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Molecular Mechanical Switch-Based Solid-State Electrochromic Devices**

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Synthesis of [2]Rotaxane R1•4PF_6 and its Precursor Dumbbell-Shaped Compound D2

The routes employed to synthesize the [2]rotaxane **R1**•4PF_6 and its respective dumbbell-shaped compound **D2**, are outlined in Schemes S1–S2. The aldehyde **5** (Scheme S1) was obtained in 81% yield by reacting 4-hydroxy-3,5-diisopropyl-benzaldehyde[1] (**3**) with 2-(2-chloroethoxy)ethanol (**4**) under alkylation conditions (K_2CO_3/KI/DMF) at 100 ˚C. Treating **5** with TsCl in the presence of Et_3N and DMAP in CH_2Cl_2 solution gave the tosylate **6** which was then reacted, without purification, with $NaBH_4$ in MeOH, to afford the benzyl alcohol **7** in an overall yield of 67%. Alkylation (K_2CO_3/LiBr/18C6/MeCN) of 1-acetoxy-5-hydroxy-naphthalene[2] (**8**) with **5** produced the intermediate ester **9**, which was subjected to saponification (KOH/MeOH) to yield the diol **10** (overall 72%). Preparation of the [2]rotaxane **R1**•4PF_6 (Scheme S2) was completed by alkylating **10** with the tosylate[4] **11** in MeCN in the presence of K_2CO_3, LiBr, and 18C6 to afford the dumbbell-shaped compound **D2** in 68% yield. The template-directed synthesis of the [2]rotaxane **R1**•4PF_6 was accomplished by reacting **D2**, the dicationic salt[3] **12**•2PF_6, and 1,4-bis(bromomethyl)benzene (**13)** in DMF at RT for 10 d. The [2]rotaxane **R1**•4PF_6 was isolated after addition of H_2O in 85% 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.

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-hydroxynaphthalene[2] (**6),** α,α´-[1,4-phenylenebis (methyl lene)]bis(4,4´-bipyridium) bis(hexafluorophosphate)[3] (**12**•2PF_6), and the tosylate[4] **9** 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 5. A solution of 4-hydroxy-3,5-diisopropylbenzaldehyde (**3**) (2.06 g, 10 mmol), 2-(2-chloroethoxy)ethanol (**4**) (1.31 g, 11 mol), K_2CO_3 (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 (SiO_2: EtOAc/hexane, 1/1) to give the alcohol **5 (**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 7. A solution of the alcohol **5** (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 **6** 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 **7** (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 10. A solution of benzyl alcohol (**7**) (1.35 g, 3.0 mmol), 1-acetoxy-5-hydroxynaphthalene (**8**) (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 **9** 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 **10 (**948 mg, overall 72%) as an off-white solid. M.p. 68–70 ^oC; ^1H 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) $[M]^+$.

Dumbbell-Shaped Compound D2 A solution of the diol **10** (131.6 mg, 0.3 mmol), the tosylate **11** (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 Dumbbell-shaped compound **D2 (**270 mg, 68%) as a yellow solid. M.p. 104–107^oC; ^1H 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) $[M]^+$.

[2]Rotaxane R1•4PF$_6$. A solution of the dumbbell-shaped compound **D2** (207 mg, 0.1 mmol), **12**•2PF$_6$ (332 mg, 0.3 mmol) and 1,4-bis(bromomethyl)benzene (**13**) (124 mg, 0.3 mmol) in anhydrous DMF (11 mL) was stirred at room temperature for 6 d. The reaction mixture was subjected directly to column chromatography (SiO_2) and unreacted **D2** 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 **R1**•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 **R1**•4PF$_6$ (662 mg, 72%) as a green solid. M.p. 202-204^{o}C (decomp); ^{1}H NMR (500 MHz, CD_3CN) δ = 1.09–1.23 (m, 15 H), 1.28–1.31 (m, 18 H), 2.62 (q, *J* = 7.8 Hz, 2 H), 3.13 (t, *J* = 5.6 Hz, 1 H), 3.40–3.45 (m, 2 H), 3.71–4.52 (m, 28 H), 5.47–5.77 (m, 8 H), 6.00, 6.05, 6.15 and 6.27 (4 x s, 2 H), 6.62–6.87 (m, 4 H), 7.07–7.73 (m, 36 H), 8.65–9.04 (m, 8 H); MS (FAB) *m/z* (%) 2275 (12) $[M–PF_6]^+$, 2130 (18) $[M–2PF_6]$+, 1985 (7) $[M–3PF_6]^+$.

