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Electrochemical Deposition of Highly-conducting Metal Dithiolene Films

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Electrochemical deposition has been used to prepare a thin film of neutral 4',4-(3-alkyl)-thiophene-5',5-hydogen-nickel and copper dithiolenes (Ni-C2, Cu-C2). The application of molecular electrodeposition provides a means to solution process molecular semiconductors of poor solubility, which results from the strong intermolecular interaction required for charge transport. Both Ni-C2 and Cu-C2 form continuous 10 thin films that show intense NIR absorptions, extending to 1800 nm and 2000 nm respectively giving evidence for the strong intermolecular interactions in the solid state. Both films are highly conducting and temperature dependence of resistance gave an activation energy of 0.42 eV and 0.072 eV respectively, with the near-metallic behaviour of Cu-C2 attributed to the additional presence of an unpaired electron.

Introduction

15 Metal bis-1,2-dithiolene complexes, comprising two unsaturated bidentate ligands, each bound to a central atom through two sulfur donor atoms, have been investigated since the 1960s.[1] While their magnetic properties have been of interest,[2] it is their optical and electronic properties in particular that have made 20 them attractive candidates for study for the last 50 years.[2,3,4,5] Many neutral metal dithiolene complexes show strong absorptions in the near infrared region (NIR) and have been successfully employed in Q-switching lasers, photodetectors,[6] semiconductors for field-effect transistors,[7] molecular metals and 25 superconductors.[8,9,10,11]

The unsaturated, non-innocent ligands give rise to a square planar core geometry with metals such as Ni, Pd or Pt, and reversible redox processes.[12] These properties, tunable by changing the 30 metal, extending the ligand conjugation or varying the side chains, make dithiolene complexes ideal for charge transport if the packing of the molecule results in strong intermolecular interaction.[2] One very intruiging area of dithiolene complex research has involved the synthesis of single-component 35 molecular metals through strong intermolecular interactions that close the bandgap in the solid.[13,14,15,16] A serious challenge exists in this field however, since the necessary strong intermolecular interactions typically result in dithiolene complexes having extremely-low solubility which prohibits processing or device 40 incorporation. Furthermore, this situation can be viewed as symptomatic of molecular conducting materials in general, where the desirable strong intermolecular interactions are always balanced against the need to maintain solubility for solution processing, or volatility for vapour processing.[17,18,19,20]

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We have previously presented electrochemical molecular deposition as a suitable method for the formation of films of insoluble molecules onto conductive substrates. The method involves disolving the more soluble anionic form of a molecule, 50 which is then electrochemically oxidised into the insoluble neutral form which deposits onto the conducting substrate.[21,22,23]

The electrodeposition of metal dithiolene molecules, based on [Ni(b-3ted)$_2$], was initially investigated by Dalgleish et al. 55 However, the film conductivity was hindered by their packing, owing to twisting of the peripheral thienyl groups.[22] Further work gave a film of neutral [Cu(mi-5hdt)$_2$], demonstrating unique stabilisation of a small, neutral, NIR-absorbing Cu-dithiolene complex in the solid state,[23] contrasting with anionic Cu-60 dithiolenes which are non NIR absorbing.[24,25,26]

In this work, we have designed and studied new Ni and Cu dithiolene complexes, aimed at achieving highly-conducting single-component molecular films. The novel 4',4-(3-alkyl)-65 thiophene-5',5-hydogen-nickel and copper dithiolenes were prepared in their soluble, monoanionic form. By including sterically undemanding H-atoms on the dithiolene, the ligands were designed to enable an extended, largely planar structure to occur in the solid state, such that strong intermolecular 70 interactions could be achieved to give high film conductivity, as observed in similar α-quarterthiophene analogues.[27,28,29] Electrochemical deposition of the neutral molecules through oxidation of the soluble anions was then used to form the films. Due to the very strong intermolecular interactions that result, the 75 neutral complexes in the films are completely insoluble.

