Amphiphilic Molecular Design as a Rational Strategy for Tailoring Bicontinuous Electron Donor and Acceptor Arrays: Photoconductive Liquid Crystalline Oligothiophene–C_{60} 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.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–C_{60} dyad 1Amphi (Chart 1).6 Together with contrasting results for a nonamphiphilic reference (1Lipo), we highlight a crucial role of the amphiphilic design both in structuring and in photoconductivity.

The molecular structures of 1Amphi and 1Lipo are identical to each other except for the terminal wedges. 1Amphi bears a hydrophilic wedge with triethylene glycol chains and, on the other side, a hydrophobic wedge with paraffinic chains. In contrast, 1Lipo possesses only the paraffinic wedges. We also prepared compounds 2 and 3, which are equivalent to the donor and acceptor components of 1Amphi, respectively. They are all soluble in CH_2Cl_2, where the absorption spectral profiles (Figure S3) and redox properties (Figure S4) of 1Amphi and 1Lipo were essentially identical to one another.6

Dyad 1Amphi 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-1Amphi 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 1Amphi, the observed layer width is almost twice as large as the distance from the paraffinic end to the fullerene unit (~5.5 nm; Figure 2, I). Thus, each repeating layer consists of laterally coupled tail-to-tail pairs of 1Amphi, and such layers are connected at the fullerene-appended hydrophilic head part of 1Amphi to form a 2D lamellar structure. In this configuration, the hydrophilic and paraffinic wedges are separated by 5.3 nm.

Similar to 1Amphi, nonamphiphilic 1Lipo 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-1Amphi and (b,d) LC-1Lipo.
mixtures of 2 and 3 formed neither regular structures nor photocconductivity (black). Noteworthy, LC-I_{Lipo} (red) was much less conductive than LC-I_{Amphi}, where the photocurrent was only 1/10 that of I_{Amphi} observed under identical conditions. This result is interesting since the electron transfer efficiencies in LC-I_{Amphi} and LC-I_{Lipo}, judging from their fluorescence quenching profiles (Figure S6), 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 (φS/φmax in cm2/V·s) of LC-I_{Amphi} (4.1 × 10−3) was markedly greater than that of the 2/3 mixture (1.2 × 10−4) but almost comparable to that of LC-I_{Lipo} (3.7 × 10−4). However, the charge carrier, generated in LC-I_{Lipo}, was shorter-lived than that in LC-I_{Amphi}, suggesting the presence of a larger number of trapping sites in LC-I_{Lipo}. This is in accord with the aforementioned low structural integrity of LC-I_{Lipo} (Figure 2, II) and its poor photoconducting nature in a macroscopic scale (Figure 3b).

In summary, we have demonstrated that amphiphilic molecular design 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 I_{Amphi}, I_{Lipo}, 2, and 3, and supporting Figures S1–S6. This material is available free of charge via the Internet at http://pubs.acs.org.

References


(7) See Supporting Information.
Supporting Information

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1. Measurements and methods

Unless otherwise noted, all commercial reagents were used as received. Tetrahydrofuran (THF) was refluxed over a mixture of Na and benzophenone under argon, and freshly distilled prior to use. CH$_2$Cl$_2$ was dried over CaH$_2$ under argon and freshly distilled prior to use.

$^1$H and $^{13}$C NMR spectra were recorded at 25 °C on a JEOL model NM-Excalibur 500 FT NMR spectrometer operating at 500 and 125 MHz, respectively, where chemical shifts were determined with respect to non-deuterated solvents as internal references. Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrometry was performed on an Applied Biosystems model Voyager-DE$^\text{TM}$ STR mass spectrometer using $\alpha$-cyano-4-hydroxycinnamic acid (CHCA) or dithranol as a matrix in a reflector mode.

Recycling preparative size-exclusion chromatography (SEC) was performed with CHCl$_3$ or THF as an eluent using JAIGEL 1H (pore size: 20–30 Å), 2H (40–50 Å), and 3H (> 50 Å) columns on a JAI model LC-908 recycling HPLC system equipped with a JASCO model MD-2010 variable-wavelength UV-Vis detector.

Electronic absorption, fluorescence, and infrared spectra were recorded on a JASCO model V-570 UV/VIS/NIR spectrophotometer, a JASCO model FP-6500 spectrofluorometer, and a JASCO model FT/IR-610$^{\text{plus}}$ Fourier transform infrared spectrometer, respectively. Differential scanning calorimetry (DSC) was performed on a Mettler-Toledo model DSC 822$^\text{e}$ differential scanning calorimeter, where the temperature was calibrated with In (430 K) and Zn (692.7 K) standard samples using sealed Al pans. Cooling and heating profiles were recorded and analyzed using a Mettler-Toledo STAR$^\text{e}$ software system. Cyclic voltammetry (CV) was performed on an ALS/[H] CH Instruments model 619B electrochemical analyzer using platinum wire working and counter electrodes and a SCE reference electrode. Sample solutions (0.1 mM) containing Bu$_4$NPF$_6$ (0.1 M) as a supporting electrolyte were degassed by several freeze–pump–thaw cycles prior to measurements.

Small-angle X-ray scattering (SAXS) measurements were carried out at 30 °C using a synchrotron radiation X-ray beam with a wavelength of 1.00 Å at the BL40B2 in SPring-8. Samples were placed 1810 mm apart from an imaging-plate (IP) detector, and exposed to the X-ray beam for 60 seconds. The scattering was detected using a Rigaku model R-AXIS VII imaging plate (IP) system with a resolution of the IP of 100 $\mu$m per pixel. Prior to the measurements, powder samples of 1$_{\text{Amphi}}$ and 1$_{\text{Lipo}}$ were put into a 0.5-mm thick glass capillary,
and annealed under a reduced pressure as follows. $1_{\text{Amphi}}$: heating at 145 °C for 1 min, cooling to 135 °C at a rate of 1 °C/h, and then natural cooling to 25 °C. $1_{\text{Lipo}}$: heating at 120 °C for 1 min, cooling to 110 °C at a rate of 1 °C/h, and then natural cooling to 25 °C.

