Supporting Information

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The Molecule-Electrode Interface in Single-Molecule Transistors

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Synthesis of [2]Rotaxane AR•4PF_6 and SR•4PF_6, and Their Precursor Dumbbell-Shaped Compounds AD and SD.

The routes employed to synthesize the [2]rotaxane **AR**•4PF_6 and **SR**•4PF_6, via their respective dumbbell-shaped compounds **AD** and **SD**, are outlined in Schemes S1–S3. The aldehyde **3** (Scheme S1) was obtained in 81% yield by reacting 4-hydroxy-3,5-diisopropyl-benzaldehyde[1] (**1**) with 2-(2-chloroethoxy)ethanol (**2**) under alkylation conditions (K_2CO_3/KI/DMF) at 100 ˚C. Treating **3** with TsCl in the presence of Et_3N and DMAP in CH_2Cl_2 solution gave the tosylate **4** which was then reacted, without purification, with $NaBH_4$ in MeOH, to afford the benzyl alcohol **5** in an overall yield of 67%. Alkylation (K_2CO_3/LiBr/18C6/MeCN) of 1-acetoxy-5-hydroxynaphthalene[2] (**6**) with **5** produced the intermediate ester **7**, which was subjected to saponification (KOH/MeOH) to yield the diol **8** (overall 72%).

Preparation of the [2]rotaxane **AR**•4PF_6 (Scheme S2) is completed by alkylating **8** with the tosylate[4] **9** in MeCN in the presence of K_2CO_3, LiBr, and 18C6 to afford the alcohol **10** in 68% yield. This alcohol was converted to the dumbbell-shaped compound **AD** by reacting it with thioctic acid (**11**) under esterification conditions (DCC/DMAP/CH_2Cl_2). The template-directed synthesis of the [2]rotaxane **AR**•4PF_6 was accomplished by reacting **AD**, the dicationic salt[3] **12**•2PF_6, and 1,4-bis(bromomethyl)benzene (**13)** in DMF at RT for 10 d. The [2]rotaxane **AR**•4PF_6 was isolated after addition of H_2O in 77% yield as an analytically pure green solid after chromatography on silica gel using a 1 % NH_4PF_6 solution in Me_2CO as the eluent.

The sequence steps employed in the synthesis of [2]rotaxane **SR**•4PF_6 and its precursor dumbbell-shaped compound **SD** is summarized in Scheme S3. The aldehyde **15**

was produced in 58% yield by alkylating **1** with the tosylate[4] **14** using conventional conditions (K_2CO_3/LiBr/18C6/MeCN). Subsequent tosylation of **15** with TsCl afforded the tosylate **16** in 86% yield. The moderate yielding (27%) alkylation of **8** with **16** was achieved in MeCN in the presence of 18C6 to produce the alcohol **17**. A two-step reaction involving firstly a reduction using $NaBH_4$ in MeOH and then an esterification (DCC/DMAP/CH_2Cl_2) of the alcohol with thioctic acid (**11**) converted **17** into the dumbbell-shaped compound **SD** in an overall yield of 93%. The template-directed synthesis of the [2]rotaxane **SR**•$4PF_6$ was achieved in 34% yield from **SD** using the protocol already described for the preparation of **UR**•$4PF_6$.

Experimental Section

General Methods: Chemicals were purchased from Aldrich and used as received. The compounds 4-hydroxy-3,5-diisopropyl-benzaldehyde[1] (**1**), 1-acetoxy-5-hydroxy-naphthalene [2] **(6),** α,α′-[1,4-phenylenebis (methylene)]bis(4,4′-bipyridium) bis(hexa fluorophosphate)[3] (**12**•$2PF_6$), and the tosylates[4] **9** and **14** were all prepared according to literature procedures. Solvents were dried following methods described in the literature.[5] All reactions were carried out under an anhydrous argon atmosphere. Thin layer chromatography (TLC) was performed on aluminum sheets coated with silica-gel 60F (Merck 5554). The plates were inspected by UV light and, if required, developed in I_2 vapor. Column chromatography was carried out by using silica-gel 60 (Merck 9385, 230-400 mesh). Melting points were determined on an Electrothermal 9100 melting point apparatus and are uncorrected. All ^1H and ^{13}C NMR spectra were recorded on either (i) a Bruker ARX500 (500 MHz and 125 MHz, respectively) or (ii) a Bruker

Avance500 (500 MHz and 125 MHz, respectively), using residual solvent as the internal standard. Samples were prepared using $CDCl_3$, CD_3COCD_3 or CD_3CN purchased from Cambridge Isotope Labs. All chemical shifts are quoted using the δ scale, and all coupling constants (*J*) are expressed in Hertz (Hz). Fast atom bombardment (FAB) mass spectra were obtained using a ZAB-SE mass spectrometer, equipped with a krypton primary atom beam, utilizing a *m*-nitrobenzyl alcohol matrix. Cesium iodide or poly(ethylene glycol) were employed as reference compounds. Electrospray mass spectra (ESMS) were measured on a VG ProSpec triple focusing mass spectrometer with MeCN as the mobile phase. Microanalyses were performed by Quantitative Technologies, Inc.

Alcohol 3. A solution of 4-hydroxy-3,5-diisopropylbenzaldehyde (**1**) (2.06 g, 10 mmol), 2-(2-chloroethoxy)ethanol (**2**) (1.31 g, 11 mol), K_2CO_3 (2.76 g, 20 mol) and KI (20 mg) in DMF was stirred at 100^{o}C for 16 h. After cooling down to room temperature, DMF was removed in vacuo and the residue was subjected to column chromatography (SiO_2: EtOAc/hexane, 1/1) to give the alcohol **3 (**2.38 g, 81%) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 1.25 (d, *J* = 6.9 Hz, 12 H), 2.25 (bs, 1 H), 3.38 (septet, *J* = 6.9 Hz, 2 H), 3.70 (t, *J* = 4.6 Hz, 2 H), 3.79 (t, *J* = 4.6 Hz, 2 H), 3.88 (t, *J* = 4.6 Hz, 2 H), 3.96 (t, *J* = 4.6 Hz, 2 H), 7.64 (s, 2 H), 9.91 (s, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ =23.7, 26.4, 61.8, 70.2, 72.5, 73.9, 126.2, 133.1, 143.0, 158.4, 191.8; MS (EI) *m/z* (%) 295 (37) $[M+1]^+$.

