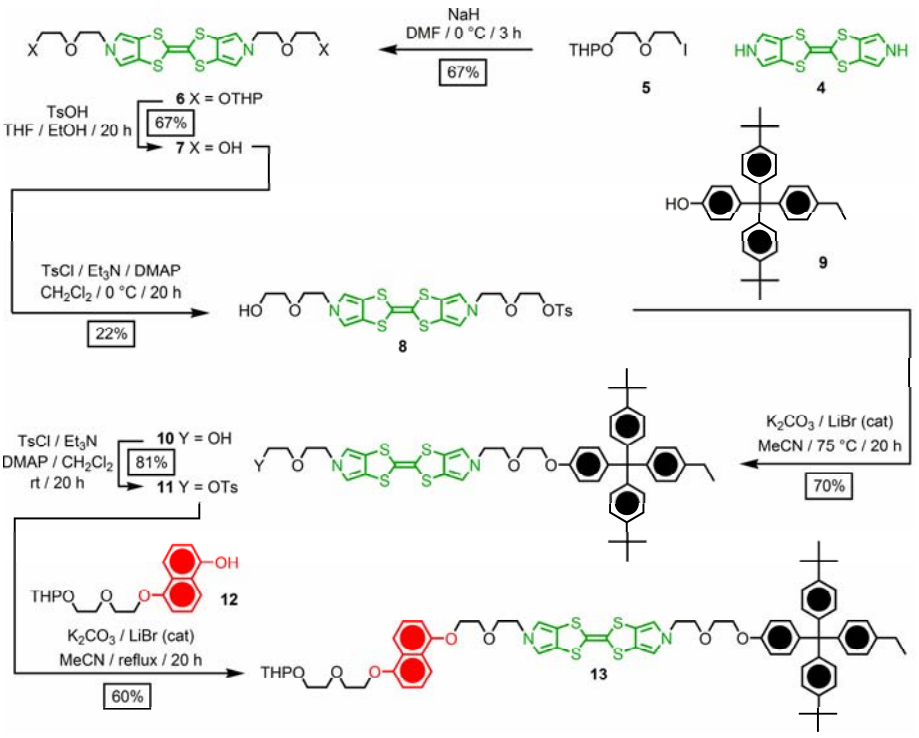
Appendix A

Syntheses of the [2]rotaxanes RBPTTF•4PF$_6$ and RBLOCK•4PF$_6$

A-1. Synthesis of the Amphiphilic [2]Rotaxane RBPTTF•4PF$_6$

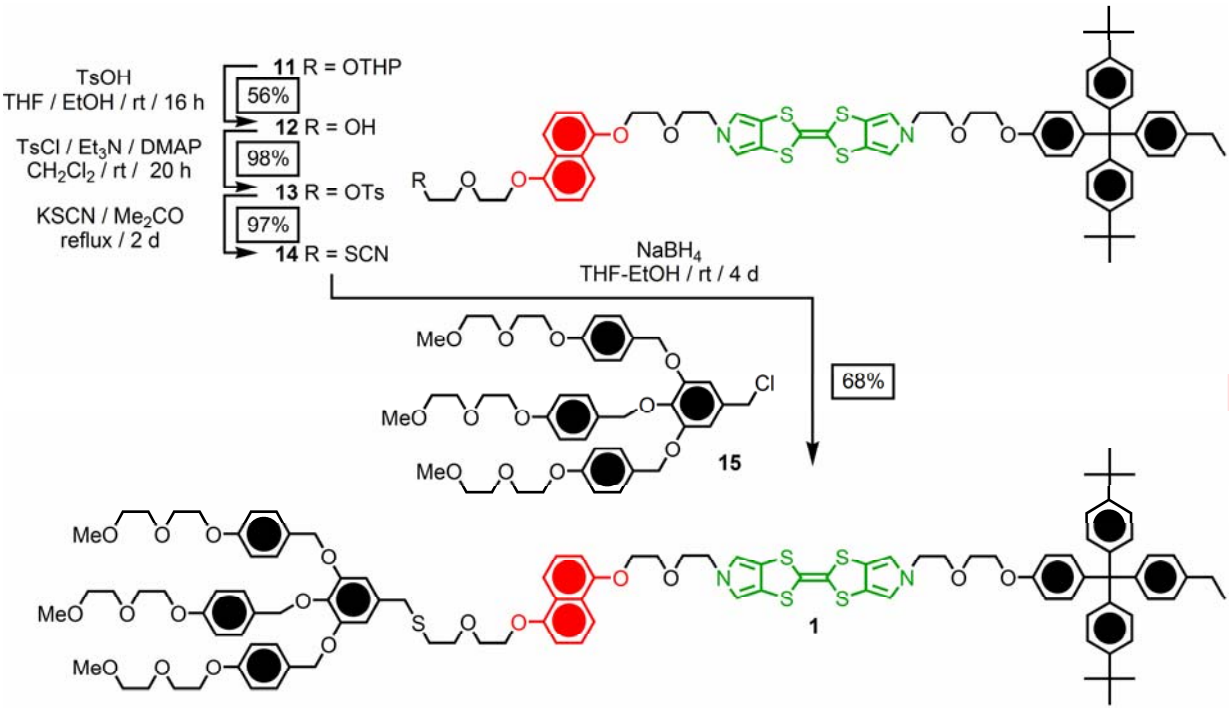
The [2]rotaxane **RBPTTF**•4PF$_6$ was synthesized according to the routes outlined sequentially in Schemes A1–A3. Alkylation of BPTTF [i] **4** with 2-[2-(2-iodoethoxy)ethoxy]tetrahydropyran [ii] (**5**) in DMF gave (Scheme A1) the BPTTF derivative **6** in 67% yield. Removal of the



Scheme A1. Synthesis of the semi-dumbbell compound **13**.

THP-protecting groups with *p*-toluenesulfonic acid (TsOH) gave the diol **7** in 67% yield. The monotosylate **8** was obtained in 22% yield by reaction of the diol **7** with one equivalent of *p*-toluenesulfonyl chloride (TsCl). Alkylation of the hydrophobic

