An Electron-Deficient Discotic Liquid-Crystalline Material

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Hexaazatriphenylene-hexacarboxy triimide **1** was synthesized and fully characterized using NMR, IR, UV/vis, and fluorescence spectroscopy. DSC and polarization microscopy showed compound **1** to be liquid crystalline over a large temperature range, while its specific mesophase ($\mathrm{Col_{ho}}$) could be determined via X-ray scattering experiments. Although the first reduction potential of **1** could not be measured directly, two closely related reference compounds **4** and **5** featured low first reduction potentials, suggesting the suitability of **1** as an acceptor material in photoinduced electron-transfer processes. The latter was confirmed via photoinduced absorption and fluorescence spectroscopy on mixed films of **1** and poly(3-hexylthiophene).

Introduction

Intensive research on π-conjugated materials during the last 2 decades has led to the development of materials with interesting optical and electronic properties and to their application in electronic devices such as field-effect transistors[1] and light-emitting diodes.[2] Most research has focused on *p*-type (semi)conducting materials. The photovoltaic cell based on π-conjugated materials may rejoice itself in ever-increasing interest and incorporates both *p*-type (donor) as well as *n*-type (acceptor) (semi)conducting materials.[3] Promising efficiencies have been obtained for bulk heterojunction photovoltaic cells, but they are not yet competitive with inorganic or hybrid photovoltaic cells.[4] The efficiency of these cells is directly related to the mobility of the charges in these devices; low mobilities increase the chance of recombination of the opposite charges. The mobility of π-conjugated materials can be improved by nanoscopic order of these systems, for instance, as a liquid-crystalline mesophase. Appropriately derivatized triphenylenes, phthalocyanines, and coronenes feature, because of their large disklike aromatic cores, hexagonal liquid-crystalline mesophases over broad temperature ranges and show high mobilities of charges parallel to their columns.[5] These systems, however, have donor characteristics while examples of liquid-crystalline acceptor materials are scarce.[6] Therefore, acceptor materials with high electron mobility are in demand.[7] In this paper we would like to present the synthesis and characterization of a new electron-deficient liquid-crystalline material **1** (Scheme 1) which combines hexaazatriphenylene (HAT)[8] as the acceptor core with 3,4,5-tridodecyloxyphenyl groups to introduce mesogenic character.

Experimental Section

General Procedures. All solvents used were p.a. quality. Tetrahydrofuran (THF) was distilled over Na/K/benzophenone. For column chromatography Merck silica gel 60 was used, while for preparative size-exclusion chromatography Bio-Rad S−X1 Beads were used. ^{1}H NMR and ^{13}C NMR spectra were recorded on an AM-400 Bruker spectrometer with frequencies of 400.1 and 100.6 MHz, respectively. Chemical shifts are given in ppm (δ) downfield from tetramethylsilane (TMS). UV/vis spectra were recorded on a Perkin-Elmer Lambda 3B spectrophotometer or on a Perkin-Elmer Lambda 900 UV/vis/NIR spectrophotometer. Fluorescence spectra were recorded on a Perkin-Elmer LS50B luminescence spectrometer and infrared

