

Quasi Temperature Independent Electron Mobility in Hexagonal Columnar Mesophases of an H-Bonded Benzotristhiophene Derivative

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Reported here are the unique properties of N,N',N''-(3,4,5-tridodecyloxyphenyl)benzo[b,b', b"]tristhiophene-2,2',2"-tricarboxamide **3** as a new H-bonded discotic liquid crystal. Polarized optical microscopy and thermal analysis as well as variable temperature IR spectroscopy and X-ray diffraction confirm the presence of two thermotropic H-bonded hexagonal columnar mesophases that cover a temperature range from <-50 to 280 °C. Intermediate lyotropic mesophases of the highly viscous material aid the alignment of the hexagonal columnar mesophases, which is essential for a detailed structural characterization and applications. Solutions of 3 in heptane at concentrations as low as 1 wt % display isotropic organo-gel phases that consist of H-bonded networks of 3 but do not contain columnar stacks. 2D-X-ray diffraction studies on aligned samples of the thermotropic hexagonal columnar mesophases and DFT calculations on a tetramer of 3 reveal a helical columnar stacking of the individual benzotristhiophene units. Charge carrier mobility measured by time-resolved microwave conductivity is about $0.02 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ in both hexagonal columnar mesophases and quasi temperature independent even across the phase transition between the two mesophases. The temperature independence is explained by the interrelation between stacking distance and mutual rotation because of the persistent intracolumnar H-bonds between amide groups. Half-life of the charge carriers, on the other hand, drastically increases in the low temperature hexagonal columnar mesophase, which is most likely a result of changing molecular dynamic and conformational states of the side chains. DFT calculations of the frontier orbitals show that the benzotristhiophene core is the sole contributor to the LUMO but does not contribute to the HOMO, whereas the trialkoxyaniline groups are the sole contributors to the HOMO. This suggests that the observed combined mobility is that of electrons alone because no hole transport is expected to occur between trialkoxyaniline groups that are spaced apart by more than 4 Å. Indeed, an electron mobility of 2×10^{-3} cm² V⁻¹ s⁻¹ but no transient signal for hole transport is obtained by timeof-flight charge carrier mobility measurements on a multi domain sample of 3.

Introduction

Self-organized columnar stacks of aromatic compounds such as discotic liquid crystals $(DLCs)^{1,2}$ and polyaromatic dendrons³ are an emerging class of organic semiconductors. Intrinsic charge carrier mobility values above 10^{-1} cm² V⁻¹ s⁻¹ have been demonstrated in bulk samples and along the columnar stacks of aligned monodomains.^{2,4} In addition to efficient charge transport and the advantages generic to organic semiconductors, such as low temperature solution processing and synthetically adjustable properties, DLCs promise an important capability of self-healing and can be used in the formation of highly anisotropic materials.

Two important limitations have hampered the broader appeal of columnar liquid crystalline materials for organic electronics: 1. the formation of aligned monodomains of the required orientation and size may be challenging;² 2. their electronic and other properties in the liquid crystal phases strongly depend on temperature

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because of changing dynamic at the molecular level and because of multiple phase transitions.⁵ Charge carrier mobility, for example, decreases by a factor of 7 with a temperature increase of only 20 °C in the hexagonal columnar mesophase (Colh) of hexakis(hexylthio)triphenylene and decreases by an order of magnitude at the phase transition from a higher ordered columnar to a less ordered Col_h mesophase.^{6,7}

Charge carrier mobility generally decreases with decreasing order of the mesophases and large steps in declining mobility are observed at phase transitions between higher and lower ordered columnar mesophases upon heating. A lesser dependence of mobility on temperature is generally observed within the temperature range of one mesophase although observed changes largely vary with the types of materials and mesophases. A decrease in charge carrier mobility with increasing temperature has been observed in the Col_b phases of most triphenylene based discotics,6,8 although temperature independent mobility values have also been reported.9 In contrast, a small increase in mobility is observed in the Col_h phases of many discotic phthalocyanines.^{7,10}

Interpretation and comparison of these results is complex because different experimental techniques have been used, such as time-resolved microwave conductivity (TRMC) and time-of-flight photoconductivity, and the temperature dependence is not only affected by changing intermolecular electronic interactions but also the charge transport mechanism as well as the number and types of defects in the discotic material.¹¹ However, changing

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intermolecular electronic interactions are most likely the dominant source of temperature dependence of charge carrier mobility in columnar mesophases, especially when mobility is measured by TRMC that provides intrinsic (short-range) values. This assumption is supported by the fact that charge carrier mobility in many higher ordered discotic columnar mesophases (e.g., helical and plastic columnar mesophases) is rather temperature independent because molecular motions are much more restricted than in conventional columnar mesophases.7,12

