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Molecular-Based Electronically Switchable Tunnel Junction Devices

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Supporting Information Available: Full experimental details and compound characterizations. Also, electrode fabrication and monolayer formation protocols

Experimental Section

General. Chemicals were purchased from Aldrich and were used as received, unless indicated otherwise. The compounds bis(4-*tert*-butylphenyl)-4-ethylphenylmethanol[10] (**4**), 2-[2-(2-chloroethoxy)ethoxy]tetrahydro-pyran[11] (**7**), toluene-4-sulfonic acid 2-(2-methoxyethoxy)ethyl ester[13] (**13**), the TTF derivative[14] (**24**), 1,1″-[1,4-phenylenebis(methylene)]bis(4,4′-bipyridin-1-ium) bis(hexafluorophosphate)[15] (**28**·2PF_6) 1,5-bis(2-(2-(2-hydroxy)ethoxy)ethoxy)naphthalene[17] (**30**), and cyclobis(paraquat-*p*-phenylene) tetrakis(hexafluorophosphate)[16] (CPBQT·4PF_6) were all prepared according to literature procedures. Solvents were dried according to literature procedures.[27] 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). Melting points were determined on an Electrothermal 9100 apparatus and are uncorrected. ^1H and ^{13}C spectra were recorded on either a Bruker AC200 (200 and 50 MHz, respectively), Bruker ARX400 (400 and 100 MHz, respectively), Bruker ARX500 or Bruker AMX500 (500 and 125 MHz, respectively) spectrometer at 300 K using residual solvent as the internal standard. All chemical shifts are quoted on a δ scale, and all coupling constants are expressed in Hertz (Hz). Electron Impact Ionization Mass Spectrometry (EIMS) was performed on a AUTO-SPEC instrument. Fast Atom Bombardment (FAB) mass spectra were obtained using a ZAB-SE mass spectrometer, equipped with krypton primary atom beam, utilizing a *m*-nitrobenzyl alcohol matrix. Microanalyses were performed by Quantitative Technologies, Inc.

4-[Bis(4-*tert*-butylphenyl)-(4-ethylphenyl)methyl]phenol (6). Compound **4** (19.6 g, 48.9 mmol) was dissolved in phenol (**5**) (80 g, excess) by warming. Concentrated aqueous HCl solution (1.8 mL) was added and a reddish-blue color was observed. The reaction mixture was heated under reflux for 4 h and then allowed to cool to room temperature, whereupon PhMe (300 mL) was added to the brown mixture. The organic phase was washed with aqueous NaOH solution (20 g/L, 7 x 150 mL) and dried ($MgSO_4$). The solvent was removed *in vacuo* and the residue was subjected to column chromatography (SiO_2:CH_2Cl_2). The colorless band (R_f = 0.15) was collected and the solvent evaporated. The resulting solid was recrystallized from hexane affording 11.7 g (50%) of the title compound **6** as a white solid. Data for **6**: m.p. 202–204 °C (lit.[10] 208–209 °C); ^{1}H NMR (200 MHz, $CDCl_3$) δ = 1.26 (t, J = 7.6 Hz, 3H), 1.34 (s, 18H), 2.66 (q, J = 7.6 Hz, 2H), 4.87 (bs, 1H), 6.69 (d, J = 8.7 Hz, 2H), 7.07–7.15 (m, 10H), 7.27 (d, J = 8.6 Hz, 4H); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 15.4, 28.3, 31.5, 34.4, 63.2, 114.1, 124.2, 126.8, 130.8, 131.1, 132.5, 139.9, 141.5, 144.2, 144.7, 148.4, 153.3; MS(EI) *m/z* (%) 476 (99) $[M]^+$; $C_{35}H_{40}O$: calcd C 88.19, H 8.46; found C 87.85, H 8.67.

2-(2-{4-[Bis(4-*tert*-butylphenyl)-(4-ethylphenyl)methyl]phenoxy}ethoxy)ethanol (8). A mixture of 4-[bis(4-*tert*-butylphenyl)-(4-ethylphenyl)methyl]phenol (**6**) (10.0 g, 21.0 mmol), KOH (2.35 g, 42.0 mmol), 2-[2-(2-chloroethoxy)ethoxy]tetrahydropyran (**7**) (8.76 g, 42.0 mmol) and LiBr (0.2 g, cat) in *n*-BuOH (150 mL) was heated under reflux for 2.5 d. After cooling to room temperature, CH_2Cl_2 (100 mL) was added and the mixture was filtered. The filtrate was concentrated *in vacuo* affording a yellow oil, which was redissolved in a mixture of CH_2Cl_2 (150 mL) and MeOH (75 mL). Concentrated HCl (5.0 mL) was added and the reaction mixture was stirred for 2.5 h at room temperature, whereupon the solvent was

removed *in vacuo*. The resulting white residue was dissolved in CH_2Cl_2, washed with H_2O (3 x 250 mL) and dried ($MgSO_4$). After removal of the solvent the residue was subjected to column chromatography (SiO_2:CH_2Cl_2/MeOH 99:1). The colorless band (R_f = 0.15) was collected and removal of the solvent afforded 9.90 g (84%) of the title compound (**8**) as a white foam. Data for **8**: ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.25 (t, J = 7.6 Hz, 3H), 1.32 (s, 18H), 2.36 (br s,w 1H), 2.64 (q, J = 7.6 Hz, 2H), 3.65–3.70 (m, 2H), 3.75–3.80 (m, 2H), 3.84–3.88 (m, 2H), 4.09–4.14 (m, 2H), 6.80 (d, J = 8.9 Hz, 2H), 7.05–7.15 (m, 10H), 7.25 (d, J = 8.6 Hz, 4H); ^{13}C NMR ($CDCl_3$, 50 MHz, 298 K) δ = 15.4, 28.3, 31.5, 34.3, 61.8, 63.2, 67.3, 69.8, 72.7, 113.2, 124.1, 126.7, 130.8, 131.1, 132.3, 140.1, 141.4, 144.2, 144.6, 148.4, 156.5; MS(EI) *m/z* (%) 564 (98), $[M]^+$; $C_{39}H_{48}O_3 \cdot 0.1CH_2Cl_2$: calcd C 81.92, H 8.47; found C 82.04, H 8.53.

