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Supplementary Information

Luminescence tuning with excellent colour homogeneity and steadiness using fluorescent molecular liquids

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Experimental Section

Materials

All starting materials and reagents, unless otherwise specified, were purchased from commercial suppliers (where noted) and used without further purification. 2-Octyldodecyloxy bromide (**BrC_8C_{12}**)[1] and 2,6-dibromo-9,10-bis(3,5-di-2-octyldodecyloxy)phenylanthracene (**1**)[2] was synthesized and purified according to reported procedures. All reactions were performed under an argon atmosphere. Column chromatography was performed using silica gel 60 N (spherical, neutral, Kanto Chemical Co., Inc.). Spectroscopic grade solvents, dichloromethane (CH_2Cl_2; DOJINDO) and *n*-hexane (DOJINDO), were used for all spectroscopic studies without further purification.

1–**BPEA** composites with **BPEA** of 0.1, 0.5, 1.0, and 5.0 mol% were prepared by mixing dilute solutions of the two components in CH_2Cl_2, followed by fast solvent evaporation. The process was repeated for three times and the resulting mixture was dried under vacuum at room temperature overnight. All measurements were carried out within 1 week after the sample preparation.

Measurements

Recycling high performance liquid chromatography (HPLC) was performed at room temperature using a GPC column (YMC-GPC T30000 ϕ 20 × 600 mm) on a LC-9225NEXT system, equipped with RI and UV-Vis detectors. ^{1}H nuclear magnetic resonance (NMR) and ^{13}C NMR spectra were recorded on a JEOL ECS-400 spectrometer at 400 MHz and 100 MHz, respectively, with tetramethylsilane used as the internal standard. Before ^{1}H and ^{13}C NMR measurements, all samples were dried up from their CH_2Cl_2 solution to check whether residual solvent remained or not. Matrix-assisted laser desorption ionization–time-of-flight mass spectra (MALDI-TOF MS) were obtained by a Shimadzu AXIMA-CFR Plus station.

Differential scanning calorimetry (DSC) was measured using Hitachi High-Tech Science DSC7000X with liquid nitrogen cooling accessory under nitrogen flow at different scan rates (where noted). Optical micrographs were taken under polarized and normal light conditions using an Olympus BX51 optical microscopy. Fluorescence microscopy images were recorded by a Leica DM2500 DIC microscope (Leica Microsystems, Wetzlar, Germany) with excitation wavelengths of 340–380 nm. The samples were sandwiched between two glass plates for both measurements. Microscopic fluorescence spectroscopy was carried out using a Leica TCS SP5 confocal laser scanning microscope (Leica Microsystems, Wetzlar, Germany) with excitation wavelength at 405 nm. The samples were sandwiched between two quartz plates for the measurements.

For all optical absorption and fluorescence measurements, thin solvent-free liquid samples were sandwiched by two quartz plates and solid powder samples were prepared by grinding with barium sulphate ($BaSO_4$). UV-Vis absorption and fluorescence spectra in both solution and solvent-free liquid state were recorded on a JASCO V-670 spectrophotometer and a JASCO FP-8300 spectrophotometer, respectively. Absolute quantum yields were determined on a Hamamatsu Photonics absolute PL quantum yield spectrometer C11347.

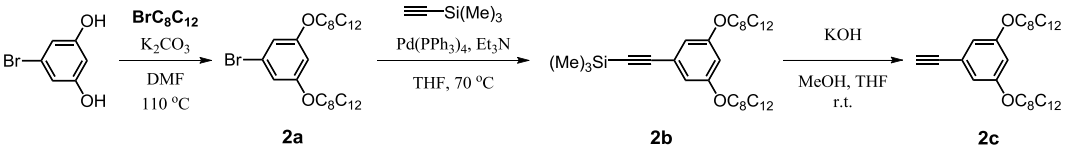
Nanosecond time-resolved fluorescence lifetime measurements were carried out by using time-correlated single photon counting (TCSPC) lifetime spectroscopy system HORIBA FluoroCube 3000U-UltraFast-SP spectrophotometer equipped with a nanosecond pulse laser (PB-375L, 375 nm) and a nanosecond photon detection module (TBX). Decay analysis and the fitting routine to determine the lifetime(s) were performed using the DAS6 software provided by IBM. The quality of the fit has been judged by the fitting parameters such as chi-squared value χ^2 (< 1.20) as well as the

visual inspection of the residuals.

Theoretic Calculation

All quantum chemical calculations were carried out using the Gaussian 09, Revision E.01 suite of programs[3] with default thresholds and algorism. The geometry optimizations of simplified models of **1**–**4** (with 2-octyldodecyl chains replaced by methyl groups) and the reference compound 9,10-bis(3,5-dimethoxyphenyl)anthracene (**DMPA**) in the ground state were performed at the B3LYP/6-31G(d) level of theory. The stationary point in the lowest single state was optimized without any assumption and characterized by frequency analysis at the same level of theory (the number of imaginary frequencies was 0). The Cartesian coordinates are given in Tables S6–10. The time-dependent density functional theory (TD-DFT) calculations at the optimized geometries were conducted at the same level of theory**.**

Synthesis and Characterization



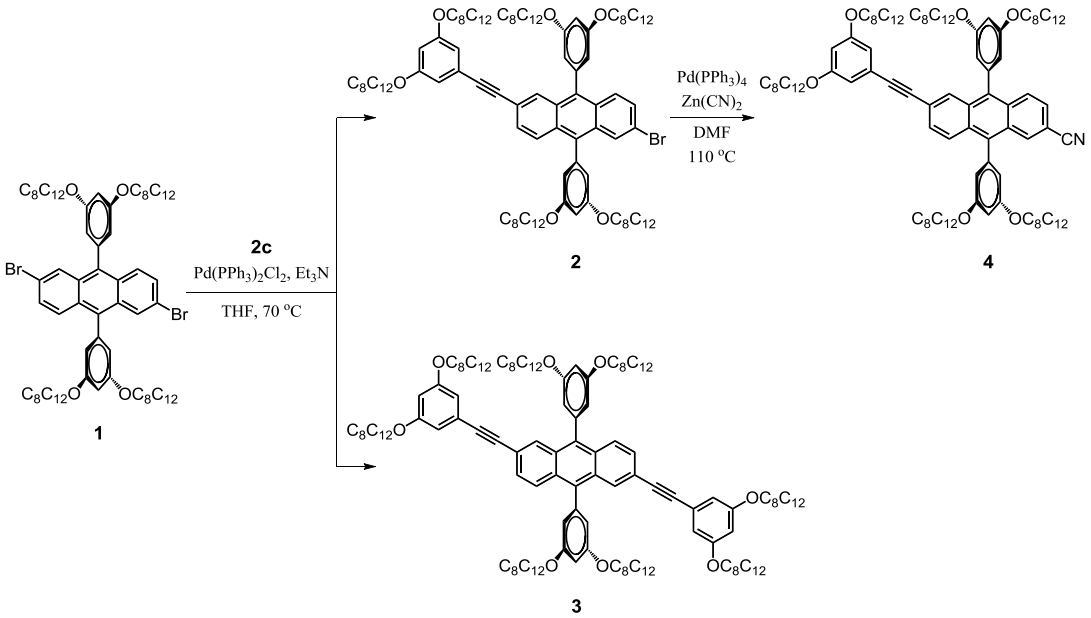
2a **2b** **2c**

Synthesis of 1-bromo-3,5-bis(2-octyldodecyloxy)benzene (2a): A mixture of 5-bromo-1,3-benzenediol (2.84 g, 10.00 mmol, Tokyo Chemical Industry Co., Ltd. (TCI)), **BrC$_8$C$_{12}$** (16.26 g, 45.0 mmol) and potassium carbonate (K_2CO_3, 16.59 g, 120.0 mmol) was stirred in dry *N*,*N*-dimethylformamide (DMF) (120 mL) at 110 °C under argon. After 24 h, the reaction mixture was filtered to remove undissolved solid and the filtrate was concentrated under reduced pressure to remove DMF. Water (50 mL) was added to the resulting residue, which was then extracted with CH_2Cl_2 (3 × 30 mL). The combined organic layer was washed with brine, dried over magnesium sulphate ($MgSO_4$), filtered and evaporated. The crude product was purified by column chromatography (SiO_2; *n*-hexane).
2a: Colorless oil (yield, 93%); TLC (*n*-hexane): R_f = 0.61; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 6.63 (d, J = 2.4 Hz, 2H), 6.36 (t, J = 2.0 Hz, 1H), 3.77 (d, J = 6.0 Hz, 4H), 1.75-1.72 (m, 2H), 1.44-1.26 (m, 64H), 0.88 (t, J = 6.4 Hz, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 161.00, 122.77, 110.13, 100.54, 71.09, 37.89, 31.93, 31.31, 30.01, 29.68, 29.66, 29.60, 29.37, 29.35, 26.82, 22.70, 14.13; MALDI-TOF MS (matrix: dithranol) calculated for $C_{46}H_{85}BrO_2$: 748.6, found: 748.3 $[M]^+$.
Synthesis of [(3,5-di-2-octyldodecyloxyphenyl)ethynyl]trimethylsilane (2b): A mixture of **2a** (4.50 g, 6.0 mmol), tetrakis(triphenylphosphine)palladium(0) ($Pd(PPh_3)_4$, 207 mg, 0.18 mmol; TCI), and copper(I) iodide (CuI, 57 mg, 0.30 mmol; Kanto Chemical Co., Inc.) was stirred in a mixture of THF (6 mL) and trimethylamine (39 mL) under argon. Ethynyl trimethylsilane (1.3 mL, 9.0 mmol) was injected and the reaction mixture was heated up to 70 °C. After 2 h, another portion of ethynyl trimethylsilane (1.3 mL, 9.0 mmol) was injected and the mixture was stirred overnight. The reaction mixture was cooled to room temperature and then filtered to remove undissolved solid. The filtrate was concentrated under reduced pressure to remove the solvents. The residue was dissolved in CH_2Cl_2 (50 mL), and then washed with saturated NH_4Cl (aq., 30 mL) and brine (30 mL). The organic layer was dried over magnesium sulphate ($MgSO_4$), filtered, and evaporated. The crude product was purified by column chromatography (SiO_2; *n*-hexane).

