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Supporting Information

Tuning the mechanoresponsive luminescence of rotaxane mechanophores by varying the stopper size

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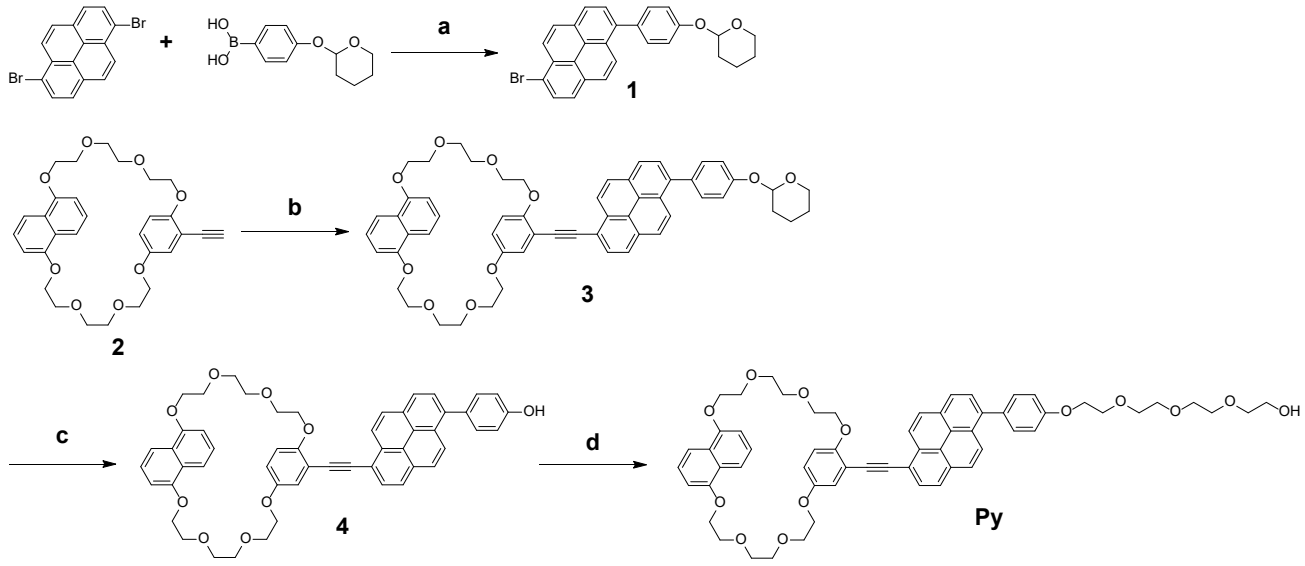
General Methods

All reagents and solvents were purchased from FUJIFILM Wako Pure Chemical Corporation, Merck, Kanto Chemical, or Tokyo Kasei. All reactions were carried out under nitrogen atmosphere. Flash silica gel column chromatography was conducted with a Biotage Isolera Flash system using SHOKO-scientific Purif-Pack-EX cartridges. Recycling preparative gel permeation chromatography (GPC) was performed with a Japan Analytical Industry LaboACE. Inhibitor-free anhydrous tetrahydrofuran (THF) was used as solvent during the polymer synthesis. Telechelic poly(tetrahydrofuran)diol (M_n = 2,000 g/mol) was dried in vacuo at 100 ºC for 1 h before use. 4,4'-Methylenebis(phenylisocyanate) and 1,4-butanediol were distilled under vacuum and stored over molecular sieves at 4 ºC and room temperature (r.t.), respectively. ^{1}H NMR spectra were measured with a JEOL JNM-ECZ400S/L1 spectrometer and all chemical shifts are reported on the δ-scale in ppm relative to the signal of tetramethylsilane (TMS at 0.00) or residual solvent protons (THF at 1.72) as an internal standard. Coupling constants (J) are quoted in Hz and relative intensities are reported. Proton-decoupled ^{13}C NMR spectra were acquired on JEOL JNM-ECZ400S/L1 spectrometer and all chemical shifts are expressed in ppm using solvent as the internal standard ($CDCl_3$ at 77.16 or THF-d_8 at 67.21). Matrix Assisted Laser Desorption Ionization Time-of-Flight (MALDI-TOF) mass spectroscopy was performed with a SHIMADZU AXIMA-Performance. High-resolution electrospray-ionization (ESI) mass spectra were measured with a Bruker Daltonics micrOTOF II. Size-exclusion chromatography (SEC) experiments were performed on a Shimadzu Nexera GPC system equipped with an GPC KF–805L column (ID = 8.0 mm, L = 300 mm, particle size = 10 μm). Samples were injected using THF as the eluent at 40 °C and a flow rate of 1.0 mL/min. Data analysis were conducted on Labosolutions software (Shimadzu) and molecular weights were calculated based on narrow-molecular-weight polystyrene calibration (1100–2,500,000 g/mol). UV-vis absorption spectra were measured on a JASCO V-750. Steady-state photoluminescence (PL) spectra of solutions were recorded with a JASCO FP-6500 and the spectra were corrected for the detector nonlinearity. Time-resolved PL measurements were carried out with a Hamamatsu Photonics Quantaurus-Tau. Quantum efficiencies were measured with a Hamamatsu Photonics Quantaurus-QY. Steady-state PL spectra of polyurethane films during stretching experiments were monitored with an Ocean Optics OEPro-FL equipped with an LLS-365 LED light source and Reflection/Backscattering Probe R400-7-UV-VIS; these spectra were not corrected. Dynamic mechanical analyses (DMA) were carried out under N_2 with a TA Instruments DMA Q800 at a heating rate of 3 °C/min, a frequency of 1 Hz, and an amplitude of 15 μm. Thermogravimetric analyses (TGA) were performed under nitrogen with a Mettler-Toledo Stare system at a rate of 10 °C/min. Differential scanning calorimetry (DSC) measurements were conducted under N_2 on a Hitachi DSC7020 at heating and cooling rates of 10 ºC/min. Stress-strain measurements were conducted under ambient conditions with a SHIMADZU AGS-100NX equipped with a 100 N load cell at strain rate of 300 mm/min. High performance liquid chromatography (HPLC) analysis was carried out on a system composed of SHIMADZU HPLC system with a GL Sciences Inc. InertSustain AQ-C18 column (ID = 4.6 mm, L = 250 mm).

Synthesis of Rotaxanes

Compounds **2**, **10**, **24** and 2-{2-[2-(2-hydroxyethoxy)ethoxy]ethoxy}ethyl *p*-toluenesulfonate were prepared according to the reported procedures.[S1,S2]



Reaction conditions: (a) K_2CO_3, $Pd(PPh_3)_4$, toluene, H_2O, reflux, 13 h; (b) **1**, $Pd(PPh_3)_4$, CuI, THF, *i*-Pr_2NH, reflux, 18 h; (c) 10% aq. HCl, THF, reflux, 1 h; (d) 2-{2-[2-(2-hydroxyethoxy)ethoxy]ethoxy}ethyl *p*-toluenesulfonate, K_2CO_3, DMF, 80 °C, 13 h.

Compound 1. An aqueous solution of K_2CO_3 (512 mg, 3.70 mmol) was added to a mixture of 1,6-dibromopyrene (500 mg, 1.39 mmol), 4-(tetrahydro-2*H*-pyran-2-yloxy)phenylboronic acid (206 mg, 0.926 mmol) and $Pd(PPh_3)_4$ (53.5 mg, 4.63×10^{-2} mmol) in toluene (100 mL) and the mixture was stirred for 13 h under reflux. After cooling to r.t., the reaction mixture was poured into chloroform (150 mL). The solution was washed with water (150 mL) and saturated aq. NaCl (150 mL). The organic layer was dried over $MgSO_4$ and filtered, and the solvent was evaporated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (eluent: gradient from hexane/chloroform = 4:1 v/v to hexane/chloroform = 2:3 v/v) and subsequently precipitated from a mixture of chloroform and hexane to afford compound **1** (193 mg, 0.422 mmol, 46%) as a white solid.
^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) = 1.62–1.80 (m, 3H), 1.93–1.97 (m, 2H), 2.04–2.15 (m, 1H), 3.68–3.73 (m, 1H), 4.00–4.06 (m, 1H), 5.57 (t, J = 3.2 Hz, 1H), 7.24–7.26 (m, 2H), 7.54 (d, J = 8.4 Hz, 2H), 7.96–8.02 (m, 3H), 8.19–8.27 (m, 4H), 8.46 (d, J = 9.2 Hz, 1H).
^{13}C NMR (100 MHz, $CDCl_3$): δ(ppm) = 18.99, 25.38, 30.56, 62.37, 96.55, 116.46, 119.95, 124.48, 125.34, 125.87, 125.91, 126.25, 127.09, 128.46, 128.71, 129.15, 130.04, 130.27, 130.57, 131.73, 134.22, 138.42, 156.70.
MS (MALDI-TOF): m/z: 456.44 (calcd. $[M]^+$ = 456.07).

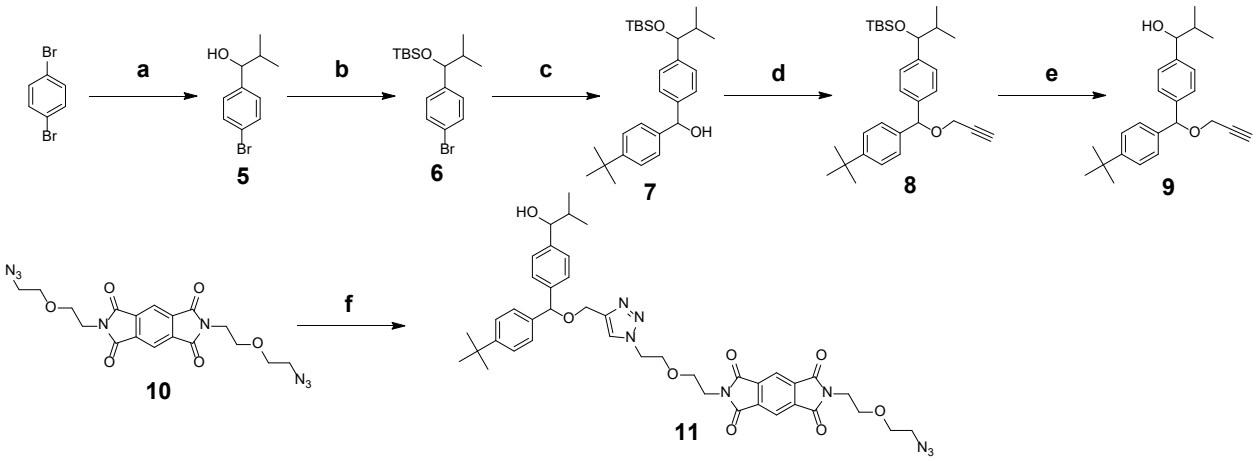
Compound 3. A mixture of compound **2**[S1] (1.02 g, 1.95 mmol), compound **1** (890 mg, 1.95 mmol), $Pd(PPh_3)_4$ (112 mg, 9.69×10^{-2} mmol), CuI (18.5 mg, 9.69×10^{-2} mmol), and *i*-Pr_2NH (5 mL) in THF (30 mL) was stirred for 18 h under reflux. After cooling to r.t., the reaction mixture was poured into ethyl acetate (150 mL). The solution was

washed with 5% aq. HCl (150 mL), saturated aq. $NaHCO_3$ (150 mL), and saturated aq. NaCl (150 mL). The organic layer was dried over $MgSO_4$ and filtered, and the solvent was evaporated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (eluent: gradient from dichloromethane to dichloromethane/acetone = 19:1 v/v) to afford compound **3** (1.48 g, 1.65 mmol, 85%) as a pale yellow solid.
^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) = 1.65–1.80 (m, 3H), 1.93–1.97 (m, 2H), 2.03–2.13 (m, 1H), 3.68–3.88 (m, 13H), 3.96–4.06 (m, 9H), 4.26–4.29 (m, 2H), 4.32–4.34 (m, 2H), 5.57 (t, *J* = 3.2 Hz, 1H), 6.24 (dd, *J* = 9.2, 3.2 Hz, 1H), 6.33 (d, *J* = 9.2 Hz, 1H), 6.79–6.85 (m, 2H), 6.95 (d, *J* = 2.8 Hz, 1H), 7.22–7.31 (m, 4H), 7.55 (d, *J* = 8.4 Hz, 2H), 7.90 (t, *J* = 8.4 Hz, 2H), 7.98–8.00 (m, 2H), 8.09 (d, *J* = 8.0 Hz, 1H), 8.15–8.25 (m, 4H), 8.77 (d, *J* = 9.2 Hz, 1H).
^{13}C NMR (100 MHz, $CDCl_3$): δ(ppm) = 18.99, 25.37, 30.56, 62.36, 67.74, 67.85, 68.44, 69.24, 69.89, 70.05, 71.00, 71.24, 71.46, 92.13, 92.67, 96.57, 105.69, 105.79, 113.69, 114.28, 114.60, 114.76, 116.26, 116.45, 118.41, 119.27, 124.37, 124.79, 124.88, 125.30, 126.00, 126.22, 126.87, 127.30, 128.14, 128.30, 128.84, 129.50, 130.46, 131.07, 131.74, 132.46, 134.35, 138.12, 152.67, 154.02, 154.41, 154.47, 156.65.
MS (MALDI-TOF): m/z: 921.67 (calcd. $[M+Na]^+$ = 921.36).

Compound 4. 10% aq. HCl (5 mL) was added to a solution of compound **3** (1.48 g, 1.65 mmol) in THF (150 mL), and the reaction mixture was stirred for 1h under reflux. After cooling to r.t., the solvent was evaporated under reduced pressure. Chloroform (250 mL) was added, and the solution was washed with water (3 × 150 mL). The organic layer was dried over $MgSO_4$ and filtered. After the solvent was evaporated under reduced pressure, the crude product was precipitated from a mixture of chloroform and hexane to afford compound **4** (1.10 g, 1.34 mmol, 82%) as a yellow solid.
^{1}H NMR (400 MHz, THF-d_8): δ(ppm) = 3.67–3.81 (m, 12H), 3.91–3.99 (m, 8H), 4.25–4.31 (m, 4H), 6.26 (s, 2H), 6.88 (t, *J* = 7.6 Hz, 2H), 6.92–6.92 (m, 1H), 6.95 (d, *J* = 8.8 Hz, 2H), 7.24 (q, *J* = 8.0 Hz, 2H), 7.43 (d, *J* = 8.8 Hz, 2H), 7.85 (d, *J* = 8.0 Hz, 2H), 7.96–8.02 (m, 2H), 8.12 (s, 2H), 8.21–8.28 (m. 3H), 8.50 (s, 1H), 8.84 (d, *J* = 9.2 Hz, 1H).
^{13}C NMR (100 MHz, THF-d_8): δ(ppm) = 14.27, 23.36, 32.37, 67.79, 68.60, 68.92, 69.34, 70.42, 70.61, 71.79, 71.90, 72.09, 72.23, 92.82, 93.05, 106.18, 106.22, 113.98, 115.01, 115.12, 115.93, 116.63, 119.26, 119.39, 124.85, 125.45, 125.51, 125.62, 125.90, 126.52, 126.71, 127.61, 127.67, 128.70 128.91, 129.46, 129.81, 131.09, 131.79, 132.21, 132.54, 133.02, 139.35, 153.39, 154.83, 155.31, 158.18.
MS (MALDI-TOF): m/z: 837.60 (calcd. $[M+Na]^+$ = 837.30).