Electrical measurements were carried out by a two-probe method using a Keithley model 4200-SCS semiconductor parameter analyzer using 8-µm-gap Au/Ti electrodes, fabricated by a photolithographic technique on a silicon wafer coated with a 300-nm thick insulating SiO$_2$ layer. The electrodes were 30-µm long and 50-nm thick. All the measurements were performed at 25 °C at a reduced pressure (< 10$^{-3}$ Pa) using a Nagase Electronic Equipment Service model GRAIL10-Helips-4-HT low-temperature prober. Photoirradiation was performed using an Asahi Spectra model MAX-301 xenon light source with a light power density of 0.91 mW mm$^{-2}$.

Flash-photolysis time-resolved microwave conductivities (FP-TRMC) and fluorescence spectra of films were measured with the identical geometries using an in situ TRMC system. A resonant cavity was used to obtain a high degree of sensitivity in the conductivity measurement. The resonant frequency and microwave power were set at ~9.1 GHz and 3 mW, respectively, so that the electric field of the microwave was small enough not to disturb the charge carrier motion. Charge carriers were photochemically generated using the third-harmonic generation (THG, $\lambda = 355$ nm) light pulses from a Spectra Physics model GCR-130 Nd:YAG laser (5–8 ns pulse duration) with an incident photon density of $4.7 \times 10^{15}$ cm$^{-2}$. The TRMC signal, picked up by a diode (rise time < 1 ns), was monitored by a Tektronics model TDS3052B digital oscilloscope. The observed conductivities were normalized, given by a photocarrier generation yield ($\phi$) multiplied by sum of the charge carrier mobilities ($\Sigma \mu$), according to the equation, $\phi \Sigma \mu = (1/eA I_0 F_{\text{light}})(\Delta P_r/P_r)$, where, $e$, $A$, $I_0$, $F_{\text{light}}$, $P_r$, and $\Delta P_r$ are the unit charge of a single electron, a sensitivity factor (S$^{-1}$ cm), an incident photon density of the excitation laser (photon cm$^{-2}$), a correction (or filling) factor (cm$^{-1}$), and a reflected microwave power and its change, respectively. The emission was guided into a Hamamatsu model C7700 high-dynamic-range streak camera to obtain a two-dimensional image of the spectral profile. All the experiments were performed at 25 °C in air.
2. Synthesis

2-1. Synthesis of 1_{Amphi}

**Reagents and Conditions:**
(a) NBS, toluene, –20 °C; (b) 2,2'-bithiophene-5-boronic acid pinacol ester, Pd(PPh₃)₄, 2 M aq. Na₂CO₃, THF, reflux; (c) NIS, CHCl₃/AcOH (1/1), 0 °C; (d) BBr₃, CH₂Cl₂; (e) 1-bromododecane, K₂CO₃, DMF; (f) 2,2':5',2''-terthiophene-5-boronic acid pinacol ester, Pd(PPh₃)₄, 2 M aq. Na₂CO₃, THF, reflux; (g) LDA, THF, –50 °C, then 2-isoproxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane; (h) Pd(PPh₃)₄, 2 M aq. Na₂CO₃, THF, reflux; (i) Ac₂O, DMAP, toluene; (j) MeI, K₂CO₃, DMF; (k) bis(pinacolato)diboron, Pd(dppe)Cl₂, KOAc, DMSO; (l) (4-toluene sulfonyl) triethylene glycol monomethyl ether, K₂CO₃, DMF; (m) 13, Pd(PPh₃)₄, 2 M aq. Na₂CO₃, THF, reflux; (n) p-TsNHNH₂, MeOH, reflux; (o) NaOMe, pyridine, then C₆₇O₆, o-dichlorobenzene, followed by irradiation, toluene; (p) HCl, AcOH, toluene, reflux; (q) DCC, DPTS, CH₂Cl₂/toluene.
**Compound 4.** To a toluene solution (35 mL) of 2-thiopheneethanol (3.51 g, 27.4 mmol) was portionwise added N-bromosuccinimide (NBS, 4.88 g, 27.4 mmol) at –20 °C under argon, and the mixture was allowed to warm to 25 °C. After 12 h, the reaction mixture was poured into an aqueous solution of KOH (10%, 100 mL) and extracted with toluene. The combined organic extract was washed with water, dried over anhydrous MgSO₄, and filtered off from an insoluble fraction. The filtrate was evaporated to dryness under a reduced pressure, and the residue was subjected to column chromatography (SiO₂, AcOEt/hexane 7/3 v/v), to allow isolation of 4 as colorless liquid (5.1 g, 24.6 mmol) in 90% yield. ¹H NMR (500 MHz, CDCl₃): δ (ppm) 6.87 (d, J = 3.5 Hz, 1H), 6.61 (d, J = 3.5 Hz, 1H), 3.81 (q, J = 6 Hz, 2H), 2.98 (t, J = 6 Hz, 1H), 1.57 (br., 1H).

**Compound 5.** To a THF solution (10 mL) of a mixture of 4 (508 mg, 2.45 mmol) and 2,2'-bithiophene-5-boronic acid pinacol ester (756 mg, 2.59 mmol) were successively added Pd(PPh₃)₄ (97 mg, 0.084 mmol) and an aqueous solution of Na₂CO₃ (2 M, 3.9 mL), and the mixture was thoroughly degassed by freeze-pump-thaw cycles and refluxed under argon overnight. The reaction mixture was poured into water (100 mL) and extracted with CHCl₃. The combined organic extract was washed with water, dried over anhydrous MgSO₄, and filtered off from an insoluble fraction. The filtrate was evaporated to dryness under a reduced pressure, and the residue was subjected to column chromatography (SiO₂, CHCl₃), followed by recrystallization with CHCl₃/hexane, to allow isolation of 5 as yellow solid (538 mg, 1.84 mmol) in 75% yield. ¹H NMR (500 MHz, CDCl₃): δ (ppm) 7.20 (dd, J₁ = 5 Hz, J₂ = 1.5 Hz, 1H), 7.14 (dd, J₁ = 5 Hz, J₂ = 1.5 Hz, 1H), 7.04 (d, J = 4 Hz, 1H), 7.01–6.99 (m, 3H), 6.77 (d, J = 4 Hz, 1H), 3.87 (q, J = 6 Hz, 2H), 3.42 (t, J = 6 Hz, 2H), 1.56 (t, J = 6 Hz, 1H). MALDI-TOF mass: calcd. for C₁₄H₁₂OS₂ 292.44, obsd. 291.91.