2b: Yellow-green oil (yield, 75%); TLC (*n*-hexane): R_f = 0.13; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 6.59 (d, J = 2.4 Hz, 2H), 6.43 (t, J = 2.4 Hz, 1H), 3.78 (d, J = 5.2 Hz, 4H), 1.74-1.71 (m, 2H), 1.42-1.26 (m, 64H), 0.88 (t, J = 6.8 Hz, 12H), 0.24 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 160.20, 124.04, 110.03, 105.29, 103.02, 70.87, 37.95, 31.95, 31.34, 30.04, 29.71, 29.67, 29.62, 29.39, 26.85, 22.72, 14.17; MALDI-TOF MS (matrix: dithranol) calculated for $C_{51}H_{94}O_2Si$: 766.7, found: 767.4 $[M]^+$.

Synthesis of 1-ethynyl-3,5-bis(2-octyldodecyloxy)benzene (2c): A mixture of **2b** (480 mg, 0.63 mmol) and potassium hydroxide (KOH, 105 mg, 1.88 mmol) was stirred in a mixture of methanol (5 mL) and THF (10 mL) at room temperature under argon. After 8 h, the reaction mixture was concentrated under reduced pressure to remove the solvents. Water (30 mL) was added to the resulting residue, which was then extracted with CH_2Cl_2 (3 × 30 mL). The combined organic layer was washed with brine, dried over magnesium sulphate ($MgSO_4$), and filtered. The product was collected via evaporation without any further purification.

2c: Yellow oil (yield, quant.); TLC (*n*-hexane): R_f = 0.19; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 6.62 (d, J = 2.4 Hz, 2H), 6.46 (t, J = 2.4 Hz, 1H), 3.78 (d, J = 5.6 Hz, 4H), 3.01 (s, 1H), 1.76-1.72 (m, 2H), 1.44-1.26 (m, 60H), 0.88 (t, J = 6.8 Hz, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 160.24, 123.02, 110.26, 103.07, 83.81, 70.92, 37.88, 31.93, 31.30, 30.02, 29.69, 29.66, 29.61, 29.37, 26.81, 22.70, 14.15; MALDI-TOF MS (matrix: dithranol) calculated for $C_{46}H_{86}O_2$: 694.7, found: 695.5 $[M]^+$.



Synthesis of 2 and 3: To a mixture of **1** (610 mg, 0.36 mmol), bis(triphenylphosphone)palladium(II) dichloride ($Pd(PPh_3)_2Cl_2$, 131 mg, 0.19 mmol; TCI), and copper(I) iodide (CuI, 126 mg, 0.66 mmol; Kanto Chemical Co., Inc.) in 50 mL anhydrous THF, a THF solution of **2c** (1.01 g, 1.45 mmol) and triethyl amine (3 mL) were added at 70 °C. The mixture was stirred for 120 h at 70 °C under argon. After the completion of the reaction, the solution was washed with distilled water. The organic layer was washed with brine, dried over anhydrous sodium sulphate, and the solvent was evaporated under reduced pressure. The purification, carried out by column chromatography (SiO_2, *n*-hexane/ CH_2Cl_2) and subsequent recycling HPLC with chloroform as the solvent, gave **2** (216 mg, 0.094 mmol) and **3** (111 mg, 0.038 mmol) as yellow liquids.

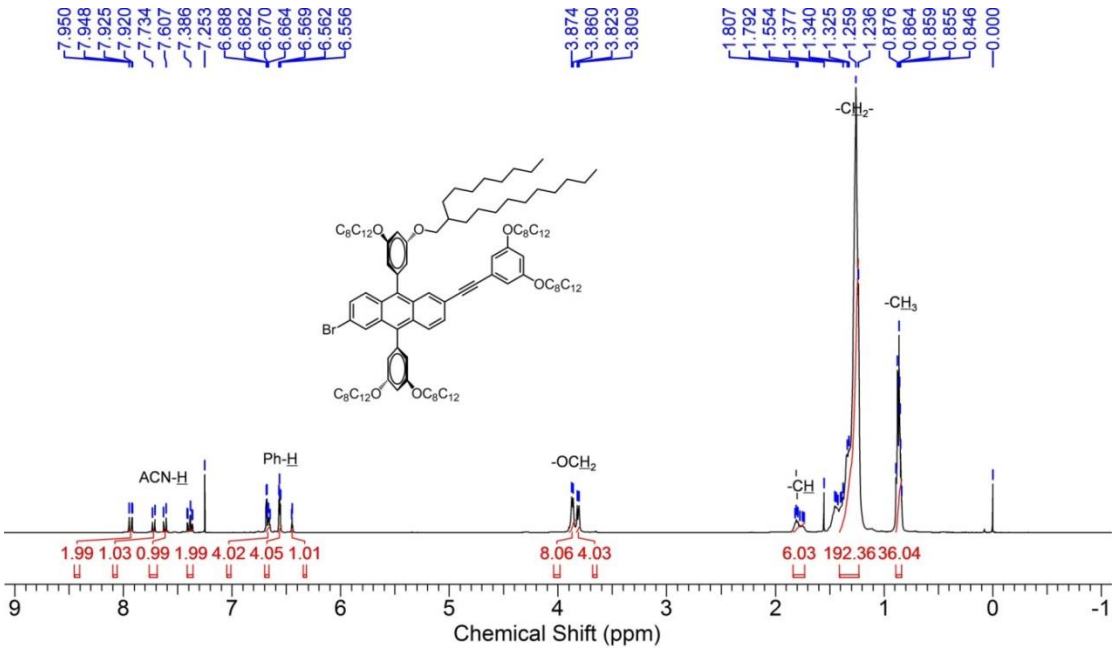
2: Yellow liquid (yield, 26%); TLC (*n*-hexane: CH_2Cl_2, 20:1 v/v): R_f = 0.25; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.94 (s, 1H), 7.92 (d, *J* = 1.6 Hz, 1H), 7.72 (d, *J* = 9.6 Hz, 1H), 7.62 (d, *J* = 9.2 Hz, 1H), 7.39 (td, *J* = 8.8, 1.2 Hz, 2H), 6.69–6.56 (m, 4H), 6.56 (t, *J* = 2.8 Hz,, 4H), 6.45 (t, *J* = 2.0 Hz, 1H), 3.86 (d, *J* = 5.6 Hz, 8H), 3.81 (d, *J* = 1.6 Hz, 4H), 1.82–1.74 (m, 6H), 1.45–1.25 (m, 192H), 0.89–0.85 (m, 36H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 160.60, 160.56, 160.30, 139.82, 139.67, 137.69, 136.47, 130.87, 130.59, 129.24, 129.17, 128.80, 128.72, 128.38, 128.01, 127.22, 124.08, 120.20, 120.04, 109.71, 109.66, 102.83, 101.07, 90.87, 89.51, 71.37, 71.25, 70.87, 38.02, 37.97, 31.92, 31.37, 30.03, 29.65, 29.36, 26.88, 22.69, 14.14; MALDI-TOF MS (matrix: dithranol) calculated for $C_{154}H_{261}BrO_6$: 2285.9, found: 2286.0 $[M]^+$.

3: Yellow liquid (yield, 10%); TLC (*n*-hexane: CH_2Cl_2, 10:1 v/v): R_f = 0.17; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.95 (s, 2H), 7.70 (d, *J* = 9.2 Hz, 2H), 7.38 (dd, *J* = 8.8, 1.6 Hz, 2H), 6.69–6.67 (m, 6H), 6.59 (d, *J* = 2.0 Hz, 4H), 6.45 (t, *J* = 1.6 Hz, 2H), 3.88–3.81 (m, 16H), 1.82–1.72 (m, 8H), 1.49–1.23 (m, 256H), 0.88–0.84 (m, 48H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 160.55, 160.30, 140.06, 137.28, 130.59, 129.61, 129.10, 127.74, 127.33, 124.14, 120.04, 109.71, 102.83, 101.06, 90.88, 89.64, 71.38, 70.89, 38.03, 37.98, 31.92, 31.34, 30.03, 29.66, 29.37, 26.85, 22.70, 14.13; MALDI-TOF MS (matrix: dithranol) calculated for $C_{202}H_{346}O_8$: 2900.7, found: 2901.2 $[M]^+$.

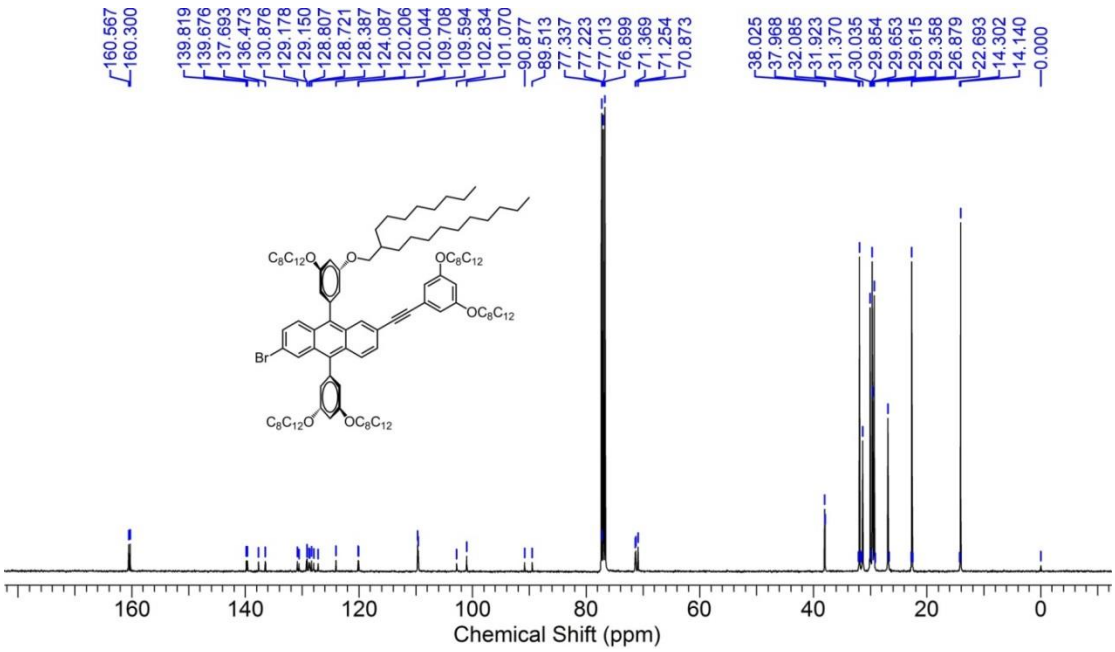
Synthesis of 4: A mixture of **2** (216 mg, 0.094 mmol), tetrakis(triphenylphosphine)palladium(0) ($Pd(PPh_3)_4$, 59 mg, 0.051 mmol; TCI), and zinc cyanide ($Zn(CN)_2$, 43 mg, 0.37 mmol; Sigma-Aldrich) in anhydrous DMF (5 mL) was stirred at 110 ^{o}C for 22 h. After the completion of the reaction, the reaction mixture was cooled to room temperature, excess chloroform was added and washed with distilled water. The organic layer was washed with brine, dried over anhydrous sodium sulphate and the solvent was evaporated under reduced pressure. The crude product was purified by silica-gel column chromatography (SiO_2, *n*-hexane/ethyl acetate). The subsequent recycling HPLC with chloroform as the solvent gave **4** (122 mg, 0.055 mmol) as a yellow liquid.