2-(2-{4-[Bis(4-*tert*-butylphenyl)-(4-ethylphenyl)methyl]phenoxy}ethoxy)ethyl Bromide (9). Ph_3P (0.95 g, 3.62 mmol) was added in one portion to an ice-cooled solution of compound **8** (1.70 g, 3.01 mmol) and CBr_4 (1.20 g, 3.62 mmol) in anhydrous CH_2Cl_2 (25 mL). The reaction mixture was stirred for 1 h at 0 °C, whereupon the ice bath was removed. After stirring for 47 h at room temperature, half of the solvent was evaporated *in vacuo* and the residue was purified by column chromatography (SiO_2:CH_2Cl_2/hexane 1:1). The colorless band (R_f = 0.4) was collected and the solvent was evaporated giving a colorless oil, which was redissolved in CH_2Cl_2 (30 mL) and concentrated to provide 1.80 g (95%) of the title compound **9** as a white foam. Data for **9**: ^{1}H NMR (200 MHz, $CDCl_3$) δ = 1.26 (t, J = 7.6 Hz, 3H), 1.34 (s, 18H), 2.66 (q, J = 7.6 Hz, 2H), 3.51 (t, J = 6.3 Hz, 2H), 3.87–3.93 (m, 4H), 4.12–4.16 (m, 2H), 6.81 (d, J = 8.9 Hz, 2H), 7.06–7.16 (m, 10H), 7.27 (d, J = 8.6 Hz, 4H); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 15.4, 28.3, 30.3, 31.5, 34.4, 63.2, 67.4, 69.8, 71.5, 113.2, 124.2, 126.7, 130.8, 131.1, 132.3, 140.0, 141.5, 144.2, 144.7, 148.4, 156.5; MS(EI) *m/z* (%) 628 (88) $[M+2]^+$; $C_{39}H_{47}BrO_2$: calcd C 74.63, H 7.55; found C 74.25, H 7.54.

2-(2-{4-[Bis(4-*tert*-butylphenyl)-(4-ethylphenyl)methyl]-phenoxy}ethoxy)ethyl Tosylate (10). A solution of TsCl (2.29 g, 12.0 mmol) in THF (15 mL) was added dropwise over 30 min to a solution of **8** (5.65 g, 10.0 mmol) and NaOH (0.52 g, 13.0 mmol) in THF (20 mL) and H_2O (10 mL) maintained at 0 °C. The mixture was stirred for a further 3.5 h at 0 °C, before being poured into ice/H_2O (100 mL) and extracted with CH_2Cl_2 (3 x 50 mL). The combined organic layers were dried ($MgSO_4$) and concentrated *in vacuo* to give a colorless oil, which was purified by column chromatography (SiO_2:gradient elution with CH_2Cl_2/hexane 1:1 to CH_2Cl_2). The colorless band (R_f= 0.5, CH_2Cl_2) was collected and the solvent evaporated to give 3.78 g (53%) of the title compound **10** as a white foam. Finally, the eluent was changed to CH_2Cl_2/MeOH 9:1 and the next colorless band was collected affording 2.51 g (44%) of unreacted starting material **8** after evaporation of the solvent. Data for **10**: ^{1}H NMR (200 MHz, $CDCl_3$) δ= 1.25 (t, J = 7.6 Hz, 3H), 1.32 (s, 18H), 2.39 (s, 3H), 2.64 (q, J = 7.6 Hz, 2H), 3.74–3.80 (m, 4H), 4.00–4.04 (m, 2H), 4.18–4.23 (m, 2H), 6.75 (d, J = 8.9 Hz, 2H), 7.05–7.14 (m, 10H), 7.23–7.31 (m, 6H), 7.81 (d, J = 8.3 Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ= 15.4, 21.7, 28.3, 31.4, 34.3, 63.2, 67.3, 68.9, 69.3, 70.0, 113.1, 124.2, 126.7, 128.1, 129.9, 130.7, 131.1, 132.3, 133.1, 140.0, 141.5, 144.2, 144.6, 144.8, 148.4, 156.5; MS(EI) *m/z* (%) 718 (27) $[M]^+$; $C_{46}H_{54}O_5S$ calcd C 76.84, H 7.57; found C 76.77, H 7.62.

2-(2-{4-[Bis(4-*tert*-butylphenyl)-(4-ethylphenyl)methyl]phenoxy}ethoxy)ethyl Iodide (11). Compound **10** (1.08 g, 1.50 mmol) was dissolved in anhydrous Me_2CO (100 mL) and NaI (2.25 g, 15.0 mmol) was added in one portion. The reaction mixture was heated under reflux for 14 h, before being cooled to room temperature and the solvent removed *in vacuo*. The white residue was dissolved in CH_2Cl_2 (100 mL), washed with H_2O (2 x 100 mL) and dried ($MgSO_4$). Concentration *in vacuo* gave 1.00 g (99%) of the title compound **11** as a white foam. Data for **11**: ^{1}H NMR (200 MHz, $CDCl_3$) δ= 1.25 (t, J = 7.6 Hz, 3H), 1.32 (s, 18H), 2.64 (q, J = 7.6 Hz, 2H), 3.29 (t, J = 6.9 Hz, 2H), 3.80–3.89 (m, 4H), 4.10–4.15 (m,

2H), 6.80 (d, J = 8.9 Hz, 2H), 7.04–7.21 (m, 10H), 7.25 (d, J = 8.5 Hz, 4H); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 2.7, 15.4, 28.3, 31.4, 34.3, 63.2, 67.3, 69.5, 72.2, 113.2, 124.1, 126.7, 130.7, 131.1, 132.3, 140.0, 141.4, 144.2, 144.6, 148.4, 156.5; MS(EI) *m/z* (%) 674 (100) $[M]^+$; $C_{39}H_{47}IO_2$: calcd C 69.43, H 7.02; found C 69.07, H 6.82.

