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## A Stable Near IR Switchable Electrochromic Polymer Based on an Indole-Substituted Nickel Dithiolene\*\*

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### Supporting information:

<sup>[†]</sup>Electronic supplementary information (ESI) available: Full experimental details for the synthesis of 1a, 1b and 1, as well as detailed experimental procedures for all calculations and experiments discussed. Fig. S1: experimental and calculated absorbance spectra for 1. Table S2: selected calculated electronic transitions for 1. Fig. S2: CV of first reduction of poly-1 showing full reversibility. See <http://dx.doi.org/10.1039/B913174D>

## Abstract

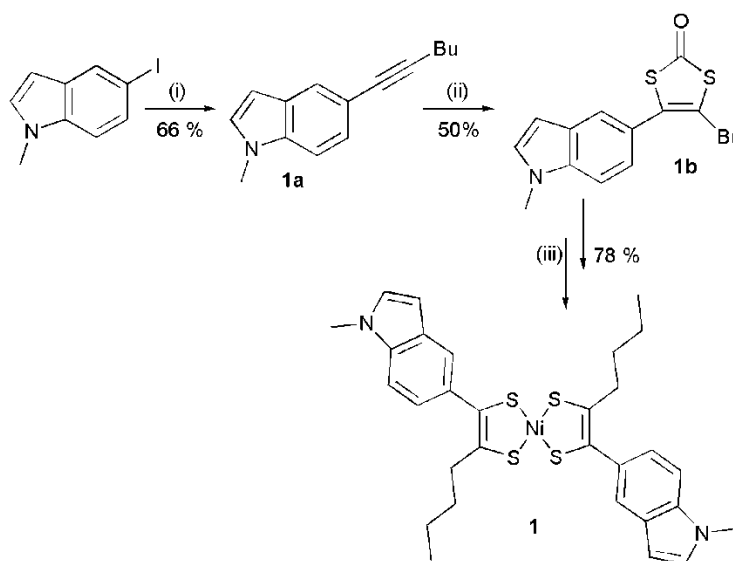
A novel nickel dithiolene-containing polymer, generated by the electropolymerisation of pendent indole units, has been prepared and shows good stability and fast reversible switching of the near infra-red absorption by varying the applied potential of the film.

## Introduction

Incorporation of nickel dithiolenes into conducting polymer films offers the possibility of stabilising the rich redox and optical properties of the dithiolene<sup>1</sup> into a stable organic framework. Previous studies have looked at dithiolene systems containing pendent thiophene groups<sup>2-4</sup> and show the optical and redox properties to be tuneable by the extent and nature of the polymerisation.<sup>5-7</sup>

We report on the synthesis of a novel polymerisable nickel dithiolene containing pendent indole functionality [Ni(mi-5htd)<sub>2</sub>] and compare the optical and redox properties of both the monomer (**1**) and the polymer film (poly-**1**) generated by oxidative electropolymerisation [(mi-5htd) = 1-(*N*-methylindol-5-yl)-hex-1-ene-1,2-dithiolate]. The allowed in-plane twist of the indole group and the restriction on the polymerisable sites imposed by the structure of the indole allow more extensive frontier orbital overlap<sup>4</sup> as well as improved polymer film morphology.

The route to the ligand precursor was developed in order to be quick and easily tuneable to allow future investigation into the effect of different alkyl substituents on the electronic and physical properties of the complexes and resultant films [Scheme 1 (see ESI† for full experimental procedures)].