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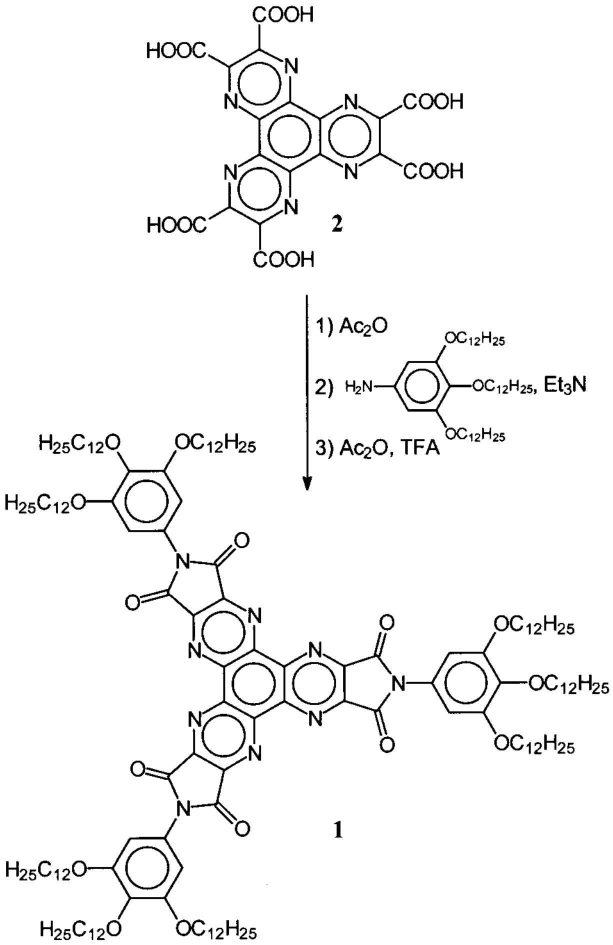
Scheme 1



spectra on a Perkin-Elmer Spectrum One using attenuated total reflection (ATR) sample accessory. Elemental analysis was performed on a Perkin-Elmer 2400 series analyzer. X-ray scattering patterns were recorded on X-ray film using a Statton camera. The sample-to-detector distances were set at either 55 or 75 mm and exposure times were in the range of 4−5 h each. The samples were sealed between two X-ray transparent sheets (either aluminum or Mylar) and subsequently sheared to produce large domains, having uniform alignment. Cyclic voltammograms were obtained in acetonitrile with 0.1 M tetrabutylammonium hexafluorophosphate as a supporting electrolyte using a Potentioscan Wenking POS73 potentiostat. A platinum disk (diameter 5 mm) was used as the working electrode, the counter electrode was a platinum plate (5 × 5 mm^2), and a saturated calomel electrode (SCE) was used as the reference electrode. Photoinduced absorption spectra were recorded between 0.25 and 3.5 eV by exciting with a mechanically modulated CW Ar ion laser (488 nm, 275 Hz) pump beam and monitoring the resulting change in transmission of a tungsten−halogen probe light through the sample (ΔT) with a phase-sensitive lock-in amplifier after dispersion by a triple-grating monochromator and detection, using Si, InGaAs, and cooled InSb detectors. The pump power incident on the sample was typically 25 mW with a beam diameter of 2 mm. The photoinduced absorption, $-\Delta T/T \approx \Delta\alpha d$, is directly calculated from the change in transmission after correction for the photoluminescence, which is recorded in a separate experiment. Photoinduced absorption spectra and photoluminescence spectra are recorded with the pump beam in a direction almost parallel to the direction of the probe beam. Samples were held at 80 K in an inert nitrogen atmosphere using an Oxford Optistat continuous flow cryostat; during measurements the temperature was kept constant within ±0.1 K.