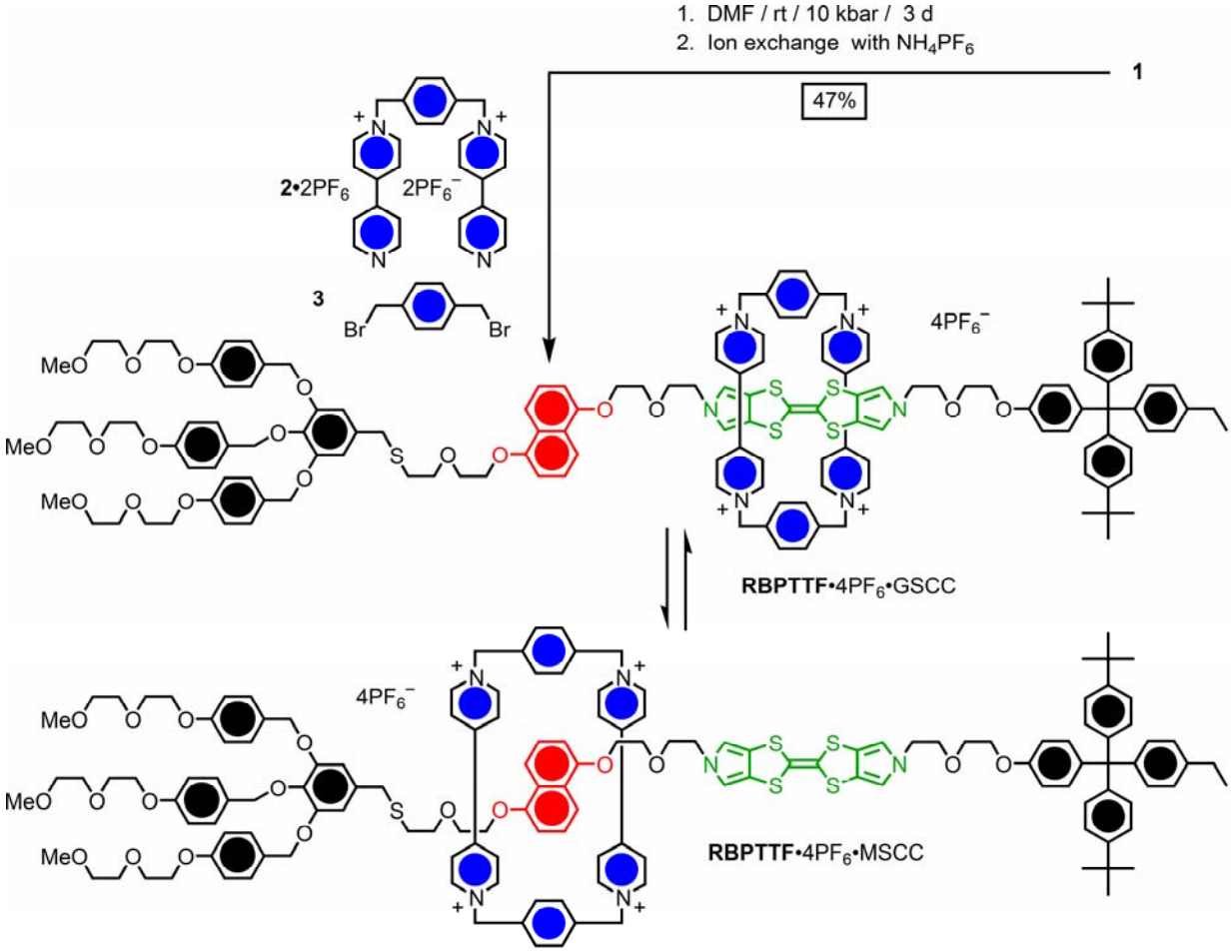
tetraarylmethane-based stopper[iii] **9** with **8** in MeCN in the presence of K_2CO_3 gave (70%) the alcohol **10**, which was tosylated using TsCl in CH_2Cl_2 affording **11** in 81% yield. Subsequently, **11** was reacted with the DNP derivative[iv] **12** under alkylation conditions (K_2CO_3 / LiBr / MeCN) affording the BPTTF derivative **13** in 60% yield, which on treatment with TsOH in THF/EtOH, gave (Scheme A2) the alcohol **14** in 56% yield. The free hydroxyl function in compound **14** was thereafter converted to a tosylate group in 98% yield (**14**→**15**) and then to a thiocyanate group in 97% yield (**15**→**16**). The thiocyanate group was reduced in situ with $NaBH_4$, and the resulting thiolate was subsequently coupled with the hydrophilic chloride[iii] **17** in THF/EtOH to



Scheme A2. Synthesis of the dumbbell compound **1**.

give the dumbbell **1** in 68% yield. Finally, the [2]rotaxane **RBPTTF**•$4PF_6$ was self-assembled (Scheme A3) under high pressure conditions by using the dumbbell

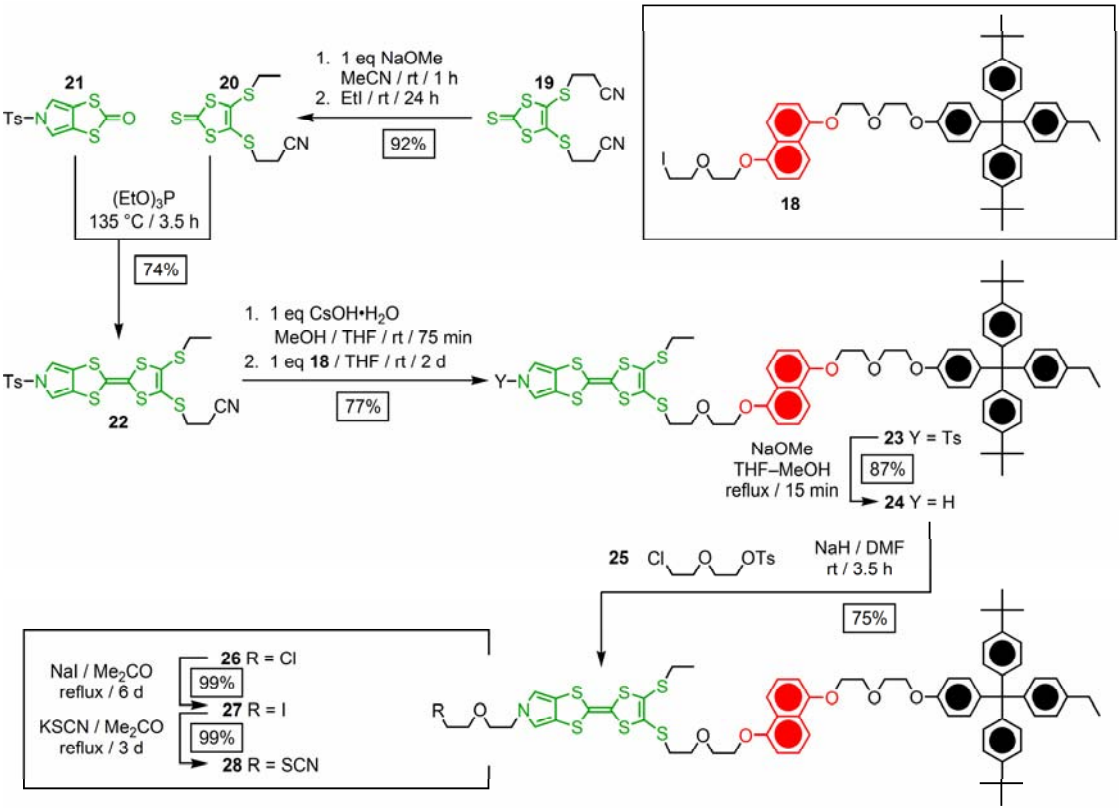
compound **1** as the template for the formation of the encircling $CBPQT^{4+}$ tetracation and the [2]rotaxane **RBPTTF**•$4PF_6$ was isolated in 47% yield from a mixture of the dumbbell compound **1**, the dicationic precursor[v] **2**•$2PF_6$, and the dibromide **3** after they had been subjected to a 10 kbar pressure in DMF at room temperature for 3 days.



Scheme A3. Synthesis of the bistable [2]rotaxane **RBPTTF**•$4PF_6$.

