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Stimuli-Responsive Luminescent Liquid Crystals: Change of Photoluminescent Colors Triggered by a Shear-Induced Phase Transition

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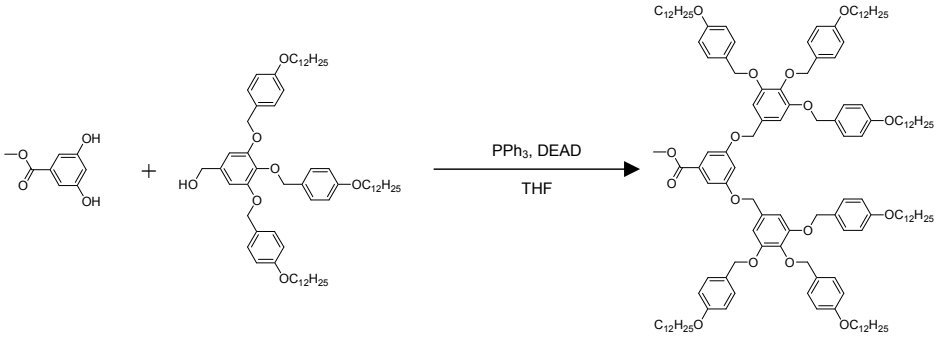
General methods and materials

All reagents and solvents were purchased from Aldrich, Tokyo Kasei, and Wako and appropriately purified, if necessary. Unless otherwise noted, all of the reactions were carried out under 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-908 chromatograph. ^{1}H NMR and ^{13}C NMR spectra were recorded on a JEOL JNM-LA400 spectrometer in $CDCl_3$ solutions (400 and 100 MHz for ^{1}H NMR and ^{13}C NMR, respectively). Chemical shifts of ^{1}H and ^{13}C NMR signals were quoted to internal standard Me_4Si (δ = 0.00) and $CDCl_3$ (δ = 77.00) respectively, and 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 a Yanaco MT-6 CHN autocorder.

Differential scanning calorimetry (DSC) measurements were performed on a NETZSCH DSC204 Phoenix calorimeter at a scanning rate of 10 °C min^{-1}. X-ray diffraction measurements were carried out on a Rigaku RINT 2500 diffractometer with a heating stage using Ni-filtered Cu Kα radiation. IR measurements were conducted on a Jasco FT/IR-660 Plus using CaF_2 plates equipped with a Mettler FP82HT hot stage. UV-vis absorption spectra were measured with a Jasco V-670 equipped with a Mettler FP82HT hot stage. Steady-state fluorescence spectra were recorded on a Jasco FP-6500 spectrofluorometer equipped with a hot stage. Time-resolved fluorescence measurements were carried out by exciting sample solutions 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 of a pyrene derivative (1)

The synthetic route used to obtain compound **1** is shown below. 1,6-Diethynylpyrene and 3,4,5-tris[*p*-(dodecan-1-yloxy)benzyloxy]benzyl alcohol were obtained according to the reported procedures.[1,2]



