Electronic Supplementary Information (ESI)

Experimental

Single Electron Transfer (SET) Reaction for Functional Group Reduction: General Procedure

Freshly cut lithium (14.0 mg, 2.00 mmol) was rolled to a foil, cut into thin strips and added to a Schlenk tube containing di-*tert*-butylbiphenyl (532 mg, 2.00 mmol), anti-bumping granules and a large stirrer bar (length approximately equal to the interior diameter of the Schlenk tube). The reaction vessel was evacuated and purged with argon three times and then stirred vigorously over three hours until the lithium had been ground to a fine powder. Tetrahydrofuran (20 mL) was added and the resulting dark blue-green solution was cooled to the required temperature. The starting material (0.50 mmol) in dry tetrahydrofuran (10 mL) was added over a period of 30 minutes by syringe pump (20 mL h^{-1}). The reaction was allowed to stir at the required temperature for a further 20 minutes and quenched by the dropwise addition of saturated aqueous ammonium chloride (5 mL). The solution was allowed to warm to ambient temperature, poured into brine (20 mL) and extracted with diethyl ether (2 × 30 mL). The organic extracts were combined, dried over $MgSO_4$ and evaporated under reduced pressure.

Electrochemical Procedures

Cyclic Voltammetry (CV)

Voltammetric measurements were carried out on a μ-Autolab (Eco-Chemie, Utrecht, Netherlands) potentiostat. A three-electrode arrangement was used in an air-tight, three-necked cryoelectrochemical cell. The cryo-cell with solid electrolyte was dried in vacuo overnight before solvent addition and electrochemical experiments. The working electrodes employed were a 1 mm (diameter) platinum electrode (housed in a Teflon™ insulating case), and a 5.4 μm (radius) platinum microdisc electrode (Cypress Systems Inc., Kansas, US) with a large area, shiny platinum wire (Goodfellow Cambridge Ltd, Cambridge, UK) used as the counter electrode. The working electrodes were all carefully polished on a clean polishing pad (Kemet, UK) using 1.0 μm and 0.3 μm aqueous-alumina slurries (Beuhler, Lake Buff, II., USA), and subsequently rinsed in de-ionised and doubly filtered water of resistivity no greater than 18 MΩ cm, taken from an Elgastat filter system (Vivendi, Bucks, UK). The electrodes were carefully dried prior to use. Before carrying out electrochemical experiments, the microdisc radius was electrochemically calibrated using a literature methodology.[1] A $Fc/Fc^+PF_6^-$ reference electrode was developed for use in THF at low temperature and has been described previously.[2] Tetra-*n*-butylammonium perchlorate was used as the supporting electrolyte in all electrochemical measurements at a concentration of 0.1 M. The solutions were degassed vigorously for 5 min using impurity-free nitrogen (BOC gases, Guildford, Surrey, UK) to remove any trace oxygen and an inert atmosphere was maintained throughout all analyses. All solutions were prepared under an atmosphere of argon using oven-dried glassware such as syringes and needles used for the transfer of moisture sensitive reagents. All low temperature experiments were conducted using a Julabo FT902 immersion cooler with temperature control for counter-cooling (JULABO UK Ltd.).

Microdisc Chronoamperometry

Microdisc chronoamperometry permits the simultaneous determination of the diffusion coefficient, *D* and the number of electrons, *n* transferred to an electroactive species of interest, provided no coupled chemistry operates on the timescale of the experiment. The time dependent current response, *I*, resulting from a diffusion-controlled reductive current after a potential step at a microdisc electrode is given in Equation 1:

$$I = -4nFDCrf(\tau) \quad (1)$$

where Equation 2 defines f(τ):

$$f(\tau) = 0.7854 + 0.8862\tau^{-1/2} + 0.2146e^{-0.7823\tau^{-1/2}} \quad (2)$$

and Equation 3 defines τ:

$$\tau = \frac{4Dt}{r^2} \quad (3)$$

F is the Faraday constant, *r* is the radius of the disc electrode and *t* the time. The above approximation (Equations 1-3) were derived by Shoup and Szabo,[3] and describes the current

response to within an accuracy of 0.6 % over all τ. Experimentally, the chronoamperometric experiment is run over a time scale incorporating a transition from transient, with a $I \propto D^{½}$ dependence, to steady-state with a $I \propto D$ dependent behaviour. Accordingly deconvolution of the parameters D and n is possible from a single scan. Fitting was achieved via ORIGIN 6.0 (Microcal Software Inc.) where, having input an accurate value for r and C, the software iterates through values of D and n until the fit of the experimental data had been optimized.

