Electronic Supplementary Information (ESI)

The electrochemically tuneable recognition properties of an electropolymerised flavin derivative

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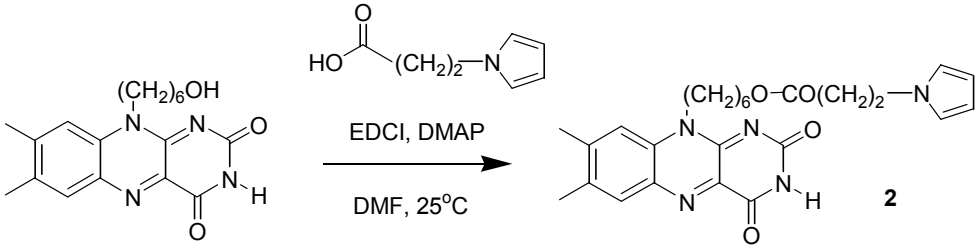
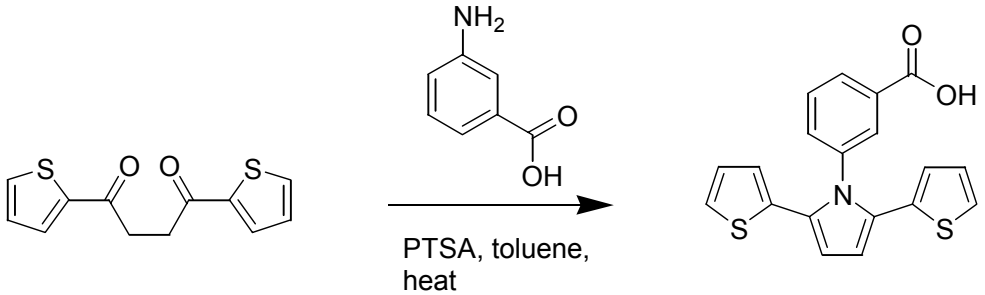
1. Synthesis

Synthesis of **2**



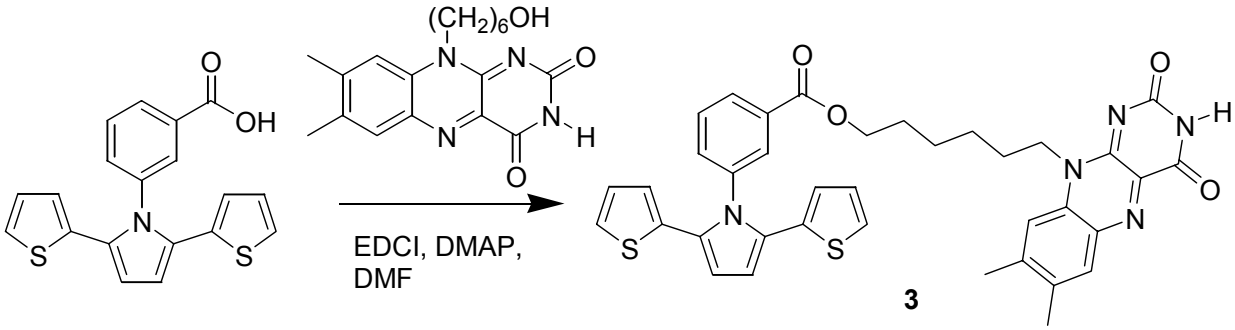
To a solution of *N*-(10)-hydroxyhexyl flavin[a] (0.45 g, 1.32 mmol) and 3-(pyrrol-1-yl) propanoic acid[b] (0.18 g, 1.32 mmol) in DMF (25 mL), were added EDCI (0.25 g, 1.32 mmol) and DMAP (0.16 g, 1.32 mmol). The resulting solution was stirred at room temperature for 7 days. The solvent was evaporated under reduced pressure, and the residue was dissolved in DCM (100 mL) and washed with water (50ml). The aqueous layer was further extracted with DCM (2 x 100 mL). The combined organic extracts were dried over $MgSO_4$, filtered and evaporated. Column chromatography (silica gel, eluting with ethyl acetate/ acetone, 90:10, v/v) afforded **2** as a yellow powder (66 %). Mp 185-184°C (dec); ν_{max} (KBr) 3436, 3103, 3028, 2926, 1721, 1675.1578, 1539, 1502, 1462, 1400, 1351, 1264, 1168, 1092, 827, 724 cm^{-1}; ^1H NMR (200 MHz, acetone-d-6) δ = 1.47 (6H, m), 1.86 (2H, m), 2.43 (3H, s), 2.55 (3H, s), 2.81 (2H, t), 4.04 (2H, t), 4.19 (2H, t), 4.70 (2H, t), 5.94 (2H, t), 6.69 (2H, t), 7.77 (1H, s), 7.83 (1H, s), 10.09 (1H, s); MS (EI) m/z = 463 (M^+); HRMS (ES+) calcd. for $C_{25}H_{29}N_5O_4$ $[M+1]^+$ 464.2292, found 464.2290.