**Compound 6.** To a CHCl₃/AcOH solution (12 mL, 1/1 v/v) of 5 (180 mg, 0.62 mmol) was portionwise added N-iodosuccinimide (NIS, 153 mg, 0.68 mmol) at 0 °C under argon. After being stirred at 0 °C for 1 h, the reaction mixture was allowed to warm to 25 °C and stirred for 3 h. Hexane was added to the reaction mixture, and the crude product precipitated was washed with hexane and recrystallized from CHCl₃, affording 6 as yellow solid (191 mg, 0.457 mmol) in 74% yield. ¹H NMR (500 MHz, CDCl₃): δ (ppm) 7.13 (d, J = 3.5 Hz, 1H), 7.00 (d, J = 3.5 Hz,
1H), 6.98 (s, 2H), 6.80 (d, J = 3.5 Hz, 1H), 6.77 (d, J = 3.5 Hz, 1H), 3.86 (q, J = 6 Hz, 2H), 3.04 (t, J = 6 Hz, 2H), 1.55 (t, J = 6 Hz, 1H). MALDI-TOF mass: calcd. for C_{14}H_{11}I_{0.5}S, 418.34, obsd. 417.82.

**Compound 7.** To a CH_{2}Cl_{2} solution (80 mL) of 5-bromo-1,2,3-trimethoxybenzene (9.88 g, 40 mmol) was slowly added, at −75 °C under argon, a CH_{2}Cl_{2} solution of BBr_{3} (1 M, 120 mL), and the mixture was allowed to warm to 25 °C. After 12 h, the reaction mixture was poured into ice/water (200 mL) and extracted with AcOEt. The combined organic extract was washed with water, dried over anhydrous MgSO_{4}, and filtered off from an insoluble fraction. The filtrate was evaporated to dryness under a reduced pressure, to afford 7 as pale solid (7.61 g, 37.1 mmol) in 93% yield. \(^1\)H NMR (500 MHz, acetone-\textit{d}_6): \(\delta\) (ppm) 8.21 (s, 2H), 7.51 (s, 1H), 6.55 (s, 2H).

**Compound 8.** To a DMF solution (25 mL) of 7 (2.50 g, 12.2 mmol) was added K_{2}CO_{3} (13.84 g, 100 mmol), and the mixture was stirred at 25 °C for 30 min. After the addition of 1-bromododecane (13 mL, 54.2 mmol), the reaction mixture was stirred at 60 °C overnight, poured into water (200 mL), and extracted with ether. The combined organic extract was washed with water, dried over anhydrous MgSO_{4}, and filtered off from an insoluble fraction. The filtrate was evaporated to dryness under a reduced pressure, and the residue was subjected to column chromatography (SiO_{2}, hexane), to allow isolation of 8 (8.46 g, 11.9 mmol) as white solid in 98% yield. \(^1\)H NMR (500 MHz, CDCl_{3}): \(\delta\) (ppm) 6.65 (s, 2H), 3.97–3.87 (m, 6H), 1.78–1.67 (m, 6H), 1.44–1.40 (m, 6H), 1.24 (br., 48H), 0.86 (t, J = 7 Hz, 9H).

**Compound 9.** To a THF solution (20 mL) of a mixture of 8 (1.43 g, 2.01 mmol) and 2,2′:5′,2″-terthiophene-5-boronic acid pinacol ester (0.752 g, 2.01 mmol) were successively added Pd(PPh_{3})_{4} (71 mg, 0.062 mmol) and an aqueous solution of Na_{2}CO_{3} (2 M, 3 mL). The mixture was thoroughly degassed by freezing-pump-thaw cycles and refluxed under argon overnight. The reaction mixture was poured into water (100 mL) and extracted with CHCl_{3}. The combined organic extract was washed with water, dried over anhydrous MgSO_{4}, and filtered off from an insoluble fraction. The filtrate was evaporated to dryness under a reduced pressure, and the residue was subjected to column chromatography (SiO_{2}, CHCl_{3}/hexane 1/2 to 1/1 v/v), followed by recrystallization with CHCl_{3}/EtOH, to allow isolation of 9 as yellow solid (1.22 g, 1.39 mmol).
in 69% yield. $^1\text{H}\text{NMR (500 MHz, CDCl}_3\text{): } \delta \text{ (ppm) 7.20 (dd, } J_1 = 5 \text{ Hz, } J_2 = 1 \text{ Hz, 1H), 7.16 (dd, } J_1 = 5 \text{ Hz, } J_2 = 1 \text{ Hz, 1H), 7.11–7.09 (m, 2H), 7.08–7.06 (m, 2H), 7.01 (dd, } J_1 = 5 \text{ Hz, } J_2 = 3.5 \text{ Hz, 1H), 6.75 (s, 2H), 4.01 (t, } J = 6.5 \text{ Hz, 4H), 3.96 (t, } J = 6.5 \text{ Hz, 2H), 1.84–1.72 (m, 6H), 1.05–1.44 (m, 6H), 1.33–1.25 (m, 48H), 0.88–0.85 (m, 9H). MALDI-TOF mass: calcd. for C$_{54}$H$_{84}$O$_3$S$_8$ 877.44, obsd. 876.63.