A-2. Synthesis of the Amphiphilic [2]Rotaxane RBLOCK•4PF$_6$

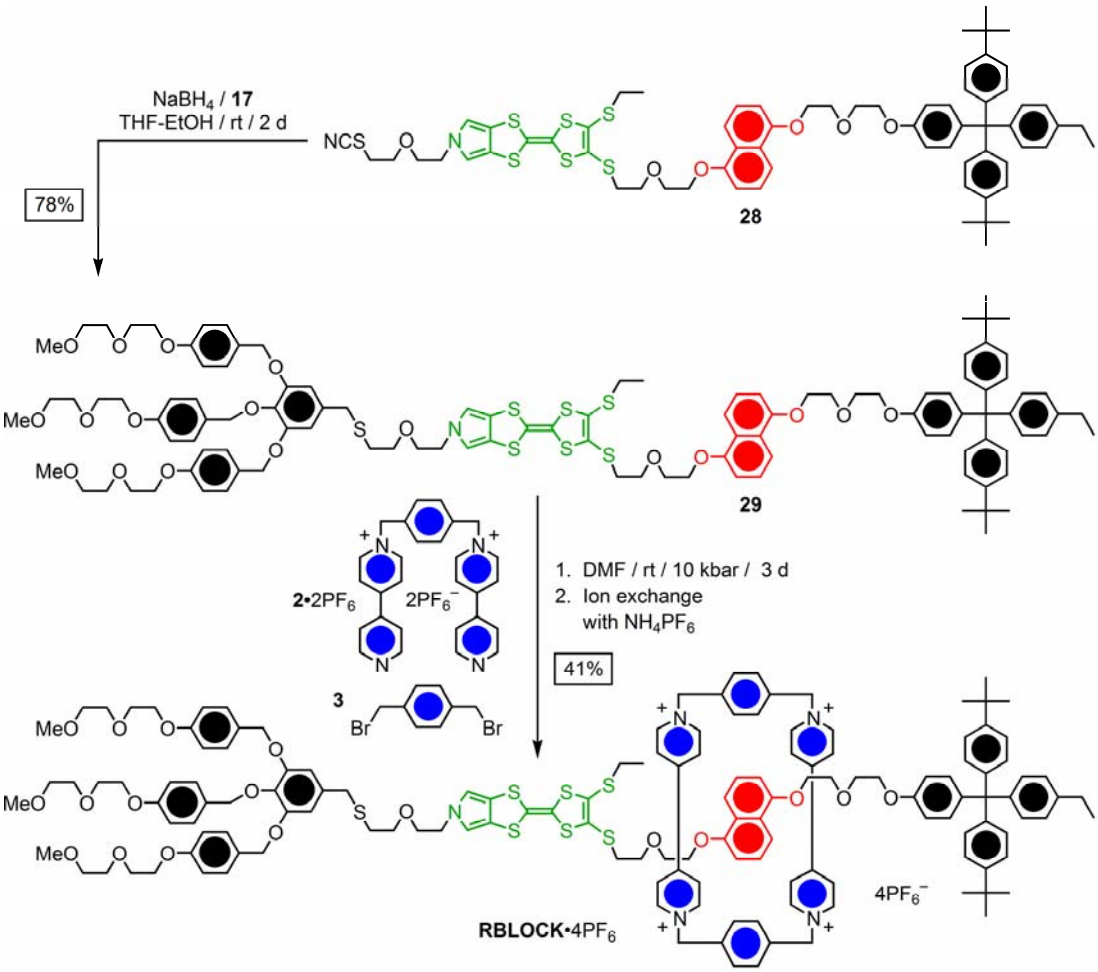
The [2]rotaxane **RBLOCK•4PF$_6$** was synthesized according to the routes outlined sequentially in Schemes A4 and A5. A THF solution of 4,5-bis(2-cyanoethylthio)-1,3-dithiole-2-thione[vi] (**19**) was treated with one equivalent of NaOMe. This procedure generated the monothiolate, which was alkylated with EtI affording compound **20** in 92% yield. Cross-coupling of 5-tosyl-(1,3)-dithiolo[4,5-*c*]pyrrole-2-one[i] (**21**) with three equivalents of the thione **20** in neat $(EtO)_3P$ gave



Scheme A4. Synthesis of the semi-dumbbell compound **28**.

(Scheme A4) the MPTTF derivative **22** (74%) in gram quantities after column chromatography. The iodide[vii] **18** was coupled with the MPTTF building block **22**, following its in situ deprotection with one equivalent of CsOH•H_2O to give **23** in 87%

yield. The tosyl protecting group on the MPTTF unit was removed in good yield (87%) using NaOMe in a THF/MeOH mixture. The resultant pyrrole nitrogen in **24** was alkylated with compound[viii] **25**, affording the chloride **26** in 75% yield. The chloride in compound **26** was initially converted to (**26**→**27**) an iodide in 99% yield and then to (**27**→**28**) a thiocyanate group in 99% yield. The thiocyanate group was reduced in situ with $NaBH_4$, and the resulting thiolate was subsequently coupled with the hydrophilic chloride[iii] **17** in THF to give the dumbbell **29** in 78% yield. Finally, the [2]rotaxane **RBLOCK**•$4PF_6$ was self-assembled (Scheme A5) under high pressure conditions by using the dumbbell compound **29** as the template for the formation of the encircling $CBPQT^{4+}$ tetracation and the [2]rotaxane **RBLOCK**•$4PF_6$ was isolated in 41% yield from a



Scheme A5. Synthesis of the [2]rotaxane **RBLOCK**•4PF_6.

mixture of the dumbbell compound **29**, the dicationic precursor[v] **2**•2PF_6, and the dibromide **3** after they had been subjected to a 10 kbar pressure in DMF at room temperature for 3 days.

A-3. Experimental Details for the Synthesis of the [2]Rotaxanes

General methods: Chemicals were purchased from Aldrich and were used as received, unless indicated otherwise. Bis(pyrrolo[3,4-*d*])tetrathiafulvalene[i] (**4**) (Scheme

A1), 2-(2-iododethoxy)-ethyl-*p*-toluenesulfonate[ii] (**5)** (Scheme A1), 4-[bis(4-*tert*-butylphenyl)(4-ethylphenyl)methyl]-phenol[iii] (**9**) (Scheme A1), compound[iv] **12** (Scheme A1), the chloride[iii] **17** (Schemes A2 and A4), 1,1′′-[1,4-phenylenebis(methylene)]bis(4,4′-bipyridin-1-ium) bis(hexafluorophosphate)[v] (**16**•2PF_6) (Schemes A3 and A5), the iodide[vii] **18** (Scheme A4), 4,5-bis(2-cyanoethylthio)-1,3-dithiole-2-thione[vi] (**19**) (Scheme A4), 5-tosyl-(1,3)-dithiolo-[4,5-*c*]pyrrole-2-one[i] (**21**) (Scheme A4), and 2-(2-chloroethoxy)-ethyl-*p*-toluenesulfonate[viii] (**25**) (Scheme A4) were all prepared according to literature procedures. Solvents were dried according to literature procedures.[ix] All reactions were carried out under an anhydrous nitrogen atmosphere. High pressure experiments were carried out in a teflon-tube on a Psika high pressure apparatus. Thin-layer chromatography (TLC) was carried out using aluminium sheets pre-coated with silica gel 60F (Merck 5554). The plates were inspected under UV light and, if required, developed in I_2 vapor. Column chromatography was carried out using silica gel 60F (Merck 9385, 0.040–0.063 mm). Deactivated SiO_2 was prepared by stirring the silica gel in CH_2Cl_2 containing 2% Et_3N for 10 min before it was filtered, washed with CH_2Cl_2 and dried. Melting points were determined on a Büchi melting point apparatus and are uncorrected. ^{1}H NMR spectra were recorded at room temperature on a Bruker ARX500 spectrometer (500 MHz), Bruker ARX400 spectrometer (400 MHz), or on a Gemini-300BB instrument (300 MHz), using residual solvent as the internal standard. ^{13}C NMR spectra were recorded at room temperature on a Gemini-300BB instrument (75 MHz), using residual solvent as the internal standard. ^{19}F NMR spectra were recorded at room temperature on a Bruker ARX400 spectrometer (376 MHz), while ^{31}P NMR spectra were recorded at room temperature on Bruker ARX400 instrument (161 MHz).

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, d = doublet, t = triplet, q = quartet, and bs = broad singlet, and m = multiplet. Samples were prepared using $CDCl_3$, CD_3COCD_3, or CD_3SOCD_3 purchased from Cambridge Isotope Labs. Electron impact ionization mass spectrometry (EI–MS) was performed on a Varian MAT 311A instrument and matrix-assisted laser-desorption/ionization time-of-flight mass spectrometry (MALDI–TOF–MS) was performed on a Kratos Kompact MALDI–TOF instrument, utilizing a 2,5-dihydroxybenzoic acid matrix, high resolution Fourier Transform matrix-assisted laser-desorption/ionisation mass spectrometry (HiRes-FT-MALDI-MS) was performed on an IonSpec 4.7 tesla Ultima Fourier Transform mass spectrometer, utilizing a 2,5-dihydroxybenzoic acid (DHP) matrix, while electrospray mass spectra (ES-MS) were obtained from a from a Sciex API III^+ mass spectrometer. Infrared (IR) spectra were recorded on a Perkin-Elmer 580 spectrophotometer. UV-vis spectra were recorded at room temperature on a Shimadzu UV-160 instrument. Microanalyses were performed by the Atlantic Microlab, Inc., Atlanta, Georgia.