Synthesis of **3**



A mixture 1,4-dithiophen-2-ylbutane-1,4-dione[c] (1.5 g, 5.8 mmol), 3-aminobenzoic acid (0.80 g, 5.8 mmol) and *para*-toluenesulfonic acid (0.150 g, 0.58 mmol) in dry toluene (15 mL) was heated to reflux using a Dean-Stark apparatus for 12 h. The toluene was removed using a rotary evaporator, and water (100 mL) was added. The crude product was removed by filtration, and purified on a silica gel column (eluting first with CH_2Cl_2 to remove the unreacted dione and then with CH_2Cl_2/ ethyl acetate 80/20, v/v) to yield the carboxylic acid derivative as an off-white powder (28 %). Mp 268-269 °C; ν_{max} (KBr) 3065, 2958, 2843, 2646, 2532, 2843, 1700, 1588, 1487, 1454, 1294, 1196, 1046, 933, 826, 763, 698, 558 cm^{-1}.^1H NMR (400 MHz, DMSO-d_6) δ = 6.59 (2H, s,), 6.68 (2H, dd), 6.87-

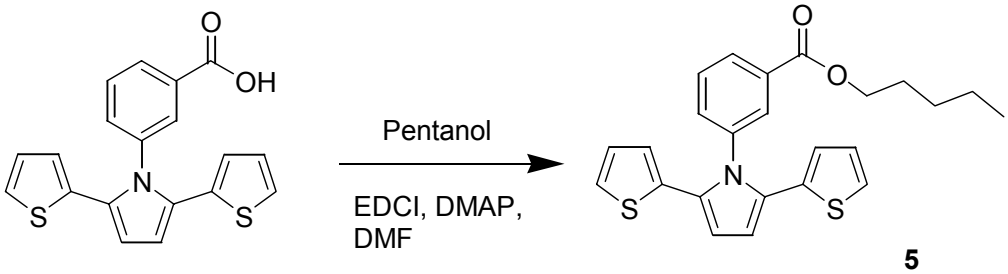
6.89 (2H, m), 7.29 (2H, dd,), 7.62-7.65 (2H, m), 7.76-7.77 (1H, m), 8.07-8.11 (1H, m), 13.32 (1H, br.s); MS (EI) m/z = 351 (M^+); HRMS (ES+) calcd. for $C_{19}H_{13}NO_2S_2$ $[M+1]^+$ 352.0460, found 352.0458.



3

To a solution of compound *N*-(10)-hydroxyhexyl flavin[a] (0.5 g, 1.46 mmol) and bis-4,4'-[(2,2'-bithienyl)-*N*-pyrrolyl]-3-carboxybenzene (0.51 g, 1.46 mmol) in DMF (25 mL) were added EDCI (0.28 g, 1.46 mmol) and DMAP (0.18 g, 1.46 mmol). The resulting solution was stirred at room temperature for 3 days. The solvent was evaporated under reduced pressure, and the residue was dissolved in DCM (100 mL) and washed with water (50ml). The aqueous layer was further extracted with DCM (2 x 100 mL). The combined organic extracts were dried over $MgSO_4$, filtered and evaporated. Column chromatography (silica gel, eluting with CH_2Cl_2/ acetone, 90:10, v/v) afforded the product as a yellow powder (28 %). Mp 233-235 ^oC; ν_{max} (KBr) 3425, 3157, 3099, 2952, 2819, 1717, 1656, 1576, 1537, 1502, 1460, 1350, 1233, 1109, 843, 767, 697 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ = 1.55 (6H, m), 1.70 (2H, m), 2.45 (3H, s), 2.55 (3H, s), 4.30 (2H, t), 4.65 (2H, t), 7.35 (1H, s), 6.48 (2H, d), 6.50 (2H, s), 6.78 (2H, m), 7.00 (2H, dd), 7.49 (2H, m), 7.98 (1H, m), 8.06 (1H, s), 8.15 (1H, m), 8.40 (1H, s); MS (EI) m/z = 675 (M^+); HRMS (ES+) calcd. for $C_{37}H_{33}N_5O_4S_2$ $[M+1]^+$ 676.2047, found 676.2046.

Synthesis of **5**



5

To a solution of compound bis-4,4'-[(2,2'-bithienyl)-*N*-pyrrolyl]-3-carboxybenzene (0.51 g, 1.46 mmol) (0.5 g, 1.46 mmol) and pentanol (0.12 g, 1.46 mmol)) in DMF (25 mL), were added EDCI (0.28 g, 1.46 mmol) and DMAP (0.18 g, 1.46 mmol). The resulting solution was stirred at room temperature for 3 days. The solvent was evaporated under reduced pressure, and the residue was dissolved in DCM (100 mL) and washed with water (50ml). The aqueous layer was further extracted with DCM (2 x 100 mL). The combined organic extracts were dried over $MgSO_4$, filtered and evaporated. Column chromatography (silica gel, eluting with hexane/ CH_2Cl_2, 3:1, v/v) afforded the product as a white powder (48 %). Mp 75-77 ^oC; ν_{max} (KBr) 3100, 2953, 2858, 1717, 1291, 1234 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ = 0.90 (3H, t), 1.38 (4H, m), 1.72 (2H, m), 4.28 (2H, t), 6.53 (4H, m), 6.80 (2H, m), 7.05 (2H, dd), 7.49 (2H, m), 7.99 (1H, m), 8.14 (1H, m); MS (EI) m/z = 421 (M^+); HRMS (ES+) calcd. for $C_{24}H_{23}NO_2S_2$ $[M+1]^+$ 422.5760, found 422.5765 .

