

Formation of stable neutral copper *bis*-dithiolene thin films by potentiostatic electrodeposition

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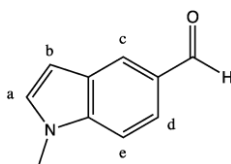
Supplementary Information

Synthesis

All reagents were used as received, unless otherwise stated. Where necessary, solvents were dried using standard laboratory methods.¹

Methylindole-5-carboxaldehyde

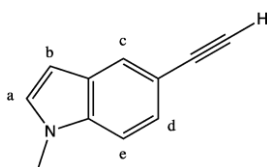
To an oven dried microwave vial (25 ml), equipped with a Teflon-coated stirrer bar, was added freshly recrystallised 5-bromo-1-methylindole (3.15 g, 15.0 mmol) and Mg turnings (401 mg, 16.5 mmol) and the flask flushed with nitrogen before being sealed using an aluminium open-top seal with a polytetrafluoroethylene (PTFE) faced septum. Dry THF (15 ml) was charged via syringe and the reaction mixture microwave-irradiated for 30 mins at 120°C, whereupon the flask was cooled to 0°C, and dry DMF (1.16 ml, 15.0 mmol) was added via syringe. The reaction mixture was stirred for 30 mins at 0°C before being warmed to room temperature. The reaction mixture was poured into a saturated solution of NH₄Cl (50 ml), and extracted with Et₂O (4 x 20 ml). The organics were combined and dried over MgSO₄ and solvent removed under reduced pressure. The product was purified by recrystallisation from hexane (2.32 g, 97 %). δ_H (250 MHz; CDCl₃) 3.84 (s, 3H, -NMe), 6.65 (dd, 1H, J = 3.1, 0.8 Hz, H_b), 7.15 (d, 1H, J = 3.1 Hz, H_a), 7.40 (d, 1H, J = 8.5 Hz, H_e), 7.80 (dd, 1H, J = 8.5, 1.5 Hz, H_d), 8.15 (dd, 1H, J = 1.5, 0.8 Hz, H_c), 10.03 (s, 1H, C(O)H).



5-Ethyny-1-methylindole

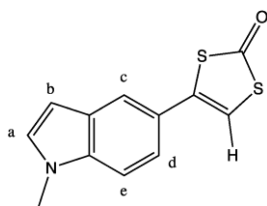
To a stirred suspension of bromomethyltriphenylphosphonium bromide (6.07 g, 13.9 mmol) in dry THF (40 ml) at -78°C was added portion-wise potassium *tert*-butoxide (3.12 g, 27.8 mmol). The reaction mixture was stirred at -78°C for 30 mins, during which time the yellow ylid formed. A solution of

1-methylindole-5-carboxaldehyde (2.21g, 13.9 mmol) was added in THF (10 ml), and the reaction was stirred for a further 30 mins at -78°C before being warmed to room temperature overnight. After 12 hours, the reaction was shown to be complete by the complete consumption of the aldehyde, observed by thin layer chromatography (TLC) and the reaction quenched by addition of NH₄Cl solution (100 ml). The product was extracted with EtOAc (4 x 100 ml) and the organics washed with brine and dried over MgSO₄. The crude product was purified by flash chromatography (Hex:EtOAc, 6:1), yielding the target material as a pale yellow oil (1.22 g, 57 %). δ_H (250 MHz; CDCl₃) 3.00 (s, 1H, CCH), 3.76 (s, 3H, -NMe), 6.47 (dd, 1H, J = 3.1, 0.8 Hz, H_b), 7.06 (d, 1H, J = 3.1 Hz, H_a), 7.24 (d, 1H, J = 8.5 Hz, H_e) 7.35 (dd, 1H, J = 8.5, 1.5 Hz, H_d), 7.81 (dd, 1H, J = 1.5, 0.8 Hz, H_c).



