

Supplementary information:

Steric effects on excimer formation for photoluminescent smectic liquid-crystalline materials

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Experimental section

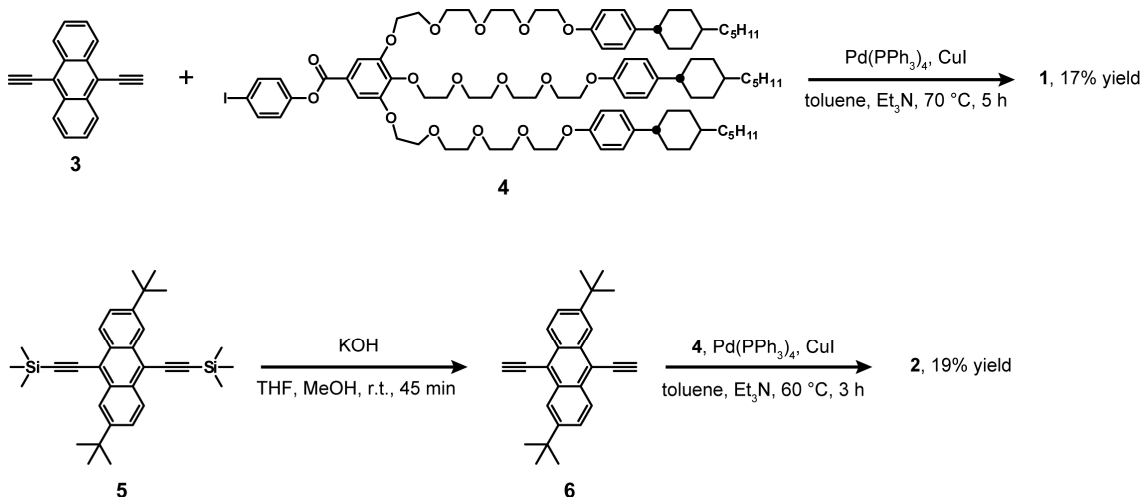
General:

All reagents and solvents were purchased from Tokyo Kasei or Kanto Kagaku, and appropriately purified, if necessary. Unless otherwise noted, all of the reactions were carried out under an argon atmosphere in dry solvents. Silica gel column chromatography was carried out with silica gel 60 from Kanto Chemicals (silica gel 60, spherical, 40-50 μm). Recycling preparative GPC was carried out with a Japan Analytical Industry LC-9201 chromatograph. ^1H NMR and ^{13}C NMR spectra were recorded on a JEOL JNM-LA400 spectrometer in CDCl_3 solution (400 and 100 MHz for ^1H NMR and ^{13}C NMR, respectively). Chemical shifts for ^1H and ^{13}C NMR were referenced to internal standards Me_4Si ($\delta = 0.00$) and CDCl_3 ($\delta = 77.00$) respectively, and are expressed by chemical shifts in ppm (δ), multiplicity, coupling constant (Hz), and relative intensity. Mass spectra were recorded on a PerSeptive Biosystems Voyager-DE STR spectrometer. Elemental analyses were carried out with an Exeter Analytical Inc. CE-440 Elemental Analyzer.

Polarizing optical microscopic images were obtained with an Olympus BX51 equipped with a Mettler FP82HT hot stage. Differential scanning calorimetry (DSC) measurements were performed on a NETZCH DSC204 Phoenix calorimeter at a scanning rate of $5\text{ }^\circ\text{C min}^{-1}$. X-ray diffraction measurements were carried out on a Rigaku RINT 2500 diffractometer with a heating stage using Ni-filtered $\text{Cu K}\alpha$ radiation. Absorption spectra were measured with a JASCO V-670 spectrophotometer equipped with integrating sphere unit ISN-800T. Emission spectra were recorded on a JASCO FP-6500 spectrofluorometer equipped with a hot stage. Time-resolved fluorescence measurements were carried out by exciting samples with a nitrogen laser pulse (337 nm), and the emission was dispersed with a Hamamatsu Photonics C-2830 disperser and monitored on a Hamamatsu Photonics M-2548 streak camera.

Synthesis:

9,10-Diethynylantracene (**3**), 4-iodophenyl 3,4,5-tris{2-[2-(2-{2-[4-(4-*trans*-pentylcyclohexyl)phenoxy]ethoxy}ethoxy)ethoxy]ethoxy}benzoate (**4**) and 2,6-di-*tert*-butyl-9,10-bis(trimethylsilyl)ethynylantracene (**5**) were obtained according to the reported procedures.¹⁻³



Scheme S1 Syntheses of **1** and **2**.

9,10-Bis[*p*-(3,4,5-tris{2-[2-(2-{2-[4-(4-*trans*-pentylcyclohexyl)phenoxy]ethoxy}ethoxy)ethoxy]ethoxy}phenylcarbonyloxy)phenylethynyl]anthracene (**1**).