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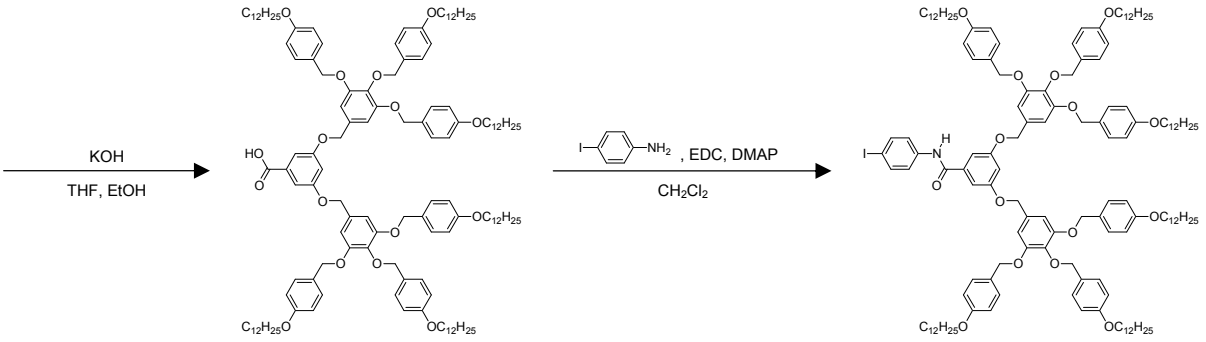
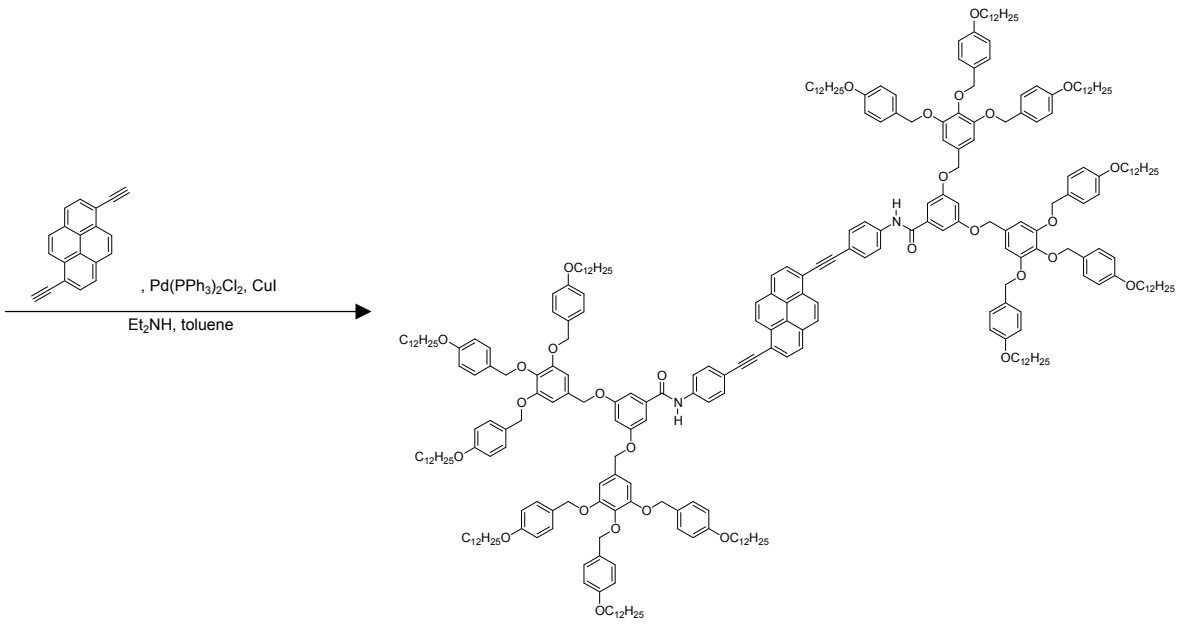


3 **4**



1

Methyl 3,5-Bis{3',4',5'-tris[*p*-(dodecan-1-yloxy)benzyloxy]benzyloxy}benzoate (2): To a solution of methyl 3,5-dihydroxybenzoate (277 mg, 1.52 mmol), 3,4,5-tris[*p*-(dodecan-1-yloxy)benzyloxy]benzyl alcohol (3.23 g, 3.35 mmol), and triphenylphosphine (PPh_3) (1.20 g, 4.56 mmol) in dry THF (100 mL), a 40 % toluene solution of diethylazodicarboxylate (DEAD) (2.1 mL, 4.56 mmol) was added dropwise very slowly to the stirred mixture at room temperature, and the reaction mixture was stirred for an additional 6 h at room temperature. After removing the solvent, the residue was dissolved in acetone. The precipitation was obtained by addition of methanol to the solution and was filtered. This precipitation was purified by twice flush column chromatography on a silica gel (eluent: ethyl acetate and hexane/ethyl acetate = 10:1 respectively) to afford compound **2** (1.38 g, 0.660 mmol) as a waxy white solid in 43 % yield.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.88 (t, *J* = 6.8 Hz, 18H), 1.26 (m, 108H), 1.73–1.81 (m, 12H), 3.90–3.96 (m, 15H), 4.93 (s, 4H), 4.95 (s, 4H), 5.02 (s, 8H), 6.72 (s, 4H), 6.75–6.78 (m, 5H), 6.87 (d, *J* = 8.4 Hz, 8H), 7.26–7.32 (m, 14H).