**Compound 10.** A THF solution of LDA (0.95 M, 1.4 mL) was slowly added at −50 °C to a THF solution (50 mL) of 9 (1.05 g, 1.20 mmol), and the mixture was stirred for 30 min, allowed to warm to −5 °C, and then cooled to −50 °C. To this reaction mixture was added 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1.3 mL, 6.37 mmol), and the resulting solution was stirred at −50 °C for 1 h and then allowed to warm to 25 °C. The reaction mixture was poured into an aqueous solution of NH$_4$Cl (1 M, 100 mL) and extracted with AcOEt. The combined organic extract was washed with water, dried over anhydrous Na$_2$SO$_4$, and filtered off from an insoluble fraction. The filtrate was evaporated to dryness under a reduced pressure, and the residue was subjected to repeated reprecipitations from CH$_2$Cl$_2$/MeOH, affording 10 as yellow solid (1.18 g, 1.18 mmol) in 98% yield. $^1\text{H}\text{NMR (500 MHz, CDCl}_3\text{): } \delta \text{ (ppm) 7.51 (d, } J = 3.5 \text{ Hz, 1H), 7.21 (d, } J = 3.5 \text{ Hz, 1H), 7.13 (d, } J = 3.5 \text{ Hz, 1H), 7.10 (s, 2H), 7.07 (d, } J = 3.5 \text{ Hz, 1H), 6.75 (s, 2H), 4.01 (t, } J = 6.5 \text{ Hz, 4H), 3.96 (t, } J = 6.5 \text{ Hz, 2H), 1.84–1.72 (m, 6H), 1.05 (br., 6H), 1.34 (s, 12H), 1.25 (br., 48H), 0.86 (t, } J = 7 \text{ Hz, 9H). MALDI-TOF mass: calcd. for C$_{60}$H$_{95}$BO$_5$S$_3$ 1003.40, obsd. 1002.72.

**Compound 11.** To a THF solution (15 mL) of a mixture of 6 (106 mg, 0.252 mmol) and 10 (306 mg, 0.304 mmol) were successively added Pd(PPh$_3$)$_4$ (29 mg, 0.025 mmol) and an aqueous solution of Na$_2$CO$_3$ (2 M, 3 mL), and the mixture was thoroughly degassed by freezing-pump-thaw cycles and refluxed under argon overnight. The reaction mixture was poured into water (20 mL) and extracted with CHCl$_3$. The combined organic extract was washed with water, dried over anhydrous MgSO$_4$, and filtered off from an insoluble fraction. The filtrate was evaporated to dryness under a reduced pressure, and the residue was subjected to column chromatography (SiO$_2$, CHCl$_3$), followed by recrystallization with CHCl$_3$/EtOH, to allow isolation of 11 as red solid (236 mg, 0.202 mmol) in 80% yield. $^1\text{H}\text{NMR (500 MHz, CDCl}_3\text{): } \delta \text{ (ppm) 7.11 (s, 2H), 7.07–7.05 (m, 7H), 7.01 (s, 1H), 7.00 (d, } J = 3.5 \text{ Hz, 1H), 6.78 (d, } J = 3.5 \text{ Hz,}
1H), 6.75 (s, 2H), 4.01 (t, $J = 6.5$ Hz, 4H), 3.96 (t, $J = 6.5$ Hz, 2H), 3.87 (q, $J = 6$ Hz, 2H), 3.05 (t, $J = 6$ Hz, 2H), 1.82–1.72 (m, 6H), 1.56 (t, $J = 6$ Hz, 1H), 1.46 (br., 6H), 1.25 (br., 48H), 0.86 (t, $J = 7$ Hz, 9H). MALDI-TOF mass: calcd. for $\text{C}_{68}\text{H}_{94}\text{O}_4\text{S}_6$ 1167.86, obsd. 1166.29.

**Compound 2.** A toluene/Ac$_2$O solution (10 mL, 5/1 v/v) of a mixture of 11 (97 mg, 0.0834 mmol) and DMAP (2 mg, 0.0016 mmol) was refluxed under argon overnight. The reaction mixture was evaporated to dryness under a reduced pressure, and the residue was subjected to column chromatography (SiO$_2$, CHCl$_3$/hexane 1/1 v/v), to allow isolation of 2 as red solid (100 mg, 0.0826 mmol) in 99% yield. $^1$H NMR (500 MHz, CDCl$_3$): δ (ppm) 7.11–7.68 (m, 11H), 6.76–6.75 (m, 3H), 4.29 (t, $J = 6.5$ Hz, 2H), 4.01 (t, $J = 6.5$ Hz, 4H), 3.96 (t, $J = 6.5$ Hz, 2H), 3.12 (br. 2H), 2.08 (s, 3H), 1.84–1.71 (m, 6H), 1.47 (br. 6H), 1.25 (br., 48H), 0.86 (t, $J = 6.5$ Hz, 9H). MALDI-TOF mass: calcd. for $\text{C}_{70}\text{H}_{96}\text{O}_5\text{S}_6$ 1209.9, obsd. 1208.89.

**Compound 12.** To a DMF solution (40 mL) of (4-bromobenzoyl)propionic acid (3.01 g, 12.7 mmol) were successively added MeI (1.5 mL, 26.2 mmol) and K$_2$CO$_3$ (4.86 g, 35.2 mmol) under argon. After being stirred at 25 °C overnight, the reaction mixture was poured into water (100 mL) and extracted with AcOEt. The combined organic extract was washed with water, dried over anhydrous MgSO$_4$, and filtered off from an insoluble fraction. The filtrate was evaporated to dryness under a reduced pressure, and the residue was subjected to column chromatography (SiO$_2$, CH$_2$Cl$_2$), to allow isolation of 12 as white solid (3.05 g, 11.3 mmol) in 96% yield. $^1$H NMR (500 MHz, CDCl$_3$): δ (ppm) 7.83 (d, $J = 6.5$ Hz, 2H), 7.59 (d, $J = 6.5$ Hz, 2H), 3.69 (s, 3H), 3.25 (t, $J = 6.5$ Hz, 2H), 2.75 (t, $J = 6.5$ Hz, 2H).

**Compound 13.** To a DMSO solution (50 mL) of a mixture of 12 (2.48 g, 9.15 mmol) and bis(pinacolato) diboron (2.81 g, 11.06 mmol) were successively added Pd(dpdpf)Cl$_2$•CH$_2$Cl$_2$ (227 mg, 0.278 mmol) and KOAc (2.75 g, 28.02 mmol), and the mixture was thoroughly degassed by freezing-pump-thaw cycles. After being stirred at 80 °C for 3 h, the reaction mixture was poured into water (100 mL) and extracted with toluene. The combined organic extract was washed with water, dried over anhydrous MgSO$_4$, and filtered off from an insoluble fraction. The filtrate was evaporated to dryness under a reduced pressure, and the residue was subjected to column chromatography (SiO$_2$, CH$_2$Cl$_2$ to CH$_2$Cl$_2$/AcOEt 10/1 v/v), to allow isolation of 13 as
yellow solid (2.90 g, 9.11 mmol) in 100% yield. \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) (ppm) 7.93 (d, \(J = 8\) Hz, 2H), 7.87 (d, \(J = 8\) Hz, 2H), 3.69 (s, 3H), 3.31 (t, \(J = 6.5\) Hz, 2H), 2.75 (t, \(J = 6.5\) Hz, 2H), 1.37 (s, 12H).