Compound 6. Compound **4** (0.80 g, 2.83 mmol) was dissolved in anhydrous DMF (30 mL), cooled to 0 ºC, and degassed (N_2, 10 min) before the iodide **5** (2.50 g, 8.33 mmol) followed by NaH (0.80 g of a 60% suspension in mineral oil, 20.0 mmol) was added to the yellow solution. The reaction mixture was stirred for 3 h at 0 ºC, whereupon the reaction mixture was diluted with CH_2Cl_2 (500 mL), washed with brine (10 × 150 mL) and dried ($MgSO_4$). Removal of the solvent gave a brown oil which was purified by column chromatography (deactivated SiO_2: CH_2Cl_2/MeOH 19:1). The broad yellow band (R_f = 0.6) was collected and concentrated, affording 1.19 g (67%) of the title

compound **6** as a yellow oil. Data for **6**: ^{1}H NMR (CD_3SOCD_3, 300 MHz) δ 1.40–1.80 (m, 12H), 3.40–4.00 (m, 20H), 4.54 (bs, 2H), 6.82 (s, 4H); ^{13}C NMR (CD_3SOCD_3, 75 MHz) δ 19.6, 25.6, 30.8, 50.3, 61.7, 66.4, 70.1, 70.7, 98.5, 114.2, 117.2, 119.5; MS(EI) *m/z* 626 (M^+, 24), 542 (18), 458 (10). Anal. Calcd for $C_{28}H_{38}N_2O_6S_4$: C, 53.65; H, 6.11; N, 4.47. Found: C, 53.78; H, 6.09; N, 4.43.

Compound 7. A solution of compound **6** (1.14 g, 1.82 mmol) in THF–EtOH (50 mL, 1:1 v/v) was degassed (N_2, 10 min) before TsOH•H_2O (~10 mg, cat) was added. The yellow solution was stirred for 20 h at room temperature, whereupon it was diluted with CH_2Cl_2 (100 mL). The combined organic phase was washed with a saturated aqueous $NaHCO_3$ solution (200 mL), H_2O (300 mL) and dried ($MgSO_4$). Concentration in vacuo gave a yellow powder, which was subjected to column chromatography (deactivated SiO_2: CH_2Cl_2/MeOH 24:1). The greenish yellow band (R_f = 0.3) was collected and the solvent evaporated to give 0.56 g (67%) of the title compound **7** as a yellow powder. Data for **7**: mp 138–139 °C; ^{1}H NMR (CD_3SOCD_3, 300 MHz) δ 3.39–3.42 (m, 8H), 3.64 (t, J = 5.2 Hz, 4H), 4.00 (t, J = 5.2 Hz, 4H), 4.59 (t, J = 5.2 Hz, 2H), 6.82 (s, 4H); ^{13}C NMR (CD_3SOCD_3, 75 MHz) δ 49.8, 60.2, 70.2, 72.2, 113.7, 116.7, 118.9; MS(MALDI–TOF) *m/z* 458 (M^+, 100). Anal. Calcd for $C_{18}H_{22}N_2O_4S_4$: C, 47.14; H, 4.83; N, 6.11; S, 27.97. Found: C, 47.04; H, 4.83; N, 6.08; S, 27.73.

Compound 8. TsCl (0.57 g, 2.99 mmol) dissolved in anhydrous CH_2Cl_2 (30 mL) was added dropwise over 20–30 min to an ice-cooled solution of the diol **7** (1.30 g, 2.83 mmol), Et_3N (2 mL, 1.5 g, 14 mmol), and DMAP (~10 mg, cat) in anhydrous CH_2Cl_2 (90 mL). The reaction mixture was stirred for 20 h (0 °C to rt), whereupon Al_2O_3 (10 g,

Brockmann 1, neutral) was added and the solvent removed. The resulting green powder was directly subjected to column chromatography (deactivated SiO_2) and 0.90 g (41%) of the bistosylate was eluted with CH_2Cl_2, whereupon the eluent was changed to CH_2Cl_2/MeOH (99:1) and the yellow band (R_f = 0.5) containing the desired monotosylate was collected and concentrated to give 0.38 g (22%) of the title compound **8** as a yellow solid. Finally, 0.45 g (34%) of the starting material **7** was eluted CH_2Cl_2/MeOH (23:2). Data for **8**: ^{1}H NMR (CD_3SOCD_3, 300 MHz) δ 2.42 (s, 3H), 3.36–3.66 (m, 10H), 3.93–4.11 (m, 6H), 4.59 (t, J = 5.2 Hz, 1H), 6.74 (s, 2H), 6.83 (s, 2H), 7.46 (d, J = 8.0 Hz, 2H), 7.75 (d, J = 8.0 Hz, 2H); ^{13}C NMR (CD_3SOCD_3, 75 MHz) δ 21.1, 49.5, 49.7, 60.2, 67.7, 69.8, 70.1, 70.2, 72.1, 113.6, 113.7, 116.7, 116.8, 118.9, 127.6, 130.1, 132.5, 144.9 (one line is missing/overlapping); MS(MALDI–TOF) *m/z* 612 (M^+, 100). Anal. Calcd for $C_{25}H_{28}N_2O_6S_5$: C, 49.00; H, 4.61; N, 4.57; S, 26.16. Found: C, 48.83; H, 4.66; N, 4.67; S, 25.97.

Compound 10. A solution of the monotosylate **8** (0.37 g, 0.60 mmol) and **9** (0.86 g, 1.80 mmol) in anhydrous MeCN (50 mL) containing K_2CO_3 (0.50 g, 3.6 mmol), LiBr (10 mg, cat) and 18-crown-6 (~10 mg, cat), was heated at 75 ºC for 20 h. After cooling down to room temperature the reaction mixture was filtered and the residue washed thoroughly with MeCN (20 mL). The combined organic phase filtrate was concentrated in vacuo and the yellow residue was purified by column chromatography (deactivated SiO_2: CH_2Cl_2/Me_2CO 97:3). The yellow band (R_f = 0.2) was collected and the solvent evaporated to give 0.38 g (70%) of the title compound **10** as a yellow foam. Data for **10**: ^{1}H NMR (CD_3SOCD_3, 300 MHz) δ 1.17 (t, J = 7.6 Hz, 3H), 1.26 (s, 18H), 2.53 (q, J = 7.6 Hz, 2H), 3.39–3.49 (m, 4H), 3.62–3.71 (m, 6H), 3.99–4.02 (m, 6H), 4.59 (t, J = 5.2

Hz, 1H), 6.80–6.84 (m, 6H), 7.01–7.12 (m, 10H), 7.28–7.31 (m, 4H); MS(EI) *m/z* 917 (M^+, 55), 105 (100). Anal. Calcd for $C_{53}H_{60}N_2O_4S_4$: C, 69.39; H, 3.05; N, 6.59; S, 13.98. Found: C, 69.63; H, 2.91; N, 6.63; S, 13.73.

Compound 11. A solution of compound **10** (0.38 g, 0.41 mmol), TsCl (0.16 g, 0.82 mmol), Et_3N (0.5 mL, 0.35 g, 3.3 mmol), and DMAP (~10 mg, cat) in anhydrous CH_2Cl_2 (150 mL) was stirred at room temperature for 20 h. Al_2O_3 (10 g, Brockmann 1, neutral) was added, whereupon the solvent was removed and the residue was purified by column chromatography (deactivated SiO_2: CH_2Cl_2/Me_2CO 99:1). The yellow band ($R_f = 0.15$) was collected and the solvent evaporated to give 0.35 g (81%) of the title compound **11** as a yellow foam. Data for **11**: ^{1}H NMR (CD_3COCD_3, 300 MHz) δ 1.18 (t, $J = 7.5$ Hz, 3H), 1.29 (s, 18H), 2.43 (s, 3H), 2.60 (q, $J = 7.5$ Hz, 2H), 3.61–3.66 (m, 4H), 3.75–3.79 (m, 4H), 3.98–4.16 (m, 8H), 6.64 (s, 2H), 6.73 (s, 2H), 6.81 (d, $J = 9.0$ Hz, 2H), 7.09–7.15 (m, 10H), 7.28–7.32 (m, 4H), 7.45 (d, $J = 8.4$ Hz, 2H), 7.78 (d, $J = 8.4$ Hz, 2H); MS(FT-MALDI) *m/z* 1093 (M^+ + Na, 2), 1070 (M^+, 100), 921 (15). Anal. Calcd for $C_{60}H_{66}N_2O_6S_5$: C, 67.26; H, 6.21; N, 2.61; S, 14.96. Found: C, 65.78; H, 6.24; N, 2.36; S, 14.91.

