Supporting Information

Asymmetric Cyclophanes Permit Access to Supercooled Nematic Liquid Crystals with Stimulus-Responsive Luminescence

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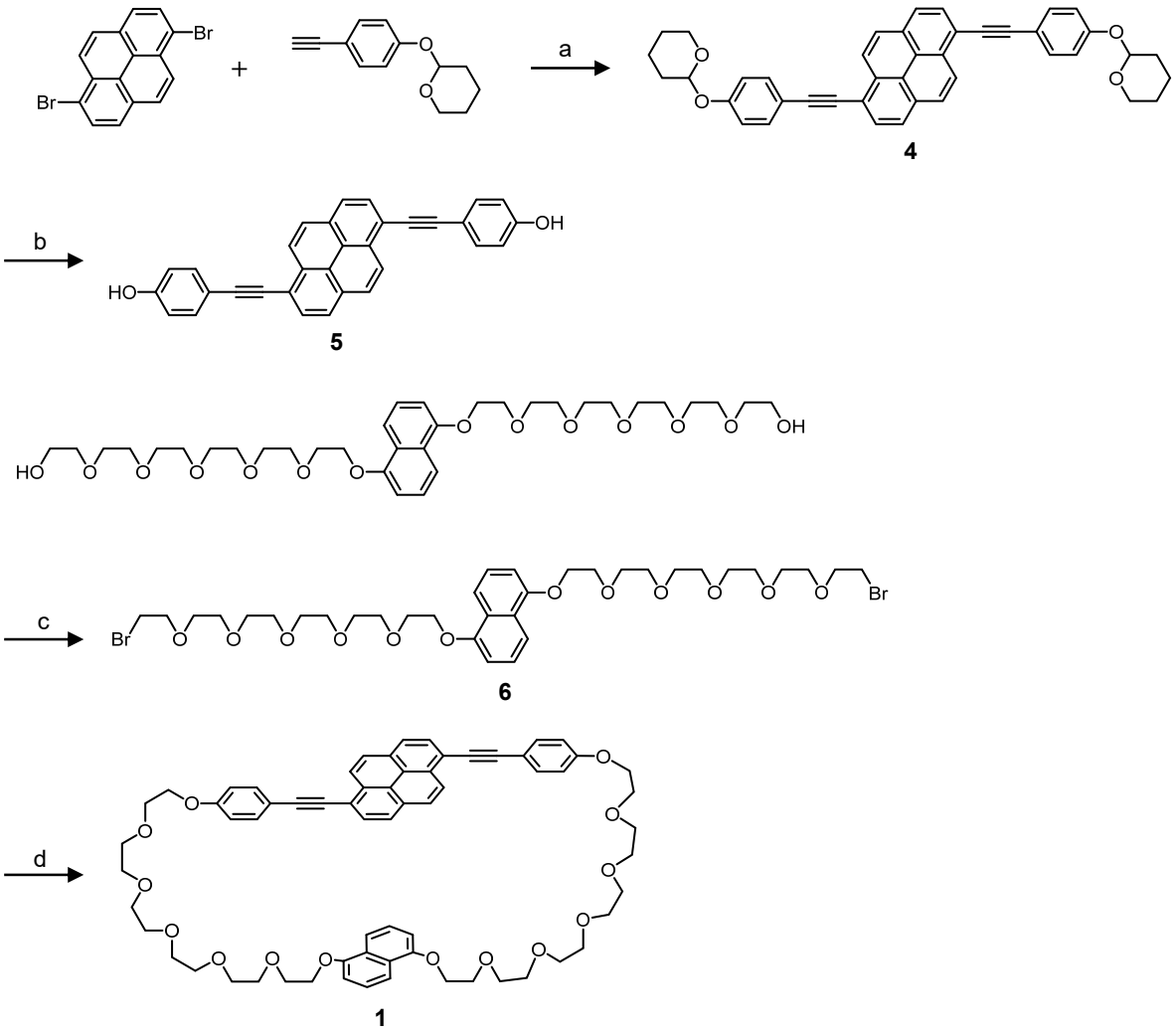
General methods and materials

