Supporting Information

Rotaxanes as Mechanochromic Fluorescent Force Transducers in Polymers
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General Methods
All reagents and solvents were purchased from Aldrich, Tokyo Kasei, Merck, Kanto Chemical, or Wako. Inhibitor-free anhydrous tetrahydrofuran (THF) (Sigma-Aldrich) was used as solvent for the polymer syntheses. Poly(tetrahydrofuran) (PTHF, number-average molecular weight, $M_n = 2,000$ g/mol) was dried in vacuo at 100 °C for 1 h before use. 4,4’-Methylenebis(phenyl isocyanate) (MDI) and 1,4-butanediol (BDO) were distilled under vacuum and stored over molecular sieves at 5 °C. Unless otherwise noted, all reactions were carried out under nitrogen atmosphere. Flash silica gel column chromatography was carried out with a Biotage Isolera Flash system using Biotage Flash Cartridges or SHOKO-scientific Purif-Pack-EX cartridges. Silica gel from Kanto Chemicals (silica gel 60 N, spherical, 63-210 μm) was used when flash silica gel column chromatography was conducted in a conventional manner. $^1$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. High resolution electrospray ionization (ESI) mass spectra were obtained on a Thermo Scientific Exactive. UV-vis absorption spectra were measured on a JASCO V-550. Steady-state photoluminescence spectra of solutions or films (except spectra in conjunction with deformation experiments) were recorded on a JASCO FP-6500 and the spectra were corrected for the detector nonlinearity. Steady-state fluorescence spectra of films made in conjunction with deformation experiments were recorded on an Ocean Optics QEPro-FL equipped with an LLS-385 LED light source and a Reflection/Backscattering Probe R400-7-UV-VIS and the spectra were used without correction. Time-resolved photoluminescence measurements were carried out with a Hamamatsu Photonics Quantaurus-Tau. All emission experiments were conducted at r.t. Differential scanning calorimetry (DSC) measurements were carried out under N$_2$ on Mettler-Toledo Star$^e$ DSC at heating and cooling rates of 10 °C/min. Thermogravimetric analyses (TGA) were carried out under N$_2$ with a Mettler-Toledo Star$^e$ system by heating from 30 to 650 °C at a rate of 10 °C/min. Stress–strain measurements were performed under ambient conditions with a Zwick/Roell Z010 tensile tester equipped with a 200 N load cell at a strain rate of 100 mm/min. Dynamic mechanical analyses (DMA) were carried out under N$_2$ on a TA Instruments DMA Q800 at a heating rate of 3 °C/min, a frequency of 1 Hz, and an amplitude of 15 μm. Size-exclusion chromatography (SEC) experiments were performed on an Agilent 1200 series HPLC system equipped with an Agilent PLgel mixed guard column (particle size = 5 μm) and two Agilent PLgel mixed-D columns (ID = 7.5 mm, L = 300 mm, particle size = 5 μm). Signals were recorded by a UV detector (Agilent 1200 series), an Optilab REX interferometric refractometer, and a miniDawn TREOS light scattering detector (Wyatt Technology Corp.). Samples were run using THF as the eluent at 30 °C and a flow rate of 1.0 mL/min. Data analyses were done on Astra software (Wyatt Technology Corp.) and molecular weights were determined based on narrow-molecular-weight polystyrene calibration (from 580 to 364,000 g/mol). Sonication experiments were performed using a Branson Model 450 ultrasonic 1/2 in-horn sonicator equipped with a 13 mm sonicator tip. A MX07R-20 refrigerating/heating bath obtained from VWR was used to maintain a constant solution temperature during sonication experiments. Emission spectra obtained in
conjunction with the sonication experiments were recorded on a PTI C720 fluorescence spectrometer using right angle illumination. For excitation, a XeArc lamp was used along with a PETI 814 photomultiplier detection system.

**Synthesis**

![Chemical structure](image)

Conditions: K₂CO₃, DMF, 80 °C, 12 h.

**Compound 5.** A mixture of tris(p-tert-butylphenyl)(4-hydroxyphenyl)methane⁵¹ (563 mg, 1.12 mmol), 3,6,9,12-tetraoxapentadec-14-yn-1-yl tosylate⁵² (474 mg, 1.23 mmol), and K₂CO₃ (462 mg, 3.35 mmol) in DMF (40 mL) was vigorously stirred under nitrogen atmosphere for 12 h at 80 °C. The suspension was cooled to room temperature and poured into a mixture of saturated aq. NH₄Cl (200 mL) and ethyl acetate (100 mL). The organic layer was separated, washed with saturated aq. NH₄Cl (3 × 100 mL) and saturated aq. NaCl (100 mL), dried over MgSO₄ and filtered, before the solvent was evaporated. The crude product was purified by flash column chromatography on silica gel (eluent: hexane/ethyl acetate = 9:1 v/v) to afford compound 5 (638 mg, 0.887 mmol, 80%) as a white solid. m.p. 163 °C.

¹H NMR (400 MHz, CDCl₃): δ = 1.29 (s, 27H), 2.40 (t, J = 2.4 Hz, 1H), 3.66–3.74 (m, 12H), 3.84 (t, J = 5.0 Hz, 2H), 4.10 (t, J = 4.8 Hz, 2H), 4.19 (d, J = 2.4 Hz, 2H), 6.78 (d, J = 8.8 Hz, 2H), 7.07 (d, J = 8.8 Hz, 8H), 7.23 (d, J = 8.4 Hz, 6H).

¹³C NMR (100 MHz, CDCl₃): δ = 31.51, 34.41, 58.53, 63.16, 67.32, 69.24, 69.89, 70.54, 70.75, 70.78, 70.92, 74.66, 79.78, 113.17, 124.16, 130.84, 132.34, 139.85, 144.25, 148.40, 156.67. HRMS (ESI): m/z: 741.4479 (calcd. [M+Na]+ = 741.4495).

![Chemical structure](image)

Conditions: (a) K₂CO₃, DMF, 80 °C, 24 h; (b) LiAlH₄, THF, 0 °C → r.t., 2 h.

**Compound 6.** A mixture of bis(p-tert-butylphenyl)bis(4-hydroxyphenyl)methane⁵³ (1.70 g, 3.66 mmol), ethyl 2-bromoisobutyrate (785 mg, 4.02 mmol), and K₂CO₃ (1.52 g, 11.0 mmol) in DMF (100 mL) was vigorously stirred under nitrogen atmosphere for 24 h at 80 °C. The suspension was cooled to room temperature and poured into a mixture of saturated aq. NH₄Cl (300 mL) and ethyl acetate (200 mL). The organic layer was washed with saturated aq.
NH₄Cl (3 × 100 mL) and saturated aq. NaCl (100 mL), dried over MgSO₄ and filtered, before the solvent was evaporated. The crude product was purified by flash column chromatography on silica gel (eluent: hexane/ethyl acetate = 4:1 v/v) to afford compound 6 (890 mg, 1.54 mmol, 42%) as a white solid. m.p. 91 °C. ¹H NMR (400 MHz, CDCl₃): δ = 1.21 (t, J = 7.2 Hz, 3H), 1.30 (s, 18H), 1.59 (s, 6H), 4.21 (q, J = 7.2 Hz, 2H), 4.61 (s, 1H), 6.68–6.70 (m, 4H), 7.00–7.05 (m, 8H), 7.22 (d, J = 8.8 Hz, 4H). ¹³C NMR (100 MHz, CDCl₃): δ = 14.21, 25.60, 31.51, 34.43, 34.44, 61.52, 62.97, 79.10, 114.12, 117.67, 124.23, 130.78, 132.00, 132.52, 139.87, 141.04, 144.20, 148.55, 153.38, 153.47, 174.54. HRMS (ESI): m/z: 601.3283 (calcd. [M+Na]^+ = 601.3294).

