Chem. Eur. J. **2003**

Supporting Information

for

Amphiphilic Bistable Rotaxanes

By

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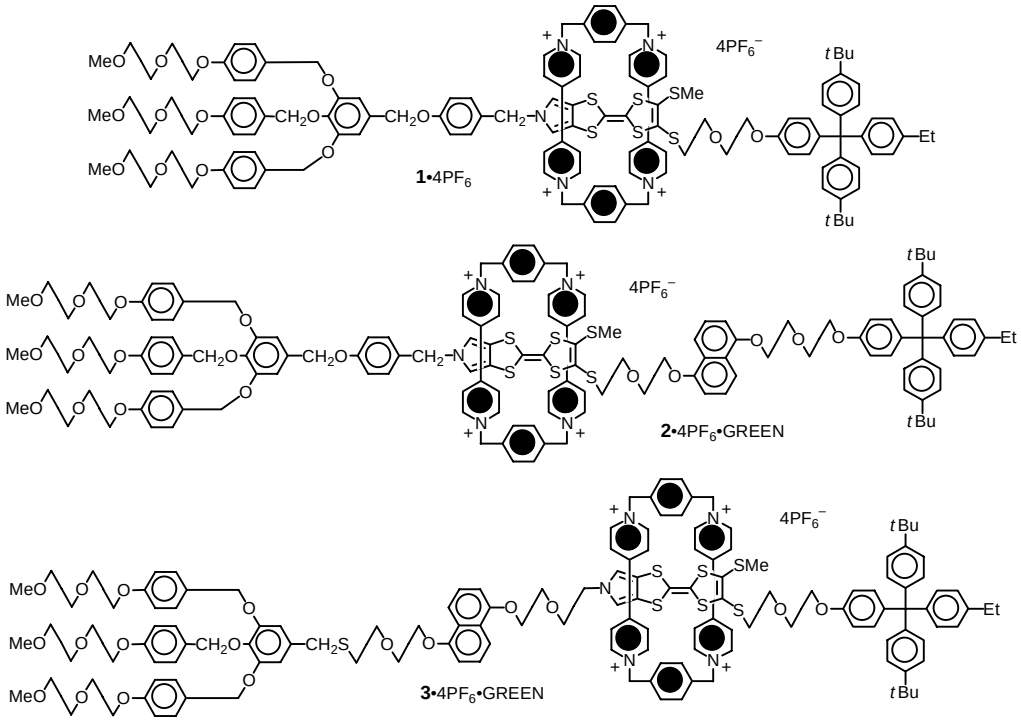


Introduction

In this supplement, we provide details on calculations of the binding constants between $CBPQT^{4+}$ and the semi-dumbbells **24** and **18** using the UV/Vis dilution method. We also provide more details on the separation of the two translational isomers of the slow two-station [2]rotaxane $\mathbf{2}^{4+}$ and the ^{1}H NMR spectroscopic characterization of **2**•$GREEN^{4+}$. Finally, we provide synthetic details and experimental procedures for the two-station [2]rotaxane **29**•$4PF_6$ that were discussed in ref. [54].

Determination of binding constant (K_a) using the UV/Vis dilution method.

Single-station [2]pseudorotaxane ***24*⊂*CBPQT*•*4PF*$_6$**: Mixing $CBPQT•4PF_6$ and the semi-dumbbell compound **24** in equimolar proportions in Me_2CO at 298 K produced a green-colored solution as a result of the appearance of a CT absorption band, centered on λ_{max} 805 (Figure S1). The absorbance A (at λ_{max}) was measured at several different absolute concentrations (c)

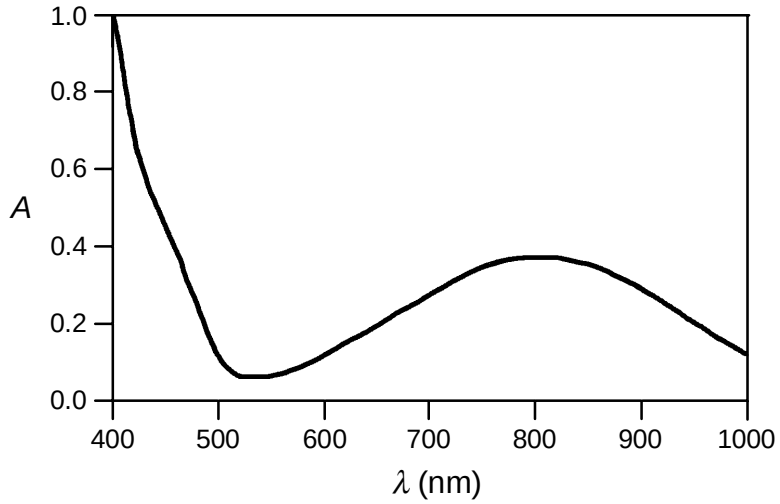


Figure S1. Absorption spectrum (Me_2CO, 298 K) recorded on a 1:1 mixture (8.34×10^{-4} M) of the semi-dumbbell **24** and $CBPQT^{4+}$.

in the range of 2×10^{-4} to 9×10^{-4} M. Measurements were carried out from dilutions of two different stock solutions, which resulted (Table S1) in 15 data points [c/A, $1/A^{1/2}$].