Compound 13. A solution of the tosylate **11** (0.64 g, 0.60 mmol) and **12** (0.26 g, 0.79 mmol) in anhydrous MeCN (50 mL) containing K_2CO_3 (0.34 g, 2.4 mmol), LiBr (10 mg, cat) and 18-crown-6 (~10 mg, cat), was heated under reflux for 2 d. After cooling down to room temperature the reaction mixture was filtered and the residue washed with MeCN (2 × 50 mL). The combined organic phase filtrate was concentrated in vacuo and the yellow oily residue was purified by column chromatography (deactivated SiO_2:

CH_2Cl_2/EtOH 97:3). The yellow band was collected and the solvent evaporated affording 0.44 g (60%) of the title compound **13** as a yellow foam. Data for **13**: ^{1}H NMR (CD_3COCD_3, 300 MHz) δ 1.20 (t, J = 7.6 Hz, 3H), 1.29 (s, 18H), 1.49–1.53 (m, 6H), 2.60 (q, J = 7.6 Hz, 2H), 3.37–3.48 (m, 1H), 3.54–3.64 (m, 1H), 3.75–4.00 (m, 14H), 4.08–4.13 (m, 6H), 4.29–4.32 (m, 4H), 4.63 (bs, 1H), 6.76 (s, 2H), 6.77 (s, 2H), 6.84 (d, J = 8.9 Hz, 2H), 6.94–6.97 (m, 2H), 7.09–7.15 (m, 10H), 7.30–7.44 (m, 6H), 7.80 (d, J = 8.4 Hz, 1H), 7.85 (d, J = 8.4 Hz, 1H); MS(FT–MALDI) *m/z* 1269 (M^+ + K, 10), 1253 (M^+ + Na, 10), 1230 (M^+, 100).

Compound 14. A solution of compound **13** (0.40 g, 0.32 mmol) in THF–EtOH (40 mL, 1:1 v/v) was degassed (N_2, 10 min) before TsOH•H_2O (~10 mg, cat) was added. The yellow solution was stirred for 16 h at room temperature, whereupon it was diluted with CH_2Cl_2 (50 mL). The combined organic phase was washed with a saturated aqueous $NaHCO_3$ solution (50 mL), H_2O (50 mL) and dried ($MgSO_4$). Concentration in vacuo gave a yellow oil, which was subjected to column chromatography (deactivated SiO_2: CH_2Cl_2/EtOAc 1:1). The yellow band (R_f = 0.4) was collected and the solvent evaporated to give 0.21 g (56%) of the title compound **14** as a yellow foam. Data for **14**: ^{1}H NMR (CD_3COCD_3, 300 MHz) δ 1.24 (t, J = 7.6 Hz, 3H), 1.33 (s, 18H), 2.64 (q, J = 7.6 Hz, 2H), 3.50–3.75 (m, 5H), 3.82–3.86 (m, 4H), 3.91–3.94 (m, 2H), 3.97–4.03 (m, 4H), 4.08–4.19 (m, 6H), 4.32–4.36 (m, 4H), 6.80 (s, 2H), 6.81 (s, 2H), 6.89 (d, J = 8.9 Hz, 2H), 6.99–7.01 (m, 2H), 7.13–7.20 (m, 10H), 7.33–7.48 (m, 6H), 7.83–7.89 (m, 2H); MS(FT–MALDI) *m/z* 1185 (M^+ + K, 5), 1169 (M^+ + Na, 20), 1146 (M^+, 100).

Compound 15. A solution of compound **14** (0.20 g, 0.17 mmol), TsCl (0.068 g, 0.35 mmol), Et_3N (0.2 mL, 0.14 g, 1.4 mmol), and DMAP (~10 mg, cat) in anhydrous CH_2Cl_2 (50 mL) was stirred at room temperature for 20 h, whereupon the solvent was removed and the yellow solid was purified by column chromatography (deactivated SiO_2: CH_2Cl_2/EtOAc 19:1). The yellow band ($R_f = 0.6$) was collected and the solvent evaporated to give 0.22 g (98%) of the title compound **15** as a yellow foam. Data for **15**: ^{1}H NMR (CD_3COCD_3, 300 MHz) δ 1.20 (t, J =7.5 Hz, 3H), 1.33 (s, 18H), 2.36 (s, 3H), 2.60 (q, J = 7.5 Hz, 2H), 3.77–3.83 (m, 6H), 3.86–3.96 (m, 6H), 4.07–4.15 (m, 6H), 4.20–4.25 (m, 4H), 4.29–4.32 (m, 2H), 6.75 (s, 2H), 6.77 (s, 2H), 6.83 (d, J = 9.0 Hz, 2H), 6.94–6.97 (m, 2H), 7.09–7.15 (m, 10H), 7.30–7.35 (m, 7H), 7.39 (t, J = 8.5 Hz, 1H), 7.77–7.83 (m, 4H); MS(FT–MALDI) *m/z* 1300 (M^+, 100).

Compound 16. The tosylate **15** (0.22 g, 0.17 mmol) was dissolved in anhydrous Me_2CO (50 mL) and KSCN (0.49 g, 5.04 mmol) was added in one portion. The yellow reaction mixture was heated under reflux for 1 d, whereupon additional KSCN (0.49 g, 5.04 mmol) was added. The reaction mixture was heated under reflux for further 1 d before being cooled to room temperature. After removal of the solvent, the yellow residue was dissolved in CH_2Cl_2 (100 mL), washed with H_2O (2 × 50 mL) and dried ($MgSO_4$). Concentration in vacuo gave 0.20 g (97%) of the title compound **16** as a yellow foam. Data for **16**: ^{1}H NMR (CD_3COCD_3, 500 MHz) δ 1.20 (t, J =7.6 Hz, 3H), 1.29 (s, 18H), 2.60 (q, J = 7.6 Hz, 2H), 3.37 (t, J = 5.7 Hz, 2H), 3.78–3.81 (m, 4H), 3.89 (t, J = 4.6 Hz, 2H), 3.93–3.95 (m, 2H), 3.99 (t, J = 4.6 Hz, 2H), 4.04–4.08 (m, 2H), 4.09–4.13 (m, 6H), 4.29–4.31 (m, 2H), 4.33–4.35 (m, 2H), 6.76 (s, 2H), 6.77 (s, 2H), 6.84 (d, J = 8.8 Hz, 2H), 6.95–6.98 (m, 2H), 7.10–7.15 (m, 10H), 7.30–7.32 (m, 4H), 7.37 (t, J = 8.5

Hz, 1H), 7.42 (t, J = 8.5 Hz, 1H), 7.81 (d, J = 8.5 Hz, 1H), 7.85 (d, J = 8.5 Hz, 1H); MS(FT–MALDI) *m/z* 1226 (M^+ + K, 15), 1210 (M^+ + Na, 15), 1187 (M^+, 100); IR (KBr) ν 2154 (S-C≡N) cm^{-1}.

Dumbbell 1. Compound **16** (0.19 g, 0.16 mmol) and the chloride **17** (0.14 g, 0.18 mmol) were dissolved in anhydrous THF/EtOH (2:1 v/v, 50 mL), after which powdered $NaBH_4$ (0.060 g, 1.6 mmol) was added in one portion. The reaction mixture was stirred for 1 d at room temperature whereupon additional $NaBH_4$ (0.060 g, 1.6 mmol) was added and the reaction mixture was stirred for further 3 d at room temperature. Thereafter, it was poured into an ice cooled saturated aqueous NH_4Cl solution (50 mL) and extracted with CH_2Cl_2 (2 × 50 mL). The combined organic extracts were dried ($MgSO_4$) and concentration in vacuo gave a yellow oil, which was purified by column chromatography (deactivated SiO_2: CH_2Cl_2/EtOAc 3:2). The yellow band (R_f = 0.4) was collected and the solvent evaporated affording 0.21 g (68%) of the title compound **1** as a yellow foam Data for **1**: ^{1}H NMR (CD_3COCD_3, 500 MHz) δ 1.20 (t, J = 7.6 Hz, 3H), 1.29 (s, 18H), 2.60 (m, 4H), 3.29 (s, 9H), 3.48–3.50 (m, 6H), 3.62–3.64 (m, 6H), 3.75–3.82 (m, 14H), 3.84–3.86 (m, 2H), 3.92–3.94 (m, 4H), 4.07–4.12 (m, 12H), 4.24–4.27 (m, 2H), 4.30–4.32 (m ,2H), 4.87 (s, 2H), 4.96 (s, 4H), 6.74 (s, 2H), 6.74 (s, 2H), 6.75 (s, 2H), 6.80–6.98 (m, 10H), 7.10–7.15 (m, 10H), 7.28–7.41 (m, 12H), 7.79 (d, J = 8.6 Hz, 1H), 7.83 (d, J = 8.6 Hz, 1H); MS(MALDI–TOF) *m/z* 1925 (M^+, 100). Anal. Calcd for $C_{110}H_{128}N_2O_{18}S_5$: C, 68.58; H, 6.70; N, 1.45. Found: C, 68.41; H, 6.75; N, 1.29.