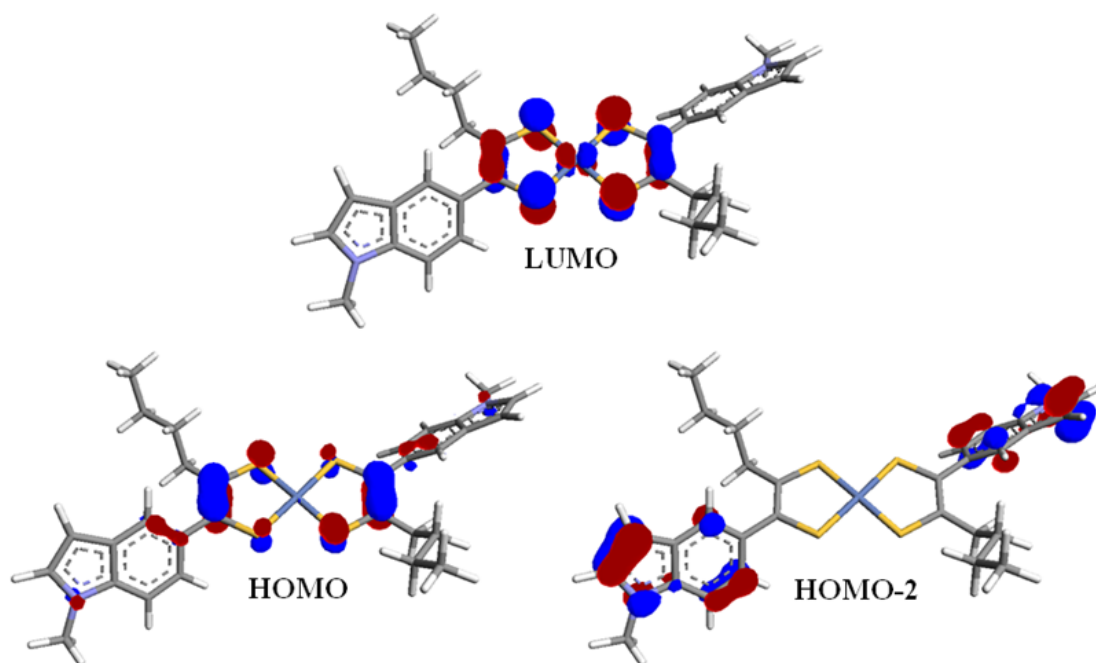


**Scheme 1.** Synthetic route towards **1**: (i) Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>, CuI, NEt<sub>3</sub>, 1-hexyne, DMF; (ii) diisopropylxanthogen disulfide, AIBN, Benzene (iii) [TMA][OH], NiCl<sub>2</sub>·6H<sub>2</sub>O, THF, MeOH.

Under Sonogashira conditions,<sup>8</sup> the alkyne was generated from the *N*-methyl-5-iodoindole<sup>9</sup> and converted to the dithiol-2-one by an analogous route to that described by Gareau.<sup>10</sup> The target material was isolated as a **1**[TMA] salt by reaction of the dithiol-2-one with [TMA][OH] in THF, followed by the addition of NiCl<sub>2</sub>Cl.6H<sub>2</sub>O. Neutral **1** was isolated by passing a DCM solution of **1**[TMA] over a silica plug.

The complex has been depicted and modelled in the trans configuration as nickel dithiolenes, with unsymmetrically substituted ligands, have previously been shown to crystallise preferentially in this way.<sup>11</sup> A combined NMR<sup>12</sup> and computational approach to investigate *cis/trans* isomerism in solution is ongoing and will be reported elsewhere.

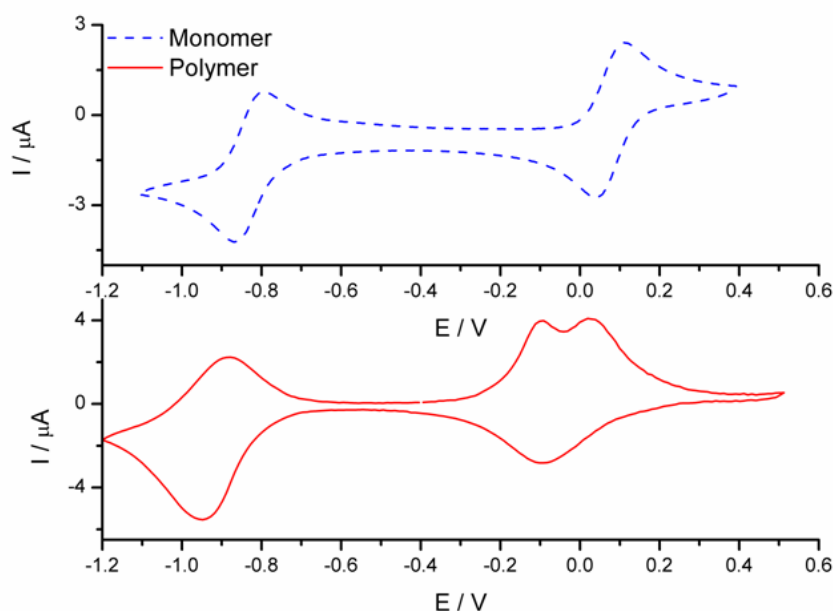
Density functional theory (DFT) calculations showed HOMO and LUMO orbitals distributed over the whole dithiolene unit, with symmetries in keeping with previous calculations.<sup>13</sup> Time-dependent DFT calculations showed good agreement with the experimentally determined absorption spectrum and showed the low energy NIR absorption [841 nm (11,890 cm<sup>-1</sup>)] to be due to a mixed HOMO and HOMO-2 to LUMO transition, indicating extensive indole contribution to the electronic properties of the complex [Fig. 1 (Fig. S1, Table S1, see ESI† for details)].