UV/Vis dilution experiment for the semi-dumbbell 24 and CBPQT^{4+} in Me_2CO at 298 K.

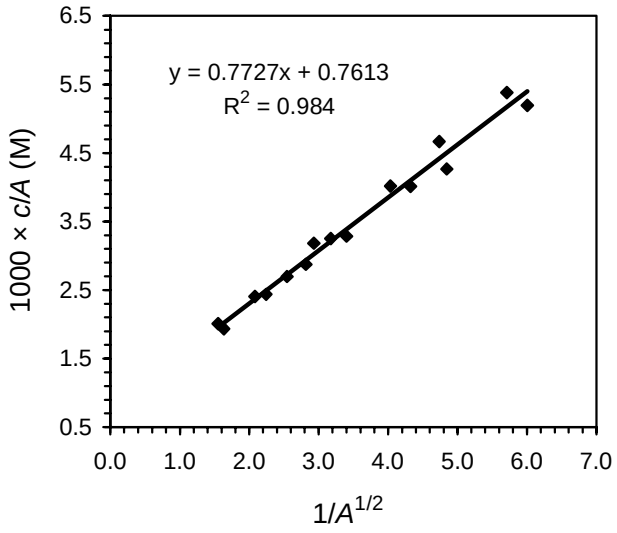
Optical path length: $l = 1$ cm
$CBPQT^{4+}$ in Me_2CO: $= 2$ L mol^{-1} cm^{-1} at $= 805$ nm
Semi-dumbbell **24** in Me_2CO: $= 0$ L mol^{-1} cm^{-1} at $= 805$ nm
Total "background": $= 2$ L mol^{-1} cm^{-1} at $= 805$ nm

Table S1. The absorbance A_m for a 1:1 mixture of CBPQT^{4+} and 24 was measured at $_{max}$ = 805 nm and subtracted the "backgroundabsorbance" (at = 805 nm) equal to $A_b = 2\ M^{-1} \times c$ giving $A = A_m - A_b = A_m - 2\ M^{-1} \times c$.

	c	A_m	A	$1/A^{1/2}$	1000 c/A
exp 1	0.000834	0.417	0.41533	1.55168	2.00803
—	0.000555	0.232	0.23089	2.08112	2.40374
—	0.000370	0.117	0.11626	2.93282	3.18252
—	0.000247	0.062	0.06151	4.03219	4.01587
—	0.000165	0.031	0.03067	5.71009	5.37985
—	0.000416	0.155	0.15417	2.54685	2.69836
—	0.000208	0.045	0.04458	4.73599	4.66535
exp 2	0.000727	0.377	0.37555	1.63181	1.93585
—	0.000485	0.200	0.19903	2.24150	2.43682
—	0.000323	0.100	0.09935	3.17254	3.25100
—	0.000215	0.054	0.05357	4.32055	4.01344
—	0.000144	0.028	0.02771	6.00712	5.19631
—	0.000363	0.127	0.12627	2.81412	2.87470
—	0.000182	0.043	0.04264	4.84297	4.26869
—	0.000284	0.087	0.08643	3.40144	3.28582

Plotting c/A against $1/A^{1/2}$ afforded a straight line with slope □ of $(1/K_a \quad l)^{1/2}$ and a y intercept y_0 of $1/\quad l$, where is the molar extinction coefficient for the CT band of the complex and l is the optical path length, according[1] to Equation S1 in Figure S2. The linear relationship (see Figure S2) between c/A and $1/A^{1/2}$ was demonstrated by calculation of the correlation coefficient and a value of 0.984 was obtained. The K_a and . values were obtained from the

relationship $K_a = y_0/\alpha^2$, where α and $y_0 = 1/\ l$ is the slope and y-intercept of the line, respectively.



$$\frac{c}{A} = \left(\frac{1}{K_a \varepsilon\, l}\right)^{1/2} \cdot \frac{1}{A^{1/2}} + \frac{1}{\varepsilon\, l} \qquad \text{(S1)}$$

$y_0 = 0.0007613$ and $\alpha = 0.0007727$

$K_a = y_0/\alpha^2 \Rightarrow K_a \approx 1300\ \text{M}^{-1}$

Figure S2. A linear plot of c/A against $1/A^{1/2}$ for a 1:1 mixture of $CBPQT^{4+}$ and the semi-dumbbell **24**. The absorbance A was measured (298 K) at different absolute concentrations c of $CBPQT^{4+}$ (equal to that of **24**) in the range 2×10^{-4} to 9×10^{-4} M. The 15 data points which resulted from dilutions of two different stock solutions have been fitted to a best straight line, giving a correlation coefficient of 0.984.

From the above plot, $y_0 = 0.7613 \times 10^{-3}$ M and $\alpha = 0.7727 \times 10^{-3}$ M. Hence $K_a = 1300 \pm 200\ \text{M}^{-1}$ ($\varepsilon = 1310\ \text{L mol}^{-1}\ \text{cm}^{-1}$) for the association between $CBPQT^{4+}$ and the semi-dumbbell **24** in Me_2CO at 298 K, which corresponds to a free energy of complexation[2] ($-\Delta G°$) of 4.2 kcal mol^{-1}.