Methyl-(2-(2-methoxy)ethoxy)ethoxybenzoate (14). Toluene-4-sulfonic 2-(2-methoxy-ethoxy) ethyl ester **13** (100 g, 0.36 mol) and methyl 4-hydroxybenzoate **12** (50.5 g, 0.33 mol) were dissolved in anhydrous MeCN (200 mL). K_2CO_3 (77.0 g, 0.56 mol) was added and the mixture was heated under reflux for 48 h. The reaction mixture was cooled to room temperature and filtered. The filtrate was evaporated to dryness and the resulting residue was redissolved in CH_2Cl_2 (150 mL). The organic phase was washed with H_2O (3 x 100 mL) and dried ($MgSO_4$). The solvent was removed to give a yellow oil. Although the product contained a small amount of starting material, it was used in the next step without further purification. Data for **14**: ^{1}H NMR ($CDCl_3$) δ= 3.38 (s, 3H), 3.55–3.58 (m, 2H), 3.70–3.73 (m, 2H), 3.85–3.88 (m, 2H), 4.17–4.20 (m, 2H), 6.92 (d, J = 8.8 Hz, 2H), 7.97 (d, J = 9.2 Hz, 2H).

(2-(2-Methoxy)ethoxy)ethoxybenzyl Alcohol (15). Compound **14** (32.5 g, 128 mmol) was dissolved in anhydrous THF (150 mL). $LiAlH_4$ (4.9 g, 128 mmol) was added portionwise to this solution with cooling as necessary. After addition of the reducing agent, the reaction was stirred at room temperature for 1 h, after which time H_2O was added carefully until gas evolution ceased. The reaction mixture was diluted with EtOAc (100 mL) and filtered. The filtrate was concentrated *in vacuo*, and the residue was dissolved in CH_2Cl_2 (150 mL). The organic phase was washed with H_2O (3 x 100 mL), dried ($MgSO_4$) and the solvents were removed *in vacuo* to give an oil which was subjected to column chromatography (SiO_2:EtOAc). The colorless band (R_f = 0.7) was collected to give 17.3 g (60%) of the title compound **15** as a colorless oil. Data for **15**: ^{1}H NMR (400 MHz, $CDCl_3$) δ= 3.35 (s, 3H),

3.52–3.58 (m, 2H), 3.65–3.71 (m, 2H), 3.77–3.85 (m, 2H), 4.07–4.12 (m, 2H), 4.55 (s, 2H), 6.86 (d, J = 8.6 Hz, 2H), 7.24 (d, J = 8.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 59.1, 64.8, 67.5, 69.8, 70.7, 71.9, 114.7, 128.6, 133.5, 158.3; MS(FAB) m/z (%) 226 (67) $[M]^+$.

(2-(2-Methoxy)ethoxy)ethoxybenzyl Chloride (16). The alcohol **15** (6.0 g, 26.5 mmol) was dissolved in anhydrous CH_2Cl_2 (50 mL) under an Ar atmosphere. Thionyl chloride (2.3 mL, 26.5 mmol) was added dropwise over a period of 10 min. The reaction was found to be complete by tlc (EtOAc, R_f= 0.8) following the addition of the thionyl chloride. The organic phase was washed with H_2O (3 x 50 mL), dried and the solvent removed *in vacuo* to yield 6.4 g (98%) of the title compound **16** as a yellow oil. The product was used without further purification. Data for **16**: ^{1}H NMR (400 MHz, $CDCl_3$) δ= 3.49 (s, 3H), 3.61–3.56 (m, 2H), 3.74–3.67 (m, 2H), 3.88 (m, 2H), 4.16–4.11 (m, 2H), 4.55 (s, 2H), 6.87 (d, J = 8.6 Hz, 2H), 7.28 (d, J = 8.6 Hz, 2H).

Methyl 3,4,5-Tris-[(2-(2-methoxy)ethoxy)ethoxybenzyloxy]benzoate (18). K_2CO_3 (5.5 g, 39.8 mmol) and methyl 3,4,5-trihydroxybenzoate **17** (0.8 g, 4.4 mmol) were suspended/dissolved in anhydrous DMF (150 mL) and degassed (Ar, 10 min). This procedure resulted in the development of a brown color. The chloride **16** (6.4 g, 26.1 mmol) was added dropwise to this brown solution at room temperature over a period of 20 min. The reaction mixture was stirred at 80 °C for 16 h during which time the color of the reaction mixture darkened considerably. After cooling, most of the DMF was removed *in vacuo*, and the residue was dissolved in CH_2Cl_2 (150 mL). The organic phase was washed with H_2O (5 x 150 mL), dried ($MgSO_4$) and solvent removed *in vacuo*. The resultant residue was subjected to column chromatography (SiO_2:EtOAc). The colorless band (R_f = 0.4) was collected and the solvent evaporated to yield 2.9 g (82%) of the title compound **18** as a colorless oil. Data for **18**: ^{1}H NMR (400 MHz, $CDCl_3$) δ= 3.37 (s, 9H), 3.55–3.57 (m, 6H), 3.70–3.72 (m, 6H), 3.86–3.84 (m, 9H), 4.09–4.11 (m, 2H), 4.10–4.15 (m, 4H), 4.99 (s, 2H),

5.06 (s, 4H), 6.78 (d, J = 8.8 Hz, 2H), 6.91 (d, J = 8.8 Hz, 4H), 7.31–7.35 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 51.9, 58.8, 67.1, 69.5, 70.5, 70.8, 71.7, 74.3, 108.9, 114.0, 114.3, 124.8, 128.7, 128.9, 129.0, 129.6, 129.8, 142.1, 152.4, 158.4, 166.4; $C_{44}H_{56}O_{14}$: calcd C 65.33, H 6.98; found C 64.95, H 6.69.