Py. A mixture of compound **4** (218 mg, 0.268 mmol), 2-{2-[2-(2-hydroxyethoxy)ethoxy]ethoxy}ethyl toluenesulfonate (112 mg, 0.321 mmol), and K_2CO_3 (111 mg, 0.803 mmol) in DMF (50 mL) was stirred for 13 h at 80 °C. After cooling to r.t., the reaction mixture was poured into ethyl acetate (150 mL). The solution was washed with saturated aq. NH_4Cl (3 × 150 mL). The organic layer was dried over $MgSO_4$ and filtered, and the solvent was evaporated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (eluent: gradient from dichloromethane/acetone 19:1 v/v to dichloromethane/acetone = 3:1 v/v) and subsequently precipitated from a mixture of chloroform and hexane to afford **Py** (217 mg, 0.219 mmol, 82%) as a yellow solid.
^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) = 2.73 (br, 1H), 3.63–3.65 (m, 2H), 3.71–3.88 (m, 22H), 3.94–4.04 (m, 10H), 4.26–4.28 (m, 4H), 4.32–4.34 (m, 2H), 6.24 (dd, *J* = 9.2, 3.2 Hz, 1H), 6.33 (d, *J* = 9.2 Hz, 1H), 6.79–6.85 (m, 2H), 6.95 (d, *J* = 3.2 Hz, 1H), 7.12 (d, *J* = 8.8 Hz, 2H), 7.25–7.31 (m, 2H), 7.55 (d, *J* = 8.4 Hz, 2H), 7.88–7.92 (m, 2H), 7.97–8.00 (m, 2H), 8.09 (d, *J* = 8.0 Hz, 1H), 8.15–8.25 (m, 4H), 8.77 (d, *J* = 9.2 Hz, 1H).
^{13}C NMR (100 MHz, $CDCl_3$): δ(ppm) = 61.92, 67.68, 67.79, 67.89, 68.47, 69.27, 69.93, 70.08, 70.48, 70.77, 70.83, 71.00, 71.26, 71.49, 72.68, 92.15, 92.67, 105.72, 105.82, 113.72, 114.33, 114.63, 114.69, 114.78, 116.31, 118.46, 119.28, 124.39, 124.82, 124.90, 125.32, 126.02, 126.16, 126.90, 127.35, 128.15, 128.32, 128.88, 129.53, 130.48,

131.08, 131.80, 132.47, 133.74, 138.06, 152.69, 154.04, 154.44, 154.49, 158.35.
MS (MALDI-TOF): m/z: 1013.68 (calcd. $[M+Na]^+$ = 1013.41).



Reaction conditions: (a) i) *n*-BuLi, THF, –78 °C, 30 min; ii) isobutyraldehyde, THF, r.t., 4 h; iii) H^+; (b) *tert*-butyldimethylchlorosilane, imidazole, DMF, r.t., 22 h; (c) i) *n*-BuLi, THF, –78 °C, 30 min; ii) 4-*tert*-butylbenzaldehyde, THF, r.t., 6 h; iii) H^+; (d) propargyl bromide, NaH, DMF, 0 °C → r.t., 20 h; (e) tetrabutylammonium fluoride, THF, 50 °C, 66 h; (f) compound **9**, CuI, chloroform, *i*-Pr_2NEt, 40 °C, 3 h.

Compound 5. A hexane solution of *n*-BuLi (ca. 1.6 mol/L, 14.6 mL, 23.3 mmol) was added to the mixture of 1,4-dibromobenzene (5.0 g, 21.1 mmol) and THF (20 mL) at –78 °C and the mixture was stirred for 30 minutes. Then isobutyraldehyde (2.13 mL, 23.3 mmol) was added to the mixture dropwise at the same temperature, and the reaction mixture was stirred for 4 h at r.t. Subsequently, saturated aq. NH_4Cl (5 mL) and ethyl acetate (150 mL) were added to the reaction mixture. The solution was washed with water (4 × 150 mL) and saturated aq. NaCl (150 mL). The organic layer was dried over $MgSO_4$ and filtered, and the solvent was evaporated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (eluent: gradient from hexane to hexane/ethyl acetate = 9:1 v/v) to afford compound **5** (4.16 g, 18.2 mmol, 86%) as a colorless liquid.
^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) = 0.80 (d, J = 7.2 Hz, 3H), 0.97 (d, J = 6.4 Hz, 3H), 1.84 (d, J = 3.6 Hz, 1H), 1.88–1.96 (m, 1H), 4.34–4.37 (m, 1H), 7.19 (d, J = 8.0 Hz, 2H), 7.46 (d, J = 8.4 Hz, 2H).
^{13}C NMR (100 MHz, $CDCl_3$): δ(ppm) = 18.13, 18.94, 35.32, 79.34, 121.21, 128.40, 131.33, 142.62.
MS (MALDI-TOF): m/z: 250.98 (calcd. $[M+Na]^+$ = 251.00).

Compound 6. *Tert*-butyldimethylchlorosilane (3.14 g, 20.8 mmol) was added to a solution of compound **5** (3.98 g, 17.3 mmol) and imidazole (3.54 g, 52.0 mmol) in DMF (100 mL) and the mixture was stirred under nitrogen atmosphere for 22 hours at r.t. The reaction mixture was then poured into ethyl acetate (150 mL). The solution was washed with saturated aq. NH_4Cl (4 × 150 mL). The organic layer was dried over $MgSO_4$ and filtered, and the solvent was evaporated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (eluent: gradient from hexane to hexane/ethyl acetate = 97:3 v/v) to afford compound **6** (4.11 g, 12.0 mmol, 69%) as a colorless liquid.
^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) = –0.22 (s, 3H), 0.01 (s, 3H), 0.77 (d, J = 6.8 Hz, 3H), 0.86–0.88 (m, 12H), 1.74–1.82 (m, 1H), 4.29 (d, J = 6.0 Hz, 1H), 7.13 (d, J = 8.0 Hz, 2H), 7.41 (d, J = 8.4 Hz, 2H).
^{13}C NMR (100 MHz, $CDCl_3$): δ(ppm) = –4.95, –4.42, 17.92, 18.33, 19.16, 25.97, 36.71, 79.64, 120.58, 128.58, 130.91, 143.68.
MS (MALDI-TOF): m/z: 364.84 (calcd. $[M+Na]^+$ = 365.09).

Compound 7. A hexane solution of *n*-BuLi (ca. 1.6 mol/L, 8.19 mL, 13.1 mmol) was added to the mixture of compound **6** (4.09 g, 11.9 mmol) and THF (10 mL) at –78 °C and the mixture was stirred for 30 minutes. Then 4-*tert*-butylbenzaldehyde (2.19 mL, 13.1 mmol) was added to the mixture dropwise at the same temperature, and the reaction mixture was stirred for 6 h at r.t. Subsequently, saturated aq. NH_4Cl (5 mL) and ethyl acetate (150 mL) were added to the reaction mixture. The solution was washed with water (4 × 150 mL) and saturated aq. NaCl (150 mL). The organic layer was dried over $MgSO_4$ and filtered, and the solvent was evaporated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (eluent: gradient from hexane to hexane/dichloromethane = 4:1 v/v) to afford compound **7** (3.45 g, 8.09 mmol, 68%) as a colorless liquid.
^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) = –0.23 (s, 3H), 0.00 (s, 3H), 0.77 (d, J = 6.8 Hz, 3H), 0.86–0.88 (m, 12H), 1.31 (s, 9H), 1.76–1.84 (m, 1H), 2.15 (d, J = 3.6 Hz, 1H), 4.31 (d, J = 6.0 Hz, 1H), 5.82 (d, J = 3.6 Hz, 1H), 7.22 (d, J = 8.0 Hz, 2H), 7.26–7.31 (m, 4H), 7.37 (d, 8.4 Hz, 2H).
^{13}C NMR (100 MHz, $CDCl_3$): δ(ppm) = –4.93, –4.39, 18.00, 18.36, 19.36, 26.01, 31.49, 34.67, 36.73, 76.08, 80.04, 125.49, 125.76, 126.04, 126.11, 126.57, 126.63, 126.90, 141.04, 142.16, 143.93, 143.97, 150.55.
MS (MALDI-TOF): m/z: 449.24 (calcd. $[M+Na]^+$ = 449.29).

Compound 8. NaH (60% dispersion in paraffin liquid, 347 mg, 8.69 mmol) was added to a solution of compound **7** (3.40 g, 7.97 mmol) in DMF (100 mL), and subsequently a toluene solution of propargyl bromide (ca. 9.2 mol/L, 0.787 mL, 7.24 mmol) was added to the mixture at 0 °C. After stirring the reaction mixture for 20 h at r.t., ethyl acetate (150 mL) was added to the reaction mixture. The solution was washed with saturated aq. NH_4Cl (2 × 150 mL) and saturated aq. NaCl (150 mL). The organic layer was dried over $MgSO_4$ and filtered, and the solvent was evaporated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (eluent: gradient from hexane to hexane/dichloromethane = 7:3 v/v) to afford compound **8** (3.06 g, 6.58 mmol, 91%) as a colorless liquid.
^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) = –0.24 (s, 3H), 0.00 (s, 3H), 0.77 (d, J = 6.8 Hz, 3H), 0.86–0.88 (m, 12H), 1.31 (s, 9H), 1.76–1.84 (m, 1H), 2.45 (t, J = 2.0 Hz, 1H), 4.13 (d, J = 2.4 Hz, 2H), 4.30 (d, J = 6.0 Hz, 1H), 5.63 (s, 1H), 7.21 (d, J = 8.4 Hz, 2H), 7.26–7.27 (m, 4H), 7.35 (d, J = 8.4 Hz, 2H).
^{13}C NMR (100 MHz, $CDCl_3$): δ(ppm) = –4.93, –4.39, 14.30, 18.02, 18.36, 19.37, 22.81, 26.01, 31.49, 31.74, 34.65, 36.72, 55.83, 74.56, 80.09, 81.52, 125.43, 126.86, 126.95, 127.31, 127.41, 138.12, 139.50, 139.56, 144.08, 144.12, 150.63, 150.67.
MS (MALDI-TOF): m/z: 487.08 (calcd. $[M+Na]^+$ = 487.30).

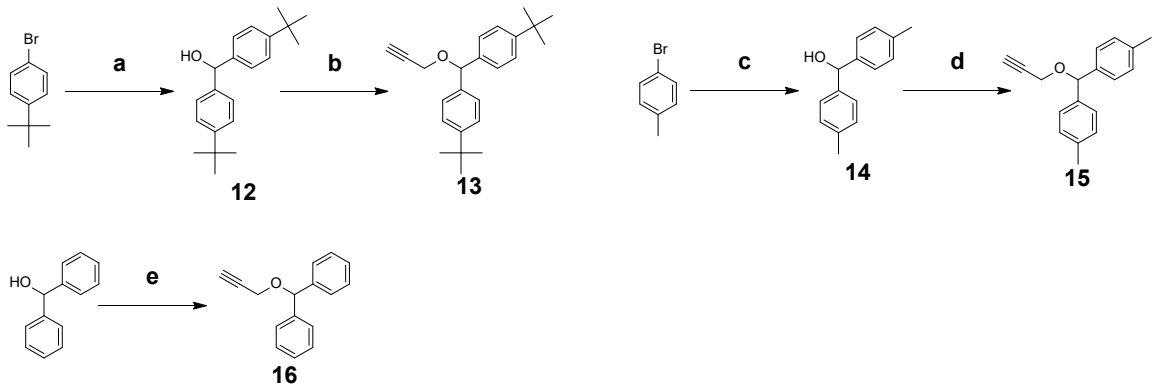
Compound 9. A mixture of compound **8** (1.00 g, 2.15 mmol) and a THF solution of tetrabutylammonium fluoride (ca. 1 mol/L, 3.23 mL, 3.23 mmol) in THF (50 mL) was stirred for 66 h at 50 °C. The reaction mixture was poured into ethyl acetate (150 mL). The solution was washed with water (2 × 150 mL) and saturated aq. NaCl (150 mL). The organic layer was dried over $MgSO_4$ and filtered, and the solvent was evaporated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (eluent: gradient from hexane to hexane/ethyl acetate = 4:1 v/v) to afford compound **9** (588 mg, 1.68 mmol, 78%) as a white solid.
^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) = 0.79 (d, J = 6.8 Hz, 3H), 0.99 (d, J = 6.8 Hz, 3H), 1.30 (s, 9H), 1.78 (d, J = 3.2 Hz, 1H), 1.90–1.98 (m, 1H), 2.45 (t, J = 2.4 Hz, 1H), 4.14 (d, J = 2.4 Hz, 2H), 4.33–4.36 (m, 1H), 5.64 (s, 1H), 7.26–7.29 (m, 4H), 7.34–7.36 (m, 4H).
^{13}C NMR (100 MHz, $CDCl_3$): δ(ppm) = 18.38, 19.18, 31.46, 34.65, 35.35, 55.87, 74.64, 79.95, 79.99, 81.39, 125.51, 126.77, 127.12, 127.24, 138.05, 140.59, 143.13, 150.73.
MS (MALDI-TOF): m/z: 373.95 (calcd. $[M+Na]^+$ = 373.21).

Compound 11. A mixture of compound **10**[S1] (919 mg, 2.08 mmol), compound **9** (485 mg, 1.38 mmol), CuI (264 mg, 1.38 mmol) and *i*-Pr_2NEt (5 mL) in chloroform (70 mL) was stirred for 3 h at 40 °C. The reaction mixture was poured into chloroform (100 mL), and the solution was washed with 5% aq. HCl (150 mL), saturated aq. $NaHCO_3$ (150 mL) and saturated aq. NaCl (150 mL). The organic layer was dried over $MgSO_4$ and filtered, and the solvent was evaporated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (eluent: gradient from dichloromethane to dichloromethane/ethyl acetate = 1:4 v/v) to afford compound **11** (369 mg, 0.466 mmol, 34%) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) = 0.78 (d, J = 6.8 Hz, 3H), 0.99 (d, J = 6.8 Hz, 3H), 1.29 (s, 9H), 1.89–1.98 (m, 1H), 2.01 (t, J = 3.2 Hz, 1H), 3.30 (t, J = 4.8 Hz, 2H), 3.65–3.71 (m, 4H), 3.77–3.84 (m, 4H), 3.92–3.98 (m, 4H), 4.32–4.35 (m, 1H), 4.48 (t, J = 5.2 Hz, 2H), 4.57 (s, 2H), 5.50 (s, 1H), 7.26–7.35 (m, 8H), 7.69 (s, 1H), 8.23 (s, 1H), 8.23 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ(ppm) = 18.43, 19.20, 31.46, 34.61, 35.30, 38.04, 38.09, 50.26, 50.64, 62.30, 67.68, 68.15, 69.07, 69.99, 79.92, 79.95, 82.52, 118.48, 124.13, 125.47, 126.75, 127.03, 127.08, 127.11, 137.08, 137.35, 138.63, 141.14, 143.08, 145.45, 150.51, 166.25.

