Supplementary Material

Comparative electrochemical and impedance studies of self-assembled rigid-rod molecular wires and alkanethiols on gold substrates

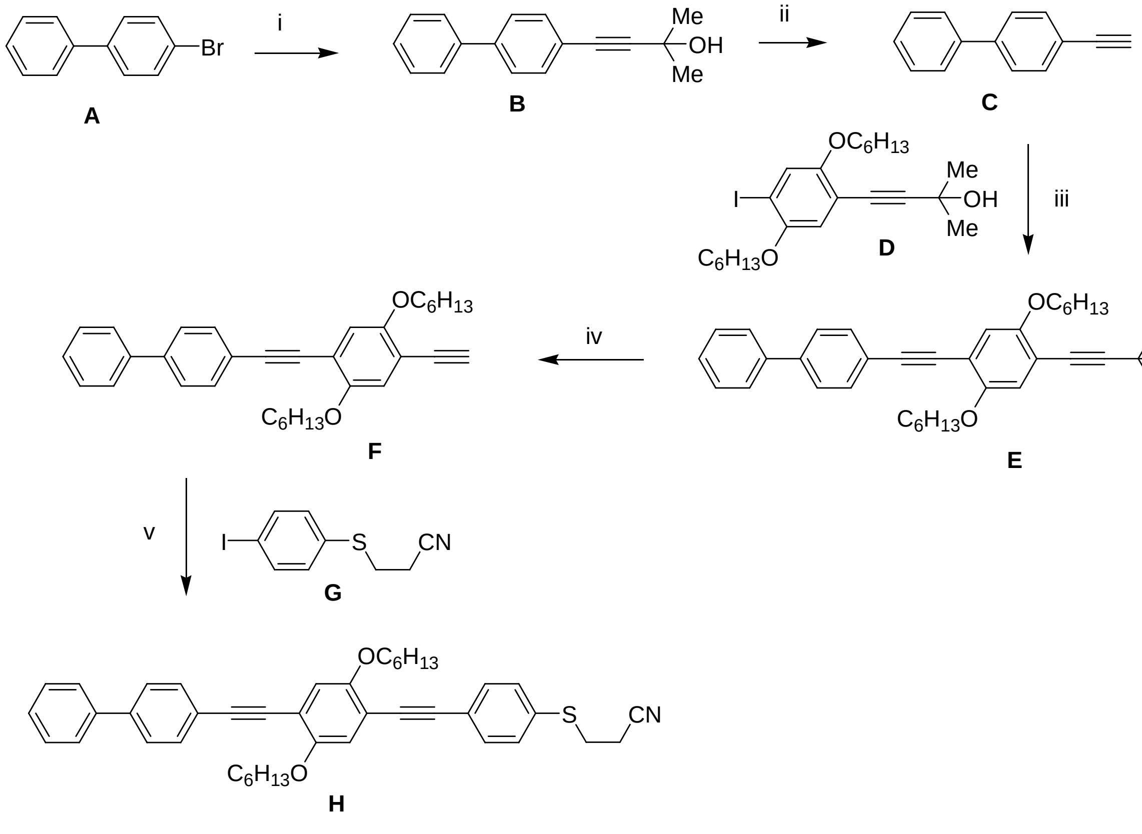
Francisco A. Aguiar,[a] Rui Campos[a], Changsheng Wang,[a] Rukkiat Jitchati,[a,b] Andrei S. Batsanov,[a] Martin R. Bryce,[a] and Ritu Kataky*[a]

[a] *Department of Chemistry, Durham University, South Road, Durham, DH1 3LE, UK. E-mail: Ritu.kataky@durham.ac.uk*

[b] *Advanced Organic Materials and Devices Laboratory, Department of Chemistry, Faculty of Science, Ubon Ratchathani University, Warinchumrap, Ubon Ratchathani 34190, Thailand*

Synthesis. Details of the equipment used and general procedures are the same as those reported previously.[1]

The synthesis of **H** is shown in Scheme S1.



