Electrochemical Deposition of Highly-conducting Metal Dithiolene Films

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All materials were purchased from commercial suppliers and used without further purification. 1H-NMR spectra were recorded on a Bruker 400MHz spectrometer fitted with a broadband BBI inverse probe recording spectra at 399.90 MHz. Spectra were referenced internally to residual solvent, chemical shifts are quoted in δ ppm. Electron ionisation mass spectra (EI) were recorded on a Bruker 3.0 T Apex II Spectrometer. Elemental analysis was carried out at the Metropolitan University of London. Powder EPR spectra were measured on a Bruker ER200D X-band spectrometer at room temperature and simulations were carried out using the Bruker EPR simulation package SimFonia. Solution UV/Vis/NIR measurements were carried out on a Jasco V-570UV/Vis/NIR spectrophotometer controlled by the proprietary software using a quartz cell with 1cm pathlength. Cyclic voltammetry measurements were carried out in freshly distilled DCM containing 0.3 M Tetrabutylammonium tetrafluoroborate electrolyte in a three electrode system, purged with house N2 for 30 min prior to the experiment. A polished 0.2 mm2 Pt working electrode sealed in glass was used in conjunction with a Pt counter electrode and an Ag/AgCl reference electrode that was calibrated against Fe/Fe+ after each experiment. The measurements were carried out at room temperature on µAutolab Type III potentiostat controlled by General Purpose Electrochemistry Software (GPES) software. CV experiments were carried out at varying rates between 25-500 mV s⁻¹ and SWV experiments were carried out using a step potential of 0.01 V, modulation amplitude of 0.10005 V and modulation and interval times of 0.05 s and 0.5 s, respectively. Conductivity measurements were performed on bottom gate/bottom contact devices based on a heavily n-doped silicon gate electrode with a 300 nm layer of thermally grown silicon dioxide. The 20 interdigitated source and drain electrodes were 100 nm gold (platinum) fabricated using photolith on a 2-3 nm titanium carbide layer deposited using an Advantest R6245 DC Voltage/Current Source/Calibrator. Prior to deposition the chips were cleaned in various individual solvents (acetonitrile, water, IPA, chloroform) and dried under nitrogen.

25 Syntheses

Potassium isopropyl xanthate, (iPrOCS2K)
To a solution of KOH (56.1 g, 1 mol) in IPA (200 cm³) placed in ice, CS₂ (96 cm³, 1.0 mol) was added at a rate of one drop per 10 seconds, whilst stirring rapidly. Upon complete addition the mixture was stirred for another hour in ice, then filtered and the precipitate was washed with EtOH (100 cm³) and DE (200 cm³) being dried overnight at 100°C, yielding a yellow/white powder (171 g, 0.98 mol, 98%). 1H-NMR (CHCl₃/400 MHz): δ 5.45 (7, 1H) 1.15 (d, 6H); CHN: C₆H₁₈KOS₂: (calc.: C: 27.56, H: 4.05) found: C: 27.50, H: 4.02;
2-Chloroaecetyl-5-Ethylphiphene
2-Ethylthiophene (6.10 cm³, 0.0544 mol) was added to a stirred mixture of chloroacetyl chloride (9.00 cm³, 0.056 mol) and anhydrous aluminium chloride (7.47 g, 0.056 mol) in dry CS₂ (150 cm³) to afford a red solution that gradually turned dark. The mixture was stirred at room temperature overnight, refluxed for 1h and cooled in an ice bath. Under vigorous stirring, HCl (1N) was cautiously added to the cooled mixture, and the brown organic layer was separated, washed with HCl, sodium carbonate and H₂O, dried over magnesium sulphate and the solvent removed in vacuum to afford an orange oil (9.10 g, 0.048 mol, Yield: 89%). 1H-NMR (CHCl₃/400 MHz): δ 7.63 (d, 1H, J=3.9Hz), 6.87 (d, 1H, J=3.9 Hz), 4.54 (s, 2H), 2.90 (q, 2H, J=7.4Hz), 1.34 (t, 3H, J=7.4Hz); 4-(5-Ethyl)-thiophene-2yl)-1,3-dithiole-2-one
4-(5-Ethyl)-thiophene-2yl)-1,3-dithiole-2-one (8.10 g, 0.0429 mol) and iPrOCS (10.25 g, 0.0588 mol) were suspended in acetone (200 cm³) and refluxed for 3h. Mixture was cooled to room temperature, filtered and washed with chloroform. Solvent was removed from the combined filtrates and crude intermediate was resuspended in CHCl₃ (30 cm³). Perchloric acid (70%) (8 cm³) was added dropwise to the stirred solution which was then refluxed overnight. The solution was poured onto ice water and extracted with chloroform. Combined extracts were dried over anh. sodium sulfate. After evaporation the crude product was purified using flash column chromatography using hexane/ethyl acetate (10:1) as eluent mix, to yield a brown oil (5.10 g, 0.022 mol, Yield: 52%).
1H-NMR (CHCl₃/400 MHz): δ 6.86 (d, 1H, J=3.6Hz), 6.70 (d, 1H, J=3.6 Hz), 6.63 (s, 1H), 2.84 (q, 2H, J=8.0Hz), 1.32 (t, 3H, J=8.0Hz); Bis(2-(5-ethylthiophene-2yl)-1,2-dithiole)nickel TBA, (TBA-Ni-C2)
4-(5-Ethyl)-thiophene-2yl)-1,3-dithiole-2-one (0.379 g, 1.6 mmol) were added to a stirred solution of 0.1M sodium methoxide (NaOMe) in EtOH (50 cm³) under argon and stirred for 1h. Tetrabutylammonium bromide ([TBA][Br]) (0.267 g, 0.83 mmol) were added and stirred until dissolved. Subsequently, nickel chloride hexahydrate (NiCl₂·6H₂O) (0.197 g, 0.8 mmol) in EtOH (15 cm³) was added dropwise over 20
45 min. The resulting suspension was stirred overnight before being concentrated and further precipitated with diethyl ether to yield a purple solid (0.450 g, 0.6 mmol, 77%).

