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Synthesis of novel pyrene discotics for potential electronic applications

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Abstract—Novel pyrene discotics, 6,7,15,16-tetrakis(alkylthio)quinoxalino[2′,3′:9,10]phenanthro[4,5-*abc*]phenazines, TQPP-[SR]$_4$, were synthesized efficiently. The HOMO and LUMO energy levels of TQPP-[SR]$_4$ were estimated to be 5.57 eV and 2.97 eV, respectively. The average saturation hole mobility of TQPP-[$C_{12}H_{25}$]$_4$ was $\sim 10^{-3}$ cm^2 V^{-1} s^{-1}.

1. Introduction

Developing organic materials for use in organic light-emitting diodes (OLEDs),[1–3] organic field-effect transistors (OFETs),[4–7] and phototransistors[8,9] has been the target of many research groups. Discotic liquid-crystalline mesophases are quasi-two-dimensional molecules, which typically consist of a rigid central aromatic core to which three to eight extended flexible chains are attached.[10] These molecules usually pack in the form of well-defined columns that may form one-dimensional paths for charge transport along the stacked conjugated cores due to efficient intermolecular π–π orbital overlap within the stacks.[11] Materials that self-assemble to form columnar discotic liquid crystals were shown to demonstrate high charge-carrier mobilities.[12] These materials offer several advantages in electronic technologies.[13]

Columnar liquid crystals are known to have an increased mobility in the direction along the columnar axis.[14] In liquid crystalline hexabenzocoronene derivatives, mobility values of up to 0.5 cm^2 V^{-1} s^{-1} were reported.[15] Important factors that govern the performance of discotic liquid crystals in device applications are charge injection/collection at the interfaces and charge transport within the bulk material. The degree of order within the columnar stack and therefore the overlap between the π-orbitals affects this charge transport in the material. Lehmann et al. recently reported high charge-carrier mobility in discotic mesogens of hexaazatrinaphthylenes substituted with six alkylsulfanyl chains.[16] The authors reported mobility, using a pulse-radiolysis time-resolved microwave-conductivity technique,[17] of up to 0.87 cm^2 V^{-1} s^{-1} for the hexadecylsulfanyl hexaazatrinaphthylene in the liquid crystalline phase.[16] We have reported a high charge-carrier mobility of an amorphous hexaazatrinaphthylene.[18] Harris' group recently reported the synthesis and properties of liquid-crystalline bisphenazines as potential electron-transport materials.[19] In this Letter, we report the synthesis and properties of novel pyrene discotic materials.

The synthesis of 6,7,15,16-tetrakis(alkylthio)quinoxalino[2′,3′:9,10]phenanthro[4,5-*abc*]phenazine—referred to hereafter as TQPP-[SR]$_4$ (**1**)—is shown in Scheme 1. 1,2,6,7-Tetraketopyrene[20] (TKP), **3**, was prepared by the oxidation of 1,2-diketopyrene **2**, which was the product of a three-step synthesis from pyrene (path 1).[21] Alternatively, TKP was prepared by the catalytic oxidation of pyrene using ruthenium(III) chloride and *meta* sodium periodate (path 2).[22] Condensation of TKP with 1,2-dichloro-4,5-phenylenediamine **4** furnished 6,7,15,16-tetrachloroquinoxalino[2′,3′:9,10]phenanthro[4,5-*abc*]phenazine **5**, which upon reaction with alkylthiols (RSH) yielded TQPP-[SR]$_4$, **1**.

The new compounds were characterized by ^{1}H and ^{13}C NMR spectroscopy, HR-MALDI-TOF, and elemental analysis. A complete investigation of the phase

