Pressure effects in the synthesis of isomeric rotaxanes

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Electronic supplementary information

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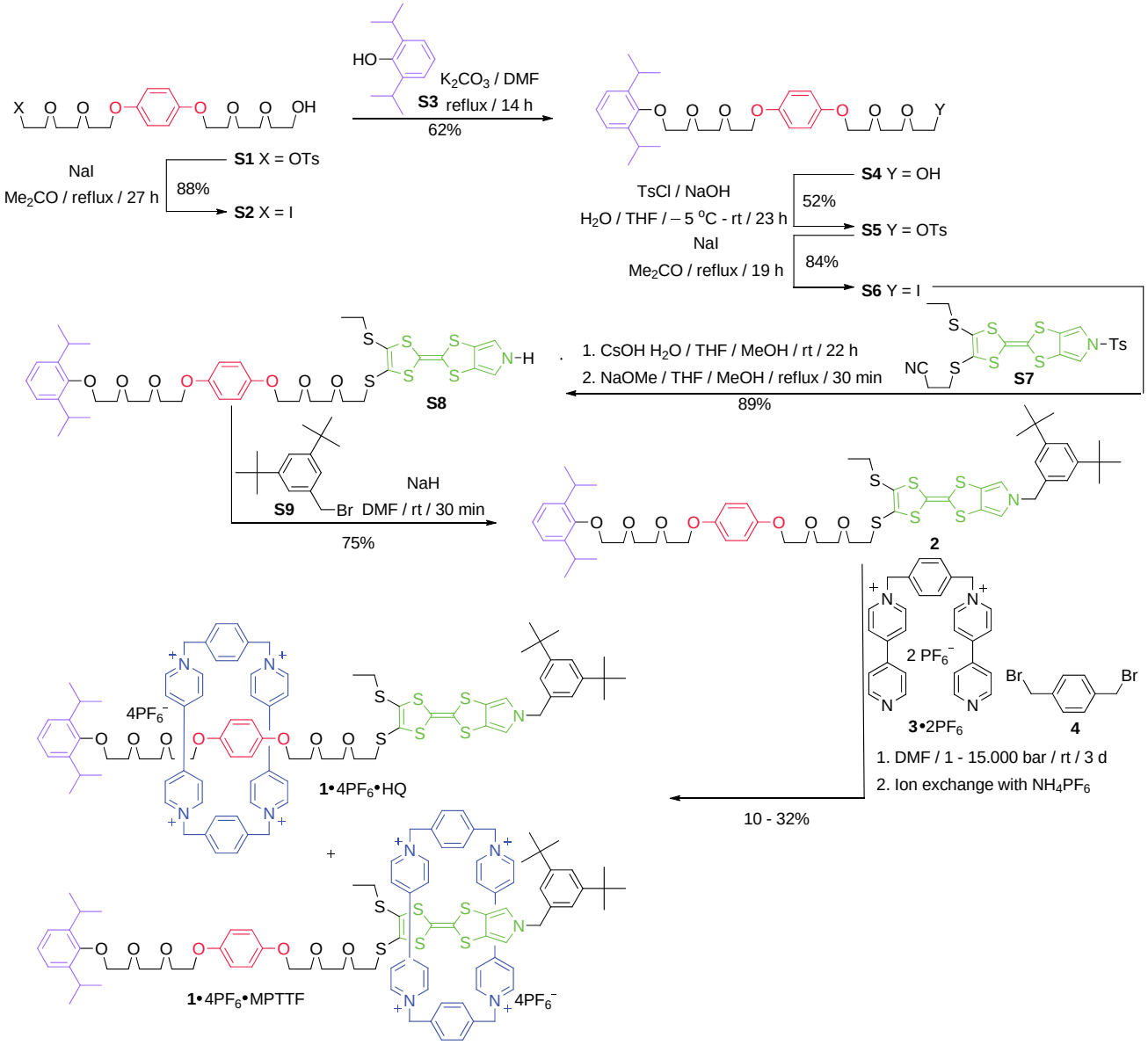
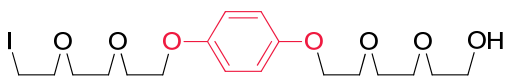
Experimental procedures

General methods

Chemicals were purchased from Sigma-Aldrich or Fluka and were used as received. The compounds, 1,1′′-[1,4-phenylenebis(methylene)]bis(4,4′-bipyridinium) bis(hexafluorophosphate) (**3**•2PF_6),[S1] 1,4-bis(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)benzene (**7**),[S2] cyclobis(paraquat-*p*-phenylene) tetrakis(hexafluorophosphate) (CBPQT•4PF_6),[S1] 1,4-bis-[2-(2-(2-hydroxyethoxy)ethoxy)ethoxy]benzene monotosylate (**S1**),[S3] 2-[4-(2-cyanoethylthio)-5-ethylthio-1,3-dithiole-2-yliden]-5-tosyl-(1,3)-dithiolo[4,5-c]pyrrole (**S7**),[S4] 3,5-di-*t*-butyl-bromomethylbenzene (**S9**),[S5] 1-iodo-2-(2-methoxyethoxy)ethane,[S6] 1-iodo-2-[2-(2-methoxyethoxy)ethoxy]ethane,[S6] and 3-((5-(methylthio)-2-(5-tosyl-5H-[1,3]dithiolo[4,5-*c*]pyrrol-2-ylidene)-1,3-dithiol-4-yl)thio)propanenitrile[S4] were all prepared according to literature procedures. All reactions were carried out under an anhydrous nitrogen atmosphere unless otherwise stated. THF was distilled from Na/benzophenone immediately prior to use, while MeOH was distilled from Mg immediately before use. CH_2Cl_2 was distilled before use. DMF was allowed to stand over molecular sieves (4 Å) for at least 3 days prior to use, while Me_2CO was dried over Drierite for at least 3 days before use. Petroleum ether used had boiling point 60–80 °C. NaI was dried in an oven at 160 °C for 24 h before use. High pressure reactions were performed in a specially made teflon-tube, using a Shicka high pressure apparatus. Thin-layer chromatography (TLC) was carried out using aluminum sheets precoated with silica gel 60F (Merck 5554). The plates were inspected under UV light (254 nm) and, if required, developed in I_2 vapor. Column chromatography was carried out using silica gel 60F (Merck 9385, 0.040–0.063 mm). Melting points (M.p.) were determined on a Büchi melting point apparatus and are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded at room temperature at 400 MHz and 100 MHz, respectively, on a Bruker ADVANCED III spectrometer using residual non- deuterated solvent as the internal standard. The solvent signals were assigned by Nudelman *et al.*[S7] All chemical shifts are quoted on a δ scale, and all coupling constants (J) are expressed in Hertz (Hz). The following abbreviations are used in listing the NMR spectra: s = singlet, bs = broad singlet, d = doublet, t = triplet, q = quartet, and m = multiplet. Samples were prepared using $CDCl_3$, CD_3CN, or CD_3SOCD_3 purchased from Cambridge Isotope Labs or Sigma-Aldrich. Matrix assisted laser-desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MS) was performed on a Bruker Autoflex III Smartbeam mass spectrometer, utilizing a 2,5-dihydroxybenzoic acid matrix, while electrospray ionization mass spectrometry (ESI-MS) was performed on a Thermo Finnigan MAT SSQ710 single stage quadropole mass spectrometer. UV-Vis-NIR spectroscopic data were recorded on a Shimadzu UV-1601PC spectrophotometer. Elemental analyses were performed by the Atlantic Microlabs, Inc., Atlanta, Georgia.

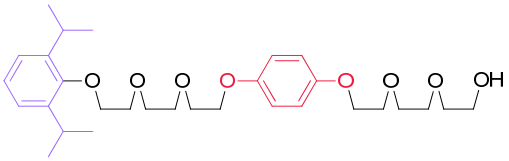
Synthesis of the [2]rotaxane 1•4PF$_6$



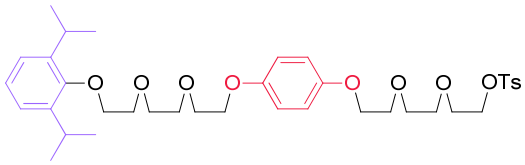


Compound S2. A mixture of the monotosylate **S1** (8.05 g, 2.15 mmol) and anhydrous NaI (9.12 g, 60.8 mmol) in anhydrous Me_2CO (300 mL) was heated under reflux for 27 h, whereafter the reaction mixture was cooled to room temperature. The precipitate was filtered off, washed with Me_2CO (2 × 50 mL), and the combined organic phases were concentrated. The resulting residue was dissolved in CH_2Cl_2 (300 mL), washed with a saturated aqueous solution of $Na_2S_2O_3$ (100 mL), H_2O (3 × 100 mL), and dried ($MgSO_4$). Removal of the solvent gave a yellow oil, which was purified using column chromatography (SiO_2, Me_2CO:petroleum ether 3:1 v/v) affording the title compound **S2** as a bright yellow semi-crystalline compound (6.50 g, 88%). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 2.47 (t, J = 6.2 Hz, 1H, CH_2CH_2OH), 3.26 (t, J = 6.8 Hz, 2H, ICH_2CH_2O), 3.61–3.63 (m, 2H, OCH_2), 3.67–3.78 (m, 12H, 6 × OCH_2), 3.82–3.85 (m, 4H, 2 × OCH_2), 4.07–4.10 (m, 4H, 2 × OCH_2),

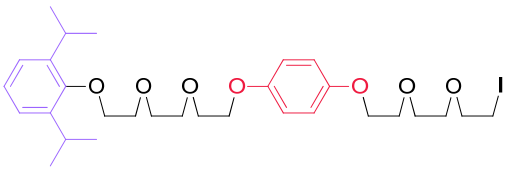
6.84 (s, 4H, 4 × HQ Ar-*H*); ^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ 3.1, 62.0, 68.2, 68.3, 70.1, 70.1, 70.5, 70.6, 71.0 (two lines overlapping), 72.2, 72.8, 115.8 (two lines overlapping), 153.2, 153.3; MS (MALDI–TOF) *m/z* 507 ([M + Na]$^+$, 100), 484 (M^+, 60); MS(HiRes-FT-ESI) calcd for $C_{18}H_{29}IO_7Na^+$ 507.0851; found 507.0853. Anal. Calcd. for $C_{18}H_{29}IO_7$: C, 44.64; H, 6.04. Found: C, 44.80; H, 6.13.



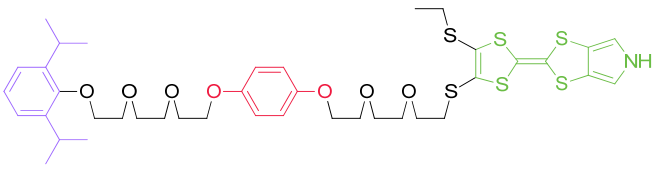
Compound S4. A mixture of **S2** (5.02 g, 4.10 mmol), 2,6-diisopropylphenol (**S3**) (2.01 g, 11.3 mmol), and K_2CO_3 (2.93 g, 2.21 mmol) in anhydrous DMF (100 mL) was heated under reflux for 14 h. After cooling to room temperature, the reaction mixture concentrated and the residue was dissolved in CH_2Cl_2 (200 mL), washed with H_2O (3 × 150 mL), and dried ($MgSO_4$). Removal of the solvent gave a brown oil which was purified using column chromatography (SiO_2, EtOAc) providing the title compound **S4** as a light brown oil (3.46 g, 62%). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 1.21 (d, J = 6.8 Hz, 12H, 2 × CH(C*H*$_3$)$_2$), 2.41 (t, J = 6.2 Hz, 1H, CH_2CH_2O*H*), 3.39 (septet, J = 6.8 Hz, 2H, 2 × C*H*(CH$_3$)$_2$), 3.61–3.63 (m, 2H, OC*H*$_2$), 3.68–3.75 (m, 6H, 3 × OC*H*$_2$), 3.77–3.79 (m, 4H, 2 × OC*H*$_2$), 3.82–3.93 (m, 8H, 4 × OC*H*$_2$), 4.07–4.15 (m, 4H, 2 × OC*H*$_2$), 6.84 (s, 4H, 4 × HQ Ar-*H*), 7.09 (s, 3H, 3 × diisopropyl Ar-*H*); ^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ 24.1, 26.2, 61.8, 68.1, 68.1, 69.9, 70.0, 70.4, 70.6, 70.8, 71.0, 71.1, 72.5, 73.9, 115.6, 115.6, 124.0 (two lines are overlapping), 124.6, 141.9, 153.1, 153.2; MS (MALDI-TOF) *m/z* 557 ([M + Na]$^+$, 100), 534 (M^+, 40); MS(HiRes-FT-ESI) calcd for $C_{30}H_{46}O_8Na^+$ 557.3085; found 557.3082. Anal. Calcd. for $C_{30}H_{46}O_8$•½EtOAc: C, 66.41; H, 8.71. Found: C, 66.66; H 8.72.



