Supporting Information

Linearly Polarized Photoluminescence from an Asymmetric Cyclophane Showing Thermo- and Mechanoresponsive Luminescence

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Synthesis of compounds 1 and 2

The synthetic routes to prepare compounds 1 and 2 are shown in Schemes S1 and S2. 2-(4-Ethynyl-phenoxy)-tetrahydro-2H-pyran, pentaethylene glycol p-toluenesulfonate, and 2-(2-(2-methoxyethoxy)ethoxy)ethyl 4-methylbenzenesulfonate were synthesized according to reported procedures.\textsuperscript{S1-S3}

Scheme S1

Conditions: (a) Pd(PPh\textsubscript{3})\textsubscript{4}, Cul, THF, (i-Pr)\textsubscript{2}NH, 80 °C, 24 h; (b) Pyridinium p-toluenesulfonate, H\textsubscript{2}O, THF, 60 °C, 5 h; (c) LiBr, K\textsubscript{2}CO\textsubscript{3}, CH\textsubscript{3}CN, reflux, 24 h; (d) CBr\textsubscript{4}, PPh\textsubscript{3}, CH\textsubscript{2}Cl\textsubscript{2}, 0 °C → r.t., 2.5 h; (e) K\textsubscript{2}CO\textsubscript{3}, DMF, 80 °C, 32 h.

Scheme S2

Conditions: K\textsubscript{2}CO\textsubscript{3}, DMF, 80 °C, 24 h.
4,7-Bis(4-(tetrahydro-2H-pyran-2-yloxy)phenylethynyl)-2,1,3-benzothiadiazole (3). A mixture of 4,7-dibromo-2,1,3-benzothiadiazole (2.00 g, 6.80 mmol), 2-(4-ethynylphenoxy)-tetrahydro-2H-pyran (3.03 g, 15.0 mmol), Pd(PPh3)4 (393 mg, 0.340 mmol), CuI (65.0 mg, 0.341 mmol), and distilled (i-Pr)2NH (30 mL) in THF (20 mL) was degassed and stirred for 24 h at 80 °C. After cooling to room temperature, the reaction suspension was poured into a mixture of 5% aq. HCl (100 mL) and chloroform (200 mL). The organic phase was washed with H2O (2 × 100 mL), followed by saturated aq. NaCl, dried over MgSO4, filtered, and the solvent was evaporated. The crude product was purified by flash column chromatography on silica gel (eluent: hexane/chloroform = 1:9) to afford compound 3 (3.22 g, 6.00 mmol) as a yellow solid in a yield of 88%.

1H NMR (400 MHz, CDCl3): δ = 1.60–1.76 (m, 6H), 1.87–1.93 (m, 4H), 1.97–2.06 (m, 2H), 3.61–3.66 (m, 2H), 3.87–3.93 (m, 2H), 5.48 (t, J = 3.2 Hz, 2H), 7.07 (d, J = 8.8 Hz, 4H), 7.60 (d, J = 8.8 Hz, 4H), 7.75 (s, 2H). 13C NMR (100 MHz, CDCl3): δ = 18.75, 25.24, 30.34, 62.19, 84.53, 96.32, 97.80, 115.52, 116.56, 117.23, 132.28, 133.57, 154.52, 157.88. MS (MALDI-TOF): m/z: 559.11 (calcd. [M+Na]+ = 559.17).

4,7-Bis(4-hydroxyphenylethynyl)-2,1,3-benzothiadiazole (4). A mixture of 3 (1.20 g, 2.23 mmol), pyridinium p-toluenesulfonate (112 mg, 0.446 mmol), H2O (5 mL) and THF (150 mL) was stirred for 6 h at 60 °C and subsequently cooled to room temperature. After most of the THF was evaporated, the mixture was poured into chloroform (300 mL). The organic phase was washed with saturated aq. NaCl (2 × 100 mL), dried over MgSO4, filtered, and the solvent was evaporated. The crude product was purified by flash column chromatography on silica gel (eluent: dichloromethane/ethylacetate = 9:1) to afford compound 4 (673 mg, 1.83 mmol) as an orange solid in a yield of 82%.

1H NMR (400 MHz, DMSO-d6): δ = 6.86 (d, J = 8.8 Hz, 4H), 7.48 (d, J = 8.8 Hz, 4H), 7.87 (s, 2H), 10.14 (s, 2H). 13C NMR (100 MHz, DMSO-d6): δ = 84.17, 97.75, 111.89, 116.01, 116.19, 132.20, 133.43, 153.78, 158.79. MS (MALDI-TOF): m/z: 368.03 (calcd. [M]+ = 368.06).