All reagents and solvents were purchased from Aldrich and Tokyo Kasei. Unless otherwise noted, all reactions were carried out under nitrogen atmosphere. Silica gel column chromatography was carried out with a Biotage Isolera Flash system. ^{1}H NMR spectra were recorded on a JEOL JNM-ECX 400 spectrometer and all chemical shifts are quoted on the δ-scale in ppm relative to the signal of tetramethylsilane (at 0.00) as an internal standard. Proton-decoupled ^{13}C NMR spectra were recorded on a JEOL JNM-ECX 400 spectrometer and all chemical shifts (δ) are reported in ppm using residual solvent as the internal standard ($CDCl_3$ at 77.16). Coupling constants (J) are reported in Hz and relative intensities are also shown. Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectra were obtained on an AB SCIEX TOF/TOF 5800. Elemental analysis was carried out with an Exeter Analytical CE440 Elemental Analyzer. The DSC measurements were conducted using a Rigaku Thermo plus EVO DSC8230 with a heating/cooling rate of 10 ˚C/min or 5 ˚C/min under nitrogen atmosphere. Powder X-ray diffraction measurements were carried out with a Rigaku SmartLab. UV-vis absorption spectra were measured with a JASCO V-550. Steady-state fluorescence spectra were recorded on a JASCO FP-6500. Time-resolved fluorescence measurements were carried out with a Hamamatsu Photonics Quantaurus-Tau. Quantum efficiencies were measured with a Hamamatsu Photonics Quantaurus-QY. Polarized optical microscopic observations were conducted with an Olympus BX-60 optical microscope equipped with a Sony DXC-950 3CCD camera. An AS ONE hot plate NA-1 and a SCINICS cool plate CP-085 were used for the thermal treatment experiments.

Synthesis of compounds 1, 2, and 3

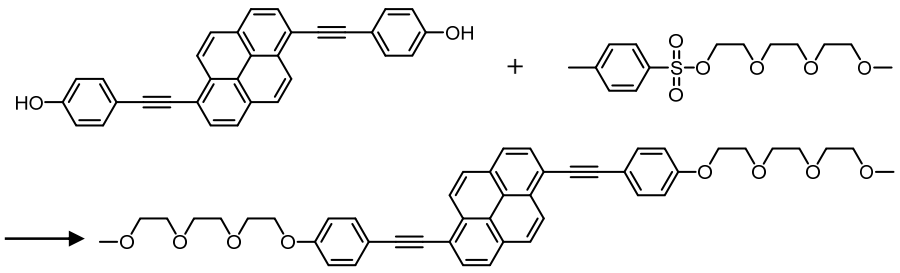
The synthetic routes used to prepare compounds **1**, **2**, and **3** are shown in Schemes S1, S2, and S3, respectively. 2-(4-Ethynyl-phenoxy)-tetrahydro-2*H*-pyran, 1,5-bis(2-[2-(2-{2-[2-(2-hydroxyethoxy)ethoxy]ethoxy}ethoxy)ethoxy]ethoxy)naphthalene, and 2-(2-(2-methoxyethoxy)ethoxy)ethyl 4-methylbenzenesulfonate were synthesized according to reported procedures.[S1-S3]

Scheme S1



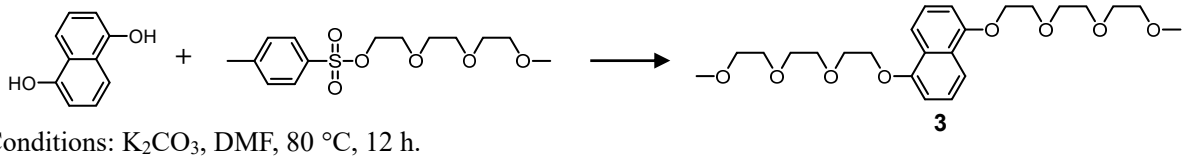
Conditions: (a) $Pd(PPh_3)_4$, CuI, THF, Et_2NH, 80 °C, 12 h; (b) 10% aq. HCl, THF, reflux, 3 h; (c) CBr_4, PPh_3, CH_2Cl_2, 0 °C → r.t., 3 h; (d) compound **5**, K_2CO_3, DMF, 80 °C, 36 h.