A quantum chemical molecular description of the dependence of charge carrier mobility on intermolecular electronic interactions based on the Markus theory has recently been provided by several groups.^{13,14} The theory predicts an increase in hopping rate (charge carrier mobility) with increasing transfer integral and decreasing reorganization energy. The transfer integral, which is a function of the overlap of frontier orbitals of adjacent molecules, crucially depends on the relative distances, positions, and orientations of stacked aromatic cores. An increase in temperature usually leads to an increase of the stacking distance and translational mobility of discotic molecules that both cause a decrease in transfer integral. Similarly strong effects on the transfer integral have changes in rotational angle of stacked molecules because the area of overlapping π -systems changes with mutual rotation depending on the shape of the aromatic core.

H-bonded stacks of discotic molecules are ideal materials for probing this model because the columnar stacking distance as well as relative orientations and locations are controlled by H-bonds and, consequently, welldefined.^{15–17} Gearba et al. reported an increase in charge carrier mobility and stacking distance with increasing temperature in H-bonded columnar discotic mesophases of hexaazatriphenylene.¹⁵ This counterintuitive experimental finding is likely a result of conformationally coupled changes in the stacking distance and mutual rotation angle governed by H-bonding between amide groups. An increase in stacking distance forces the amide groups more out-of-plane to maintain their ideal H-bonding distance and reduces the rotation angle between adjacent cores. The reduction in rotational angle apparently increases the intermolecular charge-transfer integral more than the increase in stacking distance

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^{*a*} Reagents and conditions: (i) NaOH, H₂O/ethanol, reflux; (ii) SOCl₂, PhMe, reflux; (ii) 3,4,5-tridodecyloxyaniline, NEt₃, THF, reflux.

reduces it, which is in line with theoretical findings. Paraschiv et al. also reported an increase in charge carrier mobility with increasing temperature for an H-bonded columnar DLC, but in their material the amide groups are decoupled from the columnar stacks of triphenylene cores *via* aliphatic spacers.¹⁶ This decoupling improves solubility and mesomorphism but complicates a correlation between the orientation of amide groups and the packing of discotic cores.

We report here quasi temperature independent electron mobility across a phase transition of benzotristhiophene trisphenylamide **3** as a new discotic molecule that has three phenylamide groups directly linked to its core. The observed temperature independence of intrinsic charge carrier mobility is reasoned with two opposing effects that compensate each other, the decrease of charge carrier mobility due to an increase in stacking distance with increasing temperature and the increase in charge carrier mobility due to a decrease in rotation angle. We also demonstrate the application of intermediate lyotropic mesophases to overcome the notoriously difficult processing of H-bonded discotic materials into aligned fibres and thin films.

Results and Discussion

Benzotristhiophene **3** was prepared from the earlier described benzotristhiophene tricarboxylic acid 1,¹⁸ which was converted to the acid chloride **2** and then reacted with 3,4,5-tridodecyloxyaniline to give the final product triamide **3** as a pale yellow solid (Scheme 1). The identity and the purity of the compound were established by ¹H and ¹³C NMR, IR, HRMS, HPLC, and elemental analysis.

Polarized optical microscopy (POM) of compound **3** confirms the presence of a noncrystalline soft anisotropic solid at room temperature that remains highly viscous until it clears into its isotropic liquid at 279 °C. Fan-shaped defect textures characteristic for columnar mesophases are observed only upon cooling from the isotropic liquid at the boundary between the mesophase and the isotropic liquid of a free-standing film (Figure 1).



Figure 1. a) Optical micrograph ($760 \times 360 \,\mu$ m, crossed polarizers) of a free-standing film of **3** at 281 °C with fan-shaped textures at the interface between isotropic (black) and LC areas; b) DSC graph of **3** (heating/cooling at 10 °C/min, enthalpies given for transitions on cooling); c) changes in wavenumbers with temperature of absorption maxima of selected vibrational modes in IR.

Free-standing films of 1 mm diameter are surprisingly stable in the isotropic liquid at 285 °C, which suggests some H-bonding persists even at this temperature.

A high enthalpy of 79 kJ mol⁻¹ for the transition between mesophase and isotropic liquid was determined by differential scanning calorimetry (DSC) and is additional evidence for the persistence of H-bonding over the entire temperature range of the mesophase (Figure 1b). For comparison, enthalpies for transitions between columnar discotic and isotropic liquid phases of discotic

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materials free of intermolecular H-bonds are between $2-20 \text{ kJ mol}^{-1}$.¹⁹ Compound **3** undergoes only one other phase transition at -8.9 °C (onset of peak on cooling) that indicates the formation of a higher ordered solid phase. No decomposition was observed upon heating to 290 °C, and the thermal stability of **3** determined by thermal gravimetric analysis under He is 304 °C (onset of weight loss).