Benzyl Alcohol 5. A solution of the alcohol **3** (1.62 g, 5.5 mmol), TsCl (1.14 mg, 6.0 mmol), DMAP (10 mg) and Et_3N (1.4 mL, 10 mmol) in anhydrous CH_2Cl_2 (50 mL) was

stirred for 16 h at room temperature. After addition of SiO_2 (7.0 g), the mixture was concentrated and the residue was purified by a short-path column (SiO_2: EtOAc/hexane, 1:4) to afforded the tosylate **4** as a colorless oil. The tosylate was then dissolved in MeOH (80 mL) and $NaBH_4$ (380 mg, 10 mmol) was added. The reaction mixture was stirred at room temperature for 2 h. After work-up, the crude product was purified by column chromatography (SiO_2: EtOAc/hexane, 1:4) to give the benzyl alcohol **5** (1.68 mg, overall 67%) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 1.25 (d, J = 6.9 Hz, 12 H), 2.48 (s, 3 H), 3.36 (septet, J = 6.9 Hz, 2 H), 3.83–3.91 (m, 4 H), 3.89 (t, J = 4.6 Hz, 4 H), 4.26 (t, J = 4.6 Hz, 2 H), 4.68 (s, 2 H), 7.13 (s, 2 H), 7.38 (d, J = 8.2 Hz, 2 H), 7.86 (d, J = 8.2 Hz, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 21.5, 23.9, 26.2, 65.5, 68.8, 69.1, 70.6, 73.6, 122.8, 127.9, 129.7, 132.9, 136.8, 141.9, 144.7, 152.3; MS (EI) *m/z* (%) 450.2 (47) $[M]^+$.

Diol 8. A solution of benzyl alcohol (**5**) (1.35 g, 3.0 mmol), 1-acetoxy-5-hydroxynaphthalene (**6**) (708 mg, 3.5 mmol), K_2CO_3 (828 g, 6.0 mmol), LiBr (15 mg) and 18C6 (10 mg) in MeCN (50 mL) was heated under reflux for 16 h. After cooling down to room temperature, the reaction mixture was filtered and the solid was washed with MeCN (100 mL). The combined organic filtrate was concentrated and the crude compound **7** was then dissolved in MeOH (100 mL). KOH (561 mg, 10 mmol) was added and the reaction mixture was stirred at room temperature for 4 h. After work-up, the crude product was subjected to column chromatography (SiO_2: EtOAc/hexane, 1:2) to give the diol **8 (**948 mg, overall 72%) as an off-white solid. M.p. 68–70 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 1.20 (d, J = 6.9 Hz, 12 H), 3.41 (septet, J = 6.9 Hz, 2 H), 3.95–

3.97 (m, 4 H), 4.00–4.02 (m, 2 H), 4.09 (t, J = 4.6 Hz, 2 H), 4.36 (t, J = 4.6 Hz, 2 H), 4.64 (s, 2 H), 6.82 (d, J = 6.9 Hz, 1 H), 6.87 (d, J = 7.6 Hz, 1 H), 7.25 (dd, J = 6.9, 8.5 Hz, 1 H), 7.37 (dd, J = 7.6, 8.5 Hz, 1 H), 7.77 (d, J = 8.5 Hz, 1 H), 7.88 (d, J = 8.5 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 24.0, 26.3, 65.6, 68.0, 70.0, 70.7, 73.9, 105.5, 109.3, 114.0, 114.5, 122.9, 125.0, 125.1, 125.4, 127.0, 136.6, 142.0, 151.3, 152.6, 154.4; MS (EI) *m/z* (%) 438.2 (53) $[M]^+$.

Alcohol 10. A solution of the diol **8** (131.6 mg, 0.3 mmol), the tosylate **9** (315.8 mg, 0.3 mol), K_2CO_3 (82.9 mg, 0.6 mol), LiBr (10 mg) and 18C6 (10 mg) in MeCN (50 mL) was heated under reflux for 16 h. After work-up, the crude product was subjected to column chromatography (SiO_2: EtOAc/hexane, 1:1) to give the alcohol **10 (**270 mg, 68%) as a yellow solid. M.p. 104–107^{o}C; ^{1}H NMR (500 MHz, CD_3COCD_3) δ = 1.18–1.25 (m, 15 H), 1.35 (s, 18 H), 2.63 (q, J = 7.6 Hz, 2 H), 3.49 (septet, J = 6.9 Hz, 2 H), 3.62–3.70 (m, 6 H), 3.76–3.79 (m, 2 H), 3.80–3.83 (m, 2 H), 3.97–4.00 (m, 6 H), 4.08–4.12 (m, 4 H), 4.31–4,35 (m, 6 H), 4.39 (t, J = 4.6 Hz, 2 H), 4.58, 4.59 (2 x s, 2 H), 6.46, 6.49, 6.50, and 6.51 (4 x s, 2 H), 6.84 (d, J = 7.2 Hz, 1 H), 6.86 (d, J = 7.8 Hz, 1 H), 6.98–7.02 (m, 2 H), 7.10–7.17 (m, 14 H), 6.98–7.02 (m, 2 H), 7.33 (dd, J = 7.2, 8.6 Hz, 1 H), 7.40 (dd, J = 7.8, 8.6 Hz, 1 H), 7.86 (d, J = 8.6 Hz, 1 H), 7.90 (d, J = 8.6 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 14.8, 23.4, 25.9, 27.8, 30.7, 63.0, 63.9, 67.2, 67.5, 67.5, 67.6, 67.6, 67.8, 68.0, 69.1, 69.1, 69.2, 69.2, 69.4, 69.4, 69.4, 70.3, 70.3, 70.5, 70.5, 74.0, 105.6, 109.8, 113.1, 114.2, 116.3, 116.4, 116.4, 116.5, 122.2, 124.0, 125.0, 125.1, 126.6, 130.4, 130.7, 131.8, 134.7, 134.8, 138.2, 139.5, 141.1, 141.3, 144.3, 144.6, 148.1, 152.0, 154.4, 154.4, 156.8; MS (FAB) *m/z* (%) 1318 (100) $[M]^+$.