3,4,5-Tris-[(2-(2-methoxy)ethoxy)ethoxybenzyloxy]benzyl Alcohol (19). Compound **18** (2.9 g, 3.6 mmol) was dissolved in anhydrous THF (75 mL). $LiAlH_4$ (0.14 g, 3.6 mmol) was added portionwise to this solution with cooling as necessary. After addition of the reducing agent, the reaction was stirred at room temperature for 1 h, after which time H_2O was added carefully until gas evolution ceased. The reaction mixture was diluted with EtOAc (100 mL) and filtered. The filtrate was concentrated *in vacuo*, and the residue was dissolved in CH_2Cl_2 (100 mL). The organic phase was washed with H_2O (3 x 100 mL), dried ($MgSO_4$) and removed *in vacuo* to give an oil which was subjected to column chromatography (SiO_2:EtOAc). The colorless band (R_f = 0.3) was collected to give 1.9 g (70%) of the title compound **19** as a colorless oil. Data for **19**: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 3.26 (s, 9H), 3.46–3.49 (m, 6H), 3.60–3.62 (m, 6H), 3.76–3.73 (m, 6H), 3.99–4.03 (m, 6H), 4.41 (br s, 2H), 4.83 (s, 2H), 4.86 (s, 4H), 6.56 (s, 2H), 6.71 (d, J = 8.8 Hz, 2H), 6.81 (d, J = 8.8 Hz, 4H), 7.20–7.26 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 58.3, 64.0, 66.8, 69.1, 70.0, 70.2, 71.3, 74.1, 105.5, 113.6, 113.9, 128.6, 128.9, 129.6, 129.8, 136.6, 136.8, 152.3, 157.9; $C_{43}H_{56}O_{13}$: calcd C 66.14, H 7.23; found C 65.80, H 7.15.

3,4,5-Tris-[(2-(2-methoxy)ethoxy)ethoxybenzyloxy]benzyl Chloride (20). Compound **19** (1.0 g, 1.28 mmol) and 2,6-di-*tert*-butyl-4-methyl pyridine (0.52 g, 2.56 mmol) were dissolved in anhydrous CH_2Cl_2 (50 mL) under an Ar atmosphere. Thionyl chloride (93 µL, 1.3 mmol) was added dropwise over a period of 10 min. The reaction was complete as indicated by tlc (EtOAc, R_f = 0.5) following the addition of the thionyl chloride. The organic phase was washed with H_2O (3 x 50 mL), dried and the solvent removed *in vacuo* to yield

0.98 g (97%) of the title compound **20** as a pink oil which solidified on standing. Data for **20**: ^{1}H NMR ($CDCl_3$) δ = 3.39 (s, 9H), 3.56–3.62 (m, 6H), 3.69–3.75 (m, 6H), 3.82–3.89 (m, 6H), 4.06–4.18 (m, 6H), 4.48 (s, 2H), 4.92 (s, 2H), 5.01 (s, 4H), 6.66 (s, 2H), 6.79 (d, J = 8.8 Hz, 2H), 6.91 (d, J = 8.8 Hz, 4H), 7.25–7.34 (m, 6H).

4-{3,4,5-Tris-[(2-(2-methoxy)ethoxy)ethoxybenzyloxy]benzyloxy}benzyl Alcohol (22). K_2CO_3 (1.56 g, 11.3 mmol), 4-hydroxybenzyl alcohol **21** (1.4 g, 11.3 mmol) were suspended/dissolved in DMF (75 mL) and degassed (Ar, 10 min). The chloride **20** (3.0 g, 3.8 mmol) was added dropwise over a period of 15 min. The reaction mixture was stirred at 80 °C for 16 h. The reaction mixture was cooled and most of the DMF removed *in vacuo*. The residue was dissolved in CH_2Cl_2 (75 mL) and washed with brine (2 x 50 mL) and H_2O (2 x 50 mL). The solvent was removed *in vacuo* and the residue was subjected to column chromatography (SiO_2:gradient elution with EtOAc to EtOAc/MeOH 90:10). The colorless band (R_f = 0.3) was collected to yield 2.0 g (61%) of the title compound **22** as a colorless oil. Data for **22**: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 3.43 (s, 9H), 3.62–3.63 (m, 6H), 3.75–3.78 (m, 6H), 3.90–3.92 (m, 6H), 4.13–4.22 (m, 6H), 4.65 (s, 2H), 4.97 (s, 2H), 4.98 (s, 2H), 5.06 (s, 4H), 6.72 (s, 2H), 6.84 (d, J = 6.8 Hz, 2H), 6.91–6.94 (m, 6H), 7.26–7.36 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 59.0, 64.8, 67.3, 67.4, 69.7, 70.1, 70.7 (3), 70.9, 71.9 (2), 74.6, 107.2, 114.2, 114.5, 114.9, 128.5, 129.0 (2), 129.3, 130.1, 130.2, 132.3, 133.5, 137.9, 152.9, 158.1, 158.4, 158.5.

4-{3,4,5-Tris-[(2-(2-methoxy)ethoxy)ethoxybenzyloxy]benzyloxy}benzyl Chloride (23). Compound **22** (1.8 g, 2.0 mmol) and 2,6-di-*tert*-butyl-4-methyl pyridine (0.83 g, 4.1 mmol) were dissolved in anhydrous CH_2Cl_2 (50 mL) under an Ar atmosphere. Thionyl chloride (0.15 mL, 2.0 mmol) was added dropwise over a period of 5 min. The reaction was complete by tlc (EtOAc/MeOH 90:10, R_f = 0.4) following the addition of the thionyl chloride. The organic phase was washed with H_2O (3 x 50 mL), dried, the solvent removed *in vacuo* and

the residue subjected to column chromatography (SiO_2:gradient elution with EtOAc to EtOAc/MeOH 90:10). The colorless band (R_f = 0.4) was collected to yield 2.0 g (61%) of the title compound **23** as a colorless oil. Data for **23**: ^{1}H NMR (400 MHz, $CDCl_3$) 3.42 (s, 9H), 3.62–3.63 (m, 6H), 3.75–3.78 (m, 6H), 3.90–3.92 (m, 6H), 4.13–4.22 (m, 6H), 4.55 (s, 2H), 4.94 (s, 2H), 4.96 (s, 2H), 5.05 (s, 4H), 6.72 (s, 2H), 6.84 (d, J = 6.8 Hz, 2H), 6.91–6.94 (m, 6H), 7.26–7.36 (m, 8H).