Preparative Electrolyses

Preparative electrolysis was conducted using a platinum foil electrode (4 cm^2 area) with a 40 mL solution of **I** (5.6×10^{-5} mol) in THF (0.1 M TBAP) at 20 °C and -74 °C ± 2 °C. The solution was reduced at the required constant potential versus a $Fc/Fc^+PF_6^-$ reference electrode in THF within a cryo-cell until the required charge was passed. The counter electrode was a platinum mesh (Goodfellow Cambridge Ltd, Cambridge, UK) housed within a separate compartment (containing 0.1 TBAP in THF) with a glass sintered frit. Following electrolyses, saturated aqueous ammonium chloride (2-3 mL), water (10 mL) and diethyl ether (20 mL) was added. The organic layer was separated and washed with aqueous hydrochloric acid (1 M, 6-8 × 10 mL), saturated aqueous sodium bicarbonate (10 mL) and then saturated aqueous sodium chloride (10 mL). The organic layer was dried over magnesium sulfate and then evaporated under reduced pressure to give an oil. ^{1}H NMR was used to characterise the crude product

Electrochemical Reagents

Tetra-n-butylammonium perchlorate, TBAP (Fluka), was used as received without any further purification. Anhydrous tetrahydrofuran (THF) was purified by filtration through two columns of activated alumina (grade DD-2) as supplied by Alcoa, employing the method of Grubbs et al.[4]

Analytical Techniques

^{1}H NMR spectra were recorded using a Bruker AV400 (400 MHz) spectrometer in $CDCl_3$ and referenced to tetramethylsilane ($SiMe_4$) as an internal standard. Signal positions were recorded in δ (ppm) with the abbreviations s, d, t, q, quint., sept., br, app., and m denoting singlet, doublet, triplet, quartet, quintet, septet, broad, apparent and multiplet respectively. All coupling constants, J, are quoted in Hz.

Mass spectra (*m/z*) and accurate mass (HRMS) were recorded in chemical ionisation (CI^+) mode on an Agilent 6890 Series GC System (column: ZB.5, 15m long, 0.25 ID) at an ionisation voltage of 60 eV and a source temperature of 150 ºC using amyl acetate as the lock-mass and NH_3 as CI gas. The data were controlled and stored by the Micromass Masslynx 3.5 software.

Infra-red spectra were recorded on a Bruker Tensor 27 FT-IR spectrometer. Compounds were analysed as thin films on NaCl plates. Absorption peaks are quoted in wavenumbers (cm^{-1}) and the abbreviations used in their description are broad (br), strong (s) and weak (w).

Melting points were determined using Griffin Melting Point Apparatus with a mercury thermometer and are uncorrected.

Reactions were monitored by thin-layer chromatography (TLC). TLC was performed on Merck Kieselgel 60 F_{254} 0.25 mm pre-coated aluminum backed silica plates. Compounds were visualised with UV light and/or by staining with basic potassium permanganate solution.

Synthesis and Characterisation of Compounds

***2-[{3-[(trans-4-(methoxymethoxy)cyclohexyl]oxy}propyl)thio]naphthalene,* I**

2-Naphthalenethiol (216 mg, 1.43 mmol) was added to a solution of the iodide: *t*rans-1-(3-iodopropoxy)-4-(methoxymethoxy)cyclohexane (400 mg, 1.21 mmol) and potassium carbonate (200 mg, 1.40 mmol) in dimethylformamide (3 mL) and was stirred under argon at ambient temperature for 19 hours. The reaction was diluted with diethyl ether (50 mL) and saturated aqueous sodium thiosulfate (20 mL). The organic layer was separated and washed with water (2 × 20 mL) and brine (20 mL), dried over $MgSO_4$ and then evaporated under reduced pressure to a crude yellow oil. Purification by chromatography [SiO_2, diethyl ether-petroleum ether, 20:80] gave the *naphthyl sulfide* (329 mg, 75%) as a colourless oil.

^{1}H NMR (400MHz, $CDCl_3$, 25 °C, TMS): δ=7.77 (m, 4H; ArC*H*), 7.45 (m, 3H; ArC*H*), 4.67 (s, 2H; OCH_2OCH_3), 3.55 (m, 3H; cyclohexane C*H*, OCH_2), 3.37 (s, 3H; OCH_2OCH_3), 3.24 (m, 1H; cyclohexane C*H*), 3.13 (t, ^3J (H,H)=7 Hz, 2H; CH_2SNaph), 1.96 (m, 6H; cyclohexane CH_2, OCH_2CH_2), 1.34 ppm (m, 4H; cyclohexane CH_2); **^{13}C NMR** (100MHz, $CDCl_3$, 25 °C) δ=134.2, 133.8, 131.7, 128.3, 127.7, 127.3, 127.0, 126.5, 126.5, 125.5, 94.7, 77.2, 74.5, 66.3, 55.2, 30.2, 29.8, 29.7, 29.4 ppm; **IR** (Film): ν =2936, 1625, 1590, 1501, 1454, 1376, 1106, 1043 cm^{-1}; **MS**

(CI+): *m/z* (%) 299 (100%) $[M–OCH_2OCH_3]^+$, 361 (10%) $[M+H]^+$; **HRMS** $C_{21}H_{28}O_3S$ (M) requires 360.1759, M^+ found 360.1757 (-0.6 ppm).

