Supplementary Material (ESI) for Chemical Communications

Supplementary information

Unusually Rapid Heterogeneous Electron Transfer through a Saturated Bridge 18 Bonds in Length

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1. Synthesis of bridge 2

5 was synthesized following the procedures developed by Warrener *et al.*[11]

Synthesis of tetraether 6

To a solution of **5** (3 g, 6.7 mmol) in DMF (150 mL) in ice bath was added NaH (3.3 g, 0.14 mol) (6 g oiled, added after washing with light petroleum), after 1 h stirring under argon, MeI (8 mL) was slowly added, kept stirring for another 5 h, then H_2O (100 mL) was added to the mixture to quench the reaction. After 30 min stirring, the mixture was extracted with CH_2Cl_2 (3 × 150 mL), washed with H_2O (6 × 200 mL), evaporation of CH_2Cl_2 gave **6** (3.10 g, 91%), ^{1}H NMR (300 MHz, $CDCl_3$): δ: 1.16-1.87 (d, 2H), 1.43-1.47 (d, 2H), 1.79 (s, 2H), 1.85 (4H), 2.00 (4H), 2.33 (4H), 2.85 (4H), 3.30-4.42 (20H), 6.04 (4H). ^{13}C NMR (300 MHz, $CDCl_3$) δ: 31.01 (CH_2), 37.16 (CH), 41.87 (CH), 42.34 (CH), 45.44 (CH), 46.30 (CH), 49.23 (C, cq), 58.71 (CH_3), 67.58 (CH_2O, 136.35 (CH=CH).

Synthesis of diester 7

To the solution of **6** (3 g, 5.98 mmol) in benzene (20 ml) were added DMAD (0.5 g, 3.52 mmol) and $RuH_2CO(PPh)_3$ (0.07 g, 0.08 mmol), the resulting mixture was heated up to

120°C and kept stirring at this temperature for 2 days. After this time, the solvent was removed under reduced pressure. The residue was loaded onto a silica plug and eluted with CH_2Cl_2/EtOAc (50:50) to remove the catalyst. The solvent was evaporated and the compound was purified by column chromatography (CH_2Cl_2/EtOAc, 20/80) to afford monoadduct compound **7** (1.65 g) and the bisadduct (0.7 g): ^{1}H NMR (300 MHz, $CDCl_3$), δ: 1.16-1.18 (d, 1H), 1.30-1.34 (d, 1H), 1.42-1.45 (d, 1H), 1.60 (s, 3H), 1.76 (s, 2H), 1.85 (s, 2H), 2.02 (d, 2H), 2.08 (s, 4H), 2.28-2.29 (d, 4H), 2.61 (s, 2H), 2.84 (s, 2H), 3.27-3.36 (m, 20H), 3.76 (s, 6H), 6.04 (s, 2H). ^{13}C NMR (300 MHz, $CDCl_3$) δ: 31.03 (CH_2), 34.46 (CH), 36.96 (CH), 41.87 (CH), 42.32 (CH), 45.43 (CH), 46.03 (CH), 46.30 (CH), 48.98 (CH), 49.10 (CH), 49.30 (C, cq), 49.52 (C, cq), 51.65 (CH), 58.73 (CH_3), 67.55 (CH_2), 67.68 (CH_2), 136.37 (CH=CH), 141.67 (CH=CH), 161.47 (C=O).

Synthesis of diol 8

This step was also carried out following the procedures developed by Warrener *et al.*[11] To a solution of **7** (0.87 g, 1.35 mmol) in dry THF (100 mL) under argon was added $LiAlH_4$ (1.00 g, 26.3 mmol) in small portions. The mixture was heated at reflux for 24 h. To the cooled reaction mixture were successively added water (1.0 mL), 15% aq. NaOH (1.0 mL), and water (3.0 mL). The mixture was then filtered through a Celite pad while hot. The Celite pad was then extracted with hot THF, and the resultant slurry was filtered again through a new Celite pad. The combined THF extracts were evaporated under reduced pressure to give crude diol **8** (0.70 g, 97%), which was used for tosylation without further purification.

