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Amphiphilic Molecular Design as a Rational Strategy for Tailoring Bicontinuous Electron Donor and Acceptor Arrays: Photoconductive Liquid Crystalline Oligothiophene–C₆₀ Dyads

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Tailoring bicontinuous electron donor (D) and acceptor (A) arrays in solution-processable materials is an essential step for the realization of thin-film organic optoelectronics.¹ Casting of a D/A mixture may give rise to photoconductive bulk materials.² However, without proper choice of the components, many defects are usually formed, leading to trapping and rapid annihilation of charge carriers. In view of photovoltaics, the presence of bicontinuous D and A arrays is essential, but cast films from D/A mixtures likely contain their charge-transfer complexes. So far, nanofibers and tubes with bicontinuous D and A arrays have been obtained by self-assembly of covalently linked D–A dyads.^{3,4} Nevertheless, solution-processable bulk materials with a D/A heterojunction⁵ might be more realistic for device applications. Here we report a photoconductive liquid crystal (LC) with bicontinuous arrays of densely packed D and A components, tailored from amphiphilic oligothiophene–C₆₀ dyad **1**_{Amphi} (Chart 1).⁶ Together with contrasting results for a nonamphiphilic reference (**1**_{Lipo}), we highlight a crucial role of the amphiphilic design both in structuring and in photoconductivity.

The molecular structures of **1**_{Amphi} and **1**_{Lipo} are identical to each other except for the terminal wedges. **1**_{Amphi} bears a hydrophilic wedge with triethylene glycol chains and, on the other side, a hydrophobic wedge with paraffinic chains. In contrast, **1**_{Lipo} possesses only the paraffinic wedges. We also prepared compounds **2** and **3**, which are equivalent to the donor and acceptor components of **1**_{Amphi}, respectively. They are all soluble in CH₂Cl₂, where the absorption spectral profiles (Figure S3) and redox properties (Figure S4) of **1**_{Amphi} and **1**_{Lipo} were essentially identical to one another.⁶

Dyad **1**_{Amphi} formed a LC smectic A mesophase over a wide temperature range from 136.1 to 18.3 °C (Figure S5).⁶ Polarized optical microscopy (POM) of LC-**1**_{Amphi} displayed a typical focal-conic texture (Figure 1a). Synchrotron radiation small-angle X-ray scattering (SAXS) analysis showed sharp peaks with *d* spacings of 10.6, 5.3, 3.5, and 2.6 nm (Figure 1c), which can be indexed as (100), (200), (300), and (400) reflections of a lamellar structure with a layer width of 10.6 nm. On the basis of a CPK model of **1**_{Amphi}, the observed layer width is almost twice as large as the distance from the paraffinic end to the fullerene unit (~5.5 nm;

Chart 1. Structures of **1**_{Amphi}, **1**_{Lipo}, and References **2** and **3**

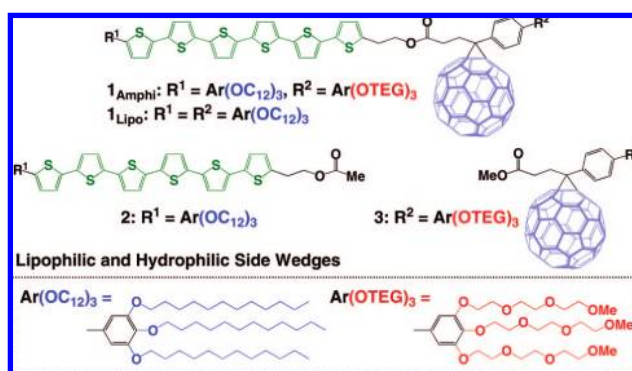


Figure 2, I). Thus, each repeating layer consists of laterally coupled tail-to-tail pairs of **1**_{Amphi}, and such layers are connected at the fullerene-appended hydrophilic head part of **1**_{Amphi} to form a 2D lamellar structure. In this configuration, the hydrophilic and paraffinic wedges are separated by 5.3 nm.

Similar to **1**_{Amphi}, nonamphiphilic **1**_{Lipo} formed a smectic A LC mesophase in a temperature range from 111.4 to 12.5 °C, as

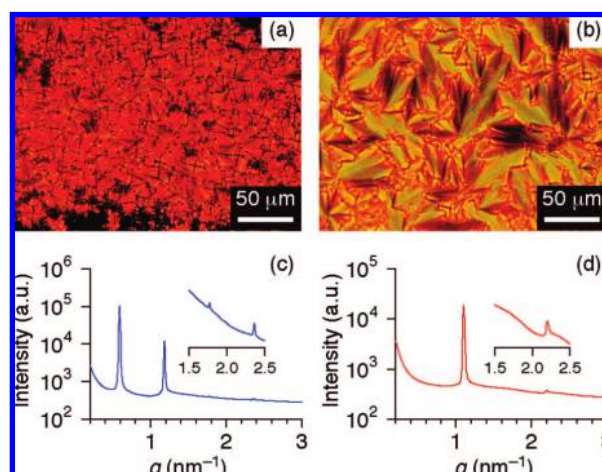


Figure 1. POMs at 33 °C and SAXS patterns at 30 °C (inset: magnified at *q* = 1.5–2.5 nm⁻¹) of (a,c) LC-**1**_{Amphi} and (b,d) LC-**1**_{Lipo}.

