Dipole-driven self-assembly of redox-active mesogenic tetracyanoanthraquinodimethanes†

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Tetracyanoanthraquinodimethane (TCAQ) derivatives having three alkoxy chains at their extremities self-assemble to form both columnar liquid crystals and fibrous aggregates through intermolecular dipole–dipole interactions. The TCAQ derivatives are redox-active, and they exhibit responses in electrochromism in the reductive potential region.

Introduction

Soft materials such as liquid crystals, gels, and polymers have attracted attention[1–4] because of their great potential as dynamically functional materials. Liquid crystals are unique among soft materials because they form ordered and dynamic molecular structures, and the use of liquid crystals with functional moieties is a useful approach to the preparation of functional soft materials.[5] It is of interest to incorporate electro-active[6] and redox-active[7] moieties into liquid crystals to develop low-dimensional (1D and 2D) conductive and photo-functional materials. Our intention here is to incorporate a polar molecule, 11,11,12,12-tetracyanoanthraquinodimethane (TCAQ)[8,9] into mesogenic molecular structures. TCAQ molecules, analogues of π-extended tetracyano-*p*-quinodimethane (TCNQ), have been reported to show redox-active and electro-active properties.[8,9] In addition, they adopt a distorted roof-shaped conformation, resulting in an intrinsic dipole moment perpendicular to the molecules, which could be useful for specific intermolecular interactions. Tetrathiafulvalene (TTF), TCNQ, TCAQ, and their derivatives can also form conductive charge-transfer complexes.[10] Although recent research has focused on the preparation of electro-active TTF-based liquid crystals[11] and nanofibers,[12] the incorporation of TCAQ or TCNQ units into these self-assembled materials has not been explored so far.

Herein, we report compounds **1–3** (Scheme 1), the first example of mesogenic TCAQ derivatives that are capable of forming both columnar liquid crystals and fibrous aggregates. We have also prepared anthraquinone (AQ) derivatives **4–6** (Scheme 1), having a similar π-conjugated framework.

Results and discussion

Molecular design and syntheses

We designed and synthesized TCAQ and AQ derivatives **1–6** as shown in Scheme 1. To induce mesomorphic properties, two benzoyloxy moieties having one, two, or three long alkoxy chains[13] were attached to the functional TCAQ and AQ cores, respectively. TCAQ derivatives **1–3** were prepared *via* the Knoevenagel condensation of **4–6** with Lehnert's reagent,[14] prepared from malononitrile, $TiCl_4$, and pyridine. Compounds **4–6** were obtained by the condensation reaction of 2,6-dihydroxyanthraquinone with two equivalents of the corresponding benzoic acid bearing alkoxy chains. The chemical structures of these new compounds were confirmed by ^1H and ^{13}C NMR spectroscopy and elemental analysis (see the Experimental section).

Liquid-crystalline properties

The thermal properties of compounds **1–6** are summarized in Table 1. Compounds **1a,b**, with three alkoxy chains at each terminal, exhibit liquid-crystalline hexagonal columnar (Col_h) phases over a wide temperature range. A fan-like texture with a large extinction along the polarizer directions is observed in the Col_h phase of **1a** under the polarizing optical microscope (Fig. 1). The X-ray diffraction pattern of **1a** at 100 °C shows four reflection peaks at 34.4 (100), 17.2 (200), 13.0 (210), and 11.4 Å (300) in the small-angle region together with a weak peak at 3.7 Å (001). The peak at 3.7 Å is due to the stacking distance of the adjacent TCAQ molecules within the column (Fig. 2). These results suggest that an ordered Col_h phase is formed for TCAQ derivatives **1a,b**. The intercolumnar distance of 39.4 Å in the Col_h phase of **1a** at 80 °C (estimated from the X-ray diffraction pattern) increases to 40.1 Å at 160 °C (see ESI†). In contrast, analogous compounds **2a,b** and **3a,b** bearing one or two alkoxy chains at each terminal of the TCAQ-based cores do not show mesomorphic behavior. These results imply that polycatenar structures are effective at inducing LC properties in the bulky TCAQ molecules.[13]