4-(1-methyl-5-indol-5-yl)-[1,3]dithiol-2-one

To a stirred solution of 5-ethynyl-1-methylindole (1.16 g, 7.47 mmol) in benzene (75 ml) was added AIBN (551 mg, 3.36 mmol) and diisopropylxanthogen disulfide (2.22 g, 8.22 mmol), and the reaction mixture stirred at reflux under a flow of nitrogen for 24 hours. The solvent was removed under reduced pressure and the crude product purified by trituration in warm methanol (6 hours), yielding pure product after filtration (1.26 g, 68 %). δ_H (360 MHz; CDCl₃) 3.82 (s, 3H, -NMe), 6.52 (d, 1H, J = 3.1 Hz, H_b), 6.73 (s, 1H, C(S)H), 7.11 (d, 1H, J = 3.1 Hz, H_a), 7.30 (dd, 1H, J = 8.5, 1.5 Hz, H_d) 7.34 (d, 1H, J = 8.5 Hz, H_e), 7.67 (bd, 1H, H_c).

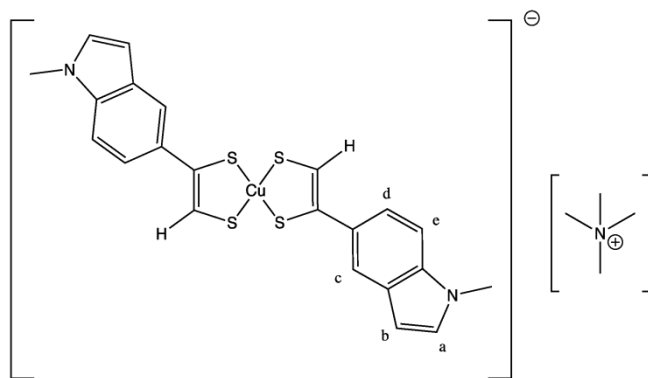


[Cu(mi-5edt)₂] (1)

To a stirred solution of freshly cut sodium (95 mg, 4.12 mmol) in dry degassed MeOH (50 ml) under nitrogen was added 4-(1-methyl-5-indol-5-yl)-[1,3]dithiol-2-one (509 mg, 2.06 mmol), and the solution stirred with gentle warming for 1 hour until complete dissolution. A solution of CuCl₂·2H₂O (175 mg, 1.03 mmol) in MeOH (25 ml) was added dropwise over 10 mins. A brown precipitate formed immediately and was stirred further for 1 hour in air, whereupon pure **1** could be isolated by filtration and washing with MeOH, affording the title compound as a brown precipitate (145 mg, 28 %). Anal. calcd. for C₂₂H₁₈N₂S₄Cu: C, 52.62; H, 3.61; N, 5.58; S, 25.54; found C, 52.69; H, 3.67; N, 5.63; S, 25.47.

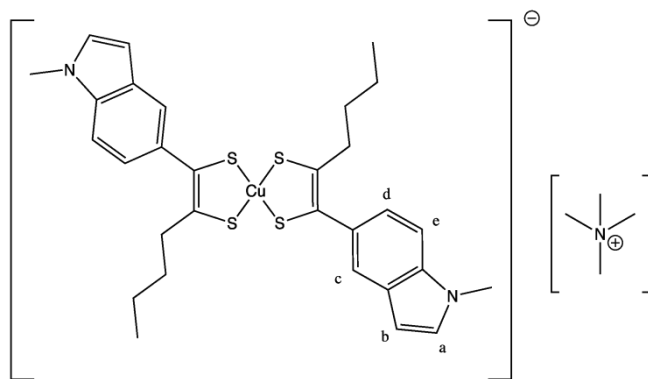
[TMA][Cu(mi-5edt)₂] ([TMA][1])