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Synthesis of ditosylate 9

To a cooled (-5 °C) solution of **8** (0.45 g, 0.85 mmol) in dry pyridine (3 mL) and CH_2Cl_2 (10 mL), was added *p*-toluenesulfonyl bromide (0.80 g, 3.39 mmol). The resulting mixture was maintained at -5 °C for 2 h, and then moved into a freezer and left there overnight. The reaction was then quenched with water (60 mL) and extracted with CH_2Cl_2 (4 × 80 mL). The combined organic extracts were washed successively with 2 M HCl (2 × 150 mL), saturated aqueous $NaHCO_3$ (100 mL) and brine (100 mL), before being dried with Na_2SO_4. Evaporation under reduced pressure gave a crude product which was purified by chromatography (CH_2Cl_2 : EtOAc, 95:5) to afford **9** (0.45 g, 67%): ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.15-1.18 (d, 1H), 1.42-1.44 (d, 1H), 1.60-1.64 (d, 1H), 1.74-1.77 (s, 3H), 1.83 (s, 4H), 1.87-1.88 (m, 2H), 1.98-2.02 (m, 7H), 2.10 (s, 1H), 2.15-2.17 (m, 1H), 2.23 (s, 2H), 2.35-2.38 (m, 1H), 2.44 (s, 6H), 2.83 (s, 2H), 3.25-3.38 (m, 20H), 3.85-3.87 (d, 2H), 4.01-4.15 (m, 2H), 6.03 (s, 2H), 7.32-7.35 (dd, 4H), 7.73-7.76 (dd, 4H). ^{13}C NMR (300 MHz, $CDCl_3$) δ: 21.54 (CH_3), 30.71 (CH_2), 31.00 (CH_2), 35.54 (CH), 36.91 (CH), 37.09 (CH), 38.22 (CH), 38.54 (CH), 38.64 (CH), 40.84 (CH), 41.85 (CH), 42.31 (CH), 45.41 (CH), 46.28 (CH), 48.29 (CH), 48.65 (CH), 48.72 (CH), 49.07 (CH), 49.19 (C, cq), 49.40 (C, cq), 58.71 (CH_3O), 67.51 (CH_2O), 67.68 (CH_2O), 68.25 (CH_2O), 72.67 (CH_2O), 127.70 (CH=CH), 127.79 (CH=CH), 129.78 (CS), 129.81 (CS), 132.86 (CH=CH), 133.07 (CH=CH), 136.35 (CH=CH), 144.69 (CH=CH), 144.71 (CS).

Synthesis of dithioacetate 10

To a solution of **9** (0.52 g, 0.58 mmol) in dry DMSO (15 mL) under argon was added KSCOMe (0.30 g, 2.63 mmol). The mixture was stirred at 80 °C for 24 h then allowed to

cool to room temperature. Water (60 mL) was added and the mixture was extracted with EtOAc (6 × 60 mL). The combined organic extracts were washed with water (5 × 200 mL), and brine (100 mL), then dried under Na_2SO_4, evaporation gave **10** (0.37 g, 92.5%): ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.14-1.l7 (d, 1H), 1.41-1.44 (d, 1H), 1.73-1.78 (m, 4H), 1.78 (s, 4H), 1.90-1.93 (m, 2H), 1.97-1.98 (d, 3H), 2.02 (s, 1H), 2.13-2.17 (d, 2H), 2.23 (s, 3H), 2.30-2.31 (d, 6H), 2.79-2.88 (m, 2H), 2.96-3.02 (dd, 1H), 3.11-3.19 (dd, 1H), 3.27-3.38 (m, 20H), 6.02 (s, 1H). ^{13}C NMR (300 MHz, $CDCl_3$) δ: 27.71 (CH_3), 30.51 (CH_2), 30.57 (CH_2), 30.93 (CH_2), 31.05 (CH_2), 34.89 (CH), 35.55 (CH), 36.90 (CH), 38.89 (CH), 39.38 (CH), 41.15 (CH), 41.70 (CH), 41.86 (CH), 42.31 (CH), 43.63 (CH), 45.40 (CH), 46.27 (CH), 48.61 (CH), 48.64 (CH), 48.70 (CH), 49.10 (CH), 49.19 (C, cq), 49.40 (C, cq), 49.48 (C, cq), 58.70 (CH_3O), 67.54 (CH_2O), 67.72 (CH_2O), 136.34 (CH=CH), 195.66 (C=O), 195.88 (C=O).

Synthesis of diester 11

To a sealed pressure tube were added **10** (0.77 g, 1.09 mmol), DMAD (0.62 g, 5.5 mmol), $RuH_2CO(PPh_3)_3$ (38 mg, 4.13 x 10^{-5} mol) and benzene (5 mL). The mixture was degassed with argon before being sealed. The resulting mixture was heated to 125 ºC and stirred for 48 h. After this time the reaction mixture was cooled down then loaded onto a 10 cm silica gel plug and then eluted with CH_2Cl_2 / EtOAc (50:50) by 1 L. The solvent was evaporated and the crude product was chromatographed (CH_2Cl_2:EtOAc, 80:20) to give **11** (0.47 g, 68%) ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.30-1.34 (d, 1H), 1.58-1.61 (d, 1H), 1.70-1.81 (m, 4H), 1.86-1.90 (d, 2H), 1.95-1.98 (m, 2H), 2.05-2.07 (m, 8H), 2.15 (s, 1H), 2.21 (d, 3H), 2.29-2.33 (m, 8H), 2.61 (s, 2H), 2.81-1.90 (m, 2H), 2.97-3.03 (dd, 1H),

