Supporting Information

Mechanoresponsive luminescence and liquid-crystalline behaviour of a cyclophane featuring two 1,6-bis(phenylethynyl)pyrene groups

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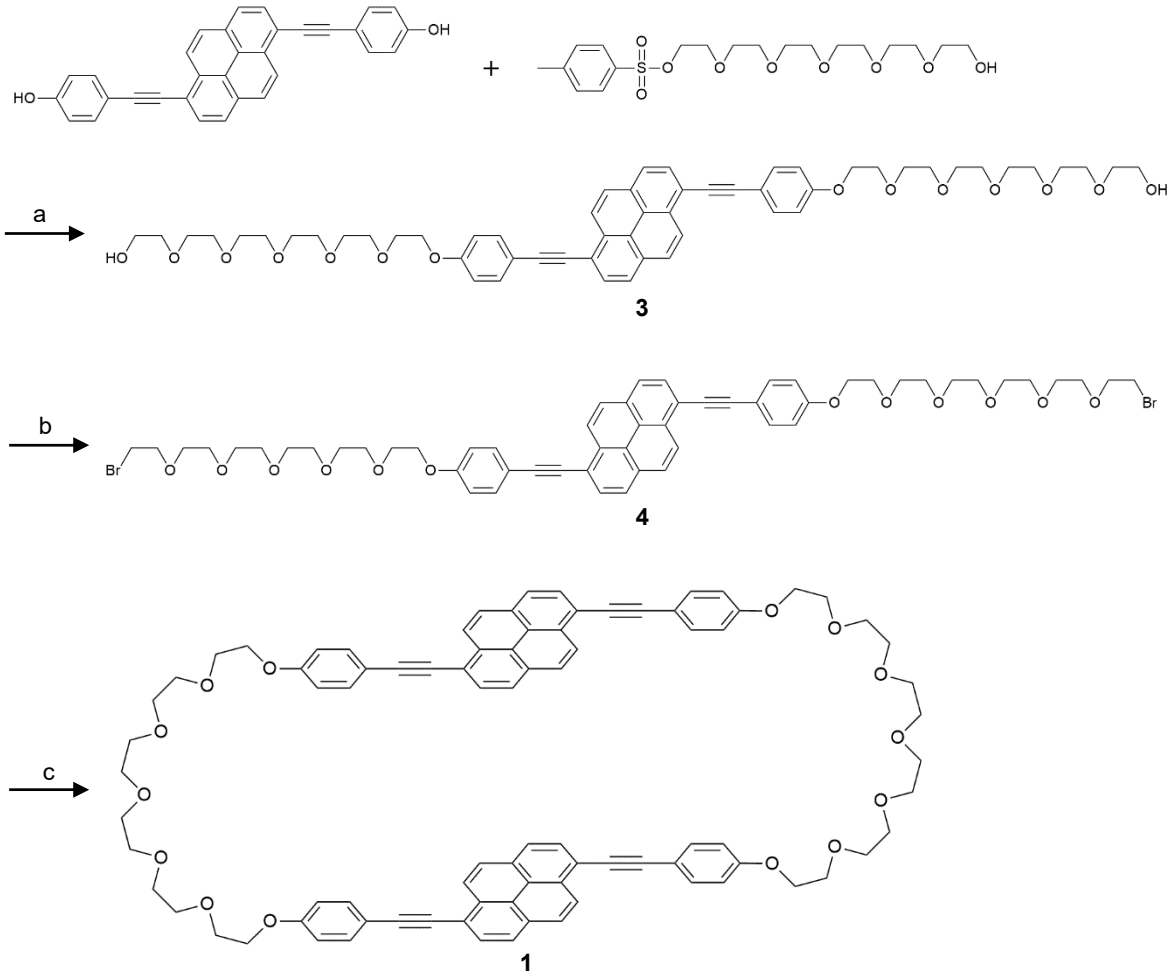
Synthesis of compound 1

The synthetic route used to prepare compound **1** is shown in Schemes S1. 1,6-Bis(4-hydroxyphenylethynyl)pyrene and hexaethyleneglycol mono-tosylate were synthesized according to reported procedures.[S1,S2]

Scheme S1



Conditions: (a) K_2CO_3, DMF, 70 °C, 12 h; (b) CBr_4, PPh_3, CH_2Cl_2, 0 °C → r.t., 3 h; (c) 1,6-bis(4-hydroxyphenylethynyl)pyrene, K_2CO_3, DMF, 70 °C, 28 h.