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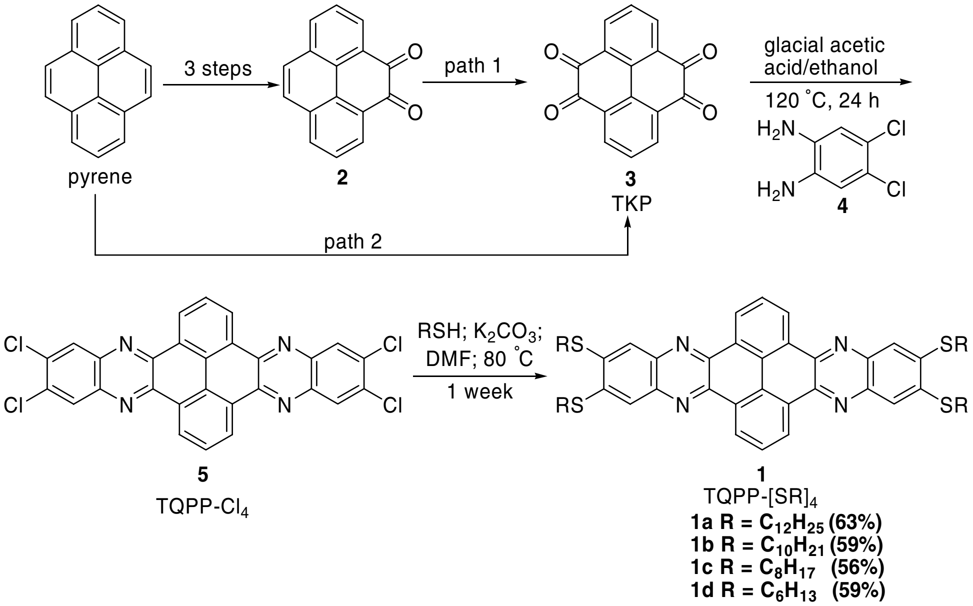

Scheme 1. Synthesis of 6,7,15,16-tetrakis(alkylthio)quinoxalino[2′,3′:9,10]phenanthro[4,5-*abc*]phenazines, TQPP-[SR]$_4$.

behaviors of TQPP-[SR]$_4$ will be reported elsewhere. Thermogravimetric analysis (TGA) showed the onset of weight loss (attributed to decomposition) at around 370 °C under air. All four TQPP-[SR]$_4$ compounds exhibited superimposable UV–vis absorption spectra with five distinct absorption bands at 254, 306, 325, 430 and 456 nm and high molar decade extinction coefficients, Figure 1. From the onset of absorption, we calculated a band gap of 2.6 eV. We further studied the reduction potentials of TQPP-[SR]$_4$ for R = $C_{12}H_{25}$, $C_{10}H_{21}$, C_8H_{17}, and C_6H_{13} using differential pulse voltammetry (DPV) experiments. For each compound, we observed two reduction processes, Table 1. The DPV graph of TQPP-[SC_8H_{17}]$_4$ is shown in Figure 2, wherein two reduction processes were observed at −1.83 V and −1.98 V (vs ferrocene/ferrocenium couple). The HOMO energy level of TQPP-[SR]$_4$ was estimated to be 5.57 eV (relative to the vacuum level) by using the reduction potential of TQPP-[SC_8H_{17}]$_4$ and the HOMO energy level of ferrocene (4.8 eV, relative to the vacuum level) as the standard.[23] The LUMO energy level was estimated to be 2.97 eV (relative to the vacuum level).

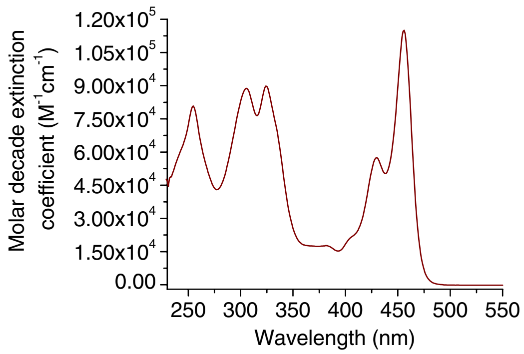

Figure 1. Absorption spectrum of TQPP-[SC_8H_{17}]$_4$ recorded in dichloromethane.

Table 1. Reduction potentials of TQPP-[SR]$_4$

Compound	R	Reduction potential[a] (V)
1a	$C_{12}H_{25}$	−1.83/−1.98
1b	$C_{10}H_{21}$	−1.83/−1.96
1c	C_8H_{17}	−1.84/−1.98
1d	C_6H_{13}	−1.83/−1.98

[a] Reduction potential values were determined versus ferrocene/ferrocenium (Fc/Fc$^+$) couple.

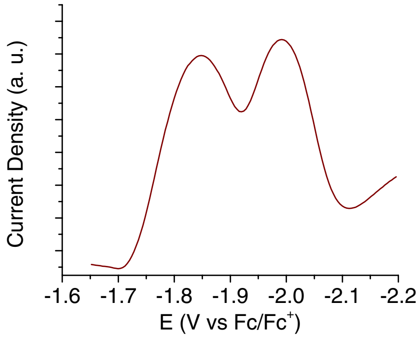

Figure 2. Differential pulse voltammetry (DPV) curve of TQPP-[SC_8H_{17}]$_4$ (potential range, 0→−2.6 V; pulse height, 25 mV; pulse width, 50 mV; scan rate, 20 mV/s).