***Tetra-n-butylammonium thionaphtholate*, IV**

2-Naphthalenethiol (167 mg, 1.04 mmol) was added to a solution of tetra-*n*-butylammonium hydroxide (1 mol dm^{-3} in methanol, 1.04 mL, 1.04 mmol). The solution was concentrated *in vacuo* and benzene (4 × 20 mL) was added to azeotrope water. The resulting residue was dried *in vacuo* to give the *salt* as a yellow solid (410 mg, 98%).

m.p. 69-71 °C (CH_3OH); **^{1}H NMR** (400MHz, CH_3OH, 25 °C, TMS): δ=7.78 (s, 1H; ArC*H*), 7.60-7.40 (m, 4H; ArC*H*), 7.25-7.15 (m, 2H; ArC*H*), 3.09 (m, 8H; CH_2N), 1.56 (m, 8H; CH_2CH_2N), 1.35 (m, 8H; CH_2CH_3), 0.96 ppm (t, ^3J (H,H)=7 Hz, 12H; CH_3); **^{13}C NMR** (100MHz, CH_3OH, 25 °C) δ=147.7, 134.8, 134.5, 129.9, 129.0, 127.4, 125.9, 125.6, 125.4, 122.5, 58.3, 23.7, 19.7, 13.0 ppm.

***2,2'-dinaphthyl disulfide* V**

1,3-Dibromo-5,5-dimethylhydantoin (593 mg, 2.08 mmol) was added to a solution of 2-naphthalenethiol (332 mg, 2.08 mmol) in dichloromethane (20 mL) and stirred under argon at ambient temperature for 18 hours. The reaction was diluted with dichloromethane (30 mL) and saturated aqueous sodium bicarbonate (30 mL) was added. The organic layer was separated and washed with brine (30 mL), dried over $MgSO_4$ and then evaporated under reduced pressure to a crude red solid. Purification by chromatography [SiO_2, petroleum ether] gave the *disulfide* (614 mg, 93%) as a white solid.

m.p. 138-140 °C (CH_2Cl_2) (lit. [5] 138-139 °C); **^{1}H NMR** (400MHz, $CDCl_3$, 25 °C, TMS): δ=8.25 (m, 2H; ArC*H*), 7.73 (m, 6H; ArC*H*), 7.61 (m, 3H; ArC*H*), 7.46 ppm (m, 3H; ArC*H*); **^{13}C NMR** (100MHz, $CDCl_3$, 25 °C) δ=134.8, 133.1, 132.4, 128.6, 128.4, 128.2, 126.5, 126.3, 123.4, 120.2 ppm.

Supporting Electrochemical Information

Determination of *n* and *D* for I at -78 °C and 20 °C

Microdisc chronoamperometric experiments were run at -78 °C. A typical chronoamperometric curve with fitting by ORIGIN™ is shown in Figure 1. A diffusion coefficient, *D* and the number of electron(s), *n* for the reduction of **I** was determined. Using the first reduction-wave, steady-state data obtained at -20 ºC and -50 ºC, *n* and *D* values were obtained and a plot of ln *D* versus T^{-1} allowed back extrapolation to obtain a *D* value for **I** at 20 ºC and is shown in Figure 2.

Tetra-*n*-butylammonium thionaphtholate, IV characterisation at 20 °C

Comparison of the peak potential positions, E_p, of **I** with overlays of cyclic voltammograms obtained for **IV** provided a clear indication that the oxidation peak is due to the naphthyl thiolate and is shown in Figure 3.

2,2'-Dinaphthyl disulfide, V characterisation at 20 °C

Sequential additions of 2,2'-dinaphthyl disulfide, **V** were added to a solution of **I** (3 mM, 0.1 M TBAP in THF). Cyclic voltammetry was recorded at 20 °C using a platinum macroelectrode after each addition and the overlayed cyclic voltammograms are shown in Figure 4.

A summary of the data obtained for the voltammetric analysis of compounds **IV** and **V** is shown in table 1.

