ORGANIC LETTERS

Counterion Induced Translational Isomerism in a Bistable [2]Rotaxane

Bo W. Laursen, Sune Nygaard, Jan O. Jeppesen,* and J. Fraser Stoddart*

Department of Chemistry and Biochemistry, University of California, Los Angeles, 405 Hilgard Avenue, Los Angeles, CA 90095-1569, USA
Department of Chemistry, Odense University (University of Southern Denmark), Campusvej 55, DK-5230, Odense M, Denmark

joj@chem.sdu.dk

SUPPORTING INFORMATION

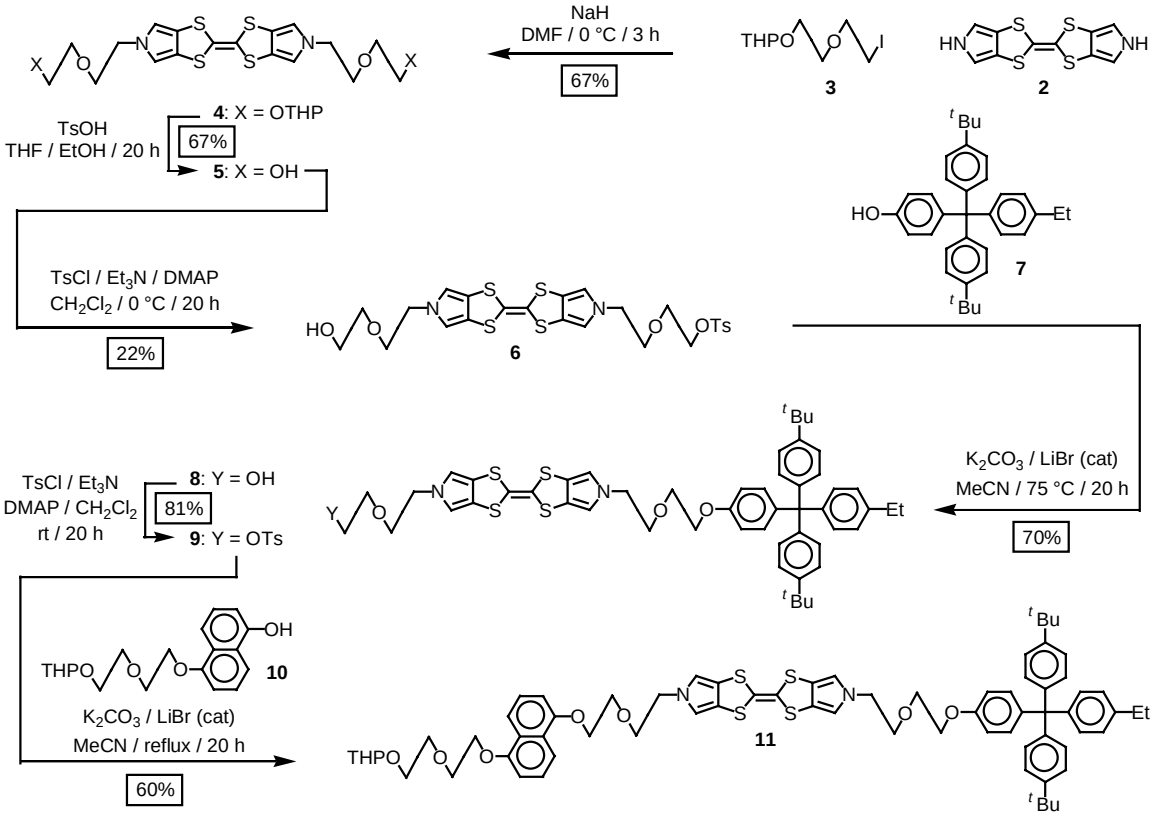
(18 Pages)

Introduction

In this supplement, we describe the experimental procedures for the syntheses of the [2]rotaxanes **1**•4PF_6 and **1**•TRISPHAT, together with spectrometric and spectroscopic characterization. We also provide more details on the preparation of Me_4N•TRISPHAT.