Scheme S2



Conditions: K_2CO_3, DMF, 80 °C, 12 h.

Scheme S3



Conditions: K_2CO_3, DMF, 80 °C, 12 h.

1,6-Bis(4-(tetrahydro-2*H*-pyran-2-yloxy)phenylethynyl)pyrene (4). A mixture of 1,6-dibromopyrene (2.00 g, 5.55 mmol), 2-(4-ethynylphenoxy)-tetrahydro-2*H*-pyran (2.47 g, 12.2 mmol), $Pd(PPh_3)_4$ (641 mg, 0.555 mmol), CuI (106 mg, 0.555 mmol), and distilled Et_2NH (30 mL) in THF (40 mL) was degassed and stirred for 12 h at 80 °C. After cooling to room temperature, methanol (10 mL) was added to the reaction mixture. The precipitate was filtered off and washed with methanol several times. The solid was then dissolved in chloroform, purified by flash column chromatography on silica gel (eluent: chloroform) and subsequently precipitated from a mixture of chloroform and hexane to afford compound **4** (3.18 g, 5.28 mmol) as a yellow solid in a yield of 95%.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.61–1.78 (m, 6H), 1.88–1.92 (m, 4H), 1.99–2.08 (m, 2H), 3.63–3.68 (m, 2H), 3.90–3.96 (m, 2H), 5.50 (t, J = 2.8 Hz, 2H), 7.12 (d, J = 8.8 Hz, 4H), 7.65 (d, J = 8.8 Hz, 4H), 8.13–8.22 (m, 6H), 8.66 (d, J = 9.2 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ =18.75. 25.24, 30.35, 62.16, 87.45, 95.69, 96.36, 116.46, 116.65, 118.86, 124.38, 125.14, 126.29, 128.10, 129.86, 131.05, 131.98, 133.17, 157.42. MS (MALDI-TOF): m/z: 602.27 (calcd. $[M]^+$ = 602.25).

1,6-Bis(4-hydroxyphenylethynyl)pyrene (5). A mixture of **4** (2.60 g, 4.31 mmol), 10% aq. HCl (6 mL), and THF (200 mL) was heated to reflux for 3 h and subsequently cooled to room temperature. Water (20 mL) was added, most of the THF was evaporated, and the solid product was filtered off. The solid was washed with water (2 × 20 mL) and a mixture of water/methanol (3/2 v/v) (2 × 20 mL), followed by methanol (5 mL). The product was dried in vacuo to afford compound **5** (1.78 g, 4.10 mmol) as an orange solid in a yield of 95%.

^{1}H NMR (400 MHz, DMSO-d6): δ = 6.90 (d, J = 8.4 Hz, 4H), 7.62 (d, J = 8.4 Hz, 4H), 8.24 (d, J = 8.0 Hz, 2H), 8.32–8.36 (m, 4H), 8.62 (d, 2H), 10.05 (s, 2H). ^{13}C NMR (100 MHz, DMSO-d6): δ = 86.35, 96.58, 112.59, 115.98, 118.31, 123.50, 125.60, 125.64, 128.47, 129.75, 130.45, 130.98, 133.38, 158.46. MS (MALDI-TOF): m/z: 434.17 (calcd. $[M]^+$ = 434.13).

1,5-Bis(2-[2-(2-{2-[2-(2-bromoethoxy)ethoxy]ethoxy}ethoxy)ethoxy]ethoxy)naphthalene (6). A solution of tetrabromomethane (2.47 g, 7.45 mmol) in dichloromethane (20 mL) was added dropwise to a solution of 1,5-bis(2-[2-(2-{2-[2-(2-hydroxyethoxy)ethoxy]ethoxy}ethoxy)ethoxy]ethoxy)naphthalene (2.05 g, 2.98 mmol) and triphenylphosphine (1.88 g, 7.15 mmol) in dichloromethane (200 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: ethyl acetate) to afford compound **6** (1.37 g, 1.68 mmol) as brownish oil in a yield of 56 %.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.44 (t, J = 6.4 Hz, 4H), 3.59–3.70 (m, 28H), 3.75–3.80 (m, 8H), 3.98 (t, J = 4.8 Hz, 4H), 4.28 (t, J = 4.8 Hz, 4H), 6.83 (d, J = 7.6 Hz, 2H), 7.34 (t, J = 8.0 Hz, 2H), 7.86 (d, J = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 30.18, 67.69, 69.58, 70.26, 70.33, 70.34, 70.36, 70.40, 70.43, 70.47, 70.76, 70.94, 105.42, 114.38, 124.86, 126.52, 154.10. MS (MALDI-TOF): m/z: 812.30 (calcd. $[M]^+$ = 812.20).