Dumbbell-Shaped compound AD. A solution of the alcohol **10** (250mg, 0.2 mmol), thioctic acid (**11**) (62 mg, 0.3 mmol), DCC (62 mg, 0.3 mmol) and DMAP (3 mg) in CH_2Cl_2 (20 mL) was stirred for 16 h at room temperature. After addition of Al_2O_3 (1 g), the mixture was concentrated and the residue was purified by a column (SiO_2: EtOAc/hexane, 1:2) to afford the dumbbell-shaped compound **AD** (267 mg, 97%) as an yellow solid. M.p. 56-58 ^oC; ^1H NMR (500 MHz, $CDCl_3$) δ = 1.20 (d, J = 6.8 Hz, 12 H), 1.23 (t, J = 7.6 Hz, 3 H), 1.29 (s, 18 H), 1.40–1.54 (m, 4 H), 1.61–1.72 (m, 2 H), 1.83–1.94 (m, 1 H), 2.37 (t, J = 7.4 Hz, 2 H), 2.40–2.51 (m, 1 H), 2.62 (q, J = 7.6 Hz, 2 H), 3.07–3.18 (m, 2 H), 3.40 (septet, J = 6.9 Hz, 2 H), 3.52–3.57 (m, 1 H), 3.63 (t, J = 4.4 Hz, 2H), 3.66 (t, J = 4.3 Hz, 2 H), 3.70–3.73 (m, 2 H), 3.78–3.81 (m, 2 H), 3.82–3.85 (m, 2 H), 3.95 (t, J = 4.4 Hz, 2 H), 3.98–4.00 (m, 6 H), 4,08–4.12 (m, 6 H), 4.28–4.31 (m, 2 H), 4.35 (t, J = 4.7 Hz, 2 H), 5.04 (s, 2 H), 6.46, 6.47 and 6.49 (3 x s, 2 H), 6.76–6.78 (dd, J = 2.4, 8.9 Hz, 2 H), 6.85 (d, J = 7.6 Hz, 1 H), 6.87 (d, J = 7.8 Hz, 1 H), 6.98–7.02 (m, 4 H), 7.10–7.17 (m, 12 H), 7.33 (dd, J = 7.6, 8.6 Hz, 1 H), 7.40 (dd, J = 7.8, 8.6 Hz, 1 H), 7.87 (d, J = 8.6 Hz, 1 H), 7.88 (d, J = 8.6 Hz, 1 H); MS (FAB) m/z (%) 1506 (100) $[M]^+$.

[2]Rotaxane AR•4PF$_6$. A solution of the dumbbell-shaped compound **AD** (150 mg, 0.1 mmol), **12**•2PF$_6$ (211 mg, 0.3 mmol) and 1,4-bis(bromomethyl)benzene (**13**) (80 mg, 0.3 mmol) in anhydrous DMF (10 mL) was stirred at room temperature for 10 d. The reaction mixture was subjected directly to column chromatography (SiO_2) and unreacted **AD** was recovered 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 band containing the [2]rotaxane **AR**•4PF$_6$ was

collected. After removal of solvent, H_2O (50 mL) was added and the resulting precipitate was collected by filtration to afford [2]rotaxane **AR**•4PF_6 (201 mg, 77%) as a green solid. M.p. 162°C (decomp); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 1.09–1.17 (m, 15 H), 1.22–1.24 (m, 18 H), 1.38–1.50 (m, 2H), 1.52–1.71 (m, 4 H), 1.83–1.94 (m, 1 H), 2.37 (t, *J* = 7.4 Hz, 2 H), 2.35–2.44 (m, 1 H), 2.58 (q, *J* = 7.8 Hz, 2 H), 3.07-3.18 (m, 2 H), 3.40 (m, 2 H), 3.52–3.57 (m, 1 H), 3.62–4.45 (m, 28 H), 5.04 (s, 2 H), 5.47–5.69 (m, 8 H), 6.01, 6.07, 6.17 and 6.26 (4 x s, 2 H), 6.57–6.89 (m, 4 H), 7.10–7.65 (m, 36 H), 8.65–9.04 (m, 8 H); MS (FAB) *m/z* (%) 2462 (10) [*M*–PF_6]$^+$, 2317 (28) [*M*–2PF_6]+, 2173 (15) [*M*–3PF_6]$^+$.

Alcohol 15. A solution of the tosylate **14** (1.19 g, 2.0 mmol), 4-hydroxy-3,5-diisopropyl-benzaldehyde (**1**) (618 mg, 3.0 mmol), K_2CO_3 (690 mg, 5.0 mol), LiBr (10 mg) and 18C6 (10 mg) in MeCN (50 mL) was heated under reflux for 16 h. After work-up, the crude product was subjected to column chromatography (SiO_2: CH_2Cl_2/EtOH, 97:3) to give the alcohol **15 (**729 mg, 58%) as a yellow oil. ^{1}H NMR (500 MHz, CD_3COCD_3) δ = 1.23 (d, *J* = 6.9 Hz, 12 H), 3.47–3.51 (m, 4 H), 3.56–3.60 (m, 6 H), 3.65–3.66 (m, 2 H), 3.69–3.72 (m, 2 H), 3.83–3.87 (m, 2 H), 3.99 (t, *J* = 4.4 Hz, 2 H), 4.30 (d, *J* = 2.1 Hz, 2 H), 4.36 (s, 2 H), 6.53 and 6.55 (2 x s, 2 H), 7.70 (s, 2 H), 9.93 (s, 1 H); ^{13}C NMR (125 MHz, CD_3COCD_3) δ =23.1, 26.1, 60.9, 67.5, 67.5, 67.6, 69.1, 69.3, 70.1, 70.4, 72.6, 74.6, 116.4, 116.5, 116.5, 125.6, 133.4, 134.7, 134.7,134.8, 134.8, 143.0, 158.5, 191.3; MS (FAB) *m/z* (%) 628 (100) [*M*]$^+$; HRMS (MALDI–TOF) calcd $C_{29}H_{40}O_7S_4$: 628.1657; found 628.1652.

Tosylate 16. A solution of the alcohol **15** (1.27, 2.0 mmol), TsCl (576 mg, 3.0 mmol), Et_3N (1.3 mL, 9mmol) and DMAP (20 mg) in anhydrous CH_2Cl_2 (50 mL) was stirred for 16 h at room temperature. After addition of Al_2O_3 (5g), the mixture was concentrated and the residue was subjected to column chromatography (SiO_2: CH_2Cl_2/EtOH, 99:1) to afforded the tosylate **16** (1.35 g, 86%) as an yellow oil. ^{1}H NMR (500 MHz, CD_3CN) δ = 1.18 (d, J = 6.9 Hz, 12 H), 2.37 (s, 3 H), 3.40–3.47 (m, 6 H), 3.58–3.61 (m, 4 H), 3.64–3.66 (m, 2 H), 3.79 (t, J = 4.5 Hz, 2 H), 3.93 (t, J = 4.5 Hz, 2 H), 4.09 (t, J = 4.5 Hz, 2 H), 4.21–4.22 (m, 2 H), 4.30 (s, 2 H), 6.44 and 6.49 (2 x s, 2 H), 7.39 (d, J = 8.1 Hz, 2 H), 7.65 (s, 2 H), 7.73 (d, J = 8.1 Hz, 2 H), 9.88 (s, 1 H); ^{13}C NMR (125 MHz, CD_3CN) δ = 20.4, 23.0, 26.0, 67.4, 67.6, 68.2, 68.9, 69.2, 69.5, 69.9, 70.0, 70.3, 74.1, 109.7, 116.3, 116.3, 116.4, 116.4, 125.5, 127.6, 129.7, 133.2, 133.3, 134.5, 134.5, 134.6, 134.6, 142.9, 144.6, 158.4, 191.1; MS (FAB) *m/z* (%) 782 (100) $[M]^+$; HRMS (MALDI–TOF) calcd for $C_{36}H_{46}O_9S_5$: 782.1745; found 782.1739.