4: Yellow liquid (yield, 58%); TLC (*n*-hexane: CH_2Cl_2, 10:1 v/v): R_f = 0.08; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.21 (s, 1H), 7.98 (s, 1H), 7.80 (t, *J* = 9.6 Hz, 2H), 7.44 (dd, *J* = 9.2, 1.2 Hz, 1H), 7.39 (dd, *J* = 9.2, 1.2 Hz, 1H), 6.69 (d, *J* = 2.4 Hz, 4H), 6.55 (dd, *J* = 5.6, 2.4 Hz, 4H), 5.46 (t, *J* = 2.0 Hz, 1H), 3.87 (d, *J* = 6.0 Hz, 8H), 3.82 (d, *J* = 5.6 Hz, 4H), 1.81–1.74 (m, 6H), 1.46–1.24 (m, 192H), 0.88–0.85 (m, 36H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 160.72, 160.69, 160.33, 139.26, 138.96, 138.83, 137.73, 130.95, 130.48, 130.04, 129.38, 128.73, 128.53, 127.62, 124.32, 123.86, 121.52, 119.70, 109.78, 109.57, 108.59, 102.97, 101.52, 91.72, 89.22, 71.40, 71.32, 70.91, 38.04, 37.98, 31.92, 31.38, 30.03, 29.65, 29.61, 29.36, 26.90, 26.86, 22.69, 14.13; MALDI-TOF MS (matrix: dithranol) calculated for $C_{155}H_{261}NO_6$: 2233.0, found: 2233.7 $[M]^+$.

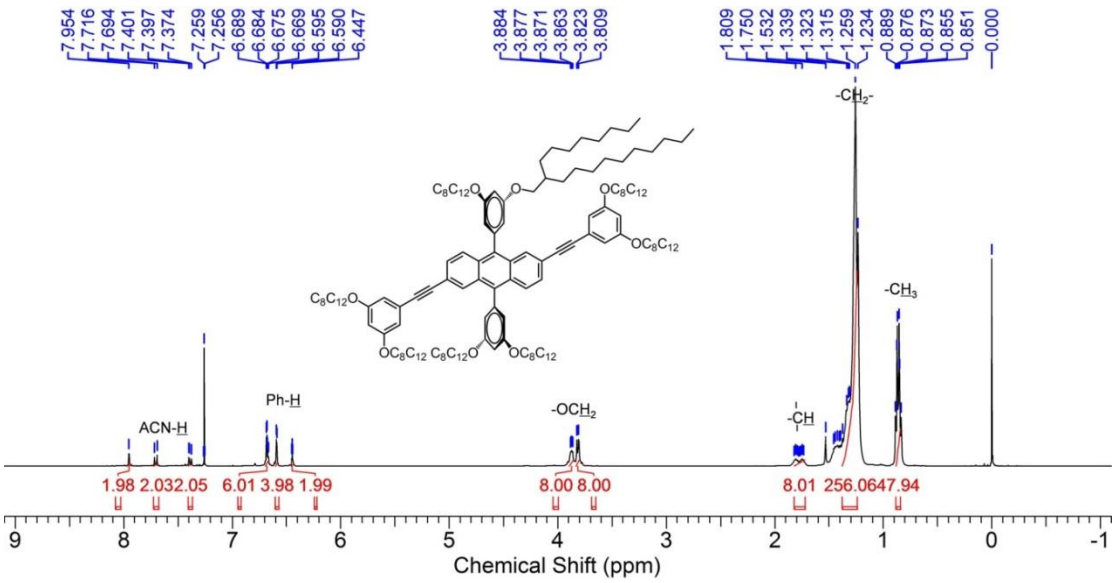
NMR spectra and MALDI-TOF MS



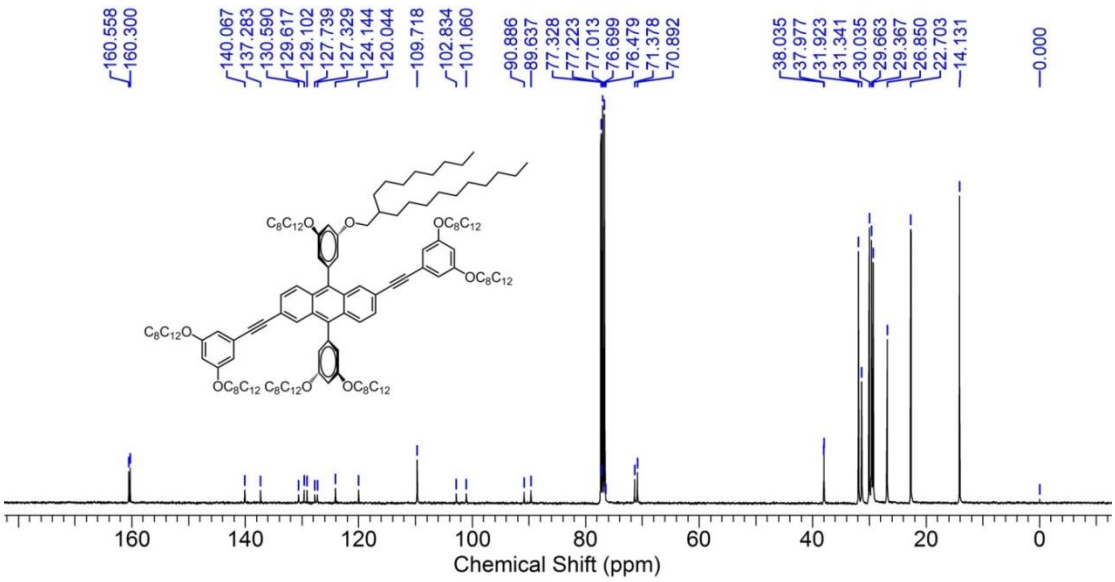
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2**.



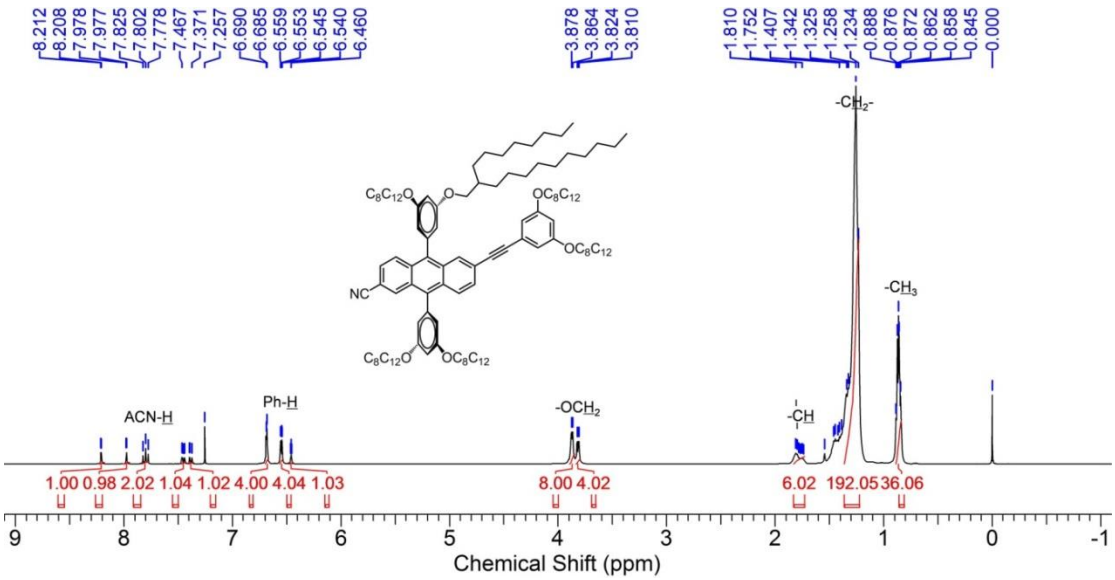
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **2**.



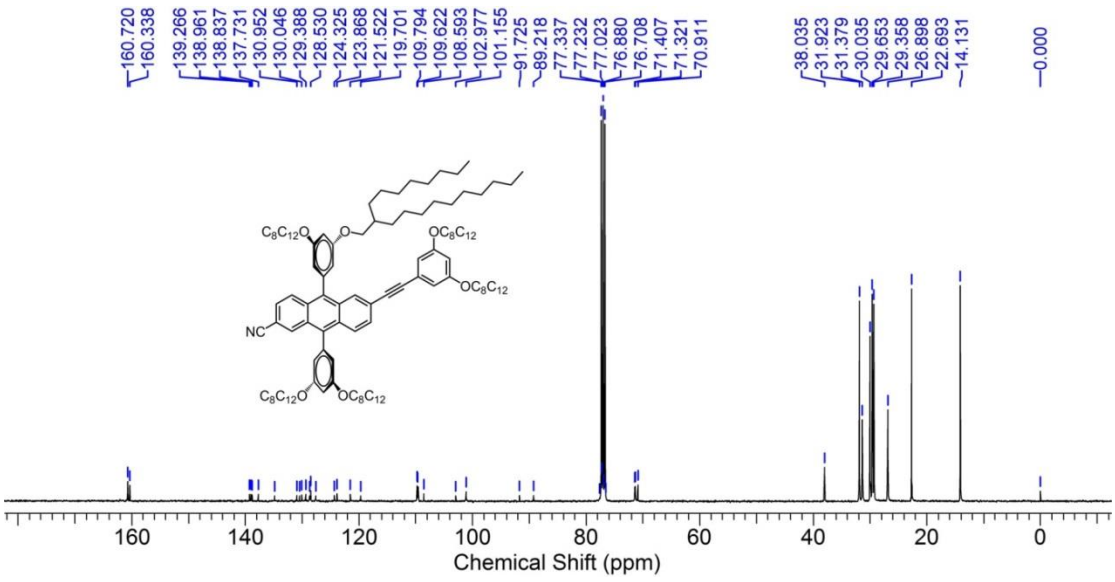
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3**.



