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ARTICLE TYPE

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 Fc/Fc⁺ 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 interdigitated source and drain electrodes were 100 nm gold (platinum) fabricated using photolith on a 2-3 nm titanium (chromium) adhesion layer. The electrode finger width and channel length were 2, 4, 8 or 20 μm and the testing was carried out in the dark either in air or in a custom-made vacuum chamber using a Keithley 2612A Dual Channel Sourcemeter or an Advantest R6245 DC Voltage/Current Source/Calibrator. Prior to deposition the chips were cleaned in various individual solvents (acetone, 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) before 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 C₄H₇KOS₂ (calc.: C: 27.56, H: 4.05) found: C:27.50, H:4.02;

2-Chloroacetyl-5-Ethylthiophene,

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-2-yl)-1,3-dithiole-2-one,

2-Chloroacetyl-5-Ethylthiophene (8.10 g, 0.0429 mol) and iPrOCS₂K (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 ash 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-2-yl)-1,3-dithiole-2-one)nickel TBA, (TBA-Ni-C2)

4-(5-Ethyl)-thiophene-2-yl)-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

45min. 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%).

$C_{32}H_{52}NNiS_6$ 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 2-Chloroacetyl-5-butylthiophene

2-Butylthiophene (3.387 g, 0.0241 mol), chloroacetyl chloride (4.25 cm³, 0.0266 mol) and anhydrous aluminium chloride (3.539 g, 0.0266 mol) in dry CS₂ (90 cm³). Brown oil was obtained (2.64g, 0.012mol, Yield: 50%).

¹H-NMR (CHCl₃/400 MHz): δ 7.61(d, 1H, J=3.7Hz), 6.84 (d, 1H, J=3.7 Hz), 4.53 (s, 2H), 2.85 (t, 2H, J=7.2Hz), 1.68 (s, 2H, J=7.6Hz), 1.39(6, 2H, J=7.6Hz), 0.93(t, 3H, J=7.6Hz);

10 4-(5-Butyl)-thiophene-2yl)-1,3-dithiole-2-one,

2-Chloroacetyl-5-butylthiophene (2.17 g, 0.010 mol) and iPrOCS₂K (1.743 g, 0.010 mol) in acetone (50 cm³). Resuspended in CHCl₃ (15 cm³) and perchloric acid (70%) (3 cm³). Flash column chromatography using petroleum ether/ethyl acetate (25:1). Product was obtained as orange oil (1.35 g, 0.006 mol, 61%).

¹H-NMR (CHCl₃/400 MHz): δ 6.85 (d, 1H, J=3.6Hz), 6.69 (d, 1H, J=3.6 Hz), 6.62 (s, 1H), 2.79 (t, 2H, J=7.3Hz), 1.66 (s, 2H, J=7.3Hz), 1.39 (6, 2H, J=7.3Hz), 0.94(t, 3H, J=7.6Hz);

15 Bis(2-(5-butylthiophene-2-yl)-1,3-dithiole-2-one)nickel TBA, (TBA-Ni-C4)

4-(5-Butyl)-thiophene-2yl)-1,3-dithiole-2-one (0.5128 g, 2 mmol) in 0.1M NaOMe in EtOH (60 cm³) stirred for 1h. [TBA][Br] (0.3224 g, 1 mmol) and NiCl₂·6H₂O (0.238 g, 1 mmol) in EtOH (15 cm³) added and stirred overnight. Red solution concentrated and precipitated with diethyl ether to afford purple solid (0.446 g, 0.006 mol, 59%).

20 $C_{36}H_{60}NNiS_6$ 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-hexylthiophene,

2-Hexylthiophene (4.34 cm³, 0.0241 mol), chloroacetyl chloride (4.25 cm³, 0.0266 mol) and anhydrous aluminium chloride (3.542 g, 0.0266 mol) in dry CS₂ (90 cm³). To yield a brown oil (3.21 g, 0.013 mol, 54%).