Variable temperature IR measurements ultimately verified the persistence of H-bonds between amide groups over the entire temperature range. Figure 1c shows the changes in peak positions with temperature for the Hbonding sensitive N-H and C=O (amide I) stretching modes and the amide II mode. All values are typical for H-bonded amide groups and vary only slightly with temperature. No abrupt change in wavenumber is observed across the phase transition between 0 and -20 °C.

Variable temperature XRD between -25 and 250 °C reveals the presence of highly ordered hexagonal columnar mesophases over the entire temperature range and across the phase transition at about -10 °C. Analysis of the diffraction patterns was best accomplished by collecting 2D patterns of the Col_h phase aligned in a fiber (Figure 2a) because reflections around $2\theta = 10^{\circ}$ are spatially separate while they overlap in the 1D diffraction patterns. The small angle reflections orthogonal to the long axis of the fiber indicate an alignment of the columnar stacks along the fiber axis, and their relative reciprocal spacing of $1:\sqrt{3}:\sqrt{4}:\sqrt{9}:\sqrt{12}:\sqrt{13}$ is characteristic of a two-dimensional hexagonal columnar arrangement. Both sharpness of the (10) peak and the observation of several higher order reflections indicate high lateral packing order.

Also of high persistence length is the intracolumnar π -stacking because it gives rise to a strong and relatively narrow wide-angle reflection at about 3.5 Å that is persistent over the entire temperature range. This reflection is perpendicular to the reflections of the hexagonal lattice, which verifies an orientation of the benzotristhiopene cores orthogonal to the stacking axis. A circular "halo" at about 4.5 nm confirms an equal distribution of the aliphatic chains around the columnar stacks. Two broad reflections at 9 Å situated at an angle of $34^{\circ} \pm 10$ to the long axis of the fiber are attributed to a periodic packing of the trialkoxyphenyl moieties that form a helical "coil" as proposed in the structural model shown in Figure 3. The determined spacing of about 9 Å corresponds to the distance between phenyl rings of every second benzotristhiopene in a helical stack and is illustrated by an arrow in Figure 3b. Similar reflections have been observed in other helical columnar stacks.²⁰



Figure 2. a) 2D diffraction pattern of a drawn fiber of 3 at 25 °C. The blue line indicates the orientation of the fiber (250 μ m in diameter) and the columnar stacks with regard to the X-ray beam. Intercolumnar diffraction peaks are orthogonal to the fiber. b) Change of *d*-spacings with temperature of the (10) and (001) reflections in the XRD patterns.

Both intra- and intercolumnar spacings increase with increasing temperature as illustrated in Figure 2b for the *d*-spacings of the (10) and (001) reflections. The lattice parameter "a" of the Col_h phase ($a = d_{(10)}/\cos 30$) increases from 33.9 Å at -25 °C to 37.5 Å at 250 °C and the intracolumnar spacing increases from 3.39 Å to 3.57 Å. Both increases appear to be linear within the high temperature Col_h phase, but about 35% of the increases occur at the phase transition between the high and low temperature Col_h phases at about -10 °C. The spacing between the phenyl groups increases by only 0.7 Å over the entire temperature range, and no change in the angular position of these broad reflections is observed.

While an increase in intracolumnar spacing with temperature is common in columnar discotic mesophases, both decreases²¹ and increases^{15,16} have been reported for the intercolumnar spacing, which emphasizes the complex relationship between conformational changes, interdigitation,

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Figure 3. Optimized (B3LYP/3-21G*) structure of a tetramer of tris-(phenylaminocarbonyl)benzotristhiophene (as a model of **3**) in a chiral columnar arrangement seen down the stack (a) and from the side (b). The arrow in (b) indicates the periodic packing of phenyl rings that gives rise to the broad reflection in XRD at 9 Å at an angle of about 34° to the axis of the stack.

and maximum space-filling of alkyl chains. However, an increase in intercolumnar spacing with temperature has been observed in all reported H-bonded Col_{h} phases^{15,16} and other helical discotic LCs.^{20,22}