MS (MALDI-TOF): m/z: 815.98 (calcd. $[M+Na]^+$ = 815.35).



Reaction conditions: (a) i) *n*-BuLi, THF,–78 °C, 2 h; ii) 4-*tert*-butylbenzaldehyde, THF, r.t., 6 h; iii) H^+; (b) propargyl bromide, NaH, DMF, 0 °C → r.t., 3 h; (c) i) *n*-BuLi, THF, –78 °C, 30 min; ii) *p*-tolualdehyde, THF, r.t., 2 h; iii) H^+; (d) propargyl bromide, NaH, DMF, 0 °C → r.t., 2 h; (e) propargyl bromide, NaH, DMF, 0 °C → r.t., 2 h.

Compound 12. A hexane solution of *n*-BuLi (ca. 1.6 mol/L, 14.7 mL, 23.5 mmol) was added to the mixture of 1-bromo-4-*tert*-butylbenzene (5.00 g, 23.5 mmol) and THF (60 mL) at –78 °C and the mixture was stirred for 2 h. Then a solution of 4-*tert*-butylbenzaldehyde (3.81 g, 23.5 mmol) in THF (20 mL) was added to the mixture dropwise at the same temperature, and the reaction mixture was stirred for 6 h at r.t. After saturated aq. NH_4Cl (5 mL) was added to the reaction mixture, dichloromethane (150 mL) was added. The solution was washed with water (150 mL) and saturated aq. NaCl (150 mL). The organic layer was dried over $MgSO_4$ and filtered, and the solvent was evaporated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (eluent: gradient from hexane/dichloromethane = 7:3 v/v to hexane/dichloromethane = 1:1 v/v) to afford compound **12** (4.81 g, 16.2 mmol, 69%) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) = 1.30 (s, 18H), 2.14 (d, J = 3.6 Hz, 1H), 5.81 (d, J = 3.2 Hz, 1H), 7.31–7.37 (m, 8H).

^{13}C NMR (100 MHz, $CDCl_3$): δ(ppm) = 31.48, 34.64, 76.05, 125.53, 126.34, 141.08, 150.51.

MS (MALDI-TOF): m/z: 319.38 (calcd. $[M+Na]^+$ = 319.20).

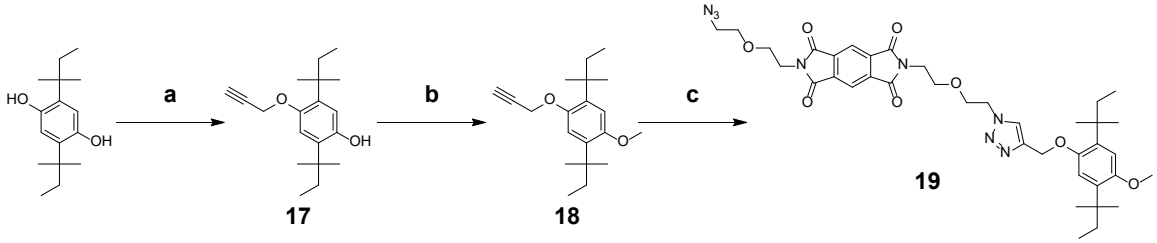
Compound 13. NaH (60% dispersion in paraffin liquid, 708 mg, 17.7 mmol) was added to a solution of compound **12** (4.81 g, 16.2 mmol) in DMF (100 mL), and subsequently a toluene solution of propargyl bromide (ca. 9.2 mol/L, 1.60 mL, 14.8 mmol) was added to the mixture at 0 °C. After stirring the reaction mixture for 3 h at r.t., ethyl acetate (150 mL) was added. The solution was washed with saturated aq. NH_4Cl (4 × 150 mL) and saturated aq. NaCl (150 mL). The organic layer was dried over $MgSO_4$ and filtered. After the solvent was evaporated under reduced pressure, the crude product was precipitated from methanol to afford compound **13** (4.43 g, 13.2 mmol, 90%) as a white solid.
^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) = 1.29 (s, 18H), 2.43 (t, J = 2.4 Hz, 1H), 4.14 (d, J = 2.0 Hz, 2H), 5.62 (s, 1H), 7.28–7.35 (m, 8H).
^{13}C NMR (100 MHz, $CDCl_3$): δ(ppm) = 31.49, 34.64, 55.87, 74.48, 80.12, 81.49, 125.46, 127.08, 138.34, 150.59.
MS (MALDI-TOF): m/z: 357.51 (calcd. $[M+Na]^+$ = 357.22).

Compound 14. A hexane solution of *n*-BuLi (ca. 1.6 mol/L, 20.1 mL, 32.2 mmol) was added to a mixture of 4-bromotoluene (5.00 g, 29.2 mmol) and THF (20 mL) at –78 °C and the mixture was stirred for 30 minutes. Then *p*-tolualdehyde (3.78 mL, 32.2 mmol) was added to the mixture dropwise at the same temperature, and the reaction mixture was stirred for 2 h at r.t. After saturated aq. NH_4Cl (5 mL) was added to the reaction mixture, ethyl acetate (150 mL) was added. The solution was washed with water (3 × 150 mL), and saturated aq. NaCl (150 mL). The organic layer was dried over $MgSO_4$ and filtered, and the solvent was evaporated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (eluent: gradient from hexane to hexane/dichloromethane = 1:4 v/v) to afford compound **14** (5.74 g, 27.0 mmol, 84%) as a white solid.
^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) = 2.12 (d, J = 3.6 Hz, 1H), 2.33 (s, 6H), 5.79 (d, J = 3.6 Hz, 1H), 7.14 (d, J = 8.0 Hz, 4H), 7.26 (d, J = 8.0 Hz, 4H).
^{13}C NMR (100 MHz, $CDCl_3$): δ(ppm) = 21.24, 75.99, 126.53, 129.24, 137.24, 141.19.
MS (MALDI-TOF): m/z: 235.40 (calcd. $[M+Na]^+$ = 235.11).

Compound 15. NaH (60% dispersion in paraffin liquid, 1.18 g, 29.5 mmol) was added to a solution of compound **14** (5.74 g, 27.0 mmol) in DMF (100 mL), and subsequently a toluene solution of propargyl bromide (ca. 9.2 mol/L, 2.56 mL, 24.6 mmol) was added to the mixture at 0 °C. After stirring the reaction mixture for 2 h at r.t., ethyl acetate (150 mL) was added to the reaction mixture. The solution was washed with saturated aq. NH_4Cl (4 × 150 mL) and saturated aq. NaCl (150 mL). The organic layer was dried over $MgSO_4$ and filtered, and the solvent was evaporated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (eluent: gradient from hexane to hexane/dichloromethane = 3:2 v/v) to afford compound **15** (5.78 g, 23.1 mmol, 94%) as a colorless liquid.
^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) = 2.32 (s, 6H), 2.44 (t, J = 2.4 Hz, 1H), 4.13 (d, J = 2.4 Hz, 2H), 5.60 (s, 1H), 7.13 (d, J = 8.0 Hz, 4H), 7.23 (d, J = 8.0 Hz, 4H).
^{13}C NMR (100 MHz, $CDCl_3$): δ(ppm) = 21.28, 55.73, 74.54, 80.00, 81.42, 127.28, 129.23, 137.40, 138.46.
MS (MALDI-TOF): m/z: 273.54 (calcd. $[M+Na]^+$ = 273.13).

Compound 16. NaH (60% dispersion in paraffin liquid, 711 mg, 17.8 mmol) was added to a solution of benzhydrol (3.00 g, 16.3 mmol) in DMF (100 mL), and subsequently a toluene solution of propargyl bromide (ca. 9.2 mol/L, 1.61 mL, 14.8 mmol) was added to the mixture at 0 °C. After stirring the reaction mixture for 2 h at r.t., ethyl acetate (150 mL) was added to the reaction mixture. The solution was washed with saturated aq. NH_4Cl (4 × 150 mL) and saturated aq. NaCl (150 mL). The organic layer was dried over $MgSO_4$ and filtered, and the solvent was evaporated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (eluent: gradient from hexane to hexane/dichloromethane = 7:3 v/v) to afford compound **16** (3.27 g, 14.7 mmol, 99%) as a colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) = 2.46 (t, J = 2.4 Hz, 1H), 4.16 (d, J = 2.4 Hz, 2H), 5.67 (s, 1H), 7.22–7.41 (m, 10H).
^{13}C NMR (100 MHz, $CDCl_3$): δ(ppm) = 55.81, 74.75, 79.77, 81.64, 127.32, 127.76, 128.51, 141.17.
MS (MALDI-TOF): m/z: 245.28 (calcd. $[M+Na]^+$ = 245.09).



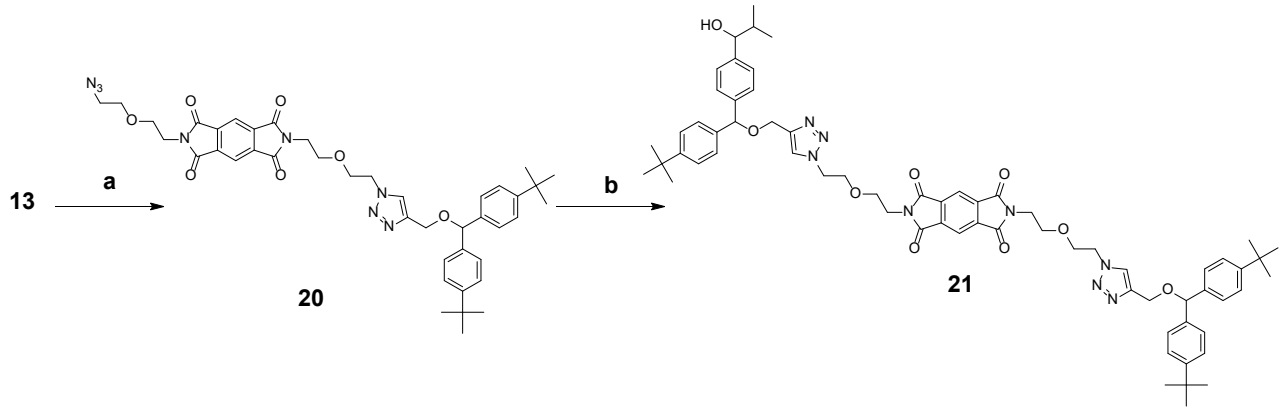
Reaction conditions: (a) propargyl bromide, NaH, DMF, 0 °C → r.t., 25 h; (b) iodomethane, Cs_2CO_3, acetonitrile, reflux, 14 h; (c) compound **10**, CuI, chloroform, *i*-Pr_2NEt, 40 °C, 2 h.

Compound 17. NaH (60% dispersion in paraffin liquid, 879 mg, 22.0 mmol) was added to a solution of 2,5-di(*tert*-amyl)hydroquinone (5.00 g, 20.0 mmol) in DMF (100 mL), and subsequently a toluene solution of propargyl bromide (ca. 9.2 mol/L, 2.61 mL, 24.0 mmol) was added to the mixture at 0 °C, and the reaction mixture was stirred for 25 h at r.t. After water (2 mL) was added to the reaction mixture, ethyl acetate (150 mL) was added. The solution was washed with saturated aq. NH_4Cl (2 × 150 mL) and saturated aq. NaCl (150 mL). The organic layer was dried over $MgSO_4$ and filtered, and the solvent was evaporated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (eluent: gradient from hexane/dichloromethane = 19:1 v/v to hexane/dichloromethane = 4:1 v/v) to afford compound **17** (1.34 g, 4.65 mmol, 23%) as a colorless liquid.
^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) = 0.63 (t, J = 7.6 Hz, 3H), 0.68 (t, J = 7.6 Hz, 3H), 1.29 (s, 6H), 1.35 (s, 6H),1.77–1.85 (m, 4H), 2.48 (t, J = 2.4 Hz, 1H), 4.41 (s, 1H), 4.64 (d, J = 2.4 Hz, 2H), 6.50 (s, 1H), 6.85 (s, 1H).
^{13}C NMR (100 MHz, $CDCl_3$): δ(ppm) = 9.64, 9.72, 27.65, 28.01, 33.48, 33.64, 37.93, 38.08, 56.97, 74.78, 79.68, 114.78, 116.84, 132.02, 135.96, 147.95, 150.42.
MS (MALDI-TOF): m/z: 288.18 (calcd. $[M]^+$ = 288.21).

Compound 18. A mixture of compound **17** (966 mg, 3.35 mmol), iodomethane (523 mg, 3.68 mmol) and Cs_2CO_3 (2.18 g, 6.70 mmol) in acetonitrile (100 mL) was stirred for 14 h under reflux. The reaction mixture was poured into ethyl acetate (150 mL), and the solution was washed with saturated aq. NH_4Cl (150 mL) and saturated aq. NaCl (150 mL). The organic layer was dried over $MgSO_4$ and filtered, and the solvent was evaporated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (eluent: gradient from hexane to hexane/dichloromethane = 9:1 v/v) to afford compound **18** (870 mg, 2.88 mmol, 86%) as a colorless liquid.
^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) = 0.61–0.66 (m, 6H), 1.31 (s, 6H), 1.33 (s, 6H), 1.76–1.84 (m, 4H), 2.48 (t, J = 2.4 Hz, 1H), 3.78 (s, 3H), 4.65 (d, J = 2.4 Hz, 2H), 6.73 (s, 1H), 6.87 (s, 1H).
^{13}C NMR (100 MHz, $CDCl_3$): δ(ppm) = 9.70, 27.82, 28.03, 33.51, 33.77, 38.29, 38.30, 56.01, 56.95, 74.75, 79.73, 112.83, 114.66, 134.77, 135.41, 150.27, 152.75.
MS (MALDI-TOF): m/z: 302.75 (calcd. $[M+H]^+$ = 303.23).