**Compound 7.** A solution of compound 6 (890 mg, 1.54 mmol) in THF (10 mL) was slowly added to a suspension of LiAlH₄ (70.0 mg, 1.85 mmol) in THF (50 mL) at 0 °C and the mixture was stirred for 2 h at room temperature. The reaction was then quenched by the dropwise addition of water, before more water (250 mL) and ethyl acetate (150 mL) were added. The organic layer was separated, washed with water (2 × 100 mL) and saturated aq. NaCl (100 mL), dried over MgSO₄ and filtered, before the solvent was evaporated. The crude product was purified by flash column chromatography on silica gel (eluent: hexane/ethyl acetate = 3:2 v/v) to afford compound 7 (534 mg, 0.995 mmol, 65%) as a colorless liquid. ¹H NMR (400 MHz, CDCl₃): δ = 1.29 (s, 6H), 1.30 (s, 18H), 2.18 (t, J = 6.8 Hz, 1H), 3.58 (d, J = 6.8 Hz, 2H), 4.71 (s, 1H), 3.58 (d, J = 6.8 Hz, 2H), 3.58 (d, J = 6.8 Hz, 2H), 6.70 (d, J = 8.8 Hz, 2H), 6.84 (d, J = 8.8 Hz, 2H), 7.01–7.08 (m, 8H), 7.23 (d, J = 8.4 Hz, 4H). ¹³C NMR (100 MHz, CDCl₃): δ = 23.29, 31.51, 34.46, 63.10, 70.54, 80.60, 114.16, 122.33, 124.28, 130.79, 132.05, 132.53, 139.73, 142.85, 144.12, 148.64, 152.44, 153.57. HRMS (ESI): m/z: 559.3176 (calcd. [M+Na]^+ = 559.3188).

**Conditions:** K₂CO₃, DMF, 80 °C, 18 h.

**Compound 8.** A mixture of compound 7 (500 mg, 0.864 mmol), 3,6,9,12-tetraoxapentadec-14-yn-1-yl tosylate52 (501 mg, 1.30 mmol), and K₂CO₃ (358 mg, 2.65 mmol) in DMF (100 mL) was vigorously stirred under nitrogen atmosphere for 18 h at 80 °C. The suspension was cooled and poured into a mixture of saturated aq. NH₄Cl (200 mL) and ethyl acetate (100 mL). The organic layer was separated, washed with saturated aq. NH₄Cl (4 × 100 mL) and saturated aq. NaCl (100 mL), dried over MgSO₄ and filtered, before the solvent was evaporated. The crude product was purified by flash column chromatography on silica gel (eluent: dichloromethane/acetone = 6:1 v/v) to afford compound 8 (537 mg, 0.715 mmol, 83%) as a white waxy solid. ¹H NMR (400 MHz, CDCl₃): δ = 1.28 (s, 6H), 1.30 (s, 18H), 2.16 (t, J = 6.4 Hz, 1H), 2.40 (t, J = 2.4 Hz, 1H), 3.58 (d, J = 6.4 Hz, 2H), 3.65–3.73 (m, 12H), 3.84 (t, J = 4.8 Hz, 2H), 4.10 (t, J = 4.8 Hz, 2H), 4.19 (d, J = 2.4 Hz, 2H), 6.78 (d, J = 8.8 Hz, 2H), 6.84 (d, J = 8.8 Hz, 2H), 7.04–7.08 (m, 8H), 7.23 (d, J = 8.4 Hz, 2H)

S4
Hz, 4H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 23.27, 31.47, 34.39, 58.49, 63.04, 67.32, 69.20, 69.85, 70.45, 70.50, 70.71, 70.74, 70.89, 74.65, 79.76, 80.50, 113.23, 122.27, 124.20, 130.75, 131.97, 132.22, 139.67, 142.74, 144.10, 148.53, 152.44, 156.73. HRMS (ESI): m/z: 773.4378 (calcd. [M+Na]$^+$ = 773.4393).

Conditions: dioxane, reflux, 18 h.

**Compound 9.** A mixture of naphthalene-1,4,5,8-tetracarboxylic dianhydride (1.50 g, 5.59 mmol) and 2-(2-aminoethoxy)ethanol (2.35 g, 22.4 mmol) in 1,4-dioxane (70 mL) was stirred for 18 h under reflux. After cooling to room temperature, the reaction mixture was poured into 5% aq. HCl (200 mL). The precipitate was filtered and washed with water (3 × 50 mL) and methanol (3 × 50 mL), before it was dried *in vacuo* to afford compound 9 (1.81 g, 4.09 mmol, 73%) as a brownish solid that was used in the next step without further purification.

Conditions: (a) PBr$_3$, DMF, 70 °C, 4 h; (b) NaN$_3$, DMF, 60 °C, 24 h.

**Compound 10.** PBr$_3$ (1.86 mL, 19.8 mmol) was added to a solution of compound 9 (3.80 g, 8.59 mmol) in DMF (200 mL) and the mixture was stirred for 4 h at 70 °C. After cooling to room temperature, the reaction mixture was slowly poured into 5% aq. NaHCO$_3$ (200 mL). The resulting precipitate was filtered and washed with water (5 × 50 mL) and MeOH (3 × 50 mL). The solid residue was dissolved in chloroform and the solution was dried over MgSO$_4$ and filtered, before the solvent was evaporated. The crude product was purified by flash column chromatography on silica gel (eluent: chloroform) to afford compound 10 (4.10 g, 7.22 mmol, 84%) as pale yellow crystalline solid. m.p. 187 °C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 3.42 (t, $J$ = 6.0 Hz, 4H), 3.84 (t, $J$ = 6.0 Hz, 4H), 3.89 (t, $J$ = 5.6 Hz, 4H), 4.49 (t, $J$ = 5.6 Hz, 4H), 8.77 (s, 4H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 30.68, 39.64, 67.79, 70.63, 126.66, 126.80, 131.15, 163.00. HRMS (ESI): m/z: 588.9579 (calcd. [M+Na]$^+$ = 588.9586).

**Compound 11.** NaN$_3$ (1.72 g, 26.4 mmol) was added to a solution of compound 10 (1.50 g, 2.64 mmol) in DMF (200 mL) and the mixture was stirred for 24 h at 60 °C. After cooling to room temperature, the reaction mixture was poured into water (200 mL). The resulting precipitate was filtered and washed with water (5 × 50 mL). The solid residue was dissolved in chloroform and the solution was dried over MgSO$_4$ and filtered, before the solvent was evaporated. The crude product was purified by flash column chromatography on silica gel (eluent: chloroform) to afford compound 11.
(1.29 g, 2.61 mmol, 99%) as white crystalline solid. m.p. 151 °C. 1H NMR (400 MHz, CDCl3): δ = 3.32 (t, J = 4.8 Hz, 4H), 3.72 (t, J = 4.8 Hz, 4H), 3.88 (t, J = 6.0 Hz, 4H), 4.49 (t, J = 6.0 Hz, 4H), 8.76 (s, 4H). 13C NMR (100 MHz, CDCl3): δ = 39.74, 50.81, 68.04, 69.94, 126.72, 126.89, 131.15, 163.11. HRMS (ESI): m/z: 515.1393 (calcd. [M+Na]⁺ = 515.1404).

Conditions: CuSO₄, sodium ascorbate, CHCl₃, H₂O, r.t., 12 h.