*Two-station [2]pseudorotaxane **18**⊂CBPQT•4PF$_6$*: Mixing equimolar amounts of the semi-dumbbell **18** and CBPQT•4PF_6 in Me_2CO at 298 K produced a brown-colored solution. CT absorption bands were observed at 545 nm (DNP/$CBPQT^{4+}$) and 745 nm (MPTTF/$CBPQT^{4+}$). The absorbance A was measured at 545 nm and at 745 nm at several different absolute concentrations (c) in the range of 10^{-5} to 10^{-3} M. Measurements were carried out from dilutions of two different stock solutions, which resulted in 22 (DNP/$CBPQT^{4+}$), and 22

(MPTTF/CBPQT^{4+}) data points [c/A, $1/A^{1/2}$]. For each probe the linear relationship between c/A and $1/A^{1/2}$ was demonstrated by calculation of the correlation coefficients and values of 0.917 (DNP/CBPQT^{4+}) and 0.959 (MPTTF/CBPQT^{4+}) were obtained. Using a similar data treatment as described for **24**⊂CBPQT•4PF$_6$ gave the following and K_a values. Data for **18**⊂CBPQT•4PF$_6$: UV/Vis (Me$_2$CO, 298 K): λ_{max} = 545 nm (ε = 760 L mol^{-1} cm^{-1}, K_a = 25 000 ± 3000 M^{-1}), 745 nm (ε = 590 L mol^{-1} cm^{-1}, K_a = 25 000 ± 3000 M^{-1}).

Separation of the two translational isomers of the slow two-station [2]rotaxane 2^{4+}.

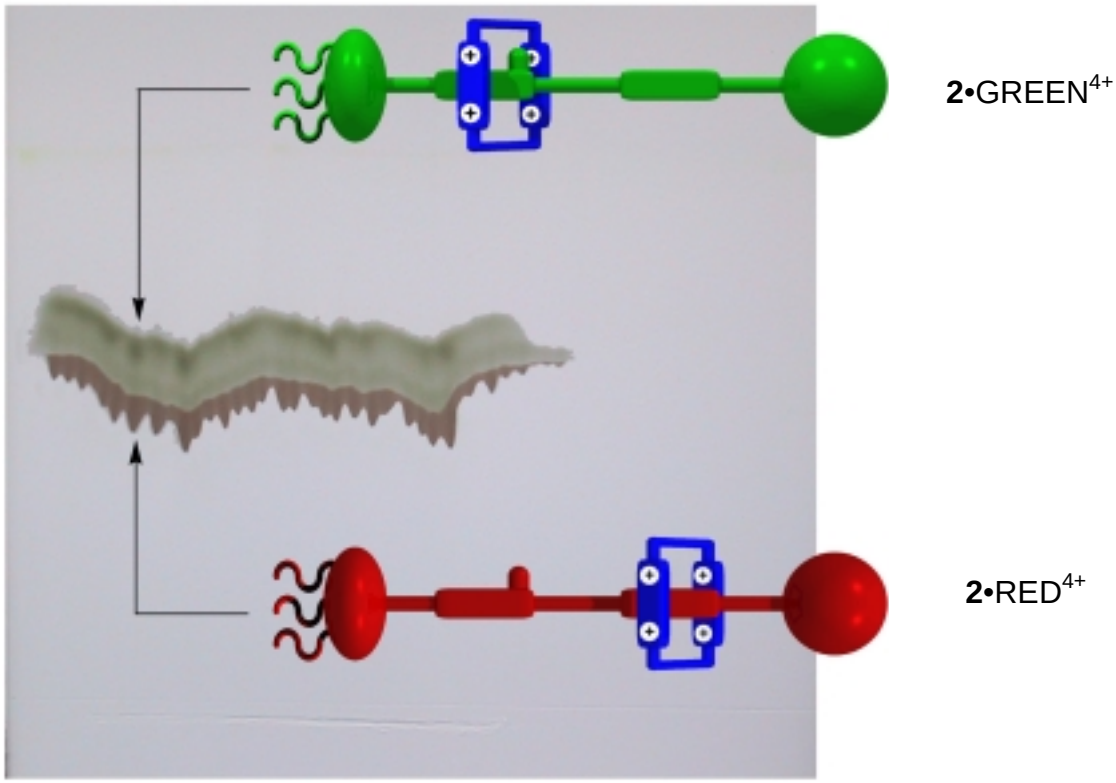


Figure S3. A preparative thin-layer chromatogram, showing the separation of **2**•RED^{4+} from **2**•GREEN^{4+}.

UV/Vis spectrum of isolated 2•GREEN^{4+}.