**Compound 14.** K\(_2\)CO\(_3\) (21.06 g, 152 mmol) was added to a DMF solution (100 mL) of 7 (5.21 g, 25.4 mmol), and the mixture was stirred at 25 °C for 30 min. After the addition of (4-toluenesulfonyl)triethylene glycol monomethyl ether (36.4 g, 114.3 mmol), the reaction mixture was stirred at 60 °C overnight, poured into water (200 mL), and extracted with CH\(_2\)Cl\(_2\). The combined organic extract was washed with water, dried over anhydrous MgSO\(_4\), and filtered off from an insoluble fraction. The filtrate was evaporated to dryness under a reduced pressure, and the residue was subjected to column chromatography (SiO\(_2\), AcOEt to AcOEt/MeOH 4/1 v/v), to allow isolation of 14 (16.9 g, 24.5 mmol) as colorless liquid in 96% yield. \(^1\)H NMR (500 MHz, CDCl\(_3\)):
\[
\delta \text{ (ppm) } 6.72 \text{ (s, 2H)}, 4.11-4.08 \text{ (m, 6H)}, 3.81 \text{ (t, } J = 5 \text{ Hz, 4H)}, 3.75 \text{ (t, } J = 5 \text{ Hz, 2H)}, 3.70-3.67 \text{ (m, 6H)}, 3.64-3.60 \text{ (m, 12H)}, 3.53-3.51 \text{ (m, 6H)}, 3.35 \text{ (s, 9H)}.
\]

**Compound 15.** To a THF solution (10 mL) of a mixture of 13 (1.70 g, 5.34 mmol) and 14 (2.47 g, 3.84 mmol) were successively added Pd(PPh\(_3\))\(_4\) (134 mg, 0.116 mmol) and an aqueous solution of Na\(_2\)CO\(_3\) (2 M, 6 mL), and the mixture was thoroughly degassed by freezing-pump-thaw cycles and refluxed under argon overnight. The reaction mixture was poured into brine (100 mL) and extracted with CHCl\(_3\). The combined organic extract was washed with brine, dried over anhydrous MgSO\(_4\), and filtered off from an insoluble fraction. The filtrate was evaporated to dryness under a reduced pressure, and the residue was subjected to column chromatography (SiO\(_2\), CHCl\(_3\) to CHCl\(_3\)/MeOH 100/5 v/v), to allow isolation of 15 as colorless liquid (2.16 g, 2.86 mmol) in 74% yield. \(^1\)H NMR (500 MHz, CDCl\(_3\)):
\[
\delta \text{ (ppm) } 7.95 \text{ (d, } J = 8 \text{ Hz, 2H)}, 7.54 \text{ (d, } J = 8 \text{ Hz, 2H)}, 6.78 \text{ (s, 2H)}, 4.17 \text{ (t, } J = 5 \text{ Hz, 4H)}, 4.13 \text{ (t, } J = 5 \text{ Hz, 2H)}, 3.81 \text{ (t, } J = 5 \text{ Hz, 4H)}, 3.75 \text{ (t, } J = 5 \text{ Hz, 2H)}, 3.67-3.66 \text{ (m, 6H)}, 3.63 \text{ (s, 3H)}, 3.60-3.55 \text{ (m, 12H)}, 3.48-3.44 \text{ (m, 6H)}, 3.29-3.25 \text{ (m, 11H)}, 2.71 \text{ (t, } J = 6.5 \text{ Hz, 2H)}. \text{ MALDI-TOF mass: calcd. for } C_{38}H_{58}O_{15} 754.86, \text{ obsd. 754.37.}
\]

**Compound 16.** p-Toluenesulfonyl hydrazide (259 mg, 1.39 mmol) was added to a MeOH solution (1 mL) of 15 (872 mg, 1.16 mmol), and the mixture was refluxed under argon overnight.
After the reaction mixture was evaporated to dryness under a reduced pressure, the residue was subjected to column chromatography (SiO$_2$, CH$_2$Cl$_2$ to CH$_2$Cl$_2$/MeOH 100/2 v/v), to give a mixture (881 mg) of cis- and trans-16 containing ca. 10% of the starting compound, which was used for the synthesis of compound 3 without further purification. MALDI-TOF mass: calcd. for C$_{45}$H$_{66}$N$_2$O$_{16}$S 923.07, obsd. 923.19.