Alcohol 17. A solution of the tosylate **16** (177 mg, 0.23 mmol), the diol **8** (131 mg, 0.30 mmol), K_2CO_3 (138 mg, 1.00 mol), LiBr (5 mg) and 18C6 (5 mg) in MeCN (20 mL) was heated under reflux for 16 h. After work-up, the crude product was subjected to column chromatography (SiO_2: EtOAc/hexane, 2:1) to give the alcohol **17 (**65 mg, 27%) as a yellow oil. ^{1}H NMR (500 MHz, CD_3COCD_3) δ = 1.19 (d, J = 6.9 Hz, 12 H), 1.29 (dd, J = 1.3, 6.9 Hz, 12 H), 3.48–3.55 (m, 4 H), 3.68–3.70 (m, 4 H), 3.74–3.76 (m, 2 H), 3.78–3.80 (m, 2 H), 3.87–3.90 (m, 2 H), 3.97–4.13 (m, 10 H), 4.35–4.37 (m, 4 H), 4.39–4.41 (m, 4 H), 4.58 (s, 2 H), 6.52, 6.53, 6.58 and 6.60 (4 x s, 2 H), 7.01 (d, J = 7.6 Hz, 1 H), 7.04 (d, J = 7.6 Hz, 1 H),7.13 (s, 2 H), 7.01 (dd, J = 7.6, 8.5 Hz, 1 H), 7.41 (dd, J = 7.6,

8.5 Hz, 1 H), 7.76 (s, 2 H), 7.89 (d, J = 8.5 Hz, 1 H), 7.91 (d, J = 8.5 Hz, 1 H), 9.98 (s, 1 H); ^{13}C NMR (125 MHz, CD_3COCD_3) δ =23.1, 23.4, 25.9, 26.1, 59.5, 63.7, 63.9, 67.6, 67.6, 67.9, 68.0, 69.2, 69.2, 69.4, 69.6, 70.0, 70.4, 70.5, 70.5, 74.0, 74.2, 105.6, 109.7, 109.8, 114.2, 114.2, 116.3, 116.4, 116.5, 122.2, 125.0, 125.1, 125.6, 126.7, 133.4, 134.7, 134.7, 134.7, 134.8, 138.2, 141.1, 143.0, 152.0, 154.3, 154.4, 158.5, 169.8, 191.2; MS (FAB) *m/z* (%) 1048 (39) $[M]^+$; HRMS (MALDI–TOF) calcd for $C_{56}H_{72}O_{11}S_4$: 1048.3957; found 1048.3916.

Dumbbell-Shaped Compound SD. $NaBH_4$ (7.6 mg, 0.20 mmol) was added to a solution of the alcohol **17** (60.0 mg, 0.06 mmol) in MeOH (10 mL) and the reaction mixture was stirred for 2 h at room temperature. After work-up, the crude compound was dissolved in a solution of thioctic acid (**11**) (74.0 mg, 0.36 mmol), DCC (74.0 mg, 0.36 mmol) and DMAP (1.0 mg) in CH_2Cl_2 (10 mL). The reaction mixture was stirred for 16 h at room temperature. After addition of Al_2O_3 (1 g), the mixture was concentrated and the residue was purified by column chromatography (SiO_2: EtOAc/hexane, 1:2) to give the dumbbell-shaped compound **SD** (76.0 mg, 93%) as an yellow solid.^{1}H NMR (500 MHz, CD_3COCD_3) δ = 1.16 (d, J = 6.9 Hz, 12 H), 1.18 (d, J = 6.9 Hz, 12 H), 1.40–1.46 (m, 4 H), 1.56–1.69 (m, 8 H), 1.81–1.87 (m, 2H), 2.01 (t, J = 4.9 Hz, 4 H), 2.38–2.44 (m, 2 H), 3.04–3.09 (m, 2 H), 3.12–3.17 (m, 2 H), 3.39–3.49 (m, 4 H), 3.51–3.57 (m, 2H), 3.61–3.64 (m, 4 H), 3.67–3.69 (m, 2 H), 3.72–3.75 (m, 2 H), 3.77–3.80 (m, 2 H), 3.87–3.90 (m, 2 H), 3.93–3.96 (m, 6 H), 4.05 (t, J = 4.7 Hz, 2 H), 4.28–4.31 (m, 4 H), 4.33–4.36 (m, 4 H), 5.01 (s, 2 H), 5.02 (s, 2 H), 6.44, 6.45, 6.51 and 6.52 (4 x s, 2 H), 6.95 (d, J = 7.6 Hz, 1 H), 6.98 (d, J = 7.6 Hz, 1 H),7.11 (s, 2 H), 7.12 (s, 2 H), 7.34 (dd, J = 7.6, 8.5 Hz, 1

H), 7.36 (dd, J = 7.6, 8.5 Hz, 1 H), 7.83 (d, J = 8.5 Hz, 1 H), 7.85 (d, J = 8.5 Hz, 1 H); ^{13}C NMR (125 MHz, CD_3COCD_3) δ = 23.4, 23.4, 24.5, 25.5, 25.9, 33.5, 34.3, 38.1, 39.9, 56.1, 65.6, 67.6, 67.7, 67.9, 68.1, 69.2, 69.2, 69.4, 69.6, 70.2, 70.5, 70.5, 74.0, 74.1, 105.6, 109.7, 109.8, 114.2, 114.2, 116.4, 116.4, 116.5, 116.5, 124.0, 124.0, 125.0, 125.1, 126.6, 132.5, 134.7, 134.8, 134.8, 141.7, 153.0, 153.0, 154.3, 154.4, 172.4; MS (FAB) *m/z* (%) 1426 (39) $[M]^+$.