AQ derivatives **6a,b** show nematic and smectic C liquid-crystalline phases, while compounds **4a,b** and **5a,b** do not exhibit mesomorphic behavior. A Schlieren texture with 2-brush and 4-brush disclinations, which is characteristic of nematic phases, is observed for **6a,b** under the polarizing optical microscope (Fig. 3a). Upon further cooling from the nematic phases, **6a,b** exhibit a smectic C phase over a wide temperature range. Fig. 3b shows the characteristic fingerprint texture observed for **6a** in the smectic C phase at 190 °C on cooling (see ESI† for **6b**). The X-ray

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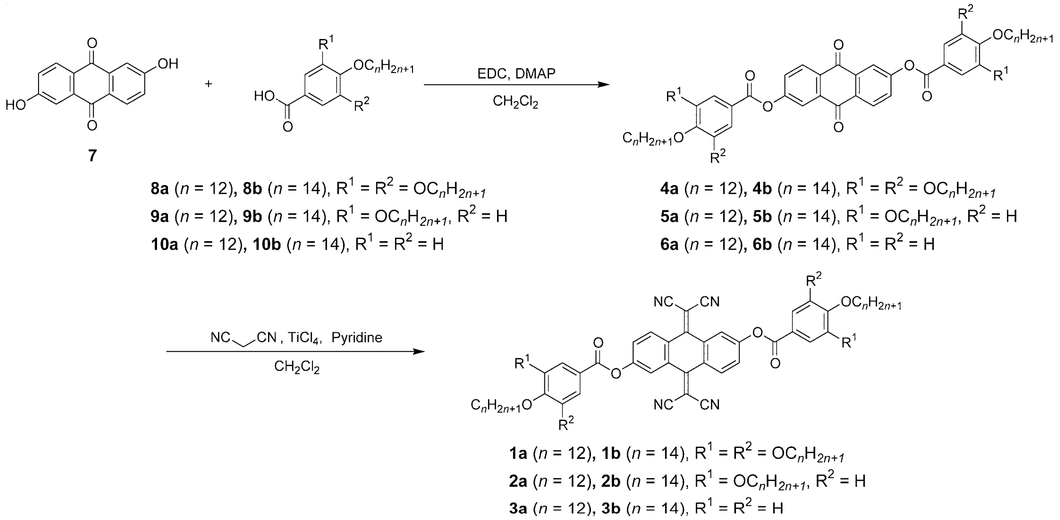

Scheme 1 Synthesis of tetracyanoanthraquinodimethane (TCAQ) derivatives (**1–3**) and anthraquinone (AQ) derivatives (**4–6**).

Table 1 Thermal behavior of **1–6**

Compound	Phase transition[a]
1a	Cr −10 (42) $\mathrm{Col_h}$ 168 (24) Iso
1b	$\mathrm{Cr_1}$ 2 $\mathrm{Cr_2}$ 61 (9) $\mathrm{Col_h}$ 161 (22) Iso
2a	$\mathrm{Cr_1}$ 54 $\mathrm{Cr_2}$ 74 $\mathrm{Cr_3}$ 101 $\mathrm{Cr_4}$ 110 (15) Iso
2b	$\mathrm{Cr_1}$ 7 $\mathrm{Cr_2}$ 61 $\mathrm{Cr_3}$ 115 $\mathrm{Cr_4}$ 121 (45) Iso
3a	$\mathrm{Cr_1}$ 124 $\mathrm{Cr_2}$ 136 (17) Iso
3b	Cr 131 (18) Iso
4a	$\mathrm{Cr_1}$ 5 $\mathrm{Cr_2}$ 69 $\mathrm{Cr_3}$ 96 (90) Iso
4b	$\mathrm{Cr_1}$ 7 $\mathrm{Cr_2}$ 27 $\mathrm{Cr_3}$ 73 (105) Iso
5a	$\mathrm{Cr_1}$ 21 $\mathrm{Cr_2}$ 62 $\mathrm{Cr_3}$ 145 (114) Iso
5b	$\mathrm{Cr_1}$ 21 $\mathrm{Cr_2}$ 49 $\mathrm{Cr_3}$ 142 (128) Iso
6a	$\mathrm{Cr_1}$ 65 $\mathrm{Cr_2}$ 77 $\mathrm{Cr_3}$ 132 (20) SmC 184 (2) N 223 (2) Iso
6b	$\mathrm{Cr_1}$ 91 $\mathrm{Cr_2}$ 103 $\mathrm{Cr_3}$ 114 (17) SmC 197 (1) N 206 (1) Iso

[a] Transition temperatures (°C) and enthalpies of transition (kJ $\mathrm{mol^{-1}}$, in parentheses) determined by DSC on second heating (first heating reflects recrystallization conditions) at 5 °C $\mathrm{min^{-1}}$. Cr: crystalline; N: nematic; SmC: smectic C; $\mathrm{Col_h}$: hexagonal columnar; Iso: isotropic.