Compound S5. A mixture of **S4** (3.22 g, 6.02 mmol) and NaOH (2.26 g, 56.5 mmol) in THF:H_2O (10:1 v/v, 110 mL) was cooled to 0 °C, before a solution of TsCl (1.26 g, 6.62 mmol) in THF (20 mL) was added over a period of 1 h. Subsequently, the reaction mixture was stirred at 0 °C for 8 h and then slowly allowed to reach room temperature. After stirring for additional 14 h at room temperature, the reaction mixture was poured into a mixture of ice and water (50 mL) and then extracted with CH_2Cl_2 (3 × 50 mL). The combined organic phase was washed with a saturated aqueous solution of NaCl (50 mL), H_2O (2 × 50 mL), and dried ($MgSO_4$). Removal of the solvent gave a light brown oil which was purified using column chromatography (SiO_2, EtOAc:petroleum ether 1:2 v/v) affording the title compound **S5** as a light yellow oil (2.16 g, 52%). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 1.21 (d, J = 6.8 Hz, 12H, 2 × CH(C*H*$_3$)$_2$), 2.42 (s, 3H, Ts C*H*$_3$), 3.39 (septet, J = 6.8 Hz, 2H, 2 × C*H*(CH$_3$)$_2$), 3.59–3.62 (m, 2H, OC*H*$_2$), 3.64–3.66 (m, 2H, OC*H*$_2$), 3.68-3.70 (m, 2H, OC*H*$_2$), 3.77–3.80 (m, 6H, 3 × OC*H*$_2$), 3.84−3.93 (m, 4H, 2 × OC*H*$_2$), 4.00–4.11 (m, 4H, 2 × OC*H*$_2$), 4.13–4.18 (m, 4H, 2 × OC*H*$_2$), 6.83 (s, 4H, 4 × HQ Ar-*H*), 7.09 (s, 3H, 3 × diisopropyl Ar-*H*), 7.32 (d, J = 8.2 Hz, 2H, 2 × Ts Ar-*H*), 7.79 (d, J = 8.2 Hz, 2H, 2 × Ts Ar-*H*); ^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ 21.6, 24.1, 26.2, 68.0, 68.1, 68.7, 69.2, 69.9, 70.0, 70.6, 70.7, 70.8, 71.0, 71.1, 73.9, 115.6, 115.6, 124.0 (two lines are overlapping), 124.6, 128.0, 129.8, 133.1, 141.8, 144.8, 153.1, 153.2; MS (MALDI-TOF) *m/z* 711 ([M + Na]$^+$, 100), 688 (M^+, 25); MS(HiRes-FT-ESI) calcd for $C_{37}H_{52}O_{10}SNa^+$ 711.3174; found 711.3180. Anal. Calcd. for $C_{37}H_{52}O_{10}S·H_2O$: C, 62.87; H, 7.70; S, 4.54 Found: C, 63.16; H, 7.47; S 4.75.

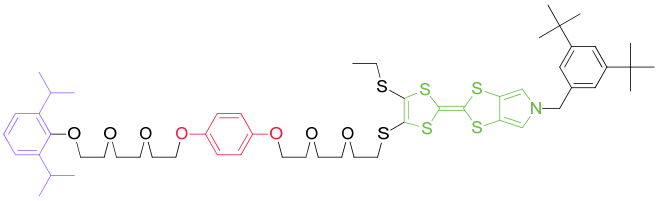


Compound S6. A mixture of the monotosylate **S5** (1.98 g, 2.88 mmol) and anhydrous NaI (1.72 g, 5.11 mmol) in anhydrous Me_2CO (100 mL) was heated under reflux for 19 h, where after the reaction mixture was cooled to room temperature. The precipitate was filtered off, washed with Me_2CO (2 × 25 mL) and the combined organic phases were concentrated. The resulting residue was dissolved in CH_2Cl_2 (75 mL), washed with a saturated aqueous solution of $Na_2S_2O_3$ (50 mL), H_2O (2 × 50 mL), and dried ($MgSO_4$). Removal of the solvent gave a faint yellow oil, which was purified using column chromatography (SiO_2, EtOAc:petroleum ether1:1 v/v) providing the title compound **S6** as a faint yellow oil (1.56 g, 84%). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 1.21 (d, J = 6.8 Hz, 12H, 2 × CH(CH_3)$_2$), 3.26 (t, J = 6.8 Hz, 2H, ICH_2CH$_2$O), 3.39 (septet, J = 6.8 Hz, 2H, 2 × CH(CH$_3$)$_2$), 3.67–3.70 (m, 2H, OCH_2), 3.72–3.75 (m, 2H, OCH_2), 3.76−3.79 (m, 4H, 2 × OCH_2), 3.80–3.89 (m, 6H, 3 × OCH_2), 3.91–3.93 (m, 4H, 2 × OCH_2), 4.07–4.11 (m, 4H, 2 × OCH_2), 6.83 (s, 4H, 4 × HQ Ar-H), 7.09 (s, 3H, 3 × diisopropyl Ar-H); ^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ 3.0, 24.3, 26.4, 68.2, 69.9, 70.1, 70.2, 70.4, 70.8, 71.0, 71.1, 71.2, 72.2, 74.0, 115.7, 115.7, 124.1 (two lines are overlapping), 124.7, 142.0, 153.2, 153.3; MS (MALDI-TOF) m/z 667 ([M + Na]$^+$, 100), 644 (M$^+$, 72); MS(HiRes-FT-ESI) calcd for $C_{30}H_{45}IO_7Na^+$ 667.2103; found 667.2098. Anal. Calcd. for $C_{30}H_{45}IO_7$•H_2O: C, 54.38; H 7.15. Found: C, 54.64; H, 6.98.

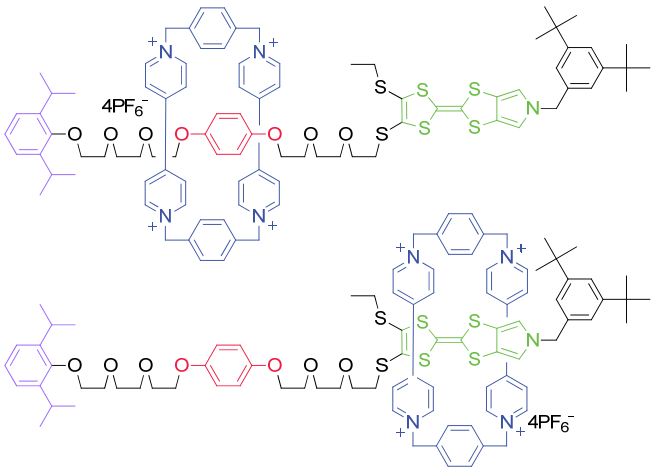


Compound S8. A solution of compound **S6** (619 mg, 0.96 mmol) and the MPTTF compound **S7** (543 mg, 0.93 mmol) in anhydrous THF (100 mL) was degassed (N_2, 15 min) before a solution of CsOH·H_2O (162 mg, 0.97 mmol) in anhydrous MeOH (0.5 mL) was added over a period of 4 h at room temperature. Thereafter, the reaction mixture was stirred for 22 h before the solvent was removed in vauco. The resulting residue was dissolved in CH_2Cl_2 (100 mL), washed with H_2O (3 × 150 mL), and dried ($MgSO_4$). Removal of the solvent gave a yellow oil, which was purified using gradient-column chromatography (SiO_2, *i*) CH_2Cl_2 *ii*) CH_2Cl_2: EtOAc 1:1 v/v). A mixture of the tosylated and detosylated product was collected, whereupon the solvent was removed to give a yellow oil. This mixture was suspended in anhydrous THF:MeOH (1:1 v/v, 150 mL) and degassed (N_2, 15 min) before NaOMe (25% v/v MeOH, 3 mL, 708 mg, 14.0 mmol) was added in one portion, whereupon the reaction mixture was heated under reflux for 30 min. After being cooled to room temperature, the solvent was removed in vauco and the residue was dissolved in CH_2Cl_2 (150 mL), washed with H_2O (3 × 100 mL), and dried ($MgSO_4$). Removal of the solvent gave a yellow oil, which was purified using column chromatography (SiO_2, CH_2Cl_2:EtOAc 10:1 v/v) to afford the title compound **S8** as an orange oil (730 mg, 89%). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 1.20 (d, J = 6.8 Hz, 12H, 2 × CH(CH_3)$_2$), 1.30 (t, J = 7.4 Hz, 3H, CH$_2$CH_3), 2.85 (q, J = 7.4 Hz, 2H, CH_2CH$_3$), 3.01 (t, J = 6.8 Hz, 2H, OCH$_2$CH_2S), 3.38 (septet, J = 6.8 Hz, 2H, 2 × CH(CH$_3$)$_2$), 3.65–3.72 (m, 4H, 2 × OCH_2), 3.76–3.88 (m, 12H, 6 × OCH_2), 3.91-3.93 (m, 2H, OCH_2), 4.05–4.09 (m, 4H, 2 × OCH_2), 6.56 (d, J = 2.8 Hz, 2H, 2 × pyrrole α-H), 6.82 (s, 2H, 2 × HQ Ar-H), 6.83 (s, 2H, 2 × HQ Ar-H), 7.09 (s, 3H, 3 × diisopropyl Ar-H), 8.50 (bs, 1H, NH); ^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ 15.2, 24.3, 26.4, 30.6, 35.5, 68.2, 68.2, 70.1, 70.2, 70.3, 70.7, 70.7, 70.9, 71.0, 71.2, 74.0, 115.7, 115.7, 124.0, 124.2 (two lines are overlapping), 124.8, 126.6, 128.5, 142.0, 153.1, 153.2 (two lines are overlapping); MS (MALDI-TOF) m/z 874 ([M + Na]$^+$, 8), 851 (M$^+$, 100); MS(HiRes-FT-ESI) calcd for

$C_{40}H_{53}NO_7S_6Na^+$ 874.2038; found 874.2040. Anal. Calcd. for $C_{40}H_{53}NO_7S_6 \bullet ½CH_2Cl_2$: C, 54.37; H, 6.08; N, 1.57; S, 21.50. Found: C, 54.51; H, 6.08; N, 1.60; S, 21.83.