C<sub>6</sub>H<sub>5</sub>NaNNiS<sub>2</sub> CHN (calc.: C:54.76, H:7.47, N:2.0) found: C:54.60 H:7.39 N:1.89; Mass (EI) m/z = 457.9 [M+H]+.

Other compounds were prepared analogously.

5-Chloroacetyl-5-butylthiophene

2-Butylthiophene (3.387 g, 0.0241 mol), chloroacetyl chloride (4.25 cm<sup>3</sup>, 0.0266 mol) and anhydrous aluminium chloride (3.542 g, 0.0266 mol) in dry C<sub>6</sub>H<sub>6</sub> (90 cm<sup>3</sup>). Brown oil was obtained (2.64 g, 0.012 mol, Yield: 54%).

1H-NMR (CDCl<sub>3</sub>/400 MHz): δ 7.61 (d, 1H, J=3.7 Hz), 6.84 (d, 1H, J=3.7 Hz), 4.53 (s, 2H), 2.85 (t, 2H, J=7.2 Hz), 1.68 (5, 2H, J=7.2 Hz), 1.39 (6, 2H, J=6.7 Hz), 0.93 (3H, J=7.6 Hz);

6-Chloroacetyl-6-hexylthiophene

2-Chloroacetyl-5-hexylthiophene (3.333 g, 0.0136 mol) and iPrOCS<sub>2</sub>K (2.864 g, 0.0164 mol) in acetone (80 cm<sup>3</sup>). Resuspended in CHCl<sub>3</sub> (15 cm<sup>3</sup>) and perchloric acid (30 cm<sup>3</sup>). Flash column chromatography using hexane/ethyl acetate (10:1) as eluent mix. Product was obtained as orange oil (1.39 g, 0.006 mol, 54%).

1H-NMR (CDCl<sub>3</sub>/400 MHz): δ 6.68 (d, 1H, J=3.5 Hz), 6.59 (d, 1H, J=3.5 Hz), 6.62 (s, 1H), 2.80 (t, 2H, J=7.1 Hz), 1.67 (5, 2H, J=7.5 Hz), 1.41-1.25 (m, 6H), 0.89 (t, 3H, J=6.7 Hz);

Bis(2-(5-hexylthiophene-2-yl)-1,2-dithiole-2-one), (TBA-Ni-C6)

4-(5-Hexylthiophene-2-yl)-1,3-dithiole-2-one (0.5128 g, 2 mmol) in 0.1M NaOMe in EtOH (60 cm<sup>3</sup>) added and stirred overnight. Red solution concentrated and precipitated with diethyl ether to afford purple solid (0.450 g, 0.6 mmol, 77%).