MS (MALDI): m/z: 2112.41 (calcd $[M + Na]^+$ = 2112.48).

Elemental analysis: Calcd.(%) for $C_{136}H_{200}O_{16}$: C, 78.12; H, 9.64. Found: C, 77.85; H, 9.94.

3,5-Bis{3',4',5'-tris[*p*-(dodecan-1-yloxy)benzyloxy]benzyloxy}benzoic acid (3): Compound **2** (1.38 g, 0.660 mmol) was dispersed in a mixture of ethanol/THF (2:1 v/v, 150 ml) containing KOH (111 mg, 1.98 mmol). To this suspension was added water (1 ml) and the suspension was stirred for 5 h under a refluxed condition. After removing the solvent, the residue was poured into a mixture of 5 % hydrochloric acid/chloroform. The organic phase was washed with brine and was dried over $MgSO_4$, filtered, and evaporated. The residue was recrystalized from acetone to afford **3** (1.23 g, 0.592 mmol) as a waxy white solid in 90 % yield.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.88 (t, *J* = 6.8 Hz, 18H), 1.26 (m, 108H), 1.73–1.81 (m, 12H), 3.90–3.96 (m, 12H), 4.93 (s, 4H), 4.96 (s, 4H), 5.02 (s, 8H), 6.73 (s, 4H), 6.76 (d, *J* = 8.4 Hz, 4H), 6.82 (t, *J* = 2.4 Hz, 1H), 6.87 (d, *J* = 8.8 Hz, 8H), 7.26–7.33 (m, 14H).

MS (MALDI): m/z: 2099.09 (calcd $[M + Na]^+$ = 2098.47).

Elemental analysis: Calcd.(%) for $C_{135}H_{198}O_{16}$: C, 78.07; H, 9.61. Found: C, 77.82; H, 9.69.

***N*-4-Iodophenyl 3,5-bis{3',4',5'-tris[*p*-(dodecan-1-yloxy)benzyloxy]benzyloxy}benzamide (4):** To a solution of **3** (1.10 g, 0.530 mmol) in dry CH_2Cl_2 (50 ml) was added 4-iodoaniline (116 mg, 0.530 mmol) and D-MAP (13.0 mg, 0.106 mmol). To the solution was added EDC (203 mg, 1.06 mmol) dissolved in dry CH_2Cl_2 (20 ml) dropwise, stirred at room temperature for 12 h. 5 % hydrochloric acid was added to the reaction mixture and the reaction mixture was washed with sat. NH_4Cl aq followed by sat. NaCl aq, dried over $MgSO_4$, filtered, and evaporated. The crude product was purified by flush column chromatography on a silica gel (eluent: chloroform) to afford compound **4** (0.889 g, 0.391 mmol) as a waxy white solid in 74 % yield.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.88 (t, *J* = 6.8 Hz, 18H), 1.26 (m, 108H), 1.73–1.81 (m, 12H), 3.90–3.96 (m, 12H), 4.94 (s, 4H), 4.97 (s, 4H), 5.02 (s, 8H), 6.70 (s, 4H), 6.72 (t, *J* = 2.0 Hz, 1H), 6.76 (d, *J* = 8.4 Hz, 4H), 6.86 (d, *J* = 8.0 Hz, 8H), 7.00 (d, *J* = 2.0 Hz, 2H), 7.26–7.32 (m, 12H), 7.42 (d, *J* = 8.4 Hz, 2H), 7.65 (d, *J* = 8.4 Hz, 2H), 7.73 (s, 1H).