[2]Rotaxane RBPTTF•4PF$_6$. A solution of the dumbbell **1** (0.20 g, 0.10 mmol), **2**•2PF_6 (0.22 g, 0.31 mmol), and the dibromide **3** (0.082 g, 0.31 mmol) in anhydrous

DMF (8 mL) was transferred to a teflon-tube and subjected to 10 kbar of pressure at room temperature for 3 d. The greenish brown solution was directly subjected to column chromatography (deactivated SiO_2) and unreacted dumbbell 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 greenish brown band was collected. Most of the solvent was removed in vacuo ($T < 30$ °C), followed by addition of H_2O (100 mL). The resulting precipitate was collected by filtration, washed with H_2O (2 × 20 mL) and Et_2O (2 × 30 mL) and dried in vacuo over P_2O_5, affording 0.15 g (47%) of the title compound **RBPTTF**•$4PF_6$ as a brown solid. Data for **RBPTTF**•$4PF_6$: The data given below are for the 1:1 mixture of the two translational isomers; ^{19}F NMR (CD_3COCD_3, 376 MHz) δ –72.4 (d); ^{31}P NMR (CD_3COCD_3, 161 MHz) δ –144.2 (septet); MS(ES) *m/z* 1369 ($[M - 2PF_6]^{2+}$, 15), 864 ($[M - 3PF_6]^{3+}$, 80), 612 ($[M - 4PF_6]^{4+}$, 100). Anal. Calcd for $C_{146}H_{160}F_{24}N_6O_{18}P_4S_5$•$2H_2O$: C, 57.25; H, 5.40; N, 2.74; S, 5.23. Found: C, 57.05; H, 5.20; N, 2.82; S, 5.04.

2-Cyanoethylthio-5-ethylthio-1,3-dithiole-2-thione (20). A solution of compound **19** (6.09 g, 20.0 mmol) in anhydrous MeCN (150 mL) was degassed (N_2, 5 min) before a solution of NaOMe (7.6 mL of a 2.75 M solution in MeOH, 20.9 mmol) was added dropwise to the yellow solution via a syringe over a period of 45 min at room temperature. The red mixture was stirred for 15 min, whereupon EtI (3.9 mL, 7.70 g, 49.5 mmol) was added in one portion and the reaction mixture was stirred for 24 h at room temperature. The solvent was evaporated and the resulting red oil was dissolved in CH_2Cl_2 (250 mL), washed with H_2O (3 × 200 mL) and dried ($MgSO_4$). Removal of the solvent gave a red oil, which was purified by column chromatography (SiO_2:

CH_2Cl_2/cyclohexane 4:1). The second yellow band ($R_f = 0.35$) was collected and concentrated, affording a yellow oil, which was repeatedly dissolved in CH_2Cl_2 (2 × 50 mL) and concentrated to give 5.14 g (92%) of the title compound **20** as a red oil which solidified upon standing to give a yellow solid. Data for **20**: mp 49.5–50.5°C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.36 (t, $J = 7.4$ Hz, 3H), 2.74 (t, $J = 7.1$ Hz, 2H), 2.95 (q, $J = 7.4$ Hz, 2H), 3.08 (t, $J = 7.1$ Hz, 2H); ^{13}C NMR $CDCl_3$, 75 MHz) δ 14.8, 18.7, 30.8, 31.8, 117.1, 129.3, 142.4, 210.2; MS(EI) *m/z* 279 (M^+, 100), 88 (84); IR (KBr) ν 2247 cm^{-1} (C≡N). Anal. Calcd for $C_8H_9NS_5$: C, 34.38; H, 3.25; N, 5.01; S, 57.36. Found: C, 34.60; H, 3.22; N, 5.07; S, 57.48.

2-{4-(2-Cyanoethylthio)-5-ethylthio-1,3-dithiole-2-yliden}-5-tosyl-(1,3)-dithiolo[4,5-*c*]-pyrrole (22). Ketone **21** (1.87 g, 6.01 mmol) and thione **20** (1.68 g, 6.01 mmol) were suspended in distilled $(EtO)_3P$ (50 mL) and heated to 135 °C (during heating the two solids dissolved leaving a red solution and after 10–15 min a yellow orange precipitate was formed). Two additional portions of **20** (each containing 0.84 g, 3.01 mmol) were added after 15 and 30 min, respectively. The red reaction mixture was stirred for another 3 h at 135 °C, cooled to room temperature and addition of MeOH (150 mL) yielded a yellow solid, which was filtered and washed with MeOH (3 × 50 mL). The yellow solid was subjected to column chromatography (SiO_2: CH_2Cl_2) and the yellow band ($R_f = 0.4$) was collected and the solvent evaporated to give a yellow solid, which was dissolved in CH_2Cl_2/MeOH (1:1 v/v, 500 mL) and concentrated to approximately half of its volume to precipitate the product. The yellow crystals were collected by filtration, washed with MeOH (50 mL) and dried in vacuo to give 2.40 g, (74%) of the title compound **22** as yellow needles. Data for **22**: mp 200–201 °C; ^{1}H NMR

(CD_3SOCD_3, 300 MHz) δ 1.25 (t, J = 7.3 Hz, 3H), 2.38 (s, 3H), 2.84 (t, J = 6.6 Hz, 2H), 2.89 (q, J = 7.3 Hz, 2H), 3.11 (t, J = 6.6 Hz, 2H), 7.39 (s, 2H), 7.46 (d, J = 8.3 Hz, 2H), 7.82 (d, J = 8.3 Hz, 2H); ^{13}C NMR (CD_3SOCD_3, 75 MHz) δ 15.0, 18.1, 21.1, 29.9, 30.9, 112.3, 112.8 (2 signals), 117.8, 118.9, 124.0, 125.9, 126.0, 126.8, 129.8, 130.4, 134.4, 145.9; MS(EI) *m/z* 542 (M^+, 11), 387 ($[M - Ts]^+$, 28), 184 (55), 105(100), 91 (65); IR (KBr) ν 2250 cm^{-1} (C≡N). Anal. Calcd for $C_{20}H_{18}N_2O_2S_7$: C, 44.25; H, 3.34; N, 5.16; S, 41.35. Found: C, 44.40; H, 3.34; N, 5.23; S, 41.42.

Compound 23: A solution of the iodide **18** (0.95 g, 1.05 mmol) and **22** (0.55 g, 1.01 mmol) in anhydrous THF (70 mL) was degassed (N_2, 10 min) before a solution of $CsOH•H_2O$ (0.174 g, 1.04 mmol) in anhydrous MeOH (5.0 mL) was added dropwise via a syringe over a period of 75 min at room temperature. Subsequently, the reaction mixture was stirred for 2 d at room temperature, whereupon the yellow reaction mixture was diluted with CH_2Cl_2 (150 mL), washed with brine (150 mL), H_2O (2 × 150 mL) and dried ($MgSO_4$). Removal of the solvent gave a yellow foam, which was purified by column chromatography (SiO_2: CH_2Cl_2/cyclohexane 9:1). The broad yellow band (R_f = 0.35) was collected and concentrated, affording a yellow foam, which was repeatedly dissolved in CH_2Cl_2 (2 × 30 mL) and concentrated to give 0.99 g (77%) of the title compound **23** as a yellow foam. Data for **23**: ^{1}H NMR (CD_3COCD_3, 300 MHz) δ 1.20 (t, J = 7.6 Hz, 3H), 1.23 (t, J = 7.4 Hz, 3H), 1.29 (s, 18H), 2.38 (s, 3H), 2.61 (q, J = 7.6 Hz, 2H), 2.84 (q, J = 7.4 Hz, 2H), 3.10 (t, J = 6.3 Hz, 2H), 3.84 (t, J = 6.3 Hz, 2H), 3.93–3.99 (m, 4H), 4.02–4.06 (m, 2H), 4.14–4.19 (m, 2H), 4.27–4.33 (m, 4H), 6.84 (d, J = 9.0 Hz, 2H), 6.89–6.97 (m, 2H), 7.06–7.14 (m, 10H), 7.24 and 7.27 (AB q, J = 2.1 Hz, 2H), 7.28–7.43 (m, 8H), 7.80–7.85 (m, 4H); MS(MALDI–TOF) *m/z* 1265

(M^+, 22), 1111 ([*M* + H – Ts]$^+$, 100); HiRes-FT-MALDI-MS *m/z* 1265.3580 (calcd for $C_{70}H_{75}NO_7S_7^+$ 1265.3583). Anal. Calcd for $C_{70}H_{75}NO_7S_7$: C, 66.37; H, 5.97; N, 1.11; S, 17.72. Found: C, 65.88; H, 5.94; N, 1.30; S, 17.75.