¹H-NMR (CHCl₃/400 MHz): δ 6.86(d, 1H, J=3.5Hz), 6.69 (d, 1H, J=3.5 Hz), 6.62 (s, 1H), 2.80 (t, 2H, J=7.7Hz), 1.67 (s, 2H, J=7.5Hz), 1.4-1.25 (m, 6H), 0.89(t, 3H, J=6.7Hz);

25 4-(5-Hexyl)-thiophene-2yl)-1,3-dithiole-2-one,

2-Chloroacetyl-5-hexylthiophene (3.333 g, 0.0136 mol) and iPrOCS₂K (2.864 g, 0.0164 mol) in acetone (80 cm³). Resuspended in CHCl₃ (15 cm³) and perchloric acid (70%) (3 cm³). Flash column chromatography using hexane/ethyl acetate (10:1) as eluent mix. Product was obtained as brown oil (1.90 g, 0.0067 mol, 49%).

30 ¹H-NMR (CHCl₃/400 MHz): δ 7.62(d, 1H, J=3.7Hz), 6.85(d, 1H, J=3.6 Hz), 4.51(s, 1H), 2.85(t, 2H, J=7.5Hz), 1.7(5, 2H, J=7.5Hz), 1.44-1.29 (m, 6H), 0.91(t, 3H, J=7.0Hz);

Bis(2-(5-hexylthiophene-2-yl)-1,3-dithiole-2-one)nickel TBA, (TBA-Ni-C6)

4-(5-Hexyl)-thiophene-2yl)-1,3-dithiole-2-one (0.5690 g, 2 mmol) in 0.2M NaOMe in EtOH (30 cm³) stirred for 1h under argon. [TBA][Br] (0.323g, 1 mmol) and NiCl₂·6H₂O (0.238g, 1mmol) in EtOH (15 cm³) added and stirred overnight. Red solution concentrated and

35 precipitated with diethyl ether to afford purple solid (0.406 g, 0.5 mmol, 50%).

$C_{40}H_{68}NNiS_6$ CHN (calc.: C:59.02, H:8.42, N:1.72) found: C:58.86, H:8.27, N:1.65; Mass (EI) m/z = 570.0 [M+H]⁺

2-Chloroacetyl-5-octylthiophene,

2-Octylthiophene (5.26 cm³, 0.0241 mol), chloroacetyl chloride (4.25 cm³, 0.0266 mol) and anhydrous aluminium chloride (3.545 g, 0.0266 mol) in dry CS₂ (80 cm³) to afford a dark red suspension which gradually turned brown. Afford an orange oil (mp: 5 °C) (3.82 g, 0.014 mol, 58%).

¹H-NMR (CHCl₃/400 MHz): δ (d, 1H, J=3.6Hz), 6.68 (d, 1H, J=3.6 Hz), 6.62 (s, 1H), 2.79 (s, 2H, J=7.2Hz), 1.67 (s, 2H, J=7.5Hz), 1.3-1.25 (m, 10H), 0.88(t, 3H, J=6.6Hz);

4-(5-Octyl)-thiophene-2yl)-1,3-dithiole-2-one,

2-Chloroacetyl-5-octylthiophene (3.493 g, 0.0128 mol) and iPrOCS₂K (2.678 g, 0.0153 mol) in acetone (80cm³). Resuspended in CHCl₃ (15 cm³), perchloric acid (70%) (3 cm³). Flash column chromatography using hexane/ethyl acetate (10:1) as eluent mix. Product was obtained as brown oil. (2.24 g, 0.007 mol, 56%).

45 ¹H-NMR (CHCl₃/400 MHz): δ 7.62(d, 1H, J=3.7Hz), 6.85(d, 1H, J=3.6 Hz), 4.51(s, 1H), 2.85(t, 2H, J=7.5Hz), 1.7(5, 2H, J=7.5Hz), 1.44-1.29(10H), 0.91(t, 3H, J=7.0Hz);

Bis(2-(5-octylthiophene-2-yl)-1,3-dithiole-2-one)nickel TBA, (TBA-Ni-C8)

50 4-(5-Octyl)-thiophene-2yl)-1,3-dithiole-2-one (0.503 g, 1.6 mmol) in 0.2M NaOMe in EtOH (25 cm³) stirred for 1h under argon. [TBA][Br] (0.258 g, 0.8 mol) and NiCl₂·6H₂O (0.1902 g, 0.8 mmol) in EtOH (15 cm³) 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]⁺; $C_{44}H_{76}NNiS_6$ CHN (calc.: C:60.73, H:8.8, N:1.61) found: C:60.63, H:8.85, N:1.59;