Synthesis of Tris{*N*-(3,4,5-tridodecyloxyphenyl)}-1,4,5,8,9,12-hexaazatriphenylene-2,3,6,7,10,11-hexacarboxy Triimide (1). {Chemical Abstracts Nomenclature for **1**: 2,7,12-tris(3,4,5-tridodecyloxyphenyl)-1H-pyrrolo[3,4-b]-bispyrrolo[3′,4′:5,6]pyrazino[2,3-f:2′,3′-h]quinoxaline-1,3,6,8,-11,13(2H,7H,12H)-hexone.} Hexaazatriphenylene hexacarboxylic acid (**2**, 1.05 g, 2.00 mmol) was suspended in acetic anhydride (50 mL) and heated to 115 °C to obtain a homogeneous solution. After being stirred for another 15 min at 115 °C, the solution was subsequently cooled and freed from excess acetic anhydride. The remaining dark solid was dissolved in THF (25 mL) and a solution of 3,4,5-tridodecyloxyaniline (6.46 g, 10.0 mmol) in THF (25 mL) was added. The solution was stirred at room temperature for 2 h, triethylamine (0.84 mL, 6.0 mmol) was added, and the solution was then stirred overnight. The solvent was removed, the remaining oil was dissolved in toluene (100 mL), and then acetic anhydride (50 mL) and trifluoroacetic acid (1 mL) were added. After being stirred for 3 days at 80 °C, the solution was evaporated and the residue was filtered over silica using dichloromethane as the eluent. The filtrate was concentrated and the residue was dissolved in toluene. Soxhlet extraction with molecular sieves for 1 day gave a water-free material. After further purifications via preparative size-exclusion chromatography using dichloromethane as the eluent, the product was obtained as a brown-red waxy solid (2.78 g, 1.19 mmol, 60%). ^{1}H NMR (400 MHz, CDCl$_3$): δ 6.78 (s, 6H), 4.03 (t, J = 6.4 Hz, 18H), 1.87−1.74 (m, 18H), 1.52−1.47 (m, 18H), 1.37−1.25 (m, 144H), 0.91−0.86 (m, 27H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 161.2, 153.6, 148.3, 145.2, 139.4, 125.5, 105.5, 73.7, 69.7, 31.9, 30.5, 29.8, 29.7, 29.7, 29.5, 29.4, 29.3, 26.2, 22.6, 14.0. Elemental analysis calcd for $C_{144}H_{231}N_9O_{15}$ (%): C, 74.3; H, 10.0; N, 5.4. Found: C, 74.0; H, 10.3; N, 5.3. IR (ATR): ν 2921, 2852, 1742, 1595, 1503, 1467, 1440, 1387, 1336, 1276, 1232, 1118, 720 cm^{-1}.

Synthesis of Tris{*N*-(3,4,5-trimethoxyphenyl)}-1,4,5,8,9,-12-hexaazatriphenylene-2,3,6,7,10,11-hexacarboxy Triimide (4). {Chemical Abstracts Nomenclature for **4**: 2,7,12-tris(3,4,5-trimethoxyphenyl)-1H-pyrrolo[3,4-b]bispyrrolo[3′,4′:5,6]pyrazino[2,3-f:2′,3′-h]quinoxaline-1,3,6,8,11,13(2H,7H,12H)-hexone.} Hexaazatriphenylene hexacarboxylic acid (**2**, 0.85 g, 1.62 mmol) was suspended in acetic anhydride (30 mL) and heated to 115 °C to obtain a homogeneous solution. After being stirred for another 15 min at 115 °C, the solution was subsequently cooled and freed from excess acetic anhydride. The remaining dark solid was dissolved in acetonitrile (50 mL) and 3,4,5-trimethoxyaniline (3.01 g, 16.4 mmol) was added. The solution was stirred at room temperature for 1 day after which acetic anhydride (15 mL) and trifluoroacetic acid (1 mL) were added. After the solution was stirred for 2 days at 70 °C, the solvents were evaporated and the residue was filtered over silica using acetonitrile as the eluent. Recrystallizations from acetonitrile yielded the product as a dark red solid (0.75 g, 0.80 mmol, 49%). ^{1}H NMR (400 MHz, CD$_3$CN): δ 6.93 (s, 6H), 3.94 (s, 18H), 3.90 (s, 9H). ^{13}C NMR (100 MHz, CD$_3$CN): δ 162.8, 153.8, 148.5, 145.7, 138.6, 126.6, 104.9, 60.0, 56.0. Elemental analysis calcd for $C_{45}H_{33}N_9O_{15}$ (%): C, 57.5; H, 3.5; N, 13.4. Found: C, 56.2; H, 3.8; N, 13.1. IR (ATR): ν 1733, 1594, 1504, 1461, 1419, 1336, 1272, 1227, 1122, 997, 920, 813, 723 cm^{-1}.