Compounds 12 and 4. A mixture of sodium ascorbate (496 mg, 2.50 mmol) and copper(II) sulfate (200 mg, 1.25 mmol) in water (4 mL) was added to a solution of compound 5 (600 mg, 0.834 mmol) and compound 11 (616 mg, 1.25 mmol) in chloroform (15 mL) and the mixture was vigorously stirred for 12 h at r.t.. The suspension was poured into a mixture of water (100 mL) and chloroform (100 mL). The organic layer was separated, washed with saturated aq. NaCl (2 × 100 mL), dried over MgSO₄ and filtered, and the solvent was evaporated. The crude product was purified by flash column chromatography on silica gel (eluent: gradient from dichloromethane/aceton = 9:1 to dichloromethane/aceton = 1:1 v/v) and recycling GPC (eluent: chloroform) to afford compound 12 (179 mg, 0.148 mmol, 18%) as a pale yellow waxy solid and compound 4 (549 mg, 0.284 mmol, 68%) as a pale yellow solid.

Compound 12: 1H NMR (400 MHz, CDCl3): δ = 1.30 (s, 27H), 3.30 (d, J = 4.8 Hz, 2H), 3.63–3.73 (m, 14H), 3.78–3.90 (m, 8H), 4.08 (t, J = 4.8 Hz, 2H), 4.42–4.50 (m, 6H), 4.53 (s, 2H), 6.76 (d, J = 9.2 Hz, 2H), 7.08 (d, J = 8.8 Hz, 8H), 7.23 (d, J = 8.8 Hz, 6H), 7.68 (s, 1H), 8.73–8.77 (m, 4H). 13C NMR (100 MHz, CDCl3): δ = 31.43, 34.31, 39.60, 39.67, 50.24, 50.68, 63.06, 64.55, 67.21, 67.91, 68.17, 68.95, 69.64, 69.78, 69.87, 70.53, 70.61, 70.64, 70.80, 113.08, 124.07, 126.41, 126.69, 126.73, 126.79, 130.74, 131.09, 131.14, 132.23, 139.75, 144.17, 148.29, 156.56, 162.90. HRMS (ESI): m/z: 1233.5972 (calcd. [M+Na]⁺ = 1233.6001).

Compound 4: m.p. 199 °C. 1H NMR (400 MHz, CDCl3): δ = 1.29 (s, 54H), 3.63–3.72 (m, 24H), 3.78–3.88 (m, 12H), 4.08 (t, J = 4.8 Hz, 4H), 4.43–4.48 (m, 8H), 4.55 (s, 4H), 6.76 (d, J = 8.8 Hz, 4H), 7.05–7.09 (m, 16H), 7.22 (d, J = 8.4 Hz, 2H), 7.67 (s, 2H), 8.77 (s, 4H). 13C NMR (100 MHz, CDCl3): δ = 31.45, 34.34, 39.64, 50.26, 63.09, 64.57, 67.24, 68.16, 68.98, 69.67, 69.81, 70.55, 70.63, 70.66, 70.82, 113.10, 123.86, 124.09, 126.56, 126.85, 130.77, 131.23, 132.26,
139.79, 144.18, 144.93, 148.32, 156.58, 162.89. HRMS (ESI): m/z: 1952.0631 (calcd. [M+Na]+ = 1952.0598).

Condition: \( \text{Pd(PPh}_3\text{)}_4, \text{CuI, Et}_2\text{NH, THF, 70 °C, 22 h.} \)

**Compound 13.** A mixture of 4,7-dibromo-2,1,3-benzothiadiazole (917 mg, 3.12 mmol), 1-ethynyl-4-propoxybenzene (500 mg, 3.12 mmol), \( \text{Pd(PPh}_3\text{)}_4 \) (180 mg, 0.156 mmol), CuI (29.7 mg, 0.156 mmol), and \( \text{Et}_2\text{NH} \) (20 mL) in THF (20 mL) was stirred under nitrogen atmosphere for 2 h at 70 °C. After cooling to room temperature, the reaction mixture was poured into ethyl acetate (150 mL) and the organic layer was washed with 5% aq. HCl (2 × 100 mL), saturated aq. NaHCO\(_3\) (100 mL), and saturated aq. NaCl (100 mL). The organic layer was dried over MgSO\(_4\) and filtered, and the solvent was evaporated. The crude product was purified by flash column chromatography on silica gel (eluent: gradient from hexane/chloroform = 1:1 v/v to hexane/chloroform = 1:2 v/v) and subsequently precipitated from a mixture of chloroform and hexane to afford compound 13 (439 mg, 1.17 mmol, 38%) as a yellow solid. m.p. 101 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta = 1.06 \) (t, \( J = 7.2 \) Hz, 3H), 1.79–1.88 (m, 2H), 3.96 (t, \( J = 6.8 \) Hz, 2H), 6.91 (d, \( J = 9.2 \) Hz, 2H), 7.59 (t, \( J = 9.2 \) Hz, 2H), 7.64 (d, \( J = 7.6 \) Hz, 1H), 7.83 (d, \( J = 7.6 \) Hz, 1H). \(^1^3\)C NMR (100 MHz, CDCl\(_3\)): \( \delta = 10.58, 22.56, 69.60, 83.58, 79.43, 114.00, 114.17, 114.64, 117.13, 132.03, 132.34, 133.55, 153.07, 154.17, 159.92. HRMS (ESI): m/z: 394.9828 (calcd. [M+Na]+ = 394.9830).

Condition: \( \text{Pd(PPh}_3\text{)}_4, \text{CuI, i-Pr}_2\text{NH, THF, 80 °C, 16 h.} \)

**Compound 14.** A mixture of 4,7-dibromo-2,1,3-benzothiadiazole (1.00 g, 3.40 mmol), 3-(4-ethynylphenoxy)propan-1-ol\(^{54}\) (599 mg, 3.40 mmol), \( \text{Pd(PPh}_3\text{)}_4 \) (196 mg, 0.170 mmol), CuI (32.4 mg, 0.170 mmol), and i-Pr\(_2\)NH (20 mL) in THF (20 mL) was stirred under nitrogen atmosphere for 16 h at 80 °C. After cooling to room temperature, the reaction mixture was poured into ethyl acetate (150 mL) and the organic layer was washed with 5% aq. HCl (2 × 100 mL), saturated aq. NaHCO\(_3\) (100 mL), and saturated aq. NaCl (100 mL). The organic layer was dried over MgSO\(_4\) and filtered, and the solvent was evaporated. The crude product was purified by flash column chromatography on silica gel (eluent: gradient from dichloromethane to dichloromethane/ethyl acetate = 3:1 v/v) to afford compound 14 (654 mg, 1.68 mmol, 50%) as a yellow solid. m.p. 116 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta = 1.62 \) (t, \( J = 5.2 \) Hz, 1H), 2.05–2.09 (quin, 2H), 3.89 (q, \( J = 6.0 \) Hz, 2H), 4.17 (t, \( J = 6.0 \) Hz, 2H), 6.93 (d, \( J = 8.8 \) Hz, 2H), 7.60 (d, \( J = 8.8 \) Hz, 2H), 7.64 (d, \( J = 7.6 \) Hz, 1H), 7.83 (d, \( J = 7.6 \) Hz, 1H). \(^1^3\)C NMR (100 MHz, CDCl\(_3\)): \( \delta = 31.97, 59.98, 65.48, 83.68, 97.25, 114.09, 114.55, 114.62, 117.04, 132.06, 132.43, 133.58, 153.07, 154.16, 159.56. HRMS (ESI): m/z: 388.9957 (calcd. [M+H]+ = 388.9959).
The crude product was purified by flash column chromatography on silica gel.