C<sub>6</sub>H<sub>5</sub>NaNNiS<sub>2</sub> CHN (calc.: C:57.05, H:7.98, N:1.85) found: C:56.87, H:7.81 N:1.93; Mass (EI) m/z = 513.95 [M+H]+.

2-Chloroacetyl-5-octylthiophene

2-Octylthiophene (4.34 cm<sup>3</sup>, 0.0241 mol), chloroacetyl chloride (4.25 cm<sup>3</sup>, 0.0266 mol) and anhydrous aluminium chloride (3.542 g, 0.0266 mol) in dry C<sub>6</sub>H<sub>6</sub> (90 cm<sup>3</sup>). To yield a brown oil (3.21 g, 0.013 mol, 54%).

1H-NMR (CDCl<sub>3</sub>/400 MHz): δ 7.62 (d, 1H, J=3.7 Hz), 6.85 (d, 1H, J=3.6 Hz), 4.51 (s, 1H), 2.85 (t, 2H, J=7.5 Hz), 1.7 (5, 2H, J=7.5 Hz), 1.44-1.29 (m, 6H), 0.91 (t, 3H, J=7.0 Hz);

Bis(2-(5-octylthiophene-2-yl)-1,2-dithiolenickel TBA, (TBA-Ni-C8)

4-(5-Octylthiophene-2-yl)-1,3-dithiole-2-one (0.503 g, 1.6 mmol) in 0.2M NaOMe in EtOH (25 cm<sup>3</sup>) stirred for 1h under argon. [TBA][Br] (0.3224 g, 1 mmol) and NiCl<sub>2</sub>·6H<sub>2</sub>O (0.238 g, 1 mmol) in EtOH (15 cm<sup>3</sup>) added and stirred overnight. Red solution concentrated and precipitated with diethyl ether to afford purple solid (0.563 g, 6.5 mmol, 81%).

Mass (EI) m/z = 570.0 [M+H]+.

2-Chloroacetyl-5-decythiophene

2-Decylthiophene (5.26 cm<sup>3</sup>, 0.0241 mol), chloroacetyl chloride (4.25 cm<sup>3</sup>, 0.0266 mol) and anhydrous aluminium chloride (3.542 g, 0.0266 mol) in dry C<sub>6</sub>H<sub>6</sub> (80 cm<sup>3</sup>) to afford a dark red suspension which gradually turned brown. Afford an orange oil (mp: 5 ºC) (3.82 g, 0.014 mol), 87% yield.

1H-NMR (CDCl<sub>3</sub>/400 MHz): δ 7.62 (d, 1H, J=3.6 Hz), 6.68 (d, 1H, J=3.6 Hz), 6.62 (s, 1H), 2.79 (5, 2H, J=7.2 Hz), 1.67 (5, 2H, J=7.5 Hz), 1.39 (6, 2H, J=6.7 Hz), 0.91 (t, 3H, J=6.7 Hz);

Bis(2-(5-decythiophene-2-yl)-1,2-dithiolene)nickel TBA, (TBA-Ni-C8)

4-(5-Decylthiophene-2-yl)-1,3-dithiole-2-one (0.503 g, 1.6 mmol) in 0.2M NaOMe in EtOH (25 cm<sup>3</sup>) stirred for 1h under argon. [TBA][Br] (0.328 g, 0.8 mol) and NiCl<sub>2</sub>·6H<sub>2</sub>O (0.1902 g, 0.8 mmol) in EtOH (15 cm<sup>3</sup>) added and stirred overnight. Red solution concentrated and precipitated with diethyl ether to afford purple solid (0.563 g, 6.5 mmol, 81%).

Mass (EI) m/z = 626.08 [M+H]+; C<sub>41</sub>H<sub>32</sub>NaNNiS<sub>2</sub> CHN (calc.: C:60.73, H:8.8, N:1.61) found: C:60.63, H:8.85, N:1.59;

