



Supporting Information

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The Molecule-Electrode Interface in Single-Molecule Transistors

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Synthesis of [2]Rotaxane **AR•4PF₆** and **SR•4PF₆**, and Their Precursor Dumbbell-Shaped Compounds **AD** and **SD**.

The routes employed to synthesize the [2]rotaxane **AR•4PF₆** and **SR•4PF₆**, 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 (K₂CO₃/KI/DMF) at 100 °C. Treating **3** with TsCl in the presence of Et₃N and DMAP in CH₂Cl₂ solution gave the tosylate **4** which was then reacted, without purification, with NaBH₄ in MeOH, to afford the benzyl alcohol **5** in an overall yield of 67%. Alkylation (K₂CO₃/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•4PF₆** (Scheme S2) is completed by alkylating **8** with the tosylate^[4] **9** in MeCN in the presence of K₂CO₃, 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/CH₂Cl₂). The template-directed synthesis of the [2]rotaxane **AR•4PF₆** was accomplished by reacting **AD**, the dicationic salt^[3] **12•2PF₆**, and 1,4-bis(bromomethyl)benzene (**13**) in DMF at RT for 10 d. The [2]rotaxane **AR•4PF₆** was isolated after addition of H₂O in 77% yield as an analytically pure green solid after chromatography on silica gel using a 1 % NH₄PF₆ solution in Me₂CO as the eluent.

The sequence steps employed in the synthesis of [2]rotaxane **SR•4PF₆** 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**•4PF₆ was achieved in 34% yield from **SD** using the protocol already described for the preparation of **UR**•4PF₆.

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**•2PF₆), 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 I₂ 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 ¹³C 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 CDCl₃, CD₃COCD₃ or CD₃CN 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), K₂CO₃ (2.76 g, 20 mol) and KI (20 mg) in DMF was stirred at 100°C for 16 h. After cooling down to room temperature, DMF was removed in vacuo and the residue was subjected to column chromatography (SiO₂: EtOAc/hexane, 1/1) to give the alcohol **3** (2.38 g, 81%) as a colorless oil. ¹H NMR (500 MHz, CDCl₃) 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); ¹³C NMR (125 MHz, CDCl₃) 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 Et₃N (1.4 mL, 10 mmol) in anhydrous CH₂Cl₂ (50 mL) was

stirred for 16 h at room temperature. After addition of SiO₂ (7.0 g), the mixture was concentrated and the residue was purified by a short-path column (SiO₂: EtOAc/hexane, 1:4) to afford the tosylate **4** as a colorless oil. The tosylate was then dissolved in MeOH (80 mL) and NaBH₄ (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 (SiO₂: EtOAc/hexane, 1:4) to give the benzyl alcohol **5** (1.68 mg, overall 67%) as a colorless oil. ¹H NMR (500 MHz, CDCl₃) 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); ¹³C NMR (125 MHz, CDCl₃) 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), K₂CO₃ (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 (SiO₂: EtOAc/hexane, 1:2) to give the diol **8** (948 mg, overall 72%) as an off-white solid. M.p. 68–70 °C; ¹H NMR (500 MHz, CDCl₃) 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) $\delta = 24.0, 26.3, 65.6, 68.0, 70.0, 70.7, 73.9, 105.5, 109.3, 114.0, 114.5, 122.9, 125.0, 125.1, 125.4, 127.0, 136.6, 142.0, 151.3, 152.6, 154.4$; 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°C; ^1H NMR (500 MHz, CD_3COCD_3) $\delta = 1.18$ – 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) $\delta = 14.8, 23.4, 25.9, 27.8, 30.7, 63.0, 63.9, 67.2, 67.5, 67.5, 67.6, 67.6, 67.8, 68.0, 69.1, 69.1, 69.2, 69.2, 69.4, 69.4, 69.4, 70.3, 70.3, 70.5, 70.5, 74.0, 105.6, 109.8, 113.1, 114.2, 116.3, 116.4, 116.4, 116.5, 122.2, 124.0, 125.0, 125.1, 126.6, 130.4, 130.7, 131.8, 134.7, 134.8, 138.2, 139.5, 141.1, 141.3, 144.3, 144.6, 148.1, 152.0, 154.4, 154.4, 156.8$; 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 CH₂Cl₂ (20 mL) was stirred for 16 h at room temperature. After addition of Al₂O₃ (1 g), the mixture was concentrated and the residue was purified by a column (SiO₂: EtOAc/hexane, 1:2) to afford the dumbbell-shaped compound **AD** (267 mg, 97%) as a yellow solid. M.p. 56-58 °C; ¹H NMR (500 MHz, CDCl₃) 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•4PF₆. A solution of the dumbbell-shaped compound **AD** (150 mg, 0.1 mmol), **12•2PF₆** (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 (SiO₂) and unreacted **AD** was recovered with Me₂CO, whereupon the eluent was changed to Me₂CO/NH₄PF₆ (1.0 g NH₄PF₆ in 100 mL Me₂CO) and the green band containing the [2]rotaxane **AR•4PF₆** was