Synthesis of *N*-(3,4,5-Trimethoxyphenyl)pyrazine-2,3-dicarboxy Imide (5). {Chemical Abstracts Nomenclature for **5**: 2-(3,4,5-trimethoxyphenyl)-1H-pyrrolo[3,4-b]pyrazine-1,3-(2H)-dione.} Pyrazine-2,3-dicarboxylic acid (0.53 g, 3.15 mmol) was suspended in acetic anhydride (10 mL) and heated to 115 °C to obtain a homogeneous solution. After being stirred for another 15 min at 115 °C, the solution was subsequently cooled and freed from excess acetic anhydride. The residue was dissolved in THF (25 mL) whereafter 3,4,5-trimethoxyaniline (0.64 g, 3.5 mmol) and triethylamine (0.48 mL, 3.46 mmol) were added. After the solution was stirred at room temperature overnight, the solvent was removed. The residue was dissolved in a mixture of toluene (25 mL) and then acetic anhydride (25 mL) and trifluoroacetic acid (0.60 mL) were added. After the solution was stirred for 6 h at 80 °C, the suspension was cooled and the crystalline solid collected by filtration. The solid was then washed with toluene and dried in a vacuum oven at 50 °C, yielding the product as a yellow-

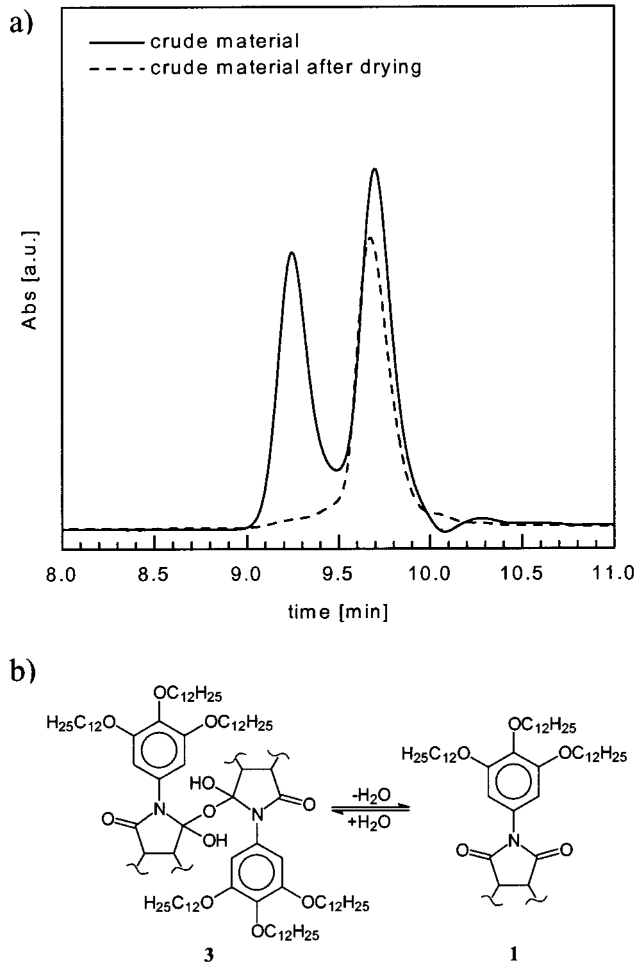


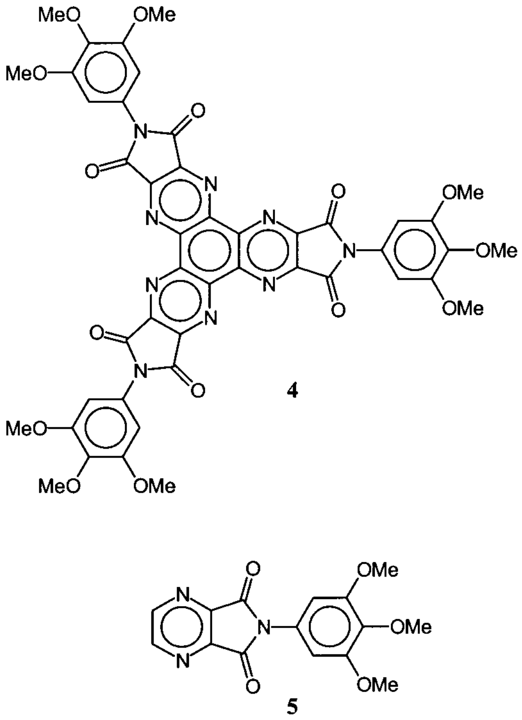
Figure 1. (a) SEC analysis of crude material before and after drying; (b) dimeric structure **3** derived from compound **1**.