Scheme S1. Reagents and conditions: i 2-methylbut-3-yn-2-ol, THF, NEt_3, $Pd(PPh)_3Cl_2$, CuI, reflux, (84% yield); ii NaOH, toluene, reflux, (97% yield); iii **C** (2.0 equiv.), **D** (1.0 equiv.), NEt_3, $Pd(PPh)_3Cl_2$, CuI, 50 ^{o}C, (91% yield); iv NaOH, toluene, reflux, (82% yield); v **F**, **G**, NEt_3, $Pd(PPh)_3Cl_2$, CuI, 50 ^{o}C, (73% yield).

4-(Biphenyl-4-yl)-2-methylbut-3-yn-2-ol (B). To the clear solution of 4-bromobiphenyl **A** (4.66 g, 20 mmol) and 2-methylbut-3-yn-2-ol (3.36 g, 40 mmol) in THF (40 cm^3) and triethylamine (80 cm^3) were added Pd(PPh$_3$)$_2$Cl$_2$ (0.85 g, 6% mmol of the bromide **A**) and CuI (0.30 g). The mixture was heated to gentle reflux and stirred for 3 h. The brown suspension was cooled to r.t. then suction filtered to remove the brown precipitate. The filtrate was evaporated under vacuum to dryness yielding a dark orange solid. The solid was purified by flash column chromatography on silica eluted with a mixture of chloroform and diethyl ether (9:1 v/v), followed by recrystallisation from cyclohexane, yielding **B** as off-white plates (3.97 g, 84%). ^{1}H NMR (CDCl$_3$, 300 MHz): 1.66 (s, 6H), 2.24 (s, 1H), 7.52 (m, 9H); ^{13}C NMR (CDCl$_3$, 75 MHz): 31.5, 65.6, 82.0, 94.4, 121.6, 126.9, 127.0, 127.6, 128.8, 132.0, 140.2, 140.9.

4-Biphenylacetylene (C). To the solution of compound **B** (3.72 g, 15.71 mmol) in toluene (100 cm^3) was added NaOH powder (0.85 g). The mixture was heated to reflux and stirred for 2.25 h under an Ar atmosphere. The brown mixture was dried of solvent by rotary evaporation and the residual solid was flash columned on silica eluted with hexanes-chloroform (2:1 v/v). The purified product **C** was obtained as white crystals (2.73 g, 97%). The analytical data were in agreement with the literature report.[2]

1-(4-Biphenylethynyl)-2,5-dihexyloxy-4-(3-hydroxy-3-methylbutynyl)benzene (E). To a solution of compounds **C** (0.356 g, 2.0 mmol) and **D**[1] (0.468 g, 1.0 mmol) in triethylamine (30 cm^3) were added Pd(PPh$_3$)$_2$Cl$_2$ (35 mg, 5% mmol of the iodide **D**) and CuI (15 mg). The mixture was stirred at r.t. for 10 min then at 50 ^{o}C for 4 h to yield a yellow suspension. The solvent was removed by rotary evaporation and the residue was flash-columned on silica, eluted with chloroform-diethyl ether 9:1 v/v), followed by recrystallistion from methanol-water to yield **E** as an off-white solid (0.49 g, 91%). Calcd for $C_{37}H_{44}O_3$: C, 82.79; H, 8.26. Found: C, 82.59; H, 8.19. ^{1}H NMR (CDCl$_3$, 300 MHz): 0.88-0.94 (m, 6H), 1.36 (m, 8H), 1.55 (m, 4H), 1.64 (s, 6H), 1.79-1.87 (m, 4H), 3.99 (t, J = 6 Hz, 2H), 4.01 (t, J = 6 Hz, 2H), 6.92 (s, 1H), 6.99 (s, 1H), 7.36 (t, J = 7.2 Hz, 1H), 7.46 (t, J = 7.5 Hz, 2H), 7.59 (m, 6H). ^{13}C NMR (CDCl$_3$, 75 MHz): 14.1, 22.6, 25.71, 25.73, 29.3, 31.4, 31.6, 65.8, 69.4, 69.6, 78.5, 86.5, 88.5, 94.6, 99.2, 113.2, 114.0, 116.7, 117.1, 122.3, 126.96, 126.99, 127.6, 128.8, 132.0, 140.3, 140.9, 153.5, 153.6.