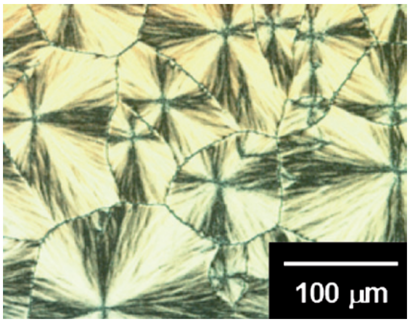

Fig. 1 Polarizing optical photomicrograph of **1a** in the $\mathrm{Col_h}$ phase at 100 °C.

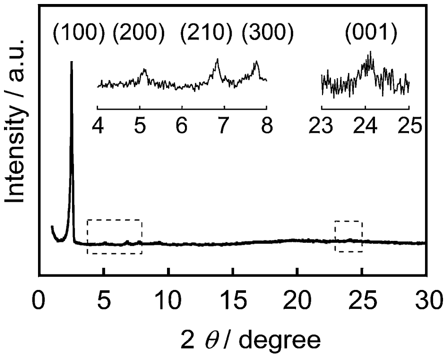

Fig. 2 X-Ray diffraction pattern of **1a** in the $\mathrm{Col_h}$ phase at 100 °C. The insets show the magnified views.

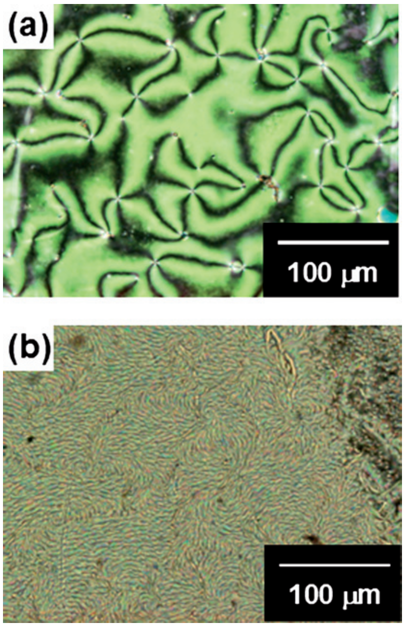

Fig. 3 Polarizing optical photomicrographs of **6a** (a) in the nematic phase at 200 °C and (b) in the smectic C phase at 190 °C on cooling.

diffraction pattern of **6a** at 140 °C shows two peaks with a *d*-spacing of 33.4 (001) and 16.5 Å (002) (see ESI†). The fully extended molecular length for **6a** is estimated to be approximately 50 Å. It is considered that the molecules are tilted and that the terminal alkoxy chains are partially interdigitated in the layered smectic C phase.

It is of interest that the phase transition behavior of **1–3** is markedly different from that of **4–6**. The conformation and polarity of their central aromatic framework are key factors for mesomorphism. While the AQ unit has a planar geometry, the TCAQ unit adopts a highly distorted roof-shaped conformation as a consequence of the strong steric repulsion between the four cyano groups and the four peri hydrogens,[8a–c,15] and thereby possesses an intrinsic dipole moment as large as 7.3 debye along the C_2 axis (Fig. 4a). Accordingly, strong longitudinal dipole–dipole interactions can facilitate the self-assembly of **1a,b** into a 1D stacked array (Fig. 4b), in which the adjacent TCAQ molecules should be arranged in an antipallarel manner. The number of molecules located in a slice of each column can be estimated as approximately 2 (see ESI†).[16,17] Moreover, nano-segregation of the highly polar TCAQ cores from the surrounding lipophilic alkoxy chains plays a crucial role in the preferable formation and stabilization of the Col_h phases. The intercolumnar distance of 39.7 Å in the Col_h phase of **1a** at 100 °C, estimated by the X-ray diffraction measurement, is shorter than the fully extended molecular length of approximately 50 Å (Fig. 4b). The interdigitation of the terminal alkoxy chains between the neighboring columns would occur in the Col_h phase.