orange crystalline material (0.84 g, 2.7 mmol, 85%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.02 (s, 2H), 6.68 (s, 2H), 3.90 (s, 3H), 3.89 (s, 6H). ^{13}C NMR (100 MHz, $(CD_3)_2SO$): δ 163.9, 153.0, 149.0, 146.7, 137.6, 126.9, 105.5, 60.1, 56.1. Elemental analysis calcd for $C_{15}H_{13}N_3O_5$ (%): C, 57.1; H, 4.2; N, 13.3. Found: C, 57.1; H, 4.0; N, 13.3. IR (ATR): ν 1736, 1601, 1508, 1470, 1459, 1384, 1321, 1239, 1168, 1125, 1099, 996, 822, 758, 733, 658 cm^{-1}.

Results and Discussion

HAT-hexacarboxylic acid **2**, one of the starting materials in the synthesis of HAT-hexacarboxy triimide **1**, was synthesized in four steps from the commercially available hexaketocyclohexane.[9] After dehydration with acetic anhydride, the obtained HAT-hexacarboxy trianhydride was reacted with 3,4,5-tridodecyloxyaniline. Intramolecular ring closure was facilitated by the addition of another portion of acetic anhydride.

Scheme 2



Size-exclusion chromatographic (SEC) analyses of the crude reaction mixture showed two distinct peaks, of which the one with the highest retention time was the desired compound HAT-hexacarboxy triimide **1** (Figure 1a). The other peak corresponded to a molecular weight twice that of **1** (according to SEC standards based on polystyrene). Furthermore, IR spectroscopy (ν = 3446 cm^{-1}) showed the presence of hydroxy groups, suggesting the formation of a dimeric structure in which two molecules of **1** were covalently bonded via an ether linkage between the imide groups (**3**, Figure 1b). To test this assumption and investigate the reversibility of the hydration of **1**, the crude reaction mixture was thoroughly dried. From the disappearance of the peak at short retention time after drying could be concluded that indeed a dimer is formed via a reversible hydration. HAT-hexacarboxy triimide **1** could finally be obtained in 60% yield after purification of the crude reaction mixture using SEC. The model compounds **4** and **5** (Scheme 2) were prepared in a similar fashion. Detailed chemical analysis showed that all data are in full agreement with the proposed structures (see Experimental Section).

TGA of **1** showed no weight loss up to 300 °C, whereas polarization microscopy revealed a clearing temperature of 269 °C. DSC measurements featured in the heating run a melting transition at -24 °C ($\Delta H = 35$ kJ mol^{-1}) and a transition from the liquid-crystalline state to the isotropic melt at 269 °C ($\Delta H = 6.1$ kJmol^{-1}). The cooling run exhibited reversible behavior, showing transitions at 251 °C ($\Delta H = -2.4$ kJ mol^{-1}) and at -30 °C ($\Delta H = -34$ kJ mol^{-1}). The texture of the liquid-crystalline state suggested a hexagonal columnar mesophase. To obtain more insight into the specific ordering of the mesophase, X-ray scattering experiments were performed at room temperature. A typical X-ray pattern revealed three main features: a series of reflections at relatively low angles, a broad ring corresponding to an average spacing of 0.45 nm, and a reflection at large angles corresponding to a Bragg spacing of 0.34 nm. The latter is a typical feature often observed in columnar mesophases arising due to regular stacking of the discotic mesogens. The low-angle reflections, corresponding to Bragg spacings of 3.9, 1.95, and 1.69 nm, indicated a two-dimensional arrangement of the columnar cross sections on a hex-