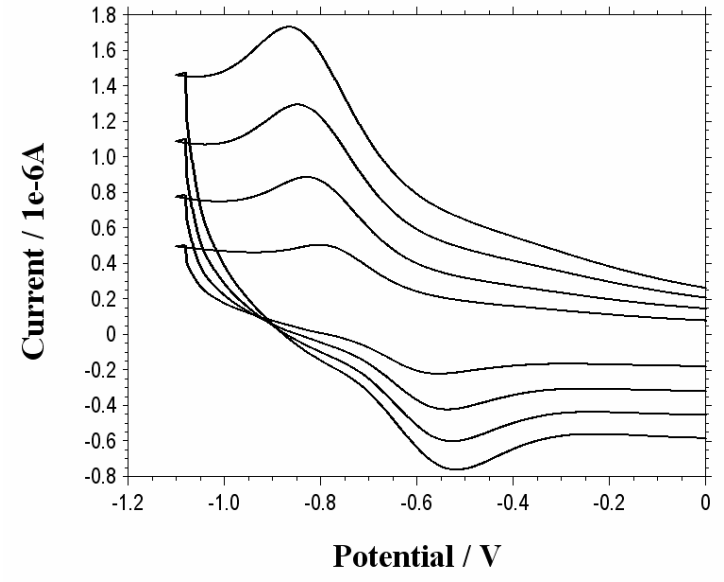
a. C. Frier, J-L Décout and M. Fontecave, *J. Org. Chem.,* 1997, **62**, 3520.
b. C. J. Pickett and K. S. Ryder, *J. Chem. Soc. Dalton Trans.*, 1994, 2181.
c. A .Merz and F. Ellinger *Synthesis*, 1991, 462.

2. Electrochemical measurements.

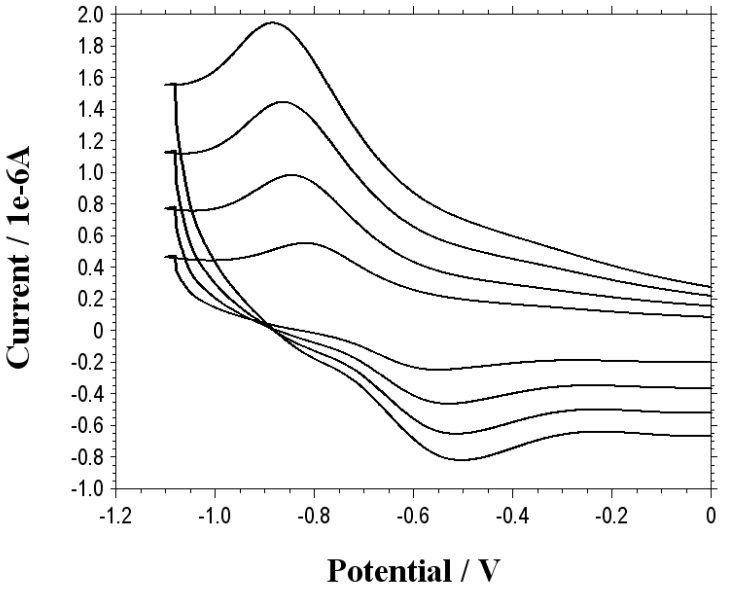
All electrochemical experiments were performed using a CH Instruments 620A electrochemical workstation. The electrolyte solution (0.1 M) was prepared from recrystallised Bu_4NPF_6 using either dry acetonitrile, toluene or dichloromethane. The solution was rigorously purged with nitrogen prior to use, and all electrochemical data were recorded under a nitrogen atmosphere. A three electrode configuration was used with a platinum disc (2mm diameter) working electrode, a Ag /AgCl reference electrode and a platinum wire as the counter electrode. Scan rate (unless otherwise stated) was 0.5 Vs^{-1}.

The redox-based enhancement in recognition was calculated using a thermodynamic cycle which can be expressed mathematically using: $K_a(red)/K_a(ox)=e^{(nF/RT)(E_{½}(bound) - E_{½}(unbound))}$. $K_a(red)$ and $K_a(ox)$ are the association constants in the reduced and oxidized forms, and $E_{½}(bound)$ and $E_{½}(unbound)$ are the half-wave redox potentials in the receptor bound and unbound states.

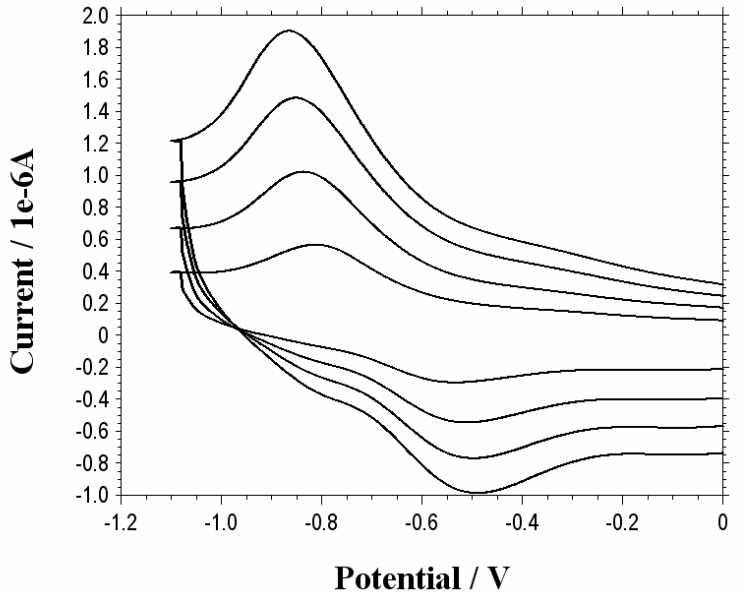
Selected electrochemical data for derivative **2**