MS (MALDI): m/z: 2300.59 (calcd $[M + Na]^+$ = 2299.41).

Elemental analysis: Calcd.(%) for $C_{141}H_{202}INO_{15}$: C, 74.34; H, 8.94; N, 0.61. Found: C, 74.38; H, 9.10; N, 0.57.

1,6-Bis[*p*-(3,5-bis{3,4,5-tris[*p*-(dodecan-1-yloxy)benzyloxy]benzyloxy}benzamido)phenylethynyl]pyrene (1): To a suspension of **4** (440 mg, 0.193 mmol), 1,6-diethynylpyrene (21.0 mg, 8.40×10^{-2} mmol), dry toluene (30 ml) and freshly distilled Et_2NH (5 ml) was added CuI (1.60 mg, 8.40×10^{-3} mmol) and $PdCl_2(PPh_3)_2$ (5.90 mg, 8.40×10^{-3} mmol). After stirring for 20 h at 50 °C, toluene and Et_2NH were removed with a rotary evaporator. The residue was dissolved in chloroform and this organic phase was washed with 5 % hydrochloric acid followed by sat. NH_4Cl aq and sat. NaCl aq, dried over $MgSO_4$, filtered, and evaporated. The residue was purified by column chromatography on a silica gel (eluent: chloroform) and GPC (eluent: chloroform) to afford **1** (114 mg, 2.52×10^{-2} mmol) as a transparent orenge solid in 30 % yield.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.87 (m, 36H), 1.25 (m, 216H), 1.77 (m, 24H), 3.90–3.96 (m, 24H), 4.95 (s, 8H), 5.00 (s, 8H), 5.03 (s, 16H), 6.73 (s, 8H), 6.86–6.88 (m, 10H), 6.87 (d, *J* = 8.4 Hz, 16H), 7.05 (d, *J* = 2.0 Hz, 4H), 7.26–7.32 (m, 24H), 7.73 (s, 8H), 7.86 (s, 2H), 8.17–8.22 (m, 6H), 8.70 (d, *J* = 9.2 Hz, 2H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 14.13, 22.70, 26.09, 29.33, 29.37, 29.47, 29.65, 29.69, 31.92, 67.99, 68.08, 70.55, 71.18, 74.84, 88.5, 95.3, 106.23, 107.36, 114.10, 114.43, 119.74, 125.16, 128.15, 128.86, 129.15, 129.83, 129.92, 130.09, 131.59, 131.99, 132.65, 138.12, 138.43, 153.19, 158.93, 160.07, 165.36.

MS (MALDI): m/z: 4572.45 (calcd $[M + Na]^+$ = 4570.08).

Elemental analysis: Calcd.(%) for $C_{302}H_{412}N_2O_{30}$: C, 79.71; H, 9.13; N, 0.62. Found: C, 79.56; H, 9.40; N, 0.65.

The number of molecules of 1 per micelle

Lattice parameter for micellar cubic phase (a) is calculated by using the equation: $a = (4^{1/2}d_{200} + 5^{1/2}d_{210} + 6^{1/2}d_{211})/3$. The number of molecules of **1** per micelle in the cubic lattice (n) is calculated by using the equation: $n = a^3\rho N_A/(8M)$ where a is lattice parameter, ρ (= 1 g cm^{-3}) is assumed density, N_A is Avogadro's number and M is molecular weight of **1**.[2]

Thermoanalysis for 1 in the cubic and shear-induced columnar phases

For the micellar cubic phase, the quenched sample of **1** from the isotropic state was used for the 2nd heating measurement (Figure S1a). The sample of **1** in the shear-induced columnar phase was prepared on a glass substrate by shearing the sample of **1** in the micellar cubic phase.