Results and Discussion

The complexes were sythesised through a precursor route tailored to yield the correct functionality of the back bone,[8,30,31] via the α-halo carbonyl and its subsequent reaction with a xanthate-ester, 80 followed by the acid catalysed ring closure to produce the 1,3-dithiolene-2-one ligand precursor. This can then be conveniently converted to the dianion in situ and reacted with the nickel dichloride salt to give the mono anionic complex (Fig. 1). The identity and purity of the sythesised complexes were shown by 85 NMR, MS and CHN (ESI, Fig. S1†). A series of Ni complexes with varying alkyl chains was synthesised (Fig. 1) and for comparison of the electrodeposited products, the Cu analogue with ethyl chain was also synthesised.
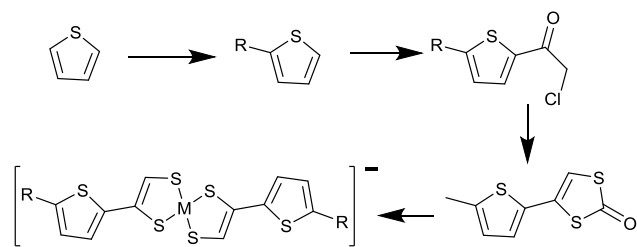
Figure 1: Synthesis of anionic dithiolene complexes as tetrabutylammonium salts for M = Ni, R = Ethyl, Butyl, Hexyl, Octyl, Decyl, Dodecyl, labelled as TBA-Ni-CX (X = 2, 4, 6, 8, 10, 12 respectively); and as tetramethylammonium salt for M = Cu, R = Ethyl, labelled as TMA-Cu-C2.

Electronic Absorption of TBA-Ni-CX compounds

The absorption spectrum for TBA-Ni-CX (TBA = tetrabutylammonium) is shown in Figure 2, with all compounds showing essentially identical spectra with two major peaks at 319 nm and 982 nm and molar absorption coeffcients of 31700 $M^{-1}cm^{-1}$ and 10500 $M^{-1}cm^{-1}$, respectively. Extension of the alkyl chain had negligible impact on the absorbance spectra as any increase in electron inductive effect is not significant and the thienyl pendant groups are already electron rich. The small band in the visible region is responsible for the dark red appearance of the salt. Significant red-shifts compared with less-conjugated analogues[28] are the result of the pendant thiophene rings giving more delocalised frontier orbitals and a decrease in the energy gap, in keeping with increased delocalisation, enabled by only containing two pendant thienyl groups, allowing for greater planarity.

DFT and TD-DFT calculations were carried out on the neutral and monoanionic form of Ni-C1 using B3PW91/6-31+G(d) incorporating dichloromethane (DCM) as the solvent and the TD-DFT results are included in Figure 2. Reasonable qualitative agreement with the experimentally observed spectrum is observed, as although the energy of the NIR transition was underestimated by 1300 cm^{-1}, the peak at 546 nm was clearly reproduced. Similar calculations on the neutral species showed the NIR transition to be only slightly higher in energy and without the peak in the visible region. This was expected as NIR absorption is due to the HOMO → SOMO/LUMO (for anion/neutral) transition of the π electron, while the visible transition was primarily due to the SOMO→ LUMO+3 transition. The former is expected to be stronger in the neutral form while the latter should not occur.[32] This is a well documented effect for nickel dithiolenes and electrochemical reduction of the complexes has been used to switch the NIR absorption.[32,33,34]
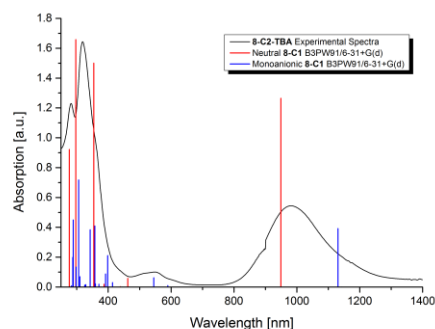

Figure 2: Experimental spectrum of TBA-Ni-C2 in DCM and calculated transitions for monoanionic and neutral Ni-C1 calculated at B3PW91/6-31+G(d) using DCM within the PCM

In contrast to the anionic Ni complexes, TMA-Cu-C2 showed no low energy absorption (Figure S2†), which is as expected since the additional electron prevents the NIR HOMO → SOMO transition observed in the Ni analogue.