1-(4-Biphenylethynyl)-2,5-dihexyloxy-4-ethynylbenzene (F). By analogy to the synthesis of **C**, compound **E** (0.48 g, 0.894 mmol) and NaOH powder (0.28 g) were refluxed in toluene (30 cm^3) for 40 min. The crude product was purified by flash-column chromatography on silica, eluent chloroform-hexane, 9:1 v/v) and recrystallisation from chloroform-ethanol, to afford **F** as a pale-yellow solid (0.35 g, 82%); m.p.: 64.2-64.9 ^{o}C. Calcd for $C_{34}H_{38}O_2$: C, 85.31; H, 8.00. Found: C, 85.29; H, 7.99. Maldi-Tof MS: m/z 478.4. ^{1}H NMR ($CDCl_3$, 400 MHz): 0.90 (m, 6H), 1.35 (m, 8H), 1.53 (m, 4H), 1.83 (m, 4H), 3.35 (s, 1H), 4.01 (m, 4H), 6.99 (s, 1H), 7.01 (s, 1H), 7.37 (t, *J* = 7 Hz, 1H), 7.46 (t, *J* = 7 Hz, 2H), 7.61 (m, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): 13.99, 14.01, 22.58, 22.63, 25.6, 25.7, 29.2, 29.3, 31.5, 31.6, 69.7, 80.0, 82.2, 86.5, 94.9, 122.7, 114.8, 117.0, 117.9, 122.3, 126.98, 127.0, 127.6, 128.8, 132.0, 140.4, 141.0, 153.5, 154.2.

1-(4-Biphenylethynyl)-4-[4-(2-cyanoethylsulfanyl)phenyl]ethynyl-2,5-dihexyloxybenzene (H). To the solution of compounds **F** (0.293 g, 0.612 mmol) and **G** (0.212 g, 0.733 mmol) in triethylamine (40 cm^3) were added $Pd(PPh_3)_2Cl_2$ (21 mg, 5% mmol relative to **F**) and CuI (15 mg). The mixture was stirred at r.t. for 2 h and at 50 ^{o}C for an additional 2 h to yield a yellow-orange suspension. The mixture was rotary evaporated to dryness and the residue was directly flash columned on silica (eluted with chloroform) to yield **1** a yellow solid (0.285 g, 73%). A single crystal for X-ray analysis was obtained by recrystallisation from toluene-cyclohexane mixture. Mp: 116.2-116.8 ^{o}C. Calcd for $C_{43}H_{45}NO_2S$: C, 80.71; H, 7.09; N, 2.19. Found: C, 80.98; H, 7.11; N, 2.20. ^{1}H NMR ($CDCl_3$, 400 MHz): 0.91 (m, 6H), 1.38 (m, 8H), 1.57 (m, 4H), 1.88 (m, 4H), 2.63 (t, *J* = 7.4 Hz, 2H), 3.17 (t, *J* = 7.4 Hz, 2H), 4.05 (dt, 4H), 7.02 (s, 1H), 7.04 (s, 1H), 7.3-7.4 (m, 3H), 7.44-7.51 (m, 4H), 7.61-7.63 (m, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): 14.03, 14.06, 18.23, 22.63, 22.67, 25.76, 25.79, 29.35, 29.38, 29.86, 31.62, 31.64, 69.69, 69.78, 86.68, 87.42, 93.97, 95.00, 113.66, 114.47, 116.99, 117.02, 117.06, 117.75, 122.38, 122.82, 127.02, 127.66, 128.84, 128.88, 130.46, 132.02, 132.33, 133.77, 140.38, 141.03, 153.72, 153.79.

X-Ray Crystallography. The X-ray molecular structure of **H** is shown in Figure S1.