[2]Rotaxane SR•4PF$_6$. A solution of the dumbbell-shaped compound **SD** (55 mg, 0.04 mmol), **12**•2PF$_6$ (108.8 mg, 0.15 mmol) and 1,4-bis(bromomethyl)benzene (**13**) (40.7 mg, 0.15 mmol) in DMF (5 mL) was stirred at room temperature for 10 d. The reaction mixture was subjected directly to column chromatography (SiO_2) and **SD** was recovered 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 band containing the [2]rotaxane **SR**•4PF$_6$ was collected. After removal of solvent, H_2O (20 mL) was added and the resulting precipitate was collected by filtration to give the pure [2]rotaxane **SR**•4PF$_6$ (32 mg, 34%) as a green solid. M.p. 139^{o}C (decomp); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 1.08–1.22 (m, 24 H), 1.42–1.48 (m, 4 H), 1.60–1.69 (m, 8H), 1.69–1.73 (m, 2 H), 2.35–2.39 (m, 4 H), 2.42–2.47 (m, 2 H), 3.11–3.14 (m, 2 H), 3.15-3.21 (m, 2 H), 3.37–3.45 (m, 4 H), 3.57–3.61 (m, 2 H), 3.71–4.42 (m, 28 H), 5.03 (s, 2 H), 5.04 (s, 2 H), 5.47–5.76 (m, 8 H), 6.00, 6.07, 6.19 and 6.23 (4 x s, 2 H), 6.76–6.90 (m, 2 H), 7.07–7.77 (m, 24 H), 8.68–9.05 (m, 8 H); MS (FAB) *m/z* (%) 2528 (10) $[M–PF_6]^+$, 2383 (30) $[M–2PF_6]$+, 2238 (11) $[M–3PF_6]^+$.

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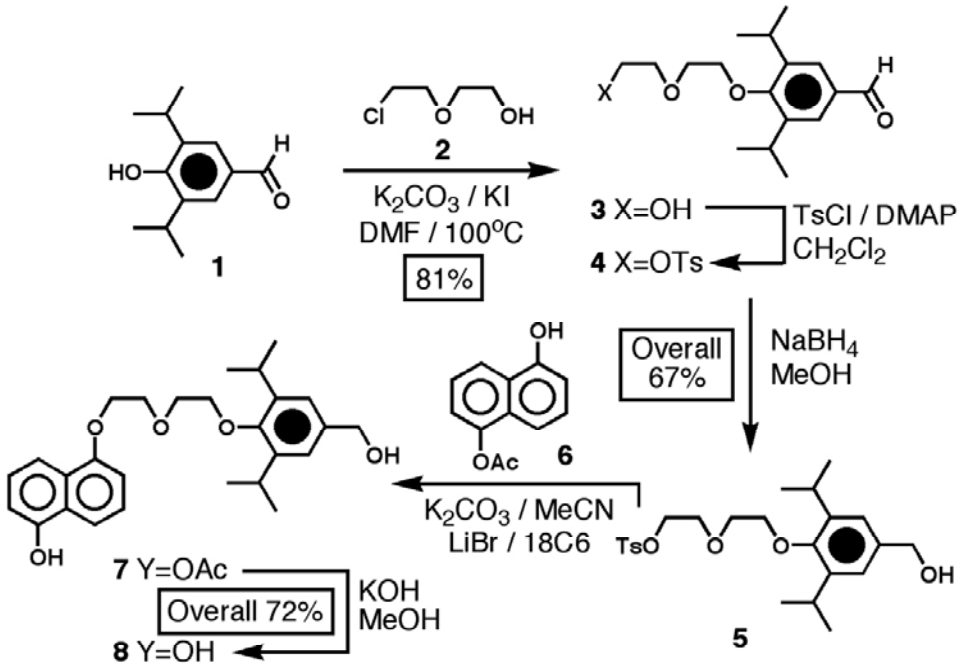
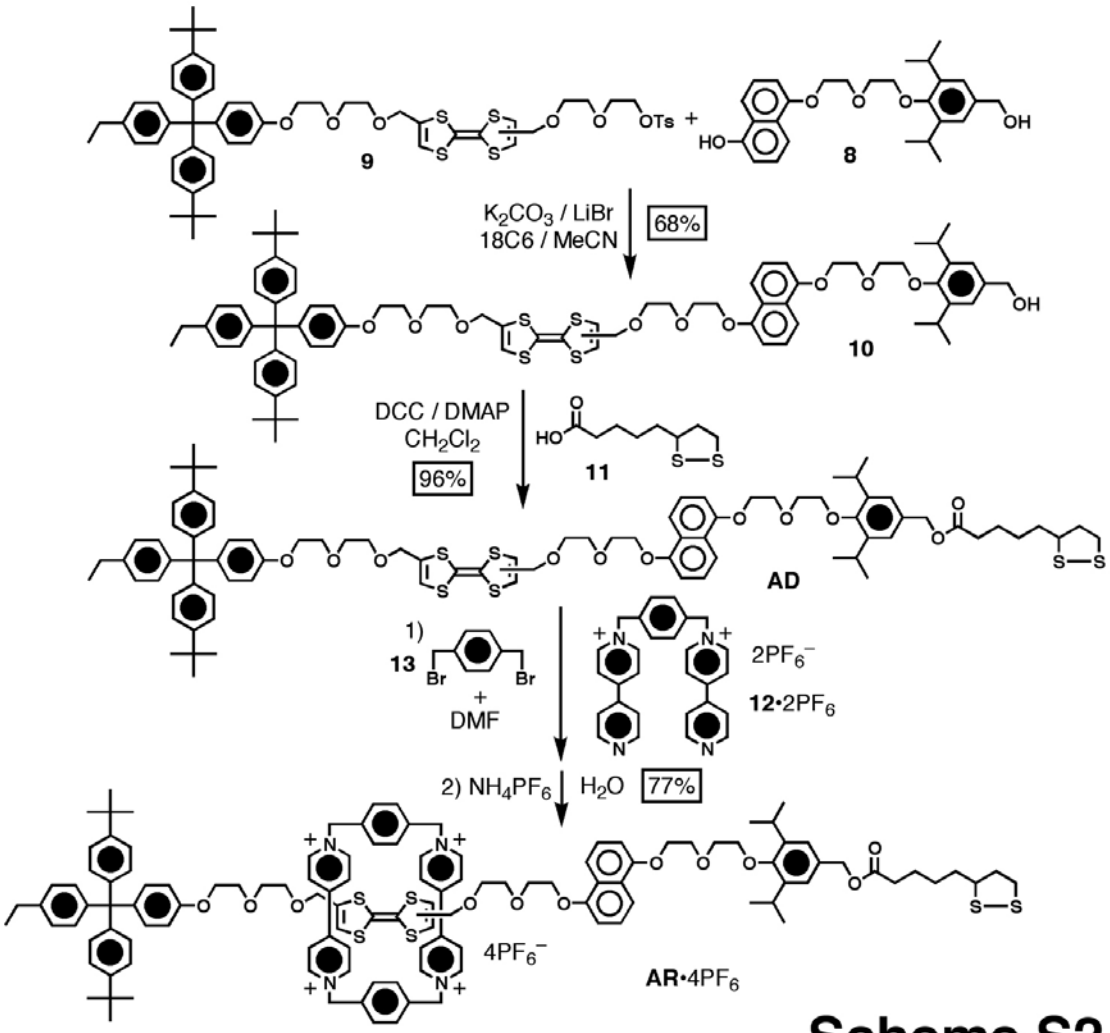
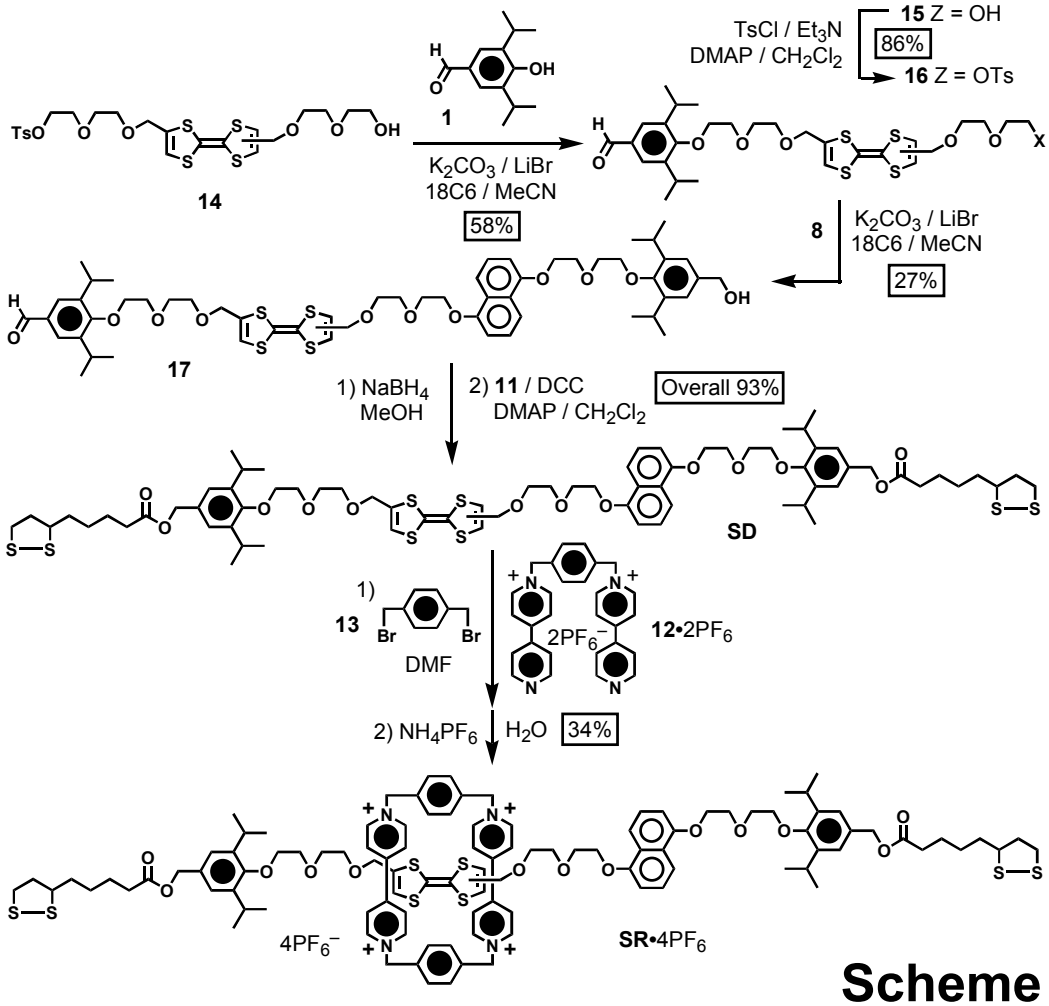