EPR

TBA-Ni-CX were investigated in the solid state by room temperature powder EPR spectroscopy (Fig S3, Table S3). Except for TBA-Ni-C2, which showed a rhombic type signal with g_1 = 2.123, g_2= 2.004 and g_3= 1.997, all compounds displayed axial type signals with g∥ and g⊥ lying at around 2.1 and 2.03 respectively. This corresponds to results reported for similar nickel centres where ^{61}Ni (I = 3/2) enriched samples were used to show that 30-40% of the spin density resides in the metal d orbitals while the rest is spread over the ligand system,[32,35,36] also backed up by electronic structure calculations.[34] While the axial symmetry is expected for the square planar centres, the slight distortion giving rise to the rhombic type signal for compound TBA-Ni-C2 is not unusual and has been reported before for other nickel dithiolene salts.[36,37]

Electrochemistry

TBA-Ni-CX exhibited completely reversible redox processes in DCM at around -0.3 V and -1.1 V corresponding to the changes from the neutral to monoanionic then dianionic form. Additional, irreversible oxidations close to the solvent window were also observed. The energy of the LUMO of the neutral complex was estimated from the first reduction (Table 1) and a representative voltammogram is shown in Figure 3. The small changes observed between the compounds lie within the experimental error and in combination with the spectroscopic data suggest that the compounds have very similar electronic properties.

Table 1: Ni-CX and Cu-C2 redox potentials against Fc/Fc$^+$. $E_{1/2}$ for reversible potentials and peak potential for irreversible processes*, plus extracted LUMO energy values.[38]

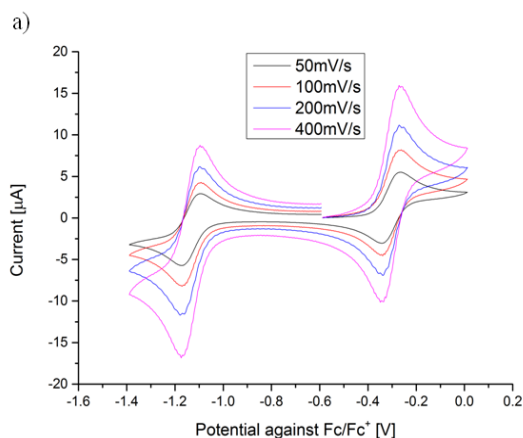| Compound	E_{red2} [V]	E_{red1} [V]	E_{ox} [V]	LUMO [eV]
Ni-C2	-1.13	-0.30	0.83*	-4.42
Ni-C4	-1.14	-0.32	0.83*	-4.41
Ni-C6	-1.15	-0.33	0.82*	-4.39
Ni-C8	-1.12	-0.32	0.81*	-4.40
Ni-C10	-1.13	-0.30	0.83*	-4.42
Ni-C12	-1.14	-0.31	0.83*	-4.41
Cu-C2	-1.37*	-0.32		-4.40

a)

Figure 3: CV voltammograms of TBA-Ni-C2 in DCM at different scan rates, using 0.3 M [TBA][BF$_4$] as supporting electrolyte

[5] The potential of E_{red1} and thus the calculated LUMO energy are very similar to those observed for the phenyl substituted analogues, consistent with the small contributions of the pendant groups to the LUMO.[39,40] For Cu-C2, the 1-/0 oxidation, important for the subsequent electrodeposition experiments, is [10] similar to that of the Ni complexes. The E_{ox} value of 0.82 V for the Ni complexes is very similar to that observed for the phenyl substituted analogues, and slighlty smaller than the previously reported tetrakis thienyl substituted analogue, suggesting that the increased planarity of the thienyl ring may allow for more [15] delocalisation of the additional charges, while avoiding the electron induction effects of the additional, twisted thienyl moieties. The values, however, remain well above that of the more delocalised [Ni(dmit)$_2$] (dmit = 2-thioxo-1,3-dithiole-4,5-dithiol).[41]