Dumbbell 2. A solution of compound **S8** (424 mg, 0.50 mmol) in anhydrous DMF (50 mL) was degassed (N_2, 15 min) before NaH (55–65% v/v in mineral oil, 398 mg, 9.95 mmol) was added in one portion. Subsequently, the reaction mixture was stirred at room temperature for 15 min, where after 3,5-di-*t*-butyl-bromomethylbenzene (**S9**) (156 mg, 0.55 mmol) was added. The reaction mixture was stirred for another 15 min at room temperature before the reaction was terminated by carefully and slowly addition of H_2O (50 mL). The resulting yellow mixture was extracted with CH_2Cl_2 (4 × 50 mL), and the combined organic phases were washed with H_2O (4 × 50 mL), a saturated aqueous solution of NaCl (50 mL), H_2O (4 × 50 mL), and dried ($MgSO_4$). Removal of the solvent gave a yellow oil, which was purified by column chromatography (SiO_2, CH_2Cl_2:EtOAc 20:1 v/v) providing the dumbbell **2** as an orange oil (394 mg, 75%). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 1.21 (d, J = 6.8 Hz, 12H, 2 × CH(CH_3)$_2$), 1.29 (m, 21H, CH_2CH_3 + 2 × C(CH_3)$_3$), 2.84 (q, J = 7.4 Hz, 2H, CH_2CH_3), 3.00 (t, J = 6.8 Hz, 2H, OCH$_2CH_2$S), 3.39 (septet, J = 6.8 Hz, 2H, 2 × CH(CH_3)$_2$), 3.65–3.72 (m, 4H, 2 × OCH_2), 3.78–3.88 (m, 12H, 6 × OCH_2), 3.91–3.93 (m, 2H, OCH_2), 4.05–4.10 (m, 4H, 2 × OCH_2), 4.95 (bs, 2H, NCH_2), 6.49 (s, 2H, 2 × *t*-Bu Ar-*H*), 6.83 (s, 2H, 2 × HQ Ar-*H*), 6.84 (s, 2H, 2 × HQ Ar-*H*), 6.99 (s, 2H, 2 × pyrrole α-*H*), 7.09 (s, 3H, 3 × diisopropyl Ar-*H*), 7.37 (s, 1H, *t*-Bu Ar-*H*); ^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ 15.2, 24.3, 26.4, 30.6, 31.6, 35.0, 35.5, 68.2, 68.2, 70.1, 70.2, 70.2, 70.7, 70.7, 70.9, 71.1, 71.2, 74.0, 115.7, 115.7, 119.2, 121.9, 122.3, 124.1 (two lines are overlapping), 124.7, 142.0, 151.6, 153.2, 153.2 (seven signals are overlapping); MS (MALDI-TOF) *m/z* 1076 ([M + Na]$^+$, 7), 1053 (M$^+$, 100); MS(HiRes-FT-ESI) calcd for $C_{55}H_{75}NO_7S_6Na^+$ 1076.3760; found 1076.3761. Anal. Calcd. for $C_{55}H_{75}NO_7S_6$: C, 62.64; H, 7.17; N, 1.33; S, 18.24. Found: C, 62.53; H, 6.96; N, 1.26; S, 17.96.



[2]Rotaxanes 1•4PF$_6$•HQ and 1•4PF$_6$•MPTTF. *General procedure*: A solution of the dumbbell **2** (30 mM, 1 eq.), 1,1′′-[1,4-phenylenebis-(methylene)]bis(4,4′-bipyridinium) bis(hexafluorophosphate) (**3**•2PF$_6$) (3 eq.), and 1,4-bis(bromomethyl)benzene (**4**) (3 eq.) in anhydrous DMF was transferred to a teflon-tube and subjected to the desired pressure ($1 - 15 \times 10^{-3}$ bar) at room temperature for 3 d. The suspension was directly subjected to column chromatography (SiO_2) and unreacted dumbbell was eluted with Me_2CO, whereupon the eluent was changed to Me_2CO/NH_4PF_6 (1 g NH_4PF_6 in 100 mL Me_2CO) and the coloured band containing the [2]rotaxane **1**•4PF$_6$ was collected. The fractions containing the [2]rotaxane **1**•4PF$_6$ was concentrated in vauco to a volume of approximately 15 mL, before H_2O (50 mL) was added. The suspension was cooled on an ice-bath for 30 min and the resulting precipitate was collected by filtration, washed with H_2O (3 × 10 mL) and Et_2O (2 × 10 mL) affording the [2]rotaxane **1**•4PF$_6$ as a coloured solid.

Experiment A. Dumbbell **2** (301 mg, 0.29 mmol), **3**•2PF_2 (609 mg, 0.86 mmol), and the dibromide **4** (288 mg, 0.86 mmol) were dissolved in anhydrous DMF (10 mL), whereupon the reaction mixture was stirred at room temperature at 1 bar. Yields:[S8] **1**•4PF_6•HQ (43mg, 7%); **1**•4PF_6•MPTTF (16mg, 3%).
Experiment B. Dumbbell **2** (100 mg, 0.10 mmol), **3**•2PF_2 (201 mg, 0.28 mmol), and the dibromide **4** (64.8 mg, 0.28 mmol) were dissolved in anhydrous DMF (3 mL), and then subjected to 5 kbar of pressure at room temperature. Yields:[S8] **1**•4PF_6•HQ (33 mg, 16%); **1**•4PF_6•MPTTF (30 mg, 15%).
Experiment C. Dumbbell **2** (105 mg, 0.10 mmol), **3**•2PF_2 (210 mg, 0.30 mmol), and the dibromide **4** (69 mg, 0.29 mmol) were dissolved in anhydrous DMF (3 mL), and then subjected to 10 kbar of pressure at room temperature. Yields:[S8] **1**•4PF_6•HQ (27 mg, 12 %); **1**•4PF_6•MPTTF (42 mg, 20 %).
Experiment D. Dumbbell **2** (300 mg, 0.28 mmol), **3**·2PF_2 (609 mg, 0.86 mmol), and the dibromide **4** (228 mg, 0.86 mmol) were dissolved in anhydrous DMF (10 mL), and then subjected to 15 kbar of pressure at room temperature. Yields:[S8] **1**•4PF_6•HQ (50 mg, 8 %); **1**•4PF_6•MPTTF (141 mg, 23 %).

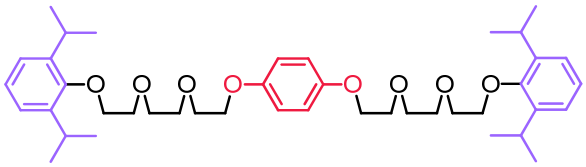
For experiments A–D similar analytical data were obtained. The following analytical data are for the mixture of the two isomeric [2]rotaxanes **1**•4PF_6•HQ and **1**•4PF_6•MPTTF. MS (ESI) *m/z* 932 ([M – 2PF_6]$^{2+}$), 572 ([M – 3PF_6]$^{3+}$), 524 ([M – 4PF_6]$^{3+}$), 465 ([M − 2PF_6]$^{4+}$), 393 ([M − 4PF_6]$^{4+}$);. MS(HiRes-FT-ESI) calcd. for [$C_{91}H_{107}F_{24}N_5O_7P_4S_6$–3$PF_6$]$^{3+}$ 572.8707; found 572.8708. Anal. Calcd for $C_{91}H_{107}F_{24}N_5O_7P_4S_6$: C, 50.72; H, 5.00; N, 3.25; S, 8.93. Found: C, 50.50; H, 5.04; N, 3.31; S, 8.93.

*Separation of the isomeric [2]rotaxanes **1**•4PF_6•HQ and **1**•4PF_6•MPTTF*.
The two isomers of **1**•4PF_6 were separated using preparative thin layer chromatography (PTLC), which was performed at room temperature using Me_2CO/NH_4PF_6 (1.0 g NH_4PF_6 in 100 mL Me_2CO) as the eluent. After eluation, the green band containing **1**•4PF_6•MPTTF was extracted into Me_2CO. The solvent was removed in vauco, and the residue was dissolved in MeCN, providing a green solution, which was evaporated in vauco to give **1**•4PF_6•MPTTF as a green solid. Data for **1**•4PF_6•MPTTF. ^{1}H NMR (400 MHz, CD_3CN, 298 K) δ 1.17 (d, J = 6.8 Hz, 12H, 2 × CH(CH_3)$_2$, 1.40 (s, 18H, 2 × C(CH_3)$_3$), 1.51 (t, J = 7.4 Hz, 3H, CH_3CH$_2$), 3.03 (q, J = 7,4 Hz, 2H, CH$_3$CH_2), 3.17 (t, J = 6.2 Hz, 2H, OCH$_2$CH_2S), 3.39 (septet, J = 6.8 Hz, 2H, 2 × CH(CH$_3$)$_2$), 3.51–3.69 (m, 12H, 6 × OCH_2), 3.77–3.82 (m, 4H, 2 × OCH_2), 3.84–3.91 (m, 4H, 2 × OCH_2), 4.00–4.01 (m, 2H, OCH_2), 5.19 (bs, 2H, NCH_2), 5.71 (s, 4H, 2 × N$^+$CH_2), 5.73 (s, 4H, 4 × N$^+$CH_2), 6.56 (d, J = 9.0 Hz, 2H, 2 × HQ Ar-*H*), 6.64 (s, 2H, 2 × pyrrole α-*H*), 6.71 (d, J = 9.0 Hz, 2H, 2 × HQ Ar-*H*), 7.06–7.14 (m, 3H, 3 × diisopropyl Ar-*H*), 7.27 (s, 2H, 2 × *t*-Bu Ar-*H*), 7.54 (s, 1H, *t*-Bu Ar-*H*), 7.57 (bs, 4H, 4 × β-*H*), 7.73 (s, 4H, 4 × xylyl-*H*), 7.74 (s, 4H, 4 × xylyl-*H*), 7.98 (bs, 4H, 4 × β-*H*), 8.82 (bs, 4H, 4 × α-*H*), 8.99 (bs, 2H, 2 × α-*H*), 9.05 (bs, 2H, 2 × α-*H*).

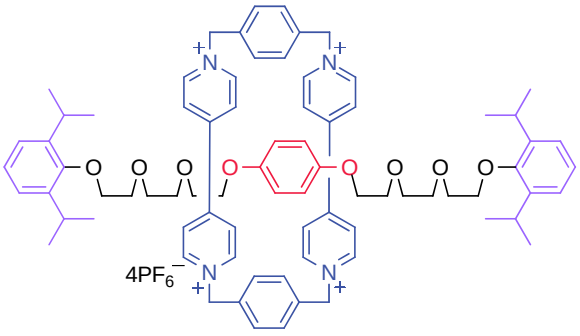
Since **1**•4PF_6•HQ is more polar than **1**•4PF_6•MPTTF, it was not possible to obtain a pure fraction of **1**•4PF_6•HQ from the above PTLC experiment. However, it was possible to isolate a mixture of **1**•4PF_6•HQ and **1**•4PF_6•MPTTF with a ratio of 81:19 in favor of **1**•4PF_6•HQ. Data given below are for **1**•4PF_6•HQ obtained from this mixture. Data for **1**•4PF_6•HQ. ^{1}H NMR (400 MHz, CD_3CN, 298 K) δ 1.11 (d, J = 6.8 Hz, 12H, 2 × CH(CH_3)$_2$, 1.40 (s, 18H, 2 × C(CH_3)$_3$), 1.50 (t, J = 7.4 Hz, 3H, CH_3CH$_2$), 3.03 (q, J = 7.4 Hz, 2H, CH$_3$CH_2), 3.17 (t, J = 6,2 Hz, 2H, OCH$_2$CH_2S), 3.32 (septet, J = 6.8 Hz, 2H, 2 × CH(CH$_3$)$_2$), 3.56–3.59 (m, 12H, 6 × OCH_2), 3.65–3.70 (m, 4H, 2 × OCH_2), 3.74-3.86 (m, 4H, 2 × OCH_2), 3.89–4.00 (m, 2H, OCH_2), 4.03 (s, 4H, 4 × HQ Ar-*H*), 5.18 (bs, 2H,

NCH_2), 5.63–5.81 (m, 8H, 4 × N$^+$CH_2), 6.65 (s, 2H, 2 × pyrrole α-*H*), 7.04−7.11 (m, 3H, 3 × diisopropyl Ar-*H*), 7.13 (d, *J* = 1.6 Hz, 2H, 2 × *t*-Bu Ar-*H*), 7.39 (t, *J* = 1.6 Hz, 1H, *t*-Bu Ar-*H*), 7.81–7.83 (m, 16H, 8 × xylyl-*H* + 8 × β-*H*), 8.91–8.93 (m, 8H, 8 × α-*H*).