2-Decylthiophene

55 To a solution of thiophene (10.66 cm³, 0.1188 mol) in THF (100 cm³) was added n-BuLi in hexane (2.5M, 47 cm³, 0.115 mol) slowly at -78°C. 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 H₂O, extracted with DE and dried with sodium sulphate. The crude material was obtained as an orange oil upon evaporation. Distillation at 170°C 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 (s, 2H, J=7.3Hz), 1.40-1.25 (m, 14H), 0.91 (t, 3H, J=6.7Hz);

2-Chloroacetyl-5-decylthiophene,

- 5 2-Decylthiophene (2.900 g, 0.013 mol), chloroacetyl chloride (1.13 cm³, 0.014 mol) and anhydrous aluminium chloride (1.614 g, 0.014 mol) in CS₂ (75 cm³) to afford an orange suspension that gradually turned into a dark red solution. Afforded an orange oil. (2.352 g, 0.0078 mol, Yield: 60%).

¹H-NMR (CHCl₃/400 MHz): δ 7.62 (d, 1H, J=3.9Hz), 6.85 (d, 1H, J=3.9 Hz), 4.54 (s, 1H), 2.85 (t, 2H, J=7.5Hz), 1.7 (s, 2H, J=6.8Hz), 1.40-1.20 (14H), 0.88 (t, 3H, J=6.7Hz);

- 10 **4-(5-Decyl)-thiophene-2-yl)-1,3-dithiole-2-one,**

2-Chloroacetyl-5-decylthiophene (3.020 g, 0.010 mol) and iPrOCS₂K (3.30 g, 0.0189 mol) in acetone (90 cm³). Resuspended in CHCl₃ (15 cm³), perchloric acid (70%) (3 cm³). Crude product was obtained as brown oil and sufficiently pure to continue (2.08 g, 0.006 mol, 61%).

¹H-NMR (CHCl₃/400 MHz): δ 6.86 (d, 1H, J=3.6Hz), 6.69 (d, 1H, J=3.6Hz), 6.63 (s, 1H), 2.79 (t, 2H, J=7.7Hz), 1.66 (s, 2H, J=7.7Hz),

- 15 1.4-1.23 (m, 16H), 0.88(t, 3H, 6.9Hz);

Bis(2-(5-decylthiophene-2-yl)-1,2-dithiole)nickel TBA, (TBA-Ni-C10)

4-(5-Decyl)-thiophene-2-yl)-1,3-dithiole-2-one (0.5442 g, 1.6 mmol) in 0.2M NaOMe in EtOH (25 cm³) stirred for 1h under argon. [TBA][Br] (0.258 g, 0.8 mmol) and NiCl₂·6H₂O (0.1902 g, 0.8 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%).

- 20 Mass (EI) m/z= 682.0 [M+H]⁺; C₄₈H₈₄NNiS₆ CHN (calc.: C:62.24, H:9.14, N:1.51) found: C:61.9 H:9.05 N:1.41;

2-Dodecylthiophene

To a solution of thiophene (10.60 cm³, 0.119 mol) in THF (100cm³) was added n-BuLi in hexane (1.6M, 74.5 cm³, 0.119 mol) slowly at -78°C. The solution was stirred for 1h then 1-bromo-dodecane (30.5 cm³, 0.119 mol) was added dropwise. The reaction was warmed to RT and stirred for 3h before being poured into H₂O and extracted with diethyl ether. Dried with sodium sulphate, the crude material was obtained as an orange oil upon evaporation. Distillation at 160°C under reduced pressure afforded a clear oil composed of the target product and unreacted 1-bromo-dodecane in a 2:1 ratio (29.9 g, 0.079 mol, 66%).