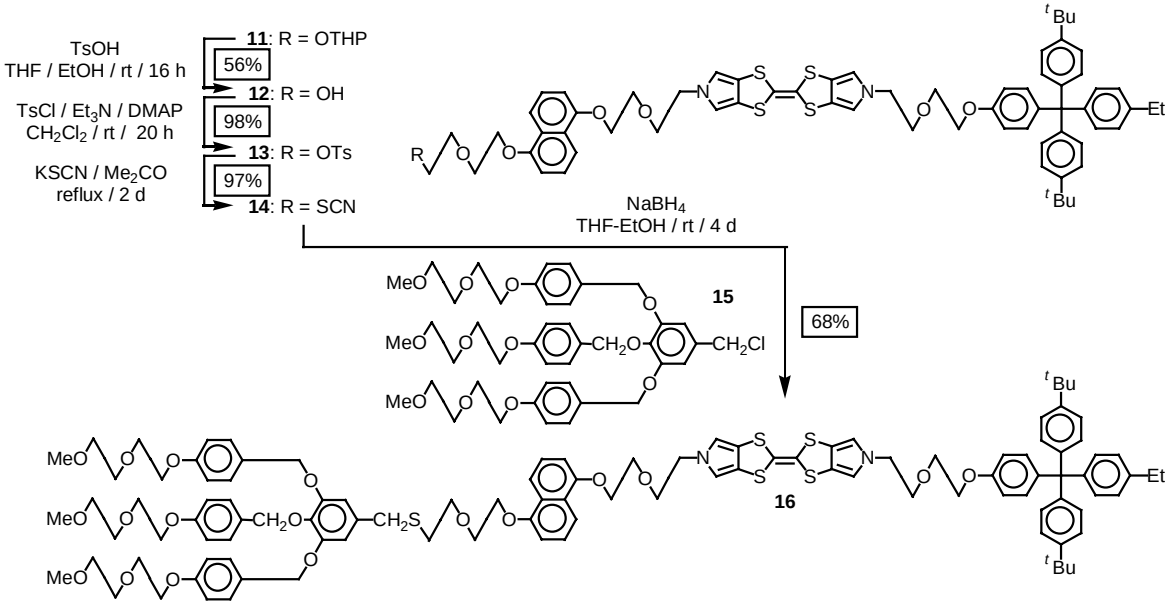
Synthesis of the Amphiphilic [2]Rotaxane 1•4PF_6

The [2]rotaxane **1**•4PF_6 was synthesized according to the routes outlined sequentially in Schemes S1–S3. Alkylation of BPTTF[1] **2** with 2-[2-(2-iodoethoxy)ethoxy]tetrahydropyran[2] (**3**) in DMF gave (Scheme 1) the BPTTF derivative **4** in 67% yield. Removal of the THP-protecting groups with *p*-toluenesulfonic acid (TsOH) gave the diol **5** in 67% yield. The



Scheme S1. Synthesis of the semi-dumbbell compound **11**.