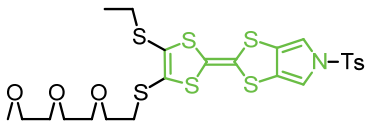
Syntheses of the [2]rotaxanes 5•4PF$_6$ and 6•4PF$_6$



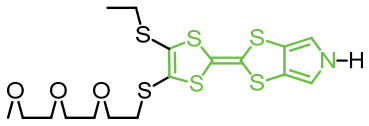
Dumbbell S10. A mixture of 1,4-bis[2-(2-(2-hydroxyethoxy)ethoxy)ethoxy]benzene ditosylate[S9] (1.02 g, 1.50 mmol), 2,6-diisopropylphenol (**S3**) (603 mg, 3.38 mmol), and K_2CO_3 (950 mg, 6.87 mmol) in anhydrous DMF (25 mL) was heated under reflux for 22 h. After cooling to room temperature, the reaction mixture was concentrated in vauco. The residue was dissolved in CH_2Cl_2 (50 mL), washed with H_2O (2 × 50 mL), and dried ($MgSO_4$). Removal of the solvent gave a bright yellow oil, which was purified using gradient-column chromatography (SiO_2, *i*) CH_2Cl_2, *ii*) CH_2Cl_2:EtOAc 1:1 v/v) to give the dumbbell compound **S10** as a faint yellow oil (724 mg, 69%). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) *δ* 1.22 (d, *J* = 6.8 Hz, 24H, 4 × CH(CH_3)$_2$), 3.39 (septet, *J* = 6.8 Hz, 4H, 4 × C*H*(CH$_3$)$_2$), 3.76–3.79 (m, 8H, 4 × OCH_2), 3.85–3.89 (m, 8H, 4 × OCH_2), 3.91–3.93 (m, 4H, 2 × OCH_2), 4.08–4.10 (m, 4H, 2 × OCH_2), 6.83 (s, 4H, 4 × HQ Ar-*H*), 7.09 (s, 6H, 6 × diisopropyl Ar-*H*); ^{13}C NMR (100 MHz, $CDCl_3$, 298 K) *δ* 24.1, 26.2, 68.1, 70.0, 70.6, 71.0 , 71.1, 73.9, 115.6, 124.0, 124.6, 141.9, 153.1, 153.2; MS(HiRes-FT-ESI) calcd for $C_{42}H_{62}O_8Na$ 717.4338; found 717.4336. Anal. Calcd. for $C_{42}H_{62}O_8$•½EtOAc: C, 71.51; H, 9.00; O, 19.49. Found: C, 71.45; H, 8.97; O 19.86.



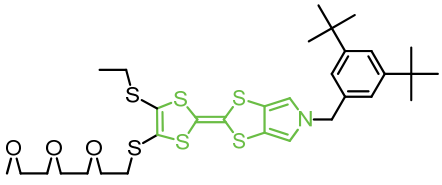
[2]Rotaxane 5•4PF$_6$. A solution of dumbbell **S10** (187 mg, 0.27 mmol), **3**•2PF$_2$ (706 mg, 0.80 mmol), and **4** (195 mg, 0.86 mmol) in anhydrous DMF (9 mL) was subjected to a pressure of 10 kbar at room temperature for 3 d. The suspension was directly subjected to column chromatography (SiO_2) and unreacted dumbbells were eluted with Me_2CO, whereupon the eluent was changed to Me_2CO/NH_4PF_6 (1 g NH_4PF_6 in 100 mL Me_2CO). A red colored band containing **5**•4PF$_6$ was collected and concentrated in vauco to a volume of approximately 15 mL before H_2O (50 mL) was added. The suspension was cooled on an ice bath for 30 min and the resulting precipitate was collected by filtration, washed with H_2O (3 × 10 mL) and Et_2O (2 × 10 mL) to give [2]rotaxane **5**•4PF$_6$ as a red powder (54.7 mg, 0.03 mmol, 11 %). M.p. > 250 °C; ^{1}H NMR (400 MHz, CD_3CN, 298 K): *δ* 1.14 (d, *J* = 6.8 Hz, 24H, 4 × CH(CH_3)$_2$, 3.34 (septet, , *J* = 6.8 Hz, 4H, 4 × C*H*(CH$_3$)$_2$), 3.60 (s, 4H, 2 × OCH_2), 3.69 – 3.70 (m, 4H, 2 × OCH_2), 3.96 – 3.97 (m, 8H, 4 × OCH_2), 4.01 – 4.03 (m, 4H, 2 × OCH_2), 4.06 (s, 8H, 4 × HQ Ar-*H* + 2 × OCH_2), 5.75 (s, 8H, 4 × N$^+$CH_2), 7.07 – 7.14 (m, 6H, 6 × diisopropyl Ar-*H*), 7.84 – 7.86 (m, 16H, 8 × xylyl-*H* + 8 × β-*H*), 8.98 (d, *J* = 7.0 Hz, 8H, 8 × α-*H*); MS(ESI): *m/z* (%) 752 ([M – 2PF$_6$]$^{2+}$), 453 ([M – 3PF$_6$]$^{3+}$), 404 ([M – 4PF$_6$]$^{3+}$), 303 ([M – 4PF$_6$]$^{4+}$); MS(HiRes-FT ESI) calcd for $C_{78}H_{94}F_6N_4O_8P$ 453.2225; found: 453.2222; Anal. Calcd for $C_{78}H_{98}F_{24}N_4O_{10}P_4$ (**5**•4PF$_6$•2H_2O): C, 51.15; H, 5.39; N, 3.03; O, 8.74. Fould: C, 51.43; H, 5.34; N, 3.10; O, 8.53.



Compound S11. A solution of MPTTF compound **S7** (996 mg, 1.84 mmol) in anhydrous THF (150 mL) was degassed (N_2, 15 min) before a solution of CsOH•H_2O (323 mg, 1.92 mmol) in anhydrous MeOH (1.0 mL) was added over a period of 1 h at room temperature. Subsequently, 1-iodo-2-[2-(2-methoxyethoxy)ethoxy]ethane (525 mg, 1.92 mmol) was added in one portion, whereafter the reaction mixture was stirred for 5 h before the solvent was evaporated in vauco. The resulting residue was dissolved in CH_2Cl_2 (150 mL), washed with H_2O (3 × 150 mL), and dried ($MgSO_4$). Removal of the solvent gave a yellow oil, which was purified using gradient-column chromatography (SiO_2, *i*) CH_2Cl_2 *ii*) CH_2Cl_2:MeOH 98:2 v/v) providing the title compound **S11** as an yellow oil (956 mg, 82%). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 1.30 (t, J = 7.4 Hz, 3H, CH_3CH$_2$), 2.41 (s, 3H, Ts-CH_3), 2.84 (q, J = 7.4 Hz, 2H, CH$_3$CH_2), 2.99 (t, J = 6.8 Hz, 2H, OCH$_2$CH_2S), 3.37 (s, 3H, CH_3O), 3.52−3.55 (m, 2H, OCH_2), 3.63−3.68 (m, 8H, 4 × OCH_2), 6.93 (s, 2H, 2 × pyrrole α-*H*), 7.30 (d, J = 8.4 Hz, 2H, 2 ×Ts Ar-*H*), 7.72 (d, J = 8.4 Hz, 2H, 2 × Ts Ar-*H*); ^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ 15.1, 21.7, 30.5, 35.4, 59.0, 70.0, 70.5, 70.6, 70.6, 71.9, 111.3, 114.8, 116.8, 126.6, 127.0, 127.2, 127.2, 128.5, 130.1, 135.4, 145.5 (two signals are overlapping); MS (ESI) *m/z* 658 ([M + Na]$^+$), 636 ([M + H]$^+$), 481([M - Ts + H]$^+$); MS(HiRes-FT-ESI) calcd for $C_{24}H_{29}NO_5S_7Na$ 657.9983; found 657.9972; Anal. Calcd. for $C_{24}H_{29}NO_5S_7$: C, 45.33; H, 4.60; O, 2.20; S, 35.29. Found: C, 45.40; H, 4.62; O, 2.26; S 35.08.

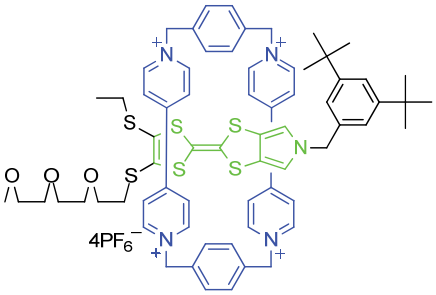


Compound S12. A solution of MPTTF compound **S11** (894 mg, 1.41 mmol) in anhydrous THF:MeOH (1:1 v/v 250 mL) was degassed (N_2, 15 min) before NaOMe (25–30% v/v MeOH, 3 mL, 708 mg, 14.0 mmol) was added in one portion, whereupon the reaction mixture was heated under reflux for 30 min. After being cooled to room temperature, the solvent was removed in vauco and the residue was dissolved in CH_2Cl_2 (100 mL), washed with H_2O (2 × 150 mL), and dried ($MgSO_4$). Removal of the solvent gave a yellow oli, which was purified by column chromatography (SiO_2, CH_2Cl_2:EtOAc 9:1 v/v) to give the title compound **S12** as a yellow semi-crystalline compound (600 mg, 89%). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 1.31 (t, J = 7.4 Hz, 3H, CH_3CH$_2$), 2.86 (q, J = 7.4 Hz, 2H, CH$_3$CH_2), 3.01 (t, J = 6.8 Hz, 2H, OCH$_2$CH_2S), 3.37 (s, 3H, CH_3O), 3.53−3.55 (m, 2H, CH_2O), 3.64–3.69 (m, 8H, 4 × CH_2O), 6.60 (s, 1H, pyrrole α-*H*), 6.61 (s, 1H, pyrrole α-*H*), 8.32 (bs, 1H, N*H*); ^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ 15.1, 30.5, 35.4, 59.0, 70.1, 70.5, 70.6, 70.6, 72.0, 109.8, 119.9, 126.5, 128.5 (two signals are overlapping); MS(HiRes-FT-ESI) calcd for $C_{17}H_{23}NO_3S_6Na^+$ 503.9895; found 503.9902; Anal. Calcd. for $C_{17}H_{23}NO_3S_6$: C, 42.38; H, 4.81; N, 2.91; S, 39.93. Found: C, 42.52; H, 4.89; N, 3.05; S, 40.03.

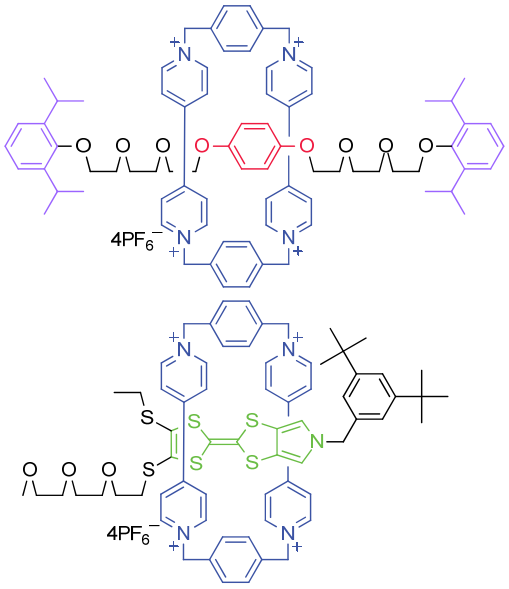


Dumbbell S13. A solution of the MPTTF compound **S12** (586 mg, 1.22 mmol) in anhydrous DMF (100 mL) was degassed (N_2, 15 min) before NaH (55–65% v/v in mineral oil, 934 mg, 4.23 mmol) and 3,5-di-*t*-butyl-bromomethylbenzene (**S9**) (385 mg, 1.36 mmol) were added in one portion. Subsequently, the reaction mixture was stirred at room temperature for 45 min before the reaction was terminated by carefully and slowly addition of H_2O (100 mL). The resulting yellow mixture was extracted with CH_2Cl_2 (3 × 100 mL) and the combined organic phases were washed with a saturated aqueous solution of NaCl (100 mL), H_2O (3 × 100 mL), and dried ($MgSO_4$). Removal of the solvent in vauco gave a yellow oil, which was puri-

fied by column chromatography (SiO_2, CH_2Cl_2:EtOAc 9:1 v/v) affording the dumbbell **S13** as a yellow oil (684 mg, 82%). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 1.24 (t, J = 7.4 Hz, 3H, CH_3CH_2), 1.30 (s, 18H, 2 × $C(CH_3)_3$), 2.85 (q, J = 7.4 Hz, 2H, CH_3CH_2), 3.00 (t, J = 6.8 Hz, 2H, OCH_2CH_2S), 3.37 (s, 3H, CH_3O), 3.53−3.55 (m, 2H, CH_2O), 3.64−3.75 (m, 8H, 4 × CH_2O), 4.96 (bs, 2H, NCH_2), 6.49 (s, 2H, 2 × *t*-Bu Ar-*H*), 6.99 (s, 1H, pyrrole α-*H*), 7.00 (s, 1H, pyrrole α-*H*), 7.37 (s, 1H, *t*-Bu Ar-*H*); ^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ 15.1, 30.5, 31.4, 34.9, 35.4, 59.1, 70.1, 70.5, 70.6, 70.6, 72.0, 119.1, 121.8, 122.2, 151.5 (seven signals are overlapping); MS(HiRes-FT-ESI) calcd for $C_{32}H_{45}NO_3S_6Na$ 706.1616; found 706.1620. Anal. Calcd. for $C_{32}H_{45}NO_3S_6$: C, 56.18; H, 6.63; N, 2.05; S 28.12. Found: C, 56.22; H, 6.73; N, 2.18; S, 27.95.