Density functional theory calculations (B3LYP/3-21G*) were performed on a tetramer²³ of amide 3 without alkoxy substituents to better understand the intermolecular interactions inside the columnar stacks (Figure 3). The B3LYP hybrid density functional has been earlier used to successfully describe columnar arrangements of hydrogen-bonded amides of trimesic acid.²⁴ As expected, the optimized geometry shows a π -stacking arrangement of the molecules reinforced by hydrogen bonding between the amide fragments of the adjacent molecules. The calculated stacking distance of 3.59 Å is larger than the 3.39 Å observed by XRD in the low-temperature phase even though a similar stacking distance was observed in the high-temperature phase (3.57 Å).²⁵

All amide groups in the model rotate out of the thiophene plane by 40° and the adjacent molecules rotate by an equivalent angle of 40° vs the stacking axis to engage in hydrogen bonding interactions (N...H distance

1.81 Å). This creates a helical stack with a pitch of 9 molecules $(9 \times 40 = 360^\circ)$, but, due to the C3 symmetry of 3, the unit cell of the stack is only 3 molecules long. We note that the high symmetry of this arrangement is broken if the stacking distance is reduced to 3.39 Å as observed by XRD in the low-temperature phase. To maintain the hydrogen bonding, the rotation of amide groups must be reduced to $\sim 37^{\circ}$, which increases the mutual rotation between benzotrithiophene cores. The model also implies that the increase in stacking distance with temperature observed by XRD must be accompanied by a decrease in rotational displacement between adjacent benzotristhiophene units because of the persistent intermolecular H-bonding between amide groups. This interdependency between stacking distance and mutual rotation is proposed to be one reason for the observed temperature independent charge carrier mobility discussed below.

In the optimized geometry, the phenyl rings are only slightly rotated out of the plane of the amide groups (\sim 5°) and interact with each other through H...H contacts (2.46 Å) forming a helical "coil" around the column. The distance between the turns of the coil (which corresponds to the distance between the centers of the Ph rings of each second molecule) is \sim 9 Å and in good agreement with the XRD data.

We note that due to a prochiral nature of benzotrithiophene, either chiral (RRRR is shown in Figure 3) or racemic (RSRS is given in the SI) columnar stacks can be formed by **3**. However, neither the diffraction data nor the calculated small difference in energy (<1 kcal/mol in favor of the racemic tetramer) allow for a clear differentiation between the two structures. Structurally, the chiral and racemic stacks only differ in the mutual positions of sulfur atoms in the neighboring molecules, which, nevertheless, might have a profound effect on charge transport through the benzotristhiophene stacks.

Other unusual features of this material that may affect charge transport are the locations of frontier orbitals depicted in Figure 4. The trialkoxyaniline groups contribute to 100% to the HOMO of 3, whereas the benzotristhiophene core contributes 100% to the LUMO, which suggests that hole transport must be facilitated through the trialkoxyaniline groups and electron transport through the benzotristhiophene cores.

The contribution of the trialkoxyaniline groups to the HOMO is supported by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) measurements. Triamide **3** displays an irreversible oxidation wave at $E_{ox} = 1.07$ V vs Ag/AgCl (DPV) in benzonitrile solution that corresponds to the formation of the radical cation on the trialkoxyaniline groups rather than the benzotristhiophene core. E_{ox} of the unsubstituted benzotristhiophene has been reported to be 1.39 V¹⁸ and is increased to 1.86 V by the electron withdrawing carboethoxy substituents in a triester of **1**. A value similar to that of triester of **1** (X = OEt) is expected for the benzotristhiophene triamide core.²⁶

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⁽²³⁾ The distortion of the benzotrithiophene core in the top and bottom molecules (Figure 3b) is an "edge effect". All distance were measured between the inner two molecules where this effect is less apparent. Unfortunately, we presently can not model longer oligomers of this compound or periodic boundary conditions.

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Figure 4. Contributions to frontier orbitals of 3 calculated by DFT (B3LYP/3-21G*; methyl for dodecyl groups); degenerated HOMO + HOMO-1 at -5.51 eV (top) and degenerated LUMO + LUMO+1 at -2.06 eV (bottom).

Furthermore an E_{HOMO} of -5.4 eV is obtained based on $E_{\rm ox}$ of **3** using ferrocene as internal standard (-4.8 - $E_{\rm ox}$ (vs Fc/Fc⁺)),²⁷ which is in excellent agreement with the calculated E_{HOMO} of -5.51 eV. The calculated E_{LUMO} is rather high (-2.06 eV). A corresponding electrochemical reduction would be expected at -2.3 V vs Ag/AgCl, which is outside the electrochemical transparency window of the electrolyte and was not observed.