3.12-3.20 (dd, 1H), 3.20-3.35 (m, 20H), 3.77 (s, 6H). ^{13}C NMR (300 MHz, $CDCl_3$) δ: 26.62 (CH_3), 27.71 (CH_3), 30.52 (CH_2), 30.57 (CH_2), 30.94 (CH_2), 31.08 (CH), 34.45 (CH), 34.89 (CH), 35.54 (CH), 36.72 (CH), 38.88 (CH), 39.39 (CH), 41.17 (CH), 41.70 (CH), 43.62 (CH), 46.02 (CH), 48.61 (CH), 48.65 (CH), 48.70 (CH), 48.95 (CH), 49.07 (CH), 49.19 (C, cq), 49.51 (C, cq), 51.66 (CH), 58.74 (CH_3O), 67.66 (CH_2O), 141.67 (C=C), 161.46 (COS), 195.91 (COO).

Synthesis of diacid 2

To a solution of **11** (470 mg, 0.56 mmol) in THF (30 mL) was added 2 M NaOH (aq) (10 mL). The mixture was degassed, and then heated at reflux under argon atmosphere for 20 h. The reaction mixture was allowed to room temperature, then 5 M HCl (20 mL) aqueous solution was added, and the mixture was kept stirring for another 4 h. The precipitated product was filtered and dried under vacuum to afford final product **2** (0.35 g, 80%) ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.43-1.47 (d, 2H), 1.85-1.86 (d, 2H), 1.99-2.22 (m, 16H), 2.37-2.41 (d, 6H), 2.60-2.65 (d, 2H), 2.81 (s, 2H), 3.40 (12H), 3.55 (s, 8H). ^{13}C NMR (300 MHz, $CDCl_3$) δ: 31.45 (CH_2), 31.69 (CH_2), 37.21 (CH), 39.55 (CH), 43.75 (CH), 45.76 (CH), 46.17 (CH), 49.20 (C, cq), 49.27 (C, cq), 49.42 (C, cq), 49.82 (CH), 50.14 (CH), 58.54 (CH_3O), 67.81 (CH_2O), 145.62 (C=C), 164.59 (C=C).

2. Characterization of 2

Bridge **2** was insoluble in most common organic solventswith the exception of partial solubility in dimethyl formamide (DMF). Due to the repeated units in **2**, the chemical shifts for the ^{1}H and ^{13}C signals in NMR spectra are difficult to assign. Therefore bridge

2 was also characterized using electrospray negative-ion FTICR mass spectroscopy. The measured *m/z* was 735.338038 (negative ion, lost one proton), compared to the theoretical formula weight (736.310881). The standard deviation was only 45 ppm, which gave strong evidence that the synthesized compound is bridge **2**.

3. Electrode fabrication

The working gold electrodes were prepared by sealing 1.0 mm diameter polycrystalline gold wire (>99.99%, Goodfellow, Cambridge, UK) with EPON ® Resin 825 and EPI-CURE ® 3271 curing agent, Shell Chemical Company (Houston, Texas) in glass tubes with copper wires attached for electrical connection. The gold electrodes were polished to a mirror-like finish successively with 1.0 μm, 0.3 μm and 0.05 μm alumina slurries (Buehler, U.S.A) on microcloth pads (Buehler, U.S.A). After removal of the trace alumina from the surface by rinsing with water and brief cleaning in an ultrasonic bath, the electrodes were further cleaned by cycling between –0.3 V and +1.5 V versus Ag/AgCl in 0.05 M H_2SO_4 solution at a scan rate of 100 mVs^{-1} until reproducible scans were recorded (typically 50 cycles).

4. The preparation of self-assembled monolayer of bridge 2

The monolayer of bridge **2** was self-assembled on gold by incubating the cleaned gold electrode in the 1 mM bridge solution in DMF for 24 h. The bridges will stand on the gold substrate via pseudo-covalent bonds between sulfur and gold. The electrode was dried under a stream of nitrogen, then incubated in 5 mM ferrocenemethylamine solution in pH 8.0 phosphate buffer containing 40 mM EDC and 10 mM NHS for 24 h. After

rinsing with copious amounts of Milli Q water, cyclic voltammetry was carried out in 1M $HClO_4$ solution.

5. Electrochemistry measurements

Cyclic voltammetry was performed with a BAS-l00B electrochemical analyser (Bioanalytical System Inc. Lafayette, USA) and a conventional three-electrode system, comprising a gold working electrode, a platinum foil as the auxiliary electrode and an Ag/AgCl 3.0 M NaCl electrode (from BAS) as reference. All potentials were quoted relative to Ag/AgCl reference at room temperature, all the cyclic voltammetry measurements were carried out in 1 M $HClO_4$ aqueous solution.