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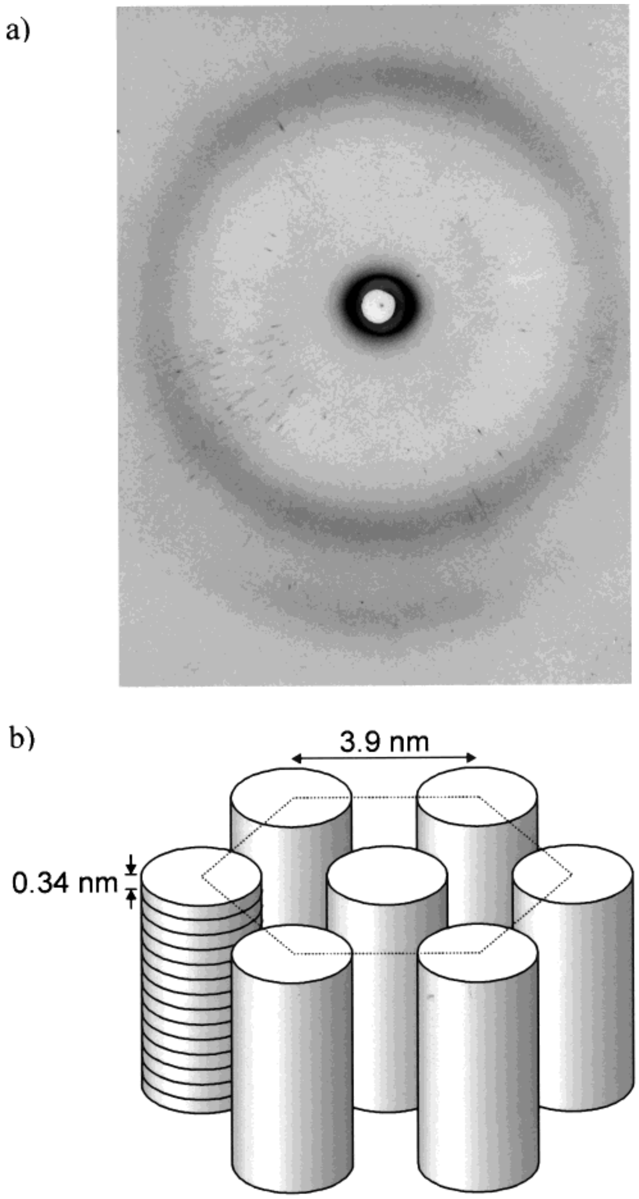

Figure 2. (a) X-ray scattering pattern of compound **1** (edge-on view, shearing direction is top to bottom); (b) the real space representation of the columnar mesophase.

agonal lattice with $a_{\text{hex}} = 3.9$ nm where the individual reflections are given by

$$\frac{1}{{d_{hk}}^2} = \frac{4}{3a^2}(h^2 + k^2 + hk) \qquad (1)$$

The X-ray exposures from macroscopically aligned samples confirmed these findings. A typical example is shown in Figure 2a. The low-angle Bragg reflections in this pattern are oriented along the equator, indicating that the columnar axes are oriented in the meridional direction, perpendicular to the X-ray beam. Consequently, the reflection indicating regular stacking of the discotic mesogens is also oriented along the meridional direction as well.

The optical properties of triimide **1** in solution were determined by measuring UV/vis and fluorescence spectroscopy. UV/vis spectroscopy of compound **1** in chloroform and dodecane showed three distinct absorption bands at 277, 318, and 438 nm. When the polarity of the solvent was gradually increased by an admixture of THF or acetonitrile, a strong hypsochromic shift of the absorption band at 438 nm could be observed in UV/vis spectroscopy. Fluorescence of compound **1** in solution was measured by excitation of samples at 438 nm. The spectra all featured a weak emission band at 501 nm independent of the solvent polarity. Preliminary SANS measurements showed scattering of compound **1** in dodecane and THF, suggesting aggregation in these solvents, while **1** appeared to be molecularly dissolved in chloroform.