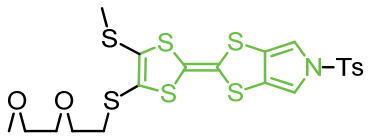
[2]Rotaxane 6•4PF$_6$. A solution of the dumbbell **S13** (252 mg, 0.37 mmol), **3**•2PF_2 (777 mg, 1.10 mmol), and **4** (290 mg, 1.10 mmol) in anhydrous DMF (12 mL) was subjected to a pressure of 10 kbar at room temperature for 3 d. The suspension was directly subjected to column chromatography (SiO_2) and unreacted dumbbell were eluted with Me_2CO, whereupon the eluent was changed to Me_2CO/NH_4PF_6 (1 g NH_4PF_6 in 100 mL Me_2CO). A green colored band containing **6**•4PF_6 was collected and concentrated in vauco to a volume of approximately 15 mL before H_2O (50 mL) was added. The suspension was cooled on an ice bath for 30 min and the resulting precipitate was collected by filtration, washed with H_2O (3 × 10 mL) and Et_2O (2 × 10 mL) to give the [2]rotaxane **6**•4PF_6 as a green powder (151 mg, 0.08 mmol, 23 %). ^{1}H NMR (400 MHz, CD_3CN, 298 K): δ 1.40 (s, 18H, 2 × $C(CH_3)_3$), 1.51 (t, J = 7.4 Hz, 3H, CH_3CH_2), 3.03 (q, J = 7.4 Hz, 2H, CH_3CH_2), 3.09 (s, 3H, CH_3O), 3.17 (t, J = 6,8 Hz, 2H, OCH_2CH_2S), 3.38 – 3.41 (m, 2H, CH_2O), 3.58 – 3.60 (m, 2H, CH_2O), 3.72 - 3.75 (m, 2H, CH_2O), 3.80 – 3.85 (m, 2H, CH_2O), 3.87 (t, J = 6.8 Hz, 2H, OCH_2CH_2S), 5.20 (s, 2H, NCH_2), 5.74 (s, 8H, 4 × N^+CH_2), 6.65/6.66 (AB q, J = 2.2 Hz, 2H, 2 × pyrrol α-*H*), 7.28 (d, J = 2.0 Hz, 2H, 2 × *t*-Bu Ar-*H*), 7.54 (t, J = 2.0 Hz, 1H, *t*-Bu Ar-*H*), 7.62 (bs, 4H, 4 × β-*H*), 7.75 (s, 4H, 4 × xylyl-*H*), 7.76 (s, 4H, 4 × xylyl-*H*), 8.00 (bs, 4H, 4 × β-*H*), 8.85 (bs, 4H, 4 × α-*H*), 9.00 (bs, 2H, 2 × α-*H*), 9.08 (bs, 2H, 2 × α-*H*); MS (ESI): *m/z* (%) 746 ($[M - 2PF_6]^{2+}$), 449 ($[M - 3PF_6]^{3+}$), 400 ($[M - 4PF_6]^{3+}$), 300 ($[M - 4PF_6]^{4+}$); MS(HiRes-FT ESI) calcd for $C_{66}H_{77}F_{12}N_5O_3P_2S_6$ ($[M - 2PF_6]^{2+}$) 746.6814; found: 746.6818; Anal Calcd for $C_{68}H_{77}F_{24}N_5O_3P_4S_6$: C, 45.76; H, 4.35; N, 3.92; S, 10.78. Found: C, 45.47; H, 4.32; N, 4.01; S, 10.55.



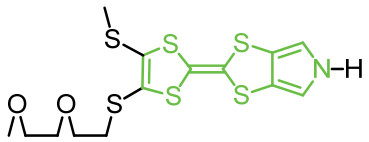
Mixtures of the [2]rotaxanes 5•4PF$_6$ and 6•4PF$_6$. *General procedure*: A solution of the dumbbell **S10** (30 mM,1 eq.), the dumbbell **S13** (30 mM,1 eq.), **3**•2PF$_6$ (3 eq.), and **4** (3 eq.) in anhydrous DMF was subjected to a pressure of 1 or 10×10^{-3} bar at room temperature for 3 d. The suspension was directly subjected to column chromatography (SiO_2) and unreacted dumbbells were eluted with Me_2CO, whereupon the eluent was changed to Me_2CO/NH_4PF_6 (1 g NH_4PF_6 in 100 mL Me_2CO) and the colored band containing a mixture of **5**•4PF$_6$ and **6**•4PF$_6$ was collected and concentrated in vauco to a volume of approximately 15 mL before H_2O (50 mL) was added. The suspension was cooled on an ice bath for 30 min and the resulting precipitate was collected by filtration, washed with H_2O (3 × 10 mL) and Et_2O (2 × 10 mL).

Experiment A: Dumbbell **S10** (103 mg, 0.15 mmol), dumbbell **S13** (100 mg, 0.15 mmol), **3**•2PF$_6$ (317 mg, 0.45 mmol), and the dibromide **4** (102 mg, 0.45 mmol) were dissolved in anhydrous DMF (5 mL), whereupon the reaction mixture was stirred at 1 bar. Yields:[S10] **5**•4PF$_6$ (16.2 mg, 6%); **6**•4PF$_6$ (2.9 mg, 1%).
Experiment B: Dumbbell **S10** (104 mg, 0.15 mmol), dumbbell **S13** (103 mg, 0.15 mmol), **3**•2PF$_6$ (316 mg, 0.45 mmol), and the dibromide **4** (101 mg, 0.44 mmol) were dissolved in anhydrous DMF (5 mL), whereupon the reaction mixture was transferred to a teflon-tube and subjected to a pressure of 10 kbar. Yields:[S10] **5**•4PF$_6$ (25 mg, 9%), **6**•4PF$_6$ (39 mg, 15%).

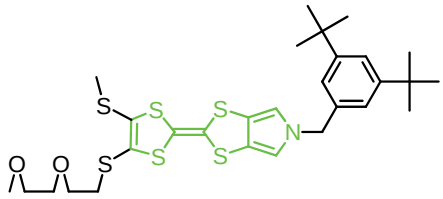
Synthesis of the dumbbell compound 8



Compound S14. A solution of 3-((5-(methylthio)-2-(5-tosyl-5H-[1,3]dithiolo[4,5-*c*]pyrrol-2-ylidene)-1,3-dithiol-4-yl)thio)propane-nitrile (1.71 g, 3.23 mmol) and 1-iodo-2-(2-methoxyethoxy)ethane (84 mg, 3.65 mmol) in anhydrous THF (200 mL) was degassed (N_2, 30 min) before a solution of CsOH•H_2O (462 mg, 2.75 mmol) in anhydrous MeOH (0.5 mL) was added over a period of 3 h at room temperature. After stirring the reaction mixture for additional 24 h at room temperature, the solvent was evaporated in vauco. The resulting residue was dissolved in CH_2Cl_2 (100 mL), washed with H_2O (3 × 200 mL), and dried ($MgSO_4$). Removal of the solvent gave a yellow oil which was purified by column chromatography (SiO_2, CH_2Cl_2) affording the title compound **S13** as a yellow solid (1.49 g, 80%). M.p. 85−87 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 2.41 (s, 6H, Ts-C*H*$_3$ + SC*H*$_3$), 2.98 (t, J = 6.8 Hz, 2H, OCH$_2$C*H*$_2$S), 3.37 (s, 3H, C*H*$_3$O), 3.52−3.54 (m, 2H, OC*H*$_2$), 3.61−3.63 (m, 2H, OC*H*$_2$), 3.66 (t, J = 6.8 Hz, 2H, OC*H*$_2$CH$_2$S), 6.93 (s, 2H, 2 × pyrrole α-*H*), 7.28 (d, J = 8.6 Hz, 2H, 2 × Ts Ar-*H*), 7.71 (d, J = 8.6 Hz, 2H, 2 × Ts Ar-*H*); ^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ 19.1, 21.7, 35.4, 59.1, 70.1, 70.4, 71.9, 111.3, 114.6, 127.0, 127.1, 127.2, 130.1, 130.4, 135.4, 145.5 (three signals are overlapping); MS(HiRes-FT-ESI) calcd for $C_{21}H_{23}NO_4S_7^+$ 576.9667; found 576.9672; Anal. Calcd. for $C_{21}H_{23}NO_4S_7$: C, 43.65; H, 4.01; N, 2.42; S, 38.84. Found: C, 43.40; H, 3.93; N, 2.38; S, 38.62.



Compound S14. A suspension of the MPTTF compound **S14** (745 mg, 1.29 mmol) in anhydrous THF:MeOH (1:1 v/v, 150 mL) was degassed (N_2, 40 min) before NaOMe (25–30% v/v MeOH, 3.6 mL, 850 mg, 15.7 mmol) was added in one portion, whereupon the reaction mixture was heated under reflux for 1 h. After being cooled to room temperature, the solvent was evaporated in vauco and the residue dissolved in CH_2Cl_2 (100 mL), washed with H_2O (5 × 200 mL), and dried ($MgSO_4$). Removal of the solvent gave a yellow oil, which was purified by column chromatography (SiO_2, CH_2Cl_2:EtOAc 10:1 v/v) to give the title compound **S14** as a yellow solid (600 mg, 89%). M.p. 114−115 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 2.43 (s, 3H, SCH_3), 3.01 (t, J = 6.8 Hz, 2H, OCH$_2$CH_2S), 3.38 (s, 3H, CH_3O), 3.54−3.56 (m, 2H, CH_2O), 3.63–3.65 (m, 2H, CH_2O), 3.68 (t, J = 6.8 Hz, 2H, OCH_2CH$_2$S), 6.60 (d, J = 2.6 Hz, 2H, 2 × pyrrole α-H), 8.31 (bs, 1H, NH); ^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ 19.1, 21.1, 35.3, 59.1, 70.1, 70.4, 109.8, 119.9, 120.0, 124.2, 130.5 (three signals are overlapping); MS(HiRes-FT-ESI) calcd for $C_{14}H_{17}NO_2S_6^+$ 422.9578; found 422.9592; Anal. Calcd. for $C_{14}H_{17}NO_2S_6$: C, 39.69; H, 4.04; N, 3.31; S, 45.41. Found: C, 39.85; H, 3.98; N, 3.15; S 45.13.



Dumbbell 8. A solution of the MPTTF compound **S14** (434 mg, 1.02 mmol) and 3,5-di-*t*-butyl-bromomethylbenzene (**S9**) (319 mg, 1.13 mmol) in anhydrous DMF (75 mL) was degassed (N_2, 15 min) before NaH (55–65% v/v in mineral oil, 335 mg, 8.38 mmol) was added in one portion. Subsequently, the reaction mixture was stirred at room temperature for 1 h, before the reaction was terminated by carefully and slowly addition of H_2O (250 mL). The resulting yellow mixture was extracted with CH_2Cl_2 (3 × 200 mL), after which the combined organic phases were dried ($MgSO_4$). Removal of the solvent in vauco gave a yellow oil, which was purified by column chromatography (SiO_2, CH_2Cl_2: EtOAc 10:1 v/v) to give the dumbbell compound **8** as a yellow oil (482 mg, 88%). ^{1}H NMR (400 MHz, CD_3SOCD_3, 298 K) δ 1.25 (s, 18H, 2 × C(CH_3)$_3$), 2.44 (s, 3H, SCH_3), 2.98 (t, J = 6.4 Hz, 2H, OCH$_2$CH_2S), 3.22 (s, 3H, CH_3O), 3.41−3.43 (m, 2H, CH_2O), 3.51−3.53 (m, 2H, CH_2O), 3.57 (t, J = 6.4 Hz, 2H, OCH_2CH$_2$S), 5.02 (bs, 2H, NCH_2), 6.93 (s, 2H, 2 × pyrrole α-H), 7.11 (d, J = 1.8 Hz, 2H, 2 × t-Bu Ar-H), 7.31 (t, J = 1.8 Hz, 1H, t-Bu Ar-H); ^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ 18.3, 31.1, 34.4, 34.9, 53.8, 58.0, 69.1, 69.4, 71.1, 107.4, 113.7, 116.9, 117.0, 121.0, 121.1, 121.6, 129.5, 137.1, 150.5 (two signals are overlapping); MS(HiRes-FT-ESI) calcd for $C_{29}H_{39}NO_2S_6^+$ 625.1300; found 625.1319.