1,5-bis[2-(2-{2-(2-hydroxyethoxy)ethoxy}ethoxy)ethoxy]ethoxyethoxy-naphthalene (5). A mixture of 1,5-dihydroxynapthalene (371 mg, 2.32 mmol), pentaethylene glycol p-toluenesulfonate (2.00 g, 5.10 mmol), lithium bromide (20.0 mg, 0.232 mmol), K2CO3 (1.60 g, 11.6 mmol), and MeCN (120 mL) was stirred and refluxed for 24 h. After cooling to room temperature, most of MeCN was evaporated. Then, dichloromethane (200 mL) was added and the mixture was passed through celite pad. The organic phase was washed with 5% aq. NaOH (2 × 50 mL), followed by saturated aq. NaCl, dried over MgSO4, filtered, and the solvent was evaporated. The crude product was purified by flash column chromatography on silica gel (eluent: dichloromethane/acetone = 9:1) to afford compound 5 (1.05 g, 1.75 mmol) as a colorless liquid in a yield of 76%.

1H NMR (400 MHz, CDCl3): δ = 2.84 (br, 2H), 3.56–3.58 (m, 4H), 3.63–3.71 (m, 24H), 3.79–3.82 (m, 4H), 3.98–4.01 (m, 4H), 4.28–4.31 (m, 4H), 6.84 (d, J = 7.6 Hz, 2H), 7.34 (t, J = 8.0 Hz, 2H), 7.86 (d, J = 8.0 Hz, 2H). 13C NMR (100 MHz, CDCl3): δ = 61.78, 67.98, 69.89, 70.35, 70.62, 70.68, 70.75, 71.07, 72.62, 105.74, 114.69, 125.17, 126.84, 154.41. MS (MALDI-TOF): m/z: 600.32 (calcd. [M]+ = 600.31).

1,5-bis[2-(2-{2-(2-bromoethoxy)ethoxy}ethoxy)ethoxy]ethoxyethoxy-naphthalene (6). A solution of tetrabromomethane (1.38 g, 4.16 mmol) in dichloromethane (20 mL) was added dropwise to a solution of 5 (1.00 g, 1.75 mmol) in dichloromethane (20 mL) and stirred at room temperature for 24 h. The mixture was evaporated. The crude product was purified by flash column chromatography on silica gel (eluent: dichloromethane/acetone = 9:1) to afford compound 6 (1.05 g, 1.75 mmol) as a colorless liquid in a yield of 76%.

1H NMR (400 MHz, CDCl3): δ = 2.84 (br, 2H), 3.56–3.58 (m, 4H), 3.63–3.71 (m, 24H), 3.79–3.82 (m, 4H), 3.98–4.01 (m, 4H), 4.28–4.31 (m, 4H), 6.84 (d, J = 7.6 Hz, 2H), 7.34 (t, J = 8.0 Hz, 2H), 7.86 (d, J = 8.0 Hz, 2H). 13C NMR (100 MHz, CDCl3): δ = 61.78, 67.98, 69.89, 70.35, 70.62, 70.68, 70.75, 71.07, 72.62, 105.74, 114.69, 125.17, 126.84, 154.41. MS (MALDI-TOF): m/z: 600.32 (calcd. [M]+ = 600.31).
1.66 mmol) and triphenylphosphine (1.05 g, 4.00 mmol) in dichloromethane (200 mL) at 0 °C. The reaction mixture was subsequently stirred for 2.5 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 = 4:1) to afford compound 6 (898 mg, 1.24 mmol) as brownish oil in a yield of 74 %.

1H NMR (400 MHz, CDCl3): \( \delta = 3.45 \) (t, \( J = 6.0 \) Hz, 4H), 3.64–3.72 (m, 20H), 3.76–3.82 (m, 8H), 4.00 (t, \( J = 4.8 \) Hz, 4H), 4.30 (t, \( J = 4.8 \) Hz, 4H), 6.84 (d, \( J = 7.6 \) Hz, 2H), 7.35 (t, \( J = 8.0 \) Hz, 2H), 7.86 (d, \( J = 8.4 \) Hz, 2H). 13C NMR (100 MHz, CDCl3): \( \delta = 30.53, 68.12, 70.03, 70.71, 70.77, 70.86, 70.87, 70.92, 71.21, 71.38, 105.85, 114.81, 125.29, 126.96, 154.54 \). MS (MALDI-TOF): m/z: 747.20 (calcd. [M+Na]+ = 747.15).

Cyclophane 1. A solution of compound 4 (300 mg, 0.814 mmol) and compound 6 (592 mg, 0.814 mmol) in DMF (25 mL) was dropwise added to a suspension of K2CO3 (2.24 g, 16.3 mmol) in DMF (300 mL) at 80 °C over 8 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. NH4Cl (300 mL) and ethyl acetate (200 mL). The organic phase was washed with saturated aq. NH4Cl (3 \( \times 100 \) mL), followed by saturated aq. NaCl, the organic layer was dried over MgSO4, filtered, and the solvent was evaporated. The crude product was purified by flash column chromatography on silica gel (eluent: gradient from dichloromethane/acetone = 4:1 to dichloromethane/acetone = 7:3), recycling GPC (eluent: chloroform), and subsequently re-precipitated from a mixture of chloroform and hexane to afford compound 1 (292 mg, 0.313 mmol) as a yellow powder in a yield of 38 %.