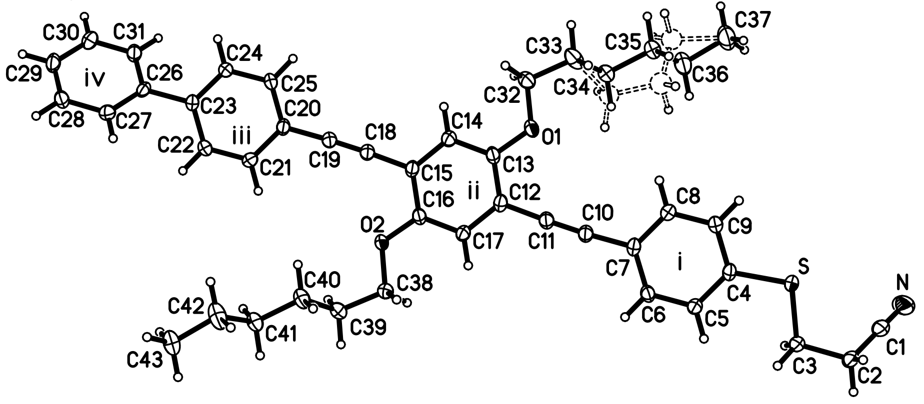
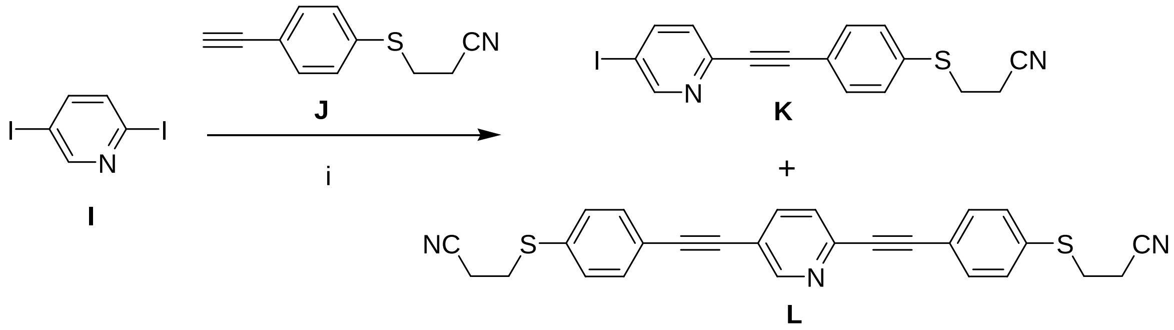


Figure S1. Molecular structure of **H** (thermal ellipsoids at 50% probability). Dihedral angles between rings: i/ii 5.5, ii/iii 5.8, iii/iv 38.9°. Disordered atoms have occupancies of 0.82 (solid) and 0.18 (dashed).

The X-ray diffraction experiment was carried out on a Bruker APEX 3-circle diffractometer with a ProteumM CCD area detector, using graphite-monochromated Mo-K_{α} radiation ($\bar{\lambda}$=0.71073 Å) and a Cryostream (Oxford Cryosystems) open-flow N_2 cryostat. The structure was solved by direct methods and refined by full-matrix least squares against F^2 of all reflections, using SHELXTL software (version 6.14, Bruker AXS, Madison WI, USA, 2003). *Crystal data*: $C_{43}H_{45}NO_2S$ **H**, M=639.86, T=120 K, triclinic, space group $P\bar{1}$ (No. 2), a=11.567(1), b=11.870(1), c=13.986(2) Å, α=106.21(1), β=102.50(1), γ= 94.14(1)°, U=1782.2(3) Å^3, Z=2, D_c=1.192 g cm^{-3}, μ=0.13 mm^{-1}, 25344 reflections with $2\theta\leq55°$, 8163 unique, $R_{\rm int}$=0.035, R=0.042 [6847 data with $I\geq2\sigma(I)$], w$R(F^2)$=0.122 (all data).

The synthesis of **K** is shown in Scheme S2.



Scheme S2. Reagents and conditions: i, **I**, **J** (1.0 equiv.), THF, NEt_3, $Pd(PPh)_3Cl_2$, CuI, reflux (**K**, 54% yield).