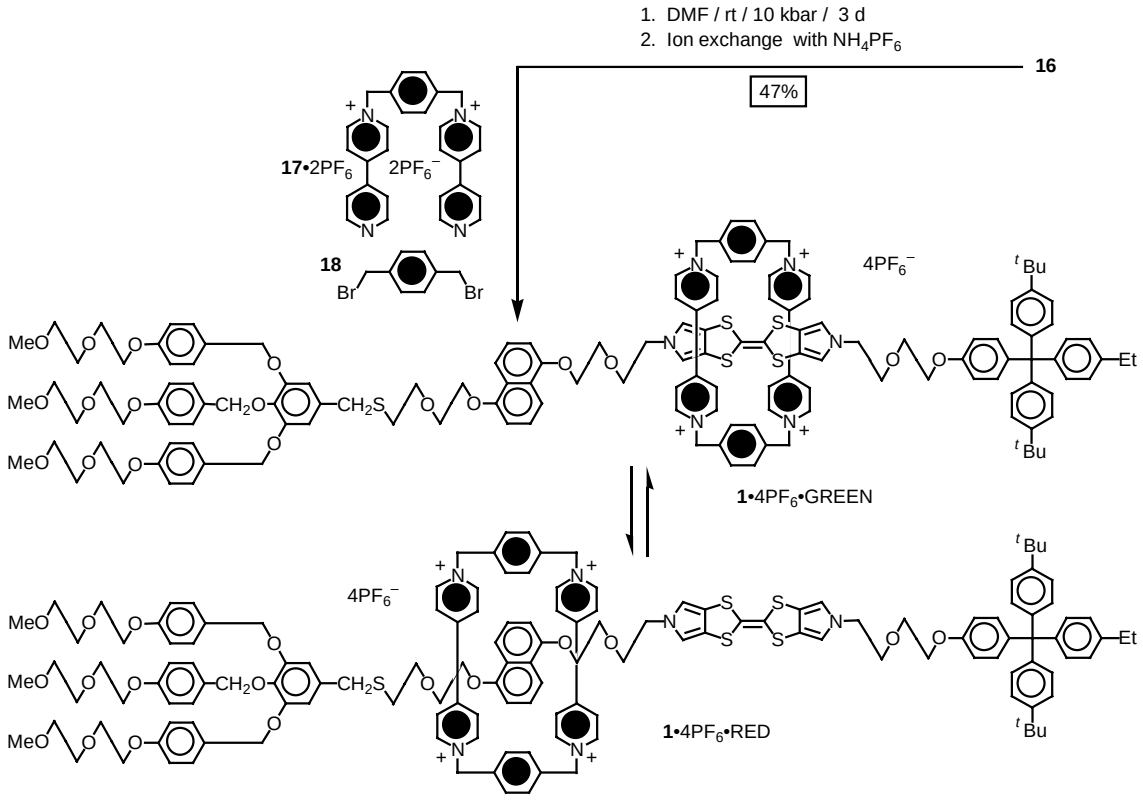
monotosylate **6** was obtained in 22% yield by reaction of the diol **5** with one equivalent of *p*-toluenesulfonyl chloride (TsCl). Alkylation of the hydrophobic tetraarylmethane-based stopper[3] **7** with **6** in MeCN in the presence of K_2CO_3 gave (70%) the alcohol **8**, which was tosylated using TsCl in CH_2Cl_2 affording **9** in 81% yield. Subsequently, **9** was reacted with the DNP derivative[4] **10** under alkylation conditions (K_2CO_3 / LiBr / MeCN) affording the BPTTF derivative **11** in 60% yield, which on treatment with TsOH in THF/EtOH, gave (Scheme 2) the alcohol **12** in 56% yield. The free hydroxyl function in compound **12** was thereafter converted to a tosylate group in 98% yield (**12**→**13**) and then to a thiocyanate group in 97% yield (**13**→**14**).The thiocyanate group was reduced in situ with $NaBH_4$, and the resulting thiolate was subsequently coupled with the hydrophilic chloride[3] **15** in THF/EtOH to give the



Scheme S2. Synthesis of the dumbbell compound **16**.

dumbbell **16** in 68% yield. Finally, the [2]rotaxane **1**•4PF_6 was self-assembled (Scheme 3) under high pressure conditions by using the dumbbell compound **16** as the template for the formation of the encircling $CBPQT^{4+}$ tetracation and the [2]rotaxane **1**•4PF_6 was isolated in

47% yield from a mixture of the dumbbell compound **16**, the dicationic precursor[5] **17**•2PF_6, and the dibromide **18** after they had been subjected to a 10 kbar pressure in DMF at room temperature for 3 days.



Scheme S3. Synthesis of the bistable [2]rotaxane **1**•4PF_6.

Experimental Details for the Synthesis of the [2]Rotaxane

General methods: Chemicals were purchased from Aldrich and were used as received, unless indicated otherwise. Bis(pyrrolo[3,4-*d*])tetrathiafulvalene[1] (**2**) (Scheme 1), 2-(2-iododethoxy)-ethyl-*p*-toluenesulfonate[2] (**3)** (Scheme 1), 4-[bis(4-*tert*-butylphenyl)(4-ethylphenyl)methyl]-phenol[3] (**7**) (Scheme 1), compound[4] **10** (Scheme 1), the chloride[3] **15** (Scheme 2), 1,1′′-[1,4-phenylenebis(methylene)]bis(4,4′-bipyridin-1-ium) bis(hexafluoro-phosphate)[5] (**17**•2PF_6) (Scheme 3) and morpholinium•TRISPHAT[6] were all prepared according to literature procedures. Solvents were dried according to literature procedures.[7] 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), which was deactivated 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 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, Fourier Transform matrix-assisted laser-desorption/ionisation mass spectrometry (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. Microanalyses were performed by the Atlantic Microlab, Inc., Atlanta, Georgia. UV-vis spectra were recorded at room temperature on a Shimadzu UV-160 instrument.

