

A Stable Near IR Switchable Electrochromic Polymer Based on an Indole-Substituted Nickel Dithiolen

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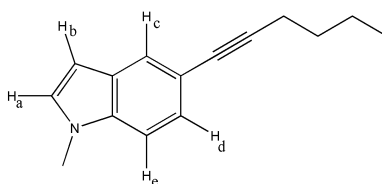
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Supplementary Information

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

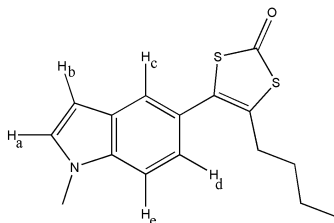
N-Methyl-5-hex-1-ynylindole (**1a**)

To a stirred, degassed solution of *N*-methyl-5-iodoindole² (3.30 g, 13.6 mmol) in dry DMF (13 ml) and freshly distilled NEt₃ (8.25 ml) under a nitrogen atmosphere was added CuI (64.6 mg, 0.340 mmol) and Pd(PPh₃)₂Cl₂ (477 mg, 0.679 mmol). Stirring was continued for 5 mins and 1-hexyne (1.87 ml, 16.3 mmol) was added and the reaction mixture was stirred under a nitrogen atmosphere at room temperature for 30 hrs. The reaction mixture was diluted with EtOAc (200 ml), filtered through celite and the organics washed with brine (2 x 200 ml), DI H₂O (2 x 200 ml) and brine (200 ml). The organics were dried over MgSO₄ and the crude product purified by flash chromatography (DCM:Hexane, 1:1) yielding the title compound as a yellow oil (1.78 g, 66%). δ_{H} (250 MHz; CDCl₃) 0.98 (t, 3H, $J = 7.0$, -CH₃), 1.44-1.70 (m, 4H, -CH₂CH₂-), 2.45 (t, 2H, $J = 6.7$, -CCCH₂-), 3.77 (s, 3H, -NMe), 6.45 (dd, 1H, $J = 3.1$, 0.8 Hz, H_b), 7.04 (d, 1H, $J = 3.1$ Hz, H_a), 7.22 (d, 1H, $J = 8.5$ Hz, H_d), 7.28 (dd, 1H, $J = 8.5$, 1.4 Hz, H_e), 7.72 (dd, 1H, $J = 1.4$, 0.8 Hz, H_c).



4-Butyl-5-(*N*-Methyl-5-indol-5-yl)-[1,3]dithiol-2-one (**1b**)

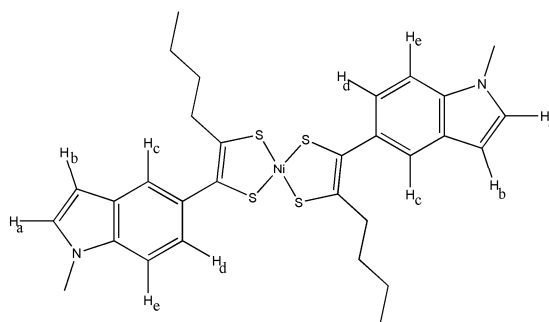
To a stirred solution of **1a** (1.78 g, 9.03 mmol) in benzene (8.5 ml) was added AIBN (635 mg, 4.06 mmol) and diisopropylxanthogen disulfide (2.51 g, 9.23 mmol) and the reaction mixture stirred at reflux under a flow of nitrogen for 50 hrs. The solvent was removed under reduced pressure and the crude product purified by flash chromatography (Hexane:Toluene, 1:1) followed by Kugelrohr distillation (64 °C at 2.0x10⁻² bar) yielding the title compound as a thick yellow oil (1.37g, 50 %). δ_{H} (250 MHz; CDCl₃) 0.85 (t, 3H, $J = 7.3$, -CH₃), 1.30 (m, 2H, -CH₂CH₃), 1.54 (m, 2H, -CH₂CH₂CH₃), 2.61 (t, 2H, $J = 7.5$, CSCH₂-), 3.83 (s, 3H, -NMe), 6.52 (dd, 1H, $J = 3.1$, 0.7 Hz, H_b), 7.13 (d, 1H, $J = 3.1$ Hz, H_a), 7.19 (dd, 1H, $J = 8.5$, 1.7 Hz, H_d), 7.35 (d, 1H, $J = 8.5$ Hz, H_e), 7.60 (dd, 1H, $J = 1.7$, 0.7 Hz, H_c); HRMS (ESI) (m/z) calcd for C₁₆H₁₇NOS₂ + H⁺: 304.0830; Found 304.08353.