Cyclophane 1. A solution of compound **6** (800 mg, 0.982 mmol) and compound **5** (427 mg, 0.982 mmol) in DMF (25 mL) was dropwise added to a suspension of K_2CO_3 (3.21 g, 19.6 mmol) in DMF (300 mL) at 80 °C over 12 h under vigorous stirring. After further stirring for 24 h at 80 °C, the reaction suspension was cooled and poured into a mixture of saturated aq. NH_4Cl (300 mL) and ethyl acetate (200 mL). The organic phase was washed with saturated aq. NH_4Cl (3 × 100 mL), followed by saturated aq. NaCl, 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), recycling GPC (eluent: chloroform), and subsequently re-precipitated from a mixture of dichloromethane and hexane to afford compound **1** (382 mg, 0.351 mmol) as a yellow powder in a yield of 36 %.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.56–3.68 (m, 28H), 3.71–3.75 (m, 8H), 3.88–3.91 (m, 8H), 4.26–4.29 (m, 4H), 6.32 (d, J = 7.6 Hz, 2H), 6.92 (t, J = 8.0 Hz, 2H), 7.05 (d, J = 8.8 Hz, 4H), 7.48 (d, J = 8.4 Hz, 2H), 7.66 (d, J = 8.8 Hz, 4H), 7.97–7.99 (m, 4H), 8.09 (d, J = 8.0 Hz, 2H), 8.56 (d, J = 9.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 67.11, 67.76, 69.54, 69.67, 70.30, 70.40, 70.41, 70.43, 70.52, 70.60, 70.62, 70.94, 87.40, 95.53, 104.87, 114.06, 115.14, 115.61, 118.46, 123.98, 124.54, 124.91, 125.85, 126.12, 127.88, 129.46, 130.70, 131.63, 133.02, 153.75, 159.11. MS (MALDI-TOF): m/z: 1086.55 (calcd. $[M]^+$ = 1086.48). Elemental analysis (%) calcd. for $C_{66}H_{70}O_{14}$: C 72.91, H 6.49, N 0.00; found: C 72.81, H 6.45, N 0.03.

1,6-Bis(2-[2-(2-methoxyethoxy)ethoxy]ethoxy)pyrene (2). A suspension of compound **5** (200 mg, 0.460 mmol), 2-(2-(2-methoxyethoxy)ethoxy)ethyl 4-methylbenzenesulfonate (366 mg, 1.15 mmol), and K_2CO_3 (318 mg, 2.30 mmol) in DMF (100 mL) was stirred for 12 h at 80 °C. After cooling to room temperature, the reaction suspension was poured into a mixture of saturated aq. NH_4Cl (200 mL) and ethyl acetate (100 mL). The organic layer was washed with saturated aq. NH_4Cl (3 × 100 mL), 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: dichloromethane/acetone = 9:1) and recycling GPC (eluent: chloroform) to afford compound **2** (283 mg, 0.389 mmol) as a yellow solid in a yield of 85%.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.40 (s, 6H), 3.56–3.58 (m, 4H), 3.67–3.72 (m, 8H), 3.76–3.79 (m, 4H), 3.89–

3.92 (m, 4H), 4.19–4.21 (m, 4H), 6.98 (d, J = 9.2 Hz, 4H), 7.65 (d, J = 8.8 Hz, 4H), 8.13–8.21 (m, 6H), 8.67 (d, J = 9.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 58.94, 67.38, 69.53, 70.47, 70.54, 70.75, 71.82, 87.25, 95.45, 114.67, 115.58, 118.60, 124.08, 124.90, 126.00, 127.84, 129.59, 130.77, 131.68, 133.02, 158.92. MS (MALDI-TOF): m/z: 726.39 (calcd. $[M]^+$ = 726.32). Elemental analysis (%) calcd. for $C_{46}H_{46}O_8$: C 76.01, H 6.38, N 0.00; found: C 75.99, H 6.38, N 0.04.