Table

Table 1. Summary of Electrochemical Data for the Reduction of **I** at 20 °C.

Compound	$E_{1/2}$ / V[a]	n	D / 10^{-10} m^2 s^{-1}	$E^{V}_{p,c}$ / μA[a,b]	$E^{IV}_{p,a}$ / μA[a,b]
IV[c,d]	-0.52	1	4.4 (± 0.01)	-2.31	-0.48
V[c,e]	-2.15	-	-	-2.33	-0.32

[a] Potentials measured versus $Fc/Fc^{+}PF_6^{-}$. [b] Subscripts p, a, and c denote peak, cathodic, and anodic, respectively with peak potentials (E_p) measured at 250 mV s^{-}1 [c] n and D values obtained from microdisc chronoamperometric experiments. [d] **IV**: $n$$Bu_4N^{+}$ $NaphS^{-}$. [e] **V**: 2,2'-dinaphthyl disulfide.

Figures

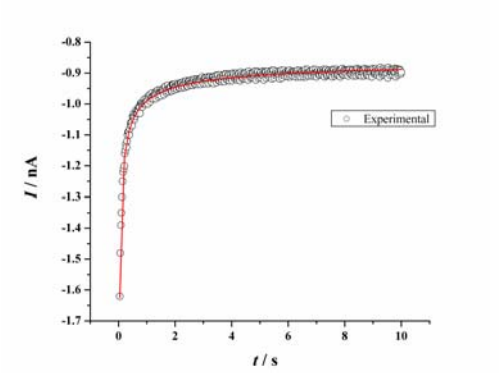

Figure 1. Typical chronoamperometric curve resulting from a potential step from a region where no faradaic processes occur to a potential at which a limiting current flows for the process of interest. Chronoamperometric curve is shown for **I** at a temperature of -78 °C. Circles (black) are experimental data and the solid line (red) shows the fitting.

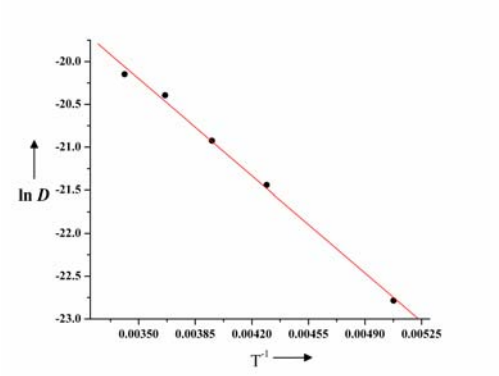

Figure 2. Plot of ln D versus T^{-1} for **I**.

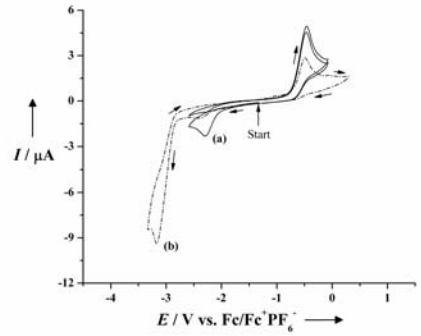

Figure 3. Characteristic cyclic voltammograms of (a) nBu$_4$N$^+$NaphS$^-$ (2.12 mM): first and second scans; (b) **I** (3 mM). Scan rate: 250 mV s^{-1} in THF (0.1 M TBAP) at 20 ºC. Electrode diameter: 1 mm; 0.1 M TBAP in THF.

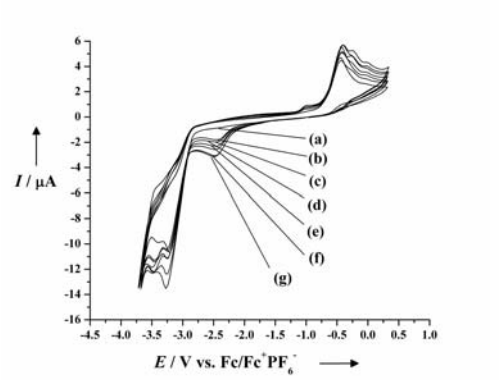

Figure 4. First (a) and second (b) scan cyclic voltammograms obtained at a 1 mm platinum disc electrode for RSNaph (3 mM, 0.1 M TBAP) in THF at 298K at scan rate: 500 mV s^{-1}. Single scan cyclic voltammograms (scan rate: 500 mV s^{-1}) obtained after sequential additions of 2,2'-dinaphthyl disulfide, **V**: (c) 117.2 μM; (d) 228.8 μM; (e) 335.2 μM; (f) 436.8 μM; and (g) 0.5 mM.

References

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