To a stirred solution of 4-(1-methyl-5-indol-5-yl)-[1,3]dithiol-2-one (297 mg, 1.20 mmol) in THF (10 ml) was added [TMA][OH]·5H₂O (478 mg, 2.64 mmol) in MeOH (2 ml). After 5 mins, CuCl₂·2H₂O (102 mg, 60 μmol) in MeOH (2 ml) was added and the reaction mixture stirred at room temperature overnight. Pure [TMA][1] was filtered off as a dark brown precipitate and washed with EtOH (292 mg, 42 %). δ_H (500 MHz; DMSO) 3.08 (s, 12H, TMA), 3.77 (s, 6H, -NMe), 6.33 (s, 2H, C(S)H), 6.39 (dd, 2H, J = 3.0, 0.5 Hz, H_b), 7.27 (d, 2H, J = 3.0 Hz, H_a), 7.31 (d, 2H, J = 8.7 Hz, H_e), 7.44 (dd, 2H, J = 8.7, 1.8 Hz, H_d), 7.70 (dd, 2H, J = 1.8, 0.5 Hz, H_c); anal. calcd. for C₂₆H₃₀N₃S₄Cu: C, 54.18; H, 5.25; N, 7.29; found C, 54.32; H, 5.37; N, 7.15; λ_{max} = 393 nm (ϵ = 11.2 × 10³ M⁻¹cm⁻¹).



[TMA][Cu(mi-5hdt)₂] ([TMA][2])

To a stirred solution of 4-Butyl-5-(1-methyl-5-indol-5-yl)-[1,3]dithiol-2-one (247 mg, 0.815 mmol) in THF (9 ml) was added [TMA][OH]·5H₂O (324 mg, 1.79 mmol) in MeOH (1 ml). After 5 mins, CuCl₂·2H₂O (72 mg, 0.407 mmol) in MeOH (1 ml) was added and the reaction mixture stirred at room temperature overnight. Pure [TMA][2] was filtered off as a bronze precipitate and washed with EtOH (292 mg, 46 %). δ_H (500 MHz; DMSO) 0.76 (t, 6H, J = 7.4 Hz, -CH₃), 1.18 (m, 4H, -CH₂CH₃), 1.48 (m, 4H, -CH₂CH₂CH₃), 2.25 (t, 4H, J = 7.6 Hz, CSCH₂), 3.09 (s, 12H, TMA), 3.77 (s, 6H, -NMe), 6.40 (d, 2H, J = 3.0 Hz, H_b), 7.09 (dd, 2H, J = 8.4, 1.1 Hz, H_d), 7.29 (d, 2H, J = 3.0 Hz, H_a), 7.33 (d, 2H, J = 8.4 Hz, H_e), 7.44 (d, 2H, J = 1.1 Hz, H_c); anal. calcd. for C₃₄H₄₆N₃S₄Cu: C, 59.31; H, 6.73; N, 6.10; found C, 59.22; H, 6.63; N, 5.98; λ_{max} = 418 nm (ϵ = 26.2 × 10³ M⁻¹cm⁻¹).



UV/Vis/NIR Spectroscopy

Measurements were recorded in laboratory grade solvents in a quartz cell of path length $l = 10$ mm on a Perkin-Elmer Lambda 9 spectrophotometer, controlled by a datalink PC, running UV/Winlab software v1.6 (Perkin-Elmer). Electrogenerated films on fluorine doped tin oxide (FTO) coated glass electrodes were fixed perpendicular to the beam in the cavity.