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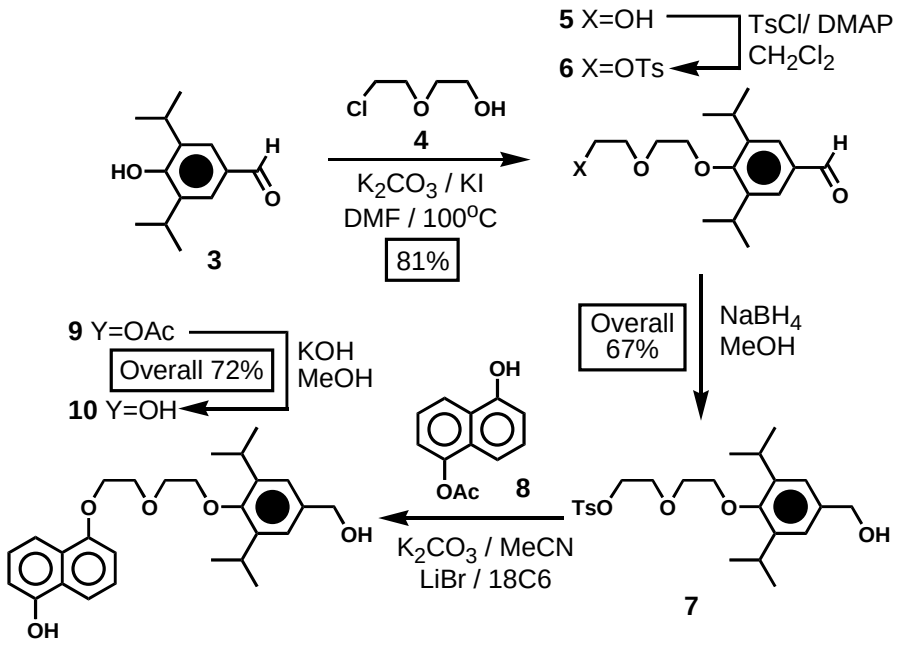
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6 X=OTs
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4
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DMF / 100°C
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3
X O O H O
Overall 67%
NaBH4
MeOH
9 Y=OAc
Overall 72%
KOH
MeOH
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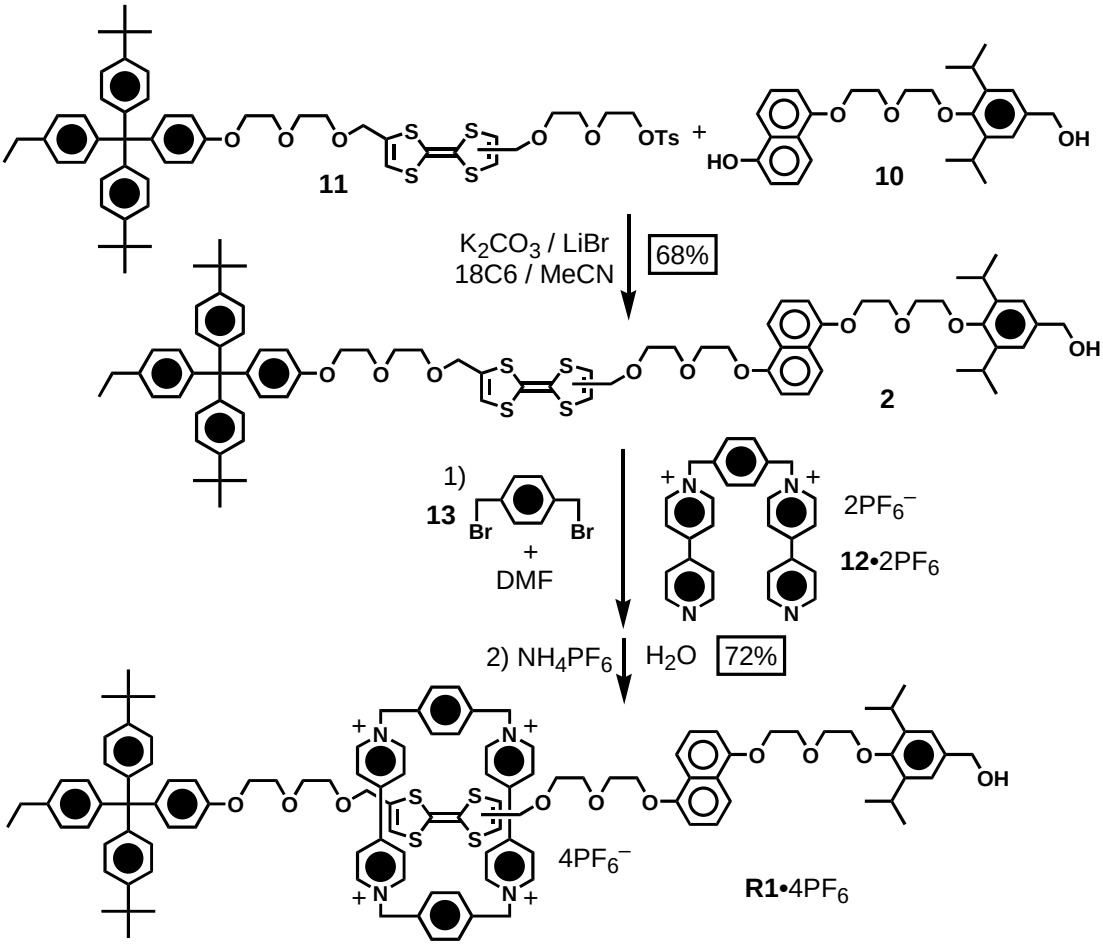
OAc
8
TsO O O OH
7
K2CO3 / MeCN
LiBr / 18C6
O O O OH
OH

Scheme S1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10
K2CO3 / LiBr
18C6 / MeCN
68%
2
1)
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Br
Br
+
DMF
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2) NH4PF6
H2O
72%
4PF6−
R1•4PF6

Scheme S2