collected. After removal of solvent, H₂O (50 mL) was added and the resulting precipitate was collected by filtration to afford [2]rotaxane **AR**•4PF₆ (201 mg, 77%) as a green solid. M.p. 162°C (decomp); ¹H NMR (500 MHz, CDCl₃) 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*-PF₆]⁺, 2317 (28) [*M*-2PF₆]⁺, 2173 (15) [*M*-3PF₆]⁺.

Alcohol 15. A solution of the tosylate **14** (1.19 g, 2.0 mmol), 4-hydroxy-3,5-diisopropylbenzaldehyde (**1**) (618 mg, 3.0 mmol), K₂CO₃ (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 (SiO₂: CH₂Cl₂/EtOH, 97:3) to give the alcohol **15** (729 mg, 58%) as a yellow oil. ¹H NMR (500 MHz, CD₃COCD₃) 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); ¹³C NMR (125 MHz, CD₃COCD₃) 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 C₂₉H₄₀O₇S₄: 628.1657; found 628.1652.

Tosylate 16. A solution of the alcohol **15** (1.27, 2.0 mmol), TsCl (576 mg, 3.0 mmol), Et₃N (1.3 mL, 9mmol) and DMAP (20 mg) in anhydrous CH₂Cl₂ (50 mL) was stirred for 16 h at room temperature. After addition of Al₂O₃ (5g), the mixture was concentrated and the residue was subjected to column chromatography (SiO₂: CH₂Cl₂/EtOH, 99:1) to afford the tosylate **16** (1.35 g, 86%) as a yellow oil. ¹H NMR (500 MHz, CD₃CN) 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); ¹³C NMR (125 MHz, CD₃CN) 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 C₃₆H₄₆O₉S₅: 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), K₂CO₃ (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 (SiO₂: EtOAc/hexane, 2:1) to give the alcohol **17** (65 mg, 27%) as a yellow oil. ¹H NMR (500 MHz, CD₃COCD₃) 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) $\delta = 23.1, 23.4, 25.9, 26.1, 59.5, 63.7, 63.9, 67.6, 67.6, 67.9, 68.0, 69.2, 69.2, 69.4, 69.6, 70.0, 70.4, 70.5, 70.5, 74.0, 74.2, 105.6, 109.7, 109.8, 114.2, 114.2, 116.3, 116.4, 116.5, 122.2, 125.0, 125.1, 125.6, 126.7, 133.4, 134.7, 134.7, 134.7, 134.8, 138.2, 141.1, 143.0, 152.0, 154.3, 154.4, 158.5, 169.8, 191.2$; MS (FAB) m/z (%) 1048 (39) $[M]^+$; HRMS (MALDI-TOF) calcd for $\text{C}_{56}\text{H}_{72}\text{O}_{11}\text{S}_4$: 1048.3957; found 1048.3916.