All OFETs of TQPP-[S$C_{12}H_{25}$]$_4$ displayed p-channel characteristics. The average saturation hole mobility was ~10^{-3} cm^2 V^{-1} s^{-1}. Standard measurement error was 10%. The average threshold voltage was −43.7 ± 5.82 V. An investigation of the electron-transport behavior of these materials is currently ongoing.

2. Experimental

2.1. General

Electrochemical measurements were carried out using an Epsilon Electrochemical Workstation from Bioanalytical Systems in differential pulse voltammetry mode. Bottom contact organic field effect transistor (OFET) testbeds were fabricated on a common gate of highly n-doped silicon with a 200 nm thick thermally grown SiO_2 dielectric layer. Source and drain electrodes were patterned using standard lithographic techniques. Gold source and drain electrodes (50 nm thick) and a titanium adhesion layer (2 nm thick) were evaporated. OFET channels had a constant width of 1 mm, but varied in channel length from 10 to 100 μm. Prior to the addition of TQPP-$[SC_{12}H_{25}]_4$, the bottom contact testbeds were modified with octyltrichlorosilane from a 2 mM solution in anhydrous hexadecane for 18 h at 25 °C. Films of TQPP-$[SC_{12}H_{25}]_4$ were spin coated at 3000 rpm from a 5 mg mL^{-1} solution in toluene heated to 80 °C under nitrogen.

A programmable Cascade probe station was used for OFET characterization under nitrogen. The field-effect saturation mobility (μ_{sat}) and threshold voltage (V_T) of TQPP-$[SC_{12}H_{25}]_4$ were calculated from transfer curves using the following expression:

$$I_D = \frac{WC_i}{2L}\mu(V_G - V_T)^2, \tag{1}$$

where I_D is the saturation drain current, L the channel length, W the channel width, C_i the dielectric layer capacitance, V_G the gate voltage, and V_T the threshold voltage.

2.2. Synthesis

2.2.1. 6,7,15,16-Tetrachloroquinoxalino[2′,3′:9,10]phenanthro[4,5-*abc*]phenazine [5]. This compound was synthesized according to a modified procedure published earlier.[24] TKP **3** (1.66 g, 6.33 mmol) and 1,2-dichloro-4,5-phenylenediamine **4** (2.24 g, 12.7 mmol) were refluxed in 200 mL of glacial acetic acid/ethanol (1:1) for 24 h at 120 °C. The mixture was cooled to room temperature and was then filtered. The resulting greenish-yellow solid was refluxed in 100 mL of 30% nitric acid at 120 °C for 2 h. The obtained yellow solid was filtered and washed with water to yield 3.1 g (90%) of **5**. This compound was used without further purification. HRMS-EI (*m*/*z*): $[M]^+$ Calcd for $C_{28}H_{10}Cl_4N_4$, 541.96596. Found: 541.96748.

2.2.2. General procedure for the synthesis of TQPP-[SR]$_4$. These were synthesized according to a modified procedure in the literature.[24] TQPP-Cl_4 (1.00 g, 1.85 mmol) and K_2CO_3 (13.7 g, 99.2 mmol) were suspended in 150 mL of dry DMF. The reaction mixture was degassed with argon for 10 min. Under argon, 44.1 mmol of RSH was added and the reaction mixture was stirred under argon for 1 week at 80 °C. The reaction mixture was then cooled to room temperature, poured into 500 mL of water and neutralized with conc. HCl. The resulting yellow-brown precipitate was filtered and washed with a copious amount of water. The solid obtained was then recrystallized twice from toluene.

2.2.3. 6,7,15,16-Tetrakis(dodecylthio)quinoxalino[2′,3′:9,10]phenanthro[4,5-*abc*]phenazine [1a]. Yield: 1.39 g (63%), orange solid, mp: 166–167 °C. ^1H NMR (C_6D_6, 60 °C, 400 MHz): δ 0.91 (12H, t, $J = 7.2$ Hz), 1.33 (64H, m), 1.45 (8H, m), 1.78 (8H, p, $J = 7.6$ Hz), 2.99 (8H, t, $J = 7.4$ Hz), 7.85 (2H, t, $J = 7.6$ Hz), 8.12 (4H, s), 9.12 (4H, d, $J = 7.6$ Hz). ^{13}C NMR (C_6D_6, 60 °C, 100 MHz): δ 14.2, 23.0, 28.9, 29.8, 30.2, 32.4, 33.7, 124.4, 126.6, 127.0, 129.6, 140.9, 141.2, 141.8. HRMS-MALDI (*m*/*z*): $[M+H]^+$: Calcd for $C_{76}H_{111}N_4S_4$, 1207.7692. Found: 1207.7561. Anal. Calcd for $C_{76}H_{110}N_4S_4$: C, 75.57; H, 9.18; N, 4.64; S, 10.62. Found: C, 75.62; H, 9.02; N, 4.69; S, 10.46.