Compound 25. Method A: A solution of compound **24** (0.53 g, 1.00 mmol) in anhydrous THF (70 mL) was degassed (Ar, 10 min) before a solution of $CsOH{\cdot}H_2O$ (0.177 g, 1.05 mmol) in anhydrous MeOH (8 mL) was added dropwise via a syringe over a period of 1 h. The mixture was stirred for 15 min, whereupon a solution of the bromide **9** (0.63 g, 1.00 mmol) in anhydrous THF (10 mL) was added in one portion and the reaction mixture was stirred for 20 h. The solvent was evaporated in vacuo and the resulting yellow residue was dissolved in CH_2Cl_2 (100 mL), washed with H_2O (2 x 100 mL) and dried ($MgSO_4$). Concentration *in vacuo* gave a orange/yellow foam, which was purified by column chromatography (SiO_2:CH_2Cl_2/hexane 4:1). The broad yellow band (R_f = 0.65) was collected and concentrated affording a yellow foam, which was repeatedly dissolved in CH_2Cl_2 (2 x 25 mL) and concentrated to give 0.78 g (76%) of **25** as a yellow foam.

Method B: A solution of compound **24** (0.75 g, 1.42 mmol) in anhydrous THF (100 mL) was degassed (Ar, 15 min) before a solution of $CsOH{\cdot}H_2O$ (0.25 g, 1.49 mmol) in anhydrous MeOH (10 mL) was added dropwise via a syringe over a period of 1 h. The mixture was stirred for 10 min, whereupon a solution of the iodide **11** (0.97 g, 1.44 mmol) in anhydrous THF (10 mL) was added in one portion and the reaction mixture was stirred for 20 h. The solvent was evaporated *in vacuo* and the resulting yellow residue was dissolved in CH_2Cl_2 (100 mL), washed with H_2O (2 x 100 mL) and dried ($MgSO_4$). Concentration *in vacuo* gave

an orange/yellow foam, which was purified by column chromatography (SiO_2:CH_2Cl_2/hexane 4:1). The broad yellow band (R_f = 0.65) was collected and concentrated to afford a yellow foam, which was repeatedly dissolved in CH_2Cl_2 (2 x 25 mL) and concentrated to give 1.32 g (91%) of the title compound **25** as a yellow foam. Data for **25**: ^{1}H NMR (200 MHz, CD_3COCD_3) δ = 1.20 (t, J = 7.6 Hz, 3H), 1.29 (s, 18H), 2.39 (s, 3H), 2.40 (s, 3H), 2.60 (q, J = 7.6 Hz, 2H), 3.03 (t, J = 6.3 Hz, 2H), 3.71–3.82 (m, 4H), 4.09 (t, J = 4.7 Hz, 2H), 6.81 (d, J = 8.9 Hz, 2H), 7.05–7.14 (m, 10H), 7.22 and 7.24 (AB q, J = 2.1 Hz, 2H), 7.31 (d, J = 8.5 Hz, 4H), 7.41 (d, J = 8.3 Hz, 2H), 7.83 (d, J = 8.3 Hz, 2H); MS(FAB) *m/z* (%) 1021 (100) $[M]^+$; $C_{55}H_{59}NO_4S_7$: calcd C 64.60; H 5.82, N 1.37; found C 64.33, H 5.63, N 1.06.

Compound 26. Compound **25** (1.32 g, 1.29 mmol) was dissolved in anhydrous THF–MeOH (1:1 v/v, 140 mL) and the solution was degassed (Ar, 10 min) before NaOMe (30% in MeOH, 3.7 mL, 1.05 g, 19.4 mmol) was added in one portion. The yellow solution was heated under reflux for 20 min before being cooled to room temperature, whereupon the solvent was evaporated. The yellow residue was dissolved in CH_2Cl_2 (150 mL), washed with H_2O (3 x 100 mL) and dried ($MgSO_4$). Concentration *in vacuo* gave a yellow foam, which was subjected to column chromatography (SiO_2:CH_2Cl_2). The yellow band (R_f = 0.6) was collected and concentrated affording 1.03 g (92%) of the title compound **26** as a yellow powder. Data for **26**: m.p. 208–209 °C (decomposition); ^{1}H NMR (200 MHz, CD_3COCD_3) δ = 1.20 (t, J = 7.6 Hz, 3H), 1.29 (s, 18H), 2.42 (s, 3H), 2.60 (q, J = 7.6 Hz, 2H), 3.05 (t, J = 6.4 Hz, 2H), 3.73–3.85 (m, 4H), 4.12 (t, J = 4.7 Hz, 2H), 6.76 (d, J = 2.8 Hz, 2H), 6.83 (d, J = 8.9 Hz, 2H), 7.06–7.14 (m, 10H), 7.31 (d, J = 8.6 Hz, 4H), 10.38 (br s, 1H); MS(FAB) *m/z* (%) 867 (100) $[M]^+$; $C_{48}H_{53}NO_2S_6$: calcd C 66.39, H 6.15, N, 1.61; found C 66.11, H 6.05, N 1.44.

Single-Station Dumbbell (27). Compound **26** (0.19 g, 0.21 mmol) and the chloride **23** (0.22 g, 0.24 mmol) were dissolved in anhydrous DMF (10 mL) and degassed (Ar, 10 min) before NaH (0.021 g of a 60% suspension in mineral oil, 0.53 mmol) was added. The reaction mixture was stirred for 45 min at room temperature, causing the initially yellow solution to become more orange. H_2O (40 mL) was added carefully (dropwise until no more gas evolution was observed), followed by addition of brine (40 mL). The yellow precipitate was filtered and dried. The crude product was purified by column chromatography (SiO_2:CH_2Cl_2/EtOAc 2:1). The yellow band (R_f = 0.35) was collected and the solvent evaporated affording a yellow oil, which was repeatedly dissolved in CH_2Cl_2 (3 x 20 mL) and concentrated to give 0.29 g (80%) of the title compound **27** as a yellow foam. Data for **27**: ^{1}H NMR (400 MHz, CD_3COCD_3) δ = 1.17 (t, J = 7.6 Hz, 3H), 1.26 (s, 18H), 2.39 (s, 3H), 2.57 (q, J = 7.6 Hz, 2H), 3.02 (t, J = 6.3 Hz, 2H), 3.26 (s, 9H), 3.44–3.49 (m, 6H), 3.59–3.64 (m, 6H), 3.72 (t, J = 6.3 Hz, 2H), 3.76–3.81 (m, 8H), 4.05–4.13 (m, 8H), 4.88 (s, 2H), 4.97 (s, 2H), 5.00 (s, 2H), 5.01 (s, 4H), 6.70 and 6.72 (AB q, J = 2.1 Hz, 2H), 6.79 (d, J = 8.7 Hz, 4H), 6.84 (s, 2H), 6.89–6.94 (m, 6H), 7.03–7.16 (m, 12H), 7.25–7.33 (m, 6H), 7.37 (d, J = 8.8 Hz, 4H); MS(FAB) *m/z* (%) 1736 (5) $[M]^+$; $C_{98}H_{113}NO_{15}S_6$: calcd C 67.75, H 6.56, N 0.81; found C 67.61, H 6.46, N 0.80.