1,5-Bis(2-[2-(2-methoxyethoxy)ethoxy]ethoxy)naphthalene (3). A suspension of 1,5-dihydroxynaphthalene (300 mg, 1.87 mmol), 2-(2-(2-methoxyethoxy)ethoxy)ethyl 4-methylbenzenesulfonate (1.49 mg, 4.68 mmol), and K_2CO_3 (1.29 mg, 9.37 mmol) in DMF (150 mL) was stirred for 12 h at 80 °C. After cooling to room temperature, the reaction suspension was poured into a mixture of saturated aq. NH_4Cl (200 mL) and ethyl acetate (100 mL). The organic layer was washed with saturated aq. NH_4Cl (3 × 100 mL), 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: dichloromethane/acetone = 9:1) and recycling GPC (eluent: chloroform) to afford compound **3** (624 mg, 1.38 mmol) as a brown liquid in a yield of 74%.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.37 (s, 6H), 3.53–3.56 (m, 4H), 3.66–3.72 (m, 8H), 3.80–3.83 (m, 4H), 3.99–4.01 (m, 4H), 4.29–4.31 (m, 4H), 6.84 (d, J = 7.6 Hz, 2H), 7.34 (t, J = 8.0 Hz, 2H), 7.86 (d, J = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 58.90, 67.77, 69.69, 70.45, 70.59, 70.86, 71.80, 105.53, 114.49, 124.93, 126.64, 154.21. MS (MALDI-TOF): m/z: 452.31 (calcd. $[M]^+$ = 452.24). Elemental analysis (%) calcd. for $C_{24}H_{36}O_8$: C 63.70, H 8.02, N 0.00; found: C 63.69, H 8.01, N 0.05.

DSC measurement for cyclophane 1 in the B-form

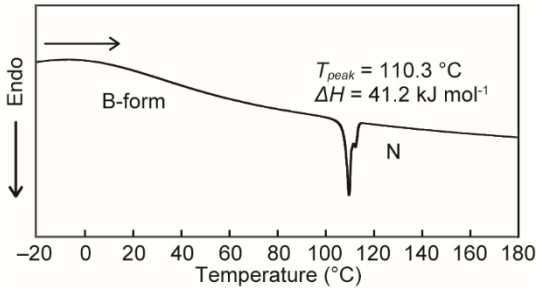


Figure S1. DSC trace (first heating) of compound **1** in the B-form. Scanning rate: 10 °C min^{-1}.

XRD patterns of cyclophane 1 in the B-form and B_{sc}-form

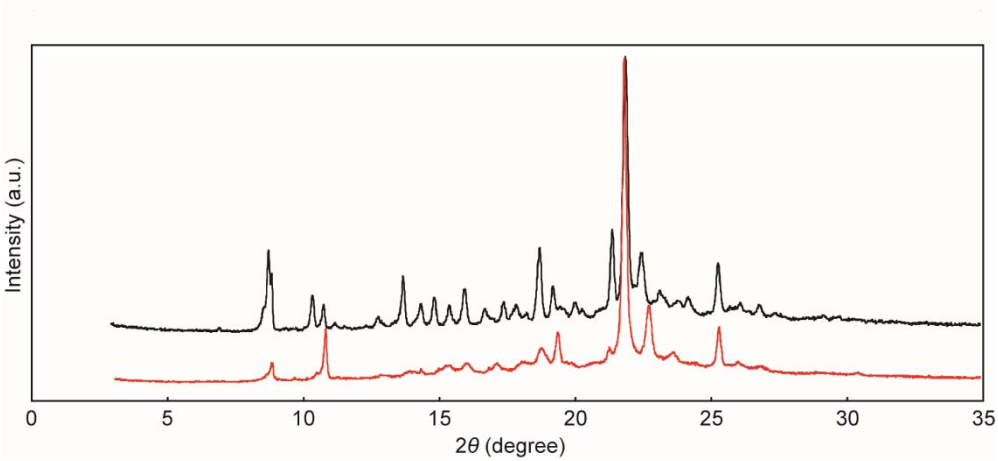


Figure S2. Comparison of the XRD patterns of the B-form (black line) and the B_{sc}-form (red line). The measurements were conducted at room temperature.