2-Decylthiophene

To a solution of thiophene (10.66 cm<sup>3</sup>, 0.1188 mol) in THF (100 cm<sup>3</sup>) was added n-BuLi in hexane (2.5M, 47 cm<sup>3</sup>, 0.115 mol) slowly at -78ºC. The solution was stirred for 1h then 1-bromo-decane (26.287 g, 0.1188 mol) was added slowly. The reaction was warmed to RT and stirred overnight before it was poured onto H<sub>2</sub>O, extracted with DE and dried with sodium sulphate. The crude material was obtained as an orange oil upon evaporation. Distillation at 170ºC and reduced pressure afforded the target product as a clear oil (16.8 g, 0.075 mol,
Yield: 63%).
1H-NMR (CHCl₃/400 MHz): 7.10 (dd, 1H, J=5.1, 1.2Hz), 6.92 (dd, 1H, J=5.0, 3.7Hz), 6.77 (d, 1H, J=3.7Hz) 2.82 (t, 2H, J=7.3Hz), 1.67 (5, 2H, J=7.3Hz), 1.40-1.25 (m, 14H), 0.91 (t, 3H, J=6.7Hz); 5-Chloroacetyl-5-decylthiophene.

2-Chloroacetyl-5-decylthiophene (2.900 g, 0.010 mol) and iPrOCS₂K (3.30 g, 0.0189 mol) in acetone (90 cm³) was added to a stirred mixture of 2-Chloroacetyl-5-decylthiophene, 4-(5-Dodecyl)-thiophene-2-yl)-1,3-dithiole-2-one, Bis(2-(5-dodecylthiophene-2-yl)-1,2-dithiolene)nickel TBA, (TBA-Ni-C₁₂) (0.258 g, 0.8 mmol) and NiCl₂ (956 mg, 5.28 mmol) in EtOH (15 cm³) added and stirred overnight. Red solution concentrated and precipitated with diethyl ether to afford purple solid (0.532 g, 5.7 mmol, 72%).

1H-NMR (CHCl₃/400 MHz): δ 7.11 (dd, 1H, J=5.1, 1.2Hz), 6.93 (d, 1H, J=5.0, 3.3Hz), 2.84 (t, 2H, J=7.4Hz), 1.7 (5, 2H, J=6.7Hz), 1.50-1.25 (m, 18H), 0.91 (t, 3H, J=6.7Hz); 5-Chloroacetyl-5-(4-ethyl-thiophene)-1,3-dithiol-2-one (547 mg, 2.40 mmol) in THF (15 ml) was added to [TMA][OH]·5H₂O (956 mg, 5.28 mmol) in MeOH (4 ml). After 5 minutes, CuCl₂·2H₂O (204 mg, 1.20 mmol) in MeOH (4 ml) was added and the reaction mixture stirred at room temperature overnight. The precipitate was filtered off and washed with EtOH (10 ml).

NMR: δH (500 MHz; CDCl₃) 1.27 (t, 6H, Me, J=7.5, 1.3 Hz c), 1.60 (s, 12H, TMA), 2.20 (q, 4H, CH₂-), J =7.3, 1.8 Hz d), 6.71 (s, 2H, C(S)H, a) 6.71 (d, 2H, -CH₃, J =7.2, 1.2Hz b) 6.89 (d, 2H, -CH₃, J=11.4, 1.2Hz c)
Figure S1: NMR of the aromatic region of TMA[Cu(Ti-C2)2]

CHN: cal: C 44.62%, H 5.24%, N 2.60% found: C 38.99%, H 5.07%, N 2.46%

The copper analogue was shown to be free of organic contaminants by NMR, as shown in Figure S1. Any attempts to purify the complex further led to degradation.

Figure S2: Electronic absorption spectra of several concentrations of TMA[Cu(Ti-C2)2] salt in MeCN. Inset: Beer-Lambert plot of the absorbance maxima against concentration
Calculations

Table S1: Frontier Orbital Energies, calculated at B3PW91/6-31+G(d); Frontier orbitals of neutral Ni-C1 as calculated for B3PW91/6-31+G(d) and displayed with an iso-surface of 0.03 electrons bohr$^{-1}$.