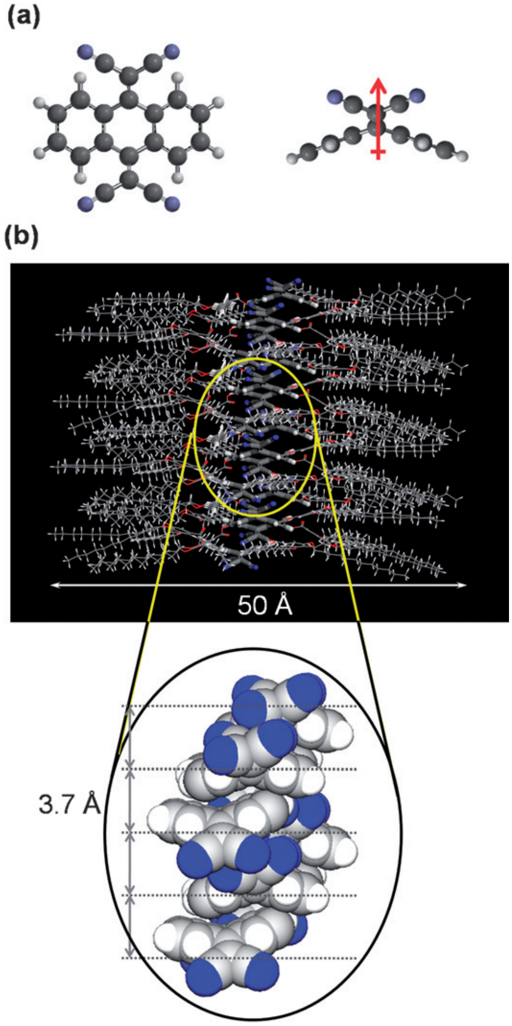

Fig. 4 (a) Optimized molecular geometry of TCAQ calculated at the B3LYP/6-31G* level: top view (left) and side view (right). An arrow indicates the dipole moment. (b) Representation of a possible self-assembled columnar structure involving twelve stacked molecules of **1a**.

Swager and co-workers reported on 3,4-dicyanothiophene-based bent-rod liquid crystals that have a large dipole moment in the lateral direction.[18] In this case, the molecules were assembled in an antiparallel manner through intermolecular dipole–dipole interactions. Mori and co-workers reported that the troponoid-based liquid crystals possessing a peripheral cyano group formed antipallarel assemblies assisted by canceling the dipole repulsion.[19] For these highly polar mesogenic molecules, the intermolecular dipole–dipole interactions should be the driving force to stabilize the LC phases.

Self-assembly in organic solvents

There are only a few examples of liquid-crystalline materials that exhibit gelation abilities in organic solvents.[5e,19b,20,21a] Mamiya *et al.* reported that carbonate-appended azobenzene derivatives with a large dipole moment self-assemble into both smectic LC phases and fibrous aggregates *via* intermolecular dipole–dipole interactions.[21a] We expected that **1–3**, having a large dipole moment perpendicular to the π-conjugated cores, could also gelate some organic solvents.

The gelation abilities of compound **1–6** were evaluated in various organic solvents at a concentration of 10 g L^{-1}. Only TCAQ derivatives **1a,b**, which are capable of forming 1D columnar LC phases, show gelation abilities in dodecane at room temperature, whereas the analogous compounds **2a,b** and **3a,b** as well as AQ derivatives **4–6** are incapable of gelating any of the solvents tested (see ESI†). Transparent gels are formed in dodecane when the heated solution of **1a** is cooled to room temperature (Fig. 5a). The DSC measurement performed on the dodecane gels of **1a** at 10 g L^{-1} exhibits a single reversible sol–gel transition at 67 °C on heating (see ESI†). The polarized optical microscopy for the gels of **1a** reveals the formation of elongated fibrous aggregates (Fig. 5b). The formed fibrous aggregates are strongly birefringent, suggesting a high degree of molecular ordering. The small-angle X-ray scattering (SAXS) pattern of the gels of **1a** shows a peak at 39.6 Å (see ESI†). This value is comparable to the intercolumnar distance observed in the Col_h phase of **1a** (39.7 Å). Therefore, the self-assembled