[Ni(mi-5hdt)₂] (**1**)

To a stirred solution of **1b** (300 mg, 0.990 mmol) in THF (10 ml) was added [TMA][OH]·5H₂O (394 mg, 2.18 mmol) in MeOH (1 ml). After 5 mins, NiCl₂·6H₂O (122 mg, 0.515 mmol) in MeOH (1 ml) was added and the reaction mixture stirred at room temperature overnight. [1][TMA] was filtered off as a bronze precipitate. [1][TMA] was dissolved in DCM and passed over a silica plug, whereupon the solution turned green. Recrystallisation in DCM/Et₂O yielded pure **1** as a dark green precipitate (235 mg, 78%). δ_{H} (250 MHz; CDCl₃) 0.84 (t, 6H, $J = 7.2$, -CH₃), 1.22-1.38 (m, 4H, -CH₂CH₃), 1.76-1.90 (m, 4H, -CH₂CH₂CH₃), 2.93 (t, 4H, $J = 7.7$, CSCH₂-), 3.85 (s, 6H, -NMe), 6.57 (d, 2H, $J = 3.2$ Hz, H_b), 7.14 (d, 2H, $J = 3.2$ Hz, H_a), 7.35 (dd, 2H, $J = 8.5$, 1.5 Hz, H_d), 7.39 (d, 2H, $J = 8.5$ Hz, H_e), 7.77 (d, 2H, $J = 1.5$, H_c); $\lambda_{\text{max}} = 841$ nm ($\epsilon =$

$23.5 \times 10^3 \text{ M}^{-1}\text{cm}^{-1}$); Anal calcd for $\text{C}_{30}\text{H}_{34}\text{N}_2\text{S}_4\text{Ni}$: C, 59.11; H, 5.62; N, 4.60; S, 21.04. Found C, 59.62; H, 5.15; N, 4.54; S, 20.98.



Experimental and calculated optical spectra of $[\text{Ni}(\text{mi-5hdt})_2]$ (**1**)

UV/Vis/NIR measurements were recorded in MeCN using a quartz cell of path length 10 mm on a Perkin-Elmer Lambda 900 spectrophotometer, controlled by a datalink PC, running UV/Winlab software. Electrochromic measurements were recorded in a quartz cell of path length 10 mm using dry MeCN and 0.1 M TBABF₄ as supporting electrolyte in a three electrode cell. The working electrode was a transparent FTO coated glass electrode (6 x 50 mm). The reference electrode was Ag/AgCl (sat. KCl) and the counter electrode was a platinum wire.

Geometry optimisations for isolated molecular units of **1** were carried out using the Gaussian 03 program,³ utilising starting structures generated using ArgusLab 4.0. The wavefunction was expanded using the Pople 6-31G* basis set for all atoms,^{4,5} coupled to the Becke three parameters hybrid exchange and the Perdew-Wang 1991 correlation functionals (B3PW91).^{6,7} 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 DCM solvation field,⁸ 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} .

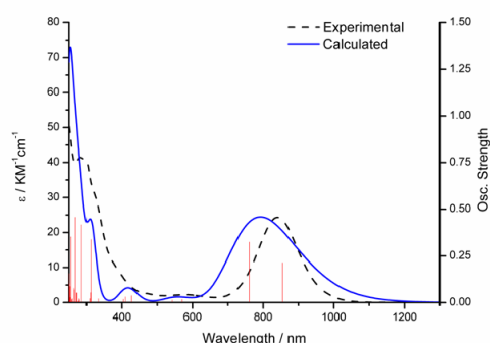


Fig S1 Experimental and calculated UV/Vis/NIR absorbance spectra of **1** in DCM showing good overall agreement of all the transitions.