1
2
K2CO3 / KI
DMF / 100°C
81%
3 X=OH
4 X=OTs
TsCl / DMAP
CH2Cl2
Overall
67%
NaBH4
MeOH
5
6
K2CO3 / MeCN
LiBr / 18C6
7 Y=OAc
Overall 72%
KOH
MeOH
8 Y=OH

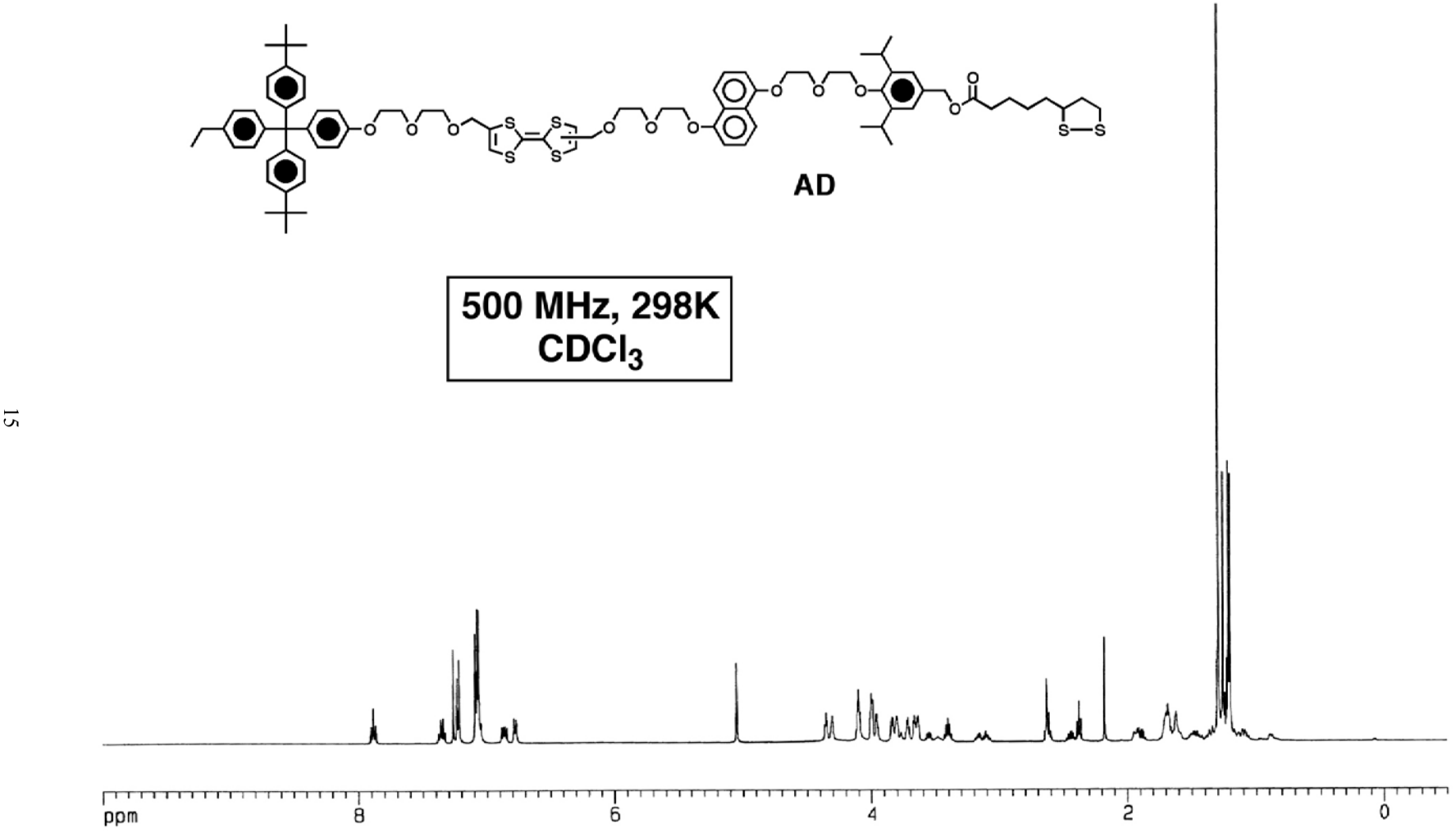
Scheme S1


9
8
K_2CO_3 / LiBr
18C6 / MeCN
68%
10
DCC / DMAP
CH_2Cl_2
96%
11
AD
1)
13
DMF
$2PF_6^-$
12•2PF_6
2) NH_4PF_6
H_2O
77%
$4PF_6^-$
AR•4PF_6

Scheme S2


TsO
14
1
K2CO3 / LiBr
18C6 / MeCN
58%
TsCl / Et3N
DMAP / CH2Cl2
15 Z = OH
86%
16 Z = OTs
8
K2CO3 / LiBr
18C6 / MeCN
27%
17
1) NaBH4
MeOH
2) 11 / DCC
DMAP / CH2Cl2
Overall 93%
SD
1)
13
DMF
2PF6−
12•2PF6
2) NH4PF6
H2O
34%
4PF6−
SR•4PF6