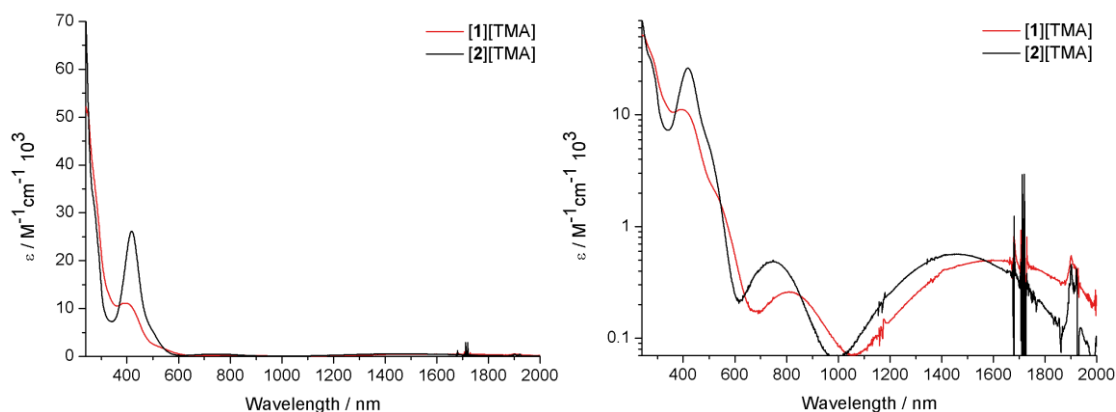


Fig. S1: Experimental UV/Vis/NIR absorbance spectra, where the absorption intensity is given as the molar extinction coefficient (ϵ): (left) [TMA][1] and [TMA][2] in MeCN showing weak absorptions in the Vis/NIR region, and a strong absorption in the UV/Vis region; (right) a logarithmic plot of [TMA][1] and [TMA][2] in MeCN, to visualise the weak Vis/NIR absorptions.

Electrochemistry

Electrochemical experiments were performed in a glass cell in dry solvent [dimethylformamide (DMF) (Sigma-Aldrich) or acetonitrile (MeCN) (Sigma-Aldrich)], and solutions were degassed with N_2 before use. The electrolyte used for analysis was tetrabutylammonium tetrafluoroborate ($TBABF_4$), and was prepared from tetrafluoroboric acid and tetrabutyl ammonium hydroxide, and recrystallised 5 times from water and dried under vacuum at $60^\circ C$ for 2 weeks. All electrochemical data were obtained using a type III μ Autolab potentiostat, connected to a PC, and controlled using General Purpose Electrochemical System (GPES) software. Cyclic voltammetry was performed at room temperature on a ~ 1 mM monomer solution, with 0.3 M electrolyte (except for DMF where 0.1 M was sufficient) in a three electrode cell. The working electrode was a ~ 3 mm² Pt disc, or a FTO coated glass slide (exposed area ~ 1 cm²). The reference electrode was Ag/AgCl (sat. KCl), calibrated against a ferrocene/ferrocenium reference (+0.55 V) in the background electrolyte, and the counter electrode was a Pt rod.

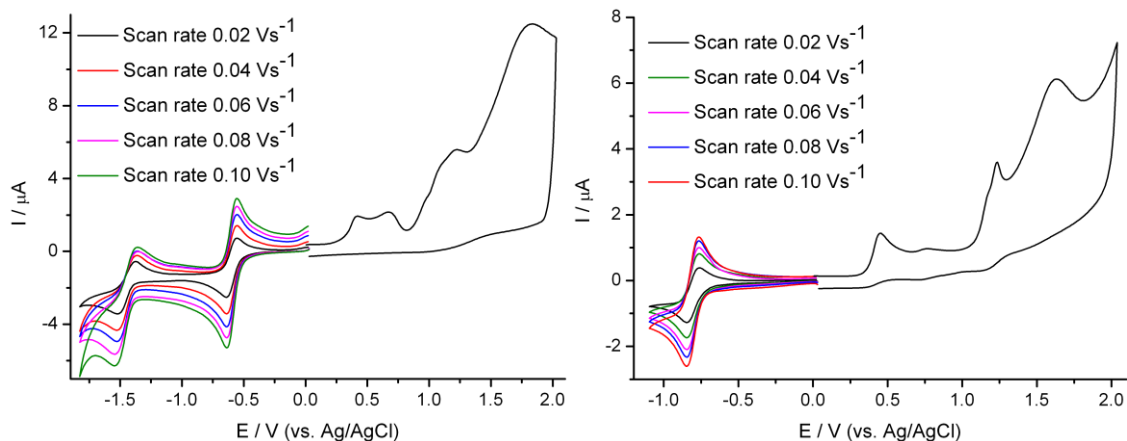


Fig. S2: Cyclic voltammetry in 0.1 M TBABF₄/MeCN, measuring the current (*I*) response to a cycled potential (*E*): (left) [TMA][1] shows two reduction processes, with the process at $E_{1/2}^1 = -1.45$ V shown to be irreversible, and the process $E_{1/2}^2 = -0.59$ V shown to be reversible. The complex also undergoes several irreversible oxidation processes at positive potentials; (right) [TMA][2] shows one reversible reduction process at $E_{1/2}^2 = -0.80$ V, as well as several irreversible oxidation processes at positive potentials.