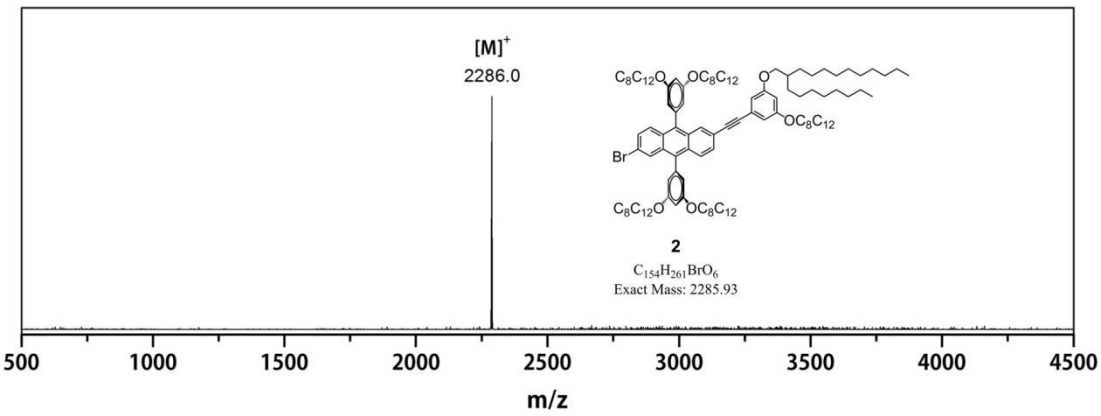
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3**.



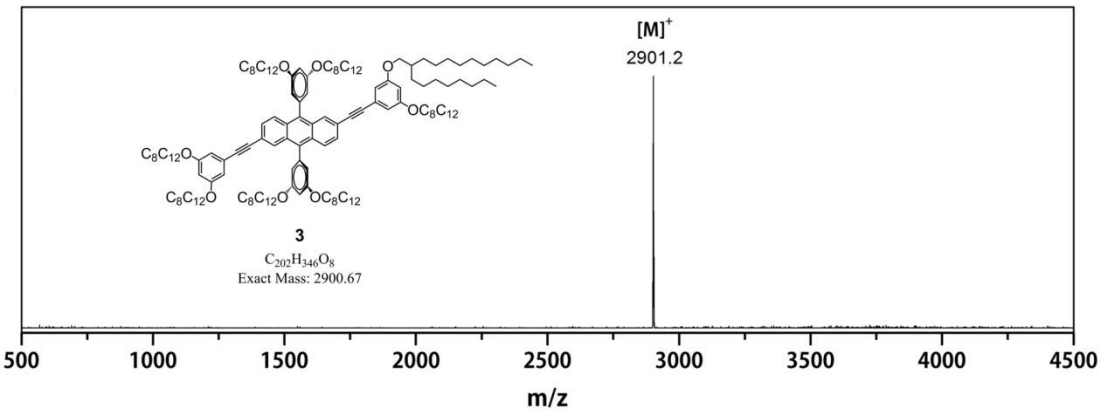
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4**.



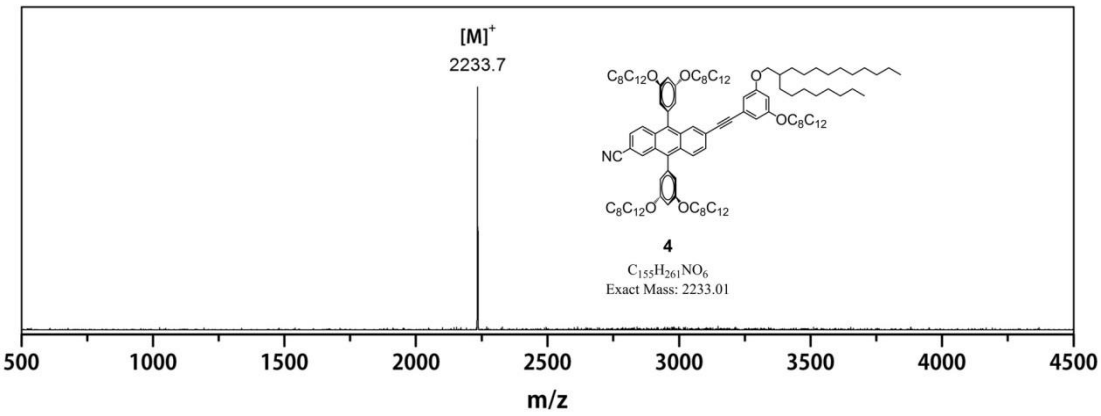
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **4**.



MALDI-TOF MS of **2**. Matrix: dithranol.



MALDI-TOF MS of **3**. Matrix: dithranol.



MALDI-TOF MS of **4**. Matrix: dithranol.

Supplementary Figures

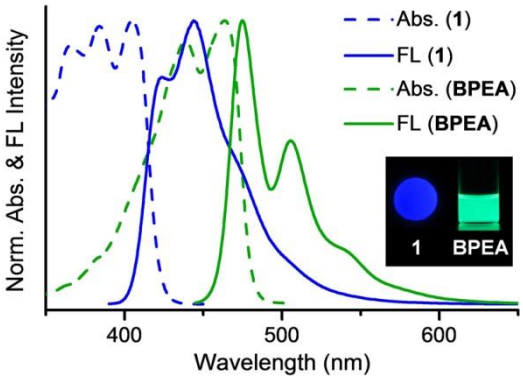


Figure S1. Normalized UV-vis absorption (dot line) and fluorescence (solid line) spectra of liquid **1** (blue) and **BPEA** in CH_2Cl_2 solution (10^{-6} M) (green). Inset, photographs of liquid **1** (a drop on a glass plate) and **BPEA** solution (CH_2Cl_2, 10^{-6} M) under irradiation of a UV lamp (365 nm).

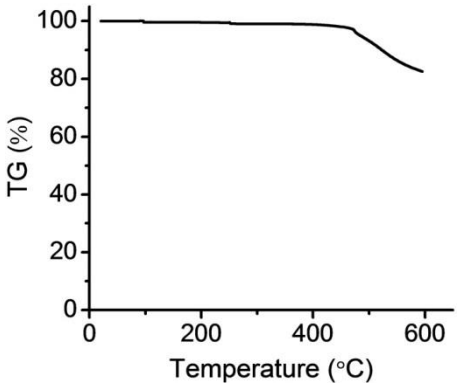


Figure S2. Thermogravimetric analysis of **BPEA**. The decomposition (5% mass loss) occurred at 485 °C.

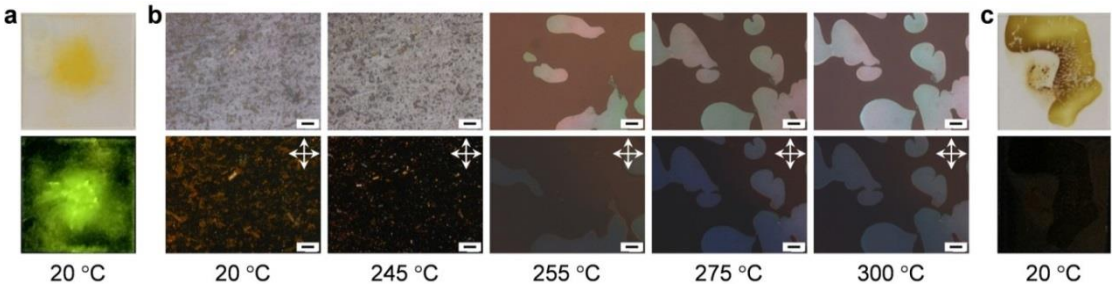


Figure S3. (**a**) Photographs of **BPEA** powders sandwiched between two glass plates under daylight conditions (upper) and under irradiation of a UV lamp (365 nm) (lower) at 20 °C; strong yellow-green emission was observed for **BPEA** powder. (**b**) Optical (upper) and polarized optical (lower) micrographs of **BPEA** sample from (**a**) recorded at different temperatures upon heating from 20 to 300 °C (as denoted below the micrographs) (scale bar, 50 μm). After melting at 255 °C, the sample turned into dark from 255 to 275 °C and lost fluidity from 275 to 300 °C, indicating intermolecular crosslinking. (**c**) Photographs of the sample from (**b**) under daylight conditions (upper) and under irradiation of a UV lamp (365 nm) (lower) at 20 °C. The resulting dark brown stuff exhibits negligible fluorescence, another indication for intermolecular crosslinking reaction.

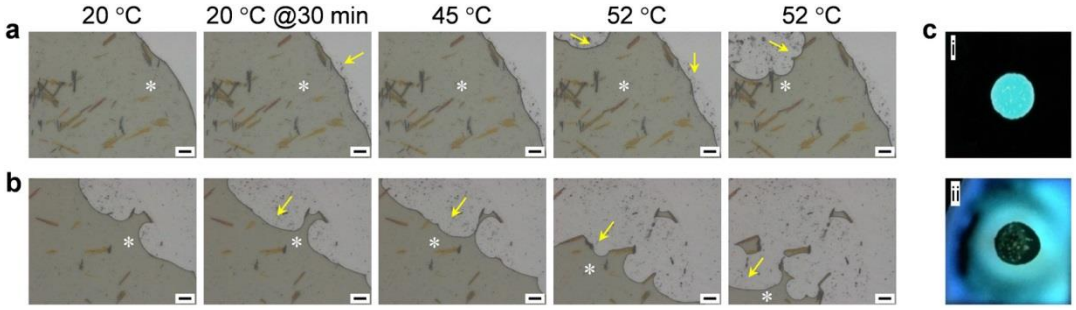


Figure S4. Optical micrographs of **1–BPEA** (5.0 mol%) composite **IV** recorded (**a**) from 20 to 52 °C (left to right, the temperature value was denoted above each micrograph) and (**b**) at 55 °C. (**c**) Photographs of **1-BPEA** (5.0 mol%) composite **IV** sandwiched between two square glass plates before (left) and after (right) heating up to 300 °C (taken under irradiation of a UV lamp (365 nm) at 20 °C). The side of the square glass is of 1.8 cm.

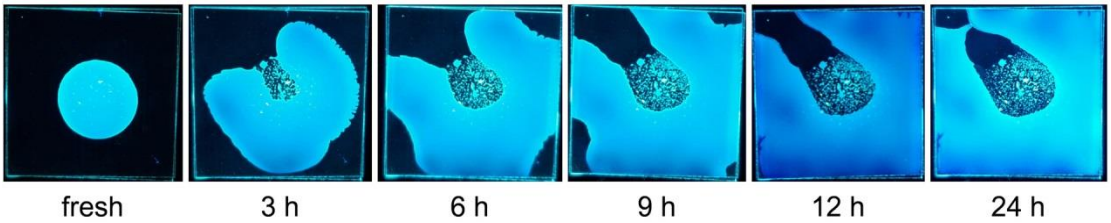


Figure S5. Photographs of a drop of **1-BPEA** (5.0 mol%) composite **IV** sandwiched between two square glass plates taken as fresh and after different time periods (denoted below each graph) under irradiation of a UV lamp (365 nm) at 20 °C. The side of the square glass is of 1.8 cm.