- 25 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 (s, 2H, J=6.7Hz), 1.50-1.25 (m, 18H), 0.91 (t, 3H, J=6.7Hz);

2-Chloroacetyl-5-dodecylthiophene,

- 30 2-Dodecylthiophene (as an unpurified 2:1 mixture with 1-bromo-dodecane) (9.160 g, 0.024 mol) was added to a stirred mixture of chloroacetyl chloride (4.25 cm³, 0.027 mol) and anhydrous aluminium chloride (3.540 g, 0.027 mol) in dry CS₂ (90cm³). After evaporation the product was obtained as a brown solid still containing the 1-bromododecane impurity (still in 2:1 ratio by NMR) (10.70 g, 0.0236 mol, 98%).

¹H-NMR (CHCl₃/400 MHz): δ (d, 1H, J=3.9Hz), 6.84(d, 1H, J=3.9Hz), 4.54(s, 2H), 2.84 (t, 2H, J=7.5Hz), 1.69 (s, 2H, J=7.2Hz), 1.43-1.23(18H), 0.87(t, 3H, J=6.7Hz);

- 35 **4-(5-Dodecyl)-thiophene-2-yl)-1,3-dithiole-2-one,**

2-Chloroacetyl-5-dodecylthiophene (4.54 g, 0.010 mol) and iPrOCS₂K (3.30 g, 0.0189 mol) in acetone (90 cm³). Resuspended in CHCl₃ (15 cm³), perchloric acid (70%) (3 cm³). Crude product was obtained as brown solid and sufficiently pure to continue (2.171 g, 0.0059 mol, 59%).

- 40 ¹H-NMR (CHCl₃/400 MHz): δ 6.85(d, 1H, J=3.6Hz), 6.68 (d, 1H, J=3.6 Hz), 6.62 (s, 1H), 2.78 (t, 2H, J=7.9Hz), 1.66 (s, 2H, J=7.9Hz), 1.4-1.25 (m, 18H), 0.89(t, 3H, J=6.6Hz); Mass (EI) m/z= 704.2[M+H]⁺;

Bis(2-(5-dodecylthiophene-2-yl)-1,2-dithiole)nickel TBA, (TBA-Ni-C12)

4-(5-Dodecyl)-thiophene-2-yl)-1,3-dithiole-2-one (0.5890 g, 1.6 mmol) in 0.2M NaOMe in EtOH (25 cm³) stirred for 1h under argon. [TBA][Br] (0.258 g, 0.8 mmol) and NiCl₂·6H₂O (0.1902 g, 0.8 mmol) in EtOH (15 cm³) added and stirred overnight. Red solution concentrated and precipitated with DE to afford purple solid (0.541 g, 5.5 mmol, 69%).

- 45 C₅₂H₉₂NNiS₆ CHN (calc.: C:63.58, H:9.44, N:1.43) found: C:58.57, H:8.86 N:0.43; Mass (EI) m/z= 738.21[M+H]⁺;

Copper (2-(5-butylthiophene-2-yl)-1,2-dithiole)2 TMA, (TMA-Cu-C2)

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).

- 50 NMR: δH (500 MHz; CDCl₃) 1.27 (t, 6H, Me, J =7.5, 1.3 Hz e), 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, -CH=, J =7.2, 1.2Hz b) 6.89 (d, 2H, =CH-, J =11.4, 1.2Hz c)