Name	$E_{1/2}^1$ / V	$E_{1/2}^2$ / V	E_{ox}^3 / V
[TMA][1]	-1.45 [§]	-0.59	0.42*
[TMA][2]	-	-0.80	0.45*

Table S1: Redox potentials of [TMA][1] and [TMA][2] in 0.1 M TBABF₄/MeCN. All processes are reversible, unless otherwise stated; *irreversible, [§]quasi reversible.

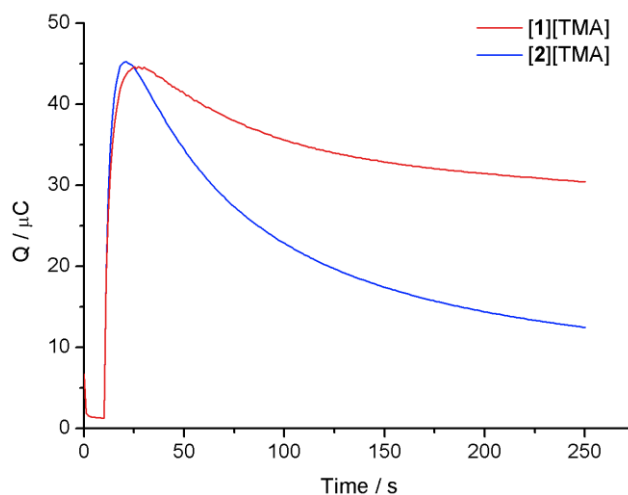


Fig. S3: Potentiostatic growth of neutral films of **1** and **2** on a platinum electrode, suggesting the deposition of a conducting film upon oxidation. Scale depicts charge (*Q*) passed at the working electrode with time.

Computational

Geometry optimisation for isolated molecules was carried out using the Gaussian 03 package,² running on

a SUSE 9.x Linux HPC cluster, comprised of 68 AMD Opteron processing cores, provided by the EaStChem Research Computing Facility (Hare cluster). The starting structure was based on the X-ray crystallographic coordinates of Ni(mi-5hdt)₂ (CCDC:xxx), and modified for a tetrahedral starting geometry using ArgusLab 4.0. The wavefunction was expanded using the Pople 6-31G* basis set for all atoms,^{3,4} and coupled to the (unrestricted) Becke three parameters hybrid exchange and the Perdew-Wang 1991 correlation functionals ((U)B3PW91).^{5,6} Optimised structures were subsequently verified as minima on the potential energy surfaces by the absence of negative values in the frequency calculations. The molecular orbital isosurfaces were generated using the cubegen utility in Gaussian 03, and visualised using ArgusLab 4.0.

TD-DFT calculations were carried out in the presence of the Tomassi polarisable continuum model (PCM) in a MeCN solvation field,⁷ with the first 50 singlet transitions calculated. Simulated spectra were generated using Gausssum 2.1 freeware program, using a full-width half-maximum value of 3000 cm⁻¹.