**Compound 15.** A solution of tetrabromomethane (4.04 g, 12.2 mmol) in dichloromethane (15 mL) was added dropwise to a solution of 1,5-bis[2-[2-(2-hydroxyethoxy)ethoxy]ethoxy]ethoxy)naphthalene\(^{55}\) (2.50 g, 4.88 mmol) and triphenylphosphine (3.07 g, 11.7 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/ethyl acetate = 4:1 v/v) to afford compound 15 (2.36 g, 3.70 mmol, 76%) as a brown oil. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 3.43\) (t, \(J = 6.4\) Hz, 4H), 3.63–3.81 (m, 20H), 3.99 (t, \(J = 4.8\) Hz, 4H), 4.29 (t, \(J = 4.8\) Hz, 4H), 6.84 (d, \(J = 8.0\) Hz, 2H), 7.34 (t, \(J = 8.0\) Hz, 2H), 7.86 (d, \(J = 8.4\) Hz, 2H). \(^13\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 30.45, 68.00, 69.90, 70.60, 70.73, 70.85, 71.08, 71.26, 105.73, 114.68, 125.16, 126.83, 154.41\). HRMS (ESI): \(m/z:\) 659.0823 (calcd. [M+Na]\(^+\) = 659.0831).

\[ \text{Conditions: (a) bromohydroquinone, K}_2\text{CO}_3, \text{DMF, 80 °C, 36 h; (b) trimethylsilylacetylene, Pd(PPh}_3)_4, \text{CuI, i-Pr}_2\text{NH, THF, 70 °C, 18 h; (c) TBAF, THF, r.t., 2 h.} \]

**Compound 16.** A solution of bromohydroquinone (518 mg, 2.74 mmol) and compound 15 (1.75 g, 2.74 mmol) in DMF (25 mL) was added over the course of 12 h and under vigorous stirring to a suspension of K\(_2\)CO\(_3\) (7.57 g, 54.8 mmol) in DMF (300 mL) at 80 °C. After stirring for 24 h at 80 °C, the solvent was evaporated. Chloroform (250 mL) was added and the organic layer was washed with saturated aq. NH\(_4\)Cl solution (3 x 300 mL) and saturated aq. NaCl (100 mL). The organic layer was dried over MgSO\(_4\) and filtered, and the solvent was evaporated. The crude product was purified by flash column chromatography on silica gel (eluent: dichloromethane/acetone = 92:8 v/v) to afford compound 16 (760 mg, 1.14 mmol, 42%) as a white solid. m.p. 76 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 3.65–3.88\) (m, 24H), 3.99–4.02 (m, 4H), 4.21–4.25 (m, 4H), 6.48–6.48 (m, 2H), 6.73–6.76 (m, 2H), 6.95 (t, \(J = 1.6\) Hz, 1H), 7.26–7.31 (m, 2H), 7.83–7.86 (m, 2H). \(^13\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 68.11, 68.16, 68.19, 69.67, 69.68, 69.84, 69.86, 70.85, 71.01, 71.05, 71.10, 105.70, 105.72, 112.71, 114.38, 114.64, 114.75, 115.09, 119.63, 125.24, 126.80, 126.82, 149.70, 153.44, 154.41, 154.44\). HRMS (ESI): \(m/z:\) 687.1769 (calcd. [M+Na]\(^+\) = 687.1781).
**Compound 17.** A mixture of compound 16 (620 mg, 0.933 mmol), trimethylsilylacetylene (914 mg, 9.31 mmol), Pd(PPh$_3$)$_4$ (54 mg, 4.7 × 10$^{-2}$ mmol), CuI (8.89 mg, 4.67 × 10$^{-2}$ mmol), and i-Pr$_2$NH (30 mL) in THF (20 mL) was stirred under nitrogen atmosphere for 18 h at 70 °C. After cooling to room temperature, the reaction mixture was poured into ethyl acetate (150 mL). The organic layer was washed with 5% aq. HCl (2 × 100 mL), saturated aq. NaHCO$_3$ (100 mL), and saturated aq. NaCl (100 mL), dried over MgSO$_4$ and filtered, and the solvent was evaporated. The crude product was purified by flash column chromatography on silica gel (eluent: gradient from dichloromethane/acetone = 95:5 v/v to dichloromethane/acetone = 92:8 v/v) to afford compound 17 (560 mg, 0.820 mmol, 88%) as a brown liquid. $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 0.23$ (s, 9H), 3.63–3.80 (m, 22H), 3.85–3.88 (m, 2H), 3.97–4.00 (m, 4H), 4.17–4.22 (m, 4H), 6.42 (d, $J = 8.8$ Hz, 1H), 6.55 (dd, $J = 2.8, 8.8$ Hz, 1H), 6.70–6.74 (m, 2H), 6.82 (d, $J = 2.8$ Hz, 1H), 7.24–7.31 (m, 2H), 7.83–7.86 (m, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 0.13, 68.00, 68.08, 69.37, 69.67, 69.76, 69.81, 70.81, 70.95, 70.96, 70.97, 71.01, 71.02, 71.06, 71.06, 98.31, 101.48, 105.70, 105.71, 113.34, 114.26, 114.59, 114.70, 116.96, 118.82, 125.22, 125.23, 126.76, 126.79, 152.49, 154.35, 154.38, 154.40. HRMS (ESI): m/z: 705.3054 (calcd. [M+Na]$^+ = 705.3071$).

**Compound 18.** A THF solution of tetrabutylammonium fluoride (ca. 1 mol/L, 0.98 mL, 0.98 mmol) was added to a solution of compound 17 (560 mg, 0.820 mmol) in THF (30 mL) at r.t.. After stirring the reaction mixture at room temperature for 2 h, ethyl acetate (150 mL) and water (200 mL) were added to the reaction mixture. The organic layer was separated, washed with saturated aq. NaCl (100 mL), dried over MgSO$_4$ and filtered, and the solvent was evaporated. The crude product was purified by flash column chromatography on silica gel (eluent: gradient from dichloromethane/acetone = 95:5 v/v to dichloromethane/acetone = 92:8 v/v) to afford compound 18 (402 mg, 0.658 mmol, 80%) as a pale brown solid. m.p. 96 °C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 3.20$ (s, 1H), 3.64–3.81 (m, 22H), 3.90–3.93 (m, 2H), 3.97–4.01 (m, 4H), 4.21–4.24 (m, 4H), 6.47 (d, $J = 8.8$ Hz, 1H), 6.56 (dd, $J = 2.8, 8.8$ Hz, 1H), 6.73–6.76 (m, 2H), 6.81 (d, $J = 2.8$ Hz, 1H), 7.25–7.31 (m, 2H), 7.83–7.86 (m, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 67.62, 67.66, 67.74, 68.98, 69.24, 69.36, 69.37, 70.36, 70.51, 70.52, 70.60, 70.60, 79.73, 81.30, 105.35, 105.40, 112.11, 113.91, 114.24, 114.37, 116.47, 118.98, 124.90, 126.39, 126.41, 152.16, 154.00, 154.03, 154.07. HRMS (ESI): m/z: 633.2658 (calcd. [M+Na]$^+ = 633.2676$).