Single-Station [2]Rotaxane (3·4PF$_6$). A solution of the dumbbell **27** (0.26 g, 0.15 mmol), **28**·2PF$_6$ (0.33 g, 0.47 mmol) and 1,4-bis(bromomethyl)benzene (**29**) (0.12 g, 0.45 mmol) in anhydrous DMF (10 mL) was stirred for 6 d at room temperature (after approx. 1 d the color changed to green and a white precipitate was formed). The green suspension was subjected directly to column chromatography (SiO_2) and the unreacted dumbbell compound 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 then the green band was collected. Most of the solvent was removed *in vacuo* (T < 30 °C) followed by addition of H_2O (30 mL). The resulting precipitate was collected by filtration, washed with Et_2O (20 mL) and dried, affording 0.035 g (8%) of the

[2]rotaxane **3**·4PF_6 as a green solid. Data for **3**·4PF_6: m.p. 135 °C (decomposition); ^{1}H NMR (400 MHz, CD_3COCD_3) δ = 1.19 (t, J = 7.6 Hz, 3H), 1.28 (s, 18H), 2.60 (q, J = 7.6 Hz, 2H), 2.64 (s, 3H), 3.28 (s, 6H), 3.29 (s, 3H), 3.29 (t, J = 6.4 Hz, 2H), 3.47–3.50 (m, 6H), 3.61–3.65 (m, 6H), 3.77–3.81 (m, 6H), 3.95 (t, J = 6.4 Hz, 2H), 3.98–4.01 (m, 2H), 4.08–4.14 (m, 6H), 4.23–4.25 (m, 2H), 4.69 (s, 2H), 4.80 (s, 4H), 4.97 (s, 2H), 5.18 (s, 2H), 5.98–6.08 (m, 8H), 6.43 and 6.45 (AB q, J = 2.1 Hz, 2H), 6.78 (s, 2H), 6.83–6.85 (m, 4H), 6.94 (d, J = 8.7 Hz, 4H), 7.07–7.12 (m, 10H), 7.18 (d, J = 8.6 Hz, 2H), 7.26–7.31 (m, 10H), 7.38 (br s, 4H), 7.69 (d, J = 8.7 Hz, 2H), 7.94–8.06 (m, 8H), 8.45 (br s, 4H), 9.16 (br s, 4H), 9.48 (br s, 4H); MS(FAB) *m/z* (%) 2691 (4) $[M - PF_6]^+$, 2546 (14) $[M - 2PF_6]^+$, 2401 (16) $[M - 3PF_6]^+$, 1738 (7) (dumbbell), 1273 (15) $[M - 2PF_6]^{2+}$, 1200.5 (35) $[M - 3PF_6]^{2+}$, 1128 (20) $[M - 4PF_6]^{2+}$; UV–vis (Me_2CO, 298 K) λ_{max} 810 nm, (ε 1400 L mol^{-1} cm^{-1}); $C_{134}H_{145}F_{24}N_5O_{15}P_4S_6$·2$H_2O$: C 56.00, H 5.23, N 2.44; found C 56.07, H 5.06, N 2.28.

2-(2-{5-[2-(2-Hydroxyethoxy)ethoxy]naphthalen-1-yloxy}ethoxy)ethyl Tosylate (30). TsCl (3.43 g, 18.0 mmol) dissolved in anhydrous CH_2Cl_2 (20 mL) was added dropwise over 20–30 min to an ice-cooled solution of the 1,5-bis[2-(2-hydroxyethoxy)ethoxy]naphthalene (6.73 g, 20.0 mmol), Et_3N (6.3 mL, 4.6 g, 45 mmol) and DMAP (~10 mg , cat) in anhydrous CH_2Cl_2 (150 mL). The reaction mixture was stirred for 16 h (0 °C to rt), whereupon it was washed with 5N HCl solution (100 mL), H_2O (3 × 250 mL) and dried ($MgSO_4$). After removal of the solvent *in vacuo* the product mixture was purified by repeated column chromatography (SiO_2:CH_2Cl_2/MeOH 24:1, up to four columns may be necessary). The second band (R_f = 0.2) containing the desired product was collected and concentrated to give 4.21 g (48%) of the title compound **30** as an off-white solid; mp 76–77.5 °C. Data for **30**: ^{1}H NMR (200 MHz, CD_2Cl_2) δ = 2.03 (t, J = 4.5 Hz, 1H), 2.37 (s, 3H), 3.69–3.82 (m, 6H), 3.87–3.92 (m, 2H), 3.96–4.01 (m, 2H), 4.16–4.22 (m, 4H), 4.28–4.32 (m, 2H), 6.84 (d, J = 8.0 Hz, 1H), 6.88 (d, J = 8.2 Hz, 1H), 7.28 (d, J = 8.0 Hz, 2H), 7.32–7.41 (m, 2H), 7.73–7.87 (m, 4H); ^{13}C NMR (CD_3SOCD_3, 50 MHz, 298 K) δ = 21.2, 60.6, 67.8, 68.0,

68.4, 69.2, 69.2, 70.2, 72.9, 106.1 (2), 114.1, 114.2, 125.6, 125.6, 126.2 (2), 127.8, 130.2, 132.6, 145.0, 154.0, 154.1; MS(FAB) *m/z* (%) 490 (100) $[M]^+$; $C_{25}H_{30}O_8S$: calcd C 61.21, H, 6.16; found C 61.13, H 6.01.