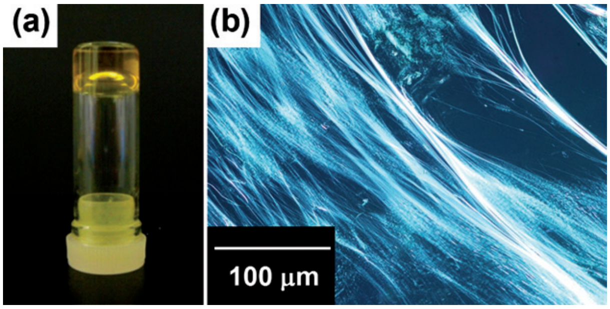

Fig. 5 (a) Photograph and (b) polarizing optical photomicrograph of the gel of **1a** in dodecane (10 g L^{-1}) at room temperature.

nanostructures of **1a** in the fibrous aggregates should be similar to those of the columnar LC structures.

Similar dipole-driven assemblies in organic solvents were reported for highly polar merocyanine dyes[21b] and cyanochalcone derivatives,[21c] in which the molecules adopted an antipallarel arrangement to cancel their dipoles. Recently, we reported pyridine-based diamide gelators with smectic layered structures.[22] Mesomorphic properties and gelation abilities are closely related since the non-mesomorphic pyridyl derivatives do not act as gelators. In the present study, a columnar structure may be related to the formation of the self-assembled fibrous aggregates in the solvents.

Electrochemical behavior

Compounds **1–6** have shown redox-active properties as characterized by cyclic voltammetry. As shown in Fig. 6a, TCAQ derivative **1a** exhibits a single reversible reduction wave at the half-wave potential ($E_{1/2}$) of −0.46 V *vs.* Ag$^+$/Ag, which is ascribed to the formation of the dianion of **1a**.[8a–c] A considerable potential difference (ΔE = 430 mV) between the cathodic and anodic peaks may arise from conformational changes between the distorted neutral **1a** and the planar dianion of **1a** during the redox process. The redox behavior of **2a,b** and **3a,b** is similar to that of **1a,b** (see ESI†). The reduction potentials of TCAQ derivatives **1–3** are shifted to more negative potentials than that of TCAQ reported by Martín and co-workers ($E_{1/2} = -0.36$ V *vs.* Ag$^+$/Ag).[9a] This behavior can be ascribed to the substitution effect of the attached benzoyloxy groups.[8b] For compound **4a**, the two reversible reduction waves appear at $E_{1/2} = -1.10$ and −1.63 V *vs.* Ag$^+$/Ag, and the redox behavior of **4b** and **6a,b** is nearly the same as that of **4a** (see ESI†). In contrast, the reduction potentials of **1–3** are observed at less negative potentials compared to those of AQ derivatives **4a,b** and **6a,b**. These results suggest that TCAQ derivatives **1–3** have higher electron-accepting capabilities than AQ derivatives **4a,b** and **6a,b**.

The spectroelectrochemical experiments have been performed for **1a** in the same electrolyte solution (Fig. 6b). The UV–vis absorption spectrum of **1a** at 0 V *vs.* Ag$^+$/Ag shows absorption peaks at 300 and 350 nm. When the applied potential is negatively increased from 0 to −1.4 V, a new broad absorption band centered around 540 nm appears, accompanied by a decrease in the absorbance at 350 nm. The visible absorption would be ascribed to the formation of the dianion of **1a** (Fig. 7a).[8a–c] By returning to 0 V, the initial UV–vis spectrum is recovered. The reversible redox cycles can also be achieved in a thin film of **1a** coated on an indium-tin-oxide (ITO)-coated glass electrode in a Bu_4NClO_4/CH_3CN electrolyte solution at room temperature. An obvious color change between yellow (**1a**) and red (dianion of **1a**) is observable during the reduction from 0 to −1.4 V (Fig. 7b). Recently, Kitagawa and co-workers reported that a thin film of Pt(II)-based metallomesogens with catecholate and 2,2′-dipyridyl ligands coated on an ITO glass electrode showed reversible redox cycles in Col$_h$ phases.[7a] In the present study, the redox reaction, accompanied by a clear color change, has been achieved for the TCAQ derivative in the columnar LC state. To our knowledge, there are few examples of redox-active columnar LC materials that show reversible electrochromic behavior during the redox reaction.