**Compound 3.** NaOMe (35 mg, 0.65 mmol) was added under argon to a pyridine solution (4.4 mL) of crude 16 (536 mg, 0.58 mmol). After being stirred at 25 °C for 15 min, the reaction mixture was mixed with an o-dichlorobenzene solution (15 mL) of C$_{60}$ (212 mg, 0.294 mmol), and the mixture was stirred at 70 °C for 22 h. The reaction mixture was evaporated to dryness under a reduced pressure, and the residue was subjected to column chromatography (SiO$_2$, toluene to toluene/MeOH 100/10 v/v), to allow isolation of a mixture of the [5,6] and [6,6] isomers of the product. The mixture was dissolved in toluene (100 mL) and irradiated by a 500-W Xe lamp to allow the [5,6] isomer to convert into the [6,6] isomer. After the complete conversion was confirmed by $^1$H NMR, the resultant solution was evaporated to dryness under a reduced pressure, affording 3 as dark brown solid (88 mg, 0.060 mmol) in 20% overall yield. $^1$H NMR (500 MHz, CDCl$_3$): δ (ppm) 7.93 (d, $J = 8$ Hz, 2H), 7.67 (d, $J = 8$ Hz, 2H), 6.89 (s, 2H), 4.24 (t, $J = 5$ Hz, 4H), 4.19 (t, $J = 5$ Hz, 2H), 3.87 (t, $J = 5$ Hz, 4H), 3.81 (t, $J = 5$ Hz, 2H), 3.75–3.72 (m, 6H), 3.68–3.60 (m, 15H), 3.54–3.51 (m, 6H), 3.55 (s, 3H), 3.34 (s, 6H), 3.23 (t, $J = 8$ Hz, 11H), 2.88 (t, $J = 8$ Hz, 2H). $^{13}$C NMR (125 MHz, CDCl$_3$): δ (ppm) 172.64, 152.83, 148.37, 147.21, 145.64, 145.08, 145.06, 145.04, 144.93, 144.89, 144.66, 144.64, 144.55, 144.52, 144.40, 144.33, 143.94, 143.62, 143.00, 142.92, 142.88, 142.86, 142.84, 142.82, 142.15, 142.00, 140.91, 140.84, 140.66, 138.38, 138.11, 137.60, 135.82, 134.91, 132.36, 126.92, 107.14, 79.53, 72.42, 71.95, 71.92, 70.84, 70.71, 70.56, 70.53, 69.82, 69.07, 59.04, 51.94, 50.50, 31.75, 29.70. MALDI-TOF mass: calcd. for C$_{98}$H$_{58}$O$_{14}$ 1459.53, obsd. 1482.27 for [M + Na]$^+$. 

**Compound 17.** To a toluene solution (8 mL) of 3 (61 mg, 0.0417 mmol) were successively added under argon AcOH (8 mL) and concentrated aqueous HCl (38%, 3.2 mL), and the mixture was heated to reflux overnight. The reaction mixture was concentrated under a reduced pressure and poured into hexane. An insoluble fraction thus formed was collected by centrifugation and subjected to repeated reprecipitations from CH$_2$Cl$_2$/hexane, to allow isolation of 17 as dark brown.
solid (55 mg, 0.038 mmol) in 91% yield. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ (ppm) 7.95 (br., 2H), 7.68 (br., 2H), 6.92 (br., 2H), 4.27 (br. 6H), 3.99–3.56 (m, 30H), 3.37 (br., 9H), 3.24 (br., 2H), 2.90 (br., 2H). MALDI-TOF mass: calcd. for C$_{97}$H$_{56}$O$_{14}$ 1445.50, obsd. 1445.37.

**Compound 1** Amphi• To a CH$_2$Cl$_2$/toluene solution (10 mL, 1/1 v/v) of a mixture of 11 (43 mg, 0.037 mmol) and 17 (55 mg, 0.038 mmol) were successively added 4-(dimethylamino)pyridinium 4-toluenesulfonate (DPTS, 11 mg, 0.037 mmol) and N,N' -dicyclohexylcarbodiimide (DCC, 40 mg, 0.194 mmol), and the mixture was heated to reflux under argon overnight. The reaction mixture was concentrated under a reduced pressure and subjected to column chromatography (SiO$_2$, CHCl$_3$ to CHCl$_3$/MeOH 100/2 v/v), followed by recycling preparative SEC (JAIGEL 2H/3H, THF), to allow isolation of 1 Amphi as dark brown solid (45 mg, 0.017 mmol) in 48% yield. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ (ppm) 7.94 (d, $J = 8.5$ Hz, 2H), 7.67 (d, $J = 8.5$ Hz, 2H), 7.10–6.95 (m, 11H), 6.89 (s, 2H), 6.77–6.75 (m, 3H), 4.31 (t, $J = 6.5$ Hz, 2H), 4.24 (t, $J = 5$ Hz, 4H), 4.20 (t, $J = 5$ Hz, 2H), 4.01 (t, $J = 6.5$ Hz, 2H), 3.96 (t, $J = 6.5$ Hz, 12H), 3.87 (t, $J = 5$ Hz, 4H), 3.81 (t, $J = 5$ Hz, 2H), 3.74–3.73 (m, 6H), 3.67–3.62 (m, 12H), 3.54–3.51 (m, 6H), 3.56 (s, 3H), 3.42 (s, 6H), 3.23 (t, $J = 8$ Hz, 2H), 3.13 (t, $J = 6$ Hz, 2H), 2.91 (t, $J = 8$ Hz, 2H), 1.84–1.72 (m, 6H), 1.48 (br., 6H), 1.24 (br., 48H), 0.86 (t, $J = 6$ Hz, 9H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ (ppm) 171.88, 153.20, 152.73, 148.21, 146.99, 145.45, 144.96, 144.93, 144.90, 144.81, 144.76, 144.53, 144.51, 144.44, 144.28, 144.15, 143.83, 143.50, 143.48, 142.77, 142.72, 142.68, 141.99, 141.90, 141.88, 140.81, 140.53, 139.36, 137.98, 137.49, 136.30, 135.85, 135.66, 135.59, 135.53, 135.40, 132.31, 128.96, 126.86, 126.39, 124.35, 124.26, 124.16, 124.00, 123.94, 123.48, 123.30, 107.06, 104.55, 79.49, 77.44, 77.42, 76.56, 73.60, 72.45, 71.98, 71.96, 70.87, 70.74, 70.60, 70.57, 69.83, 69.29, 69.09, 64.72, 59.11, 50.57, 32.25, 32.08, 30.49, 29.92, 29.90, 29.88, 29.85, 29.82, 29.78, 29.73, 29.59, 29.56, 29.55, 26.30, 26.28, 22.88, 14.34. MALDI-TOF mass: calcd. for C$_{165}$H$_{148}$O$_{17}$S$_6$ 2595.38, obsd. 2617.56 for [M + Na]$^+$. UV-vis (CH$_2$Cl$_2$, 25°C): $\lambda_{\text{max}}$/nm ($\varepsilon$/M$^{-1}$ cm$^{-1}$) 700 (76), 453 (67600), 328 (56500), 260 (156000).