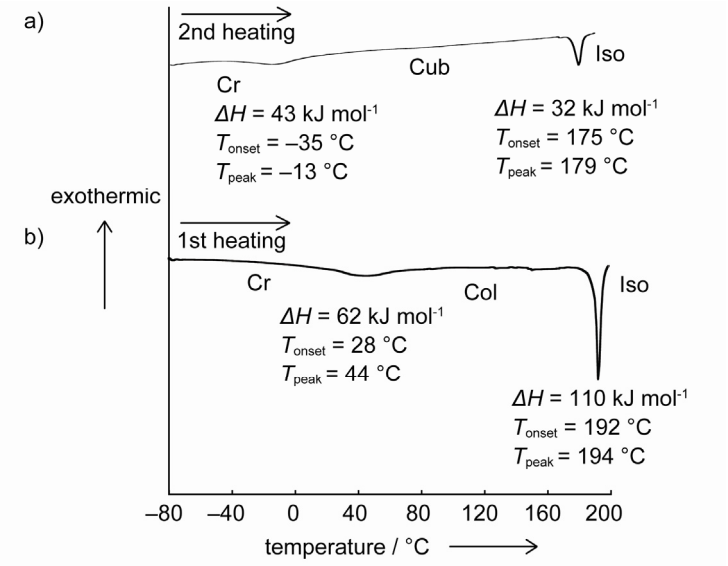


Figure S1. The differential scanning calorimetry (DSC) trace of **1**; a) in the cubic phase in the second heating at the rate of 10 °C min^{-1} and b) in the shear-induced columnar phase in the first heating at the rate of 10 °C min^{-1}.

Fluorescence decay profiles

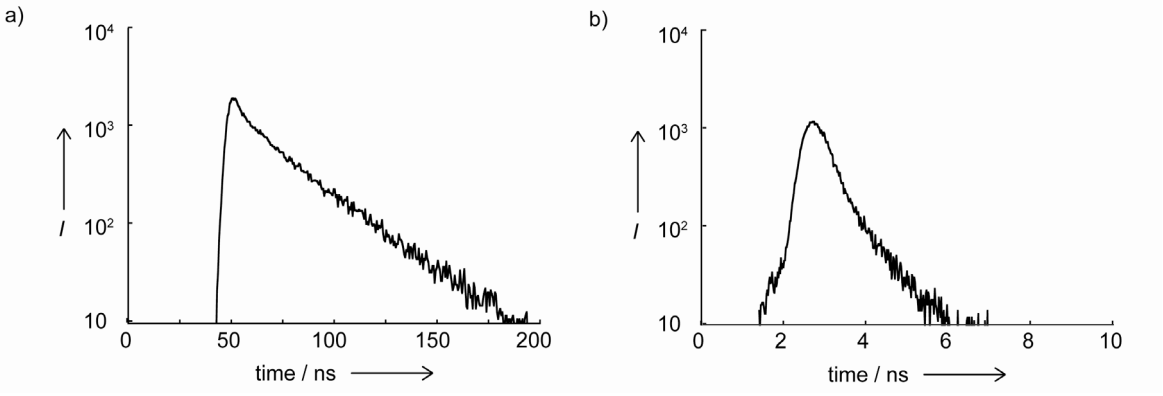


Figure S2. Time-resolved fluorescence decay profiles of **1**; a) in the cubic phase at 160 °C and b) in the shear-induced columnar phase at 160 °C.

References

[1] S. Leroy-Lhez, F. Fages, *Eur. J. Org. Chem.* **2005**, 2684–2688.

[2] V. Percec, W.-D. Cho, P. E. Mosier, G. Ungar, D. J. P. Yeardley, *J. Am. Chem. Soc.* **1998**, *120*, 11061–11070.