Scheme S3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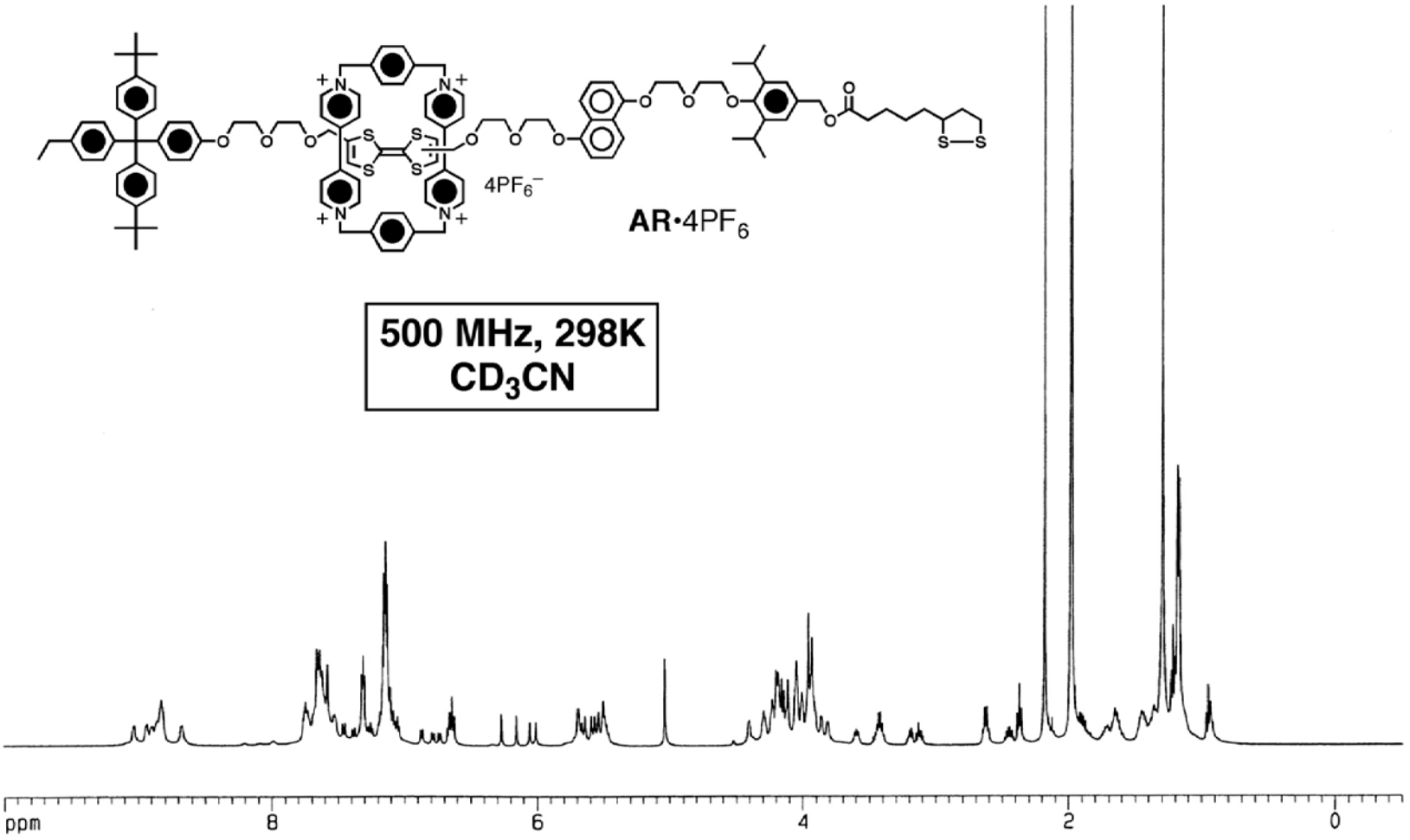
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AR·4PF6
500 MHz, 298K
CD3CN
ppm
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