Characterization of the [2]rotaxane 1•4PF$_6$

Absorption spectroscopy. The UV/Vis/NIR absorption spectra (MeCN, 298 K) recorded of different mixtures of the two isomers of the [2]rotaxane **1**•4PF$_6$ (c = 0.6 mM) are shown in Fig. S1. The charge transfer (CT) absorption band observed at 490 nm is associated with isomer where CBPQT•4PF$_6$ encircles the HQ station, while the CT absorption band observed at 820 nm is associated with the isomer where CBPQT•4PF$_6$ encircles the MPTTF station.

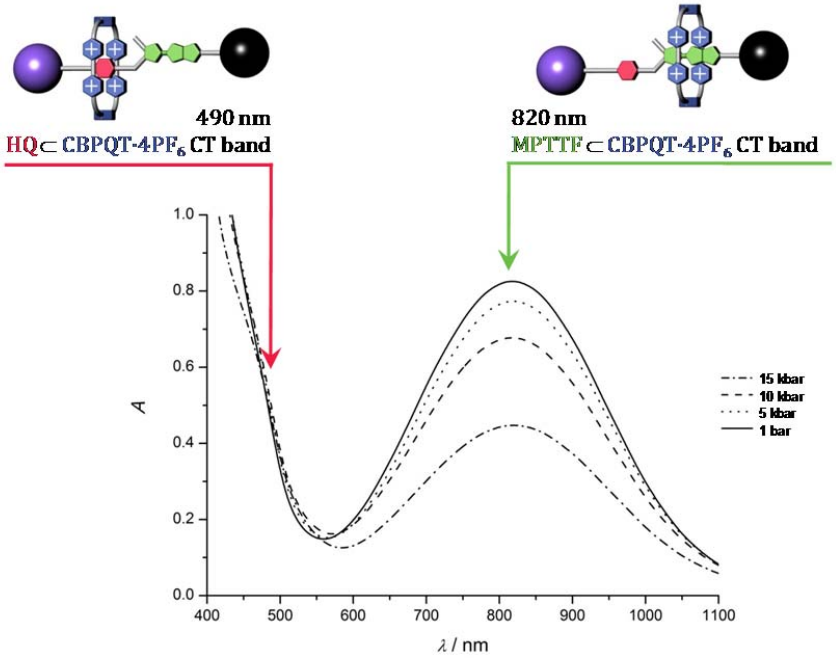


Fig. S1 UV/Vis/NIR absorption spectra (MeCN, 298 K) recorded of different mixtures of the two isomers of the [2]rotaxane **1**•4PF$_6$ (c = 0.6 mM) obtained from the clipping reaction carried out at (a) 1 bar, (b) 5 kbar, (c) 10 kbar, and (d) 15 kbar.

^{1}H NMR spectroscopy. The ^{1}H NMR spectrum (400 MHz, CD$_3$CN, 298 K) recorded of the [2]rotaxane **1**•4PF$_6$ synthesized at 5 kbar is shown in Fig. S3. The descriptions used to assign the signals in the ^{1}H NMR spectra are in Fig. S2. The partial ^{1}H NMR spectra (400 MHz, CD$_3$CN, 298 K) shown in Fig. S4 illustrate how the isomeric distribution of the two different isomers of the [2]rotaxane **1**•4PF$_6$ change when the pressure is varied from 1 bar to 15 kbar. In Fig. S2–S4, a red color indicates that CBPQT•4PF$_6$ encircle the HQ station, while a green color indicates that CBPQT•4PF$_6$ encircles the MPTTF station.

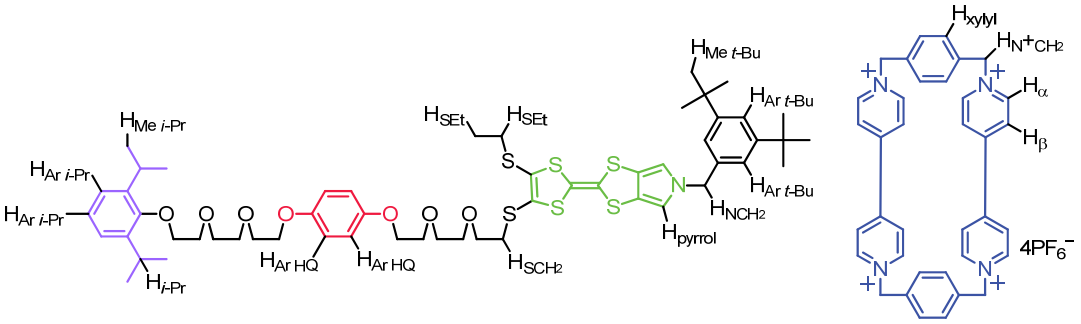
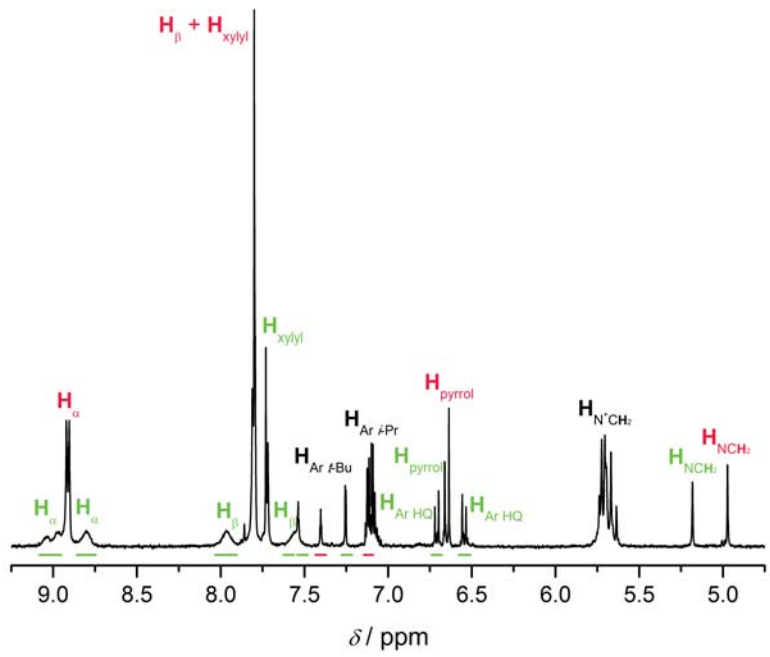


Fig. S2 Descriptions used to assign the signals in the ^{1}H NMR spectra (Fig. S3 and S4) recorded of the [2]rotaxane **1**•4PF$_6$.

(a)



(b)

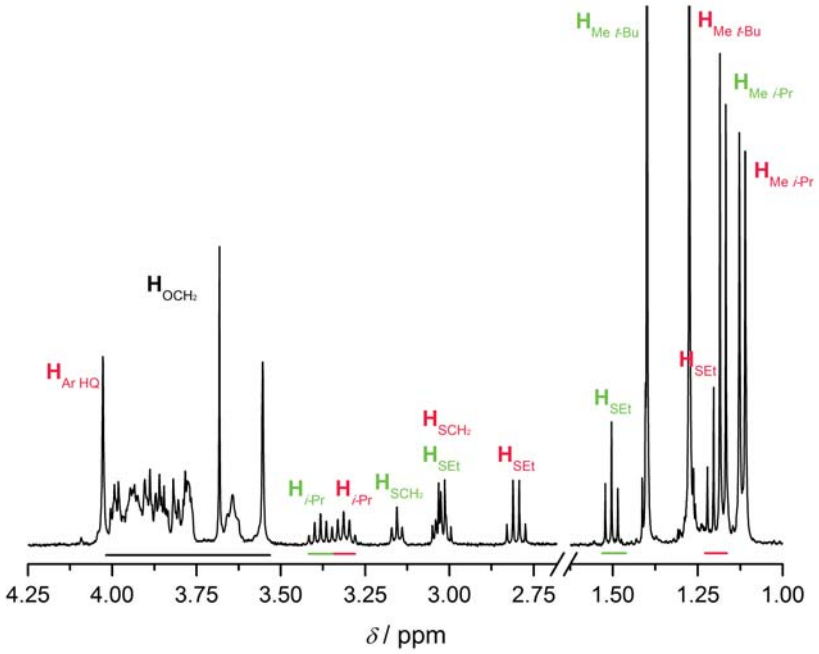


Fig. S3 Partial ^{1}H NMR spectra (400 MHz, CD_3CN, 298 K) recorded of an isomeric mixture of the [2]rotaxane **1**•4PF_6 (c = 2.76 mM). Assignment of the signals is based on the descriptions shown in Fig. S2. The assignments in red are associated with the isomer where CBPQT•4PF_6 encircles the HQ station, while the assignments in green are associated with the isomer where CBPQT•4PF_6 encircles the MPTTF station.

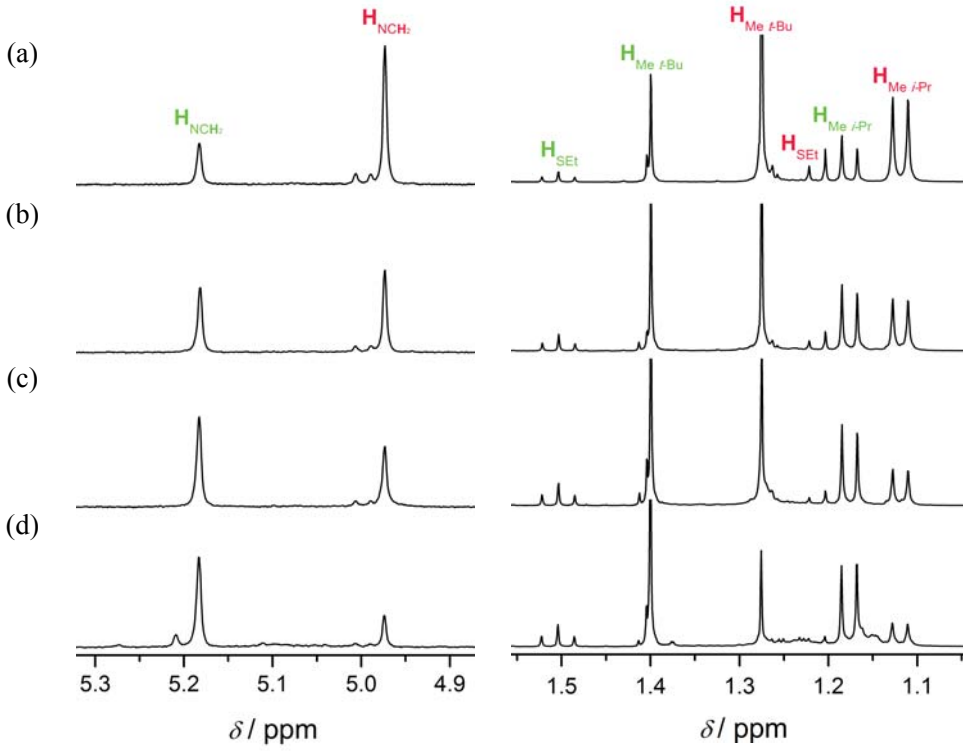


Fig. S4 Partial ^{1}H NMR spectra (400 MHz, CD_3CN, 298 K) recorded of different mixtures of the two isomers of the [2]rotaxane **1**•4PF_6 obtained from the clipping reaction carried out at (a) 1 bar, (b) 5 kbar, (c) 10 kbar, and (d) 15 kbar. The singlet at δ 4.97 ppm corresponds to the NCH_2 resonance when CBPQT•4PF_6 encircles the HQ station and the singlet at δ 5.18 ppm corresponds to the NCH_2 resonance when CBPQT•4PF_6 encircles the MPTTF station. From the integrals of the two different NCH_2 resonances, the ratio of the two isomeric rotaxanes was obtained. The change in ratio between the two different isomers is also evident from the signals associated with the CH_2CH_3 (δ 1.20 and 1.50 ppm), the $C(CH_3)_3$ (δ 1.28 + 1.48 ppm), and the $CH(CH_3)_2$ (δ 1.12 + 1.18 ppm) protons, where the assignments in red are associated with the isomer where CBPQT•4PF_6 encircles the HQ station, while the assignments in green are associated with the isomer where CBPQT•4PF_6 encircles the MPTTF station.