![Diagram](https://via.placeholder.com/150)

Conditions: Pd(PPh$_3$)$_4$, CuI, Et$_2$NH, THF, 70 °C, 12 h.
**Compound 3.** A mixture of compound 13 (439 mg, 1.18 mmol), compound 18 (718 mg, 1.18 mmol), Pd(PPh₃)₄ (136 mg, 0.118 mmol), CuI (22.5 mg, 0.118 mmol), and Et₂NH (30 mL) in THF (20 mL) was stirred under nitrogen atmosphere for 12 h at 70 °C. After cooling to room temperature, the reaction mixture was poured into ethyl acetate (150 mL). The organic layer was separated, washed with 5% aq. HCl (2 × 100 mL), saturated aq. NaHCO₃ (100 mL), and saturated aq. NaCl (100 mL), dried over MgSO₄ and filtered, and the solvent was evaporated. The crude product was purified by flash column chromatography on silica gel (eluent: gradient from dichloromethane to dichloromethane/acetone = 9:1 v/v) to afford compound 3 (794 mg, 0.879 mmol, 75%) as an orange waxy solid. ¹H NMR (400 MHz, CDCl₃): δ = 1.05 (t, J = 7.6 Hz, 3H), 1.78–1.87 (m, 2H), 3.66–4.01 (m, 30H), 4.18 (t, J = 4.8 Hz, 2H), 4.23 (t, J = 4.8 Hz, 2H), 6.52 (d, J = 9.2 Hz, 1H), 6.64 (dd, J = 3.2, 8.8 Hz, 1H), 6.72 (t, J = 8.0 Hz, 2H), 6.91 (d, J = 8.8 Hz, 2H), 7.01 (d, J = 3.2 Hz, 1H), 7.24–7.30 (m, 2H), 7.60 (d, J = 9.2 Hz, 2H), 7.72 (s, 2H), 7.83 (d, J = 8.4 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃): δ = 10.48, 22.44, 67.90, 67.94, 67.97, 69.43, 69.49, 69.54, 69.63, 69.66, 69.70, 70.69, 70.76, 70.80, 70.86, 70.88, 70.90, 70.91, 84.38, 89.44, 94.12, 97.82, 105.55, 105.58, 112.80, 114.23, 114.27, 114.43, 114.55, 114.57, 116.96, 117.18, 117.46, 118.45, 125.07, 125.09, 126.59, 131.99, 132.32, 133.48, 152.53, 154.21, 154.28, 154.29, 159.80. HRMS (ESI): m/z: 925.3352 (calcd. [M+Na]⁺ = 925.3346).

**Condition:** Pd(PPh₃)₄, CuI, Et₂NH, THF, 80 °C, 10 h.

**Compound 19.** A mixture of compound 14 (400 mg, 0.655 mmol), compound 18 (280 mg, 0.720 mmol), Pd(PPh₃)₄ (37.9 mg, 3.28 × 10⁻² mmol), CuI (6.3 mg, 3.3 × 10⁻² mmol), and Et₂NH (30 mL) in THF (20 mL) was stirred under nitrogen atmosphere for 10 h at 80 °C. After cooling to room temperature, the reaction mixture was poured into ethyl acetate (150 mL). The organic layer was separated and washed with 5% aq. HCl (2 × 100 mL), saturated aq. NaHCO₃ (100 mL) and saturated aq. NaCl (100 mL), dried over MgSO₄ and filtered, and the solvent was evaporated. The crude product was purified by flash column chromatography on silica gel (eluent: gradient from dichloromethane/acetone = 9:1 v/v to dichloromethane/acetone = 7:3 v/v) to afford compound 19 (420 mg, 0.457 mmol, 70%) as an orange waxy solid. ¹H NMR (400 MHz, CDCl₃): δ = 1.66 (t, J = 5.2 Hz, 1H), 2.05–2.13 (m, 4H), 3.67–4.02 (m, 28H), 4.16–4.20 (m, 4H), 4.24 (t, J = 4.8 Hz, 2H), 6.53 (d, J = 9.2 Hz, 1H), 6.65 (dd, J = 3.2, 8.8 Hz, 1H), 6.72 (t, J = 8.0 Hz, 2H), 6.93 (d, J = 8.8 Hz, 2H), 7.01 (d, J = 3.2 Hz, 1H), 7.22–7.31 (m, 2H), 7.61 (d, J = 8.8 Hz, 2H), 7.73 (s, 2H), 7.83 (d, J = 8.4 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃): δ = 31.97, 59.89, 65.48, 68.00, 68.04, 68.07, 69.52, 69.66, 69.75, 69.78, 69.81, 70.79, 70.87, 70.91, 70.96, 70.98, 71.01, 84.52, 89.49, 94.22, 97.76, 105.66, 105.69, 112.88, 114.35, 114.54, 114.63, 114.65, 114.69, 117.11, 117.22, 117.61, 118.55, 125.17, 125.19, 126.70, 132.15, 132.42, 133.60, 152.63, 154.30, 154.31.
154.38, 159.56. HRMS (ESI): m/z: 941.3290 (calcd. [M+Na]$^+$ = 941.3295).

Conditions: CuSO$_4$, sodium ascorbate, CHCl$_3$, H$_2$O, 5 °C, 24 h.

**Compound 2.** A mixture of sodium ascorbate (96.6 mg, 0.488 mmol) and copper(II) sulfate (38.9 mg, 0.244 mmol) in water (1 mL) was added to a solution of compound 3 (147 mg, 0.163 mmol), compound 5 (117 mg, 0.163 mmol), and compound 12 (197 mg, 0.167 mmol) in chloroform (0.5 mL) and the mixture was vigorously stirred for 24 h at 5 °C. The suspension was poured into a mixture of water (100 mL) and chloroform (100 mL), before the organic layer was separated, washed with saturated aq. NaCl (100 mL), dried over MgSO$_4$ and filtered, and the solvent was evaporated. The crude product thus obtained was purified by flash column chromatography on silica gel (eluent: gradient from dichloromethane/acetone = 9:1 v/v to dichloromethane/acetone = 3:7 v/v) and recycling GPC (eluent: chloroform) to afford compound 2 (82.3 mg, 2.90 × 10^{-2} mmol, 18%) as a brown solid. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 1.06 (t, $J$ = 7.6 Hz, 3H), 1.29 (s, 54H), 1.80–1.89 (m, 2H), 3.51–4.13 (m, 78H), 4.56 (t, $J$ = 5.2 Hz, 4H), 4.69 (s, 4H), 5.81 (d, $J$ = 2.8 Hz, 1H), 5.89 (d, $J$ = 8.8 Hz, 1H), 6.01 (dd, $J$ = 3.2, 9.2 Hz, 1H), 6.11–6.15 (m, 2H), 6.63–6.71 (m, 2H), 6.76 (d, $J$ = 8.8 Hz, 4H), 6.91–6.95 (m, 4H), 7.07 (d, $J$ = 8.4 Hz, 16H), 7.22 (d, $J$ = 8.4 Hz, 12H), 7.62 (d, $J$ = 8.8 Hz, 2H), 7.68 (d, $J$ = 7.6 Hz, 1H), 7.78 (s, 2H), 7.79 (d, $J$ = 7.6 Hz, 1H), 8.51 (s, 4H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 10.63, 22.63, 31.49, 34.39, 38.71, 50.50, 63.15, 64.70, 67.22, 67.30, 67.54, 67.66, 68.04, 68.59, 68.91, 69.54, 69.74, 69.81, 69.87, 70.04, 70.07, 70.62, 70.68, 70.70, 70.72, 70.87, 71.06, 71.25, 71.35, 71.40, 71.49, 71.51, 71.74, 84.49, 89.47, 93.25, 98.35, 103.64, 103.67, 110.63, 110.90, 113.17, 114.34, 114.36, 114.84, 114.98, 116.48, 116.76, 117.55, 123.76, 124.13, 124.87, 124.99, 125.01, 125.22, 130.82, 131.44, 132.13, 132.32, 132.66, 133.69, 139.84, 144.24, 148.39, 151.11, 152.87, 153.23, 153.26, 154.27, 154.48, 156.66, 160.11, 163.22. HRMS (ESI): m/z: 1416.7147 (calcd. [M+2H]$^{2+}$ = 1416.7153).
Conditions: CuSO₄, sodium ascorbate, CHCl₃, H₂O, r.t., 24 h.