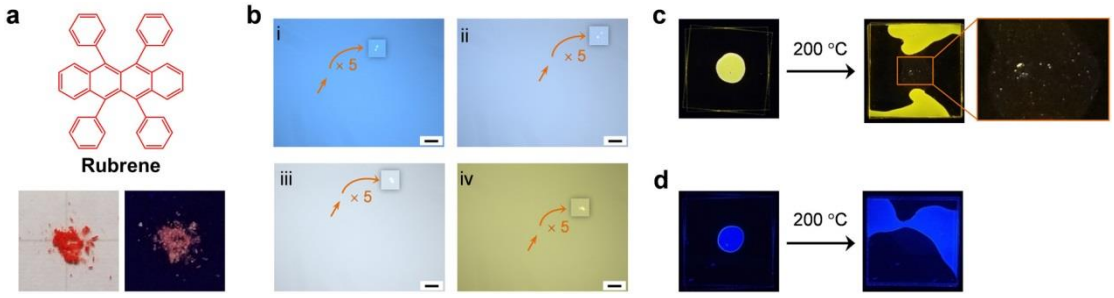


Figure S6. (**a**) Chemical structure (upper) and photographs (lower) (taken under daylight conditions (left) and under irradiation of a UV lamp (365 nm)) of rubrene. (**b**) Fluorescence micrographs for **1**–rubrene composites with 0.1 (i), 0.5 (ii), 1.0 (iii), and 5.0 (iv) mol% of rubrene at 20 °C. Scale bar, 50 μm. λ_{ex}: 340–380 nm. Photographs of (**c**) **1**-rubrene (5.0 mol%) composite and (**d**) pure liquid **1** sandwiched between two square glass plates before and after heating up to 200 °C (taken under irradiation of a UV lamp (365 nm) at 20 °C). The side of the square glass is of 1.8 cm.

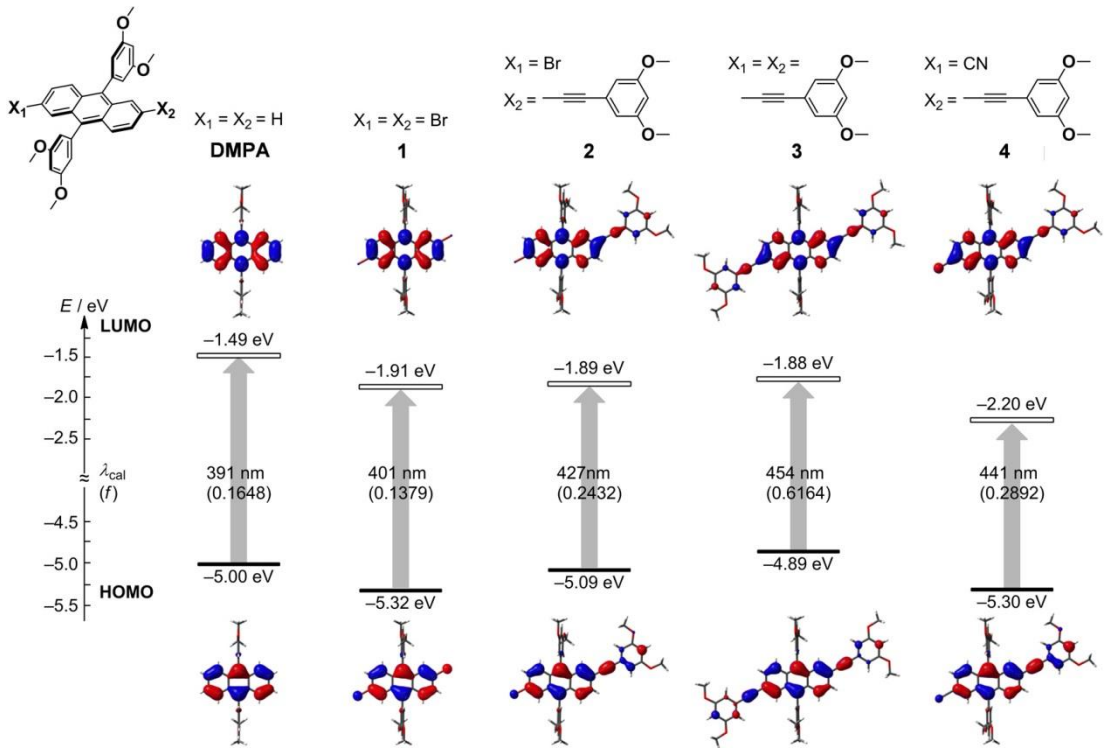


Figure S7. Kohn-Sham molecular orbitals and electronic transitions for 9,10-bis(3,5-dimethoxyphenyl)-anthracene (**DMPA**) and simplified models of **1**–**4** (with 2-octyldodecyl chains replaced by methyl groups) in the ground state calculated at the B3LYP/6-31G(d)//B3LYP/6-31G(d) level of theory.

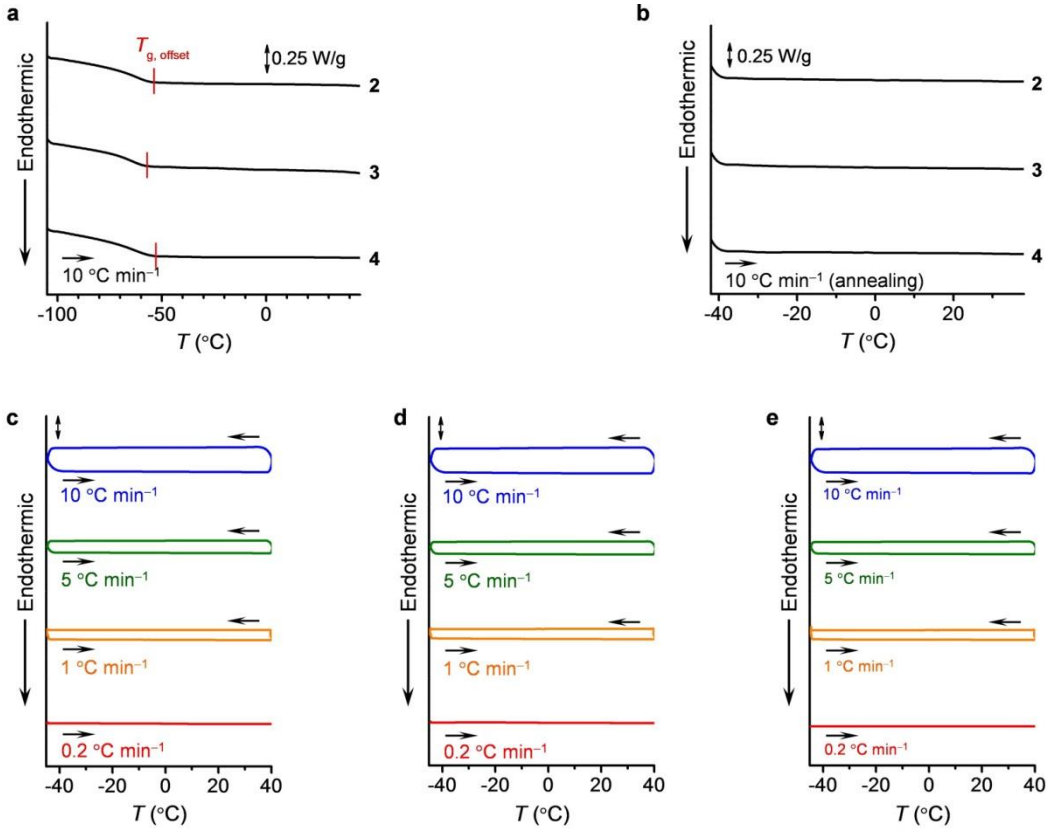


Figure S8. DSC thermograms of **2**, **3**, and **4** (**a**) during the first heating scan from −105 to 45 °C at 10 °C min^{-1} under nitrogen flow ($T_{g, offset}$: the offset temperature of the *glass*-to-*isotropic liquid* transition), and (**b**) during the heating scan from −45 to 40 °C at 10 °C min^{-1} after annealing at −45 °C for 12 hours. DSC thermograms of (**c**) **2**, (**d**) **3**, and (**e**) **4** during the heating/cooling cycles between −45 and 40 °C at 10 °C min^{-1} (blue line; scale bar, 1 W/g), 5 °C min^{-1} (green line; scale bar, 1 W/g), 1 °C min^{-1} (orange line; scale bar, 0.25 W/g), and 0.2 °C min^{-1} (red line; scale bar, 0.25 W/g) under nitrogen flow.

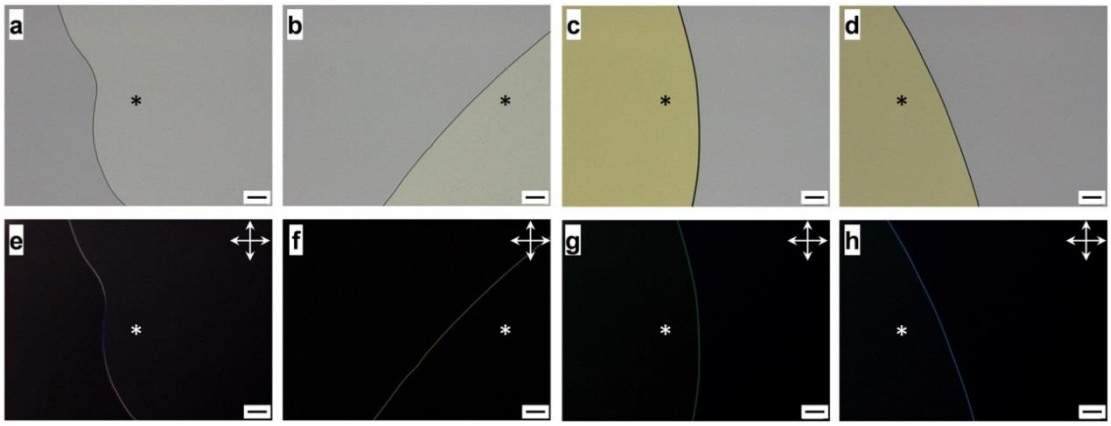


Figure S9. Optical (upper) and polarized optical (lower) micrographs of **1** (**a** and **e**), **2** (**b** and **f**), **3** (**c** and **g**), and **4** (**d** and **h**) at 20 °C. The sample area was denoted with asterisk (∗). Scale bar, 50 μm.