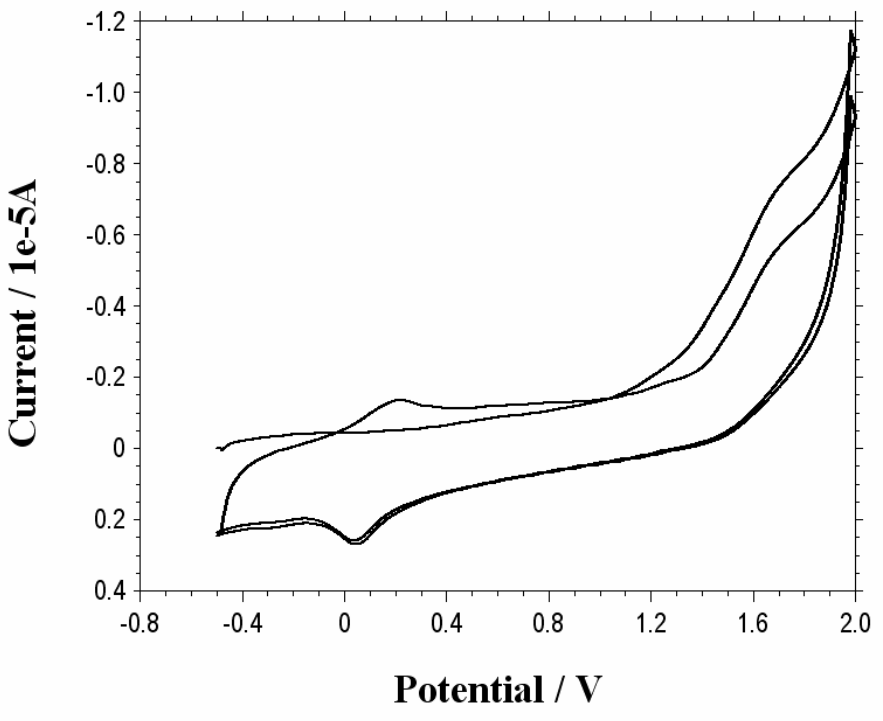
CVs of electropolymerised **2** (following two electropolymerisation cycles from acetonitrile) recorded in CH_2Cl_2 (0.1 M Bu_4NPF_6). Scan rate = 1 (largest current) , 0.75, 0.5 0.25 (smallest current) Vs^{-1}. ΔE_{fwhm} = 0.209 V, 1.19 x 10^{-7} C, Γ = 1.23 x 10^{-12} mol cm^{-2} (using 1 Vs^{-1} scan rate).



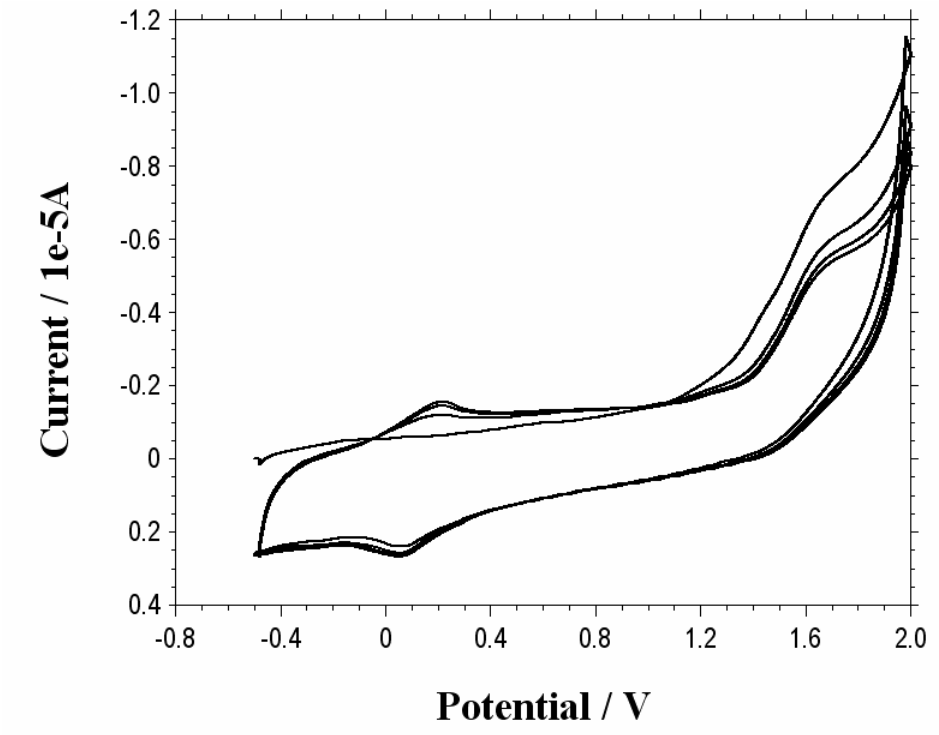
CVs of electropolymerised **2** (following four electropolymerisation cycles from acetonitrile) recorded in CH_2Cl_2 (0.1 M Bu_4NPF_6). Scan rate = 1 (largest current) , 0.75, 0.5 0.25 (smallest current) Vs^{-1}. ΔE_{fwhm} = 0.225 V, 1.59 x 10^{-7} C, Γ = 1.65 x 10^{-12} mol cm^{-2} (using 1 Vs^{-1} scan rate).