UV-vis absorption spectra of **3** in THF solution and as thin film on quartz (Figure S12 in the SI) are very similar, and the only evidence of electronic interactions between the molecules in the solid film is a slight broadening of the absorptions and changes in relative intensities. The optical gaps of 3 in solution and as thin film were calculated to 3.18 and 3.09 eV, respectively, based on the onset of the longest wavelength absorption. The optical gap is in reasonably good agreement with the calculated HOMO--LUMO gap of 3.45 eV. In fact, time-dependent DFT (TD-DFT) calculations (at the same level as the structure optimization) predict the lowest energy transition at 3.11 eV (398 nm) in the planar configuration (gas-phase minimum for individual molecule) and 3.32 eV (373 nm) for the molecule with arylamide groups twisted out-ofplane (minimum for stacked molecules). In both cases, the

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Figure 5. Charge carrier mobility (left axis, solid line, squares) and conductivity lifetime (right axis, dotted line, triangles) of compound 3 as a function of temperature.

transition is a mix of HOMO, HOMO-1, HOMO-2 (which are all close in energy) with LUMO and LUMO+1 orbital interactions and has a charge-transfer character.

The intrinsic mobility of charges in compound 3 was measured by time-resolved microwave conductivity (TRMC) measurements²⁸ at different temperatures (Figure 5). A quasi constant mobility of about 0.02 cm^2 V^{-1} s⁻¹ for the sum of charge carriers was obtained between -50 and 50 °C and, most remarkably, no abrupt change in the charge carrier mobility and its dependence on temperature was observed at the phase transition (-10 °C). While the mobility is not affected by the phase transition, the conductivity lifetime clearly changes and half-life time increases from about 50 ns in the high temperature Colh phase to almost 500 ns in the low temperature Col_h phase (Figure 5). Consequently, charge recombination and/or trapping in the low temperature Col_h phase must be less efficient than in the high temperature Col_h phase.

The observed mobility of $0.02 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ is comparable to values reported for similarly sized discotic alkoxy-substituted triphenylenes even though higher values have been observed in discotic materials with larger aromatic cores.²⁹ Also, H-bonded columnar discotic materials of similar core size have shown higher mobility^{15,16} than **3**. Considering the results of DFT calculations, it is likely that only electron mobility contributes to the combined mobility measured for 3 by TRMC, which would explain the comparably low value for the combined mobility but suggests a high value for electron mobility. Hole transport through the trialkoxyaniline groups is not feasible because their packing distance is larger than 4 Å and only the trialkoxyaniline groups but not the benzotristhiophene core

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contribute to the highest occupied orbitals (HOMO to HOMO-3) of 3 as outlined above.

A distinction between mobilities of positive and negative charge carriers is not possible by TRMC but by timeof-flight (TOF) charge carrier mobility measurements. Indeed, time-of-flight charge carrier mobility measurements on 25 μ m thick multidomain samples of 3 sandwiched between semitransparent Al electrodes on glass slides revealed a fairly nondispersive transport for electrons with a calculated mobility of up to 2×10^{-3} cm² V^{-1} s⁻¹ but no observable transient signal for holes. The macroscopic (TOF) electron mobility across a 25 μ m multidomain sample is expectedly lower than the combined intrinsic mobility measured by TRMC but only by a factor of 10. In fact, this is a surprisingly high macroscopic electron mobility considering that the measurements were taken in air on samples that are not ultra pure and with a compound that has a high E_{LUMO} . Both, the absence of a transient signal for holes and the relatively high mobility of electrons in the TOF measurements confirm that the combined mobility measured by TRMC is solely due to electrons.

The absence of an abrupt change in mobility at a phase transition has been reported before for other mesomorphic materials of high structural order because the structural changes to the columnar stacking are minimal at the phase transition.^{15,30} The estimated persistence length of the columnar stacks of 3 determined by the Scherrer equation based on the line broadening of the (001) diffraction peak is 105 Å and practically constant between -25 and 70 °C. Still surprising is that a decrease in stacking distance by 0.1 Å in 3 does not result in a measurable increase of the mobility. The most probable explanation is that an increase in charge transfer integral due to tighter packing of the stack at lower temperatures is compensated by a decrease of charge transfer integral due to an increase in mutual rotation angle between neighboring molecules (see discussion above). Increasing mobility due to thermal activation, however, may also help compensate for a decreasing mobility with increasing stacking distance.14

So, what causes the large change in lifetime if the structural changes are minimal? Warman et al. proposed that charge carrier recombination in highly ordered discotic columnar phases at time scales > 5 ns is dominated by recombination of charge carriers on separate columns by intercolumnar electron tunnelling through the layer of aliphatic chains.³¹ The authors also showed that the tunnelling process critically depends on the packing structure of the aliphatic chains among other factors. We propose here that changes to the dynamic and conformational states of the side chains are mainly responsible for the large increase in lifetime with decreasing temperature in the low temperature Col_h phase of 3 because no changes to the core packing are detected other



Figure 6. Optical micrographs $(35 \times 42 \,\mu\text{m})$ of a shear aligned thin film of 3 on glass with shear direction (arrow) parallel to one of the crossed polarizers (left) and after turning the sample ccw by 10° (right). Alignment was achieved in the lyotropic phase of 3 in heptane followed by evaporation of the solvent.

than a decrease in packing distances with decreasing temperature. Decreasing intercolumnar spacing, however, should increase the rate of recombination.