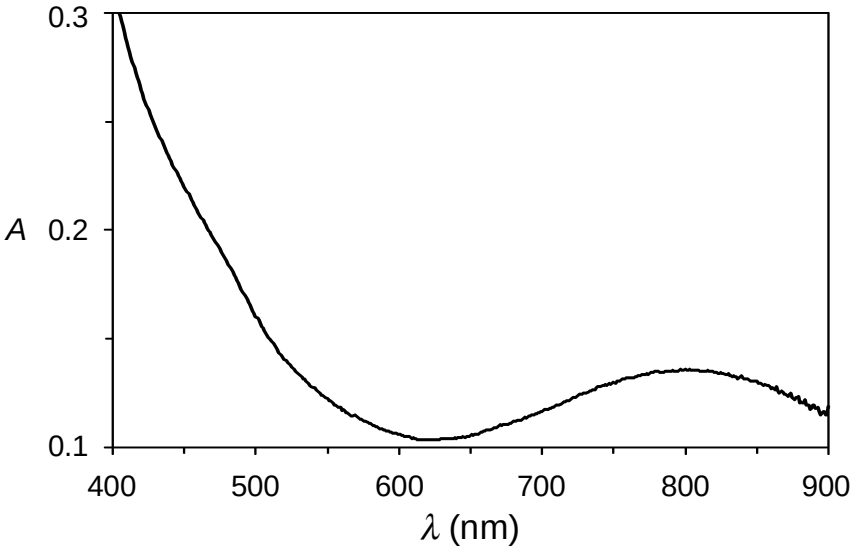


Figure S4. Absorption spectrum (Me_2CO, 298 K) recorded on a solution of the [2]rotaxane **2**•GREEN^{4+} immediately after its isolation.

^{1}H NMR spectroscopic characterization of 2•GREEN^{4+}.

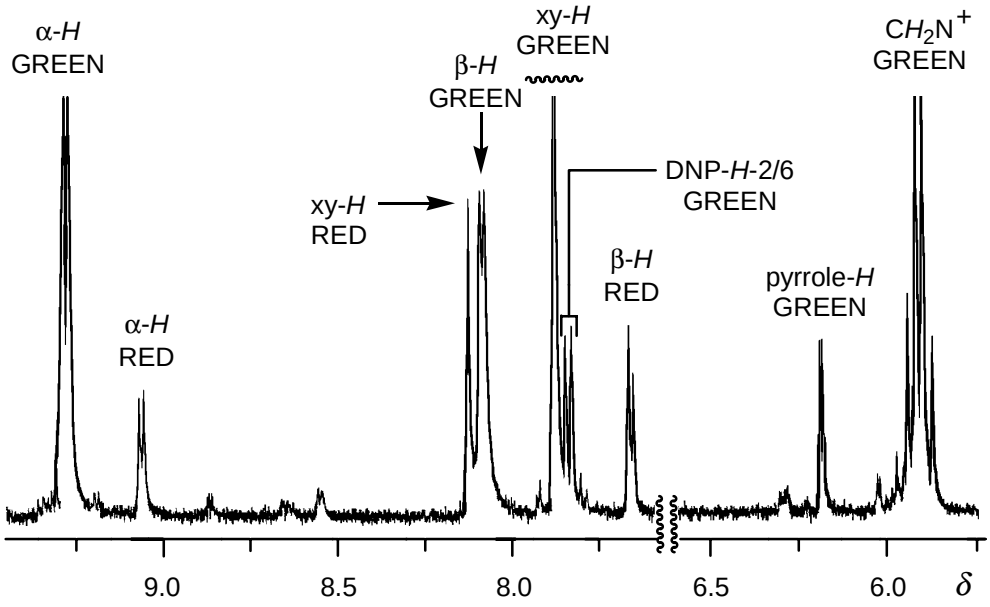
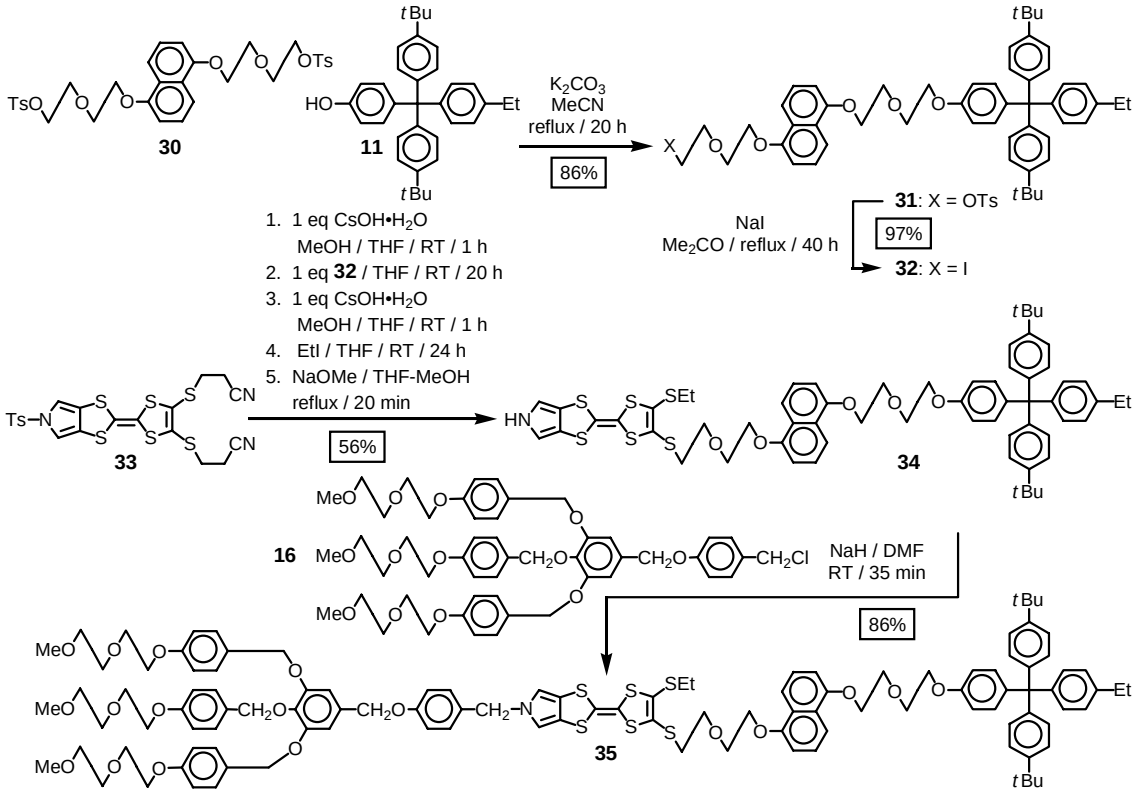