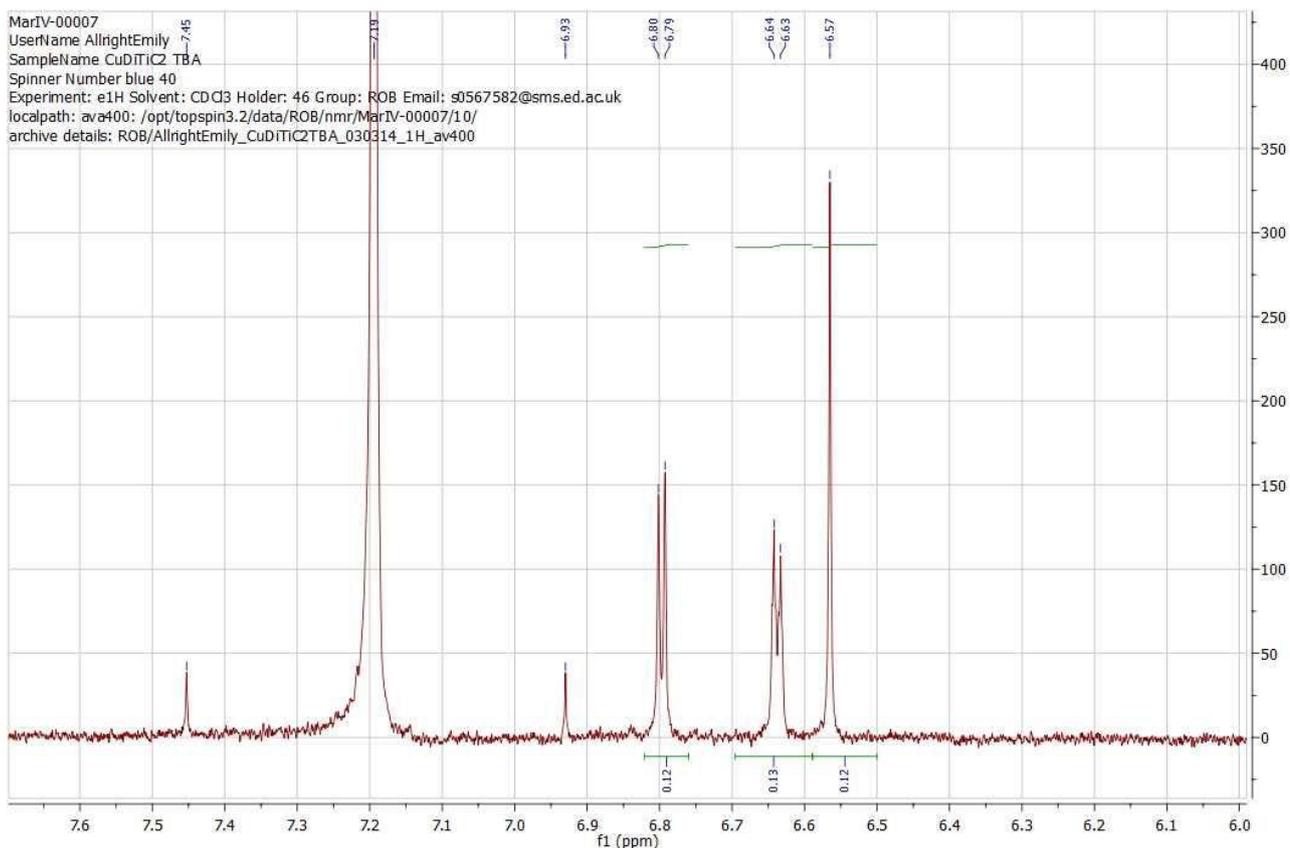


Figure S1: NMR of the aromatic region of TMA[Cu(Ti-C2)₂]

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

5 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.

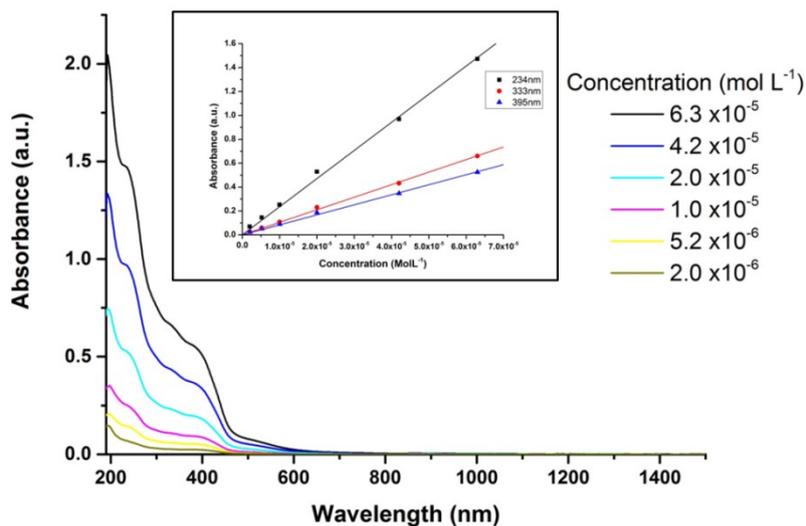


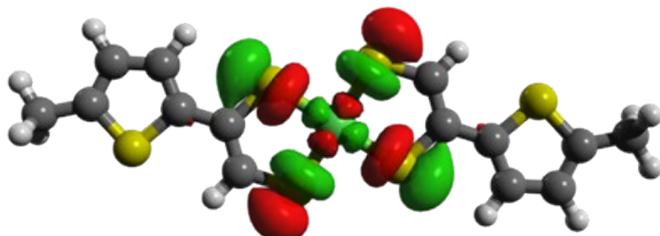
Figure S2: Electronic absorption spectra of several concentrations of TMA[Cu(Ti-C2)₂] salt in MeCN. Inset: Beer-Lambert plot of the absorbance maxima against concentration