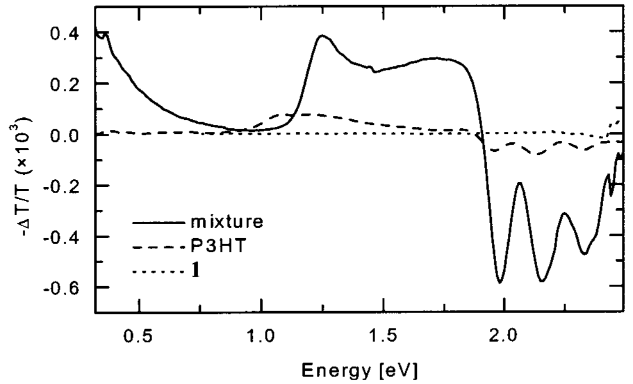

Figure 3. PIA spectra of **1**, P3HT, and a mixture of both (50/50 wt %). The spectra were recorded at 80 K utilizing a 2.54 eV (488 nm, 25 mW) excitation beam and a modulation frequency of 275 Hz.

To study the electron affinity of compound **1**, the first reduction potentials of its model compounds **4** and **5** were determined via cyclic voltammetry in acetonitrile. Both triimide **4** and monoimide **5** could be reduced reversibly, showing first reduction potentials of −0.35 and −1.06 V, respectively (conditions: 0.1 M Bu_4NPF_6 in acetonitrile, 100 mV/s, V versus standard calomel electrode). Compound **1** could not be reduced by cyclic voltammetry; it remained electrochemically silent both in solution and as a film on the electrode. This can be explained by the shielding of the aromatic core of **1** by the long peripheral alkoxy tails. The similarity of the chemical structure of HAT-hexacarboxy triimides **1** and **4**, however, suggest that **1** also has a comparably low first reduction potential of −0.35 V.

The suitability of HAT-hexacarboxy triimide **1** as an electron-acceptor material for photoinduced electron-transfer processes was investigated by mixing it with poly(3-hexylthiophene) (P3HT)[10] and measuring photoinduced absorption (PIA) and fluorescence of films of the blend (50/50 wt %). A PIA spectrum of the mixed film showed two characteristic absorption bands at 0.37 and 1.24 eV (Figure 3), which can be assigned to the radical cations of P3HT and originate from photoinduced electron transfer.[11] This is in contrast to PIA spectra of pure P3HT, featuring bands at 1.08 and 1.18 eV assigned to the triplet state, and of pure **1**, showing no photoinduced absorption at all. Because in the blend photoinduced electron transfer was observed from P3HT, our electron-deficient compound **1** should be concomi-

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tantly reduced. However, its absorption band could not be identified in the PIA spectrum of the mixed film, possibly because it coincides with one of the polaronic bands of P3HT. To test this assumption, spectroelectrochemistry was performed on a solution of model compound **4** in acetonitrile, which indeed gave an absorption band of the radical anion at 1.24 eV. The modulation frequency dependency of the PIA bands revealed that all bands follow the same recombination kinetics and that a distribution of lifetimes is present ranging up to 10 ms. The intensity of the PIA bands increased with the square root of the pump intensity, pointing to a bimolecular decay mechanism (recombination of opposite charges). Fluorescence spectroscopy of a film of the blend of both components showed complete quenching of the fluorescence of the P3HT (at 672 nm for a film of pure P3HT), which indicates that the process of photoluminescence is much slower than the competitive electron transfer.

In conclusion, we have shown that HAT-hexacarboxy triimide **1** is indeed an electron-deficient liquid-crystalline material which shows photoinduced electron transfer with P3HT as a donor. Future work will focus on the synthesis of HAT-hexacarboxy triimides substituted with *p*-type mesogenic groups and the application of these new materials and their blends in organic solar cells.

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