Figure S5. Partial ^{1}H NMR spectrum of an equilibrium mixture of the [2]rotaxanes **2**•GREEN^{4+} and **2**•RED^{4+}, recorded at 500 MHz in CD_3SOCD_3 at 410 K.

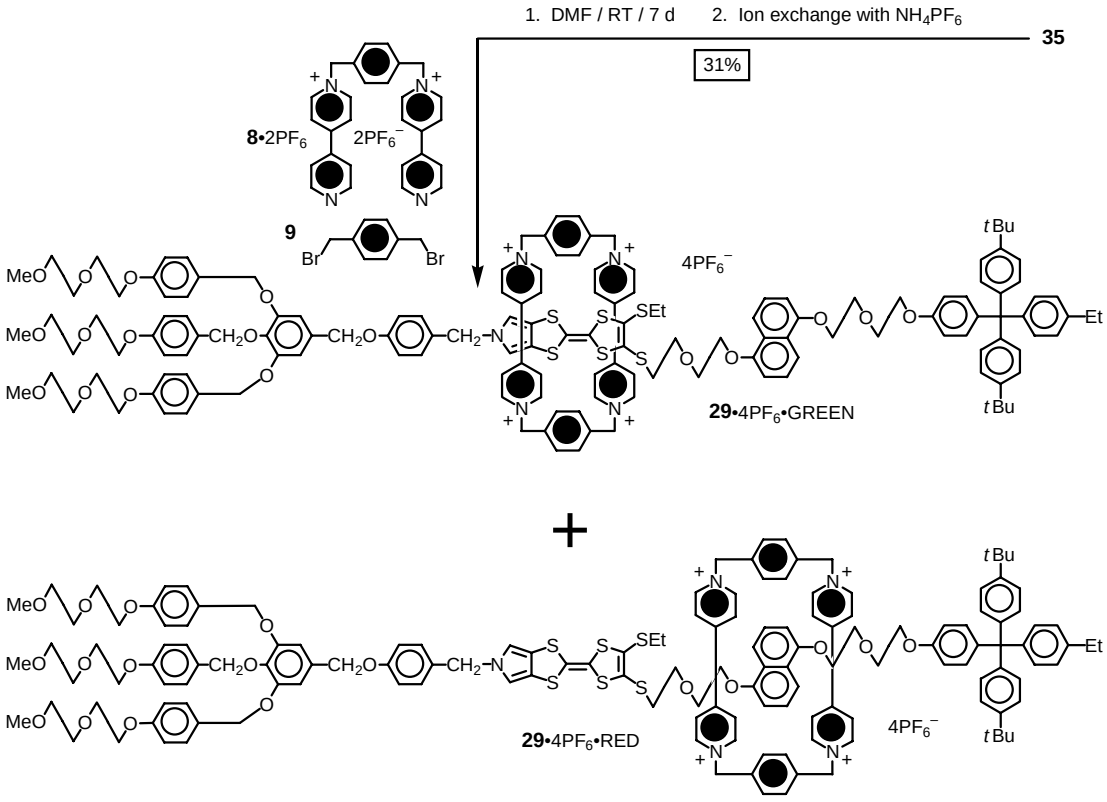
Synthesis of the two-station [2]rotaxane 29•4PF$_6$.

The [2]rotaxane **29**•4PF$_6$—in which the SMe group of **2**•4PF$_6$ has been replaced by the more bulky SEt group – was synthesized according to Schemes S1 and S2. Monoalkylation of the bistosylate[3] **30** with the hydrophobic tetraarylmethane stopper[4] **11** in MeCN gave the tosylate **31** in 86% yield. Consequent treatment of the **31** with NaI in Me_2CO gave the iodide **32** in almost quantitative yield (97%). In order to obtain the semi-dumbbell **34** directly from the MPTTF building block[5] **33**, the following reaction sequence was carried out. A THF solution of **33** was treated with one equivalent of CsOH•H_2O. This procedure generated the MPTTF-monothiolate, which was subsequently alkylated with one equivalent of **32**. The residue was then treated with another one equivalent of CsOH•H_2O, followed by addition of ethyl iodide, which effected the second deprotection/alkylation sequence. Finally, the tosyl



Scheme S1. Synthesis of the dumbbell compound **35**.

protecting group on the MPTTF unit was removed using NaOMe in a THF–MeOH mixture affording **34** in an overall yield of 56% for the five steps. The resultant pyrrole nitrogen in **34** was alkylated with the chloride[4] **16** of the hydrophilic stopper and, following purification by column chromatography, the dumbbell **35** was isolated in 86% yield. In order to synthesize the [2]rotaxane **29**•4PF_6, the tetracationic cyclophane $CBPQT^{4+}$ was introduced using a clipping procedure as shown in Scheme S2. Formation of the [2]rotaxane **29**•4PF_6 was achieved in 31% yield[6] using the dumbbell **35** as template for the formation of encircling cyclobis(paraquat-*p*-phenylene) tetracation from the dicationic precursor[7] **8**•2PF_6 and the dibromide **9**.