Compound 4. Compound **2** (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 **3** (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 **4** as a yellow oil. Data for **4**: ^{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 5. A solution of compound **4** (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 **5** as a yellow powder. Data for **5**: 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 6. 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 **5** (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 **6** as a yellow solid. Finally, 0.45 g (34%) of the starting material **5** was eluted CH_2Cl_2/MeOH (23:2). Data for **6**: ^{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 8. A solution of the monotosylate **6** (0.37 g, 0.60 mmol) and **7** (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 **8** as a yellow foam. Data for **8**: ^{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 9. A solution of compound **8** (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 **9** as a yellow foam. Data for **9**: ^{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 11. A solution of the tosylate **9** (0.64 g, 0.60 mmol) and **10** (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 **11** as a yellow foam. Data for **11**: ^{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 12. A solution of compound **11** (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 **12** as a yellow foam. Data for **12**: ^{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 13. A solution of compound **12** (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 **13** as a yellow foam. Data for **13**: ^{1}H NMR (CD_3COCD_3, 300 MHz) δ1.20 (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 14. The tosylate **13** (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 **14** as a yellow foam. Data for **14**: ^{1}H NMR (CD_3COCD_3, 500 MHz) δ1.20 (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 16. Compound **14** (0.19 g, 0.16 mmol) and the chloride **15** (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 **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 (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 1•4PF$_6$. A solution of the dumbbell **16** (0.20 g, 0.10 mmol), **17**•2PF_6 (0.22 g, 0.31 mmol), and the dibromide **18** (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 **1**•4PF_6 as a brown solid. Data for **1**•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 $C_{146}H_{160}F_{24}N_6O_{18}P_4S_5$•2$H_2O$: 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]Rotaxane 1•4TRISPHAT. Me_2CO solutions of **1**•4PF_6 (0.025 g, 0.0083 mmol) and morpholinium•TRISPHAT (0.035 g, 0.041 mmol) were mixed at room temperature and the solvent removed. The resulting solid material was redissolved in $CHCl_3$ (125 mL) and washed with milli-Q H_2O (80 mL). The two phases were separated and the aqueous phase extracted with $CHCl_3$ (2 × 30 mL). The combined organic phases were washed with milli-Q H_2O (2 × 50 mL) and dried ($MgSO_4$). Removal of the solvent gave a green solid wherefrom excess morpholinium•TRISPHAT (identified from the morpholinium signals in the ^{1}H NMR spectrum) was removed by reprecipitating the product from Me_2CO/Et_2O twice, providing 0.033 g (72%) of the title compound **1**•4TRISPHAT as a green solid. Data for **1**•4TRISPHAT: ^{31}P NMR (CD_3COCD_3, 161 MHz) δ –80.7 (s); MS(ES) *m/z* 1992 ([M – TRISPHAT]$^{2+}$, 13), 1072 ([M – TRISPHAT^{3+}, 100), 612 ([M – 4TRISPHAT]$^{4+}$, 12).

Me_4N•TRISPHAT. A solution of morpholinium•TRISPHAT (0.050 mg, 0.058 mmol) in CH_2Cl_2 (150 mL) was washed with an aqueous solution containing a large excess of Me_4N•Br followed by washing with H_2O. The two phases were separated and the organic phase dried ($MgSO_4$) before the solvent was removed, providing 0.045 g (0.053 mmol) of the title compound Me_4N•TRISPHAT as a white solid. Data for Me_4N•TRISPHAT: ^{1}H NMR (CD_3COCD_3, 400 MHz) δ 3.44 (s, 12H); ^{31}P NMR (CD_3COCD_3, 161 MHz) δ –80.7 (s).