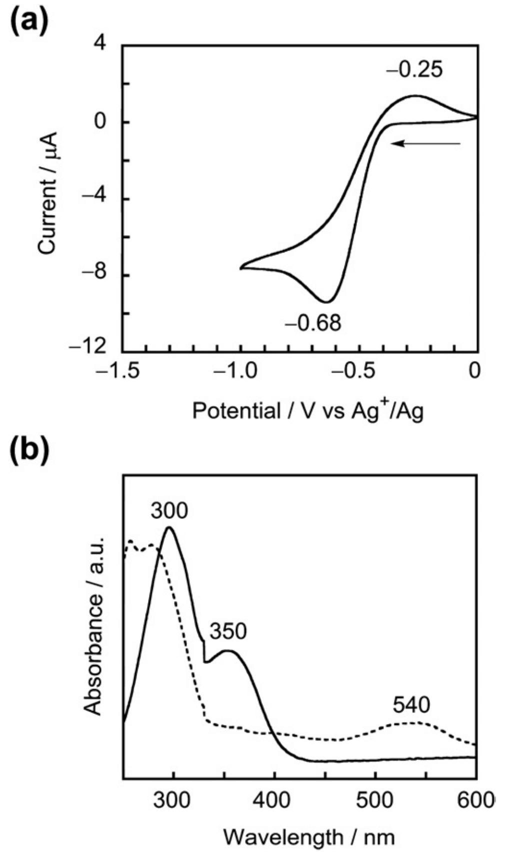

Fig. 6 (a) Cyclic voltammogram of **1a** (2.0 mM) recorded in a CH_2Cl_2 solution of Bu_4NClO_4 (0.10 M). Sweep rate is 50 mV s^{-1}. (b) UV–vis absorption spectra of **1a** observed at 0 V (solid line) and −1.4 V (dashed line) *vs.* Ag$^+$/Ag.

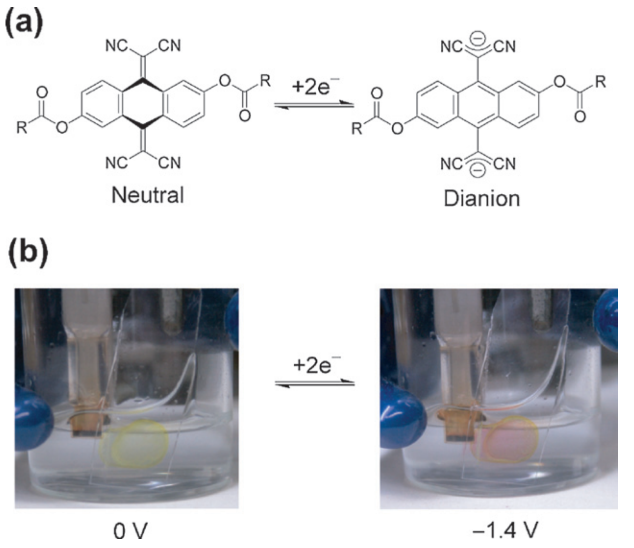

Fig. 7 (a) Structural changes in **1a,b** by redox reactions (R = 3,4,5-trialkoxyphenyl). (b) Photographs showing the electrochromic behavior of a thin film of **1a** coated on an ITO electrode in a CH_3CN solution of Bu_4NClO_4 (0.10 M): E = 0 V (left); E = −1.4 V (right).

Conclusion

We have shown self-assembled structures and properties of mesogenic molecules incorporating TCAQ and AQ. TCAQ derivatives **1a,b** based on highly polar π-conjugated cores self-assemble into columnar liquid crystals *via* the intermolecular dipole–dipole interactions and nanosegregation of polar aromatic and aliphatic moieties. In contrast, AQ derivatives **6a,b** of non-polar π-conjugated cores show nematic and smectic C phases over wide temperature ranges. Compounds **1a,b** also form fibrous aggregates in organic solvents. The reversible electrochemical reactions of **1a,b** occur in the condensed columnar liquid-crystalline state as well as in the solution state. These TCAQ-based materials are expected to be a candidate for new n-type liquid-crystalline semiconductors and self-assembled insulated molecular wires.