[20]

In contrast to DCM, when carrying out electrochemistry in acetonitrile solution, film formation was observed if a potential was applied sufficient to form the neutral compound, resulting in CV characteristics similar to those observed in previous studies [25] of metal dithiolene electrodeposition.[22,23] This contrasts with CV in the DCM solution in which no electrodeposition of the neutral species was observed. We note also that no electropolymerisation was observed, following the irreversible oxidation, attributed to the terminal alkyl groups as expected,[42] and evidenced by re-[30] dissolution of the molecular film upon re-reduction of the molecules.

Electrodeposition of Ni-C2 and Cu-C2

Films of Ni-C2 and Cu-C2 were electrodeposited onto FTO [35] (fluorine-doped tin oxide) conducting glass and interdigitated electrode substrates to investigate the optical and charge transport properties of both films. 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. Uniform films occurred at 0.96 V for Cu-C2 [40] and at 0.86 V for Ni-C2. Typical depositions of Cu-C2 at 0.96 V, (a), and Ni-C2 at 0.86 V, (b), in 0.1M TBABF$_4$ MeCN electrolyte are shown in Figure 4.
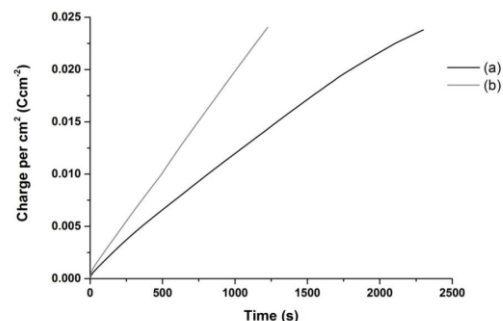

Figure 4: Deposition of 2.40×10^{-2} Ccm^{-2} of (a) Cu-C2 at 0.96 V and (b) [45] Ni-C2 at 0.86 V

The charge per cm^2 of the deposition of the films of Cu-C2 and Ni-C2 onto FTO continues to rise steadily with time suggesting that both dithiolene films are conductive and transport the current [50] to the surface of the formed film.

The initial current is very large due to the formation of the double layer and the initial adsorption of any dithiolene monoanions present at the surface of the FTO substrate. It then decreases [55] rapidly until it levels off, decreasing very slowly which indicates that the formation of the film is diffusion-dependent (Figure S4†). This is probably due to the formation of a continuous layer of neutral complex on the substrate surface, since the deposition of molecules onto already-deposited molecules is more energetically [60] favourable than the nucleation of molecules on the substrate surface.
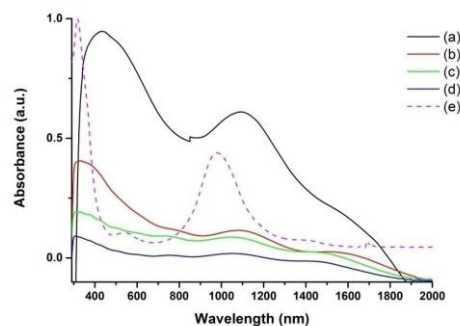
Electronic Absorption of Ni-C2 films

Figure 5: Electronic Absorption of Ni-C2 films: (a) 1.54×10^{-1} Ccm^2, (b) [65] 6.38×10^{-2} Ccm^{-2}, (c) 3.85×10^{-2} Ccm^{-2}, (d) 2.40×10^{-2} Ccm^{-2} and (e) TBA-Ni-C2 in DCM for comparison