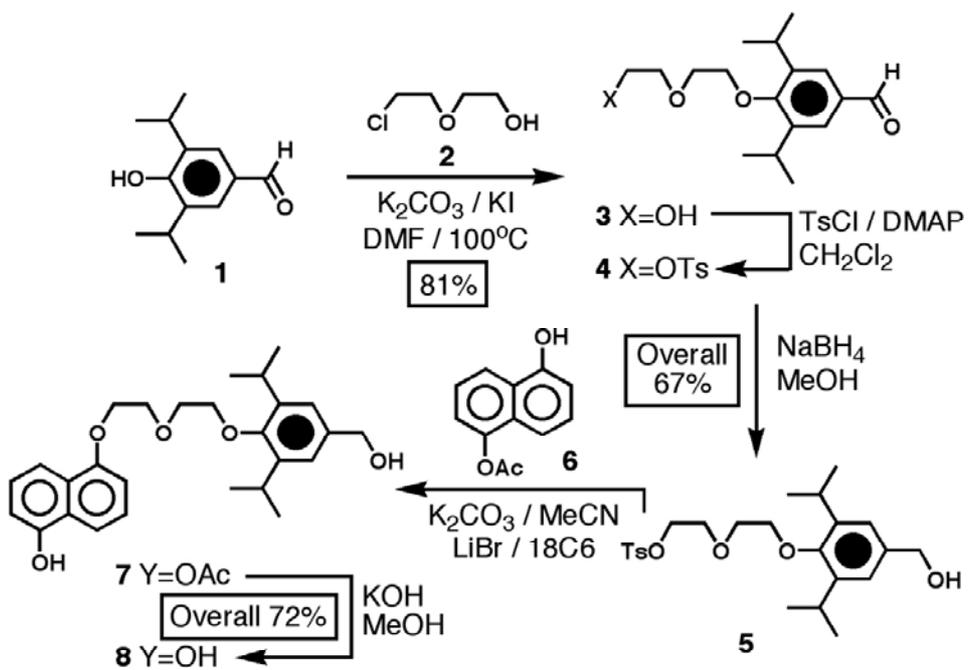
Dumbbell-Shaped Compound SD. NaBH_4 (7.6 mg, 0.20 mmol) was added to a solution of the alcohol **17** (60.0 mg, 0.06 mmol) in MeOH (10 mL) and the reaction mixture was stirred for 2 h at room temperature. After work-up, the crude compound was dissolved in a solution of thioctic acid (**11**) (74.0 mg, 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 a yellow solid. ^1H NMR (500 MHz, CD_3COCD_3) $\delta = 1.16$ (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) $\delta = 23.4, 23.4, 24.5, 25.5, 25.9, 33.5, 34.3, 38.1, 39.9, 56.1, 65.6, 67.6, 67.7, 67.9, 68.1, 69.2, 69.2, 69.4, 69.6, 70.2, 70.5, 70.5, 74.0, 74.1, 105.6, 109.7, 109.8, 114.2, 114.2, 116.4, 116.4, 116.5, 116.5, 124.0, 124.0, 125.0, 125.1, 126.6, 132.5, 134.7, 134.8, 134.8, 141.7, 153.0, 153.0, 154.3, 154.4, 172.4$; MS (FAB) m/z (%) 1426 (39) $[\text{M}]^+$.