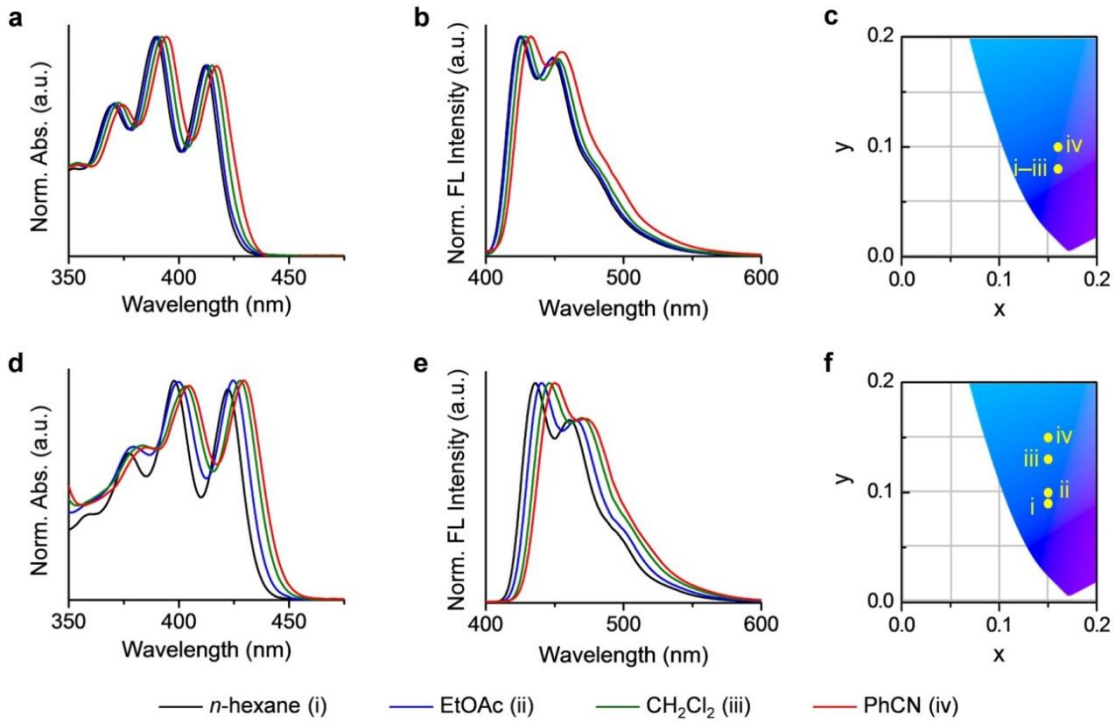


Figure S10. Normalized UV-vis absorption (**a**, **d**) and fluorescence (**b**, **e**) spectra and section of CIE 1931 chromaticity diagrams (**c**, **f**) of **2** (**a**, **b**, and **c**) and **4** (**d**, **e**, and **f**) recorded in various solvents (UV-vis, 5×10^{-6} M; fluorescence, 10^{-6} M) at 20 °C. The solvents (dielectric constant) used were: *n*-hexane (1.89), ethyl acetate (EtOAc, 6.02), dichloromethane (CH_2Cl_2, 8.93) and benzonitrile (PhCN, 26.0).

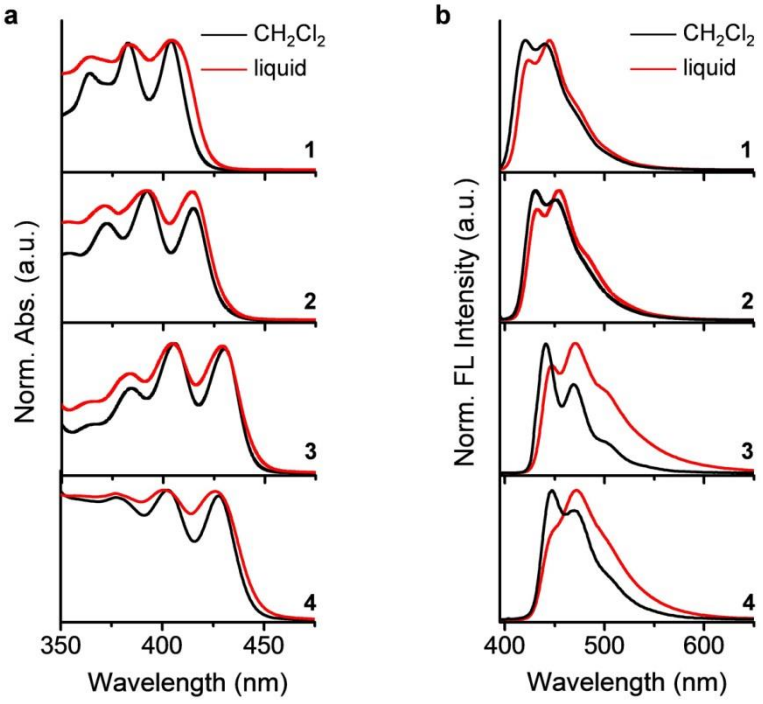


Figure S11. Normalized of UV-vis absorption (**a**) and fluorescence (**b**) spectra of **1–4** (as denoted inside) in CH_2Cl_2 (UV-vis, 10^{-6} M; fluorescence, 10^{-6} M) (black line) and solvent-free liquid state (red line).

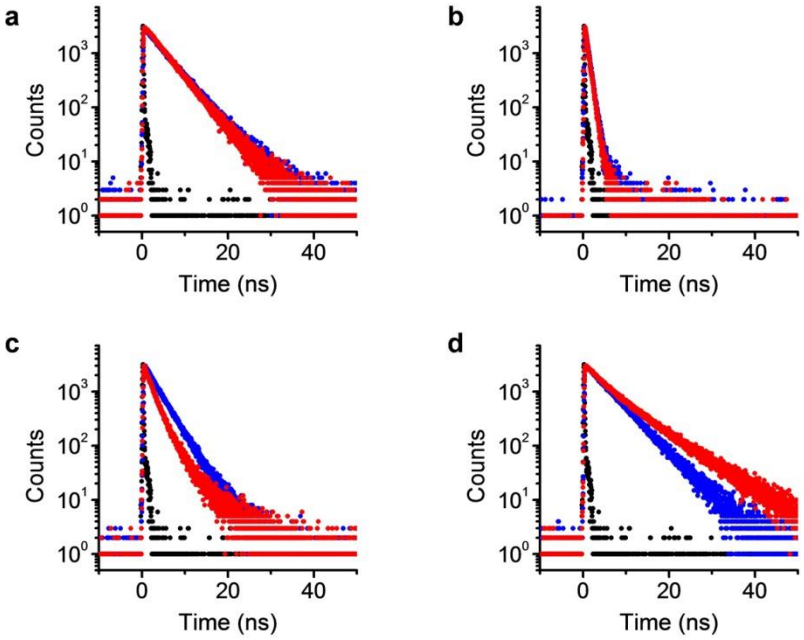


Figure S12. Nanosecond time-resolved fluorescence decay profiles of (**a**) **1**, (**b**) **2**, (**c**) **3**, and (**d**) **4** in solution (10^{-6} M) (blue) and solvent-free liquid state (red). **IRF**: Instrument response function (black). Solvent: CH_2Cl_2. λ_{ex}: 375 nm.

Supplementary Tables

Table S1. Physical characteristics ($T_{g,\ offset}$: the offset temperature of glass transition in the second heating trace) and photophysical parameters (ΔE: HOMO–LUMO energy gap; λ: wavelength; ε: absorption coefficient; and Φ_{FL}: absolute fluorescence quantum yield) of **1–4** in CH_2Cl_2 solution (10^{-5} M) and solvent-free liquid state

Compound	$T_{g,\ offset}$ (°C)[a]	ΔE, eV (nm)[b]	Absorption Feature λ_{abs}, nm (ε, 10^4 dm^3 mol^{-1} cm^{-1})		Fluorescence λ_{max}, nm (Φ_{FL})		*CIE* (*x*, *y*)	
			CH_2Cl_2	Liquid[c]	CH_2Cl_2	Liquid[c]	CH_2Cl_2	Liquid[c]
1	−50.8	3.41 (401)	364 (1.32) 383 (1.74) 404 (1.78)	364 383 404	420 (0.47)	444 (0.37)	0.16, 0.05	0.15, 0.08
2	−53.1	3.20 (427)	372 (1.34) 392 (1.79) 415 (1.55)	371 392 414	429 (0.10)	444 (0.37)	0.16, 0.13	0.17, 0.19
3	−57.8	3.01 (454)	384 (1.16) 405 (1.78) 430 (1.71)	384 405 429	441 (0.52)	455 (0.05)	0.15, 0.11	0.18, 0.26
4	−54.4	3.10 (441)	384 (1.32) 403 (1.83) 428 (1.85)	377 401 426	446 (0.68)	470 (0.22)	0.15, 0.13	0.16, 0.32

[a] Determined in the first DSC heating scan at 10 °C min^{-1} under N_2.

[b] Calculated for the simplified models of **1**–**4**, with the alkyl chains replaced by methyl groups.

[c] Prepared by sandwiching the liquid between two quartz plates.

Table S2. Photophysical parameters (λ: wavelength; ε: absorption coefficient; and Φ_{FL}: absolute fluorescence quantum yield) of **2** in various solvents of different polarities

Solvent (dielectric constant)	Absorption Feature[a] λ_{abs}, nm (ε, 10^4 dm^3 mol^{-1} cm^{-1})	Fluorescence[b] λ_{max}, nm (Φ_{FL})	*CIE* (*x*, *y*)
n-hexane (1.89)	370 (1.17) 389 (1.70) 412 (1.48)	425 (0.08)	0.16, 0.08
ethyl acetate (6.02)	371 (1.24) 390 (1.78) 413 (1.55)	436 (0.08)	0.16, 0.08
CH_2Cl_2 (8.93)	372 (1.34) 392 (1.79) 415 (1.41)	429 (0.10)	0.16, 0.08
benzonitrile (26.0)	374 (1.07) 394 (1.53) 417 (1.34)	433 (0.15)	0.16, 0.10

[a] Concentration: 5×10^{-6} M.

[b] Concentration: 10^{-6} M.