The high temperature Col_h phase of **3** fulfills all common criteria of a liquid crystalline phase but it is not liquidlike. In fact, the material is so highly viscous that no flow can be mechanically induced into a free-standing film at 275 °C. This lack of mobility impedes the processing into aligned monodomains that is important for applications as an organic semiconductor in thin-film electronics. We have previously demonstrated the application of intermediate lyotropic mesophases for the alignment of highly viscous discotic phthalocyanines³² and report here that the same methodology is applicable to H-bonded discotic LCs. Triamide 3 was aligned in both fibers (Figure 2a) and thin films (Figure 6) by extrusion from lyotropic solutions or by mechanical shear alignment of lyotropic thin films on substrates, respectively. Subsequent evaporation of the solvent (usually *n*-heptane) at elevated temperatures under vacuum generates the aligned solvent free (thermotropic) mesophases of 3 without significant disturbance of the alignment (Figure 6).

Lyotropic Col_h mesophases of **3** in *n*-heptane are best prepared at elevated temperatures (50-60 °C) by mixing equal masses of 3 and the solvent to avoid the formation of biphasic mixtures at higher solvent contents. In contrast, isotropic organo-gels of 3 in n-heptane are obtained at concentrations as low as 1% wt. IR spectroscopy of the gel confirms that all amide groups are involved in H-bonding, but no columnar stacks are detected by XRD. Consequently, isotropic H-bonded networks of 3 must have been formed that contain no or only very short columnar aggregates. A detailed investigation of the lyotropic mesomorphism and gel formation is the subject of a separate study.

Conclusion

Incorporation of three amide groups in 3 is sufficient for holding the molecules together in columnar stacks up to a temperature of 280 °C and suppresses the formation

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of crystalline phases in favor of a low temperature Col_h mesophase. The specific design of 3 ensures the formation of an isotropic liquid below its decomposition temperature and the formation of lyotropic mesophases at high concentrations as well as isotropic organo-gels at low concentrations in alkanes. Both, formation of an isotropic liquid and lyotropic mesomorphism, are essential for the preparation of uniaxially aligned fibers and films of 3 and its potential use in devices in general. The intracolumnar H-bonding between molecules of 3 in the hexagonal columnar mesophases necessitates a helical stacking of the benzotristhiophene units and couples the observed increase in stacking distance with increasing temperature with a decrease in mutual rotation of adjacent benzotristhiophene units. It is proposed here that this interdependence of stacking distance and mutual rotation angle together with the absence of major changes to the columnar structure are responsible for the observed quasi temperature independent charge carrier mobility. The combined charge mobility of $0.02 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ measured by TRMC is modest for H-bonded Col_h phases but it originates from electrons alone as confirmed by TOF charge carrier mobility measurements. This unusual behavior (for oligothiophene materials) is a consequence of the specific topology of frontier orbitals in 3: the LUMOs are localized on the benzotrithiophene unit and form electron channels in the columnar stacks, while the HOMOs are localized on the pendant trialkoxyphenyl substituents that are spaced too far apart to form channels for hole transport. We expect that changing the location of the carbonyl and amino group in the amide linker (NH attached to benzotristhiophene) would localize both HOMO and LUMO on the benzotristhiophene core. This compound should show high hole mobility but probably lower electron mobility.

Experimental Section

Synthesis of Benzo[B,b',b'']tristhiophene-2,2',2''-tricarbonyl Trichloride (2). A mixture of benzotristhiophene tricarboxylic acid 1¹⁸ (0.030 g, 0.079 mmol) in 5 mL of dry toluene was stirred at reflux for 12 h and then cooled to room temperature. Thionyl chloride (0.094 g, 0.06 mL, 0.792 mmol) was added, and the reaction mixture was stirred at reflux for 72 h. Excess of SOCl₂ was removed in vacuum, and the residue was washed with toluene (2 × 5 mL). The product was dried in vacuum to give 0.033 g (92%) of a white solid. mp: > 320 °C; IR (KBr) (cm⁻¹): 1723, 1542, 1494, 1350, 1182, 1096, 875, 842, 790, 663. ¹H NMR (DMSO-*d*6) (ppm): 8.45 (3 β -CH of thiophene); ¹³C NMR (DMSO-*d*6) (ppm): 162.8 (C=O), 136.7, 135.2, 130.5, 127.8.