Compound 3. A suspension of 1,6-bis(4-hydroxyphenylethynyl)pyrene (860 mg, 1.98 mmol), hexaethyleneglycol mono-tosylate (1.90 g, 4.35 mmol), and K_2CO_3 (1.37 g, 9.90 mmol) in DMF (200 mL) was stirred for 12 h at 70 °C. After cooling to room temperature, most of the DMF was evaporated and chloroform (300 mL) was added to the mixtue. The organic layer was washed with saturated aq. NH_4Cl (3 × 100 mL), then washed with saturated aq. NaCl (1 × 100 mL), dried over $MgSO_4$, filtered, and the solvent was evaporated. The crude product was purified by flash column chromatography on silica gel (eluent: stepwise gradient from chloroform to chloroform/methanol = 5:1) and subsequent re-precipitation from a mixture of chloroform and ethyl acetate to afford compound **3** (1.63 g, 1.69 mmol) as a yellow solid in 85% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.46 (br, 2H), 3.61–3.79 (m, 40H), 3.91–3.93 (m, 4H), 4.20–4.23 (m, 4H), 7.00 (d, J = 9.2 Hz, 4H), 7.67 (d, J = 8.8 Hz, 4H), 8.14–8.22 (m, 6H), 8.68 (d, J = 8.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 61.81, 67.65, 69.79, 70.33, 70.61, 70.63, 70.65, 70.72, 70.74, 70.74, 70.93, 72.82, 87.45, 95.71, 114.96, 115.80, 118.89, 124.41, 125.19, 126.32, 128.15, 129.88, 131.07, 131.99, 133.28, 159.20. MS (MALDI-TOF): m/z: 962.65 (calcd. $[M]^+$ = 962.45).

Compound 4. To a solution of **3** (1.30 g, 1.35 mmol) and triphenylphosphine (0.85 g, 3.24 mmol) in dichloromethane (100 mL) was added dropwise a solution of tetrabromomethane (1.12 g, 3.37 mmol) in dichloromethane (15 mL) at 0 °C. The reaction mixture was subsequently stirred for 3 h at room temperature before most of the dichloromethane was evaporated. The crude product was purified by flash column chromatography on silica gel (eluent: dichloromethane/acetone = 3:1), then purified by another flash column chromatography (dichloromethane/acetone = 1:1) and subsequent re-precipitation from a mixture of dichloromethane and hexane to afford compound **4** (1.13 g, 1.04 mmol) as a yellow solid in 77% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.47 (t, J = 12.8 Hz, 4H), 3.66–3.77 (m, 32H), 3.80 (t, J = 12.8 Hz, 4H), 3.89–3.91 (m, 4H), 4.19–4.21 (m, 4H), 6.98 (d, J = 8.8 Hz, 4H), 7.65 (d, J = 8.8 Hz, 4H), 8.13–8.21 (m, 6H), 8.67 (d, J = 9.2 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 30.45, 67.60, 69.74, 70.60, 70.66, 70.67, 70.72, 70.74, 70.96, 71.27, 87.45, 95.66, 114.89, 115.78, 118.82, 124.32, 125.14, 126.24, 128.08, 129.82, 131.00, 131.91, 133.24, 159.13. MS (MALDI-TOF): m/z: 1086.64 (calcd. $[M]^+$ = 1086.28).

Compound 1. A solution of compound **4** (500 mg, 0.459 mmol) and 1,6-bis(4-hydroxyphenylethynyl)pyrene (200 mg, 0.459 mmol) in DMF (25 mL) was added to a suspension of K_2CO_3 (1.27 g, 9.18 mmol) in DMF (200 mL) dropwise at 70 °C over 4 h under vigorous stirring. After further stirring for 24 h at 70 °C, the reaction suspension was cooled and poured into the mixture of saturated aq. NH_4Cl (300 mL) and ethyl acetate (200 mL). The organic phase was washed with saturated aq. NH_4Cl (4 × 100 mL), followed by saturated aq. NaCl (100 mL), the organic layer was dried over $MgSO_4$, filtered, and the solvent was evaporated. The crude product was purified by flash column chromatography on silica gel (eluent: dichloromethane/acetone = 3:1) and recycling GPC (eluent: chloroform) to afford compound **1** (181 mg, 0.133 mmol) as a yellow solid in 29 % yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.71–3.78 (m, 32H), 3.88–3.91 (m, 8H), 4.10–4.12 (m, 8H), 6.84 (d, J = 8.8 Hz, 8H), 7.49 (d, J = 8.8 Hz, 8H), 7.67 (d, J = 9.2 Hz, 4H), 7.75 (d, J = 7.6 Hz, 4H), 7.87 (d, J = 8.0 Hz, 4H), 8.23 (d, J = 9.2 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 67.65, 69.85, 70.90, 71.08, 87.64, 95.39, 114.75, 115.97, 118.44,

123.83, 124.76, 125.78, 127.63, 129.42, 130.63, 131.57, 133.25, 158.98. HRMS (ESI): m/z: 703.2680 (calcd. $[M+Na_2]^{2+}$ = 703.2672).