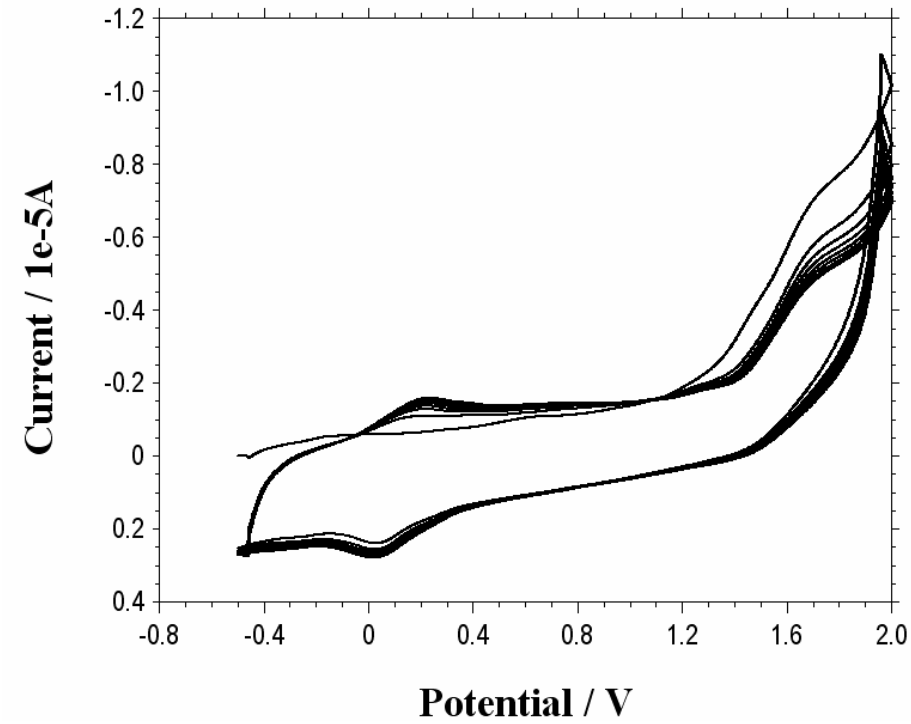
CVs of electropolymerised **2** (following eight electropolymerisation cycles from acetonitrile) recorded in CH_2Cl_2 (0.1 M Bu_4NPF_6). Scan rate = 1 (largest current) , 0.75, 0.5 0.25 (smallest current) Vs^{-1}. ΔE_{fwhm} = 0.245 V, 2.37 x 10^{-7} C, Γ = 2.45 x 10^{-12} mol cm^{-2} (using 1 Vs^{-1} scan rate).



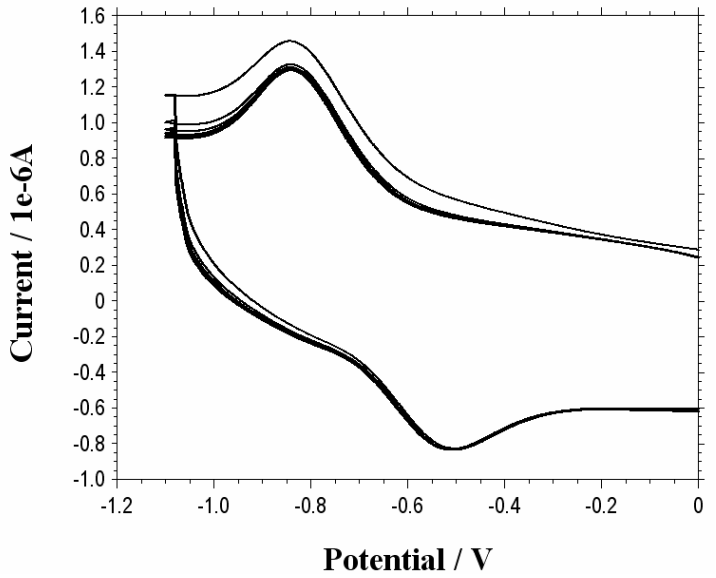
CVs showing the electropolymerisation of **2** (two cycles) recorded in CH_3CN (0.1 M Bu_4NPF_6). Scan rate = 0.5 Vs^{-1}



CVs showing the electropolymerisation of **2** (four cycles) recorded in CH_3CN (0.1 M Bu_4NPF_6). Scan rate = 0.5 Vs^{-1}