Calculations

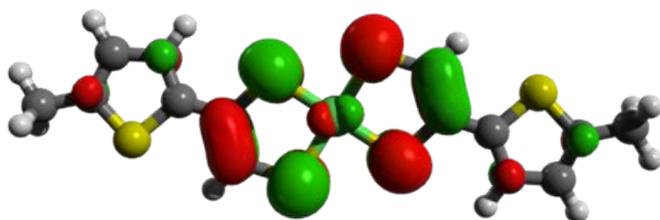
Table S1: Frontier Orbital Energies, calculated at B3PW91/6-31+G(d); Frontier orbitals of neutral Ni-C1 as calculated for B3PW91/6-31+G(d) and displayed with an iso-surface of 0.03 electrons bohr⁻¹.

5

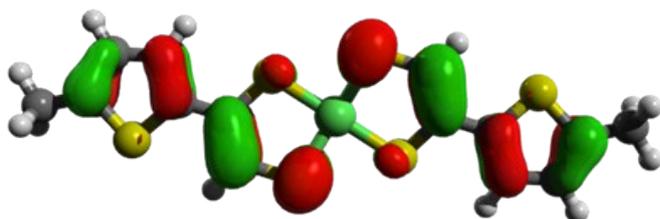
Compound	HOMO		SOMO		LUMO	
	[ht]	[eV]	[ht]	[eV]	[ht]	[eV]
Neutral Ni-C1	-0.20684	-5.63			-0.15631	-4.25
Anionic [Ni-C1] ⁻	-0.18976	-5.16	-0.16553	-4.50	-0.11487	-3.13



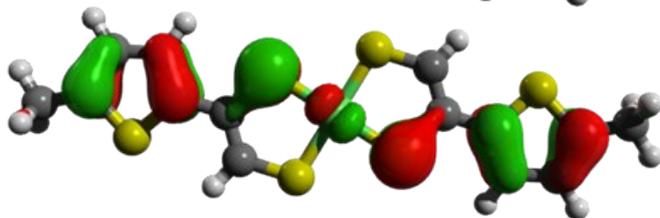
LUMO+1



LUMO



HOMO



HOMO-1

10

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.

Compound	λ calc [nm]	Oscillator Strength	Orbitals	Contribution
Neutral Ni-C1	949	0.5859	HOMO -> LUMO	97

	354	0.6945	HOMO -> LUMO+2	75
	297	0.7675	HOMO-1 -> LUMO+3	86
Anionic [Ni-C1] ⁻	1131	0.2497	HOMO -> SOMO	98
	545	0.0226	SOMO->LUMO+2	40
	398	0.1349	various	

EPR

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

Compound	g1	g2	g3
TBA-Ni-C2	2.123	2.004	1.997
Compound	g	g _⊥	
TBA-Ni-C4	2.103	2.030	
TBA-Ni-C6	2.096	2.024	
TBA-Ni-C8	2.099	2.029	
TBA-Ni-C12	2.106	2.037	

5

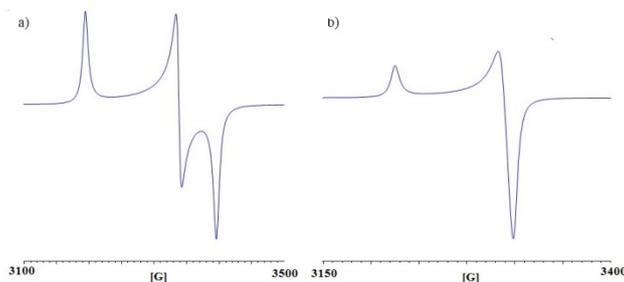


Figure S3: Room temperature powder EPR spectra of a) TBA-Ni-C2 and b) TBA-Ni-C4

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.