DSC measurements of compounds 2 and 3

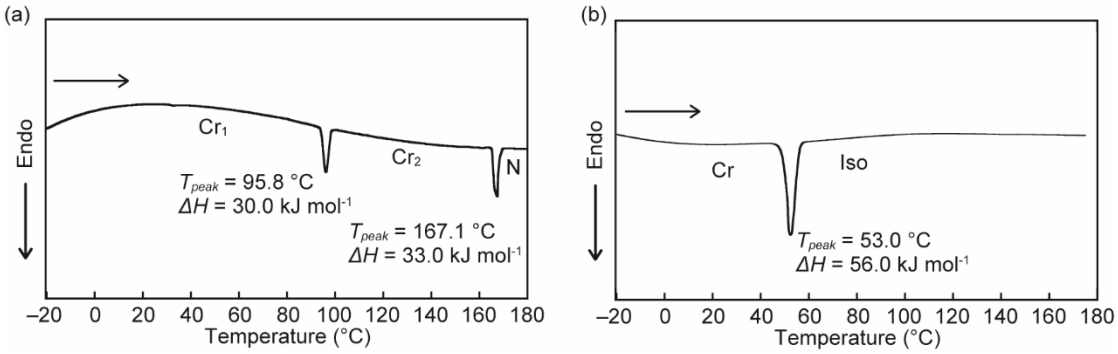


Figure S3. DSC traces (first heating) of compounds (a) **2** and (b) **3**. Scanning rate: 10 ºC min^{-1}.

POM images of compound 2 and an equimolar mixture of 2 and 3

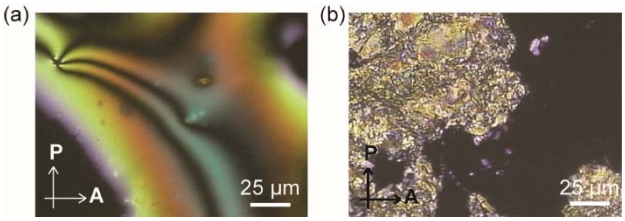


Figure S4. (a) POM image of compound **2** in the nematic phase at 180 ºC in the absence of a cover glass. (b) POM image of an equimolar mixture of compounds **2** and **3** at 100 ºC in the presence of a cover glass. The black part is associated with the isotropic state of compound **3**, whereas the bright birefringent parts mainly consist of the crystalline form of compound **2**.

Emission lifetime measurement of compound 2 in solution

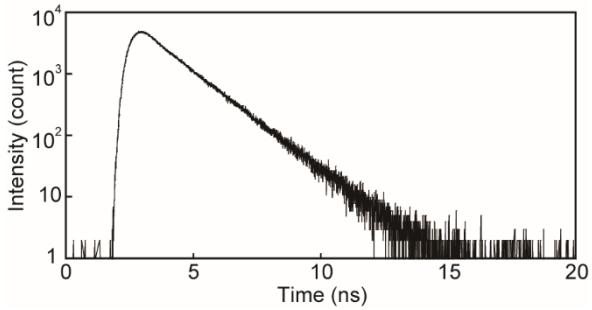


Figure S5. Emission decay profile of compound **2** in the chloroform solution. The profile was measured at room temperature with λ_{ex} = 405 nm.