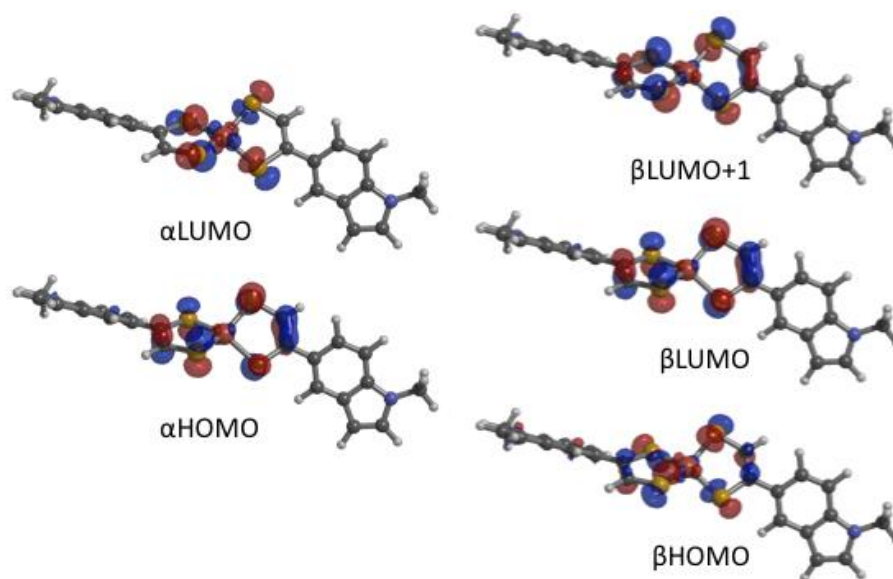


Fig. S4: Frontier molecular orbitals of **1** that contribute to the low energy absorption in the NIR region.

Observed abs. / nm	Calculated trans. / nm	Osc. Strength	Major orbital contributions
1270	1443	0.0826	β HOMO \rightarrow β LUMO (65%), β HOMO \rightarrow β LUMO+1 (18%)
	1405	0.0280	β HOMO \rightarrow β LUMO+1 (18%), β HOMO \rightarrow β LUMO (65%)
	1280	0.0281	α HOMO \rightarrow α LUMO (73%)

Table S2: TD-DFT data: (above) calculated energies and intensities of the NIR transitions observed in **1**, and major molecular orbital contributions to the NIR absorption. The data confirm the low energy absorption to be due to transitions between orbitals delocalised over the dithiolene core.

Film morphology studies

Scanning electron microscopy was performed using a Hitachi S-4300 electron microscope at 3 kV at a working distance of 5.0 mm.

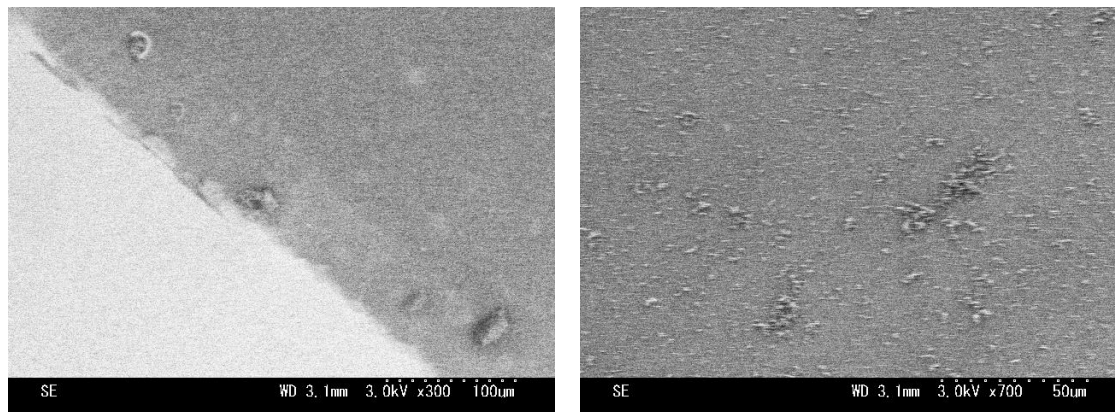


Fig. S5: Scanning electron microscopy (SEM) images of electrodeposited film of **2** on an FTO coated glass electrode; (left) edge of deposited film, with working area defined by chemically resistant Capton tape; (right) small features observed on an otherwise flat film surface. Morphology of thin film of **1** showed similar features.

The films were characterised as amorphous by thin film XRD, using a Rigaku RINT2000 diffractometer ($\text{CuK}\alpha$, $\lambda = 0.15418 \text{ nm}$). Spectra were recorded on a sample width 0.02 cm, with beam width 0.5 mm, between $2\theta = 5\text{-}50^\circ$, at a scan rate of $1.0^\circ/\text{min}$.

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