Characterization of the [2]rotaxanes 5•4PF$_6$ and 6•4PF$_6$

Absorption spectroscopy. The UV/Vis/NIR absorption spectra (MeCN, 298 K) recorded of different mixtures of the [2]rotaxanes **5**•4PF$_6$ (c = 0.4 mM) and **6**•4PF$_6$ (c = 0.4 mM) are shown in Fig. S5. The charge transfer (CT) absorption band observed at 460 nm is associated with **5**•4PF$_6$ where CBPQT•4PF$_6$ encircles the HQ station, while the CT absorption band observed at 820 nm is associated with **6**•4PF$_6$ where CBPQT•4PF$_6$ encircles the MPTTF station.

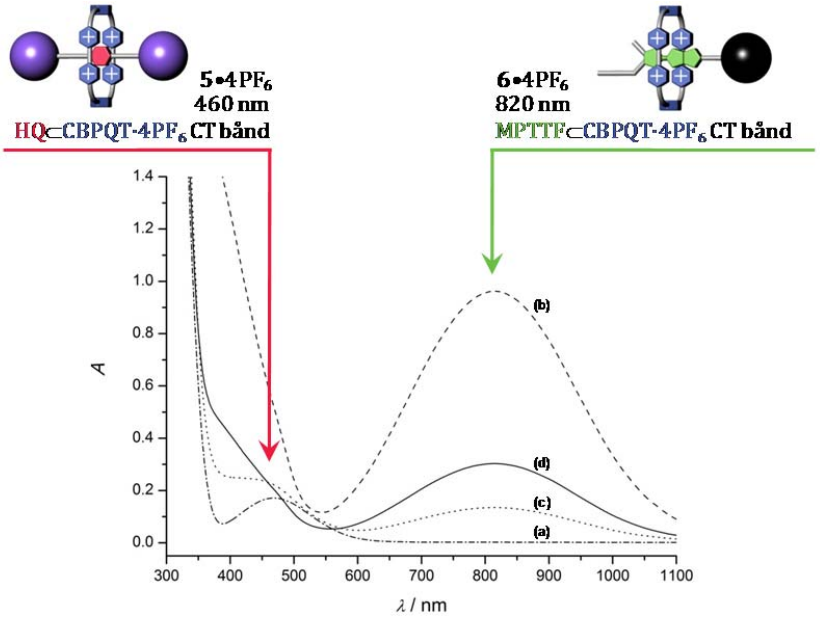


Fig. S5 UV/Vis/NIR absorption spectra (MeCN, 298 K, 0.4 mM) of (a) **5**•4PF$_6$, (b) **6**•4PF$_6$, (c) **5**•4PF$_6$ and **6**•4PF$_6$ with the ratio 85:15 (clipping reaction carried out at 1 bar), and (d) **5**•4PF$_6$ and **6**•4PF$_6$ with the ratio 39:61 (clipping reaction carried out at 10 kbar).

^{1}H NMR Spectroscopy. The ^{1}H NMR spectra (400 MHz, CD_3CN, 298 K) recorded of the [2]rotaxane **5**•4PF$_6$, [2]rotaxane **6**•4PF$_6$, and a mixture of these are illustrated in Fig. S7, Fig. S8, and Fig. S9, respectively. The descriptions used to assign the signals in the ^{1}H NMR spectra are shown in Fig. S6. In Fig. S9 the red colored signals are associated with **5**•4PF, while the assignments in green are associated with **6**•4PF$_6$.

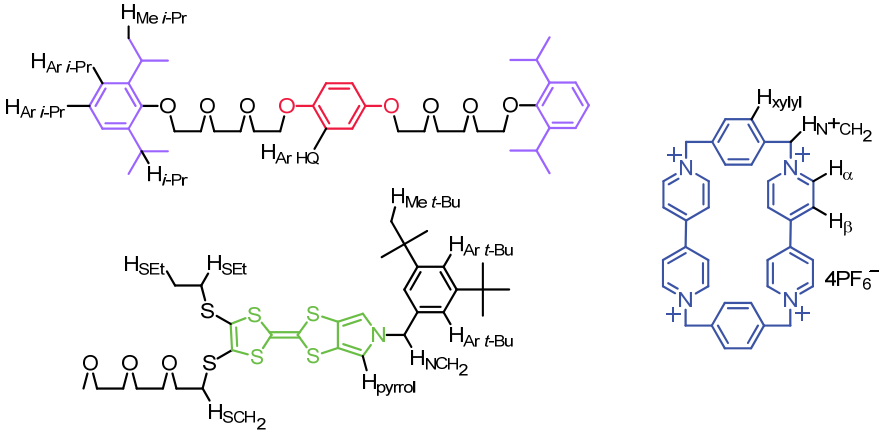


Fig. S6 Descriptions used to assign the signals in the ^{1}H NMR spectra (Fig. S7, Fig. S8, and Fig. S9) recorded of the [2]rotaxanes **5**•4PF$_6$ and **6**•4PF$_6$.

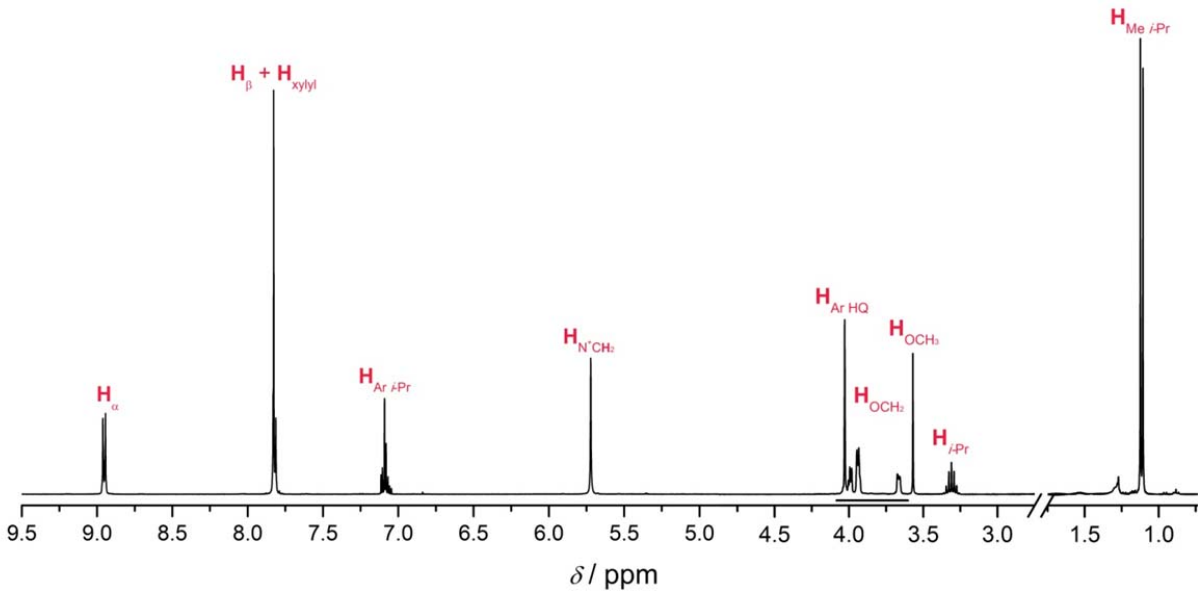


Fig. S7 Partial ^{1}H NMR spectrum (400 MHz, CD_3CN, 298 K) of [2]rotaxane **5**•4PF_6. Assignment of the signals is based on the descriptions shown in Fig. S6.

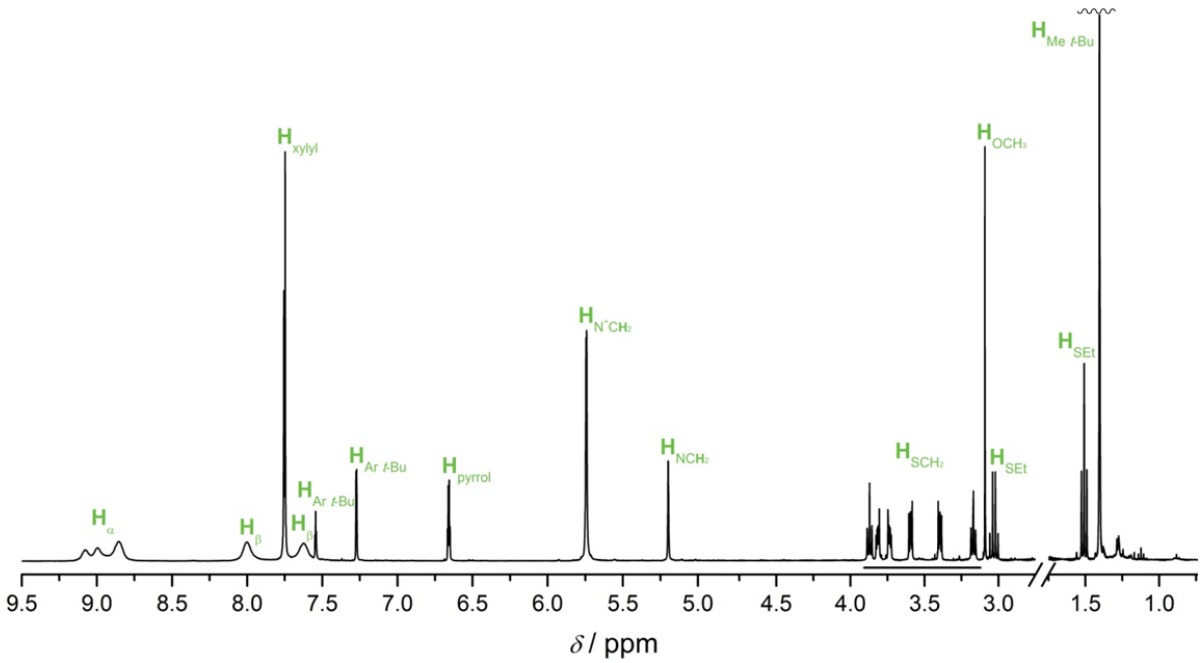


Fig. S8 Partial ^{1}H NMR spectrum (400 MHz, CD_3CN, 298 K) of [2]rotaxane **6**•4PF_6. Assignment of the signals is based on the descriptions shown in Fig. S6.

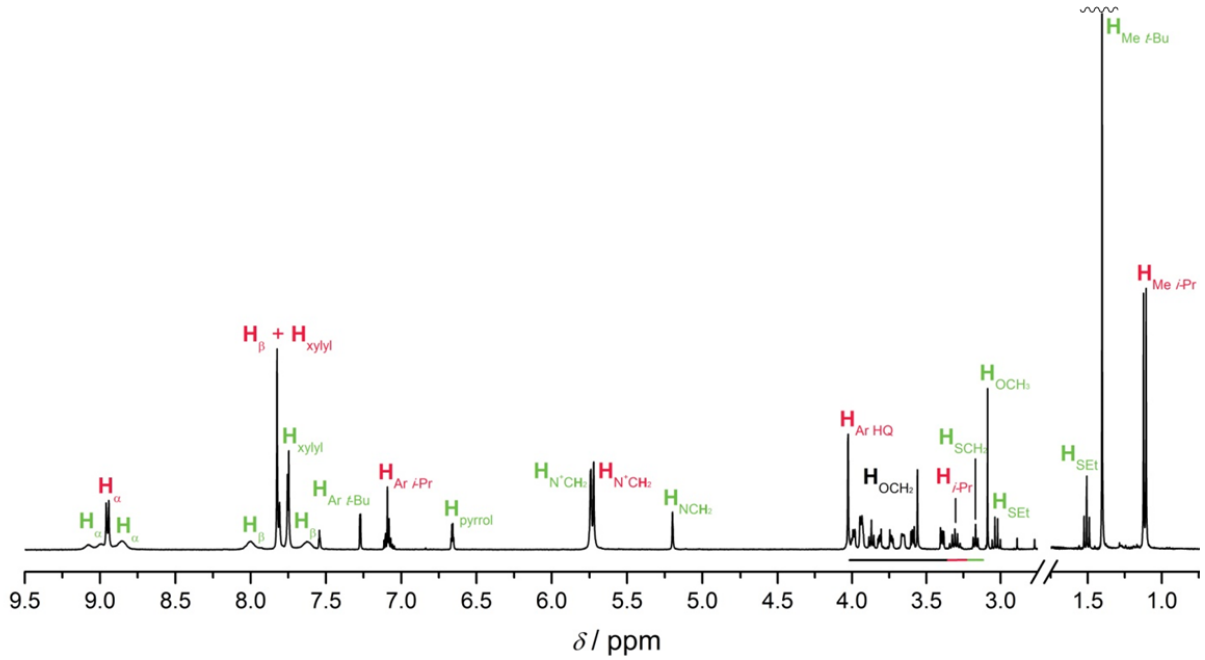


Fig. S9 Partial ^{1}H NMR spectrum (400 MHz, CD_3CN, 298 K) of a mixture of [2]rotaxane **5**•4PF_6 and **6**•4PF_6 with the ratio 85:15 (clipping reaction carried out at 10 kbar). Assignment of the signals is based on the descriptions shown in Fig. S6. The assignments in red are associated with **5**•4PF, while the assignments in green are associated with **6**•4PF_6.