Compound 19. A mixture of compound **10** (1.13 g, 2.55 mmol), compound **18** (515 mg, 1.70 mmol), CuI (324 mg, 1.70 mmol) and *i*-Pr_2NEt (5 mL) in chloroform (100 mL) was stirred for 2 h at 40 °C. The reaction mixture was poured into chloroform (100 mL), and the solution was washed with 5% aq. HCl (150 mL), saturated aq. $NaHCO_3$ (150 mL) and saturated aq. NaCl (150 mL). The organic layer was dried over $MgSO_4$ and filtered, and the solvent was evaporated under reduced pressure. The crude product was purified by flash column chromatography on silica

gel (eluent: gradient from dichloromethane/ethyl acetate = 19:1 v/v to dichloromethane/ethyl acetate = 17:3 v/v) to afford compound **19** (412 mg, 0.553 mmol, 32%) as an orange liquid.
^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) = 0.60–0.64 (m, 6H), 1.31 (s, 6H), 1.33 (s, 6H), 1.76–1.83 (m, 4H), 3.30 (t, J = 4.8 Hz, 2H), 3.66–3.69 (m, 4H), 3.78–3.81 (m, 5H), 3.86 (t, J = 5.2 Hz, 2H), 3.92 (t, J = 5.6 Hz, 2H), 3.99 (t, J = 5.6 Hz, 2H), 4.50 (t, J = 5.2 Hz, 2H), 5.17 (s, 2H), 6.75 (s, 1H), 6.87 (s, 1H), 7.72 (s, 1H), 8.28 (s, 2H).
^{13}C NMR (100 MHz, $CDCl_3$): δ(ppm) = 9.72, 9.74, 27.87, 28.02, 33.48, 33.65, 37.87, 38.12, 38.32, 50.40, 50.67, 56.08, 63.29, 67.70, 68.11, 69.12, 70.02, 113.04, 114.20, 118.50, 123.78, 134.87, 134.91, 137.19, 137.43, 145.15, 150.53, 152.48, 166.21, 166.24.
MS (MALDI-TOF): m/z: 745.49 (calcd. $[M+H]^+$ = 745.37).

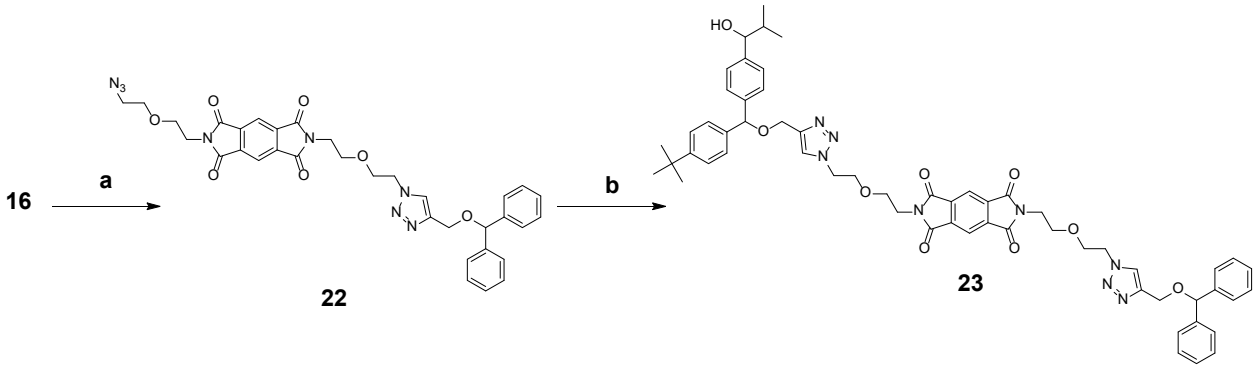


Reaction conditions: (a) compound **10**, CuI, chloroform, *i*-Pr_2NEt, 40 °C, 2 h.; (b) compound **9**, CuI, chloroform, *i*-Pr_2NEt, 40 °C, 2 h.

Compound 20. A mixture of compound **10** (1.00 g, 2.26 mmol), compound **13** (505 mg, 1.51 mmol), CuI (288 mg, 1.51 mmol) and *i*-Pr_2NEt (5 mL) in $CHCl_3$ (100 mL) was stirred for 2 h at 40 °C. The reaction mixture was poured into chloroform (100 mL), and the solution was washed with 5% aq. HCl (150 mL), saturated aq. $NaHCO_3$ (150 mL) and saturated aq. NaCl (150 mL). The organic layer was dried over $MgSO_4$ and filtered, and the solvent was evaporated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (eluent: gradient from dichloromethane/ethyl acetate = 19:1 v/v to dichloromethane/ethyl acetate = 7:3 v/v) to afford compound **20** (351 mg, 0.452 mmol, 30%) as a pale yellow liquid.
^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) = 1.29 (s, 18H), 3.30 (t, J = 4.8 Hz, 2H), 3.65–3.71 (m, 4H), 3.80 (t, J = 5.6 Hz, 2H), 3.83 (t, J = 5.2 Hz, 2H), 3.93 (t, J = 5.6 Hz, 2H), 3.98 (t, J = 5.6 Hz, 2H), 4.47 (t, J = 5.2 Hz, 2H), 4.58 (s, 2H), 5.48 (s, 1H), 7.29–7.35 (m, 8H), 7.69 (s, 1H), 8.25 (s, 2H).
^{13}C NMR (100 MHz, $CDCl_3$): δ(ppm) = 31.49, 34.62, 38.00, 38.13, 50.27, 50.69, 62.39, 67.72, 68.14, 69.12, 70.01, 82.72, 118.50, 124.06, 125.44, 126.97, 137.17, 137.44, 138.96, 145.62, 150.38, 166.23.
MS (MALDI-TOF): m/z: 799.61 (calcd. $[M+Na]^+$ = 799.35).

Compound 21. A mixture of compound **9** (100 mg, 0.285 mmol), compound **20** (210 mg, 0.270 mmol), CuI (51 mg, 0.27 mmol) and *i*-Pr_2NEt (2 mL) in chloroform (50 mL) was stirred for 2 h at 40 °C. The reaction mixture was poured into chloroform (100 mL), and the solution was washed with 5% aq. HCl (150 mL), saturated aq. $NaHCO_3$ (150 mL) and saturated aq. NaCl (150 mL). The organic layer was dried over $MgSO_4$ and filtered, and the solvent was evaporated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (eluent: gradient from dichloromethane/acetone = 19:1 v/v to dichloromethane/acetone = 7:3 v/v) to afford compound **21** (235 mg, 0.208 mmol, 77%) as a pale yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) = 0.76 (d, J = 6.8 Hz, 3H), 0.98 (d, J = 6.8 Hz, 3H), 1.28 (s, 27H), 1.87–1.96 (m, 1H), 2.13 (br, 1H), 3.67–3.70 (m, 4H), 3.80–3.83 (m, 4H), 3.90–3.94 (m, 4H), 4.32 (d, J = 6.4 Hz, 1H), 4.43 (m, 4H), 4.57 (s, 4H), 5.48 (s, 1H), 5.49 (s, 1H), 7.24–7.34 (m, 16H), 7.67 (br, 2H), 8.20 (s, 1H), 8.21 (s, 1H).
^{13}C NMR (100 MHz, $CDCl_3$): δ(ppm) = 18.42, 19.21, 31.47, 34.61, 35.31, 37.99, 38.06, 50.23, 62.34, 68.06, 68.12, 69.08, 79.91, 82.56, 82.69, 118.55, 123.99, 124.04, 125.43, 126.76, 126.94, 127.04, 127.10, 137.21, 138.66, 138.92, 141.12, 143.12, 145.47, 145.57, 150.37, 150.53, 166.16. 150.53, 152.48, 166.21, 166.24.
MS (MALDI-TOF): m/z: 1149.89 (calcd. $[M+Na]^+$ =1149.58).

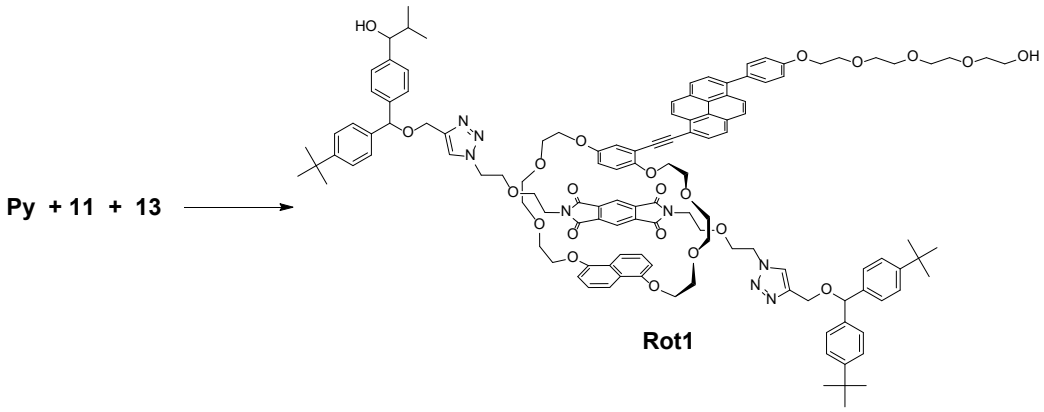


Reaction conditions: (a) compound **10**, CuI, chloroform, *i*-Pr_2NEt, 40 °C, 3 h.; (b) compound **9**, CuI, chloroform, *i*-Pr_2NEt, 40 ºC, 2 h.

Compound 22. A mixture of compound **10** (1.43 g, 3.39 mmol), compound **16** (500 mg, 2.25 mmol), CuI (428 mg, 2.25 mmol) and *i*-Pr_2NEt (10 mL) in chloroform (100 mL) was stirred for 3 h at 40 °C. The reaction mixture was poured into chloroform (100 mL), and the solution was washed with 5% aq. HCl (150 mL), saturated aq. $NaHCO_3$ (150 mL) and saturated aq. NaCl (150 mL). The organic layer was dried over $MgSO_4$ and filtered, and the solvent was evaporated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (eluent: gradient from dichloromethane/ethyl acetate = 19:1 v/v to dichloromethane/ethyl acetate = 3:2 v/v) to afford compound **22** (247 mg, 0.248 mmol, 11%) as a pale yellow solid.
^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) = 3.30 (t, J = 4.8 Hz, 2H), 3.65–3.70 (m, 4H), 3.78–3.83 (m, 4H), 3.92 (t, J = 5.2 Hz, 2H), 3.97 (t, J = 5.2 Hz, 2H), 4.47 (t, J = 5.2 Hz, 2H), 4.60 (s, 2H), 5.54 (s, 1H), 7.22–7.38 (m, 10H), 7.70 (s, 1H), 8.24 (s, 2H).
^{13}C NMR (100 MHz, $CDCl_3$): δ(ppm) = 38.02, 38.09, 50.26, 50.66, 62.39, 67.68, 68.13, 69.08, 69.97, 82.90, 118.45, 124.10, 127.28, 127.64, 128.52, 137.11, 137.39, 141.88, 145.36, 166.20.
MS (MALDI-TOF): m/z: 665.92 (calcd. $[M+H]^+$ = 665.25).

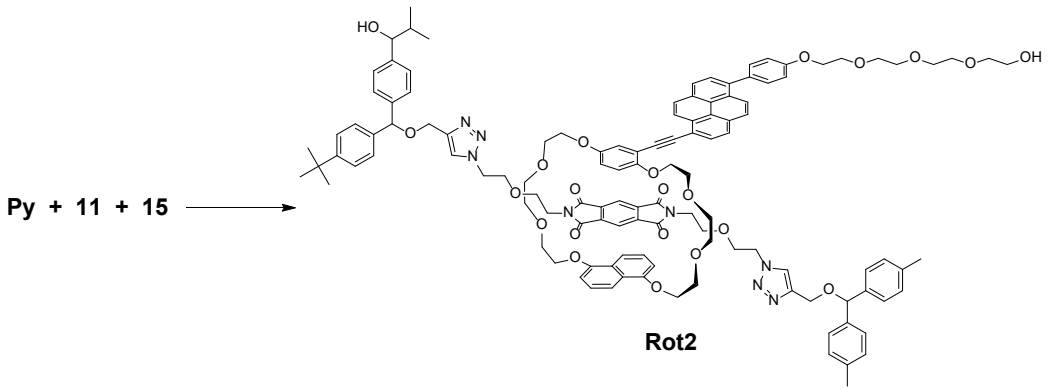
Compound 23. A mixture of compound **9** (52.6 g, 0.150 mmol), compound **22** (100 mg, 0.150 mmol), CuI (28.6 mg, 0.150 mmol) and *i*-Pr_2NEt (5 mL) in chloroform (50 mL) was stirred for 2 h at 40 °C. The reaction mixture was poured into chloroform (100 mL), and the solution was washed with 5% aq. HCl (150 mL), saturated aq. $NaHCO_3$ (150 mL) and saturated aq. NaCl (150 mL). The organic layer was dried over $MgSO_4$ and filtered, and the solvent was evaporated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (eluent: gradient from dichloromethane to dichloromethane/acetone = 3:2 v/v) to afford compound **23** (118 mg, 0.116 mmol, 77%) as a pale yellow solid.
^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) = 0.76 (d, J = 6.8 Hz, 3H), 0.97 (d, J = 6.8 Hz, 3H), 1.28 (s, 9H), 1.87–1.95 (m, 1H), 2.33 (br, 1H), 3.65–3.69 (m, 4H), 3.78–3.81 (m, 4H), 3.88–3.92 (m, 4H), 4.31 (d, J = 6.8 Hz, 1H), 4.43 (t, J = 5.2 Hz, 4H), 4.56 (s, 2H), 4.58 (s, 2H), 5.49 (s, 1H), 5.53 (s, 1H), 7.21–7.36 (m, 18H), 7.67 (br, 2H), 8.19–8.19 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ(ppm) = 18.35, 19.15, 31.41, 34.55, 35.25, 37.98, 50.17, 62.25, 62.30, 68.01, 68.99, 79.75, 82.50, 82.83, 118.46, 124.01, 125.40, 126.70, 126.98, 127.21, 127.60, 128.47, 137.12, 138.62, 141.00, 141.80, 143.12, 145.25, 145.36, 150.47, 166.10.
MS (MALDI-TOF): m/z: 1016.04 (calcd. $[M+H]^+$ = 1015.47).



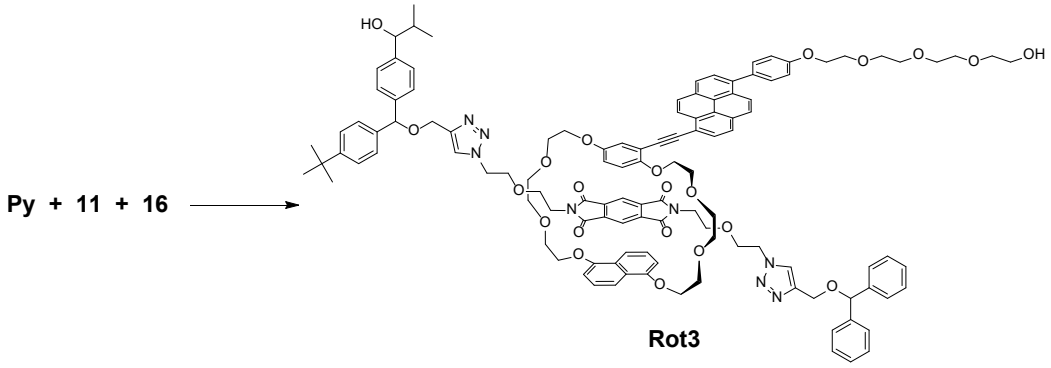
Reaction conditions: $CuSO_4$, sodium ascorbate, chloroform, H_2O, 5 °C, 13 h.