<table>
<thead>
<tr>
<th>Compound</th>
<th>HOMO [eV]</th>
<th>SOMO [eV]</th>
<th>LUMO [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neutral Ni-C1</td>
<td>-0.20684</td>
<td>-5.63</td>
<td>-0.15631</td>
</tr>
<tr>
<td>Anionic [Ni-C1]$^-$</td>
<td>-0.18976</td>
<td>-5.16</td>
<td>-0.16553</td>
</tr>
</tbody>
</table>

Table S2: Primary transition wavelengths, oscillator strengths and contributing orbitals for the first 30 excited states as calculated by TD DFT using B3PW91/6-31+G(d) and PCM dichloromethane.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\lambda$ calc [nm]</th>
<th>Oscillator Strength</th>
<th>Orbitals</th>
<th>Contribution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neutral Ni-C1</td>
<td>949</td>
<td>0.5859</td>
<td>HOMO -&gt; LUMO</td>
<td>97</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
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<td>----</td>
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<tr>
<td></td>
<td>354</td>
<td>0.6945</td>
<td>HOMO -&gt; LUMO+2</td>
<td>75</td>
</tr>
<tr>
<td></td>
<td>297</td>
<td>0.7675</td>
<td>HOMO-1 -&gt; LUMO+3</td>
<td>86</td>
</tr>
<tr>
<td>Anionic [Ni-C1]</td>
<td>1131</td>
<td>0.2497</td>
<td>HOMO -&gt; SOMO</td>
<td>98</td>
</tr>
<tr>
<td></td>
<td>545</td>
<td>0.0226</td>
<td>SOMO -&gt; LUMO+2</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td>398</td>
<td>0.1349</td>
<td>various</td>
<td></td>
</tr>
</tbody>
</table>
EPR

Table S3: Principal g values observed for the rhombic type signal and the axial type signals

<table>
<thead>
<tr>
<th>Compound</th>
<th>g1</th>
<th>g2</th>
<th>g3</th>
</tr>
</thead>
<tbody>
<tr>
<td>TBA-Ni-C2</td>
<td>2.123</td>
<td>2.004</td>
<td>1.997</td>
</tr>
<tr>
<td>Compound</td>
<td>gII</td>
<td>g┴</td>
<td></td>
</tr>
<tr>
<td>TBA-Ni-C4</td>
<td>2.103</td>
<td>2.030</td>
<td></td>
</tr>
<tr>
<td>TBA-Ni-C6</td>
<td>2.096</td>
<td>2.024</td>
<td></td>
</tr>
<tr>
<td>TBA-Ni-C8</td>
<td>2.099</td>
<td>2.029</td>
<td></td>
</tr>
<tr>
<td>TBA-Ni-C12</td>
<td>2.106</td>
<td>2.037</td>
<td></td>
</tr>
</tbody>
</table>

Electrochemical deposition

Depositions were performed using a modified three-electrode set-up. A substrate on which the molecule was being deposited was used instead of a working electrode. This was either a piece of Fluorine-doped tin oxide glass or a chip of interdigitated electrodes for conductivity measurements. The counter electrode was in a separate cell connected to the rest of the experiment by a glass frit. This was done so that any electrochemical processes occurring at this electrode would be isolated and not have any effect on the deposition process taking place. Chronocoulometry, a potential-step technique, was used to monitor the electrochemical deposition.

The electrodeposition of the dithiolene complexes was investigated in acetonitrile as the dithiolene salts were soluble and, since acetonitrile is more polar than DCM, the neutral dithiolene complexes were not soluble. Several potentials above E_{ox}=0.31 V for the Cu-C2 and E_{ox}=0.34 V for the Ni-C2 were investigated for the electrodeposition of both complexes. Depositions were attempted at 1.06 V, 0.96 V, 0.86 V and 0.76 V for both films to investigate the potential needed to electrodeposit from a solution with a dithiolene salt concentration of 5x10^{-4} mol dm^{-3} in acetonitrile. Deposition at 1.06 V resulted in black fibres rather than a uniform film for Ni-C2.

Figure S4: Deposition current of 2.40x10^{-2} Ccm^{-2} of (a) Cu-C2 and (b) Ni-C2
**Electrodeposited films**

Figure S5: SEM images of the features of Cu-C2

![SEM image of Cu-C2 features](image)

Figure S6: SEM images of the features of Ni-C2

![SEM image of Ni-C2 features](image)

Figure S7: SEM images of Cu-C2 electrodeposited on 8 \( \mu \)m x 8 \( \mu \)m interdigitated electrodes

![SEM image of Cu-C2 on interdigitated electrodes](image)

Figure S8: SEM images of Ni-C2 electrodeposited on 8 \( \mu \)m x 8 \( \mu \)m interdigitated electrodes

![SEM image of Ni-C2 on interdigitated electrodes](image)
Figure S9: Plot of resistance against temperature for the cooling of 8 μm x 8 μm interdigitated electrodes of (a) Cu-C2 and (b) Ni-C2