Synthesis of N,N',N"-(3,4,5-Tridodecyloxyphenyl)benzo[b,b', b"]tristhiophene-2,2',2"-tricarboxamide (3). To a suspension of acid chloride 2 (0.081 g, 0.187 mmol) in dry THF (30 mL) was added 3,4,5-tridodecyloxyaniline³³ (0.60 g, 0.93 mmol) and triethyl amine (0.11 mL, 0.81 mmol). The mixture was refluxed for 15 h, precipitated salt was filtered off, and the solvent was removed in vacuum. An off-white solid was obtained as crude product that was washed with acetone, hexane, and ether and finally recrystallized from THF/methanol to give 0.25 g (60%) of analytically pure compound **3** as a pale yellow solid. ¹H NMR (500 MHz, pyridine- d_6 , δ): 11.15 (s, 3H, NH), 7.6 (3H, thiophene overlapping with Py), 4.95 (Ph overlapping with H₂O), 4.26 (t, J=6.7 Hz, 6H, OCH₂), 3.95 (t, J=6.3 Hz, 12H, OCH₂), 1.90 (m, 6H, CH₂), 1.77 (m, 12H, CH₂), 1.63 (m, 6H, CH₂), 1.48 $(m, 12H, CH_2), 1.4-1.2 (m, 144H, CH_2), 0.87 (t, J=6.0 Hz, 27H)$ CH₃); (300 MHz, THF-d₈, δ): 9.28 (broad s, 3H, NH), 7.92 (broad s, 3H, thiophene), 6.80 (broad s, 6H, Ph), 3.22 (broad s, 18H, OCH₂), 1.6-1.4 (m, 18H, CH₂ partially overlapping with THF), 1.3-0.9 (m, 162H, CH₂), 0.55 (t but not fully resolved, 27H, CH₃); ¹³C NMR (75 MHz, THF-d₈, δ): 160.2 (C=O), 153.93, 142.2, 136.6, 136.0, 135.21, 132.25, 122.8, 99.9, 73.7, 69.6, 32.9, 31.5, 30.7, 30.6, 30.4, 27.3, 27.2, 25.9, 25.6, 25.3, 25.0, 14.3; IR (KBr): v = 3270 (m, v(N-H)), 3139 (w), 3079 (w), 2923 (s, v(C-H)), 2852 (s, v(C-H)), 1631 (s, v(C=O)_{amide I}), 1608 (s, v(C=C)_{arom.}), 1545 (s, amide II), 1505 (s), 1464 (s), 1424 (s), 1382 (m), 1357(m), 1306 (m), 1273 (m), 1233 (s, $\nu(C-O-C)$), 1114(s,v(C-O-C)), 1007 (m), 838 (m), 723 (m), 624 (w); UV-vis (THF): $\lambda_{max}(\varepsilon) = 332 (13000), 267 \text{ nm} (5400); HRMS (MALDI-$ ToF, m/z): $[M + H]^+$ calcd for $C_{141}H_{237}N_3O_{12}S_3$, 2261.73; found, 2261.89. Anal. Calcd for C141H237N3O12S3: C 74.85; H 10.56; N 1.86; found: C 75.02, H 10.46, N 1.59.

Spectroscopy and Spectrometry. UV-vis spectra of solutions in THF (spectroscopic grade) were recorded on a Varian Cary 50 conc. UV-visible spectrophotometer. ¹H NMR and ¹³C NMR spectra were run on Bruker NMR spectrometers (DRX 500 MHz, DPX 300 MHz, and DPX 300 MHz with autotune). Deuterated chloroform, THF, and pyridine were used as solvents, and their residual proton signals functioned as reference signals. Multiplicities of the peaks are given as s = singlet, d =doublet, t = triplet, m = multiplet. Coupling constants for firstorder spin systems are given in Hz. Data are presented in the following order (multiplicity, integration, coupling constant). Fourier Transform Infrared spectra (FT-IR) were obtained on a Bruker Vector 22. Relative peak intensities in IR are abbreviated as vs = very strong, s = strong, m = medium, w = weak, br = broad. Liquid samples were recorded as films on potassium bromide plates, and solid samples were run as potassium bromide pellets. Mass spectrometry measurements were performed by Kirk Green at the Regional Center for Mass Spectrometry, and MALDI MS data were obtained on a Waters/ Micromass Micro MX.