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2-2. **Synthesis of 1\textsubscript{Lipo}**

Reagents and Conditions: (a) Pd(PPh\textsubscript{3})\textsubscript{4}, 2 M aq. Na\textsubscript{2}CO\textsubscript{3}, THF, reflux; (b) p-TsNHNH\textsubscript{2}, MeOH, reflux; (c) NaOMe, pyridine, then C\textsubscript{60}, o-dichlorobenzene, followed by irradiation, toluene; (d) HCl, AcOH, toluene, reflux; (e) DCC, DPTS, CH\textsubscript{2}Cl\textsubscript{2}/toluene.

**Compound 18.** To a THF solution (5 mL) of a mixture of 8 (1.20 g, 1.69 mmol) and 13 (0.81 g, 2.55 mmol) were successively added Pd(PPh\textsubscript{3})\textsubscript{4} (59 mg, 0.051 mmol) and an aqeous solution of Na\textsubscript{2}CO\textsubscript{3} (2 M, 2.5 mL), an the mixture was thoroughly degassed by freezing-pump-thaw cycles and refluxed under argon overnight. The reaction mixture was poured into water (100 mL) and extracted with CHCl\textsubscript{3}. The combined organic extract was washed with water, dried over anhydrous MgSO\textsubscript{4}, and filtered off from an insoluble fraction. The filtrate was evaporated to dryness under a reduced pressure, and the residue was subjected to column chromatography (SiO\textsubscript{2}, CH\textsubscript{2}Cl\textsubscript{2}/hexane 1/4 to 2/1 v/v), followed by recrystallization with CHCl\textsubscript{3}/EtOH, to allow isolation of 18 as white solid (0.77 g, 0.94 mmol) in 55% yield. \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}): \( \delta \) (ppm) 8.01 (d, \( J = 8.5 \) Hz, 2H), 7.62 (d, \( J = 8.5 \) Hz, 2H), 6.76 (s, 2H), 4.02 (t, \( J = 6.5 \) Hz, 4H), 3.98 (t, \( J = 6.5 \) Hz, 2H), 3.70 (s, 3H), 3.33 (t, \( J = 6.5 \) Hz, 2H), 2.77 (t, \( J = 6.5 \) Hz, 2H), 1.83–1.73 (m, 6H), 1.53–1.44 (m, 6H), 1.34–1.24 (m, 48H), 0.86 (t, \( J = 6.5 \) Hz, 9H). MALDI-TOF mass: calcd. for C\textsubscript{53}H\textsubscript{88}O\textsubscript{6} 821.26, obsd. 821.58.
Compound 19.  

\( p \)-TsNHNH\(_2\) (180 mg, 0.967 mmol) was added to a MeOH solution (10 mL) of \( 18 \) (639 mg, 0.778 mmol), and the mixture was refluxed under argon overnight. After the reaction mixture was evaporated to dryness under a reduced pressure, the residue was subjected to column chromatography (SiO\(_2\), CH\(_2\)Cl\(_2\)/hexane 1/1 to 2/1 v/v), to give a mixture (529 mg) of cis- and trans-19, which was used for the synthesis of compound 20 without further purification. MALDI-TOF mass: calcd. for C\(_{60}\)H\(_{96}\)N\(_2\)O\(_7\)S 989.48, obsd. 989.60.

Compound 20.  

NaOMe (32 mg, 0.594 mmol) was added under argon to a pyridine solution (4 mL) of 19 (529 mg, 0.535 mmol). After being stirred at 25 °C for 15 min, the reaction mixture was mixed with an o-dichlorobenzene solution (40 mL) of C\(_{60}\) (584 mg, 0.810 mmol), and the mixture was stirred at 70 °C for 22 h. The reaction mixture was evaporated to dryness under a reduced pressure, the residue was subjected to column chromatography (SiO\(_2\), toluene to CHCl\(_3\)/hexane 1/1 v/v), to allow isolation of a mixture of the [5,6] and [6,6] isomers of the product. The mixture was dissolved in toluene (50 mL) and irradiated by a 500-W Xe lamp to allow the [5,6] isomer to convert into [6,6] isomer. After the complete conversion was confirmed by \(^1\)H NMR, the resultant solution was evaporated to dryness under a reduced pressure, affording 20 as dark brown solid (194 mg, 0.127 mmol) in 24% overall yield. \(^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta \) (ppm) 7.94 (d, \( J = 8.5 \) Hz, 2H), 7.69 (d, \( J = 8.5 \) Hz, 2H), 6.84 (s, 2H), 4.06 (t, \( J = 6.5 \) Hz, 4H), 4.00 (t, \( J = 6.5 \) Hz, 2H), 3.67 (s, 3H), 3.23 (t, \( J = 8 \) Hz, 2H), 2.88 (t, \( J = 8 \) Hz, 2H), 1.84–1.74 (m, 6H), 1.53–1.44 (m, 6H), 1.34–1.24 (m, 48H), 0.87–0.85 (m, 9H). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \( \delta \) (ppm) 172.53, 153.22, 148.29, 147.12, 145.54, 144.98, 144.97, 144.83, 144.79, 144.57, 144.47, 144.42, 144.31, 144.23, 143.84, 143.53, 142.92, 142.83, 142.79, 142.75, 142.73, 142.06, 141.92, 141.90, 141.20, 140.82, 140.56, 138.02, 137.55, 135.39, 134.59, 132.22, 126.89, 105.90, 79.55, 73.57, 69.36, 52.02, 50.59, 32.08, 31.85, 30.54, 29.94, 29.91, 29.87, 29.83, 29.66, 29.61, 29.56, 29.54, 26.33, 22.88, 14.34. MALDI-TOF mass: calcd. for C\(_{113}\)H\(_{88}\)O\(_5\) 1525.94, obsd. 1526.54.

Compound 21.  

To a toluene solution (10 mL) of 17 (100 mg, 0.0656 mmol) were successively added under argon AcOH (10 mL) and concentrated aqueous HCl (38%, 4 mL), and the mixture was heated to reflux overnight. The reaction mixture was evaporated to dryness under a reduced pressure. The residue was subjected to repeated reprecipitations from CHCl\(_3\)/MeOH, to
allow isolation of 21 as dark brown solid (99 mg, 0.0656 mmol) quantitatively. ¹H NMR (500 MHz, CDCl₃): δ (ppm) 7.94 (d, J = 8.5 Hz, 2H), 7.70 (d, J = 8.5 Hz, 2H), 6.84 (s, 2H), 4.06 (t, J = 6.5 Hz, 4H), 4.01 (t, J = 6.5 Hz, 2H), 3.23 (t, J = 8 Hz, 2H), 2.90 (t, J = 8 Hz, 2H), 1.85–1.77 (m, 6H), 0.87–1.25 (m, 48H), 0.88–0.85 (m, 9H). MALDI-TOF mass: calcd. for C₁₁₂H₈₆O₅ 1511.91, obsd. 1512.05.