Experimental section

General

^{1}H and ^{13}C NMR spectra were recorded on a JOEL JNM-LA400 spectrometer. Chemical shifts of ^{1}H and ^{13}C NMR signals were quoted to tetramethylsilane (δ = 0.00) and $CDCl_3$ (δ = 77.0) as internal standards, respectively. The ^{13}C NMR spectra for **5a,b** could not be taken at room temperature because of their poor solubility in $CDCl_3$. Elemental analyses were carried out with a Yanaco MT-6 CHN autocorder. Differential scanning calorimetry (DSC) measurements were performed on a NETZSCH DSC204 Phoenix calorimeter at a scanning rate of 5 °C min^{-1}. Transition temperatures were taken at the onset of transition peaks. For compound **1a**, the melting temperature was determined as the peak position in the DSC traces due to the broadness of the transition peak. A polarizing optical microscope Olympus BH-51 equipped with Mettler FP82 HT hot stage was used for visual observation. X-Ray diffraction (XRD) patterns were obtained using a Rigaku RINT-2500 diffractmeter with a heating stage using Ni-filtered CuKα radiation. Cyclic voltammetry (CV) was carried out in a CH_2Cl_2 solution of Bu_4NClO_4 (0.10 M) with Pt working and counter-electrodes, and an Ag$^+$/Ag reference electrode using an ALS CHI 600B electrochemical analyzer. *In situ* electrochromism studies were conducted in a three-electrode quartz cell with the same electrolyte system as CV using the potentiostat together with a JASCO V-670 spectrometer. Molecular mechanics calculations were performed with the COMPASS force-field using Accelrys MS Modeling (v. 4.0) softwares. The density functional theory (DFT) calculations were carried out using Wavefunction SPARTAN'04 (v. 1.0.3) programs. The ground-state geometries were optimized at the B3LYP/6-31G* level of theory.[23]

Syntheses of TCAQ derivatives 1a,b and AQ derivatives 6a,b

2,6-Bis(3,4,5-tridodecyloxybenzoyloxy)-11,11,12,12-tetracyanoanthraquinodimethane (1a). To a stirred mixture of **4a** (2.18 g, 1.4 mmol) and malononitrile (1.39 g, 21.0 mmol) in dry CH_2Cl_2 (100 mL) were slowly added $TiCl_4$ (0.8 mL) followed by pyridine (2.2 mL) at 0 °C. The mixture was refluxed for 24 h. After cooling to room temperature, the reaction mixture was added into a large amount of aqueous hydrochloric acid (*ca.* 5%). The product was extracted with $CHCl_3$, and the organic layer was washed with an aqueous $NaHCO_3$ and brine, and then dried over anhydrous Na_2SO_4. After filtration and evaporation, the product was purified by column chromatography (silica, $CHCl_3$–hexane = 1 : 1, v/v), recrystallized from $CHCl_3$–methanol, and dried under vacuum to afford **1a** as a bright yellow solid (0.42 g, 18%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.31 (d, J = 8.4 Hz, 2H), 8.15 (d, J = 2.4 Hz, 2H), 7.59 (dd, J = 8.4 and 2.4 Hz, 2H), 7.40 (s, 4H), 4.10–4.03 (m, 12H), 1.86–1.75 (m, 12H), 1.56–1.10 (m, 108H), 0.90–0.86 (m, 18H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.08, 158.77, 153.93, 153.10, 143.85, 131.85, 129.31, 127.23, 126.00, 122.19, 121.55, 112.82, 112.61, 108.87, 83.58, 73.67, 69.37, 31.91, 30.33, 29.72, 29.68, 29.64, 29.62, 29.55, 29.38, 29.35, 29.27, 26.08, 22.67, 14.10. Anal. Calcd for $C_{106}H_{160}N_4O_{10}$: C, 77.14; H, 9.77; N, 3.39%. Found: C, 77.30; H, 9.92; N, 3.19%.