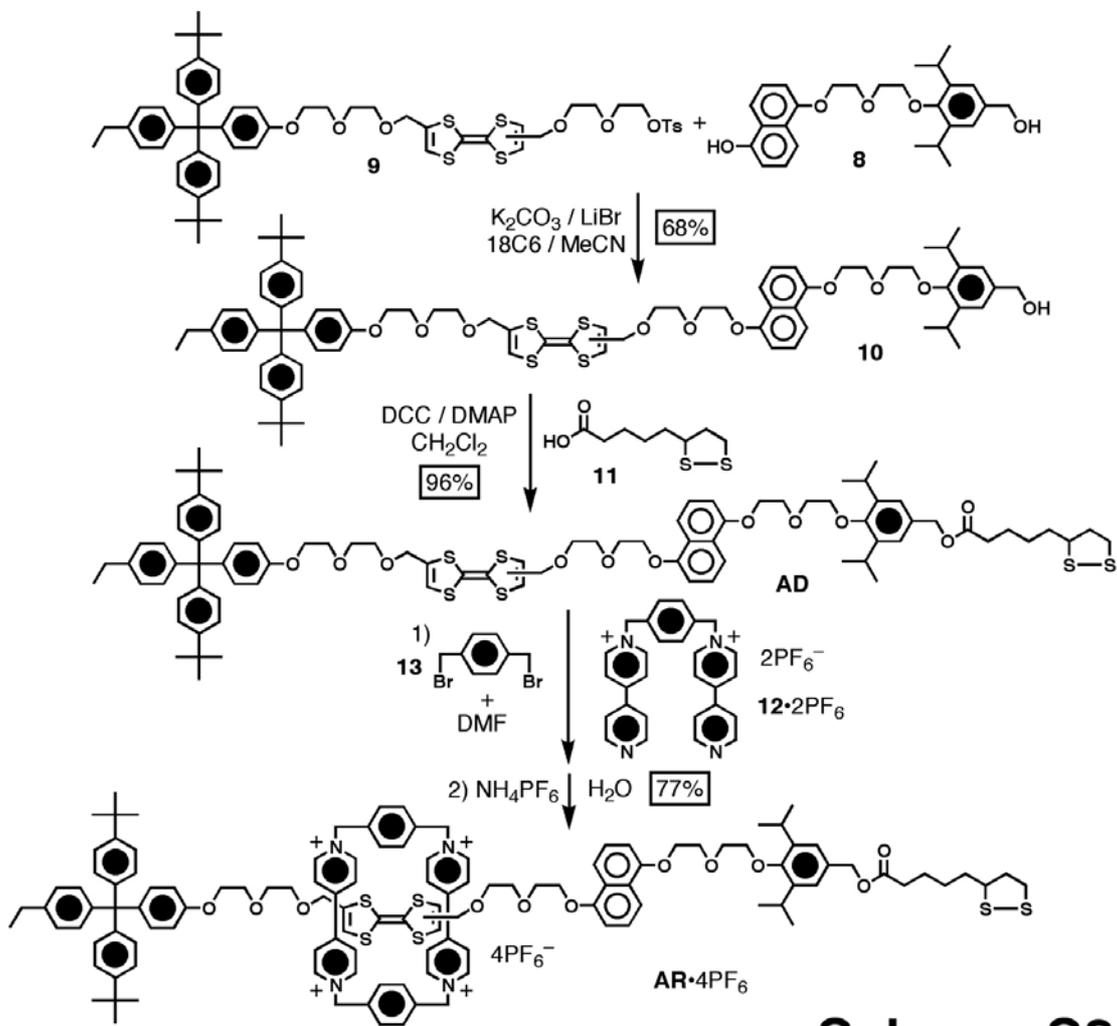
[2]Rotaxane $\text{SR}\cdot 4\text{PF}_6$. A solution of the dumbbell-shaped compound **SD** (55 mg, 0.04 mmol), **12** $\cdot 2\text{PF}_6$ (108.8 mg, 0.15 mmol) and 1,4-bis(bromomethyl)benzene (**13**) (40.7 mg, 0.15 mmol) in DMF (5 mL) was stirred at room temperature for 10 d. The reaction mixture was subjected directly to column chromatography (SiO_2) and **SD** was recovered with Me_2CO , whereupon the eluent was changed to $\text{Me}_2\text{CO}/\text{NH}_4\text{PF}_6$ (1.0 g NH_4PF_6 in 100 mL Me_2CO) and the green band containing the [2]rotaxane **SR** $\cdot 4\text{PF}_6$ 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** $\cdot 4\text{PF}_6$ (32 mg, 34%) as a green solid. M.p. 139°C (decomp); ^1H NMR (500 MHz, CDCl_3) $\delta = 1.08\text{--}1.22$ (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) $[\text{M}\text{--}\text{PF}_6]^+$, 2383 (30) $[\text{M}\text{--}2\text{PF}_6]^+$, 2238 (11) $[\text{M}\text{--}3\text{PF}_6]^+$.

References:

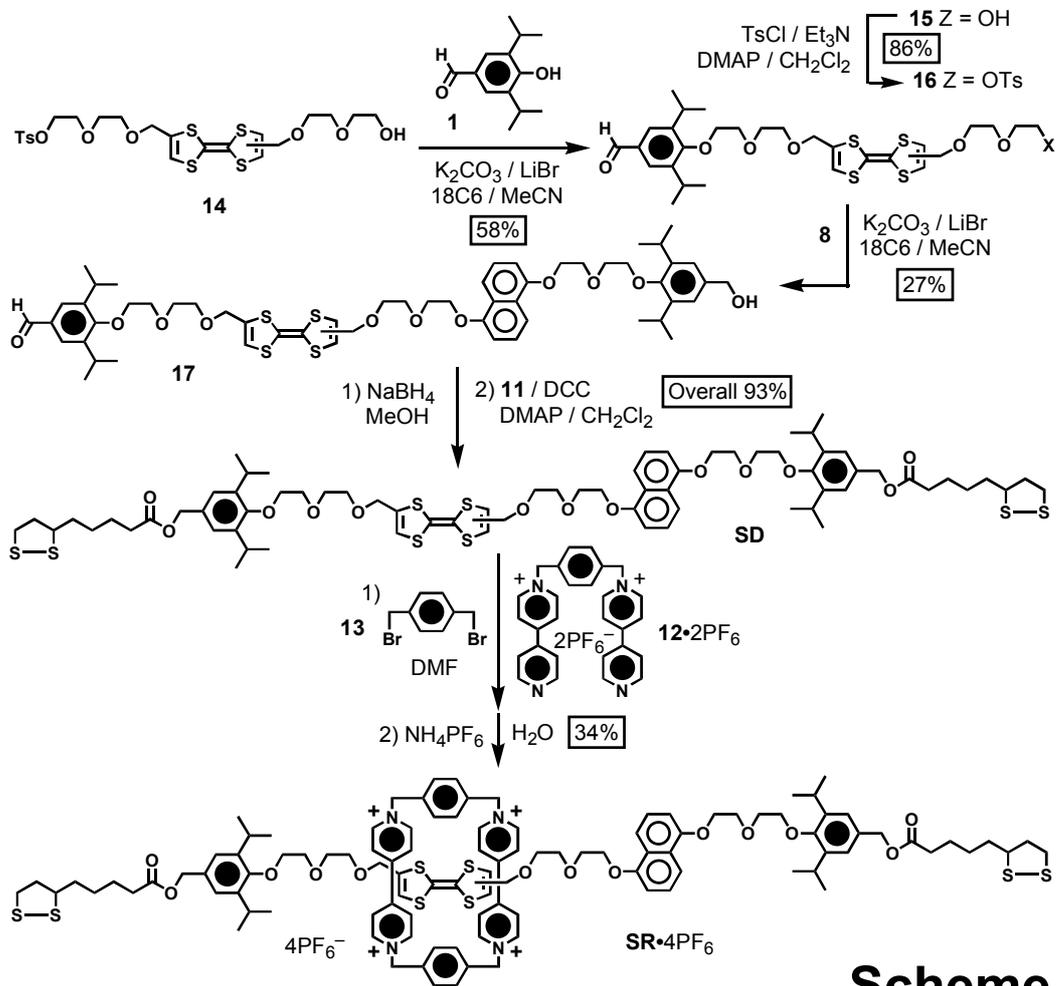
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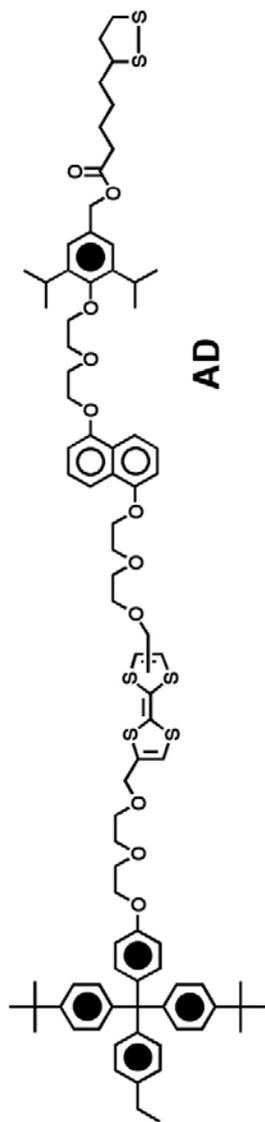
Scheme S1