**Compound 1Lipo.**  To a CH₂Cl₂/toluene solution (16 mL, 1/1 v/v) of a mixture of 11 (71 mg, 0.0607 mmol) and 21 (99 mg, 0.0656 mmol) were successively added DPTS (18 mg, 0.0595 mmol) and DCC (63 mg, 0.304 mmol), and the mixture was heated to reflux under argon overnight. The reaction mixture was concentrated under a reduced pressure and subjected to column chromatography (SiO₂, CHCl₃), followed by recycling preparative SEC (JAIGEL 2H/3H, THF) to allow isolation of 1Lipo as dark brown solid (108 mg, 0.0406 mmol) in 67% yield. ¹H NMR (500 MHz, CDCl₃): δ (ppm) 7.93 (d, J = 8.5 Hz, 2H), 7.69 (d, J = 8.5 Hz, 2H), 7.10–6.94 (m, 11H), 6.84 (s, 2H), 6.75 (s, 2H), 4.31 (t, J = 6.5 Hz, 2H), 4.06–3.96 (m, 12H), 3.24 (t, J = 8 Hz, 2H), 3.13 (br., 2H), 2.91 (t, J = 8 Hz, 2H), 1.83–1.71 (m, 12H), 1.48 (br., 2H), 1.34–1.21 (m, 12H), 1.18–1.07 (m, 18H). ¹³C NMR (125 MHz, CDCl₃): δ (ppm) 172.06, 153.37, 148.36, 147.14, 145.58, 145.08, 145.06, 145.03, 144.93, 144.88, 144.65, 144.63, 144.57, 144.51, 144.40, 144.27, 143.94, 143.62, 143.60, 142.91, 142.84, 142.81, 142.12, 142.01, 141.99, 141.30, 141.30, 140.91, 140.64, 138.09, 137.63, 135.48, 134.67, 132.35, 126.97, 124.36, 79.53, 73.57, 69.27, 50.56, 32.00, 30.47, 30.41, 29.84, 29.79, 29.75, 29.70, 29.59, 29.55, 29.51, 25.97, 29.46, 26.27, 26.25, 26.22, 26.20, 22.80, 14.23. MALDI-TOF mass: calcd. for C₁₈₀H₁₇₈O₆S₆ 2662.79, obsd. 2662.00. UV-vis (CH₂Cl₂, 25°C): λ_max/nm (ε/M⁻¹ cm⁻¹) 700 (107), 451 (65100), 328 (55100), 260 (151000).
3. Film Preparation for Spectroscopic, Photoconduction, and FP-TRMC Measurements.

**LC-1\textsubscript{Amphi} films.** A CH\textsubscript{2}Cl\textsubscript{2} solution of 1\textsubscript{Amphi} (0.1 mM) was cast onto a quartz plate (for spectroscopy and FP-TRMC) or 8-\textmu m-gap Au/Ti electrodes (for photoconduction). The resulting cast film was annealed under a reduced pressure upon heating at 145 °C for 1 min, cooling to 135 °C at a rate of 1 °C/h, and then natural cooling to 25 °C.

**LC-1\textsubscript{Lipo} films.** A CH\textsubscript{2}Cl\textsubscript{2} solution of 1\textsubscript{Lipo} (0.1 mM) was cast onto a quartz plate (for spectroscopy and FP-TRMC) or 8-\textmu m-gap Au/Ti electrodes (for photoconduction). The resulting cast film was annealed under a reduced pressure upon heating at 120 °C for 1 min, cooling to 110 °C at a rate of 1 °C/h, and then natural cooling to 25 °C.

**Films of 2, 3, and their 1:1 mixture.** A CH\textsubscript{2}Cl\textsubscript{2} solution of 2, 3, or their 1:1 mixture (0.1 mM) was cast onto a quartz plate (for spectroscopy and FP-TRMC) or 8-\textmu m-gap Au/Ti electrodes (for photoconduction). The resulting cast film was dried at 25 °C under a reduced pressure.
4. Supporting Figures

**Figure S1.** (a) $^1$H and (b) $^{13}$C NMR spectra of $^{1}$Amphi (blue) and $^{1}$Lipo (red) in CDCl$_3$ at 25 °C.
**Figure S2.** MALDI-TOF mass spectra of (a) 1<sub>Amphi</sub> and (b) 1<sub>Lipo</sub> using dithranol as a matrix.

**Figure S3.** Electronic absorption spectra of 1<sub>Amphi</sub> (blue), 1<sub>Lipo</sub> (red), 2 (green), 3 (magenta), and a 1:1 mixture of 2 and 3 (black) in CH<sub>2</sub>Cl<sub>2</sub> (10 µM) at 25 °C with an optical path length of 1 cm.
Figure S4. Cyclic voltammograms of 1_{Amph} (blue), 1_{Lipo} (red), 2 (green), and 3 (magenta) in CH$_2$Cl$_2$ at 25 °C. Two platinum wires and SCE were used as working, counter, and reference electrodes, respectively. Bu$_4$PF$_6$ (0.1 M) was used as supporting electrolyte.
Figure S5. DSC traces with phase transition temperatures (ΔH values in kJ mol⁻¹) of 1Amphi (blue) and 1Lipo (red) upon second heating/cooling at 5 °C/min under N₂. Iso: isotropic melt; SmA: smectic A mesophase.
**Figure S6.** Fluorescence spectra at 25 °C of LC-1_{Amph} (blue), LC-1_{Lipo} (red), and cast films of 2 (green) and a 1:1 mixture of 2 and 3 (black), upon excitation at 355 nm. Peaks around 710 nm are frequency-doubled harmonic peaks of the excitation light.