$\text{Pd}(\text{PPh}_3)_4$ (9.35 mg, 8.09×10^{-3} mmol) and CuI (1.54 mg, 8.09×10^{-3} mmol) were added to a mixture of **3** (18.3 mg, 8.09×10^{-2} mmol), **4** (282 mg, 0.178 mmol), dry toluene (10 mL) and freshly distilled Et_3N (3 mL). After stirring for 5 h at 70°C , the mixture was dissolved in ethyl acetate and the organic phase was washed with 5% hydrochloric acid, water and brine, then dried over anhydrous MgSO_4 . After filtration and evaporation, the resulting residue was purified by silica gel flash column chromatography (eluent: ethyl acetate/chloroform = 97:3 \rightarrow 100:0) and GPC (eluent: chloroform) to afford **1** as an orange waxy solid (44.2 mg, 17%). ^1H NMR (CDCl_3 , 400 MHz): δ 8.72-8.69 (m, 4H), 7.84 (d, $J = 8.4$ Hz, 4H), 7.68-7.65 (m, 4H), 7.48 (s, 4H), 7.31 (d, $J = 8.8$ Hz, 4H), 7.11-7.07 (m, 12H), 6.84-6.81 (m, 12H), 4.28 (t, $J = 5.2$ Hz, 4H), 4.24 (t, $J = 4.8$ Hz, 8H), 4.10-4.07 (m, 12H), 3.89 (t, $J = 4.8$ Hz, 8H), 3.84-3.81 (m, 16H), 3.75-3.65 (m, 48H), 2.42-2.33 (m, 6H), 1.85-1.81 (m, 24H), 1.42-1.17 (m, 66H), 1.05-0.95 (m, 12H), 0.88 (t, $J = 6.8$ Hz, 18H). ^{13}C NMR (100 MHz, CDCl_3): δ 164.45, 156.83, 152.52, 151.18, 143.46, 140.32, 132.93, 132.13, 127.59, 127.25, 126.93, 123.87, 122.19, 121.11, 118.42, 114.36, 109.76, 101.69, 86.68, 72.55, 70.86, 70.79, 70.73, 70.68, 70.65, 70.59, 69.81, 69.64, 69.02, 67.40, 43.71, 37.40, 37.31, 34.56, 33.64, 32.23, 26.67, 22.72, 14.13. MS (MALDI-TOF): m/z 3163.32 [$\text{M} + \text{Na}$] $^+$; calcd. 3162.90. Anal. calcd for $\text{C}_{194}\text{H}_{266}\text{O}_{34}$: C, 74.16; H, 8.53%; found: C, 74.16; H, 8.79%.

2,6-Di-*tert*-butyl-9,10-diethynylanthracene (6).

Compound **5** (35.7 mg, 7.39×10^{-2} mmol) was dispersed in a mixture of methanol/THF (7:2 v/v, 45 mL) containing KOH (12.5 mg, 0.222 mmol). The mixture was stirred for 45 min at room temperature. After removing the solvent, the residue was poured into a mixture of 5% hydrochloric acid/chloroform. The organic phase was washed with brine, dried over anhydrous MgSO₄, filtered and evaporated to afford **6** as a brown powder. The product was used directly in the next reaction.

2,6-Di-*tert*-butyl-9,10-bis[*p*-(3,4,5-tris{2-[2-(2-{2-[4-(4-*trans*-pentylcyclohexyl)phenoxy]-ethoxy}ethoxy)ethoxy]ethoxy}phenylcarbonyloxy)phenylethynyl]anthracene (2).

This compound was prepared in a similar manner to compound **1**, and was obtained as an orange waxy solid (19%). ¹H NMR (CDCl₃, 400 MHz): δ 0.88 (t, *J* = 7.2 Hz, 18H), 0.95-1.05 (m, 12H), 1.17-1.43 (m, 66H), 1.53 (s, 18H), 1.81-1.84 (m, 24H), 2.34-2.40 (m, 6H), 3.65-3.75 (m, 44H), 3.83 (t, *J* = 5.2 Hz, 16H), 3.89 (t, *J* = 5.2 Hz, 8H), 4.07-4.10 (m, 16H), 4.24 (t, *J* = 5.2 Hz, 8H), 4.28 (t, *J* = 5.2 Hz, 4H), 6.28-6.84 (m, 12H), 7.07-7.11 (m, 12 H), 7.29-7.31 (m, 4H), 7.48 (s, 4H), 7.76 (dd, *J* = 2.0 Hz, 8.8 Hz, 2H), 7.81 (d, 7.6 Hz, 4H), 8.61-8.63 (m, 4H). ¹³C NMR (100 MHz, CDCl₃): δ 164.47, 156.82, 152.50, 150.99, 149.11, 143.41, 140.30, 132.78, 131.86, 130.77, 127.58, 126.87, 126.27, 123.87, 122.21, 121.47, 121.40, 117.52, 114.33, 109.71, 101.37, 87.10, 72.53, 70.85, 70.77, 70.72, 70.68, 70.64, 70.58, 69.80, 69.62, 69.00, 67.35, 43.69, 37.39, 37.28, 35.24, 34.54, 33.62, 32.22, 30.94, 26.66, 22.72, 14.14. MS (MALDI-TOF): *m/z* 3274.73 [M + Na]⁺; calcd. 3275.02. Anal. calcd for C₂₀₂H₂₈₂O₃₄: C, 74.55; H, 8.73%; found: C, 74.64; H, 8.75%.