Spectroscopic Characterization of 1•4PF$_6$ and 1•4TRISPHAT

A comparison of the full ^{1}H NMR spectra (400 MHz) of **1**•4PF$_6$ and **1**•4TRISPHAT recorded in CD_3COCD_3 is shown in Figure S1.

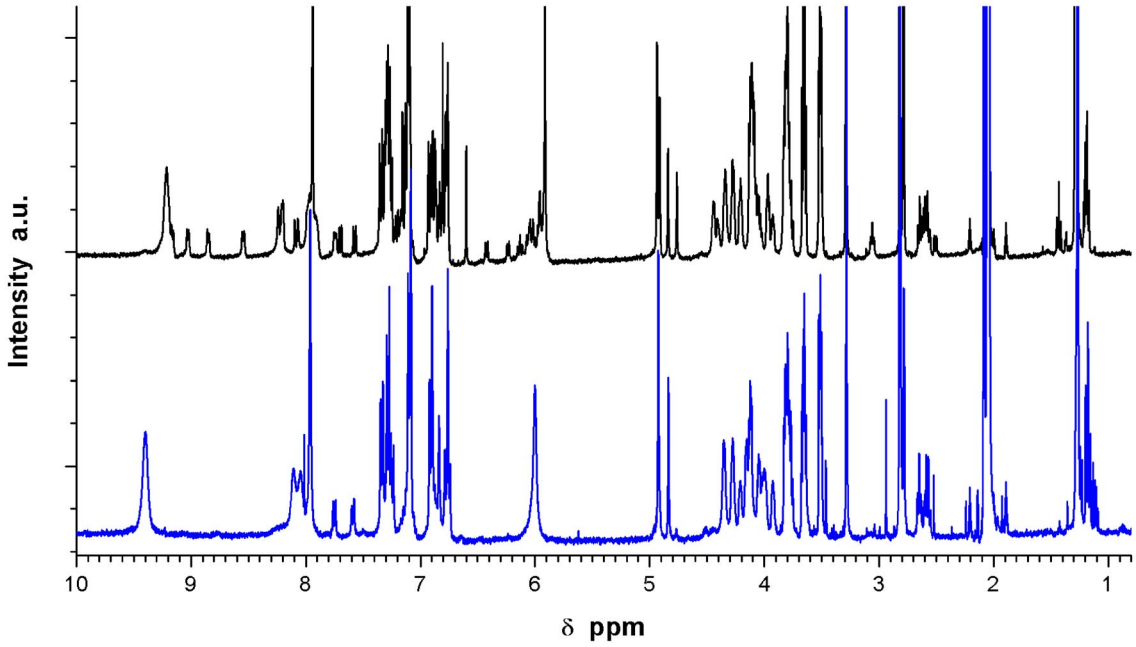


Figure S1. ^{1}H NMR spectra (400 MHz) of **1**•4PF$_6$ (black trace) and **1**•4TRISPHAT (blue trace) recorded in CD_3COCD_3 at 295 K.

Figure S2 show a comparsion of the ^{19}F NMR spectra (376 MHz) of **1**•4PF_6 and **1**•4TRISPHAT recorded in CD_3COCD_3, while Figure S3 show a comparsion of the ^{31}P NMR spectra (161 MHz) of **1**•4PF_6 and **1**•4TRISPHAT recorded in CD_3COCD_3.

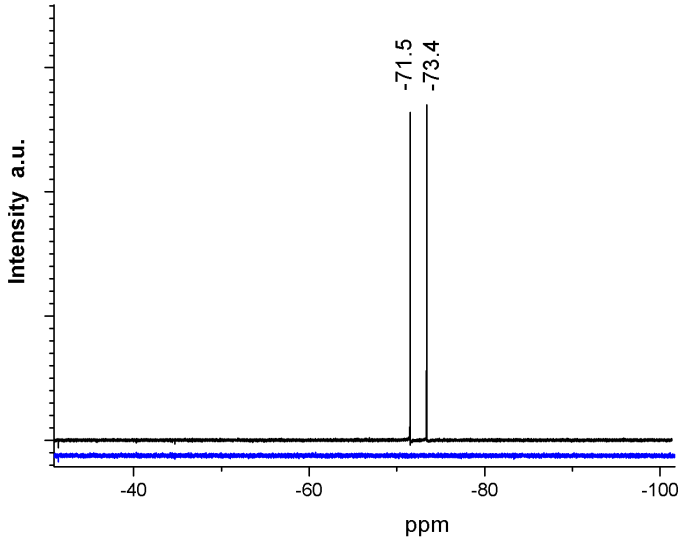


Figure S2. ^{19}F NMR spectra (376 MHz) of **1**•4PF_6 (black line) and **1**•4TRISPHAT (blue line) recorded in CD_3COCD_3 at 295 K.