**Compound 1.** A mixture of sodium ascorbate (55.5 mg, 0.280 mmol) and copper(II) sulfate (22.4 mg, 0.140 mmol) in water (1 mL) was added to a solution of compound 8 (105 mg, 0.140 mmol), compound 12 (170 mg, 0.140 mmol), and compound 19 (129 mg, 0.140 mmol) in chloroform (1 mL) and the mixture was vigorously stirred for 24 h at r.t.. The suspension was poured into a mixture of water (100 mL) and chloroform (100 mL), before the organic layer was separated, washed with saturated aq. NaCl solution (2 × 100 mL), dried over MgSO₄ and filtered, and the solvent was evaporated. The crude product was purified by flash column chromatography on silica gel (eluent: gradient from dichloromethane/acetone = 2:1 v/v to acetone) and recycling GPC (eluent: chloroform) to afford compound 1 (59.0 mg, 2.05 × 10⁻² mmol, 15%) as a brown solid. ¹H NMR (400 MHz, CDCl₃): δ = 1.28 (s, 6H), 1.29 (s, 45H), 2.05–2.11 (m, 2H), 2.24 (br, 1H), 3.50–4.13 (m, 80H), 4.18 (t, J = 6.0 Hz, 2H), 4.56 (t, J = 5.2 Hz, 4H), 4.69 (s, 4H), 5.81 (d, J = 2.8 Hz, 1H), 5.90 (d, J = 8.8 Hz, 1H), 6.02 (dd, J = 3.2, 8.8 Hz, 1H), 6.10–6.14 (m, 2H), 6.63–6.71 (m, 2H), 6.76 (d, J = 8.8 Hz, 4H), 6.84 (d, J = 8.8 Hz, 2H), 6.91–6.97 (m, 4H), 7.03–7.08 (m, 16H), 7.20–7.24 (m, 10H), 7.63 (d, J = 8.8 Hz, 2H), 7.68 (d, J = 7.6 Hz, 1H), 7.79 (s, 2H), 7.80 (d, J = 7.6 Hz, 1H), 8.51 (s, 4H). ¹³C NMR (100 MHz, CDCl₃): δ = 23.29, 31.49, 32.06, 34.39, 34.41, 38.70, 50.59, 60.07, 63.06, 63.14, 64.68, 65.64, 67.21, 67.28, 67.31, 67.53, 67.66, 68.00, 68.57, 68.88, 69.53, 69.79, 69.86, 70.04, 70.07, 70.46, 70.61, 70.66, 70.68, 70.70, 70.86, 71.04, 71.23, 71.34, 71.39, 71.49, 71.51, 71.75, 80.54, 84.61, 89.42, 93.29, 98.17, 103.63, 103.66, 110.60, 110.84, 113.15, 113.23, 114.33, 114.69, 114.85, 115.02, 116.48, 116.80, 117.45, 122.30, 123.76, 124.14, 124.22, 124.85, 124.97, 124.99, 125.21, 130.76, 130.82, 131.44, 131.98, 132.19, 132.24, 132.32, 132.64, 133.72, 139.69, 139.84, 142.76, 144.11, 144.23, 148.39, 148.56, 151.09, 152.46, 152.84, 153.22, 153.25, 154.25, 154.46, 156.64, 156.72, 159.76, 163.22. HRMS (ESI): m/z: 1451.6981 (calcd. [M+Na+H]⁺ = 1451.6986).
Synthesis of polyurethane 1-PU. DIBUTYLTIN dilaurate (3 drops) was added to a mixture of rotaxane 1 (20 mg, 6.9 \times 10^{-3} \text{ mmol}), poly(tetrahydrofuran) (M_n = 2,000 \text{ g/mol}, 3.00 g, 1.50 mmol), and 4,4’-methylenebis(phenylisocyanate) (1.31 g, 5.25 mmol) in THF (30 mL) and the mixture was stirred at room temperature for 3 h. A solution of 1,4-butane diol (315 mg, 3.50 mmol) in THF (10 mL) was then added and the reaction mixture was stirred at room temperature for 48 h. MeOH (2 mL) was added to the reaction mixture and after stirring for another 30 min the reaction mixture was poured into EtOH (500 mL). The yellow precipitate was collected by filtration, dissolved in THF (300 mL), the solution was filtered through a cotton filter, while approximately half of solvent evaporated, and the polymer was precipitated into hexane (400 mL). The precipitate was filtered and dried \textit{in vacuo} for 24 h at room temperature to afford 1-PU as a yellow rubbery solid (4.03 g, 87\%, M_n = 71 \text{ kDa}).

Synthesis of polyurethane PU. DIBUTYLTIN dilaurate (3 drops) was added to a mixture of poly(tetrahydrofuran) (M_n = 2,000 \text{ g/mol}, 3.00 g, 1.50 mmol) and 4,4’-methylenebis(phenylisocyanate) (1.20 g, 4.80 mmol) in THF (20 mL) and the mixture was stirred at room temperature for 3 h. A solution of 1,4-butane diol (270 mg, 3.00 mmol) in THF (10 mL) was then added and the reaction mixture was stirred at room temperature for 48 h. MeOH (10 mL) was added to the reaction mixture and after stirring for another 30 min the reaction mixture was poured into EtOH (400 mL). The white precipitate was collected by filtration, dissolved in CHCl_3 (300 mL), the solution was passed through a cotton filter, while approximately half of solvent evaporated, and the polymer was precipitated into hexane (400 mL). The precipitate was filtered and reprecipitated from THF (150 mL) into EtOH (400 mL). The precipitate was filtered and dried \textit{in vacuo} for 24 h at room temperature to afford PU as a white rubbery solid (3.82 g, 85\%, M_n = 115 \text{ kDa}).

Preparation of Polyurethane Films
1-PU and PU. The polymers (1-PU or PU, ca. 0.3 g) were dissolved in THF (10 mL) and the solutions were divided between three round poly(tetrafluoroethylene) molds (32 \times 3.5 mm). The molds were placed in a well-ventilated hood under an inverted funnel so that the evaporation rate was controlled. The solvent was evaporated overnight under ambient conditions and the resulting films were further dried \textit{in vacuo} at room temperature overnight.

2inPU. PU (ca. 0.3 g) was dissolved in THF (10 mL) before rotaxane 2 was added so that the concentration of the rotaxane unit was same as that in the 1-PU (1.4 \times 10^{-6} \text{ mol/1 g}). The mixture was divided between three round poly(tetrafluoroethylene) molds (32 \times 3.5 mm) and the films were dried as described above.

3,4inPU. An equimolar mixture of 3 and 4 in THF (2 mL) was added to a THF solution (8 mL) of PU (ca. 0.3 g) so that the concentrations of luminophore 3 and dumbbell 4 were same as that of rotaxane units in 1-PU (1.4 \times 10^{-6} \text{ mol/1 g}). The mixture was divided between three round poly(tetrafluoroethylene) molds (32 \times 3.5 mm) and the films were dried as described above.

Films thus prepared (thickness: 60–130 \mu m) were cut into rectangular-shaped or dog-bone-shaped specimens that were used in the various measurements. Typical dimension: 6 mm \times 20 mm.
Photophysical Properties of Cyclic Compound 3 in Solution

**Figure S1.** Picture documenting the solvatochromic luminescence behavior of compound 3. The glass vials contain solutions of 3 in hexane, toluene, tetrahydrofuran, acetone, and acetonitrile (from left to right). The concentration of all solutions was $c = 1 \times 10^{-5}$ M, except for hexane ($c = 0.7 \times 10^{-5}$ M), in which the solubility of 3 is limited. The photo was taken under excitation light at 365 nm.