Concentration dependency of the photoluminescence spectra

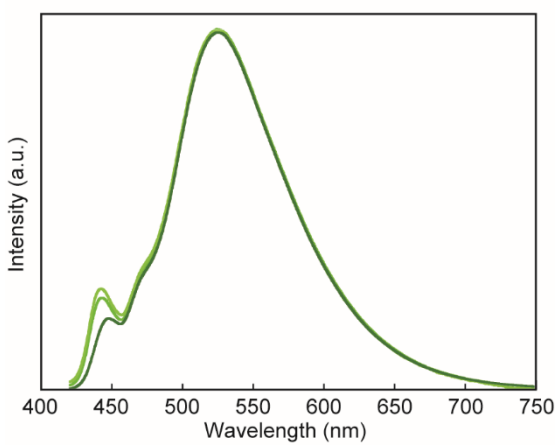


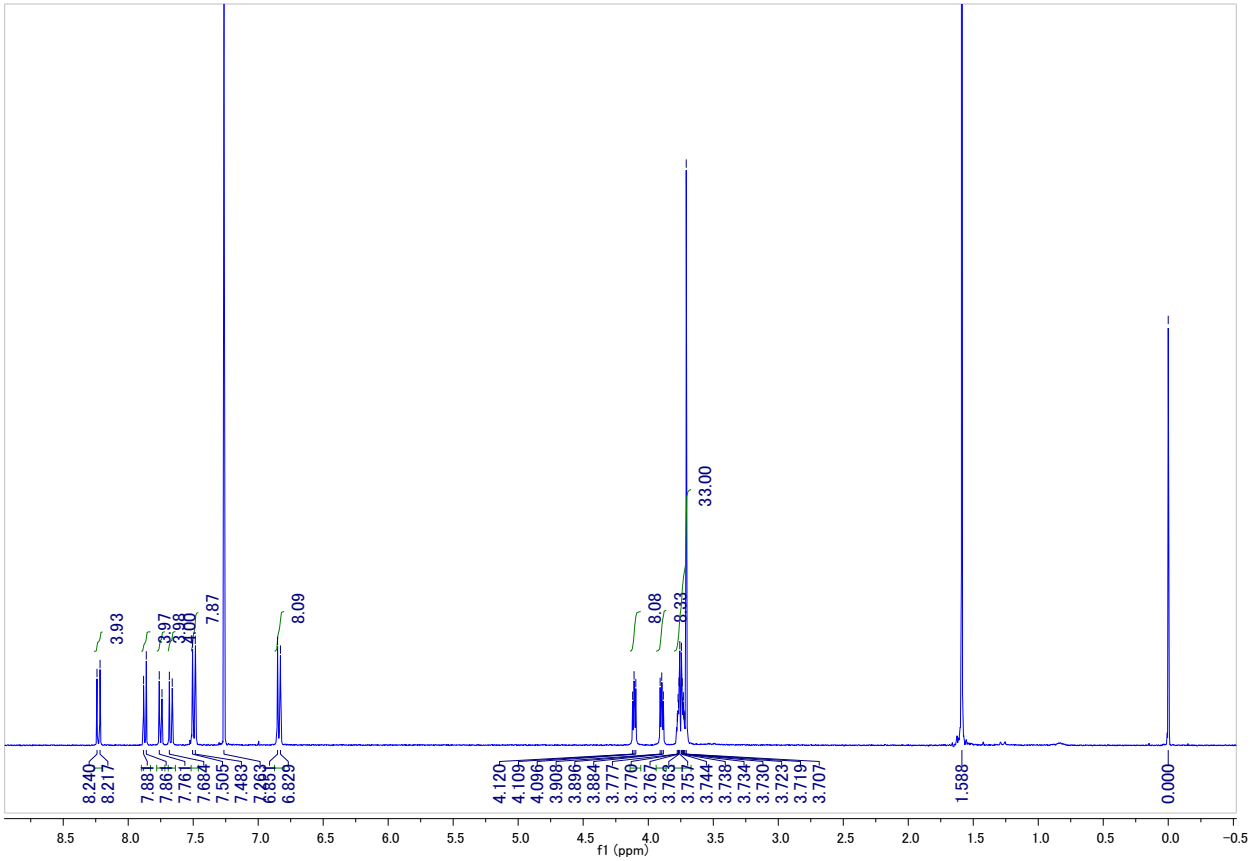
Fig. S1. Photoluminescence spectra of pyrenophane **1** in chloroform solution varying the concentration from 1.0×10^{-5} M to 1.0×10^{-7} M. All spectra were recorded at room temperature with excitation light of 400 nm.

References

S1. Y. Sagara, C. Weder and N. Tamaoki, *Chem. Mater.*, 2017, **29**, 6145–6152.

S2. A. Dif, F. Boulmedais, M. Pinot, V. Roullier, M. Baudy-Floc'h, F. M. Coquelle, S. Clarke, P. Neveu, F. Vignaux, R. Le Borgne, M. Dahan, Z. Gueroui and V. Marchi-Artzner, *J. Am. Chem. Soc.*, 2009, **131**, 14738–14746.

^{1}H NMR of Compound 1



^{13}C NMR of Compound 1