Compound 24: Compound **23** (0.85 g, 0.67 mmol) was dissolved in anhydrous THF/MeOH (1:1 v/v, 70 mL) and degassed (N_2, 10 min) before NaOMe (25% solution in MeOH, 2.3 mL, 0.54 g, 10.1 mmol) was added in one portion. The yellow solution was heated under reflux for 15 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 × 100 mL) and dried ($MgSO_4$). Concentration gave a yellow foam, which was subjected to column chromatography (SiO_2: CH_2Cl_2). The yellow band (R_f = 0.5) was collected and concentrated to provide 0.64 g (87%) of the title compound **24** as a yellow foam. Data for **24**: ^{1}H NMR (CD_3COCD_3, 300 MHz) δ 1.21 (t, *J* = 7.6 Hz, 3H), 1.26 (t, *J* = 7.3 Hz, 3H), 1.30 (s, 18H), 2.61 (q, *J* = 7.6 Hz, 2H), 2.87 (q, *J* = 7.3 Hz, 2H), 3.11 (t, *J* = 6.4 Hz, 2H), 3.86 (t, *J* = 6.4 Hz, 2H), 3.95–4.01 (m, 4H), 4.02–4.05 (m, 2H), 4.16–4.19 (m, 2H), 4.29–4.33 (m, 4H), 6.79 and 6.80 (AB q, *J* = 1.9 Hz, 2H), 6.85 (d, *J* = 9.0 Hz, 2H), 6.93 (d, *J* = 8.0 Hz, 1H), 6.96 (d, *J* = 8.0 Hz, 1H), 7.06–7.14 (m, 10H), 7.26–7.38 (m, 6H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.86 (d, *J* = 8.0 Hz, 1H), 10.36 (bs, 1H); MS(MALDI–TOF) *m/z* 1112 (M^+, 100); HiRes-FT-MALDI-MS *m/z* 1111.3452 (calcd for $C_{63}H_{69}NO_5S_6^+$ 1111.3495). Anal. Calcd for $C_{63}H_{69}NO_5S_6$: C, 68.01; H, 6.25; N, 1.26; S, 17.29. Found: C, 67.74; H, 6.36; N, 1.28; S, 17.06.

Compound 26: Compound **24** (0.61 g, 0.55 mmol) and compound **25** (0.25 g, 0.90 mmol) were dissolved in anhydrous DMF (20 mL) and degassed (N_2, 10 min) before

NaH (0.055 g of a 60% suspension in mineral oil, 1.38 mmol) was added. The reaction mixture was stirred for 3.5 h at room temperature, causing the initially yellow solution to become more orange. Brine (80 mL) was added dropwise until no more gas evolution was observed and the resulting yellow precipitate was filtered, washed with H_2O (20 mL) and dried. The crude product was purified by column chromatography (SiO_2: CH_2Cl_2). The yellow band ($R_f = 0.5$) was collected and the solvent evaporated, providing 0.50 g (75%) of the title compound **26** as a yellow foam. Data for **26**: ^{1}H NMR (CD_3COCD_3, 300 MHz) δ 1.21 (t, $J = 7.6$ Hz, 3H), 1.26 (t, $J = 7.3$ Hz, 3H), 1.30 (s, 18H), 2.61 (q, $J = 7.6$ Hz, 2H), 2.86 (q, $J = 7.3$ Hz, 2H), 3.11 (t, $J = 6.4$ Hz, 2H), 3.61–3.73 (m, 4H), 3.74–3.78 (m, 2H), 3.85 (t, $J = 6.4$ Hz, 2H), 3.94–4.00 (m, 4H), 4.02–4.05 (m, 2H), 4.08–4.12 (m, 2H), 4.15–4.19 (m, 2H), 4.28–4.34 (m, 4H), 6.76 and 6.79 (AB q, $J = 2.0$ Hz, 2H), 6.85 (d, $J = 9.0$ Hz, 2H), 6.93 (d, $J = 8.0$ Hz, 1H), 6.96 (d, $J = 8.0$ Hz, 1H), 7.06–7.13 (m, 10H), 7.26–7.38 (m, 6H), 7.83 (d, $J = 8.0$ Hz, 1H), 7.86 (d, $J = 8.0$ Hz, 1H); MS(MALDI–TOF) *m/z* 1217 (M^+, 100); HiRes-FT-MALDI-MS *m/z* 1217.3675 (calcd for $C_{67}H_{76}ClNO_6S_6^+$ 1217.3680). Anal. Calcd for $C_{67}H_{76}ClNO_6S_6$: C, 66.01; H, 6.28; N, 1.15; S, 15.78. Found: C, 66.14; H, 6.30; N, 1.20; S, 15.61.

Compound 27: The chloride **26** (0.46 g, 0.38 mmol) was dissolved in anhydrous Me_2CO (60 mL) and NaI (3.42 g, 22.8 mmol) was added in one portion. The reaction mixture was heated under reflux for 6 d, before being cooled to room temperature and the solvent removed in vacuo. The yellow residue was dissolved in CH_2Cl_2 (75 mL) and washed with H_2O (3 × 50 mL), before being dried ($MgSO_4$). Concentration in vacuo gave 0.49 g (99%) of the title compound **27** as a yellow foam. Data for **27**: ^{1}H NMR (CD_3COCD_3, 300 MHz) δ 1.21 (t, $J = 7.6$ Hz, 3H), 1.26 (t, $J = 7.3$ Hz, 3H), 1.30

(s, 18H), 2.61 (q, J = 7.6 Hz, 2H), 2.86 (q, J = 7.3 Hz, 2H), 3.11 (t, J = 6.4 Hz, 2H), 3.30 (t, J = 6.5 Hz, 2H), 3.69 (t, J = 6.5 Hz, 2H), 3.74–3.78 (m, 2H), 3.85 (t, J = 6.4 Hz, 2H), 3.95–4.01 (m, 4H), 4.02–4.06 (m, 2H), 4.08–4.12 (m, 2H), 4.16–4.19 (m, 2H), 4.29–4.34 (m, 4H), 6.77 and 6.80 (AB q, J = 2.1 Hz, 2H), 6.85 (d, J = 9.0 Hz, 2H), 6.93 (d, J = 8.0 Hz, 1H), 6.96 (d, J = 8.0 Hz, 1H), 7.06–7.14 (m, 10H), 7.26–7.38 (m, 6H), 7.83 (d, J = 8.0 Hz, 1H), 7.86 (d, J = 8.0 Hz, 1H); MS(MALDI–TOF) *m/z* 1309 (M^+, 100); HiRes-FT-MALDI-MS *m/z* 1309.3035 (calcd for $C_{67}H_{76}INO_6S_6^+$ 1309.3036). Anal. Calcd for $C_{67}H_{76}INO_6S_6$: C, 61.40; H, 5.84; N, 1.07; S, 14.68. Found: C, 61.78; H, 5.83; N, 1.11; S, 14.50.