Table 2: Peak positions of the Ni-C2 films shown in Figure 5

Film (Ccm^{-2})	Peak Positions (nm)			
2.40×10^{-2} (a)	305	758	1051	1455
3.85×10^{-2} (b)	305	757	1050	1464
6.38×10^{-2} (c)	319	786	1091	1556
1.54×10^{-1} (d)	434		1095	1668
Solvent (e)	316	551	980	

[70] The electronic absorption of the thinnest film on FTO has peaks at 305 nm, 758 nm, 1051 nm and 1455 nm (Fig. 5 (a)). The new band at low energy implies strong intermolecular interactions, most likely by π-π stacking. Apart from the broad peak at around 300 nm, all the other peaks have red-shifted and become broader, [75] also attributed to π-π stacking. Films with a low charge per cm^2,

less than 5.00×10^{-2} Ccm^{-2}, have similar peak positions, with the exception of the last peak at around 1400 nm, whereas for the thicker films the peaks start to further red-shift with increasing thickness, probably due to an increase in the extensive
5 intermolecular interactions.

Electronic Absorption of Cu-C2 films
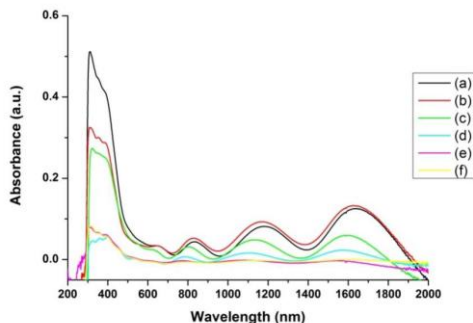
10 **Figure 6:** Electronic absorption of Cu-C2 films: (a) 5.68×10^{-2} Ccm^{-2}, (b) 4.35×10^{-2} Ccm^{-2}, (c) 2.38×10^{-2} Ccm^{-2}, (d) 5.80×10^{-3} Ccm^{-2}, (e) 2.94×10^{-3} Ccm^{-2} and (f) 2.30×10^{-3} Ccm^{-2}

The films show similar absorptions to the parent TMA-Cu-C2 in solution, between 300 nm and 600 nm, although red-shifted in a
15 similar way to the Ni-C2 species above. However, there are also three new absorptions at 830 nm, 1170 nm and 1628 nm for thicker films deposited via higher charge passed per cm^2, with corresponding weak absorptions in the thinner films. The presence of these two NIR peaks and one MIR (mid-IR) peak
20 confirms that the neutral Cu-C2 has been formed, as this complex is now isoelectronic with the NIR absorbing monoanionic TBA-Ni-C2 complex. The peaks are also very broad covering the range of 800 nm to 2000 nm compared to the previously electrodeposited neutral Cu(mi-5hdt)$_2$, which had a peak from
25 800 nm to 1500 nm.[23] This can be attributed to the greater planarity of Cu-C2 with only one substitutent on each ligand.

Scanning Electron Microscopy
SEM imaging of several films of Cu-C2 and Ni-C2 was
30 performed and representative images of the surface of the films are shown in Figures 7 and 8 and Figures S5 and S6†.
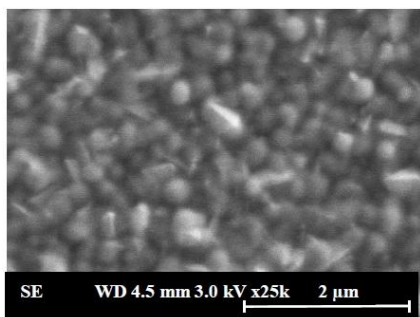

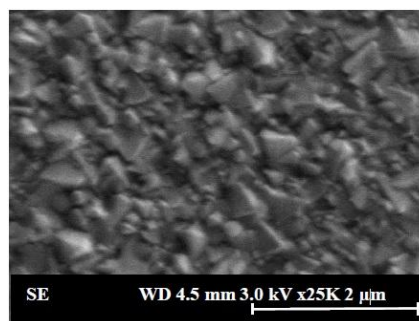**Figure 7:** SEM image of Cu-C2

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Figure 8: SEM images of Ni-C2