2-(2-{5-[2-(2-Hydroxyethoxy)ethoxy]naphthalen-1-yloxy}ethoxy)ethyl Iodide (31). Compound **30** (2.55 g, 5.20 mmol) was dissolved in anhydrous Me_2CO (100 mL) and NaI (7.64 g, 51.0 mmol) was added in one portion. The reaction mixture was heated under reflux for 1 d, before being cooled to room temperature and the solvent removed *in vacuo*. The white residue was dissolved in CH_2Cl_2 (100 mL), washed with a saturated $Na_2S_2O_3$ solution (100 mL), H_2O (150 mL) and dried ($MgSO_4$). Concentration *in vacuo* gave 2.29 g (99%) of the title compound **31** as an off-white solid. Data for **31**: mp 62.5–64 °C; ^1H NMR (300 MHz, $CDCl_3$) δ = 2.22 (br s, 1H), 3.31 (t, J = 6.8 Hz, 2H), 3.71–3.78 (m, 4H), 3.90 (t, J = 6.8 Hz, 2H), 3.96–4.01 (m, 4H), 4.27–4.32 (m, 4H), 6.84 (d, J = 8.2 Hz, 2H), 7.36 (t, J = 8.2 Hz, 2H), 7.87 (d, J = 8.2 Hz, 1H), 7.88 (d, J = 8.2 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 2.9, 61.8, 67.8, 67.9, 69.4, 69.7, 72.1, 72.6, 105.7, 105.8, 114.6, 114.7, 125.1, 125.1, 126.7 (2), 154.2 (2); MS(FAB) *m/z* (%) 446 (100) $[M]^+$; $C_{18}H_{23}IO_5$: calcd C 48.44, H 5.19; found C 48.74, H 5.32.

2-(2-{5-[2-(2-(Tetrahydropyranyloxy)ethoxy)ethoxy]naphthalen-1-yloxy}ethoxy)ethyl Iodide (32). A solution of the iodide **31** (2.20 g, 4.93 mmol), 3,4-dihydro-2*H*-pyran (0.47 mL, 0.43 g, 5.15 mmol) and *p*-TsOH·H_2O (~10 mg, cat) in anhydrous CH_2Cl_2 (75 mL) was stirred for 1.5 h at room temperature. The reaction mixture was diluted with CH_2Cl_2 (75 mL), washed with H_2O (100 mL) and then saturated aqueous $NaHCO_3$ solution (100 mL) before being dried ($MgSO_4$). Evaporation of the solvent *in vacuo* gave a reddish oil, which was purified by flash column chromatography (SiO_2:CH_2Cl_2/MeOH 24:1). The first band (R_f = 0.6) was collected and concentrated providing 2.31 g (88%) of the title compound **32** as a reddish oil. The product consists of a mixture of (*R*-) and (*S*-)enantiomers because of the

presence of a stereogenic center at the 2-position of the tetrahydropyranyl ether. Hence, the spectroscopic data below are also given for the mixture of enantiomers. Data for **32**: ^{1}H NMR (300 MHz, $CDCl_3$) δ= 1.44–1.90 (m, 6H), 3.31 (t, J = 6.8 Hz, 2H), 3.45–3.53 (m, 1H), 3.62–3.70 (m, 1H), 3.79–4.04 (m, 10H), 4.26–4.32 (m, 4H), 4.66 (t, J = 3.5 Hz, 1H), 6.83 (d, J = 8.0 Hz, 1H), 6.86 (d, J = 8.0 Hz, 1H), 7.34 (t, J = 8.0 Hz, 1H), 7.36 (t, J = 8.0 Hz, 1H), 7.86 (d, J = 8.0 Hz, 1H), 7.89 (d, J = 8.0 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ= 2.9, 19.4, 25.4, 30.5, 62.2, 66.7, 67.9, 67.9, 69.4, 69.7, 70.9, 72.1, 98.9, 105.7, 105.7, 114.5, 114.8, 124.9, 125.1, 126.7, 126.8, 154.2, 154.3; MS(FAB) *m/z* (%) 530 (100) $[M]^+$; $C_{23}H_{31}IO_6$: calcd C 52.08, H 5.89; found C 52.31, H 5.79.

THP Protected Semi-Dumbbell (33). Compound **26** (0.62 g, 0.71 mmol) and the iodide **32** (0.38 g, 0.72 mmol) were dissolved in anhydrous DMF (30 mL) and degassed (Ar, 10 min) before NaH (0.070 g of a 60% suspension in mineral oil, 1.75 mmol) was added. The reaction mixture was stirred for 1 h at room temperature, causing the initially yellow solution to become more orange. H_2O (100 mL) was added (dropwise until no more gas evolution was observed), followed by addition of brine (100 mL). The yellow precipitate was filtered, washed with H_2O (2 x 30 mL) and dried ($MgSO_4$). The crude product was purified by column chromatography (SiO_2:CH_2Cl_2/MeOH 99:1). The yellow band (R_f = 0.4) was collected and the solvent evaporated *in vacuo* affording a yellow oil, which was redissolved in CH_2Cl_2 (2 x 40 mL) and concentrated providing 0.78 g (86%) of the title compound **33** as a yellow foam. Data for **33**: ^{1}H NMR (400 MHz, CD_3COCD_3) δ= 1.17 (t, J = 7.6 Hz, 3H), 1.27 (s, 18H), 1.33–1.82 (m, 6H), 2.40 (s, 3H), 2.58 (q, J = 7.6 Hz, 2H), 3.03 (t, J = 6.4 Hz, 2H), 3.35–3.43 (m, 1H), 3.52–3.60 (m, 1H), 3.71–3.84 (m, 10H), 3.88–3.97 (m, 4H), 4.05–4.09 (m, 4H), 4.23–4.31 (m, 4H), 4.60 (t, J = 3.2 Hz, 1H), 6.73 and 6.74 (AB q, J = 2.1 Hz, 2H), 6.79 (d, J = 9.0 Hz, 2H), 6.90 (d, J = 7.7 Hz, 1H), 6.96 (d, J = 7.7 Hz, 1H), 7.04–7.12 (m, 10H), 7.26–7.40 (m, 6H), 7.78 (d, J = 8.5 Hz, 1H), 7.83 (d, J = 8.5 Hz, 1H); MS(FAB)

m/z (%) 1269 (100) $[M]^+$; $C_{71}H_{83}NO_8S_6$: calcd C 67.10, H 6.58, N 1.10; found C 67.21, H 6.63, N 1.03.