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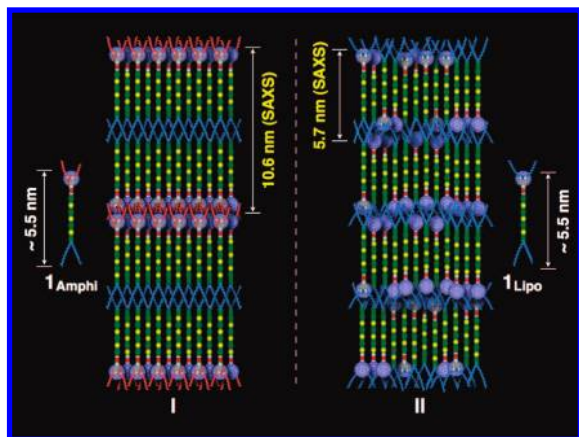


Figure 2. Schematic representations of molecular orientations in LC-**1**_{Amphi} (I) and LC-**1**_{Lipo} (II) with a smectic A mesophase.

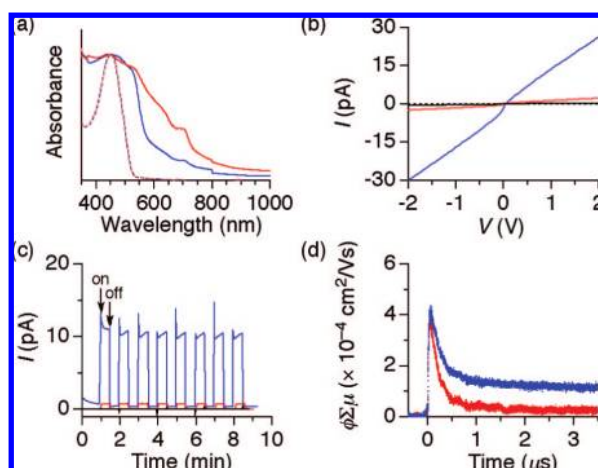


Figure 3. (a) Absorption spectra at 25 °C of **1**_{Amphi} (blue) and **1**_{Lipo} (red) in the LC state (solid curves) and in CH₂Cl₂ (broken curves), normalized at 450 nm. Photoconducting properties at 25 °C of LC-**1**_{Amphi} (blue), LC-**1**_{Lipo} (red), and a 1:1 mixture of **2** and **3** (black); (b) *I*–*V* profiles without (broken curves) and with photoirradiation (solid curves) and (c) changes in photo-generated electric current under an applied voltage of +1 V. (d) FP-TRMC profiles ($\lambda_{\text{ex}} = 355 \text{ nm}$) of LC-**1**_{Amphi} (blue) and LC-**1**_{Lipo} (red).

observed by DSC and POM profiles (Figures 1b and S5).⁶ SAXS pattern (Figure 1d) displayed intense and weak diffractions with *d* spacings of 5.7 and 2.9 nm, respectively, which were indexed as (100) and (200) reflections of a lamellar structure with a layer width of 5.7 nm (Figure 2, I). The observed width is close to the molecular length of **1**_{Lipo}. Considering that both ends of **1**_{Lipo} are paraffinic, the head/tail orientation of **1**_{Lipo} in the lamellar structure is most likely nonuniform (Figure 2, II). In relation to these structural aspects, the absorption spectrum of LC-**1**_{Lipo} was different from that of LC-**1**_{Amphi}, while both were obviously broader than those in CH₂Cl₂ (Figure 3a). In particular, a broad band observed for LC-**1**_{Lipo} at 600–800 nm suggests a charge-transfer interaction between the oligothiophene and fullerene units, which can occur unless **1**_{Lipo} adopts a uniform head/tail orientation.

As shown in Figure 3b,c, LC-**1**_{Amphi} (blue) exhibited a distinct photoconductive character. At an applied voltage of, for example, +2 V, the current at 25 °C increased abruptly from 0.09 to 26 pA (on/off ratio = 290) upon irradiation and quickly retrieved the original value when the light was turned off. In contrast, a 1:1

mixture of **2** and **3** formed neither regular structures nor photoconductivity (black). Noteworthy, LC-**1**_{Lipo} (red) was much less conductive than LC-**1**_{Amphi}, where the photocurrent was only 1/10 that of **1**_{Amphi} observed under identical conditions. This result is interesting since the electron transfer efficiencies in LC-**1**_{Amphi} and LC-**1**_{Lipo}, judging from their fluorescence quenching profiles (Figure S6),⁶ are considered equally high. Having these features in mind, we conducted flash photolysis time-resolved microwave conductivity (FR-TRMC) measurements, which are informative of the behaviors of mobile charge carriers in a short distance (~10 nm). With a 355 nm laser pulse at 25 °C (Figure 3d), the maximum conductivity ($\phi\Sigma\mu_{\text{max}}$ in cm²/V·s) of LC-**1**_{Amphi} (4.1×10^{-4}) was markedly greater than that of the **2/3** mixture (1.2×10^{-4}) but almost comparable to that of LC-**1**_{Lipo} (3.7×10^{-4}). However, the charge carrier, generated in LC-**1**_{Lipo}, was shorter-lived than that in LC-**1**_{Amphi}, suggesting the presence of a larger number of trapping sites in LC-**1**_{Lipo}. This is in accord with the aforementioned low structural integrity of LC-**1**_{Lipo} (Figure 2, II) and its poor photoconducting nature in a macroscopic scale (Figure 3b).

In summary, we have demonstrated that amphiphilic molecular design⁷ can be a rational strategy for the spontaneous formation of bicontinuous donor and acceptor arrays in liquid crystalline materials. Site-specific modification of donor–acceptor dyads with hydrophilic and paraffinic wedges not only prohibits donor–acceptor interactions leading to the trapping of charge carriers but also ensures a long-range conducting pathway in the materials. As liquid crystals are solution-processable and self-healable, our design strategy may contribute to the development of high-performance organic optoelectronics.

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Supporting Information Available: Details of synthesis and characterization of **1**_{Amphi}, **1**_{Lipo}, **2**, and **3**, and supporting Figures S1–S6. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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