The continuous films of both Ni-C2 and Cu-C2 contain features
40 of between 50 nm and 500 nm in size. SEM images of the interdigitated electrodes were recorded and the results are shown in Figures S7 and S8†. The SEM images of the interdigitated areas show that both dithiolenes deposit as a combination of a thin film and fibres. The Cu-C2 has deposited as an even layer
45 with small needle-shaped fibres crossing the electrodes. The Ni-C2 has also deposited as a thin film plus needle-shaped fibres, but in this case both types of deposition also seem to be in competition as there is no thin film for about 20 μm where the fibres have formed.

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Resistance measurements
The resistance of the electrodeposited films of Cu-C2 and Ni-C2 was measured as a function of temperature upon cooling (Figure 9, Figure S9†). The activation energy of the complexes can be
55 calculated from the temperature-dependent resistance using the following equation,

$$Ln(\sigma) = Ln(\sigma_0) - \frac{E_a}{R}\frac{1}{T}$$

where σ is the conductivity, σ_0 is the pre-exponential factor, E_a is
60 the activation energy, R is the gas constant and T is the temperature in K. This is illustrated by a plot of ln(σ) against 1/T where the gradient of the plot is -E_a/R.

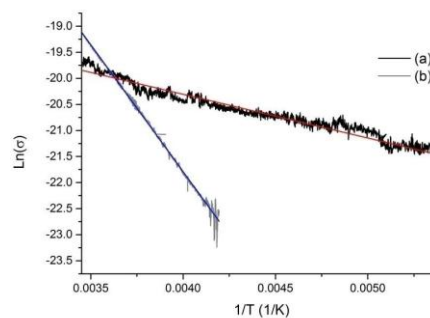**Figure 9**: Plot of Log(σ) against 1/T of (a) Cu-C2 and (b) Ni-C2

65

The activation energies of Cu-C2 and Ni-C2 were calculated to be 0.072 eV and 0.42 eV respectively. Both measurements suggest that the films contain strongly π-stacked molecules, which result in significant intermolecular interaction, showing a
70 narrow gap between the occupied and unoccupied levels. The activation energy of the Ni-C2 film broadly agrees with the electronic absorption measurements (Fig. 5), where the absorption onset around 1800 nm corresponds to a gap of around 0.7 eV and, assuming similar behaviour to a band semiconductor,

the activation energy equals the bandgap divided by two. The Cu-C2 activation energy is significantly smaller than that of Ni-C2 and does not correspond to a similar transition in the electronic absorption measurements. For Cu-C2 (Fig. 5) the absorption onset around 2000 nm corresponds to a separation of 0.6 eV. This suggests that the extra unpaired electron in the radical Cu-C2 is playing a role, giving an exceptionally low activation energy. The resulting, almost-metallic behaviour, is reminiscent of the isoelectronic Au-*bis*-dithiolene complexes that show metallic conductivity.[15]

Conclusions

We have achieved highly-conducting thin films of neutral metal-*bis*-dithiolene complexes, which in the case of M = Cu shows nearly metallic properties. This adds distinctive new examples to the limited group of such highly-conducting single-component molecular materials. As is inevitable for molecular semiconductors, our extension of the electronic delocalisation to increase intermolecular interaction also reduced the solublity of the neutral complexes and precluded solution processing. To overcome this, we applied a molecular electrodeposition approach, which we previously introduced, enabling solution processing via the soluble anionic complexes. This approach offers the possibility to further extend conjugation on the molecules, while still maintaining solution processability.

Acknowledgements

Notes and references

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† Electronic Supplementary Information (ESI) available: Synthesis of compounds and precursors; UV/Vis of TMA[Cu(Ti-C2)₂]; Computational tables; EPR spectra; SEM of electrodeposited films; resistance against T plots. See DOI: 10.1039/b000000x/

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