5-Iodo-1-[4-(2-cyanoethylsulfanyl)phenylethynyl]-pyridine (K) and **2,5-Bis[4-(2-cyanoethylsulfanyl)phenylethynyl]-pyridine (L).** 2,5-Diiodopyridine **I** (0.67 g, 2.0 mmol) and compound **J**[3] (0.40 g, 2.0 mmol) were dissolved in dry THF (30 cm^3). $Pd(PPh_3)_2Cl_2$ (46 mg) and CuI (11 mg) were added with stirring followed by triethylamine (30 cm^3). The mixture was stirred under an argon atmosphere at 50 °C for 4 h. The solution was cooled to r.t., resulting in a yellow suspension which was mixed with dichloromethane then filtered through a silica pad (washed with a small amount of dichloromethane). The filtrate was concentrated and the residue was chromatographed on silica (eluent DCM), to afford compound **K** (1st band) as a pale-yellow solid (0.42 g, 54%); Mp: 148-150 °C. Calcd for $C_{16}H_{11}IN_2S$: C, 49.24; H, 2.84; N, 7.18. Found: C, 49.44; H, 2.66; N, 7.00. ^1H NMR ($CDCl_3$, 300 MHz): δ 2.65 (t, J = 7.0 Hz, 2H), 3.19 (t, J = 7.0 Hz, 2H), 7.31 (d, J = 8.5 Hz, 1H), 7.37 (d, J = 8.5 Hz, 2H), 7.55 (d, J = 8.5 Hz, 2H), 8.00 (dd, J = 8.5 Hz, J = 1.5 Hz, 1H), 8.84 (d, J = 1.5 Hz, 1H), ^{13}C NMR ($CDCl_3$, 125 MHz): δ 18.5, 29.6, 89.1, 90.1, 92.8, 117.9, 119.6, 121.1, 128.7, 130.1, 133.0, 135.2, 142.0, 144.7, 156.4. MS (MALDI-TOF) *m/z* (%) 390.0 (100). This was followed by impure compound **L** (2nd band).