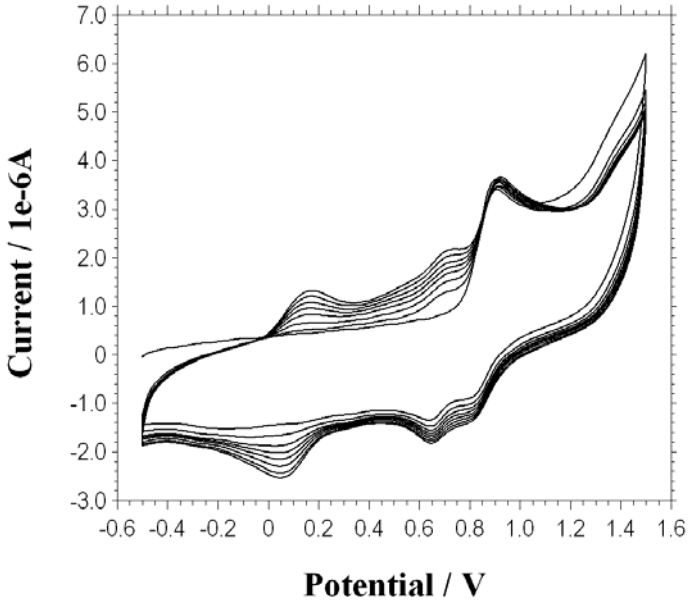


CVs showing the electropolymerisation of **2** (eight cycles) recorded in CH_3CN (0.1 M Bu_4NPF_6). Scan rate = 0.5 Vs^{-1}

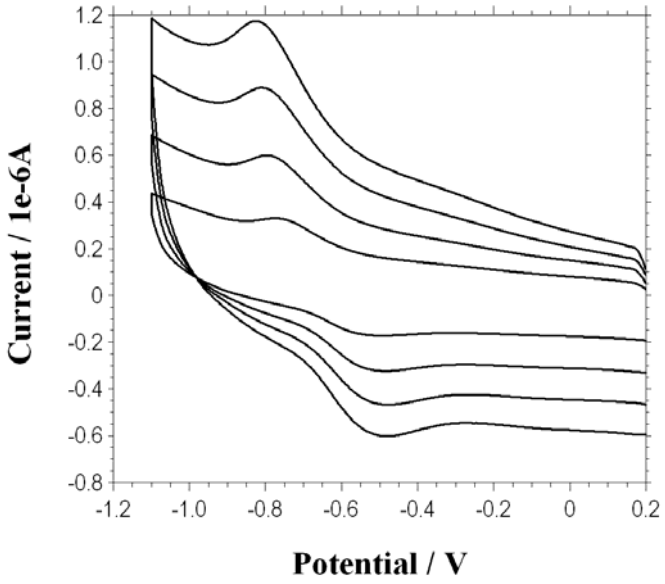


CVs of electropolymerised **2** (following two electropolymerisation cycles from acetonitrile) recorded in CH_2Cl_2 (0.1 M Bu_4NPF_6) showing six successive cycles. Scan rate = 1 Vs^{-1}

Selected electrochemical data for derivative **3**

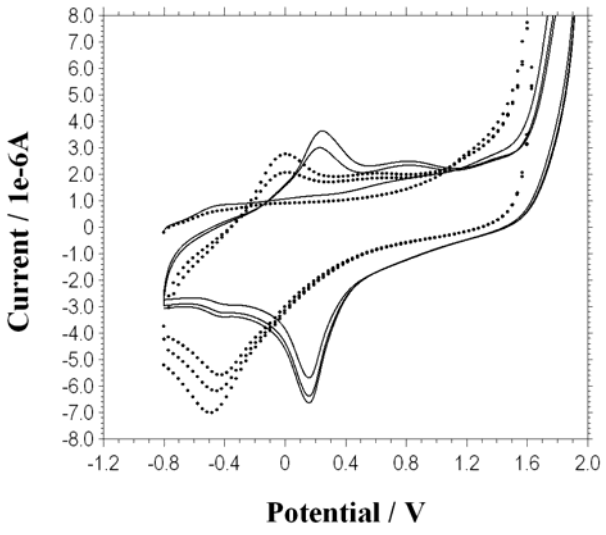


CVs showing the electropolymerisation of **3** (~2 x10^{-4} M) (eight cycles) recorded in a 0.1 M Bu_4NPF_6 CH_3CN/ toluene (1:1) solution. Scan rate = 0.5 Vs^{-1}