Mesomorphism. Polarized light microscopy was performed on an Olympus TPM51 polarized light microscope that is equipped with a Linkam variable temperature stage HCS410 and digital photographic imaging system (DITO1). Calorimetric studies were performed on a Mettler Toledo DSC 822e, and thermal gravimetric analysis was performed on a Mettler Toledo TGA SDTA 851e. Helium (99.99%) was used to purge the system at a flow rate of 60 mL/min. Samples were held at 30 °C for 30 min before heated to 550 °C at a rate of 10 °C/min. All samples were run in aluminum crucibles. XRD measurements were run on a Bruker D8 Discover diffractometer equipped with a Hi-Star area detector and GADDS software package. The tube is operated at 40 kV and 40 mA and Cu Ka1 radiation ($\lambda = 1.54187$ Å) with an initial beam diameter of 0.5 mm is used. Compound 3 was studied as self-supported bulk material and aligned fibers. Sample detector distances were varied between 15.0 and 9.0 cm. A modified Instec hot and cold stage HCS 402 operated via controllers STC 200 and LN2-P (for below ambient temperatures) was used for variable temperature

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XRD and IR measurements. Free standing films were obtained by spreading compound **3** over sharp edged holes of 1-2 mmdiameter in metal plates at a temperature of 250 °C.

Electrochemistry. Electrochemical characterization was performed with an Epsilon potentiostat in benzonitrile solution (HPLC grade) using Bu_4NPF_6 (0.1 M) as electrolyte. A Pt disk, Pt wire, and Ag/AgCl electrode were used as working, auxiliary and reference electrodes, respectively. Ferrocene was added as an internal standard at the end of the experiments, showing an E^0_{ox} of +0.45 V. Because of the relatively low solubility and strong aggregation of triamide **3**, its electrochemical characterization by CV and DPV was performed in benzonitrile at 65 °C.

Pulse-radiolysis time-resolved conductivity (PR-TRMC) measurements were performed on solid samples (30 mg) in a perspex container. The sample was placed in microwave cells consisting of a rectangular waveguide with inner dimensions of 3.55 \times 7.00 mm² that was short-circuited with a metal end plate. The materials were uniformly ionized with a nanosec pulse of 3 MeV electrons from a Van de Graff accelerator. The energy absorbed by the sample (the radiation dose, D) was accurately known from dosimetry and leads to the formation of charge carrier pairs with concentrations of $\sim 10^{21}$ m⁻³. If the charge carriers formed by ionization are mobile, the sample conductivity will increase upon irradiation. The change in conductivity of the sample was measured as a function of time by monitoring the decrease in microwave power reflected by the cell. The conductivity increases during the irradiation pulse due to the formation of mobile charge carriers. After the pulse, the conductivity decays because of trapping and/or recombination of positive and negative charges. From the value of the conductivity at the end of the pulse, an estimate of the charge carrier mobility may be obtained if the concentration of charge carriers generated by irradiation is known. Accurate estimates of the charge carrier concentrations generated by pulse radiolysis can be made for discotic materials as described previously.²⁹ The PR-TRMC technique is described more extensively in a recent review.28

Time-of-flight (TOF) measurements were preformed on 25 µm thick layers of compound 3 sandwiched between semitransparent Al electrodes on glass substrates. The TOF setup and the measurement method were similar to that described by Melnyk and Pai.³⁴ All measurements took place in air under ambient conditions (22 °C and 30% relative humidity). A Spectra-Physics (VSL-337ND-S) nitrogen laser emitting a 4 ns pulse at 337 nm served as the excitation light source. At this wavelength the Beer–Lambert attenuation coefficient is about $11 \,\mu m^{-1}$ in the layer of 3. Thus, 90% of the laser pulse is absorbed within the first 0.5 µm of the material. The thickness of this 90% absorption region is much thinner than the overall film thickness of the layer. Measurements were performed at an electric field of $30 \text{ V}/\mu\text{m}$, and the measurement circuit resistance was adjusted to ensure that the RC time constant was much less than the charge carrier transit time. The resultant transient signals were recorded on a GHz storage oscilloscope (Tektronics TDS 580D). Typically 10-12 measurements were taken under the same conditions and then averaged.

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Supporting Information Available: Spectra, chromatogram, electrochemistry, variable temperature diffraction and IR data, thermal gravimetric analysis, gel phase, calculated orbitals, and racemic columnar stack as well as TOF data. This material is available free of charge via the Internet at http://pubs.acs.org.

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