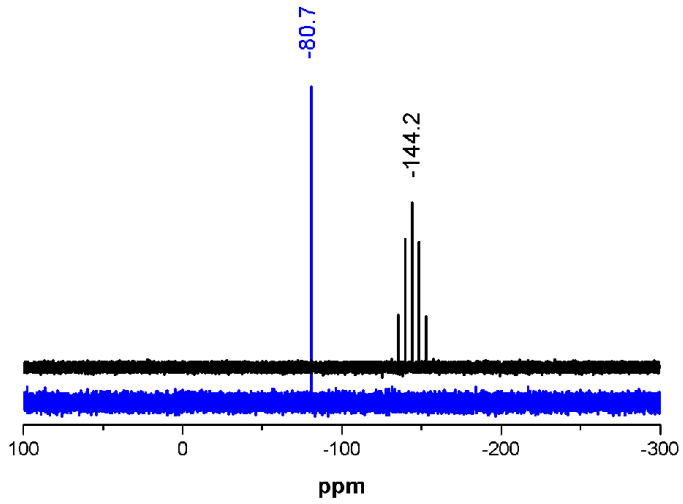
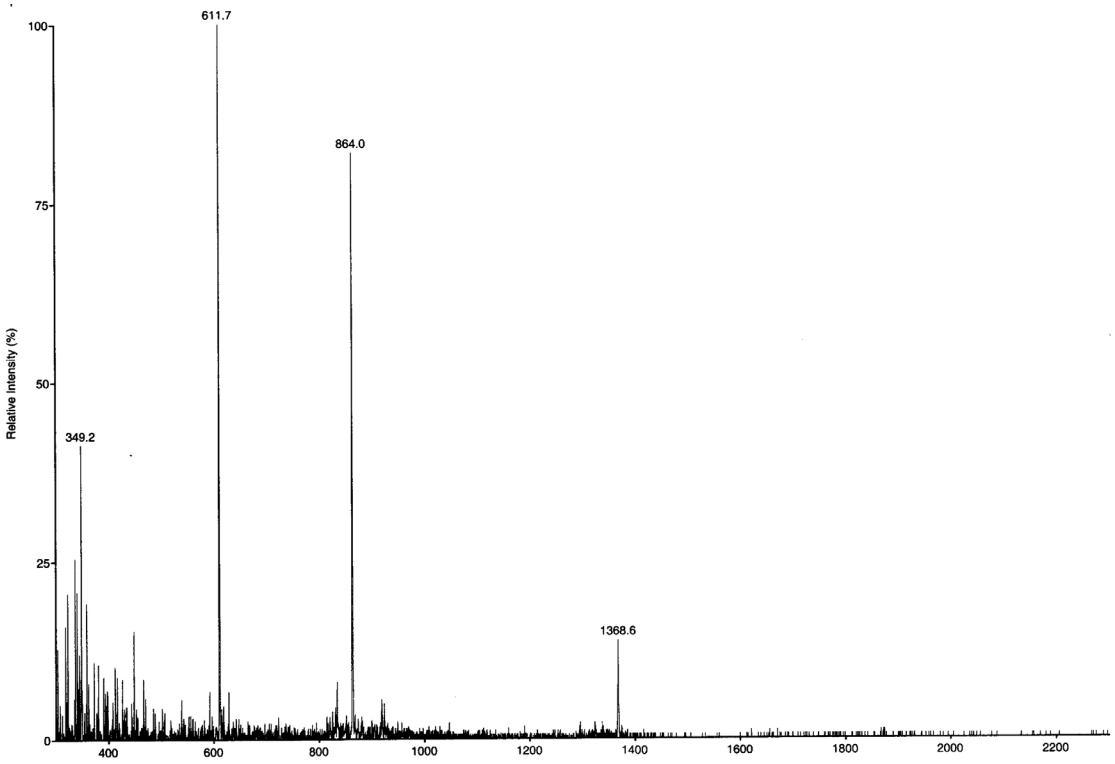


Figure S3. ^{31}P NMR spectra (161 MHz) of **1**•4PF_6 (black trace) and the product of the anion exchange **1**•4TRISPHAT (blue trace) recorded in CD_3COCD_3 at 295 K.