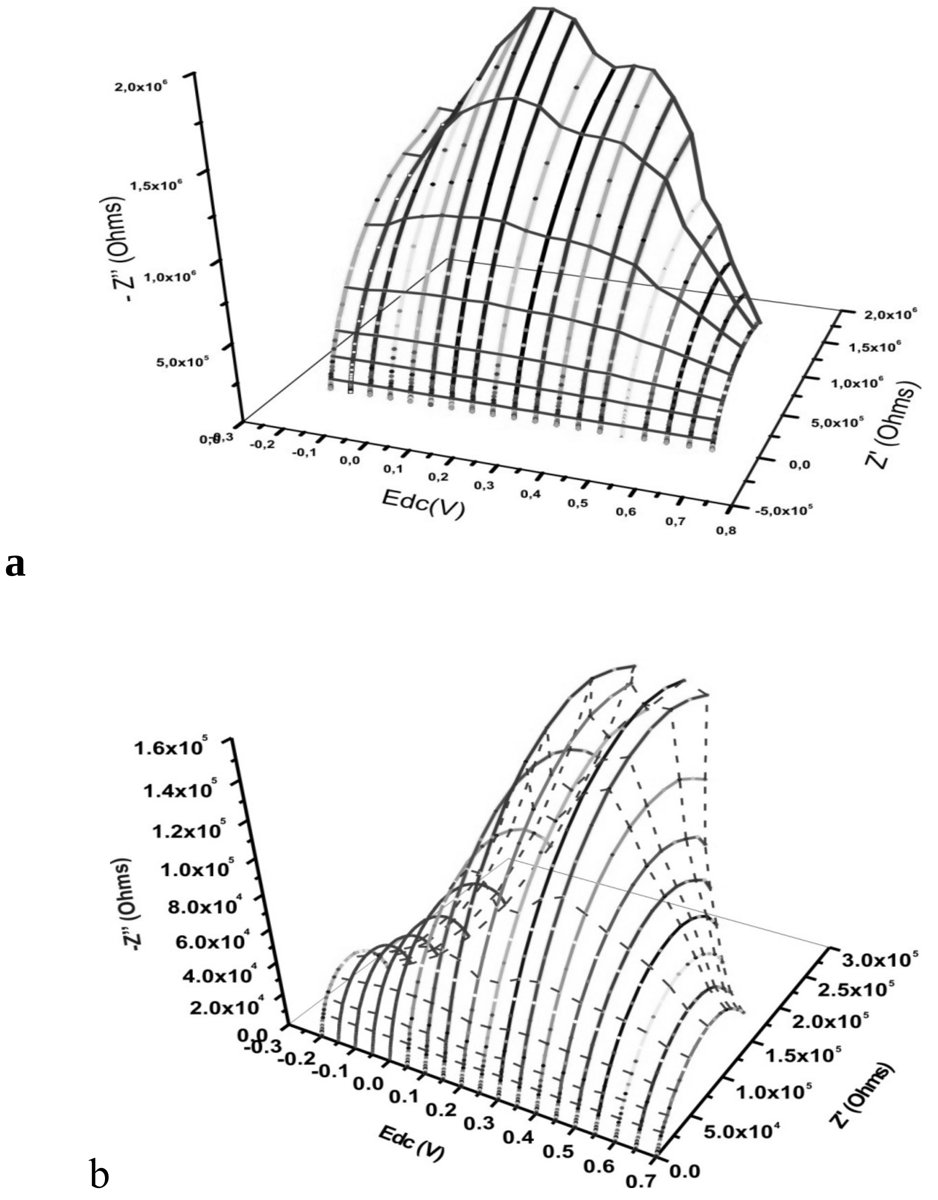


Figure S2 a and **b**. Nyquist plots for 1 mM $Fe(CN)_6^{3-/4-}$ in 0.1 M KNO_3 solution using (**a**) DDT SAM and (**b**) **2** SAM electrodes. Frequency range: 1 Hz to 100 KHz at different applied potentials.