**Figure S2.** (a) Absorption and (b) normalized photoluminescence spectra of 3 in hexane (green line), toluene (light green line), tetrahydrofuran (yellow line), acetone (orange line), and acetonitrile (red line). The concentration of all solutions was $c = 1 \times 10^{-5}$ M, except for hexane ($c = 0.7 \times 10^{-5}$ M), on account of the limited solubility of 3 in this solvent. The photoluminescence spectra were collected under excitation at 400 nm and are normalized to match the maxima.
Photophysical Properties of Rotaxane 2 in Solution

**Figure S3.** Absorption spectra of rotaxane 2 (orange solid line), luminophore 3 (black solid line), dumbbell 4 (blue solid line), and an equimolar mixture of 3 and 4 (orange dashed line) in THF. The concentration of all compounds was $c = 1 \times 10^{-5}$ M.

**Figure S4.** Photoluminescence spectra of rotaxane 2 (orange solid line), luminophore 3 (black solid line), and an equimolar mixture of 3 and 4 (orange dashed line) in THF. The photoluminescence spectra were collected under excitation at 400 nm and the concentration of all compounds was $c = 1.0 \times 10^{-5}$ M.
Photophysical Properties of Rotaxane 1 in Solution

Figure S5. (a) Absorption and (b) photoluminescence spectra of rotaxanes 1 (orange dashed line), and 2 (orange solid line), luminophore 3 (black solid line), and luminophore 19 in THF (yellow dashed line). The emission spectra were collected under excitation at 400 nm and the concentration was $c = 1.0 \times 10^{-5}$ M.
Figure S6. (a) Partial $^1$H NMR spectrum of luminophore 3. (b) Partial $^1$H NMR spectrum of rotaxane 2. (c) Partial $^1$H NMR spectrum of dumbbell 4. All spectra were measured in CDCl$_3$ at 298 K. Blue peaks represent signals ascribed to the stopper moieties.
Photophysical Properties of 1-PU in Solution

Figure S7. (a) Absorption and (b) photoluminescence spectra of solutions of 1-PU (orange line) and rotaxane 1 in THF (c = 1.0 × 10⁻⁵ M, gray line). The concentration of the 1-PU solution was adjusted so that the absorbance at 440 nm coincided with the one of rotaxane 1 in THF. The photoluminescence spectra were collected under excitation at 400 nm.
**1^H NMR Spectra of Polyurethanes 1-PU and PU**

**Figure S8.** (a) $^1$H NMR spectrum of 1-PU in THF-$d_8$. Signals are characterized as protons of polyurethane chains. No clear signals corresponding to the rotaxane mechanophores are observed, on account of their very low concentration. (b) $^1$H NMR spectrum of reference PU in THF-$d_8$. Both spectra were measured at 25 °C.
Thermal Properties of Polyurethanes 1-PU and PU

Figure S9. (a) Differential scanning calorimetry (DSC) traces of 1-PU. (b) DSC traces of PU. The heating and cooling rates were 10 °C/min.

Figure S10. (a) Thermogravimetric analyses (TGA) trace of 1-PU. (b) TGA trace of PU. The TGA were conducted under N₂ at a heating rate of 10 °C/min.
Mechanical Properties of Polyurethanes

Figure S11. (a) Dynamic mechanical analysis DMA traces of 1-PU. (b) DMA traces of PU. Each panel contains three curves obtained from 3 different samples. The measurements were conducted under N\textsubscript{2} at a heating rate of 3 °C/min, a frequency of 1 Hz, and an amplitude of 15 μm.

Figure S12. Stress-strain curves of (a) 1-PU, (b) PU, (c) 2inPU, and (d) 3,4inPU. Panels a and b show curves obtained from 6 different specimens and panels c and d show curves obtained from 5 different specimens. The experiments were conducted with a strain rate of 100 mm/min at room temperature.
Table S1. Mechanical data of the various polyurethanes extracted from tensile tests.\textsuperscript{a)}

|        | Elongation at break (%) | Stress at break (MPa) | Young’s modulus (MPa) |
|--------|--------------------------|-----------------------|-----------------------|
| 1-PU   | 782 ± 49                 | 91 ± 11               | 38 ± 4                |
| PU     | 798 ± 50                 | 94 ± 10               | 29 ± 2                |
| 2inPU  | 802 ± 61                 | 106 ± 5               | 28 ± 1                |
| 3,4inPU| 772 ± 85                 | 95 ± 14               | 24 ± 1                |

\textsuperscript{a)} All data were extracted from the stress-strain curves shown in Figure S12 and represent averages of 5–6 measurements ± standard deviation. \textsuperscript{b)} The Young’s moduli were derived from the slopes of the stress-strain curves in the strain regime of 0.5–1.0%.

Images of Polyurethane Films During Uniaxial Deformation

Figure S13. Pictures of (a) 1-PU, (b) 2inPU, (c) 3,4inPU, and (d) 1-PU under cyclic uniaxial deformation test. For each strained state, the top image shows the photoluminescence of the film; these pictures were taken in the dark under excitation with 365 nm UV light. The bottom image was taken under ambient illumination. All images were taken under the same ambient conditions.
Photoluminescence Spectra of Polyurethane Reference Films During Deformation

Figure S14. Photoluminescence spectra of a film of 2inPU recorded at a strain of 0% (black line), and upon uniaxial deformation to strains of 100% (blue line), 200% (green line), 300% (red line), 400% (orange line), 500% (yellow line), or 600% (gray line). The data show that the 2inPU film is hardly photoluminescent and that the photoluminescence of rotaxane 2, which was physically blended with the polymer, was not changed upon deformation. This confirms that mechanical activation via covalent bonds is required for activation. All photoluminescence spectra were taken in the dark at room temperature under excitation with 385 nm UV light.

Figure S15. Photoluminescence spectra of a film of 3,4inPU recorded at a strain of 0% (black line), and upon uniaxial deformation to strains of 100% (blue line), 200% (green line), 300% (red line), 400% (orange line), 500% (yellow line), or 600% (gray line). A comparison with the data shown in Figure S14 reveals that the reference films into which the luminophore 3 and dumbbell 4 were physically blended reveal a much higher photoluminescence intensity than observed for reference films containing the rotaxane 2. The data further show that the photoluminescence intensity hardly changes upon uniaxial deformation. The decrease in photoluminescence intensity observed at strains between 0% and 200% is attributed to thinning of the film. All photoluminescence spectra were taken in the dark at room temperature under excitation with 385 nm UV light.
**Photoluminescence Spectra of 1-PU Films During Deformation**

![Graphs showing photoluminescence spectra](image)

**Figure S16.** Changes of the photoluminescence spectra of a 1-PU film in a 2nd deformation cycle. (a) Photoluminescence spectra of the 1-PU film recorded in the initial state (i.e., after first stretching the sample to a length of 600% and subsequent relaxation; on account of the polyurethane’s hysteresis, this “relaxed length” is ca. 190% relative to the original length) (black line) and upon uniaxial deformation to strains of 200% (green line), 300% (red line), 400% (orange line), 500% (brown line), and 600% (gray line). (b) Photoluminescence spectra of the same film recorded before (600%, gray line), and upon releasing the stress to achieve strains of 500% (brown line), 400% (orange line), 300% (red line), 200% (green line), and the relaxed state (ca. 190% relative to the original length and same as the initial length for this 2nd deformation cycle, black line). The sample used here was the same sample whose first deformation sample is shown in Figure 3b and c. All photoluminescence spectra were taken in the dark at room temperature under excitation with 385 nm UV light.
Activation Ratio of the Mechanophores
Quantitative experiments were carried out to estimate the value of activation ratio of the mechanoluminophores introduced in 1-PU. As shown in Figure S17a, 1-PU and 3,4inPU specimens with identical dimension were prepared for this experiment. As the considerable light scattering of solid films prevents accurate absorption measurements, THF solutions (5 mg/1 mL) were prepared and their nearly identical absorbance around 440 nm and also at the excitation wavelength of 385 nm that was used in this experiment (Figure S17d) indicates that the specimens have comparable luminophore concentrations. The photoluminescence spectra were acquired just after each specimen was uniaxially deformed (λ = 600%). The experimental set up was fixed, i.e., both detector and excitation light positions were the same and excitation light intensity was also same. The 1-PU film shows a maximum fluorescence intensity of $3.2 \times 10^4$ at $\lambda = 600\%$, whereas the 3,4inPU film displays a maximum intensity of $11 \times 10^4$ under the same condition. The ratio of these values affords an activation ratio of 29%. As the photoluminescence intensity decreases after deformation due to the inherent characteristic of the polyurethane (Fig. 4c), the actual activation ratio may be substantially higher.