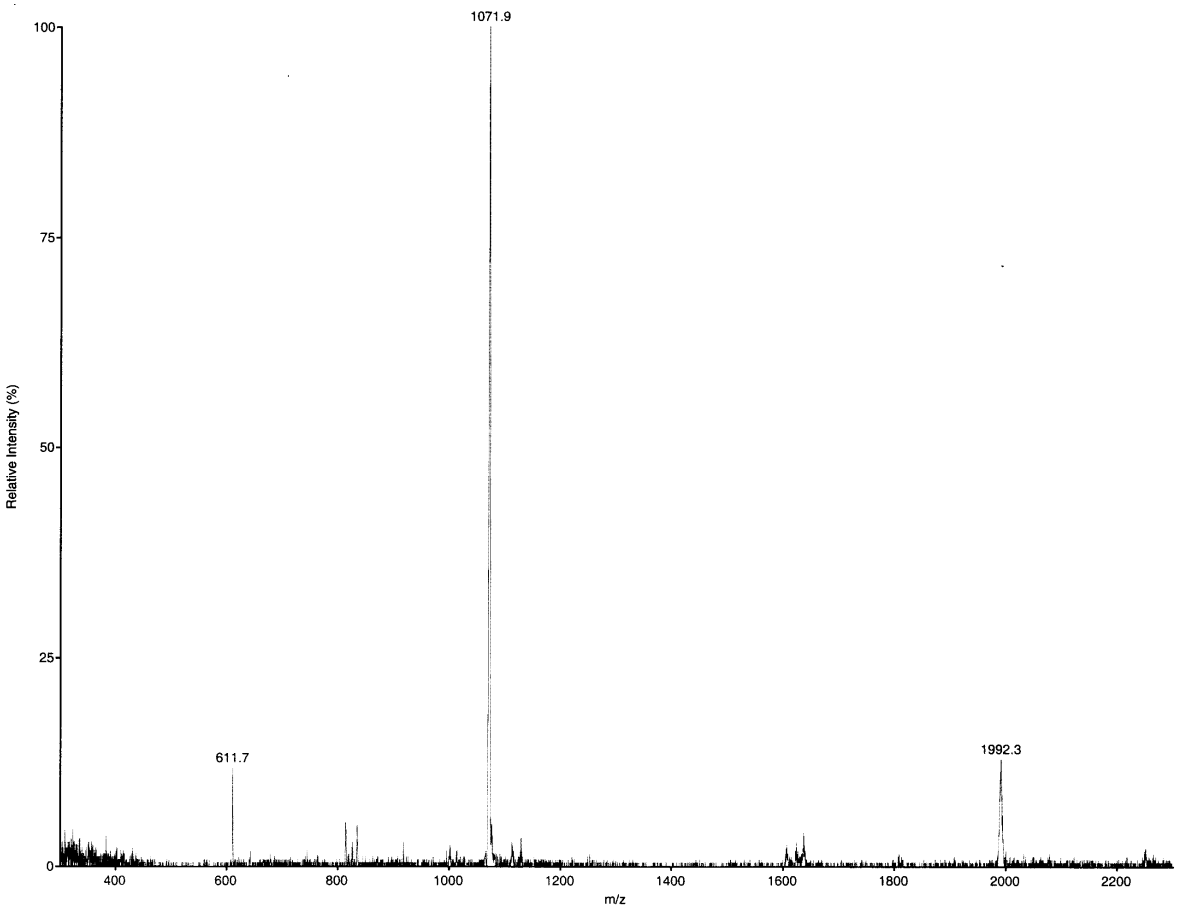
Spectrometric Characterization of 1•4PF_6 and 1•4TRISPHAT

Electrospray mass spectra (ES-MS) recorded of **1**•4PF_6 and **1**•4TRISPHAT are depicted in Figure S4 and S5, respectively.