Scheme S2. Synthesis of the [2]rotaxane **29**•4PF_6.

Experimental details for the synthesis of the [2]rotaxane 29•4PF_6.

General methods: As described in the Experimental Section, except that the compounds 1,5-bis[2-(2-(tosyl)ethoxy)ethoxy]naphthalene[3] (**30**) (Scheme S1) and 2-{4,5-bis(2-cyanoethylthio)-1,3-dithiole-2-yliden}-*N*-tosyl-(1,3)-dithiolo[4,5-*c*]pyrrole[5] (**33**) (Scheme S1) both were prepared according to literature procedures.

Compound 31: A mixture of the bistosylate **30** (1.61g, 2.50 mmol) and **11** (0.40 g, 0.84 mmol) in anhydrous MeCN (150 mL) containing K_2CO_3 (0.23 g, 1.67 mmol) was heated under reflux for 3.5 d. After cooling down to room temperature, the mixture was filtered. The filtrate was concentrated in vacuo and the oily residue was dissolved in CH_2Cl_2 (200 mL), washed with H_2O (3 × 150 mL) and dried ($MgSO_4$). After removal of the solvent the residue was subjected to column chromatography (SiO_2: CH_2Cl_2/MeOH 99:1). The colorless band (R_f = 0.1) was collected and the solvent evaporated, affording the title compound **31** (0.67 g, 86%) as a white solid. ^{1}H NMR ($CDCl_3$, 500 MHz): = 1.26 (t, *J* = 7.6 Hz, 3H), 1.34 (s, 18 H), 2.32 (s, 3H), 2.65 (q, *J* = 7.6 Hz, 2H), 3.79–3.81 (m, 2H), 3.87–3.89 (m, 2H), 3.97–3.99 (m, 2H), 4.04–4.06 (m, 2H), 4.14–4.18 (m, 4H), 4.21–4.23 (m, 2H), 4.29–4.31 (m, 2H), 6.79 (d, *J* = 8.0 Hz, 1H), 6.83 (d, *J* = 8.9 Hz, 2H), 6.86 (d, *J* = 8.0 Hz, 1H), 7.09–7.18 (m, 10H), 7.21 (d, *J* = 8.2 Hz, 2H), 7.26–7.29 (m, 4H), 7.34 (t, *J* = 8.0 Hz, 1H), 7.37 (t, *J* = 8.0 Hz, 1H), 7.80 (d, *J* = 8.2 Hz, 2H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.94 (d, *J* = 8.9 Hz, 1H); MS (FAB): *m/z* (%): 948 (100) $[M]^+$.

Compound 32: Compound **31** (0.51 g, 0.55 mmol) was dissolved in anhydrous Me_2CO (50 mL) and NaI (0.82 g, 5.46 mmol) was added in one portion. The reaction mixture was heated under reflux for 40 h, before being cooled to room temperature and the solvent removed in vacuo. The white residue was dissolved in CH_2Cl_2 (100 mL), washed with H_2O (3 × 100 mL) and dried ($MgSO_4$). Concentration in vacuo gave a colorless oil, which was

purified by column chromatography (SiO_2: CH_2Cl_2) The colorless band ($R_f = 0.4$) was collected and concentrated to give the title compound **32** (0.46 g, 97%) as a colorless oil. ^{1}H NMR ($CDCl_3$, 500 MHz): = 1.32 (t, J = 7.6 Hz, 3H), 1.39 (s, 18H), 2.71 (q, J = 7.6 Hz, 2H), 3.38 (t, J = 6.7 Hz, 2H), 3.97 (t, J = 6.7 Hz, 2H), 4.04–4.07 (m, 4H), 4.11–4.13 (m, 2H), 4.21–4.23 (m, 2H), 4.34–4.36 (m, 2H), 4.37–4.39 (m, 2H), 6.87–6.93 (m, 4H), 7.09–7.20 (m, 10H), 7.31–7.33 (m, 4H), 7.39 (t, J = 8.0 Hz, 1H), 7.43 (t, J = 8.0 Hz, 1H), 7.96 (d, J = 8.4 Hz, 1H), 7.97 (d, J = 8.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): = 2.9, 15.3, 28.2, 31.3, 34.2, 63.1, 67.3, 67.8, 67.9, 69.3, 69.9, 70.0, 72.1, 105.7, 105.7, 113.1, 114.6, 114.7, 124.0, 125.0, 125.1, 126.6, 126.7, 126.7, 130.6, 131.0, 132.1, 139.9, 141.3, 144.1, 144.5, 148.2, 154.1, 154.3, 156.5; MS (EI): *m/z* (%): 905 (33) $[M + H]^+$, 771 (25) 128 (100); elemental analysis calcd (%) for $C_{53}H_{61}IO_5$ (905.0): C 70.34, H 6.79; found: C 69.98, H 6.73.