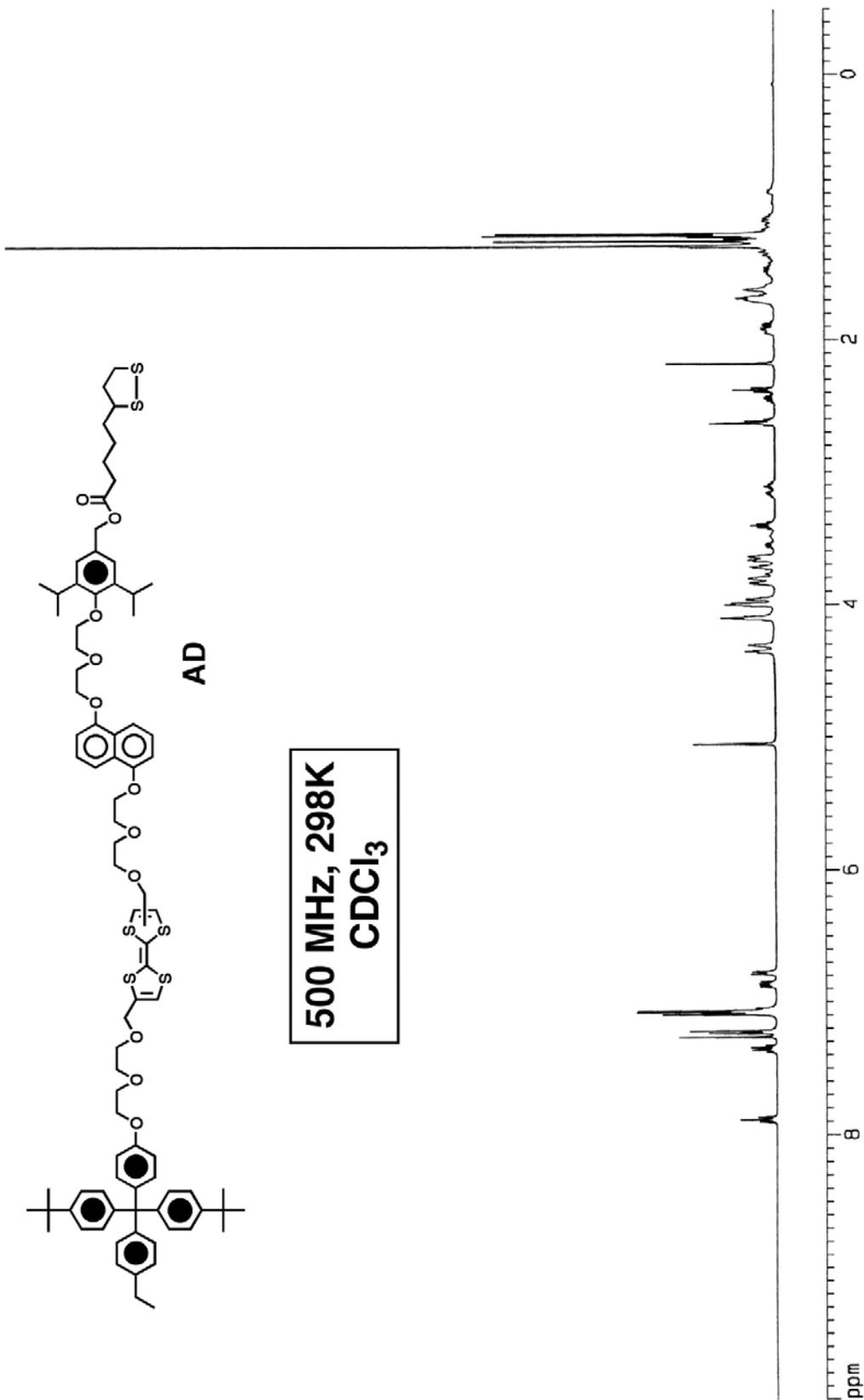
Scheme S2

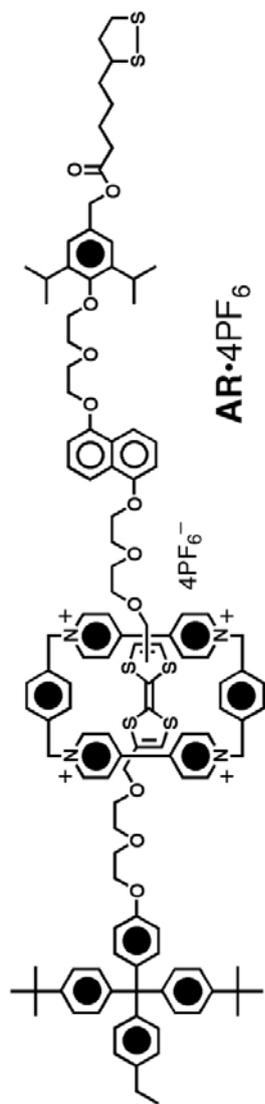


Scheme S3

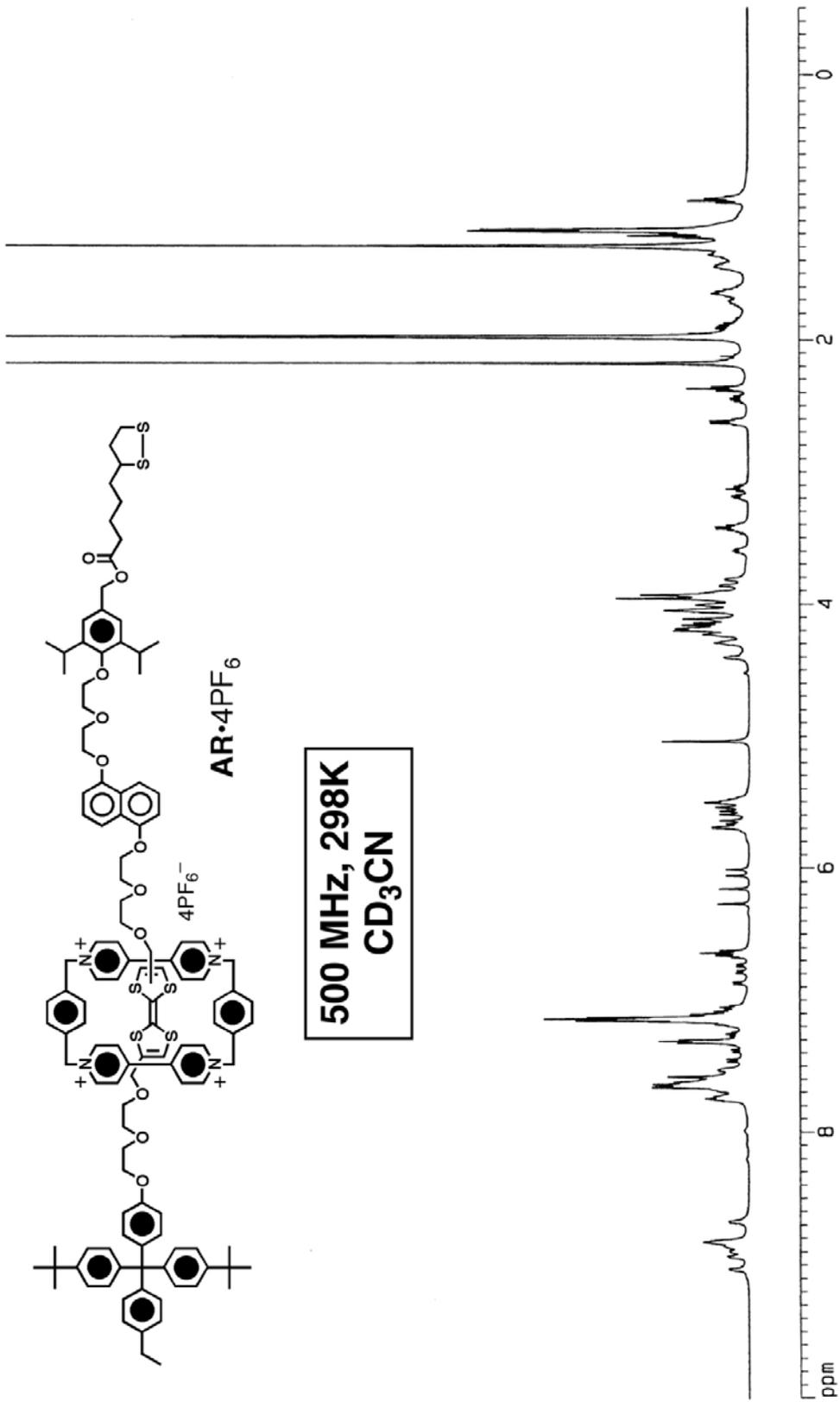


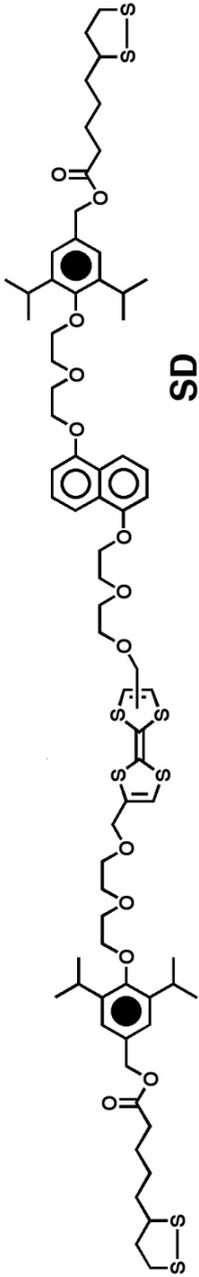
**500 MHz, 298K
CDCl₃**





500 MHz, 298K
CD₃CN





500 MHz, 298 K
CD₃COCD₃