	Actual peak	Intensity	Calculated peak
$[\mathbf{1}]^{4+}$	611.70	124.67	611.75
$[\mathbf{1}\bullet PF_6]^{3+}$	864.00	99.33	864.00
$[\mathbf{1}\bullet 2PF_6]^{2+}$	1368.60	16.667	1368.50

Figure S4. ES-MS spectrum (Me_2CO) of **1**•4PF_6 together with a table comparing the location of the actual peaks with the calculated peaks.



	Actual peak	Intensity	Calculated peak
[**1**]$^{4+}$	611.70	13.75	611.85
[**1**•TRISPHAT]$^{3+}$	1071.90	116.67	1072.00
[**1**•2TRISPHAT]$^{2+}$	1992.30	15.00	1992.30

Figure S5. ES-MS spectrum (Me_2CO) of **1**•TRISPHAT together with a table comparing the location of the actual peaks with the calculated peaks.

Titration of 1•4TRISPHAT with $Bu_4N•PF_6$

The titration was carried out by adding $Bu_4N•PF_6$ to a Me_2CO solution of **1**•4TRISPHAT and monitoring the growth/decrease of the charger transfer absorption bands at 540 and 825 nm. Figure S6 illustrates the UV-vis spectra recorded by adding $Bu_4N•PF_6$ to a Me_2CO solution of **1**•4TRISPHAT.

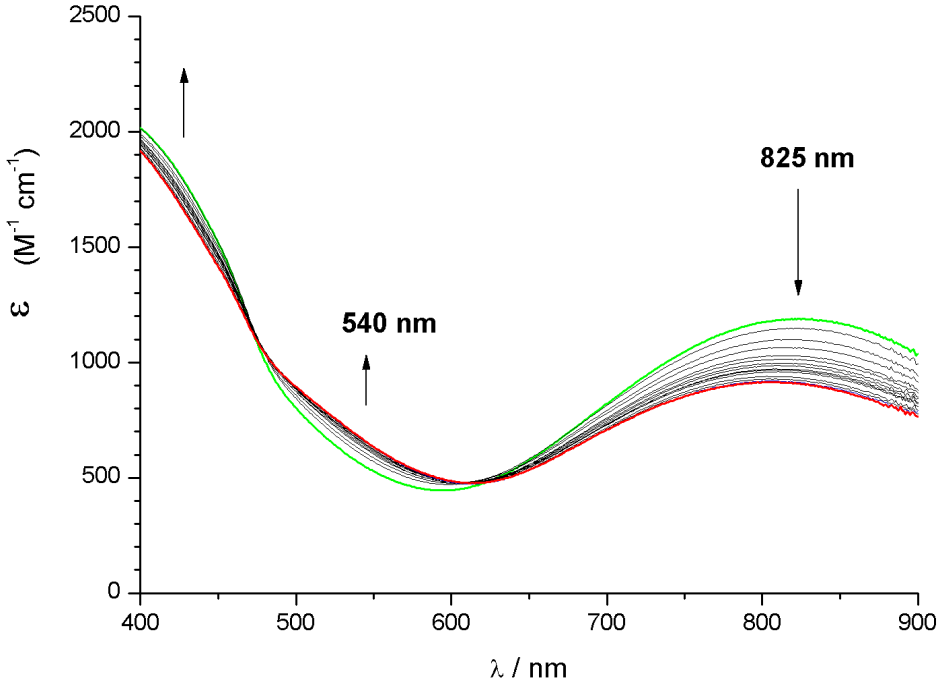


Figure S6. UV-vis spectra recorded of **1**•4TRISPHAT in Me_2CO at 295 K upon addition of increasing amounts of $Bu_4N•PF6$. The arrows show the evolution of the charge transfer bands of **1**·4TRISPHAT as $Bu_4N•PF_6$ is added. The green trace show the spectrum of the pure **1**•4TRISPHAT solution, while the red trace is after addition of three equivalents of $Bu_4N•PF_6$.

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