Compound 34: A solution of **33** (0.091 g, 0.16 mmol) in anhydrous THF (30 mL) was degassed (Ar, 10 min) before a solution of $CsOH•H_2O$ (0.028 g, 0.17 mmol) in anhydrous MeOH (1 mL) was added dropwise via a syringe over a period of 1 h. The mixture was stirred for 15 min, whereupon a solution of the iodide **32** (0.15 g, 0.17 mmol) in anhydrous THF (5 mL) was added in one portion and the reaction mixture was stirred for 20 h at room temperature. Then a new solution of $CsOH•H_2O$ (0.028 g, 0.17 mmol) in anhydrous MeOH (1 mL) was added dropwise via a syringe over a period of 1 h. The mixture was stirred for 15 min, whereupon ethyl iodide (0.13 mL, excess) was added in one portion and the reaction mixture was stirred for 24 h at room temperature. The solvent and excess ethyl iodide were removed in vacuo and the resulting yellow residue was redissolved in anhydrous THF/MeOH (1:1 v/v, 90 mL) and degassed (Ar, 10 min) before NaOMe (25% solution in MeOH, 0.55 mL, 0.13 g, 2.4 mmol) was added in one portion. The yellow solution was heated under reflux for 25 min before being cooled to room temperature, whereupon the solvent was evaporated. The

yellow residue was dissolved in CH_2Cl_2 (100 mL), washed with H_2O (3 × 50 mL) and dried ($MgSO_4$). Concentration in vacuo gave a yellow foam, which was subjected to column chromatography (SiO_2: CH_2Cl_2). The yellow band (R_f = 0.4) was collected and concentrated to provide the title compound **34** (0.10 g, 56%) as a yellow foam. ^{1}H NMR (CD_3COCD_3, 500 MHz): = 1.17 (t, *J* = 7.6 Hz, 3H), 1.19 (t, *J* = 7.5 Hz, 3H), 1.26 (s, 18H), 2.57 (q, *J* = 7.5 Hz, 2H), 2.82 (q, *J* = 7.6 Hz, 2H), 3.06 (t, *J* = 6.4 Hz, 2H), 3.80 (t, *J* = 6.4 Hz, 2H), 3.89–3.91 (m, 2H), 3.92–3.94 (m, 2H), 3.97–3.98 (m, 2H), 4.10–4.11 (m, 2H), 4.23–4.26 (m, 4H), 6.73–6.75 (m, 2H), 6.78–6.81 (m, 2H), 6.86–6.89 (m, 2H), 7.05–7.11 (m, 10H), 7.24–7.27 (m, 5H), 7.31 (t, *J* = 8.0 Hz, 1H), 7.80 (d, *J* = 8.5 Hz, 1H),7.84 (d, *J* = 8.5 Hz, 1H), 10.30 (bs, 1H); MS (FAB): *m/z* (%): 1111 (100) $[M]^+$; elemental analysis calcd (%) for $C_{63}H_{69}NO_5S_6$ (1112.6): C 68.01, H 6.25, N 1.26: found: C 68.29, H 6.32, N 1.17.

Dumbbell 35: Compound **34** (0.085 g, 0.076 mmol) and the chloride **16** (0.083 g, 0.092 mmol) were dissolved in anhydrous DMF (10 mL) and degassed (Ar, 10 min) before NaH (0.009 g of a 60% suspension in mineral oil, 0.23 mmol) was added. The reaction mixture was stirred for 35 min at room temperature, causing the initially yellow solution to become more orange. H_2O (20 mL) was added (dropwise until no more gas evolution was observed), followed by addition of brine (40 mL). The yellow precipitate was filtered, redissolved in CH_2Cl_2 (50 mL), washed with H_2O (2 × 30 mL) and dried ($MgSO_4$). Concentration in vacuo gave a yellow oil, which was purified by column chromatography (SiO_2: CH_2Cl_2/EtOAc 2:1). The yellow band (R_f = 0.4) was collected and the solvent evaporated affording a yellow oil, which was repeatedly dissolved in CH_2Cl_2 (3 × 20 mL) and concentrated providing the title compound **35** (0.13 g, 86%) as a yellow foam. ^{1}H NMR (CD_3COCD_3, 500 MHz): = 1.20 (t, *J* = 7.6 Hz, 3H), 1.24 (t, *J* = 7.4 Hz, 3H), 1.30 (s, 18H), 2.61 (q, *J* = 7.6 Hz, 2H), 2.90 (q, *J* = 7.4 Hz, 2H), 3.08 (t, *J* = 6.5 Hz, 2H), 3.29 (s, 6H), 3.29 (s, 3H), 3.49–3.51 (m, 6H), 3.64–3.66 (m, 6H),