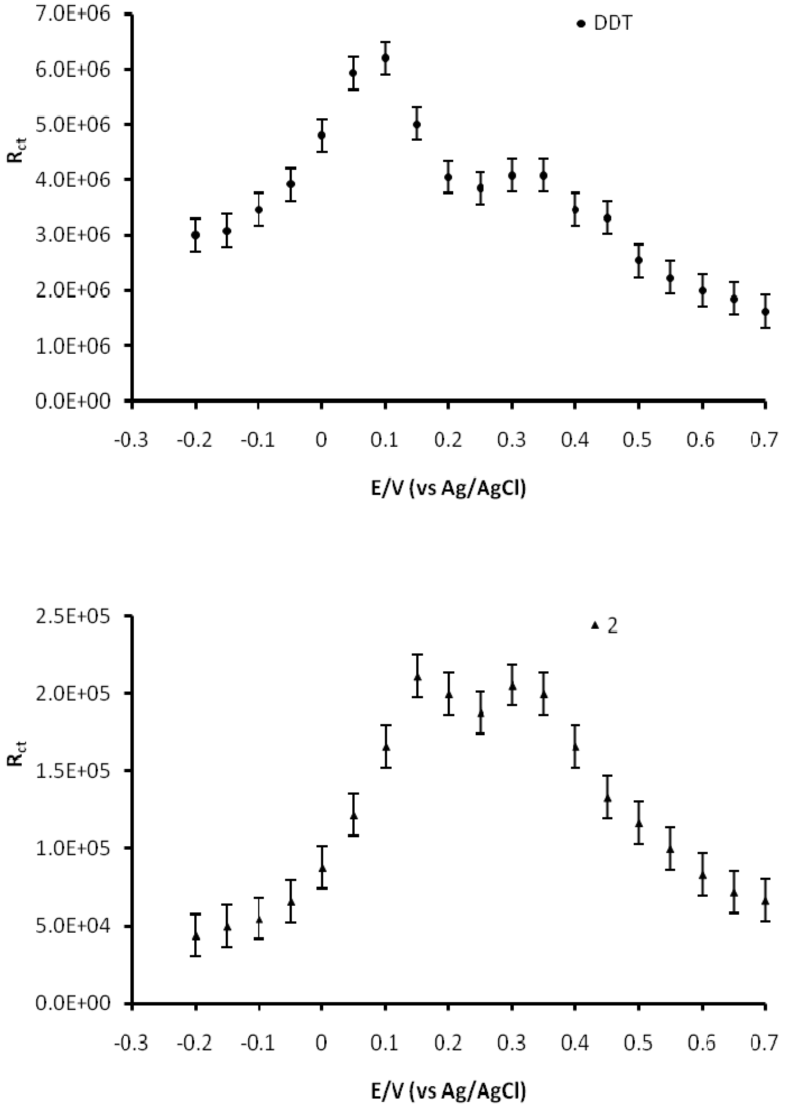


Figure S3a and b. Variation of R_{ct} of DDT SAM and **2** SAM electrodes over a potential range.

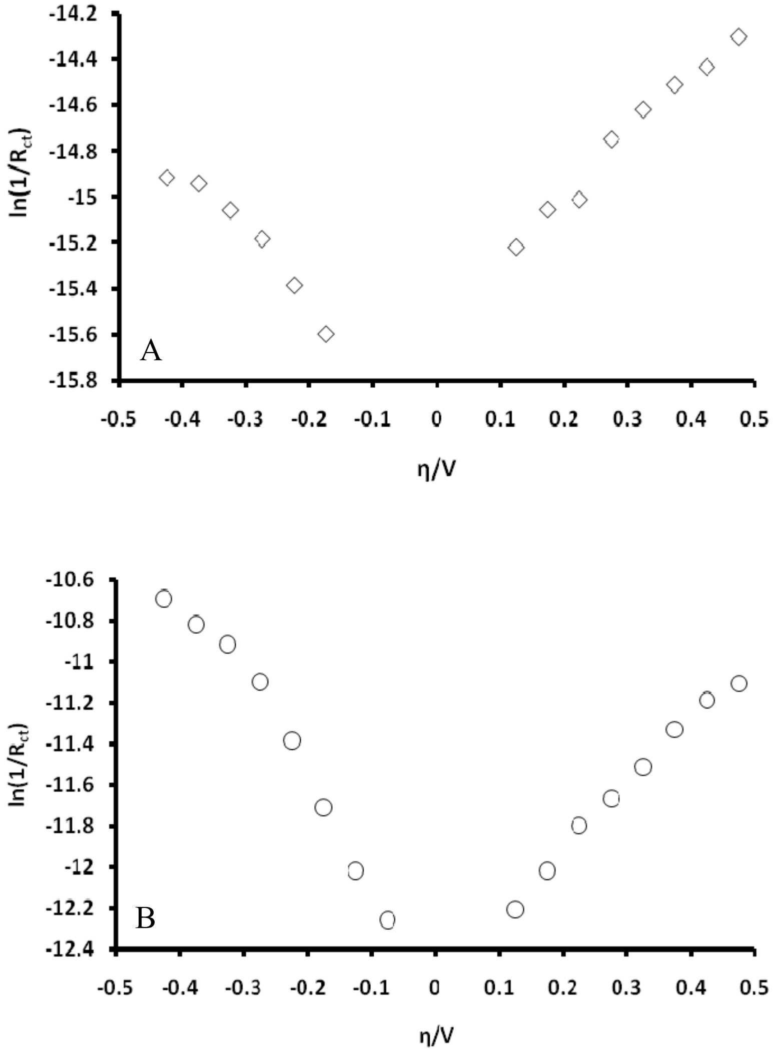


Fig. S4a and b. Tafel plots for (A) DDT SAM and (B) 2 SAM

References for the Supplementary Material

1 C. Wang, A. S. Batsanov and M. R. Bryce, *J. Org. Chem.*, 2006, **71**, 108-116.

2 E. B. Stephens and J. M. Tour, *Macromolecules*, 1993, **26**, 2420-2427.

3 C. Wang, A. S. Batsanov, M. R. Bryce and I. Sage, *Org. Lett.*, 2004, **6**, 2181-2184.