Wavelength (nm)	Osc. Strength	Major contributions
854.5271	0.2139	H-2->LUMO (31%), HOMO->LUMO (56%)
760.5873	0.3249	H-2->LUMO (62%), HOMO->LUMO (-16%)
312.5289	0.3386	H-15->LUMO (-10%), H-14->LUMO (10%), H-7->L+1 (-21%), H-3->L+1 (39%)
285.5246	0.4177	HOMO->L+2 (80%)
268.2055	0.4578	H-21->LUMO (17%), HOMO->L+4 (18%)
255.5462	0.3531	H-28->LUMO (10%), H-21->LUMO (35%), H-8->L+1 (10%)
251.2582	0.1009	H-25->LUMO (-22%), H-24->LUMO (45%)
250.2085	0.1561	H-3->L+2 (21%), H-1->L+4 (-15%)
248.8626	0.4869	H-3->L+3 (13%)

Table S1 Selected calculated transitions (those with oscillator strength <0.1 omitted for clarity) in the UV/Vis/NIR spectra from TD-DFT calculations on **1**. The data confirms the low energy absorption to be due to transitions from orbitals delocalised over the whole molecule.

Electrochemistry of [Ni(mi-5hdt)₂] (1) and (Poly-1)

Electrochemical experiments were performed in dry MeCN (Sigma-Aldrich) and solutions were degassed with N₂ before use. TBABF₄ was used as supporting electrolyte and was prepared from tetrafluoroboric acid and tetrabutyl ammonium hydroxide and recrystallised 5 times from water and dried under vacuum at 60°C for 2 weeks.

Cyclic voltammetry and electrochemical polymerisation were performed at room temperature on a *ca.* 1 mM and *ca.* 10 mM monomer solution respectively in dry, degassed MeCN using 0.1 M TBABF₄ supporting electrolyte in a three electrode cell under a nitrogen atmosphere. The working electrode was a ~3 mm² Pt disc. The reference electrode was Ag/AgCl (sat. KCl), calibrated at +0.55 V against Ferrocene/Ferrocenium in the background electrolyte, and the counter electrode was a Pt rod.

Cycling between -0.3 and 1.2 V for 20 scans at scan rates between 0.1 and 1.0 Vs⁻¹ was performed, with improved film redox behaviour observed at faster scan rates. This was attributed to a shorter residence time at strongly oxidising potentials. The redox behaviour of the grown films was investigated in monomer-free electrolyte solution initially between -0.3 and 0.4 V, but extending the range to between -1.2 and 0.4 V. The first reduction of the film (E¹_{1/2} = -0.05 V) was fully reversible (shown by a plot of peak current vs. scan rate), whereas the second reduction process (E²_{1/2} = -0.91 V) diminished at faster scan rates. This was attributed to the steric difficulty of incorporating two molar equivalents of [TBA]⁺ through the film.

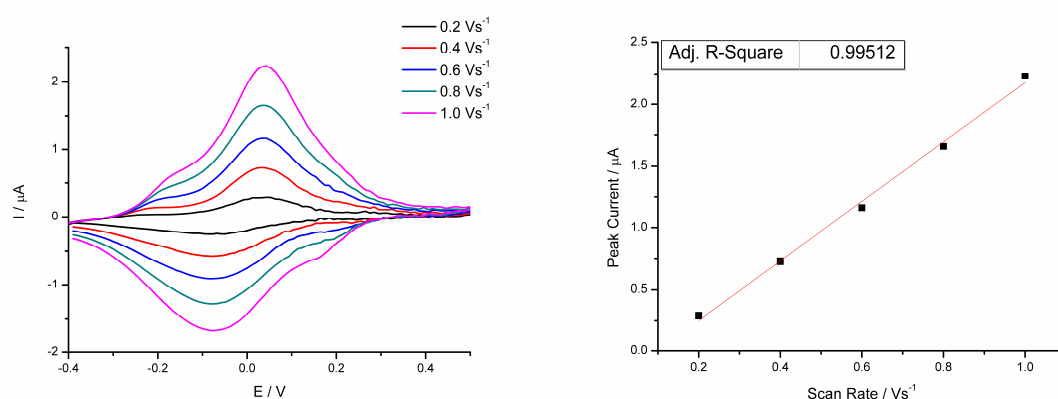


Fig S2 Cyclic voltammetry of a poly-1 coated platinum electrode in monomer free electrolyte solution showing reversibility of the first reduction process (confirmed by a plot of peak current vs. scan rate).

References

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