Semi-Dumbbell (2). A solution of compound **33** (0.70 g, 0.55 mmol) in THF–EtOH (40 mL, 1:1 v/v) was degassed (Ar, 5 min) before *p*-TsOH·H_2O (~10 mg, cat.) was added. The yellow solution was stirred for 1 d at room temperature, whereupon it was diluted with CH_2Cl_2 (150 mL). The combined organic phase was washed with a saturated aqueous $NaHCO_3$ solution (100 mL), H_2O (2 x 100 mL) and dried ($MgSO_4$). Concentration *in vacuo* gave a yellow oil, which was subjected to column chromatography (SiO_2:CH_2Cl_2/MeOH 49:1). The yellow band (R_f = 0.3) was collected and the solvent evaporated affording a yellow oil, which was redissolved in CH_2Cl_2 (2 x 20 mL) and concentrated to give 0.64 g (98%) of the title compound **2** as a yellow powder. Data for **2**: m.p. melt over a long range; ^{1}H NMR (400 MHz, CD_3COCD_3) δ = 1.19 (t, J = 7.6 Hz, 3H), 1.28 (s, 18H), 2.42 (s, 3H), 2.59 (q, J = 7.6 Hz, 2H), 3.05 (t, J = 6.4 Hz, 2H), 3.58–3.68 (m, 5H), 3.75 (t, J = 6.4 Hz, 2H), 3.79–3.82 (m, 2H), 3.84–3.86 (m, 2H), 3.90–3.93 (m, 2H), 3.95–3.98 (m, 2H), 4.08–4.11 (m, 4H), 4.26–4.31 (m, 4H), 6.75 and 6.76 (AB q, J = 2.1 Hz, 2H), 6.81 (d, J = 9.0 Hz, 2H), 6.93 (d, J = 7.8 Hz, 1H), 6.97 (d, J = 7.7 Hz, 1H), 7.06–7.13 (m, 10H), 7.28–7.42 (m, 6H), 7.79 (d, J = 8.5 Hz, 1H), 7.83 (d, J = 8.5 Hz, 1H); MS(FAB) *m/z* (%) 1185 (100) $[M]^+$; $C_{66}H_{75}NO_7S_6$: calcd C 66.80, H 6.37, N 1.18; found C 66.43, H 6.50, N 1.13.

[2]Pseudorotaxane (2·CBPQT^{4+}). Mixing equimolar amounts of the semi-dumbbell compound **2** and CBPQT·$4PF_6$ in MeCN (or Me_2CO) produced a brown colored solution. CT Bands were observed at 540 nm (NP·CBPQT^{4+}) and 785 nm (TTF-CBPQT^{4+}) in MeCN [and at 545 nm (NP·CBPQT^{4+} and 745 nm (TTF^{a}CBPQT^{4+}) in Me_2CO]. The absorbance A was measured at both 540 (545) nm and 785 (745) nm at several different concentrations (c) in the range from 10^{-5} to 10^{-3} M. Measurements were carried out following progressive dilutions of three different MeCN solutions (two different Me_2CO solutions) to give 31 (22)

for NP·CBPQT^{4+} and 32 (22) for TTF·CBPQT^{4+} data points [c/A, $1/A^{1/2}$]. Plotting c/A against $1/A^{1/2}$ afforded a straight line with a slope α of $(1/K_a\varepsilon l)$ and a y intercept, y_o, of $1/\varepsilon l$ where ε is the molar extinction coefficient for the CT band of the complex and l is the optical path length, according to the following equation,[28]

$$c/A = (1/K_a\varepsilon l)^{1/2} \cdot 1/A^{1/2} + 1/\varepsilon l$$

Linear relationships between c/A and $1/A^{1/2}$ were demonstrated by calculations of the correlation coefficients of 0.862 (0.917) and 0.971 (0.959), respectively, for the NP·CBPQT^{4+} and the TTF·CBPQT^{4+} CT bands. UV-VIS Data in MeCN at 298 K: λ_{max} 540 nm, ε = 870 L mol^{-1} cm^{-1}, K_a = 85000 ± 15000 M^{-1}; λ_{max} 785 nm, ε = 1000 L mol^{-1} cm^{-1}, K_a = 95000 ± 15000 M^{-1}. (UV-VIS Data in Me_2CO at 298 K: λ_{max} 545 nm, ε = 760 L mol^{-1} cm^{-1}, K_a = 25000 ± 3000 M^{-1}; λ_{max} 745, ε = 590 L mol^{-1} cm^{-1}, K_a = 25000 ± 3000 M^{-1}).

Electrode Fabrication: The poly-Si electrodes were fabricated as described below: Low-pressure, SiH_4 CVD was used to deposit 1500 Å of amorphous Si onto 1100 Å of SiO_2 on a <100> silicon wafer at 525 °C. The film was exposed to air at room temperature for several minutes to form a passivating SiO_2 layer, and then crystallized under N_2 at 650 °C. Poly-Si films were implanted with 55 keV P^+ ions and 1 μm film of SiO_2 was grown by CVD to prevent out-gassing of the phosphorus. The dopant phosphorous atoms were activated at 1000 °C, and then a 6:1 mixture of NH_4F (aq):HF (aq) was used to etch away the SiO_2. Electrodes were patterned using standard photolithography techniques.

Monolayer Formation: Langmuir-Blodgett films were deposited onto non-patterned substrates of identically cleaned SiO_2 and poly-Si, and contact angles of water (18.2 mega ohm, millipure) drops on the substrate were measured as a check of monolayer quality, with the following results: cleaned SiO_2 (0°); cleaned poly-Si (11°); eicosanoic acid on SiO_2

(75°); eicosanoic acid on poly-Si (72°); [2]catenane 1^{4+} on SiO_2 (108°); [2]catenane 1^{4+} on poly-Si (108°). The subphase for all monolayer transfers was 6.4 mM $CdCl_2$ (aq), adjusted to pH = 8.5 with NaOH (aq).

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