Rot1. A mixture of sodium ascorbate (120 mg, 0.605 mmol) and copper(II) sulfate (48.3 mg, 0.303 mmol) in water (1 mL) was added to a solution of compound **Py** (200 mg, 0.202 mmol), compound **11** (160 mg, 0.202 mmol) and compound **13** (67.5 mg, 0.202 mmol) in chloroform (0.5 mL) and the mixture was vigorously stirred for 13 h at 5 °C. The suspension was poured into chloroform (150 mL), and the solution was washed with water (2 × 150 mL) and saturated aq. NaCl (150 mL). The organic layer was dried over $MgSO_4$ and filtered, and the solvent was evaporated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (eluent: gradient from dichloromethane/acetone = 17:3 v/v to dichloromethane/acetone = 13:7 v/v) and recycling GPC (eluent: chloroform) to afford **Rot1** (44.4 mg, 2.10×10^{-2} mmol, 10%) as an orange solid.
^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) = 0.73–0.76 (m, 3H), 0.93–0.96 (m, 3H), 1.24–1.26 (m, 27H), 1.84–1.96 (m, 2H), 2.78–2.82 (m, 1H), 3.41–4.49 (m, 57H), 4.60 (s, 2H), 4.61 (s, 2H), 5.44–5.47 (m, 2H), 6.03 (d, J = 9.2 Hz, 1H), 6.15 (dd, J = 9.2, 3.2 Hz, 1H), 6.26–6.35 (m, 3H), 6.74–6.84 (m, 2H), 7.14 (d, J = 8.8 Hz, 2H), 7.19–7.31 (m, 18H), 7.55 (d, J = 8.4 Hz, 2H), 7.61–7.68 (m, 2H), 7.96–8.01 (m, 4H), 8.06 (s, 2H), 8.19–8.27 (m, 3H), 8.64(d, J = 9.2 Hz, 1H).
^{13}C NMR (100 MHz, $CDCl_3$): δ(ppm) = 18.33, 19.19, 31.42, 34.54, 35.28, 36.63, 36.68, 50.24, 61.86, 62.44, 67.66, 67.78, 68.02, 68.18, 68.43, 68.54, 69.46, 69.89, 69.96, 70.45, 70.73, 70.80, 70.91, 70.96, 71.04, 72.66, 79.80, 82.74, 82.83, 91.13, 93.33, 105.29, 105.37, 111.29, 112.55, 114.08, 114.31, 114.74, 115.39, 116.84, 117.89, 118.26, 123.73, 124.11, 124.24, 124.31, 124.69, 124.82, 125.38, 125.52, 125.62, 125.79, 126.13, 126.47, 126.70, 126.88, 126.94, 127.02, 127.27, 128.29, 128.49, 128.79, 129.68, 130.45, 131.24, 131.77, 132.47, 133.50, 134.25, 134.39, 138.29, 138.69, 138.88, 141.05, 143.08, 145.49, 145.53, 145.62, 150.32, 150.47, 151.84, 153.11, 153.91, 153.96, 158.40, 166.77, 166.81.
MS (ESI-TOF): m/z: 2139.9998 (calcd. $[M+Na]^+$ = 2139.9980).



Reaction conditions: $CuSO_4$, sodium ascorbate, chloroform, H_2O, 5 °C, 14 h.

Rot2. A mixture of sodium ascorbate (122 mg, 0.614 mmol) and copper(II) sulfate (49.0 mg, 0.307 mmol) in water (1 mL) was added to a solution of compound **Py** (203 mg, 0.205 mmol), compound **11** (162 mg, 0.205 mmol) and compound **15** (51.2 mg, 0.205 mmol) in chloroform (0.5 mL) and the mixture was vigorously stirred for 14 h at 5 ºC. The suspension was poured into chloroform (150 mL), and the solution was washed with water (2 × 150 mL) and saturated aq. NaCl (150 mL). The organic layer was dried over $MgSO_4$ and filtered, and the solvent was evaporated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (eluent: gradient from dichloromethane/acetone = 4:1 v/v to dichloromethane/acetone = 3:2 v/v) and recycling GPC (eluent: chloroform) to afford **Rot2** (52.0 mg, 2.56×10^{-2} mmol, 13%) as an orange solid.
^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) = 0.73–0.76 (m, 3H), 0.93–0.96 (m, 3H), 1.24–1.26 (m, 9H), 1.83–1.95 (m, 2H), 2.28 (s, 6H), 2.71 (br, 1H), 3.42–4.49 (m, 57H), 4.60 (s, 2H), 4.61 (s, 2H), 5.43–5.47 (m, 2H), 6.02 (d, J = 8.8 Hz, 1H), 6.14 (dd, J = 8.8, 2.8 Hz, 1H), 6.26–6.34 (m, 3H), 6.73–6.83 (m, 2H), 7.07–7.10 (m, 4H), 7.13 (d, J = 8.8 Hz, 2H), 7.19–7.31 (m, 14H), 7.53–7.56 (d, J = 8.4 Hz, 2H), 7.62 (s, 1H), 7.66 (s, 1H), 7.96–8.01(m, 4H), 8.06 (s, 2H), 8.19–8.27 (m, 3H), 8.64 (d, J = 9.2 Hz, 1H).
^{13}C NMR (100 MHz, $CDCl_3$): δ(ppm) = 18.34, 19.19, 21.22, 31.42, 34.56, 35.28, 36.70, 50.23, 61.86, 62.34, 62.43, 67.66, 67.77, 68.02, 68.18, 68.44, 68.59, 69.46, 69.89, 69.96, 70.44, 70.73, 70.80, 70.90, 70.96, 71.04, 72.67, 79.81, 82.75, 91.12, 93,32, 105.28, 105.37, 111.29, 112.54, 114.08, 114.31, 114.74, 115.39, 116.83, 117.88, 118.26, 123.74, 124.11, 124.23, 124.31, 124.69, 124.83, 125.42, 125.52, 125.62, 125.79, 126.12, 126.48, 126.71, 126.94, 127.02, 127.13, 127.27, 128.30, 128.50, 128.79, 129.17, 129.68, 130.45, 131.24, 131.77, 132.47, 133.51, 134.24, 134.39, 137.15, 138.30, 138.69, 139.08, 141.06, 143.08, 145.55, 150.47, 151.84, 153.10, 153.93, 158.40, 166.80.
MS (ESI-TOF): m/z: 2055.8890 (calcd. $[M+Na]^+$ = 2055.9041).



Reaction conditions: $CuSO_4$, sodium ascorbate, chloroform, H_2O, 5 °C, 18 h.

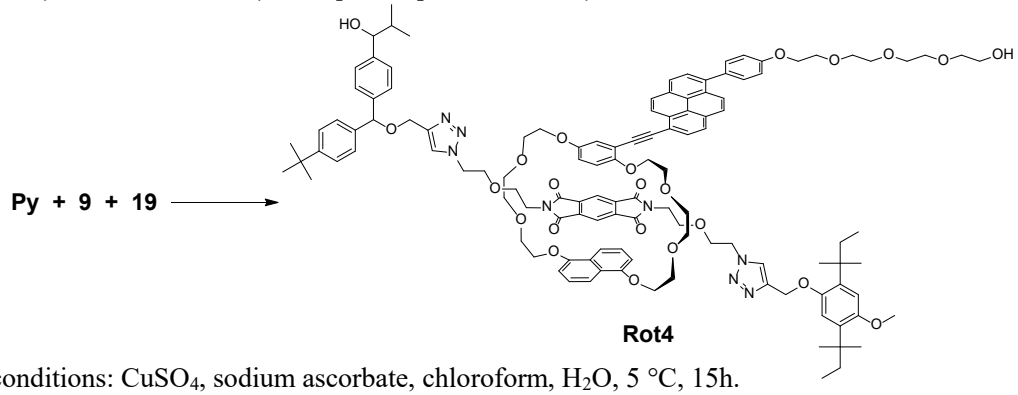
Rot3. A mixture of sodium ascorbate (120 mg, 0.605 mmol) and copper(II) sulfate (48.3 mg, 0.303 mmol) in water

(1 mL) was added to a solution of compound **Py** (200 mg, 0.202 mmol), compound **11** (160 mg, 0.202 mmol) and compound **16** (44.9 mg, 0.202 mmol) in chloroform (0.5 mL) and the mixture was vigorously stirred for 18 h at 5 ºC. The suspension was poured into chloroform (150 mL), and the solution was washed with water (2 × 150 mL) and saturated aq. NaCl (150 mL). The organic layer was dried over $MgSO_4$ and filtered, and the solvent was evaporated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (eluent: gradient from dichloromethane/acetone = 4:1 v/v to dichloromethane/acetone = 3:2 v/v) and recycling GPC (eluent: chloroform) to afford **Rot3** (13.2 mg, 6.58×10^{-3} mmol, 3%) as an orange solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) = 0.73–0.76 (m, 3H), 0.93–0.97 (m, 3H), 1.25–1.29 (m, 9H), 1.82–1.96 (m, 2H), 2.65 (br, 1H), 3.42–4.50 (m, 57H), 4.60–4.65 (m, 4H), 5.47–5.52 (m, 2H), 6.04 (d, J = 8.8 Hz, 1H), 6.16 (dd, J = 8.8, 2.0 Hz, 1H), 6.27–6.35 (m, 3H), 6.74–6.84 (m, 2H), 7.14 (d, J = 8.4 Hz, 2H), 7.21–7.36 (m, 20H), 7.55 (d, J = 8.4 Hz, 2H), 7.64 (s, 1H), 7.67 (s, 1H), 7.97–8.02 (m, 4H), 8.06 (s, 2H), 8.20–8.28 (m, 3H), 8.65 (d, J = 9.2 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ(ppm) = 18.37, 19.21, 31.44, 34.59, 35.30, 36.69, 50.28, 61.91, 62.46, 67.68, 67.80, 68.04, 68.21, 68.46, 68.51, 68.55, 68.62, 69.46, 69.88, 69.94, 69.98, 70.49, 70.78, 70.84, 70.92, 71.00, 71.07, 72.65, 79.87, 82.75, 83.04, 91.11, 93.34, 105.30, 105.38, 111.28, 112.54, 114.08, 114.31, 114.75, 115.39, 116.84, 117.88, 118.28, 123.80, 123.84, 124.11, 124.25, 124.33, 124.71, 124.84, 125.46, 125.56, 125.63, 125.80, 126.15, 126.51, 126.74, 126.96, 127.05, 127.26, 127.67, 128.33, 128.56, 128.81, 129.70, 130.47, 131.26, 131.80, 132.50, 133.50, 134.26, 134.40, 138.32, 138.69, 141.09, 141.86, 143.06, 145.41, 145.45, 145.54, 150.50, 151.84, 153.11, 153.94, 153.98, 158.43, 166.79, 166.81.

MS (ESI-TOF): m/z: 2127.8687 (calcd. $[M+Na]^+$ = 2127.8728).



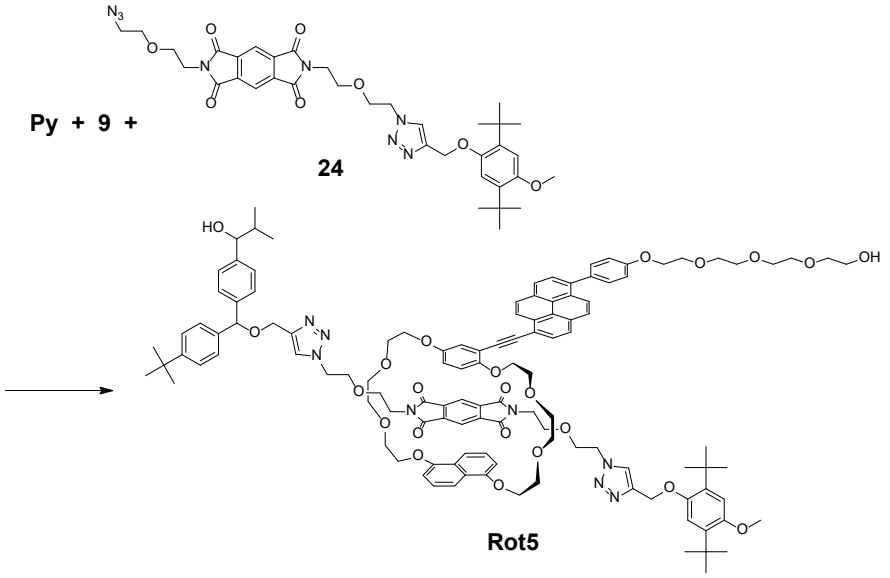
Reaction conditions: $CuSO_4$, sodium ascorbate, chloroform, H_2O, 5 °C, 15h.