Table S1 Liquid-crystalline properties of compounds **1** and **2**.

| Compound | | Thermal behaviour ^a | | | | | | | | | |
|----------|---|--------------------------------|-----------------|---------|-----------------|--------|----|-------|-----|--------|-----|
| 1 | G | -22 | M ₁ | 22 | M ₂ | 49 | Sm | 76 | SmA | 85 | Iso |
| | | | | (0.37) | | (1.7) | | (6.8) | | (12.6) | |
| 2 | G | -22 | Cr ₁ | 28 | Cr ₂ | 47 | Sm | 53 | SmA | 63 | Iso |
| | | | | (-26.4) | | (26.4) | | (2.5) | | (11.0) | |

^a Transition temperatures (°C) and transition enthalpies (kJ mol⁻¹, in parentheses) are determined by differential scanning calorimetry (DSC) on 2nd heating at 5 K min⁻¹. SmA: smectic A; Sm: unidentified monolayer smectic; M: unidentified mesophase; G: glassy; Cr: crystalline; Iso: isotropic.

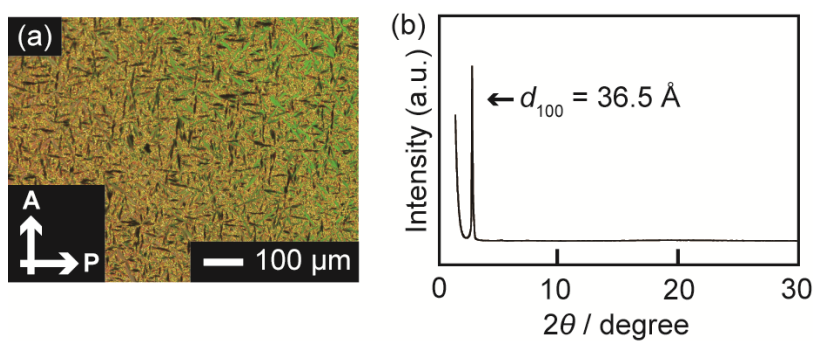


Fig. S1 (a) Polarizing optical micrograph of **2** at 55 °C and (b) XRD pattern of **2** at 55 °C.

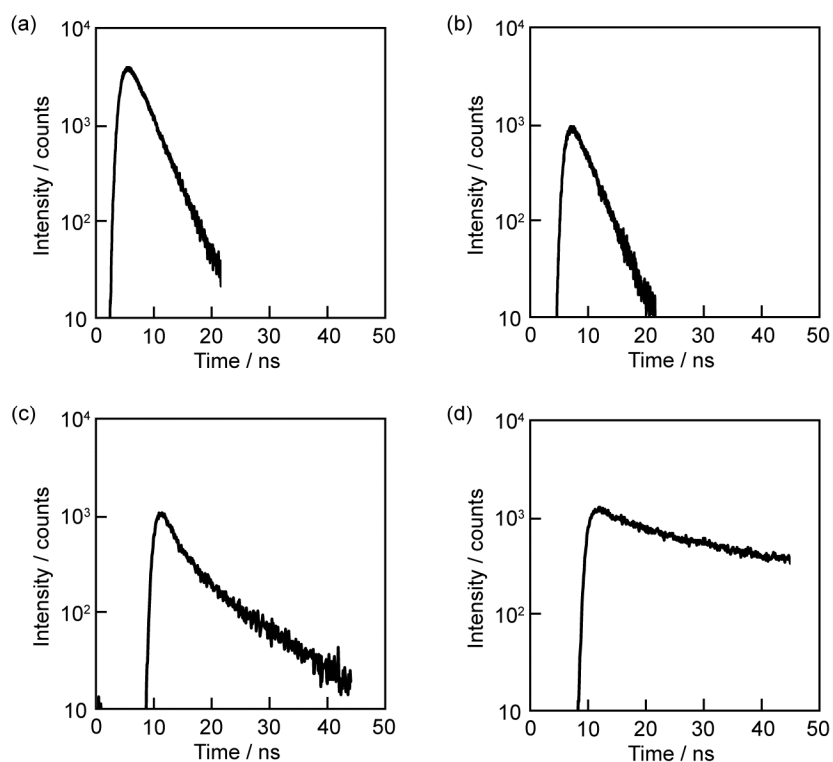


Fig. S2 Time-resolved fluorescence decay profiles of **1** and **2** ($\lambda_{\text{ex}} = 337$ nm); (a) a dichloromethane solution of **1** at room temperature, (b) a dichloromethane solution of **2** at room temperature, (c) compound **1** in the smectic A phase at 80 °C and (d) compound **2** in the smectic A phase at 55 °C.

References

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