Photographs documenting the mechanoresponsive luminescence behavior of 1

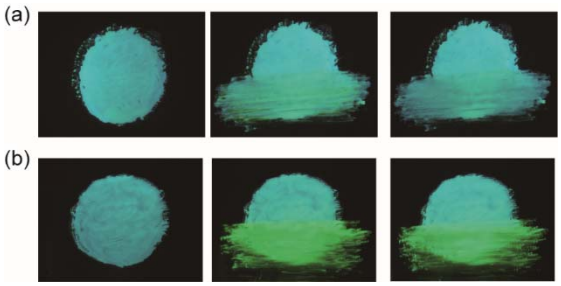


Figure S6. Photographs documenting the mechanoresponsive luminescence of cyclophane **1**. (a) Before grinding at 35 °C (left), just after grinding at 35 °C (middle) and after keeping the sample at 35 °C for 2 min (right). Green photoluminescence cannot be seen after grinding, due to the rapid recovery at this temperature. (b) Before grinding at 15 °C (left), just after grinding at 15 °C (middle) and after keeping the sample at 15 °C for 1 h (right). All images were recorded under illumination with 365 nm UV light.

Emission lifetime measurements for cyclophane 1 after grinding

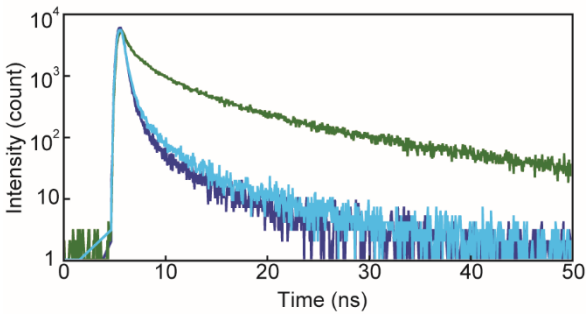


Figure S7. Emission decay profiles of cyclophane **1** in the B-form (blue line), the sample just after grinding at 25 °C (green line), and the sample after 10 min at 25 °C. The profiles were measured at room temperature with λ_{ex} = 405 nm.

XRD pattern after rapid recovery of luminescence color after mechanical grinding

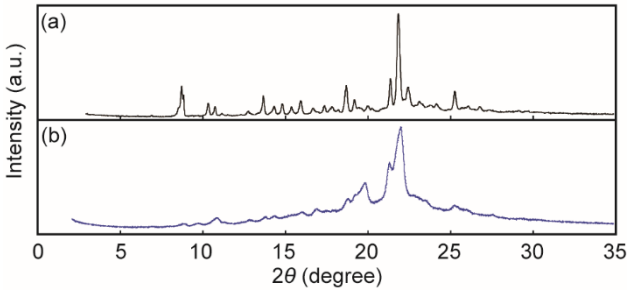


Figure S8. XRD patterns of (a) the B-form and (b) the sample after grinding at 25 °C. The bottom pattern was measured after 10 min after grinding at 25 °C. It takes 16.5 min to obtain each diffraction pattern.

Mechanoresponsive luminescence behavior of the B_{sc}-form and as-prepared powder

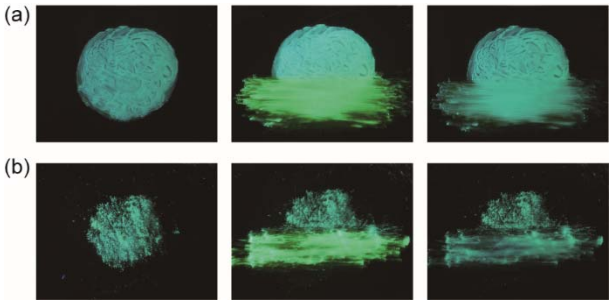


Figure S9. Photographs documenting the mechanoresponsive luminescence of the B_{sc}-form and as-prepared powder of cyclophane **1** at 25 °C. (a) The Bsc-form before grinding (left), just after grinding (middle) and after keeping the sample for 10 min (right). (b) As-prepared powder of cyclophane **1** before grinding (left), just after grinding (middle) and after keeping the sample for 10 min (right). All images were recorded under illumination with 365 nm UV light.

References

S1. Yelamaggad, C. V.; Shanker, G. *Tetrahedron* **2008**, *64*, 3760–3771.

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S3. Yoshimoto, M.; Honda, K.; Kurosawa, S.; Tanaka, M. *J. Phys. Chem. C* **2014**, *118*, 16067–16073.