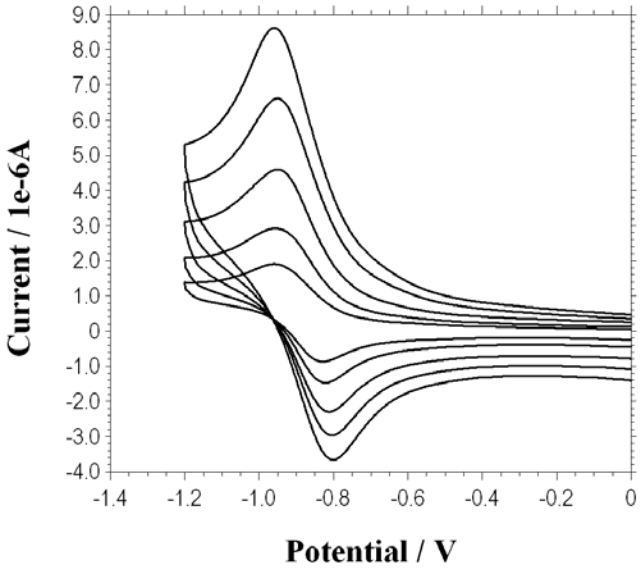


CVs of electropolymerised **3** (following eight electropolymerisation cycles from acetonitrile) recorded in CH_2Cl_2 (0.1 M Bu_4NPF_6). Scan rate = 1 (largest current) , 0.75, 0.5 0.25 (smallest current) Vs^{-1}. ΔE_{fwhm} = 0.177 V, 4.643 x 10^{-8} C, Γ = 4.8 x10^{-13} mol cm^{-2} (parameters calculated using 1 Vs^{-1} scan rate).

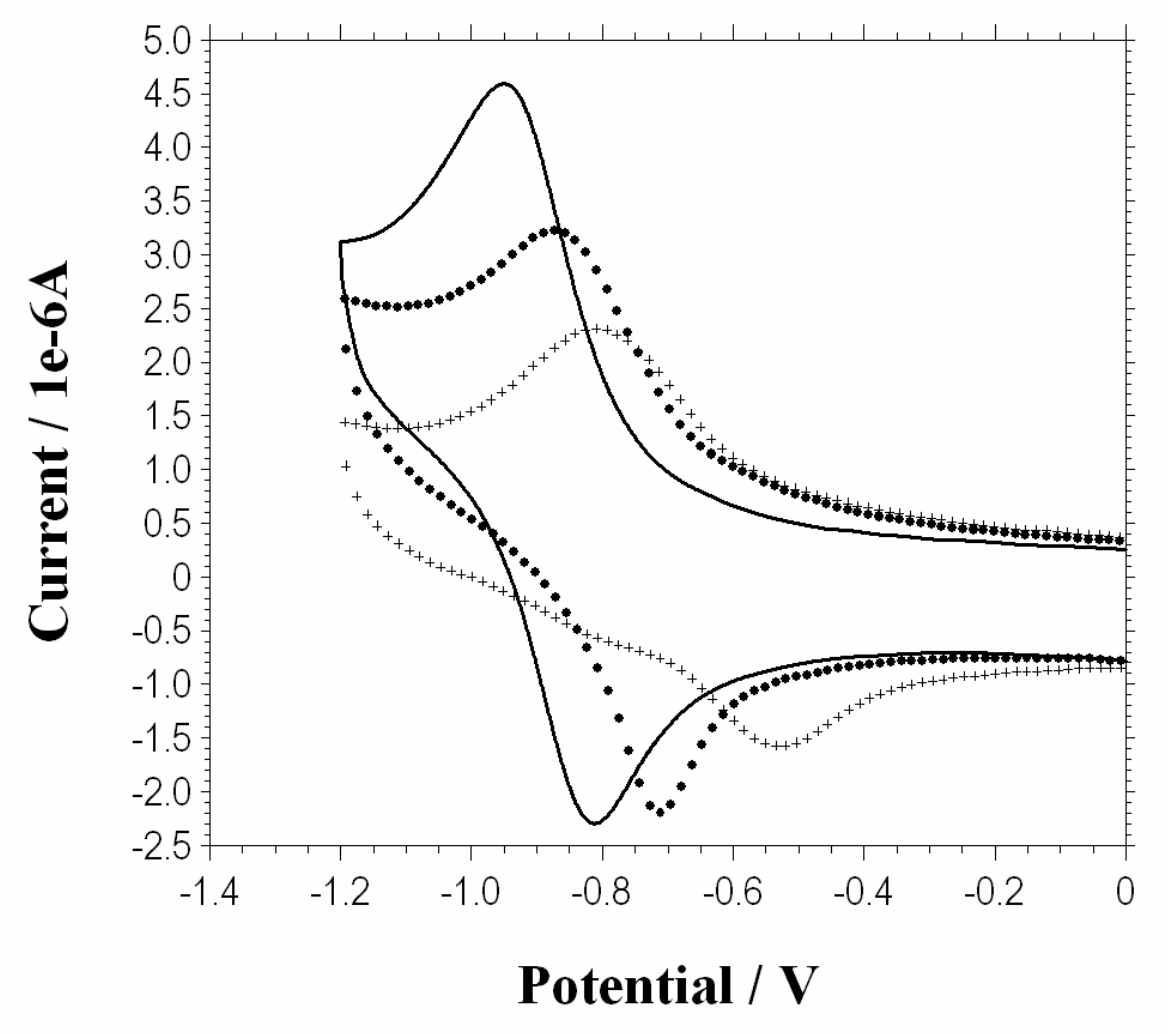
The Γ value of 4.8 x10^{-13} mol cm^{-2} and the peak current/scan rate linearity suggest a sub-monolayer coverage.