Rot4. A mixture of sodium ascorbate (125 mg, 0.632 mmol) and copper(II) sulfate (50.5 mg, 0.316 mmol) in water (1 mL) was added to a solution of compound **Py** (209 mg, 0.211 mmol), compound **19** (157 mg, 0.211 mmol) and compound **9** (73.9 mg, 0.211 mmol) in chloroform (0.5 mL) and the mixture was vigorously stirred for 15 h at 5 ºC. The suspension was poured into chloroform (150 mL), and the solution was washed with water (2 × 150 mL) and saturated aq. NaCl (150 mL). The organic layer was dried over $MgSO_4$ and filtered, and the solvent was evaporated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (eluent: gradient from dichloromethane/acetone = 4:1 v/v to dichloromethane/acetone = 3:2 v/v) and recycling GPC (eluent: chloroform) to afford **Rot4** (73.4 mg, 3.52×10^{-2} mmol, 17%) as an orange solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) = 0.59–0.63 (m, 6H), 0.73–0.76 (m, 3H), 0.93–0.96 (m, 3H), 1.25–1.32 (m, 21H), 1.76–1.96 (m, 6H), 2.83 (br, 1H), 3.43–4.50 (m, 60H), 4.60–4.61 (m, 2H), 5.16–5.17 (m, 2H), 5.46–5.46 (m, 1H), 6.02 (d, J = 9.2 Hz, 1H), 6.15 (dd, J = 8.8, 2.0 Hz, 1H), 6.26–6.35 (m, 3H), 6.73–6.83 (m, 3H), 6.86–6.87 (m, 1H), 7.14 (d, J = 8.4 Hz, 2H), 7.20–7.30 (m, 10H), 7.55 (d, J = 8.0 Hz, 2H), 7.61–7.70 (m, 2H), 7.96–8.02 (m, 4H), 8.07 (s, 2H), 8.19–8.28 (m, 3H), 8.63 (d, J = 9.2 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ(ppm) = 9.67, 9.72, 18.32, 19.17, 27.84, 28.00, 31.40, 33.45, 33.64, 34.54, 35.26,

36.66, 36.71, 38.27, 50.21, 50.24, 50.30, 56.03, 61.82, 62.40, 63.30, 67.56, 67.64, 67.73, 67.96, 68.14, 68.41, 68.51, 68.63, 69.45, 69.86, 69.96, 70.37, 70.68, 70.76, 70.87, 70.92, 71.00, 71.03, 72.72, 79.76, 79.78, 82.73, 91.08, 93.30, 105.26, 105.33, 111.24, 112.51, 113.01, 114.07, 114.14, 114.31, 114.72, 115.39, 116.76, 117.84, 118.22, 123.47, 123.49, 123.72, 123.76, 124.07, 124.12, 124.20, 124.24, 124.30, 124.67, 124.81, 125.39, 125.51, 125.58, 125.77, 126.06, 126.48, 126.69, 126.92, 127.00, 127.24, 128.29, 128.49, 128.78, 129.68, 130.42, 131.24, 131.76, 132.44, 133.50, 134.19, 134.22, 134.35, 134.37, 134.85, 134.88, 138.31, 138.67, 141.01, 143.09, 145.09, 145.13, 145.46, 145.50, 150.45, 150.56, 151.82, 152.48, 153.07, 153.88, 153.93, 158.36, 166.74, 166.77, 166.80, 166.84.
MS (ESI-TOF): m/z: 2107.9900 (calcd. $[M+Na]^+$ = 2107.9929).



Reaction conditions: $CuSO_4$, sodium ascorbate, chloroform, H_2O, 5 °C, 23 h.

Rot5. A mixture of sodium ascorbate (125 mg, 0.629 mmol) and copper(II) sulfate (50.2 mg, 0.314 mmol) in water (1 mL) was added to a solution of compound **Py** (208 mg, 0.210 mmol), compound **24**[S1] (150 mg, 0.210 mmol) and compound **9** (73.5 mg, 0.210 mmol) in chloroform (0.5 mL) and the mixture was vigorously stirred for 23 h at 5 ºC. The suspension was poured into chloroform (150 mL), and the solution was washed with water (2 × 150 mL) and saturated aq. NaCl (150 mL). The organic layer was dried over $MgSO_4$ and filtered, and the solvent was evaporated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (eluent: gradient from dichloromethane/acetone = 4:1 v/v to dichloromethane/acetone = 13:7 v/v) and recycling GPC (eluent: chloroform) to afford **Rot5** (36.8 mg, 1.79×10^{-2} mmol, 9%) as an orange solid.
^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) = 0.72–0.76 (m, 3H), 0.92–0.96 (m, 3H), 1.24–1.25 (m, 9H), 1.35–1.37 (m, 18H), 1.85–1.91 (m, 1H), 1.98–2.05 (m, 1H), 2.70 (br, 1H), 3.43–4.50 (m, 60H), 4.60–4.61 (m, 2H), 5.20–5.21 (m, 2H), 5.46–5.46 (m, 1H), 6.02 (d, J = 9.2 Hz, 1H), 6.15 (dd, J = 8.8, 2.8 Hz, 1H), 6.25–6.35 (m, 3H), 6.73–6.83 (m, 3H), 6.97–6.97 (m, 1H), 7.13 (d, J = 8.8 Hz, 2H), 7.19–7.31 (m, 10H), 7.55 (d, J = 8.4 Hz, 2H), 7.62–7.73 (m, 2H), 7.96–8.08 (m, 6H), 8.20–8.27 (m, 3H), 8.64 (d, J = 9.2 Hz, 1H).
^{13}C NMR (100 MHz, $CDCl_3$): δ(ppm) = 18.36, 19.19, 29.87, 30.02, 31.42, 34.56, 34.73, 35.28, 36.65, 50.29, 50.35, 55.91, 61.87, 62.42, 63.21, 67.65, 67.78, 67.99, 68.17, 68.42, 68.52, 68.64, 69.44, 69.90, 69.97, 70.46, 70.74, 70.80, 70.91, 70.97, 71.05, 72.63, 79.83, 82.73, 91.08, 93.31, 105.27, 105.35, 111.20, 111.65, 112.50, 112.82, 114.05, 114.29, 114.72, 115.37, 116.82, 117.85, 118.25, 123.56, 123.76, 124.10, 124.24, 124.30, 124.68, 124.82, 125.43, 125.54, 125.59, 125.77, 126.12, 126.49, 126.71, 126.93, 127.02, 127.26, 128.31, 128.51, 128.78, 129.67, 130.44, 131.24, 131.77, 132.47, 133.46, 134.23, 134.38, 136.50, 138.31, 138.68, 141.05, 143.06, 145.10, 145.14, 145.49, 145.52, 150.46, 150.57, 151.82, 152.42, 153.07, 153.90, 153.95, 158.41, 166.76.
MS (ESI-TOF): m/z: 2079.9569 (calcd. $[M+Na]^+$ = 2079.9616).

Polymer Synthesis

Synthesis of polyurethane Rot1PU, Rot2PU, and Rot4PU. Dibutyltin dilaurate (4 drops) was added to a stirred mixture of the respective rotaxane (10.0 mg), telechelic poly(tetrahydrofuran)diol (M_n = 2,000 g/mol, 3.00 g, 1.50 mmol) and 4,4'-methylenebis(phenylisocyanate) (1.26 g, 5.04 mmol) in THF (30 mL) and the mixture was stirred at r.t. for 3 h. A solution of 1,4-butanediol (297 mg, 3.30 mmol) in THF (10 mL) was then added and the reaction mixture was stirred at r.t. for an additional 42–135 h. MeOH (5 mL) was added to the reaction mixture and the reaction mixture was poured into MeOH (1500 mL) after stirring for another 30 min. The pale yellow precipitate was collected by filtration and re-dissolved in THF (100 mL). The THF solution was filtrated through a cotton filter and poured into hexane (1600 mL). The precipitate was filtered off and dried in vacuo for 15 h at r.t. to afford **Rot1PU** (4.19 g, 93%, 116 kg·mol^{-1}), **Rot2PU** (4.24 g, 94%, M_n = 132 kg·mol^{-1}), and **Rot4PU** (4.26 g, 95%, M_n = 118 kg·mol^{-1}) as yellow rubbery solids.

Synthesis of polyurethane Rot3PU and Rot5PU. Dibutyltin dilaurate (4 drops) was added to a stirred mixture of the respective rotaxane (10.0 mg), telechelic poly(tetrahydrofuran)diol (M_n = 2,000 g/mol, 3.00 g, 1.50 mmol) and 4,4'-methylenebis(phenylisocyanate) (1.28 g, 5.11 mmol) in THF (30 mL) and the mixture was stirred at r.t. for 3 h. A solution of 1,4-butanediol (297 mg, 3.30 mmol) in THF (10 mL) was then added and the reaction mixture was stirred at r.t. for an additional 24–116 h. MeOH (5 mL) was added to the reaction mixture and the reaction mixture was poured into MeOH (1500 mL) after stirring for another 30 min. The pale yellow precipitate was collected by filtration and re-dissolved in THF (100 mL). The THF solution was filtrated through a cotton filter and poured into hexane (1600 mL). The precipitate was filtered off and dried in vacuo for 15 h at r.t. to afford **Rot3PU** (4.06 g, 90%, 139 kg·mol^{-1}) and **Rot5PU** (4.25 g, 94%, M_n = 136 kg·mol^{-1}) as yellow rubbery solids.

Preparation of Polyurethane Films

Preparation of Rot1PU, Rot2PU, Rot3PU, Rot4PU and Rot5PU films. 300 mg of the polyurethanes (**Rot1PU**, **Rot2PU**, **Rot3PU**, **Rot4PU** and **Rot5PU**) were dissolved in THF (8 mL) and each solution was divided between two square poly(tetrafluoroethylene) molds (35 × 35 × 4.0 mm). The molds were placed under an inverted funnel so that the evaporation rate was controlled. The solvent was evaporated over the course of 2 h under ambient conditions and the resulting films were further dried in vacuo at r.t. for 3 h. The films thus obtained were smooth and transparent or opaque. The thicknesses of the films were 60–100 μm, which were measured by a digital caliper.

^{1}H NMR Spectra of Rotaxanes

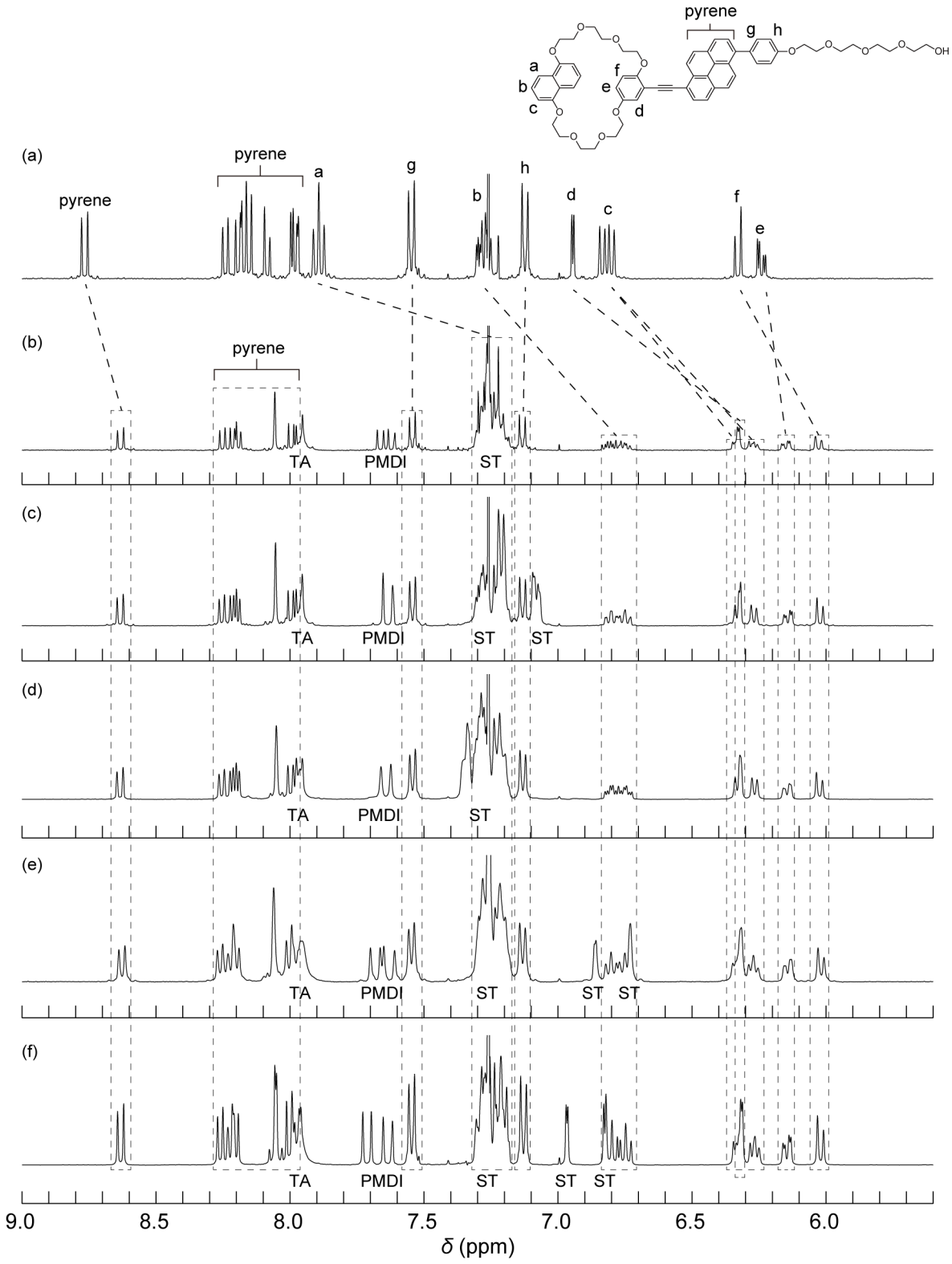


Figure S1. Aromatic region of the ^{1}H NMR spectra of (a) **Py** and the rotaxanes (b) **Rot1**, (c) **Rot2**, (d) **Rot3**, (e) **Rot4**, and (f) **Rot5**. The abbreviations "ST", "TA", "PMDI" indicate signals corresponding to the stoppers, triazole, and quencher moieties, respectively. All spectra were recorded in $CDCl_3$ at r.t. with 400 MHz.

Absorption and Fluorescence Spectra of Rotaxanes in Chloroform

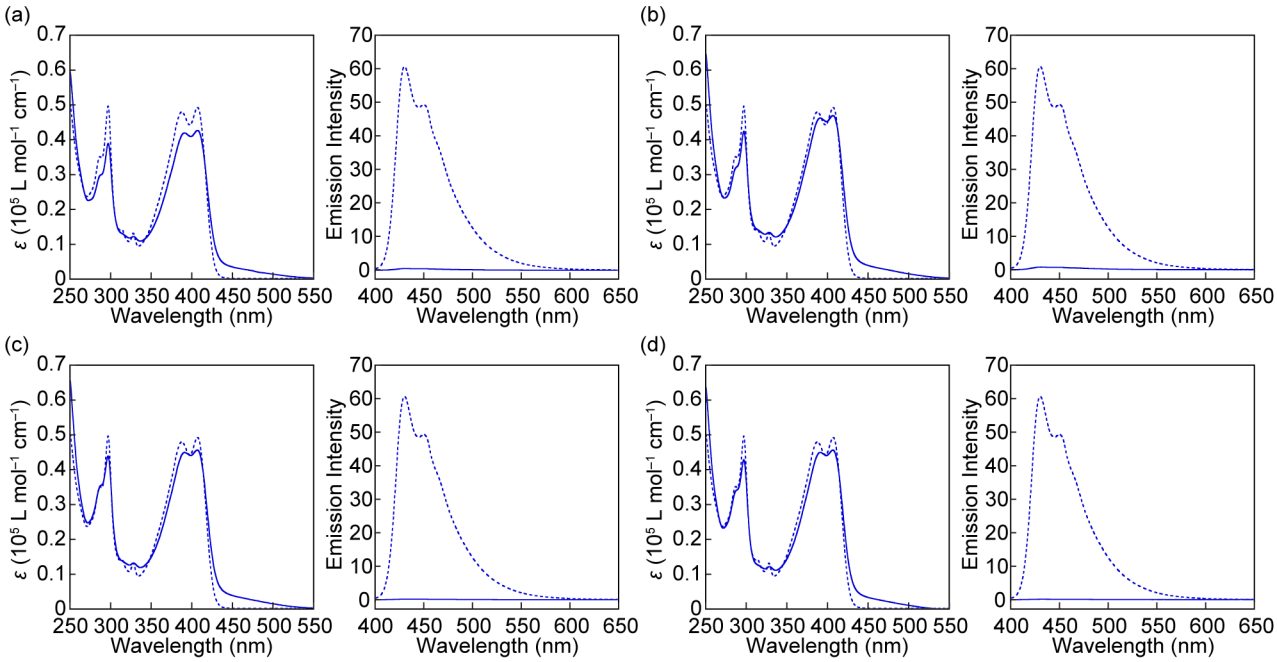


Figure S2. UV-vis absorption (left) and photoluminescence (PL, right) spectra of (a) **Rot2**, (b) **Rot3**, (c) **Rot4**, and (d) **Rot5** in chloroform (solid lines) (c = 1.0 × 10^{-5} M). The spectra recorded for **Py** are also shown in each panel (dotted lines). All PL spectra were recorded with excitation at 380 nm at r.t.