1H NMR (400 MHz, CDCl3): \( \delta = 3.57–3.65 \) (m, 20H), 3.70–3.73 (m, 4H), 3.82–3.88 (m, 8H), 4.10–4.13 (m, 4H), 4.25–4.27 (m, 4H), 6.58 (d, \( J = 7.6 \) Hz, 2H), 7.01 (d, \( J = 8.8 \) Hz, 2H), 7.10 (t, \( J = 8.0 \) Hz, 4H), 7.35 (s, 2H), 7.58–7.63 (m, 6H). 13C NMR (100 MHz, CDCl3): \( \delta = 67.36, 68.02, 69.79, 69.95, 70.59, 70.62, 70.83, 70.92, 70.95, 71.21, 84.75, 97.40, 110.23, 114.41, 115.04, 115.35, 116.77, 124.91, 126.46, 132.05, 133.59, 154.15, 154.17, 159.76 \). HRMS (ESI): m/z: 955.3442 (calcd. [M+Na]+ = 955.3446). Elemental analysis (%) calcd. for C52H56N2O12S: C 66.94, H 6.05, N 3.00; found: C 66.70, H 5.91, N 2.90.

Compound 2. A suspension of compound 4 (200 mg, 0.543 mmol), 2-(2-(2-methoxyethoxy)ethoxy)ethyl 4-methylbenzenesulfonate (432 mg, 1.36 mmol), and K2CO3 (375 mg, 2.72 mmol) in DMF (150 mL) was stirred for 24 h at 80 °C. After cooling to room temperature, the reaction suspension was poured into a mixture of saturated aq. NH4Cl (250 mL) and ethyl acetate (150 mL). The organic layer was washed with saturated aq. NH4Cl (3 \( \times 100 \) mL), washed with saturated aq. NaCl (1 \( \times 100 \) mL), dried over MgSO4, filtered, and the solvent was evaporated. The crude product was purified by flash column chromatography on silica gel (eluent: hexane/ethylacetate = 1:9) and recycling GPC (eluent: chloroform) to afford compound 2 (216 mg, 0.341 mmol) as a yellow solid in a yield of 63%.

1H NMR (400 MHz, CDCl3): \( \delta = 3.39 \) (s, 6H), 3.55–3.57 (m, 4H), 3.66–3.71 (m, 8H), 3.74–3.77 (m, 4H), 3.88–3.90 (m, 4H), 4.17–4.19 (m, 4H), 6.94 (d, \( J = 8.8 \) Hz, 4H), 7.60 (d, \( J = 8.8 \) Hz, 4H), 7.75 (s, 2H). 13C NMR (100 MHz, CDCl3): \( \delta = 59.17, 67.61, 69.73, 70.70, 70.77, 70.98, 72.03, 84.49, 97.74, 114.84, 117.20, 132.22, 133.63, 154.50, 159.59 \). HRMS (ESI): m/z: 683.2405 (calcd. [M+Na]+ = 683.2398). Elemental analysis (%) calcd. for C36H40N2O8S: C 65.44, H 6.10, N 4.24; found: C 65.16, H 6.04, N 4.21.
DSC measurements of cyclophane 1 and acyclic compound 2

Figure S1. DSC traces of (a) compound 1 on the first heating from the crystalline state, and (b) compound 2 on the first cooling and the second heating. Scanning rate: 5 °C min⁻¹.

The wavelength dependency of polarized emission

Figure S2. The ratio of photoluminescence intensity in the direction parallel and perpendicular to the rubbing direction between 530 and 650 nm (a) in the nematic phase and (b) in the crystalline phase.
**Emission lifetime measurements for the ground 1**

![Graph showing emission decay profiles](image)

**Figure S3.** Emission decay profiles recorded for compound 1 in the nematic phase (orange line), in the crystalline phase (green line), and after mechanical grinding for the crystalline state (red line). The profiles were collected at room temperature with excitation light of 405 nm.

**X-ray diffraction pattern after mechanical treatment**

![XRD patterns](image)

**Figure S4.** XRD patterns of 1 (a) in the crystalline phase after annealing the nematic phase at 60 °C for 1 h and (b) after rapid recovery of emission colour from the ground state. The patterns were recorded at room temperature.
Temperature dependency of rapid recovery behaviour

Figure S5. Photographs documenting the mechanoresponsive luminescence of cyclophane 1. (a,b) Samples in the crystalline phases that are accessed through annealing at 60 °C for 1 h from the nematic phase, (c,d) just after grinding at 15 °C, (e) after keeping sample at 15 °C for 5 min, and (f) just after keeping the sample at 40 °C. All images were recorded under illumination with 365 nm UV light.

References