Compound 28: The iodide **27** (0.48 g, 0.37 mmol) was dissolved in anhydrous Me_2CO (50 mL) and KSCN (1.78 g, 18.3 mmol) was added in one portion. The yellow reaction mixture was heated under reflux for 3 d, whereupon the reaction mixture was cooled to room temperature. After removal of the solvent, the yellow residue was dissolved in CH_2Cl_2 (100 mL), washed with H_2O (3 × 75 mL) and dried ($MgSO_4$). Concentration in vacuo gave 0.45 g (99%) of the title compound **28** as a yellow foam. Data for **28**: ^{1}H NMR (CD_3COCD_3, 300 MHz) δ 1.21 (t, J = 7.6 Hz, 3H), 1.26 (t, J = 7.3 Hz, 3H), 1.30 (s, 18H), 2.61 (q, J = 7.6 Hz, 2H), 2.87 (q, J = 7.3 Hz, 2H), 3.11 (t, J = 6.4 Hz, 2H), 3.28 (t, J = 5.7 Hz, 2H), 3.76–3.81 (m, 4H), 3.86 (t, J = 6.4 Hz, 2H), 3.94–4.01 (m, 4H), 4.03–4.06 (m, 2H), 4.11–4.14 (m, 2H), 4.16–4.19 (m, 2H), 4.29–4.34 (m, 4H), 6.77 and 6.80 (AB q, J = 2.1 Hz, 2H), 6.85 (d, J = 9.0 Hz, 2H), 6.93 (d, J = 8.0 Hz, 1H), 6.96 (d, J = 8.0 Hz, 1H), 7.06–7.14 (m, 10H), 7.26–7.38 (m, 6H), 7.83 (d, J = 8.0 Hz, 1H), 7.86 (d, J = 8.0 Hz, 1H); MS(MALDI–TOF) *m/z* 1241 (M^+, 100); HiRes-FT-MALDI-MS *m/z* 1240.3743 (calcd for $C_{68}H_{76}N_2O_6S_7^+$ 1240.3743); IR (KBr) ν 2154 cm^{-1}

(S-C≡N). Anal. Calcd for $C_{68}H_{76}N_2O_6S_7$: C, 65.77; H, 6.17; N, 2.26; S, 18.08. Found: C, 65.87; H, 6.31; N, 2.28; S, 17.83.

Dumbbell 29: The chloride **17** (0.19 g, 0.24 mmol) and compound **28** (0.25 g, 0.20 mmol) were dissolved in anhydrous THF/EtOH (2:1 v/v, 50 mL), after which powdered $NaBH_4$ (0.15 g, 3.97 mmol) was added in one portion. The reaction mixture was stirred for 2 d at room temperature, whereupon it was poured into a saturated aqueous NH_4Cl solution (50 mL), and extracted with CH_2Cl_2 (2 × 75 mL). The combined organic extracts were washed with brine (100 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 = 0.5) was collected and the solvent evaporated affording a yellow oil, which was repeatedly dissolved in CH_2Cl_2 (2 × 25 mL) and concentrated to give 0.31 g (78%) of the title compound **29** as a yellow foam. Data for **29**: ^{1}H NMR (CD_3COCD_3, 300 MHz) δ 1.21 (t, J = 7.6 Hz, 3H), 1.24 (t, J = 7.3 Hz, 3H), 1.30 (s, 18H), 2.52 (t, J = 6.4 Hz, 2H), 2.61 (q, J = 7.6 Hz, 2H), 2.84 (q, J = 7.3 Hz, 2H), 3.08 (t, J = 6.4 Hz, 2H), 3.29 (s, 9H), 3.49 (t, J = 6.4 Hz, 2H), 3.48–3.51 (m, 6H), 3.62–3.67 (m, 10H), 3.77–3.82 (m, 6H), 3.83 (t, J = 6.4 Hz, 2H), 3.93–3.98 (m, 4H), 4.01–4.18 (m, 12H), 4.26–4.32 (m, 4H), 4.91 (s, 2H), 5.03 (s, 4H), 6.73 (s, 2H), 6.76 and 6.78 (AB q, J = 2.0 Hz, 2H), 6.82 (d, J = 8.5 Hz, 2H), 6.85 (d, J = 9.1 Hz, 2H), 6.92 (d, J = 8.0 Hz, 1H), 6.94 (d, J = 8.0 Hz, 1H), 6.95 (d, J = 8.6 Hz, 4H), 7.07–7.14 (m, 10H), 7.26–7.35 (m, 8H), 7.39 (d, J = 8.6 Hz, 4H), 7.83 (d, J = 8.0 Hz, 1H), 7.86 (d, J = 8.0 Hz, 1H); MS(MALDI–TOF) *m/z* 1976 (M^+, 100), 1767 (12); HiRes-FT-MALDI-MS *m/z* 1977.7405 (calcd for $C_{110}H_{131}NO_{18}S_7^+$ 1977.7406). Anal. Calcd for $C_{110}H_{131}NO_{18}S_7$: C, 66.74; H, 6.67; N, 0.71; S, 11.34. Found: C, 66.64; H, 6.45; N, 0.77; S, 11.15.

[2]Rotaxane RBLOCK•4PF$_6$: A solution of the dumbbell **29** (0.25 g, 0.13 mmol), **2**•2PF$_6$ (0.27 g, 0.38 mmol), and the dibromide **3** (0.10 g, 0.38 mmol) in anhydrous DMF (12 mL) was transferred to a teflon-tube and subjected to 10 kbar of pressure at room temperature for 3 d. The red solution 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 (1.0 g NH_4PF_6 in 100 mL Me_2CO) and the red band was collected. Most of the solvent was removed in vacuo (T < 30 °C), followed by addition of H_2O (100 mL). The resulting precipitate was collected by filtration, washed with H_2O (2 × 20 mL) and Et_2O (2 × 30 mL) and dried in vacuo over P_2O_5, affording 0.16 g (41%) of the title compound **RBLOCK**•4PF$_6$ as a red solid. Data for **RBLOCK**•4PF$_6$: mp 170 °C (decomposed without melting); ^{1}H NMR (400 MHz, CD_3COCD_3) δ 1.18 (t, J = 7.6 Hz, 3H), 1.27 (s, 18H), 1.30 (t, J = 7.3 Hz, 3H), 2.56 (t, J = 6.2 Hz, 2H), 2.58 (q, J = 7.6 Hz, 2H), 2.72 (d, J = 8.0 Hz, 1H), 2.74 (d, J = 8.0 Hz, 1H), 2.93 (q, J = 7.3 Hz, 2H), 3.29 (s, 9H), 3.41–3.46 (m, 2H), 3.48–3.52 (m, 6H), 3.55 (t, J = 6.5 Hz, 2H), 3.63–3.69 (m, 8H), 3.71 (s, 2H), 3.74–3.82 (m, 6H), 4.02–4.22 (m, 10H), 4.34–4.45 (m, 6H), 4.48–4.62 (m, 6H), 4.90 (s, 2H), 5.04 (s, 4H), 6.01–6.14 (bm, 8H), 6.15 (t, J = 8.0 Hz, 1H), 6.24 (t, J = 8.0 Hz, 1H), 6.44 (d, J = 8.0 Hz, 1H), 6.45 (d, J = 8.0 Hz, 1H), 6.66 and 6.72 (AB q, J = 2.2 Hz, 2H), 6.78 (s, 2H), 6.80–6.96 (m, 8H), 7.03–7.10 (m, 10H), 7.26–7.34 (m, 6H), 7.40 (d, J = 8.4 Hz, 4H), 7.50–7.90 (bm, 8H), 8.10–8.50 (bm, 8H), 9.05–9.45 (bm, 8H); MS (MALDI–TOF): *m/z* 2644 ([M – 3PF$_6$]$^+$, 8) 2499 ([M – 4PF$_6$]$^+$, 8) 1977 (2), 665 ([CBPQT•PF$_6$]$^+$, 16), 561 (100); UV/Vis (MeCN, 298 K) λ_{max} 540 nm (ε 920 L mol^{-1} cm^{-1}). Anal. Calcd for $C_{146}H_{163}F_{24}N_5O_{18}P_4S_7$•2$H_2O$: C, 56.27; H, 5.40; N, 2.25; S, 7.20. Found: C, 56.23; H, 5.32; N, 2.46; S, 7.50.

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