Figure S17. (a) Dimension of specimens of 1-PU and 3,4inPU. (b) A picture of prepared specimens of 1-PU (top) and 3,4inPU (bottom) under room light. (c) A picture of prepared specimens of 1-PU (top) and 3,4inPU (bottom) under excitation light (365 nm) in dark. Pictures in panels b and c were taken at room temperature. (d) Absorption spectra of THF solutions (5 mg/1 mL) of 1-PU (green line) and 3,4inPU (black line). (e) Photoluminescence spectra of specimens of 1-PU (green line) and 3,4inPU (black line) under strain of 600%. The photoluminescence spectra were measured under excitation light of 385 nm in dark.
Time Dependency of the Emission Intensity of Stretched 1-PU and 3,4inPU

Figure S18. Changes of the normalized photoluminescence intensity of stretched PU films as a function of time after stretching. Shown are the change of the photoluminescence intensity as a function of time after films of 1-PU (red triangles) and 3,4inPU (black circles) had been strained to 600% (a) or 300% (b). The photoluminescence intensities were measured at 530 nm and normalized to the first data point recorded at \( t = 0 \) min. All photoluminescence spectra were taken in dark at room temperature under excitation with 385 nm UV light.
Emission Lifetime of 1-PU and 3,4inPU Reference Films During Deformation

**Figure S19.** Emission decay profiles of 1-PU at strains of 600% (1st cycle: blue line; 2nd cycle: red line) and 400% (1st cycle: green line; 2nd cycle: orange line) together with the emission decay profile of a 3,4inPU film at a strain of 0% (black line). Figure 4d in the manuscript displays an expansion of these decay curves. All decay profiles were collected at 530 nm upon excitation at 405 nm at room temperature.

**Figure S20.** (a) Emission decay profiles of 3,4inPU reference films at strains of 0% (black line), 400% (blue line), and 600% (red line). (b) Expansion of the initial period of the decay traces shown in panel a. No clear changes were observed in the emission decay profiles upon stretching 3,4inPU. All decay profiles were collected at 530 nm upon excitation at 405 nm at room temperature.
Thermal Effect on the Photoluminescence Properties of 1-PU and 3,4inPU

**Figure S21.** Pictures documenting thermal effect on the 1-PU (right) and 3,4inPU (left) before deformation (a) and upon uniaxial deformation to a strain of 400% (b) under room light and excitation with 365 nm UV light.

Investigation of the Heat-Induced Rotaxane De-Threading in 1-PU

**Figure S22.** (a) Size exclusion chromatography traces of 1-PU before (black line) and after (red line) heating a polymer film for 2 h at 150 °C in air. (b) Photoluminescence spectra of the 1-PU film before thermal treatment (black line), and after heating for 30 (blue line), 60 (red line), 90 (green line), and 120 min (gray line) at 150 °C in air. All photoluminescence spectra were measured at room temperature under excitation with 385 nm UV light.
Investigation of the Ultrasound-Induced Permanent Chain Cleavage in 1-PU and PU

Sonomechnochemical experiments, which represent a well-established framework to evaluate the mechanically induced covalent chain scission of polymers containing conventional mechanophores, were conducted by ultrasonication of THF solutions of 1-PU and a corresponding mixture of PU and rotaxane 2. These sonication experiments were performed using a Branson Model 450 ultrasonic 1/2 in-horn sonicator equipped with a 13 mm sonicator tip. A MX07R-20 refrigerating/heating bath from VWR was used to maintain a constant solution temperature during sonication experiments. The polymers were dissolved in THF (Romil-SpSTM, Super Purity Solvent grade) at a concentration of 1.00 mg/mL. A volume of 20 mL was introduced into a Suslick cell that was then placed in the thermostatic bath. The solutions were purged with argon for 15 min prior to sonication. A pulsed sonication of 0.5 s at a power density of 10.4 W cm$^{-2}$ intercalated with pauses of 1.0 s was performed. Aliquots (300 µL) were taken with syringes at regular time intervals. Photoluminescence spectra obtained in conjunction with the sonication experiments were recorded on a PTI C720 fluorescence spectrometer using right angle illumination. For excitation, a XeArc lamp was used along with a PETI 814 photomultiplier detection system.

Sonication for periods of up to ~60 min resulted in a gradual decrease of the molecular weight of 1-PU and PU (Figures S23 and S24) and a gradual increase of the photoluminescence intensity for the THF solution of 1-PU (Figure S23b,c). These results indicate the scission of covalent bonds and de-threading of the rotaxane upon sonication as well as nonspecific scission of covalent bonds in the polyurethane chains. The plots of photoluminescence intensity shown in Figure S24c reveal that the interlocked system without covalently-introduced polymer chains is not broken upon sonication.

Figure S23. (a) Size exclusion chromatography (SEC) traces of 1-PU before sonication (black line) and after sonication for 1 h (red line). The traces were normalized to the peak maximum of the chromatograms before sonication. (b) Changes of the photoluminescence spectra of the solutions upon sonication. (c) $M_p/M_{p0}$ (black) and photoluminescence intensity (red) as a function of sonication time. $M_p/M_{p0}$ is the ratio between the polymer’s molar mass reflected by the peak maximum of the SEC trace after sonication for time $t$ and the molar mass at $t = 0$ min. Both the $M_p/M_{p0}$ ratio (black) and photoluminescence intensity values are averages of measurements made on three different samples ± standard deviation. All sonication experiments were made with solutions of 1-PU in THF that had a concentration of $c = 1$ mg/mL.
**Figure S24.** (a) Size exclusion chromatography (SEC) traces of PU in the presence of rotaxane 2 before sonication (black line) and after sonication for 1 h (red line). The traces were normalized to the peak maximum of the chromatograms before sonication. (b) Changes of the photoluminescence spectra of the solutions upon sonication. (c) \( M_p/M_{p0} \) (black) and photoluminescence intensity (red) as a function of sonication time. \( M_p/M_{p0} \) is the ratio between the polymer’s molar mass reflected by the peak maximum of the SEC trace after sonication for time \( t \) and the molar mass at \( t = 0 \) min. Both the \( M_p/M_{p0} \) ratio (black) and photoluminescence intensity values are averages of measurements made on three different samples ± standard deviation. All sonication experiments were made with solutions of PU and rotaxane 2 in THF that had a PU concentration of \( c = 1 \) mg/mL and in which the rotaxane 2 was comparable to the content in the 1-PU solution used in Figure S23.

**Supporting Movies**

**Supporting Movie S1.** Representative movie of reversible ON/OFF switching of photoluminescence upon cyclic stretching 1-PU film.

**Supporting Movie S2.** Representative movie of reference film, 2inPU, upon cyclic stretching. No obvious increase in photoluminescence intensity was observed.

**Supporting Movie S3.** Representative movie of reference film, 3,4inPU, upon cyclic stretching. The film exhibits bright photoluminescence regardless of strain applied.

All movies were taken in the dark with excitation light of 365nm.
References

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