prepared with the following architectures: ITO/poly[(9,9-bis(3-((N,N-dimethylamino)propyl)-2,7-fluorene)-alt-2,7-(9,9-dioctylfluorene)] (PFN)/FFPTB/Ca/Al. A PFN interlayer dissolved in chloroform (CHCl$_3$) and then left to stir overnight. The probe beam was sent through a CaF$_2$ plate for supercontinuum white-light generation and directed to a prism spectograph with a scientific CCD camera (Entwicklungsbüro Streising). Liquid crystalline dyes in chloroform (20 mg mL$^{-1}$) were filled in a 2 mm quartz cuvette (Hellma QS) and mounted in a homebuilt vibrating sample holder to avoid irradiation damage during experiments. The (FWHM) diameters of the pump and the probe beams at the sample position were 350 and 75 µm, respectively. TA kinetics were obtained by delaying the pump with respect to the probe pulse, with an instrument response function of 80 fs, estimated from global analysis.

FSRS measurements were performed on the same solutions and using the same oscillator and regenerative amplifier (COHERENT Libra) as in TA. Importantly, baseline-free FSRS data were obtained via the watermarking procedure introduced previously.[66,67] The pump beam was frequency-doubled to 400 nm in order to serve as the “actinic pump;” the probe beam was further split into a “Raman probe” (spectrally broadened by supercontinuum white-light generation via a sapphire crystal, about 600–1100 nm) and a “Raman pump” (800 nm). To obtain stimulated Raman spectra, the Raman pump and Raman probe were spatiotemporally overlapped at the sample position and the probe light was detected via a grating spectograph (Acton SpectraPro SP-2500, Princeton Instruments), which was connected to a scientific CCD camera (Entwicklungsbüro Streising). Time-dependent stimulated Raman spectra were obtained by delaying the actinic pump beam. The obtained spectral resolution was about 10 cm$^{-1}$ and the instrument response was 200 fs, estimated from global analysis. The pulse energies of Raman probe, Raman pump, and actinic pump were about 20, 3000, and 380 nJ, respectively, with (FWHM) beam diameters of 100, 100, and 350 µm, respectively.

DFT Calculations: The HOMO and LUMO energy levels for the relaxed structures of 2,3-FFPTB and 2,6-FFPTB were calculated using Gaussian 09[68] on the B3LYP/6-311+G(d,p)/B3LYP/6-31G(d) level of theory.[69] The optimized geometries were verified to be minimum structures by frequency analysis: they showed only positive eigenfrequencies.

The geometries of the pairs were extracted out of the crystal structures using Mercury CSD 2.0.[70] The orbital energies were obtained for each pair by a single point calculation on the B3LYP/6-311+G(d,p) level of theory. The corresponding transfer integrals were $J_{+} = (E_{\text{HOMO}} - E_{\text{HOMO-1}})/2$ for the hole mobility and $J_{-} = (E_{\text{LUMO+1}} - E_{\text{LUMO}})/2$ for the electron mobility.[71,72]

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.
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Conflict of Interest
The authors declare no conflict of interest.

Data Availability Statement
Research data are not shared.

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