2,6-Bis(3,4,5-tritetradecyloxybenzoyloxy)-11,11,12,12-tetracyanoanthraquinodimethane (1b). This compound was prepared from **4b** (1.89 g, 1.1 mmol), malononitrile (0.35 g, 5.3 mmol), $TiCl_4$ (1.2 mL), and pyridine (2.2 mL) in dry CH_2Cl_2 (50 mL) by adopting the procedure used for **1a**, and was obtained as a bright yellow solid (0.60 g, 30%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.31 (d, J = 8.4 Hz, 2H), 8.15 (d, J = 2.4 Hz, 2H), 7.59 (dd, J = 8.4 and 2.4 Hz, 2H), 7.40 (s, 4H), 4.10–4.03 (m, 12H), 1.87–1.70 (m, 12H), 1.53–1.10 (m, 132H), 0.90–0.86 (m, 18H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.06, 158.80, 153.94, 153.10, 143.82, 131.85, 129.32, 127.23, 126.01, 122.19, 121.56, 112.82, 112.60, 108.86, 83.57, 73.67, 69.37, 31.92, 30.34, 29.75, 29.74, 29.70, 29.68, 29.66, 29.63, 29.56, 29.39, 29.38, 29.36, 29.28, 26.08, 22.68, 14.11. Anal. Calcd for $C_{118}H_{184}N_4O_{10}$: C, 77.93; H, 10.20; N, 3.08%. Found: C, 77.68; H, 10.42; N, 2.84%.

2,6-Bis(4-dodecyloxybenzoyloxy)-9,10-anthraquinone (6a). To a mixture of 2,6-dihydroxyanthraquinone 7 (0.80 g, 3.3 mmol), **10a** (2.14 g, 7.0 mmol), and 4-dimethylaminopyridine (DMAP, 0.40 g, 3.3 mmol) in dry CH_2Cl_2 (50 mL) was added dropwise a solution of 1-ethyl-3-(3-dimethylaminopropyl)-carbodiimide hydrochloride (EDC, 1.91 g, 10.2 mmol) in dry CH_2Cl_2 (50 mL). The mixture was stirred for 40 h at room temperature. After quenching with water (50 mL), the product was extracted with $CHCl_3$. The organic layer was washed with water and dried over anhydrous Na_2SO_4. After filtration and evaporation, the crude product was purified by column chromatography (silica, $CHCl_3$), recrystallized from $CHCl_3$–methanol, and dried under vacuum to give **6a** as a light-yellow solid (2.40 g, 79%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.41 (d, J = 8.0 Hz, 2H), 8.18–8.14 (m, 6H), 7.67 (dd, J = 8.0 and 2.4 Hz, 2H), 7.00 (d, J = 8.8 Hz, 4H), 4.06 (t, J = 6.4 Hz, 4H), 1.85 (quint, J = 6.4 Hz, 4H), 1.57–1.45 (m, 4H), 1.40–0.95 (m, 32H), 0.89 (t, J = 6.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 181.48, 164.08, 163.98, 155.98, 135.17, 132.53, 130.93, 129.45, 127.72, 120.51, 120.45, 114.48, 68.40, 31.91, 29.65, 29.63, 29.59, 29.55, 29.35, 29.07, 25.97, 22.69, 14.13. Anal. Calcd for $C_{52}H_{64}O_8$: C, 76.44; H, 7.90%. Found: C, 76.26; H, 7.97%.

2,6-Bis(4-tetradecyloxybenzoyloxy)-9,10-anthraquinone (6b). This compound was prepared from **7** (0.80 g, 3.3 mmol), **10b** (2.34 g, 7.0 mmol), DMAP (0.40 g, 3.3 mmol), and EDC (1.91 g, 10.2 mmol) in dry CH_2Cl_2 (50 mL) by adopting the procedure used for **6a**, and was obtained as a light-yellow solid (2.44 g, 84%). ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.40 (d, $J = 8.0$ Hz, 2H), 8.18–8.14 (m, 6H), 7.67 (dd, $J = 8.0$ and 2.4 Hz, 2H), 7.00 (d, $J = 8.8$ Hz, 4H), 4.06 (t, $J = 6.4$ Hz, 4H), 1.83 (quint, $J = 6.4$ Hz, 4H), 1.52–1.43 (m, 4H), 1.40–0.89 (m, 40H), 0.88 (t, $J = 6.8$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 181.45, 164.05, 163.99, 156.01, 135.19, 132.52, 130.95, 129.43, 127.67, 120.57, 120.41, 114.50, 68.42, 31.91, 29.68, 29.66, 29.64, 29.58, 29.54, 29.35, 29.08, 25.97, 22.68, 14.10. Anal. Calcd for $C_{56}H_{72}O_8$: C, 77.03; H, 8.31%. Found: C, 76.74; H, 8.40%.

Acknowledgements

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