3.78–3.83 (m, 8H), 3.92–3.96 (m, 4H), 3.99–4.00 (m, 2H), 4.08–4.10 (m, 2H), 4.11–4.14 (m, 6H), 4.25–4.28 (m, 4H), 4.92 (s, 2H), 4.97 (s, 2H), 4.99 (s, 2H), 5.02 (s, 4H), 6.71 and 6.74 (AB q, J = 2.0 Hz, 2H), 6.81–6.84 (m, 4H), 6.84 (s, 2H), 6.89–6.96 (m, 8H), 7.09–7.16 (m, 12H), 7.26–7.36 (m, 8H), 7.38 (d, J = 8.6 Hz, 4H), 7.84 (d, J = 8.5 Hz, 1H), 7.87 (d, J = 8.5 Hz, 1H); MS (FAB): *m/z* (%): 1981 (100) $[M]^+$, 1772 (25), 1562 (23), 1218 (33); elemental analysis calcd (%) for $C_{113}H_{129}NO_{18}S_6$ (1981.6): C 68.49, H 6.56, N 0.71; found: C 68.41, H 6.41, N 0.56.

[2]Rotaxane 29•4PF$_6$: A solution of **35** (0.12 g, 0.061 mmol), **8**•2PF$_6$ (0.17 g, 0.24 mmol) and **9** (0.065 g, 0.24 mmol) in anhydrous DMF (5 mL) was stirred for 7 d at room temperature (after approximately 1 d the color changed to reddish brown and a white precipitate was formed). The reddish brown suspension was directly subjected to column chromatography (SiO_2) and unreacted **35** was eluted with Me_2CO, whereupon the eluent was changed to Me_2CO/NH_4PF_6 (1.0 g NH_4PF_6 in 100 mL Me_2CO) and the green/red band was collected. Most of the solvent was removed in vacuo (T < 30ºC) followed by addition of H_2O (30 mL). The resulting precipitate was collected by filtration, washed with Et_2O (20 mL) and dried, affording the title [2]rotaxane **29**•4PF$_6$ (0.060 g, 31%) as a brown solid. M.p. 210ºC (decomposed without melting). The data given below are for the mixture of the two translational isomers; UV/Vis (MeCN, 298K): λ_{max} (ε) = 540 nm (806 L mol^{-1} cm^{-1}), 810 nm (505 L mol^{-1} cm^{-1}); elemental analysis calcd (%) for $C_{149}H_{161}F_{24}N_5O_{18}P_4S_6$ (3082.1): C 58.06, H 5.27, N 2.27; found: C 57.86, H 5.33, N 2.18.

*Separation of the translational isomers of **29**•4PF$_6$*: The two translational isomers were separated using preparative thin-layer chromatography (PTLC), which was performed at room temperature with Me_2CO/NH_4PF_6 (1.0 g NH_4PF_6 in 100 mL Me_2CO) as eluent. After elution, the red band containing **29**•4PF$_6$•RED was extracted into Me_2CO. The solvent was removed in

vacuo ($T < 10$ºC) and the red residue dissolved in CD_3CN, giving a red solution, which was used for ^{1}H NMR and UV/Vis spectroscopies. Although **29**•4PF_6•GREEN appears to be less polar than **29**•4PF_6•RED, it was not possible to extract a sufficient amount of **29**•4PF_6•GREEN from the silica on the PTLC plate to carry out a characterization of **29**•4PF_6•GREEN by ^{1}H NMR and UV/Vis spectroscopies.

Data for **29**•4PF_6•RED. ^{1}H NMR (CD_3CN, 500 MHz, 300K): = 1.14 (t, J = 7.6 Hz, 3H), 1.22 (s, 18H), 1.29 (t, J = 7.3 Hz, 3H), 2.31–2.34 (m, 2H), 2.52–2.57 (m, 4H), 2.92 (q, J = 7.3 Hz, 2H) 3.27 (s, 9H), 3.31–3.33 (m, 2H), 3.46–3.48 (m, 6H), 3.58–3.61 (m, 6H), 3.72–3.75 (m, 6H), 4.02–4.11 (m, 8H), 4.19–4.21 (m, 4H), 4.25–4.28 (m, 4H), 4.37–4.38 (m, 2H), 4.82 (s, 2H), 4.87 (s, 2H), 4.96 (s, 2H), 4.97 (s, 4H), 5.55–5.68 (m, 8H), 5.83 (t, J = 7.9 Hz, 1H), 5.92 (t, J = 7.9 Hz, 1H), 6.17 (d, J = 7.9 Hz, 1H), 6.22 (d, J = 7.9 Hz, 1H), 6.37 and 6.54 (AB q, J = 2.1 Hz, 2H), 6.77–6.81 (m, 4H), 6.86 (bs, 2H), 6.91–6.97 (m, 12H), 7.04–7.10 (m, 12H), 7.20–7.25 (m, 6H), 7.32–7.33 (m, 2H), 7.38–7.40 (m, 4H), 7.87 (s, 2H), 7.92 (s, 4H), 8.03 (s, 2H), 8.57 (d, J = 6.5 Hz, 2H), 8.64 (d, J = 6.5 Hz, 2H), 8.67 (d, J = 6.5 Hz, 2H), 8.90 (d, J = 6.5 Hz, 2H); UV/Vis (MeCN, 298K): $_{max}$ = 540 nm.

References and notes

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