Table S3. Photophysical parameters (λ: wavelength; ε: absorption coefficient; and Φ_{FL}: absolute fluorescence quantum yield) of **4** in various solvents of different polarities

Solvent (dielectric constant)	**Absorption Feature**[a] λ_{abs}, nm (ε, 10^4 dm^3 mol^{-1} cm^{-1})	**Fluorescence**[b] λ_{max}, nm (Φ_{FL})	***CIE*** *(x, y)*
n-hexane (1.89)	377 (1.20) 398 (1.79) 422 (1.72)	436 (0.79)	0.15, 0.09
ethyl acetate (6.02)	379 (1.06) 400 (1.51) 425 (1.52)	440 (0.61)	0.15, 0.10
CH_2Cl_2 (8.93)	384 (1.32) 403 (1.83) 427 (1.85)	446 (0.68)	0.15, 0.13
benzonitrile (26.0)	385 (1.07) 405 (1.51) 428 (1.55)	450 (1.00)	0.15, 0.15

[a] Concentration: 5×10^{-6} M.
[b] Concentration: 10^{-6} M.

Table S4. Fitting parameters (λ_{moni}: monitored wavelength; τ: decay time; and χ^2: chi-squared value) of fluorescence decays of **1**–**4** in CH_2Cl_2 solution (10^{-6} M)

Compound	λ_{moni}, nm[a]	τ, nm[b]	χ^2
1	420	4.6	1.19
2	430	0.7	1.06
3	441	3.2	1.06
4	447	5.1	1.08

[a] Recorded at their respective maximum emission wavelengths.
[b] λ_{ex} = 375 nm.

Table S5. Fitting parameters (λ_{moni}: monitored wavelength; τ: decay time; and χ^2: chi-squared value) of fluorescence decays of **1**–**4** in solvent-free liquid state

Compound[a]	λ_{moni}, nm[b]	τ[c]		χ^2
		τ**1**, ns **(α1)**	τ**1**, ns **(α1)**	
1	443	4.3	—	1.03
2	447	0.3 (0.23)	0.8 (0.77)	1.07
3	468	1.7 (0.70)	4.1 (0.30)	1.04
4	475	3.2 (0.23)	8.0 (0.77)	1.04

[a] Prepared by sandwiching the liquid between two quartz plates
[b] Recorded at their respective maximum emission wavelengths.
[c] λ_{ex} = 375 nm.

Table S6. Cartesian coordinates [Å] of the optimized structure for simplified **1**, with 2-octyldodecyl chains replaced by methyl groups.

atom	x	y	z	atom	x	y	z
C	-3.282514	0.143693	-1.735923	C	-1.663273	0.044151	5.48712
H	-1.656441	0.064486	-3.108014	C	-1.107656	1.23965	3.447373
C	-1.959315	0.084712	-2.068939	C	-0.99859	-1.185474	3.493616
C	-2.779929	0.12527	0.616769	C	-1.402937	-1.169736	4.830029
C	-0.956574	0.045643	-1.046662	C	-1.514257	1.243022	4.793628
C	-3.71358	0.164961	-0.382561	H	-0.997082	2.187509	2.931717
C	-1.376121	0.066047	0.336447	H	-0.795533	-2.114559	2.97557
C	0.416353	-0.019836	-1.369197	H	-1.973306	0.004474	6.523769
H	-4.773166	0.210349	-0.156476	O	1.738708	-2.474797	-5.33321
H	-3.102746	0.140471	1.65157	O	1.57912	2.28444	-5.596854
C	1.376121	-0.066047	-0.336447	O	-1.57912	-2.28444	5.596854
C	2.779929	-0.12527	-0.616769	O	-1.738708	2.474797	5.33321
C	0.956574	-0.045643	1.046662	C	2.14181	-2.550861	-6.691923
H	1.656441	-0.064486	3.108014	H	2.258022	-3.614029	-6.90977
C	-0.416353	0.019836	1.369197	H	3.098949	-2.039166	-6.857772
C	3.71358	-0.164961	0.382561	H	1.384084	-2.123167	-7.361379
H	3.102746	-0.140471	-1.65157	C	1.325657	3.552071	-5.009667
H	4.773166	-0.210349	0.156476	H	0.282585	3.641982	-4.679862
C	3.282514	-0.143693	1.735923	H	1.522093	4.287412	-5.792
C	1.959315	-0.084712	2.068939	H	1.991067	3.741932	-4.157443
C	0.851782	-0.032722	-2.803186	C	-1.325657	-3.552071	5.009667
C	1.663273	-0.044151	-5.48712	H	-1.991067	-3.741932	4.157443
C	1.107656	-1.23965	-3.447373	H	-1.522093	-4.287412	5.792
C	0.99859	1.185474	-3.493616	H	-0.282585	-3.641982	4.679862
C	1.402937	1.169736	-4.830029	C	-2.14181	2.550861	6.691923
C	1.514257	-1.243022	-4.793628	H	-2.258022	3.614029	6.90977
H	0.997082	-2.187509	-2.931717	H	-1.384084	2.123167	7.361379
H	0.795533	2.114559	-2.97557	H	-3.098949	2.039166	6.857772
H	1.973306	-0.004474	-6.523769	Br	-4.612955	0.196178	-3.110903
C	-0.851782	0.032722	2.803186	Br	4.612955	-0.196178	3.110903

Table S7. Cartesian coordinates [Å] of the optimized structure for simplified **2**, with 2-octyldodecyl chains replaced by methyl groups

atom	**x**	**y**	**z**	**atom**	**x**	**y**	**z**
C	-1.805388	-1.195199	-0.052298	O	5.123827	-4.349802	2.24941
H	-1.818738	0.936755	-0.073723	O	4.619038	-4.483426	-2.491443
C	-1.199855	0.047733	-0.062312	C	-2.059944	6.330514	-2.459645
C	0.379529	-2.268695	-0.047867	H	-1.618426	7.136989	-1.859451
C	0.219365	0.195666	-0.058955	H	-3.084549	6.14342	-2.112046
C	-0.981158	-2.371538	-0.041023	C	-1.673806	4.218689	3.551484
C	1.039906	-0.995671	-0.062171	H	-2.071595	3.195569	3.547573
C	0.828247	1.471631	-0.058485	H	-0.606875	4.189236	3.808301
H	-1.461721	-3.344807	-0.030392	C	4.876233	-3.738441	3.506229

H	0.987746	-3.166146	-0.04526	H	5.270965	-2.714717	3.541291
C	2.234797	1.578357	-0.065219	H	3.804033	-3.719435	3.741425
C	2.894454	2.850241	-0.051099	C	5.425434	-5.649117	-2.558423
C	3.052444	0.386265	-0.0772	H	4.979711	-6.4807	-1.996845
H	5.098603	-0.354741	-0.113843	H	6.438387	-5.460778	-2.179165
C	2.444966	-0.889332	-0.073883	C	-3.222484	-1.323246	-0.052825
C	4.258736	2.955919	-0.059589	C	-4.431937	-1.457044	-0.051226
H	2.289145	3.74944	-0.035612	C	-5.850808	-1.593665	-0.050466
H	4.744811	3.92521	-0.048992	C	-8.640657	-1.852515	-0.049321
C	5.044924	1.773583	-0.084589	C	-6.434479	-2.863984	-0.003362
C	4.476859	0.531182	-0.093677	C	-6.661872	-0.435874	-0.097575
C	-0.018258	2.708213	-0.042881	C	-8.046768	-0.579211	-0.096771
C	-1.599444	5.024648	-0.000877	C	-7.831432	-2.986739	-0.003057
C	-0.280242	3.393924	-1.225518	H	-5.823585	-3.758294	0.032486
C	-0.545112	3.173339	1.177348	H	-6.186973	0.535626	-0.134581
C	-1.331554	4.326654	1.188267	H	-9.721906	-1.908021	-0.051062
C	-1.072889	4.555094	-1.202086	O	-8.306104	-4.265159	0.04467
H	0.114849	3.048864	-2.174917	O	-8.930992	0.460678	-0.140187
H	-0.330387	2.627127	2.087465	C	-9.711211	-4.460847	0.044204
H	-2.213585	5.914418	0.058953	H	-10.184047	-3.995338	0.919071
C	3.294657	-2.124119	-0.076294	H	-10.17385	-4.063285	-0.868762
C	4.888035	-4.431877	-0.070202	C	-8.411227	1.780011	-0.194406
C	3.589057	-2.769583	-1.273668	H	-7.807618	2.012561	0.692691
C	3.794465	-2.625128	1.140962	H	-7.802756	1.936987	-1.094617
C	4.586912	-3.774558	1.133948	H	-9.278931	2.441695	-0.224601
C	4.388266	-3.926588	-1.268311	H	-9.862241	-5.541152	0.084434
H	3.214244	-2.396559	-2.220708	H	-2.08372	6.632121	-3.508378
H	3.554417	-2.109851	2.062757	H	-2.208083	4.811472	4.296271
H	5.507268	-5.318892	-0.02414	H	5.478938	-5.914873	-3.615718
O	-1.270166	5.152849	-2.412003	H	5.396771	-4.351925	4.243936
O	-1.89328	4.868426	2.308541	Br	6.950873	1.953181	-0.103963

Table S8. Cartesian coordinates [Å] of the optimized structure for simplified **3**, with 2-octyldodecyl chains replaced by methyl groups

atom	x	y	z	atom	x	y	z
C	-3.607443	1.022746	-0.015292	C	2.66801	4.397086	-3.602672
H	-3.340356	-1.092861	-0.021068	H	3.195357	3.434802	-3.631053
C	-2.843361	-0.130299	-0.012397	H	3.100816	5.06857	-4.346576
C	-1.582629	2.373767	-0.005837	H	1.607474	4.233555	-3.834554
C	-1.417882	-0.090225	-0.001497	C	2.990249	6.398779	2.448512
C	-2.945152	2.297034	-0.011771	H	3.015019	6.675512	3.504138
C	-0.760567	1.198421	0.001514	H	2.439668	7.163944	1.885344
C	-0.646009	-1.27594	-0.002425	H	4.017024	6.33902	2.064288
H	-3.549148	3.19907	-0.016416	C	-5.02888	0.96188	-0.024075
H	-1.097544	3.343379	-0.004895	C	-6.245229	0.924582	-0.02992
C	0.760593	-1.198406	-0.001506	C	5.02891	-0.96184	0.024
C	1.582665	-2.373746	0.005888	C	6.245259	-0.924548	0.029824