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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 5×10^{-4} mol dm^{-3} in acetonitrile. Deposition at 1.06 V resulted in black fibres rather than a uniform film for Ni-C2.

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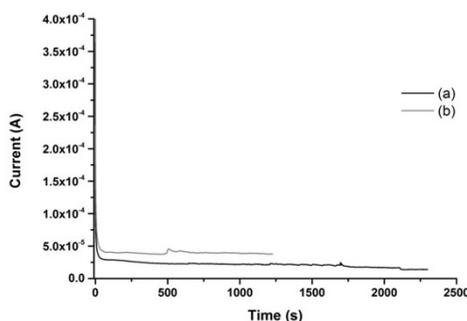


Figure S4: Deposition current of 2.40×10^{-2} Ccm⁻² of (a) Cu-C2 and (b) Ni-C2

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Electrodeposited films

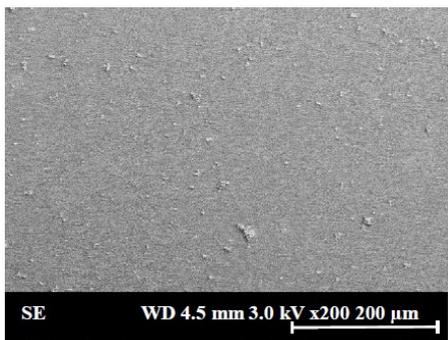


Figure S5: SEM images of the features of Cu-C2

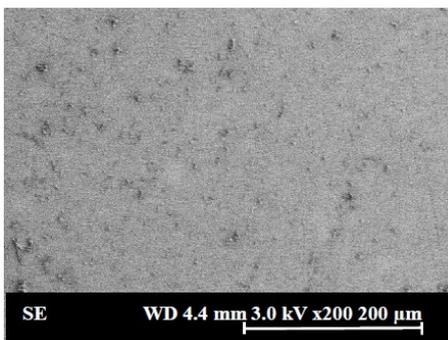


Figure S6: SEM images of the features of Ni-C2

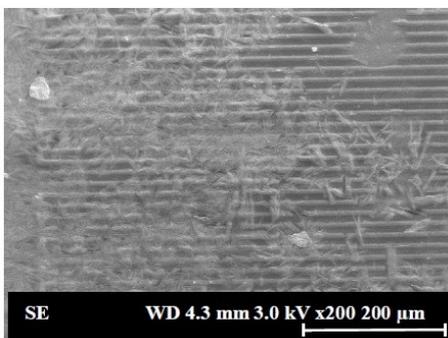


Figure S7: SEM images of Cu-C2 electrodeposited on 8 μm x 8 μm interdigitated electrodes

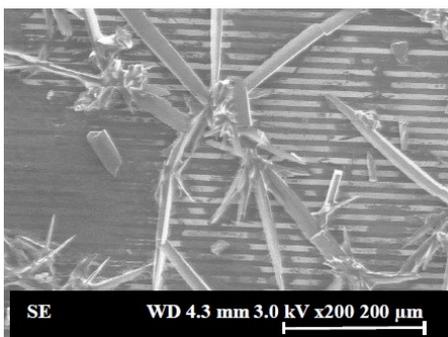


Figure S8: SEM images of Ni-C2 electrodeposited on 8 μm x 8 μm interdigitated electrodes

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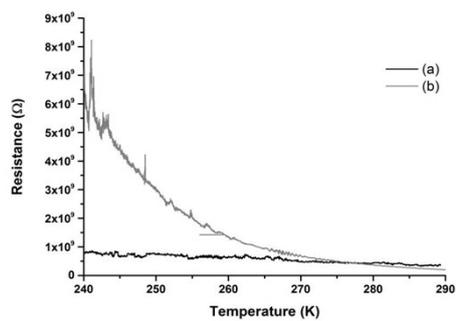


Figure S9: Plot of resistance against temperature for the cooling of 8 μm x 8 μm interdigitated electrodes of (a) Cu-C2 and (b) Ni-C2