^{1}H NMR Spectra of Polyurethanes

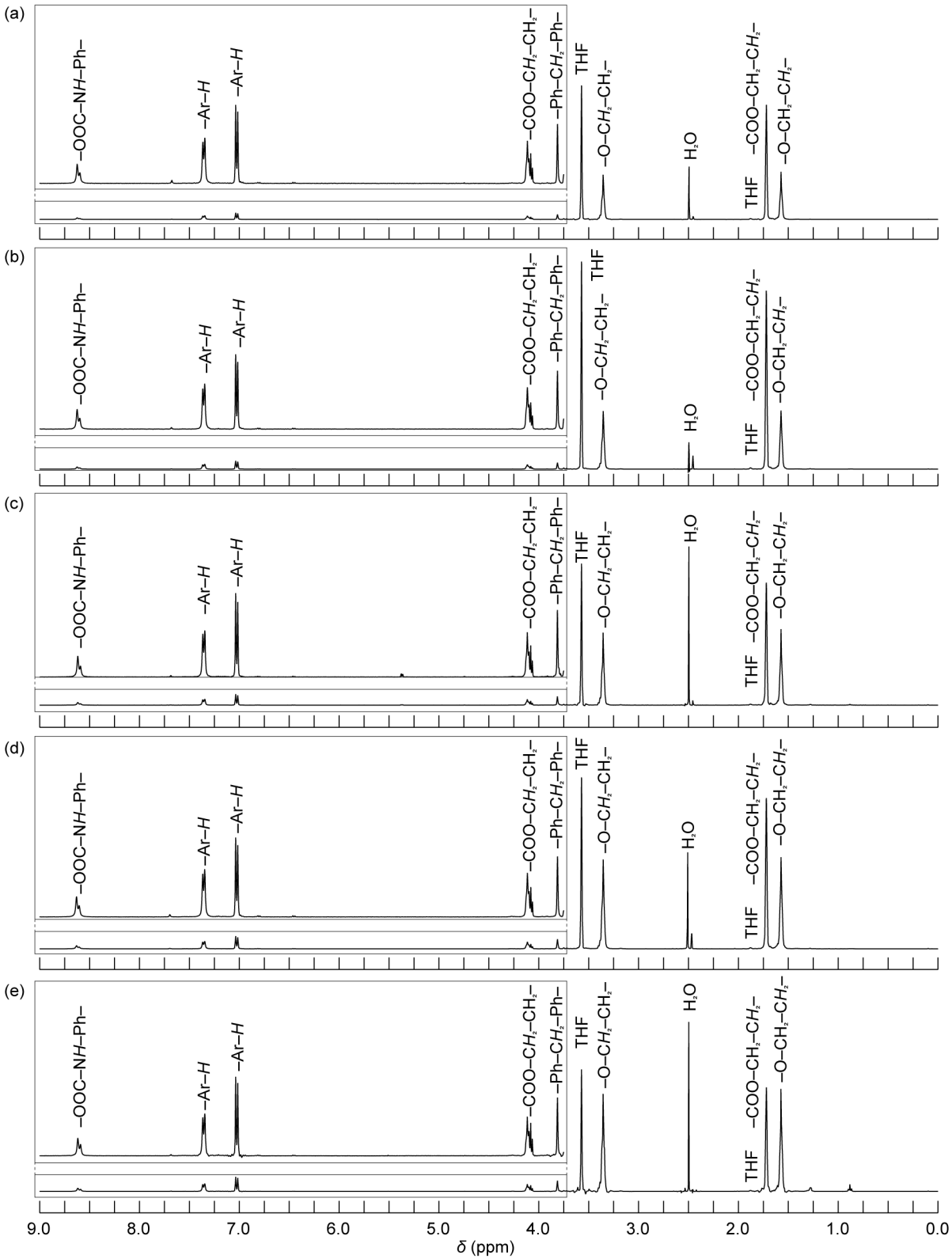


Figure S3. ^{1}H NMR spectra of (a) **Rot1PU**, (b) **Rot2PU**, (c) **Rot3PU**, (d) **Rot4PU**, and (e) **Rot5PU** in THF-d_8. The insets show the expanded spectra in low-magnetic-field regions. The signals were assigned to the protons of polyurethane chain and no signals of the rotaxane mechanophores were observed due to their low concentration in the polymers. All spectra were recorded at r.t.

Absorption and Photoluminescence Spectra of Polyurethanes in Solutions

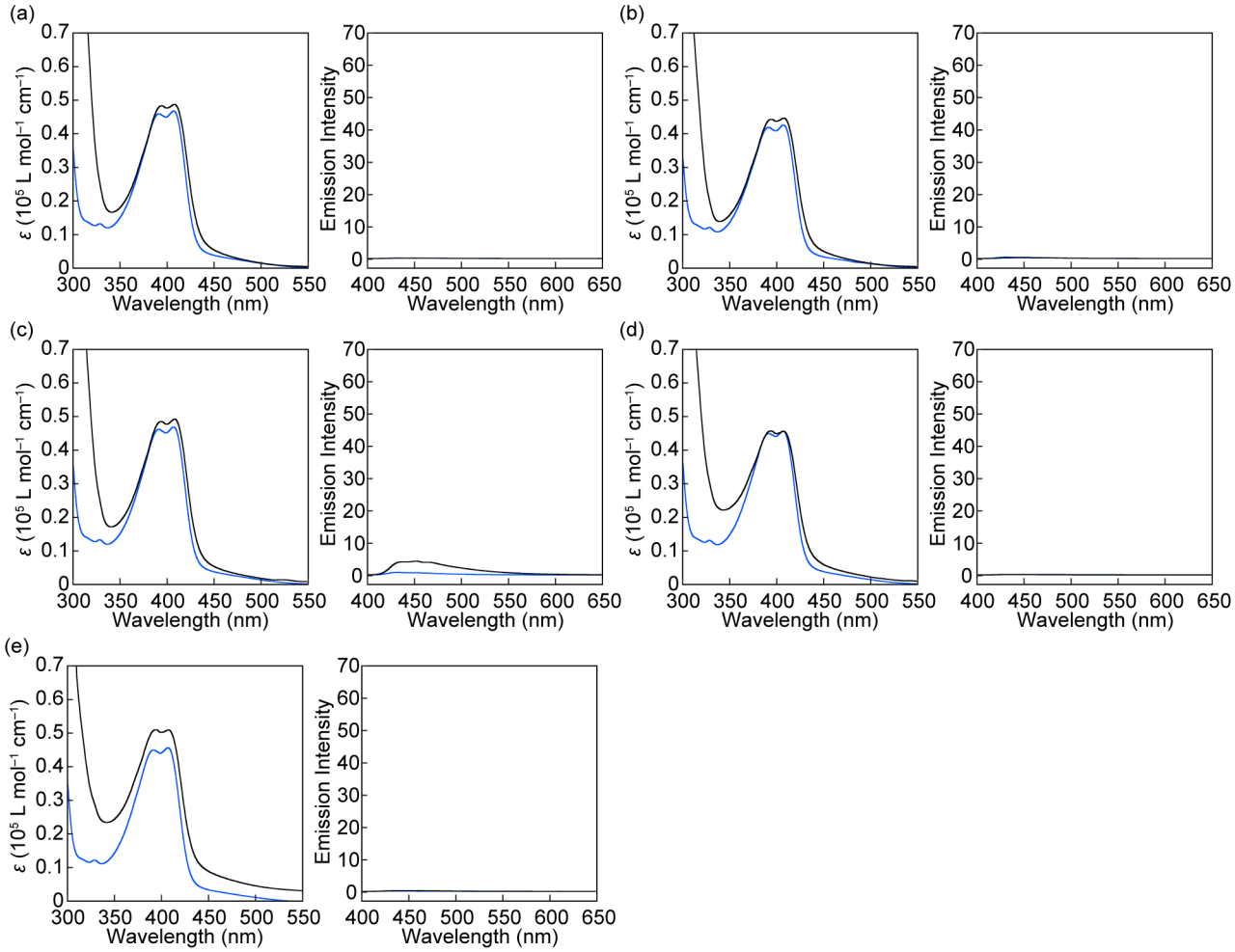


Figure S4. Absorption (left) and photoluminescence (PL, right) spectra of the individual rotaxanes in chloroform (blue lines, $c = 1.0 \times 10^{-5}$ M) and the corresponding polyurethanes in DMF (black lines). (a) **Rot1** and **Rot1PU**, (b) **Rot2** and **Rot2PU**, (c) **Rot3** and **Rot3PU**, (d) **Rot4** and **Rot4PU**, and (e) **Rot5** and **Rot5PU**. All PL spectra were recorded with excitation at 380 nm at r.t.

Thermal Treatment of Rot1 and Rot3 in Toluene

Toluene solutions of **Rot1** and **Rot3** were kept at 90 °C for 3 h. The toluene solutions of **Rot1** and **Rot3** before and after thermal treatment were investigated by fluorescence spectroscopy and high performance liquid chromatography (HPLC).

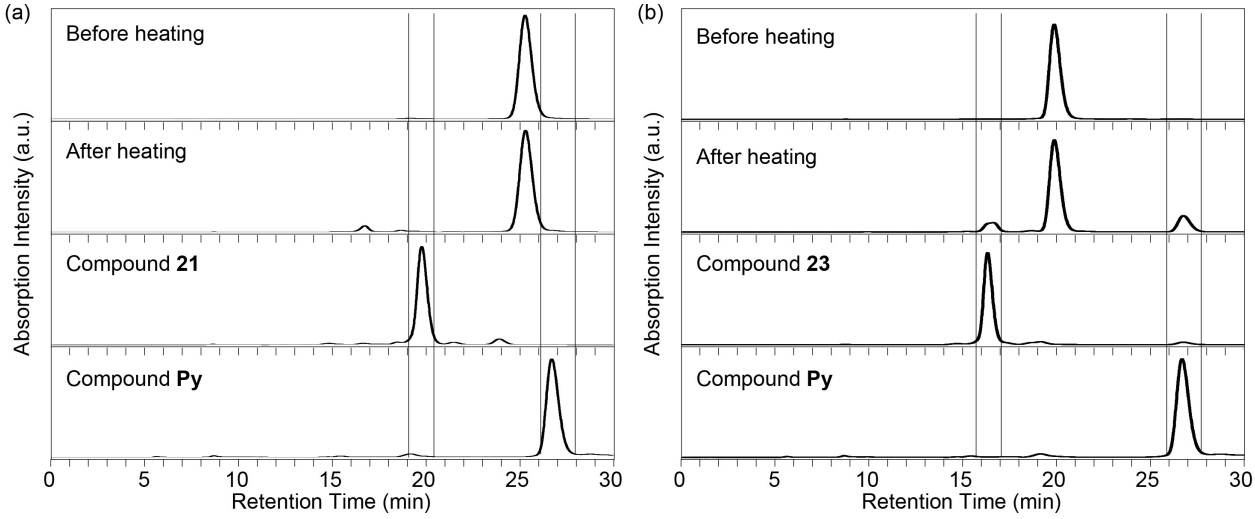


Figure S5. HPLC traces of toluene solutions of (a) **Rot1** and (b) **Rot3** before and after heating the solutions for 3 h at 90 °C. Also shown are the traces of the corresponding axle compounds **21** and **23**, and of the cyclic compound **Py**. Eluent: methanol/isopropanol = 80/20. Flow rate: 0.2 mL/min. Detection wavelength: 254 nm.

Change in the Fluorescence Intensity of Rot3 in THF at Room Temperature

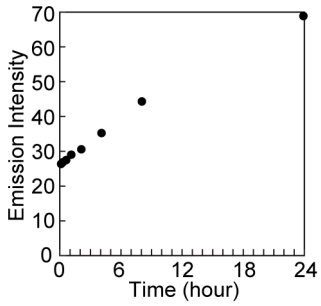


Figure S6. Plots of the fluorescence intensity recorded for **Rot3** in THF as a function of storage time of the solution at r.t. The fluorescence intensities were obtained with excitation at 380 nm at r.t.

Mechanical Properties of Polyurethanes

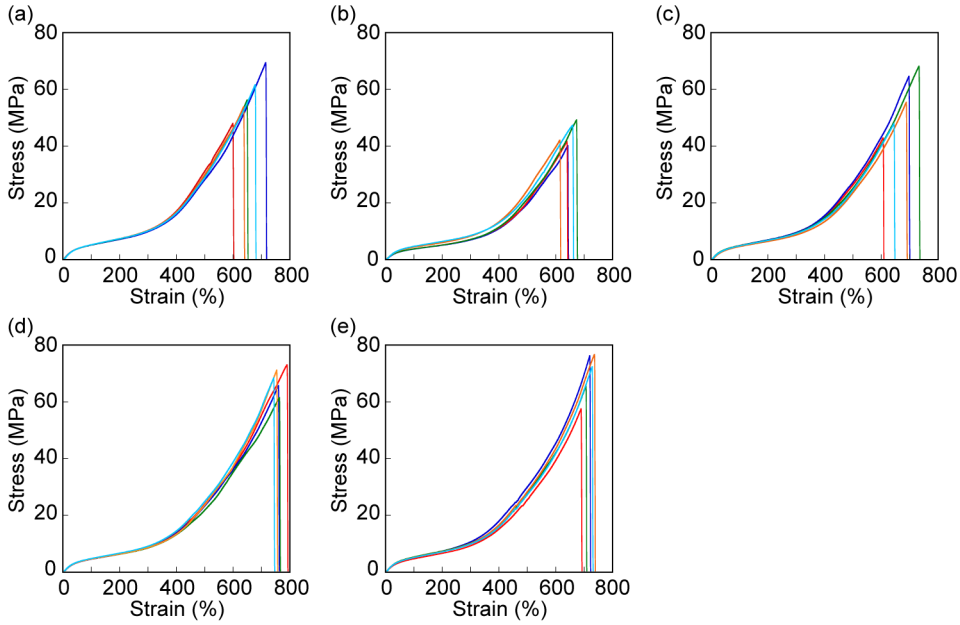


Figure S7. Stress-strain curves of (a) **Rot1PU**, (b) **Rot2PU**, (c) **Rot3PU**, (d) **Rot4PU**, and (e) **Rot5PU** films. Each graph displays data obtained from the three individual specimen. The tests were performed with a strain rate of 300 mm/min at r.t.