C	1.417906	0.090242	0.001494	C	-7.669796	0.878349	-0.036535
H	3.34037	1.092894	0.020976	C	-10.470814	0.795026	-0.04884
C	0.646033	1.275954	0.002431	C	-8.332195	-0.353743	-0.051622
C	2.945187	-2.297003	0.011805	C	-8.407138	2.085412	-0.02741
H	1.097589	-3.343362	0.004992	C	-9.798233	2.029337	-0.033682
H	3.549187	-3.199036	0.016482	C	-9.734012	-0.388412	-0.057801
C	3.607475	-1.022712	0.015261	H	-7.778125	-1.284975	-0.059246
C	2.843384	0.130327	0.01235	H	-7.872731	3.026156	-0.015803
C	-1.32563	-2.611913	0.00414	H	-11.553397	0.807529	-0.053221
C	-2.600726	-5.109945	0.030609	C	7.669826	-0.878358	0.036515
C	-1.537287	-3.298189	-1.188121	C	10.470847	-0.795119	0.048928
C	-1.749619	-3.167581	1.226345	C	8.332262	0.353711	0.051837
C	-2.383755	-4.411226	1.229621	C	8.407134	-2.085441	0.027192
C	-2.17696	-4.550172	-1.172475	C	9.79823	-2.029407	0.03352
H	-1.21996	-2.884173	-2.139132	C	9.73408	0.388339	0.058075
H	-1.576304	-2.618984	2.143827	H	7.778218	1.284959	0.059596
H	-3.097818	-6.070337	0.084595	H	7.872701	-3.026167	0.0154
C	1.32565	2.611931	-0.004129	H	11.55343	-0.807656	0.053347
C	2.60073	5.109966	-0.030588	O	-10.288307	-1.635522	-0.072699
C	1.537784	3.297954	1.188191	O	-10.61573	3.123566	-0.025949
C	1.749148	3.167851	-1.226388	O	10.615695	-3.123658	0.025614
C	2.383281	4.411497	-1.229658	O	10.28841	1.635431	0.073221
C	2.177449	4.549942	1.17255	C	-11.702781	-1.741787	-0.081253
H	1.220831	2.883742	2.139241	H	-12.147222	-1.290447	0.815683
H	1.575477	2.619438	-2.143913	H	-11.921947	-2.811082	-0.093522
H	3.097796	6.070373	-0.084573	H	-12.137717	-1.271805	-0.973242
O	-2.337732	-5.140306	-2.391996	C	-10.0145	4.40874	-0.011127
O	-2.835408	-5.045495	2.351081	H	-9.401018	4.556746	0.887276
O	2.834491	5.045998	-2.351166	H	-10.838989	5.124191	-0.007434
O	2.338703	5.139826	2.392127	H	-9.393981	4.574057	-0.901636
C	-2.989229	-6.399285	-2.448376	C	10.014426	-4.408811	0.010481
H	-3.01356	-6.676246	-3.503953	H	9.393886	-4.574317	0.900941
H	-4.016163	-6.339465	-2.064587	H	10.838892	-5.124287	0.006634
H	-2.438863	-7.164317	-1.884817	H	9.400953	-4.556586	-0.887967
C	-2.669494	-4.396289	3.602511	C	11.702888	1.741659	0.081659
H	-1.609062	-4.232704	3.834834	H	12.137892	1.271578	0.973564
H	-3.102635	-5.067599	4.346375	H	11.922084	2.810947	0.094018
H	-3.196853	-3.433998	3.630426	H	12.147235	1.290395	-0.81536

Table S9. Cartesian coordinates [Å] of the optimized structure for simplified **4**, with 2-octyldodecyl chains replaced by methyl groups

atom	x	y	z	atom	x	y	z
C	-1.275542	-1.161838	-0.047436	O	5.312627	-4.028861	-2.489005
H	-1.44156	0.963964	-0.080429	C	-2.110439	6.28961	-2.496486
C	-0.760761	0.121576	-0.06681	H	-1.717242	7.133394	-1.914424

C	0.979816	-2.077375	-0.044587	H	-3.113949	6.036218	-2.130031
C	0.643785	0.370297	-0.070218	C	-1.477425	4.301623	3.536639
C	-0.369874	-2.27676	-0.031921	H	-1.798652	3.252131	3.555995
C	1.546787	-0.760235	-0.070032	H	-0.407033	4.35544	3.77418
C	1.158589	1.687869	-0.077725	C	5.670256	-3.133998	3.482956
H	-0.780118	-3.281466	-0.012807	H	5.991688	-2.084468	3.482646
H	1.650936	-2.928669	-0.038108	H	4.606983	-3.18611	3.751245
C	2.552669	1.895538	-0.089965	C	6.208699	-5.127879	-2.556668
C	3.119157	3.213105	-0.085524	H	5.845123	-5.980876	-1.968806
C	3.45322	0.76373	-0.099545	H	7.212078	-4.851004	-2.207983
H	5.540006	0.169032	-0.145569	C	-2.679325	-1.39122	-0.041859
C	2.940126	-0.554034	-0.08733	C	-3.875952	-1.611915	-0.035261
C	4.469382	3.416163	-0.100897	C	6.775472	2.514591	-0.145154
H	2.447973	4.064045	-0.072202	C	-5.281073	-1.85135	-0.028685
H	4.881393	4.419984	-0.097277	C	-8.043473	-2.313361	-0.016224
C	5.35952	2.295046	-0.124907	C	-5.769463	-3.160999	0.023004
C	4.858081	1.010539	-0.125368	C	-6.174146	-0.755639	-0.074761
C	0.224278	2.859634	-0.064745	C	-7.544918	-0.99992	-0.06828
C	-1.520365	5.054704	-0.027992	C	-7.153776	-3.385694	0.02891
C	-0.105362	3.5062	-1.25233	H	-5.094564	-4.008066	0.058036
C	-0.315393	3.302806	1.157967	H	-5.771674	0.247874	-0.115313
C	-1.183648	4.396118	1.166175	H	-9.117771	-2.447756	-0.013631
C	-0.980212	4.607082	-1.231532	O	-7.533535	-4.694807	0.080616
H	0.299016	3.177021	-2.203468	O	-8.50295	-0.028155	-0.109982
H	-0.04718	2.787459	2.071903	C	-8.920835	-4.992914	0.084525
H	-2.196437	5.898491	0.029997	H	-9.423679	-4.562128	0.960374
C	3.877368	-1.723494	-0.086944	H	-9.413602	-4.631356	-0.827569
C	5.636943	-3.905718	-0.077501	C	-8.082118	1.325993	-0.16863
C	4.188037	-2.370927	-1.279022	H	-7.493834	1.604026	0.715631
C	4.442881	-2.158794	1.126799	H	-7.490673	1.525435	-1.071744
C	5.318216	-3.246869	1.121314	N	7.923361	2.707112	-0.157348
C	5.071509	-3.465285	-1.271979	H	-8.996414	1.921658	-0.1963
H	3.763748	-2.046942	-2.22323	H	-8.992063	-6.081276	0.126334
H	4.188258	-1.643359	2.044594	H	-2.170961	6.573277	-3.548672
H	6.322207	-4.742662	-0.030439	H	-2.041308	4.866089	4.281499
O	-1.239191	5.170559	-2.445622	H	6.256592	-5.409127	-3.610114
O	-1.76556	4.912203	2.28766	H	6.25549	-3.690878	4.216886
O	5.923554	-3.75659	2.232386				

Table S10. Cartesian coordinates [Å] of the optimized structure for 9,10-bis(3,5-dimethoxyphenyl)-anthracene (**DPA**)

atom	x	y	z	atom	x	y	z
C	0.521607	3.629348	-0.712189	C	0.046398	-0.006281	5.733242
H	0.318653	2.467073	-2.486974	C	1.23138	-0.175404	3.619814
C	0.338576	2.461314	-1.402785	C	-1.170702	0.167658	3.631892

C	0.384608	2.455233	1.401607	C	-1.155895	0.165516	5.027719
C	0.166612	1.211257	-0.723412	C	1.234325	-0.175975	5.025656
C	0.545539	3.626176	0.710432	H	2.170704	-0.30966	3.094196
C	0.18974	1.208211	0.72284	H	-2.090994	0.299104	3.076301
C	-0.022402	0.002948	-1.428001	H	0.006596	-0.000718	6.815326
H	0.692663	4.559039	1.248374	O	-2.455708	0.350818	-5.608886
H	0.404995	2.455601	2.485804	O	2.262376	-0.323542	-5.812802
C	-0.18974	-1.208211	-0.72284	O	-2.262376	0.323542	5.812802
C	-0.384608	-2.455233	-1.401607	O	2.455708	-0.350818	5.608886
C	-0.166612	-1.211257	0.723412	C	-2.527516	0.361958	-7.025364
H	-0.318653	-2.467073	2.486974	H	-3.580555	0.512764	-7.270335
C	0.022402	-0.002948	1.428001	H	-2.187584	-0.589883	-7.454575
C	-0.545539	-3.626176	-0.710432	H	-1.934227	1.180854	-7.453369
H	-0.404995	-2.455601	-2.485804	C	3.517318	-0.502651	-5.17489
H	-0.692663	-4.559039	-1.248374	H	3.781548	0.362957	-4.553499
C	-0.521607	-3.629348	0.712189	H	4.248514	-0.606898	-5.978776
C	-0.338576	-2.461314	1.402785	H	3.528941	-1.407729	-4.553661
C	-0.036055	0.004692	-2.927361	C	-3.517318	0.502651	5.17489
C	-0.046398	0.006281	-5.733242	H	-3.528941	1.407729	4.553661
C	-1.23138	0.175404	-3.619814	H	-4.248514	0.606898	5.978776
C	1.170702	-0.167658	-3.631892	H	-3.781548	-0.362957	4.553499
C	1.155895	-0.165516	-5.027719	C	2.527516	-0.361958	7.025364
C	-1.234325	0.175975	-5.025656	H	3.580555	-0.512764	7.270335
H	-2.170704	0.30966	-3.094196	H	1.934227	-1.180854	7.453369
H	2.090994	-0.299104	-3.076301	H	2.187584	0.589883	7.454575
H	-0.006596	0.000718	-6.815326	H	-0.648928	-4.564859	1.250582
C	0.036055	-0.004692	2.927361	H	0.648928	4.564859	-1.250582

References

1 H. Li, S. S. Babu, S. T. Turner, D. Neher, M. J. Hollamby, T. Seki, S. Yagai, Y. Deguchi, H. Möhwald, T. Nakanishi, *J. Mater. Chem. C*, 2013, **1**, 1943–1951.

2 F. Lu, K. Jang, I. Osica, K. Hagiwara, M. Yoshizawa, M. Ishii, Y. Chino, K. Ohta, K. Ludwichowska, K. J. Kurzydłowski, S. Ishihara, T. Nakanishi, *Chem. Sci.* 2018, **9**, 6774–6778.

3 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian 09, Revision E.01, Gaussian, Inc., Wallingford CT, 2013.