Determination of binding constants using the UV/Vis dilution method

7⊂CBPQT•4PF$_6$. Mixing the colorless cyclophane CBPQT•4PF$_6$ and the HQ thread **7** in equimolar proportions in MeCN immediately produced a light red-colored solution, as a result of the appearance (Fig. S10a) of a CT absorption band centered around λ_{max} = 464 nm. Appropriate dilutions of two independent stock solutions produced solutions with absolute concentrations (c) in the range of 10^{-3} M, which was placed in the thermostatted cell compartment of the UV/Vis spectrophotometer and allowed to equilibrate at 298 K before the absorbance A was measured at 464 nm (λ_{max}). Subsequently, the solution was repeatedly diluted with MeCN to give absorptions between 1 and 0.1. After each dilution, the solution was allowed to equilibrate at 298 K before the absorbance A was measured at 464 nm (λ_{max}), which resulted (Table S1) in 32 data points [$1/A^{½}$, c/A] for **7**⊂CBPQT•4PF$_6$.

Optical path length:	l = 1 cm	
CBPQT•PF$_6$ in MeCN	ε = 16 M^{-1} cm^{-1}	at λ = 464 nm
7 in MeCN	ε = 0.7 M^{-1} cm^{-1}	at λ = 464 nm
Total "background" (A_b)	ε = 16.7 M^{-1} cm^{-1}	at λ = 464 nm

Table S1 The absorbance A_m for 1:1 mixture of CBPQT•4PF$_6$ and **7** in MeCN was measured at λ_{max} = 464 nm at different concentrations c and subtracted the "background absorbance" (at λ_{max} = 464 nm) equal to A_b = 16.7 M^{-1} × c giving $A = A_m - A_b = A_m$ – 16.7 M^{-1} × c

c (M)	A_m	A	$1/A^{½}$	c/A (M)
0.003340	0.5846	0.5288	1.3751	0.006316
0.002884	0.4764	0.4282	1.5281	0.006735
0.002672	0.4202	0.3756	1.6317	0.007114
0.002491	0.3936	0.3520	1.6855	0.007076
0.002151	0.3195	0.2836	1.8779	0.007586
0.002138	0.3046	0.2689	1.9284	0.007949
0.001858	0.2566	0.2256	2.1055	0.008236
0.001710	0.2177	0.1891	2.2994	0.009041
0.001604	0.2087	0.1819	2.3446	0.008820
0.001386	0.1678	0.1447	2.6292	0.009579
0.001368	0.1544	0.1316	2.7571	0.010399
0.001197	0.1323	0.1123	2.9839	0.010655
0.001034	0.1090	0.0917	3.3016	0.011266
0.001094	0.1093	0.0910	3.3146	0.012024
0.003894	0.7067	0.6417	1.2484	0.006069
0.003427	0.6017	0.5445	1.3552	0.006294
0.003016	0.5072	0.4568	1.4795	0.006601
0.002654	0.4237	0.3794	1.6235	0.006995
0.002596	0.4009	0.3575	1.6724	0.007261
0.002335	0.3582	0.3192	1.7700	0.007316
0.002225	0.3158	0.2786	1.8944	0.007986
0.002055	0.2960	0.2617	1.9548	0.007853
0.001907	0.2535	0.2216	2.1241	0.008605
0.001808	0.2454	0.2152	2.1557	0.008403
0.001591	0.2042	0.1776	2.3727	0.008959

0.001635	0.1996	0.1723	2.4091	0.009488
0.001400	0.1700	0.1466	2.6116	0.009552
0.001401	0.1575	0.1341	2.7308	0.010449
0.001232	0.1383	0.1177	2.9146	0.010469
0.001201	0.1262	0.1061	3.0694	0.011316
0.001084	0.1147	0.0966	3.2176	0.011228
0.001029	0.1005	0.0833	3.4646	0.012358

Plotting c/A against $1/A^{1/2}$ afforded a straight line with slope α of $(1/K_a\varepsilon l)^{1/2}$ and a y intercept y_0 of $1/\varepsilon l$, where ε is the molar extinction coefficient for the CT band of the complex and l is the optical path length.[S11] The linear relationship (Fig. S10b) between c/A and $1/A^{1/2}$ was demonstrated by calculation of the correlation coefficient and a value of 0.989 was obtained. The K_a and ε values were obtained from the relationship[S11] $K_a = y_0/\alpha^2$, where α and $y_0 = 1/\varepsilon l$ is the slope and y-intercept of the line, respectively. The free energies of complexation ($-\Delta G^o$) where calculated using the relationship $\Delta G^o = -RT\ln K_a$, where R is the gas constant and T is the absolute temperature.

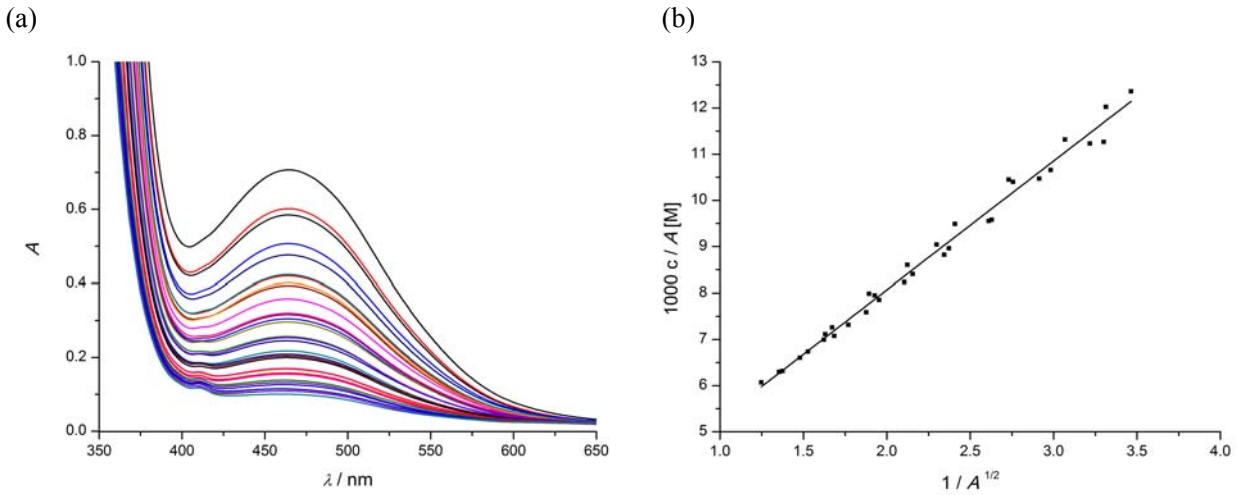


Fig. S10 (a) Absorption spectra of the pseudorotaxane **7**⊂CBPQT•4PF$_6$. (b) Linear plots of c/A against $1/A^{1/2}$ for the pseudorotaxane **7**⊂CBPQT•4PF$_6$. The absorbance A was measured at 464 nm (λ_{max}) at several different absolute concentrations (c) and the obtained data points [$1/A^{1/2}$, c/A] were fitted to the best straight line, giving correlation a coefficient of 0.989.

8⊂CBPQT•4PF$_6$. The binding constant between the MPTTF thread **8** and CBPQT•4PF$_6$ was determined using an similar approach as for **7**⊂CBPQT•4PF$_6$. Solutions with absolute concentrations (c) in the range of 10^{-3} M was subsequently repeatedly diluted with MeCN to give absorptions between 1 and 0.1. In these experiments, the CT absorption band was centered (Fig. S11a) around λ_{max} = 783 nm and a total of 30 data point were obtained (see Fig. S11b).

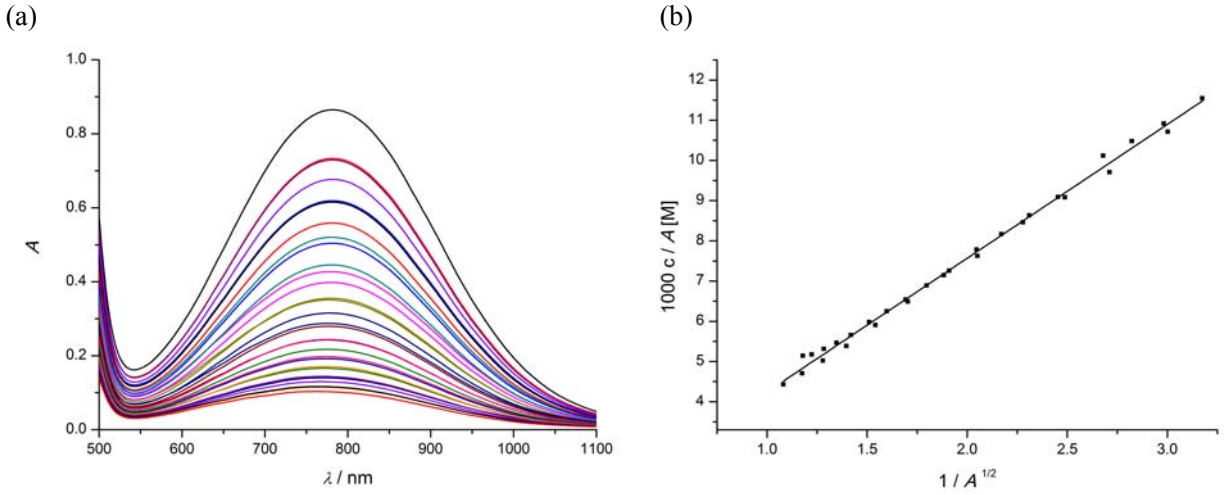


Fig. S11 (a) Absorption spectra of the pseudorotaxane **8**⊂CBPQT•4PF$_6$. (b) Linear plots of c/A against $1/A^{1/2}$ for the pseudorotaxane **8**⊂CBPQT•4PF$_6$. The absorbance A was measured at 783 nm (λ_{max}) at several different absolute concentrations (c) and the obtained data points [$1/A^{1/2}$, c/A] were fitted to the best straight line, giving correlation a coefficient of 0.996.

Notes and references

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S8 The yields of **1**•4PF_6•HQ and **1**•4PF_6•MPTTF were determined from integration of the resonances associated with the methylene protons (i.e., H_{NCH2}, see Fig. S4) located between the pyrrole ring and the 3,5-di-*t*-butylbenzene stopper.

S9 The compound was isolated as a byproduct in the synthesis of **S1**.

S10 The yields of **5**•4PF_6 and **6**•4PF_6 were determined from integration of the resonances associated with the methylene protons on the 2,6-di-*i*-propylphenylene stopper of **5**•4PF_6 and the methylene protons on the 3,5-di-*t*-butylbenzene stopper of **6**•4PF_6

S11 S. Nygaard, C. N. Hansen, J. O. Jeppesen, *J. Org. Chem.* 2007, **72**, 1617.