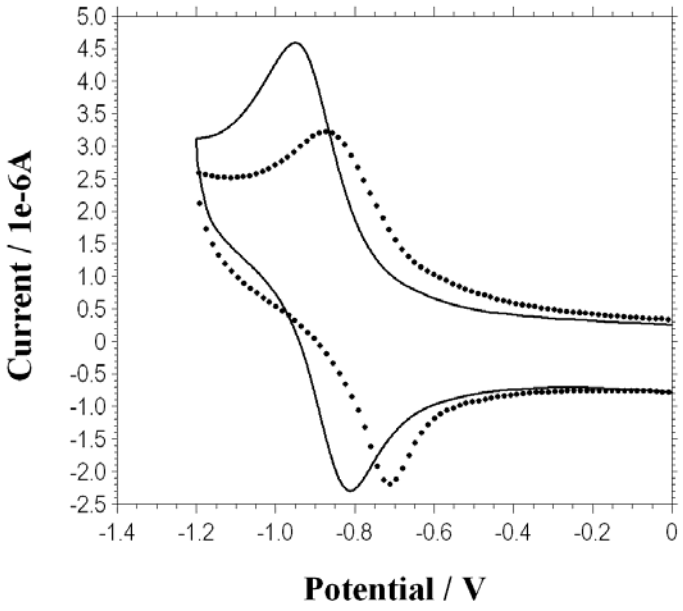
CV studies recorded in toluene/CH_3CN (1:1) between -0.8 V and +2.0 V, showing the oxidation of the electropolymerised films of 3 (——) and in the presence of a 3 x 10^{-2} M solution of 4 (·····). Scan rate = 0.5 Vs^{-1}.



CVs of electropolymerised **3** (following eight electropolymerisation cycles from acetonitrile/toluene 1:1, between -0.5 and +1.5 V) recorded in acetonitrile/toluene (1:1) (0.1 M Bu_4NPF_6). Scan rate = 1 (largest current) , 0.75, 0.5 0.25, 0.125 (smallest current) Vs^{-1}.

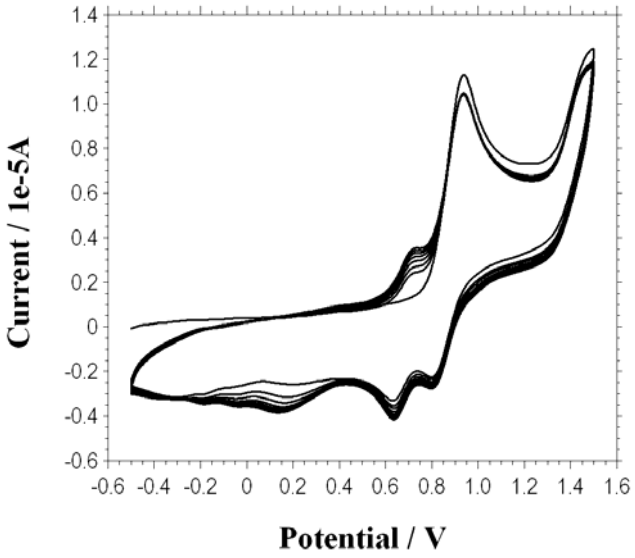


CV studies showing the reduction of the electropolymerised films (fabricated by 8 cycles between -0.5 and +1.5 V in acetonitrile/toluene, 1:1) of **3** in acetonitrile/toluene, 1:1 (——) and in the presence of a 3 x 10^{-2} M solution of **4**, first scan (·····), second scan (+ + +). Scan rate = 0.5 Vs^{-1}.

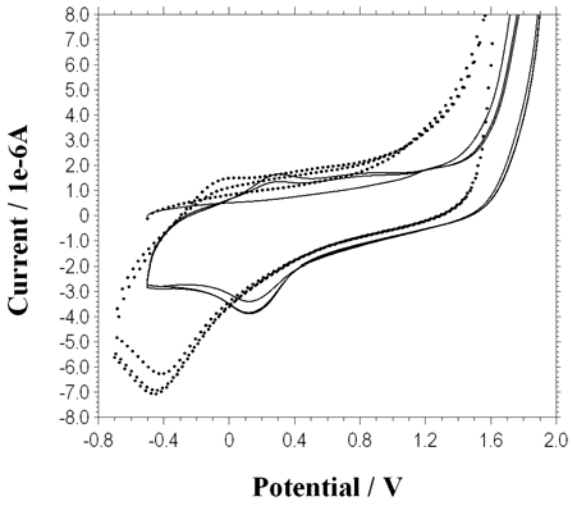


CV studies showing the reduction of the electropolymerised films (fabricated by 8 cycles between -0.5 and +1.5 V in acetonitrile/toluene, 1:1) of **3** in acetonitrile/toluene, 1:1 (—) and in the presence of a 3 x 10^{-2} M solution of **4** (·····). Scan rate = 0.5 Vs^{-1}.

Selected electrochemical data for derivative **5**



CVs showing the electropolymerisation of **5** (~2 x10^{-4} M) (eight cycles) recorded in a 0.1 M Bu_4NPF_6 CH_3CN/ toluene (1:1) solution. Scan rate = 0.5 Vs^{-1}



CV studies showing the oxidation of the as-deposited electropolymerised films of **5** in CH_3CN/toluene 1,1 (v/v) (—) and in the presence of a 3 x 10 -2 M solution of **4** (·····) .

Supplementary Material for Chemical Communications