2.2.4. 6,7,15,16-Tetrakis(decylthio)quinoxalino[2′,3′:9,10]phenanthro[4,5-*abc*]phenazine [1b]. Yield: 1.19 g (59%), yellow solid, mp: 182–183 °C. ^1H NMR (C_6D_6, 60 °C, 400 MHz): δ 0.93 (12H, t, $J = 7.2$ Hz), 1.35 (48H, m), 1.49 (8H, m), 1.82 (8H, p, $J = 7.6$ Hz), 2.97 (8H, t, $J = 7.4$ Hz), 7.66 (2H, t, $J = 7.6$ Hz), 7.87 (4H, s), 9.29 (4H, d, $J = 7.6$ Hz). ^{13}C NMR (C_6D_6, 60 °C, 100 MHz): δ 14.2, 23.1, 28.8, 29.8, 30.1, 32.4, 33.7, 124.3, 126.6, 127.0, 129.6, 140.9, 141.3, 141.7. HRMS-MALDI (*m*/*z*): $[M+H]^+$: Calcd for $C_{68}H_{95}N_4S_4$: 1095.6440. Found: 1095.6544. Anal. Calcd for $C_{68}H_{94}N_4S_4$: C, 74.54; H, 8.65; N, 5.11; S, 11.71. Found: C, 74.50; H, 8.68; N, 5.11; S, 11.52.

2.2.5. 6,7,15,16-Tetrakis(octylthio)quinoxalino[2′,3′:9,10]phenanthro[4,5-*abc*]phenazine [1c]. Yield: 1.01 g (56%), yellow solid, mp: 202–203 °C. ^1H NMR (C_6D_6, 60 °C, 400 MHz): δ 0.96 (12H, t, $H = 6.6$ Hz), 1.33 (32H, m), 1.47 (8H, m), 1.80 (8H, p, $J = 7.6$ Hz), 2.95 (8H, t, $J = 7.6$ Hz), 7.63 (2H, t, $J = 7.6$ Hz), 7.83 (4H, s), 9.24 (4H, d, $J = 7.6$ Hz). ^{13}C NMR (C_6D_6, 60 °C, 100 MHz): δ 14.3, 23.1, 28.8, 29.7, 29.8, 32.2, 33.7, 124.2, 126.5, 127.0, 129.5, 140.8, 141.1, 141.7. HRMS-MALDI (*m*/*z*): $[M+H]^+$: Calcd for $C_{60}H_{79}N_4S_4$: 983.5188. Found: 983.5269. Anal. Calcd for $C_{60}H_{78}N_4S_4$: C, 73.27; H, 7.99; N, 5.70; S, 13.04. Found: C, 73.01; H, 7.85; N, 5.77; S, 12.74.

2.2.6. 6,7,15,16-Tetrakis(hexylthio)quinoxalino[2′,3′:9,10]phenanthro[4,5-*abc*]phenazine [1d]. Yield: 0.86 g (54%), yellow solid, mp: 221–222 °C. ^1H NMR (C_6D_6, 70 °C, 400 MHz): δ 0.93 (12H, t, $J = 6.8$ Hz), 1.30 (16H, m), 1.42 (8H, p, $J = 7.4$ Hz), 1.76 (8H, p, $J = 7.5$ Hz), 2.93 (8H, t, $J = 7.4$ Hz), 7.65 (2H, t, $J = 7.6$ Hz), 7.87 (4H, s), 9.31 (4H, d, $J = 7.6$ Hz). ^{13}C NMR (C_6D_6, 60 °C, 100 MHz): δ 14.2, 22.9, 28.7, 29.3, 31.9, 33.6, 124.2, 126.5, 126.9, 129.5, 140.8, 141.1, 141.7. HRMS-MALDI (*m*/*z*): $[M+H]^+$: Calcd for $C_{52}H_{63}N_4S_4$, 871.3936. Found: 871.3853. Anal. Calcd for $C_{52}H_{62}N_4S_4$: C, 71.68; H, 7.17; N, 6.43; S, 14.72. Found: C, 71.55; H, 7.35; N, 6.40; S, 14.61.

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