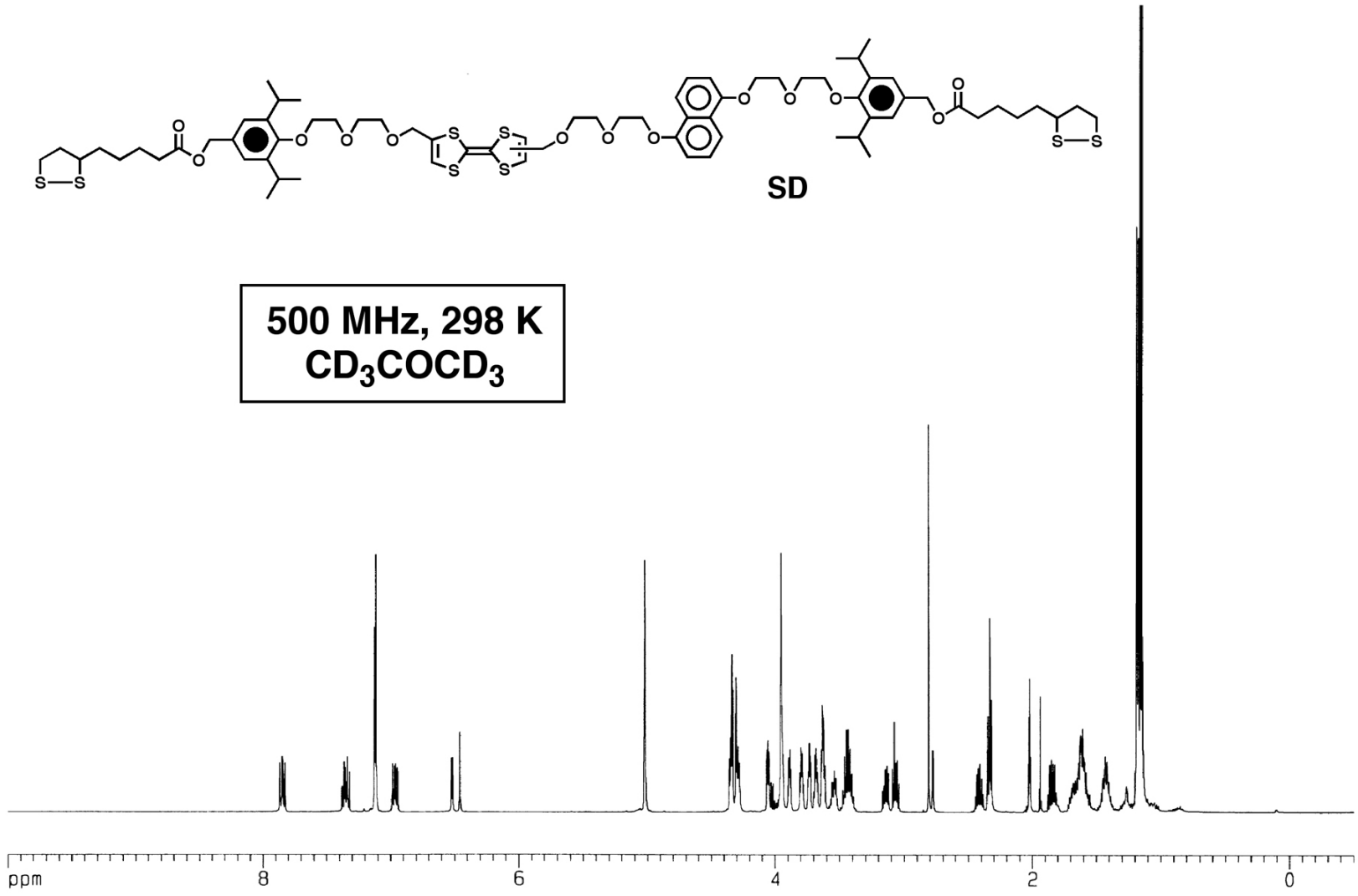
6
4
2
0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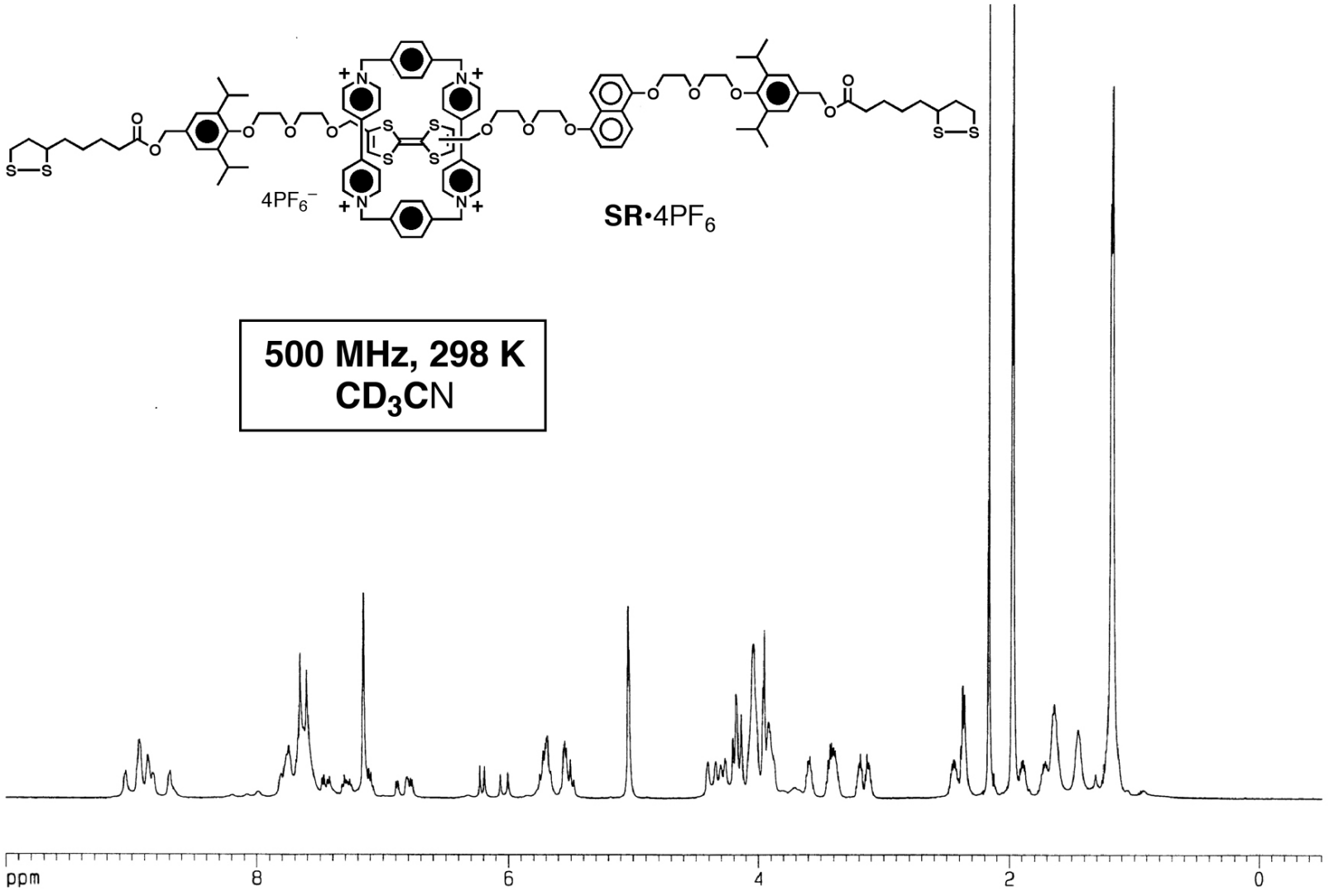
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CD3CN
ppm
8
6
4
2
0