Table S1. Overview of mechanical properties of **Rot1PU**, **Rot2PU**, **Rot3PU**, **Rot4PU**, and **Rot5PU** films as determined from stress-strain curves recorded during uniaxial tensile deformation (see Figure S7).[a)]

	Elongation at break (%)	Stress at break (MPa)	Young's modulus (MPa)[b)]
Rot1PU	656 ± 59	57.9 ± 11.6	12.3 ± 0.6
Rot2PU	646 ± 31	44.1± 5.1	9.6 ± 1.1
Rot3PU	674 ± 68	55.8 ± 13.0	11.1 ± 1.5
Rot4PU	763 ± 28	67.9 ± 6.4	11.0 ± 0.5
Rot5PU	717 ± 26	69.7 ± 12.2	12.6 ± 0.8

a) All data were extracted from the stress-strain curves shown in Figure S7 and represent averages of 5 measurements ± standard deviation. b) The Young's moduli were derived from the slopes of the stress-strain curves in the strain regime between 5–10%.

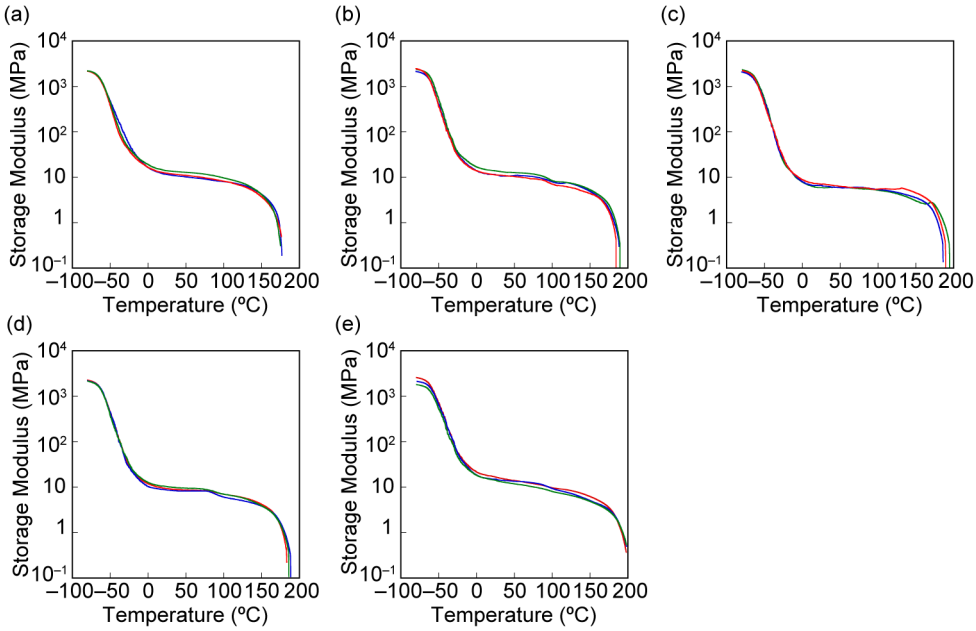


Figure S8. DMA traces of (a) **Rot1PU**, (b) **Rot2PU**, (c) **Rot3PU**, (d) **Rot4PU**, and (e) **Rot5PU** films. Each graph displays data obtained from the three individual specimen. The tests were performed under a N_2 atmosphere with a heating rate of 3 °C/mm, a frequency of 1 Hz, and an amplitude of 15 μm.

Thermal Properties of Polyurethanes

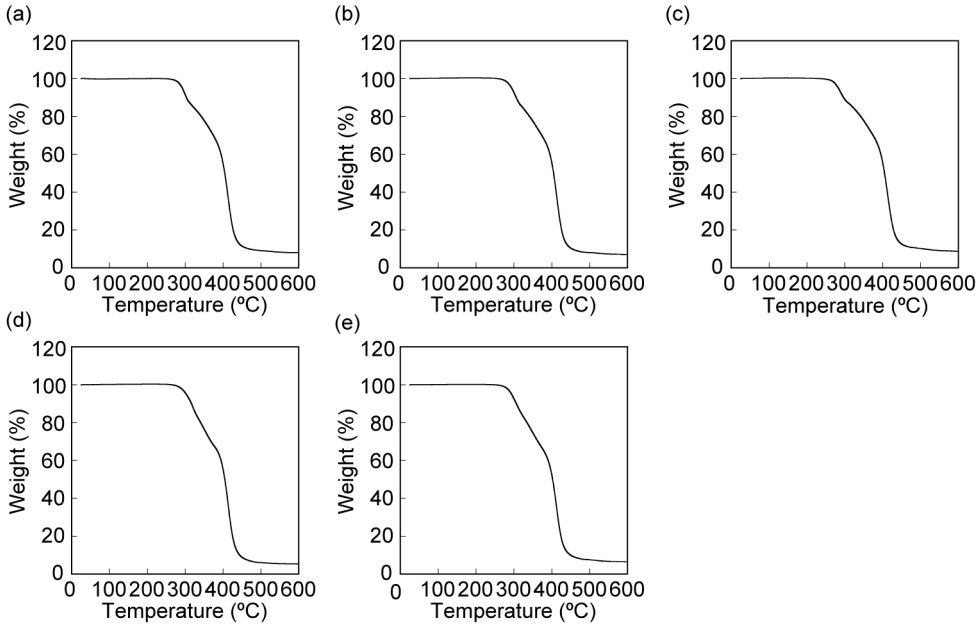


Figure S9. TGA traces of (a) **Rot1PU**, (b) **Rot2PU**, (c) **Rot3PU**, (d) **Rot4PU**, and (e) **Rot5PU**. A heating rate of 10 °C/min was used for all measurements.

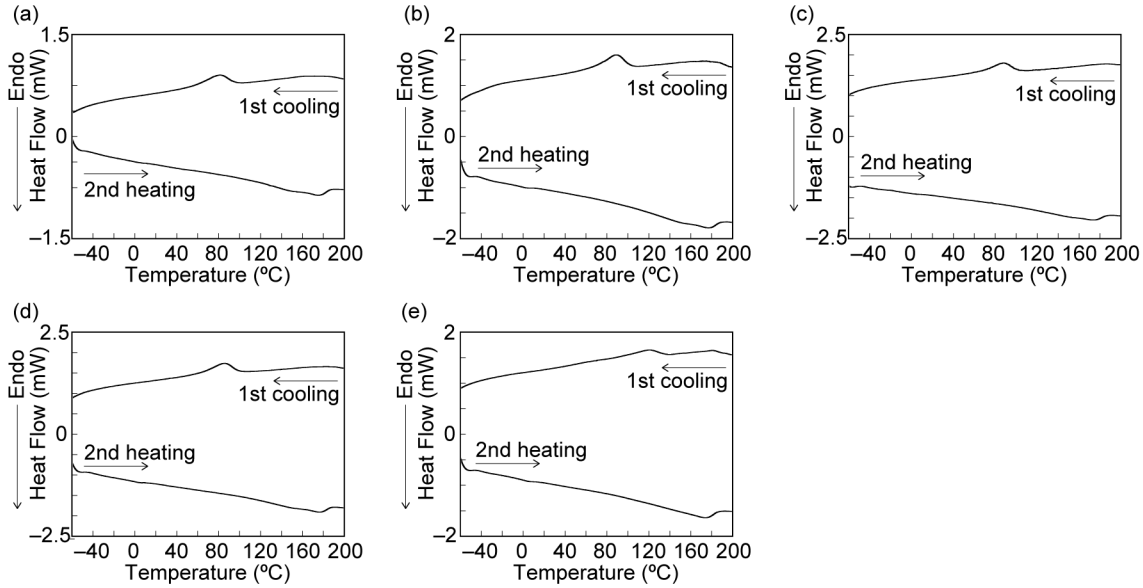


Figure S10. DSC traces of (a) **Rot1PU**, (b) **Rot2PU**, (c) **Rot3PU**, (d) **Rot4PU**, and (e) **Rot5PU**. A heating rate of 10 °C/min was used for all measurements.

MD Simulations

All-atom MD simulations were performed by using MD program GROMACS 2016.3. In the initial structure of the simulated system, the rotaxane was placed near one side of a rectangular MD simulation box and the surrounding space was filled with solvents, diethyl ether (DEE). The sizes of the simulation box were as follows: 12.0 × 6.0 × 6.0 nm^3 for **Rot1** and 10.0 × 6.0 × 6.0 nm^3 for **Rot3** and **Rot4**. The number of DEE molecules were 4940, 4288, and 4288 for **Rot1**, **Rot3**, and **Rot4**, respectively. The generalized Amber force field[S3] parameters were used for calculating inter- and intramolecular interactions. The atomic charges were calculated using the restrained electrostatic potential (RESP)[S4] methodology, based on DFT calculations (B3LYP/6-31G(d,p)) with the GAUSSIAN 16 revision C01 program. Since all bonds connected to hydrogen atoms were constrained with LINCS algorithm[S5], the time step was set to 2 fs. The long-rang Coulomb interactions were calculated with the smooth particle-mesh Ewald[S6] method with a grid spacing of 0.30 nm. The real space cutoff for both Coulomb and van der Waals interactions was 1.4 nm.

As in the usual MD simulations, pre-equilibration runs for 2 ns at 250 K and 2 ns at 300K and equilibration run for 100 ns at 300 K were sequentially performed after the steepest energy minimization. The pressure of the system for all MD simulations was kept at 1 bar.

The steered MD simulations in which the ring molecule was pulled along the specific direction to pass through the stopper of the rod molecule were performed for 10 ns using the structure after the 100 ns equilibration runs. The pulling rates were 0.54 nm ns^{-1} for **Rot1** and 0.45 nm ns^{-1} for **Rot3** and **Rot4**, respectively. The umbrella potential with a force constant of 1,000 kJ mol^{-1} nm^{-2} was applied to the center of the mass of the ring. According to the previous study,[S7] the PMF for each system was obtained from a series of umbrella sampling (US) simulations, where the energy minima of their umbrella potentials were located at equal intervals along the direction of pulling the ring and the calculated probability density distributions were overlapped. The initial positions of a series of the US simulations were selected from the trajectory of the steered MD run. The number of the US simulations was 9 for all the systems. In the US simulation, the 1 ns pre-equilibration and 5 ns equilibration runs were performed using the same umbrella potential as the steered MD. During the steered MD simulations and the US simulations, the system was maintained at 300 K and 1 bar and the atoms of the rod except hydrogen atoms were constrained to the initial positions by a harmonic potential with a force constant of 1,000 kJ mol^{-1} nm^{-2}. The values of the PMF were calculated from each set of the US simulations by the weighted histogram method (WHAM).[S8,S9]

In the MD simulations presented here, the temperature and pressure of the pre-equilibration run were maintained constant using velocity-rescaling thermostat[S10] and Berendsen barostat[S11] with the relaxation times of 0.2 and 2.0 ps, respectively. The Nosé-Hoover thermostat[S12] and Parrinello-Rahman barostat[S6] with the relaxation times of 1.0 and 5.0 ps, respectively, were used for keeping the temperature and pressure of the equilibration run.

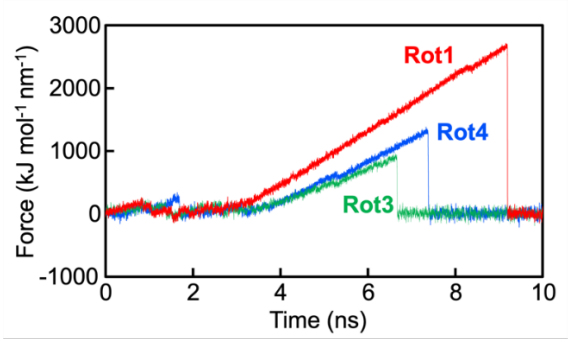


Figure S11. Time profiles of pulling force applied to the ring in the steered MD for **Rot1**, **Rot3**, and **Rot4** represented by red, green, and blue lines, respectively.

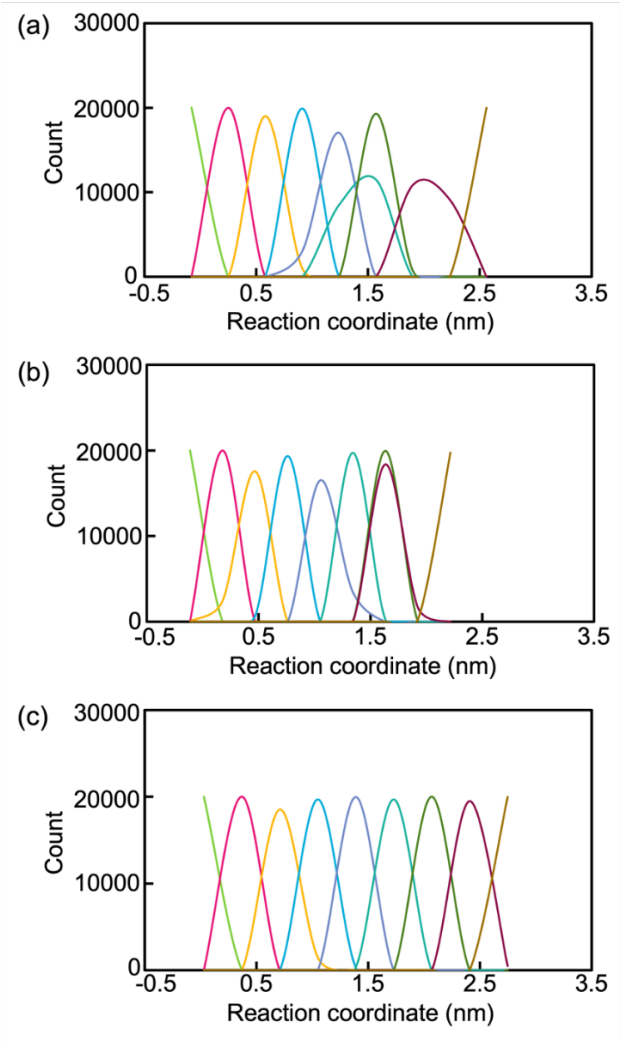


Figure S12. Apparent probability density of (a) **Rot1**, (b) **Rot3**, and (c) **Rot4** in US simulations. The curves drawn in different colors were calculated from each simulation.

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