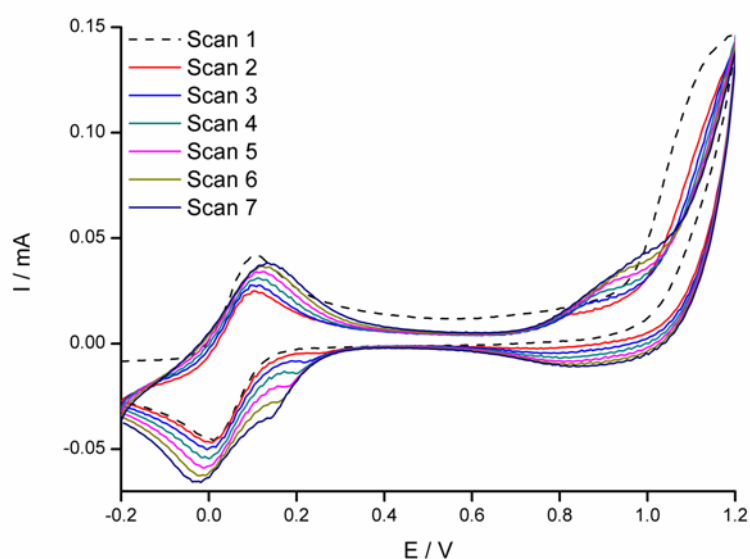
**Figure 1.** Frontier molecular orbitals of **1**.

Cyclic voltammetry<sup>‡</sup> of **1** in solution showed two reversible one-electron processes at  $E_{1/2}^1 = -0.83$  V ( $-1 \leftrightarrow -2$ ),  $E_{1/2}^2 = 0.08$  V ( $0 \leftrightarrow -1$ ) (Fig. 2), and an irreversible oxidation process above 1 V (see ESI† for details).

The first two processes correspond to sequential reduction of the neutral complex to a mono and a dianion, similar to previously reported neutral metal *bis*-dithiolene complexes.<sup>11</sup> Cycling into the third (irreversible) process resulted in the deposition of a polymer film on the electrode, and is thus attributed to the oxidation of the indole groups (Fig. 3). Cycling of the deposited film in monomer-free electrolyte solution showed two reversible processes corresponding to the sequential reduction of the polymer film, as well as an irreversible oxidation process at a similar potential to the monomer. Both reduction processes were shown to be chemically reversible (Fig. S2 ESI<sup>†</sup>), however, the second process diminished at faster scan rates ( $>0.5 \text{ Vs}^{-1}$ ), attributed to the steric difficulty in incorporating two molar equivalents of  $[\text{TBA}]^+$  into the film. The redox processes occur at similar potentials to the monomer, suggesting that, contrary to previous results from thiophene containing systems,<sup>2, 3, 7</sup> the dithiolene redox processes are largely unaffected by incorporation into a polymer film (Fig. 2), although the reason for the split oxidation process of  $\text{E}^2_{1/2}$  is not known at present. This contrast with thiophene-functionalised dithiolene complexes is likely due to the adjacent nature of possible coupling sites on the indole, compared to thiophene. Indole has previously been shown to couple at the 3 position under electrooxidative conditions<sup>14</sup> and, with the 4 and 5 positions blocked by the fused benzene ring, further coupling through the 2 position occurs, generally leading to discrete cyclic trimers<sup>15, 16</sup> or, for more hindered systems, short chain oligomers. Polymerisation of dithiolenes containing pendent indole units therefore appears to stabilise the dithiolene in a coordination polymer framework, whilst leaving the redox and optical properties largely unaffected.

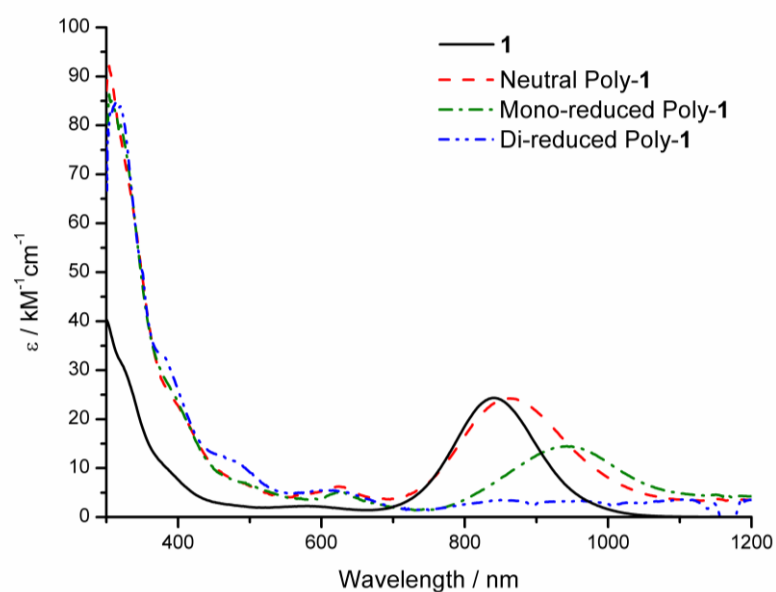


**Figure 2.** Cyclic voltammetry of **1** and poly-**1** in monomer free electrolyte solution showing clean redox behaviour and minimal change in  $\text{E}_{1/2}$  upon incorporation into a polymer film.



**Figure 3.** Electropolymerisation of  $\sim 10$  mM **1** in 0.1 M TBABF/MeCN. Peak currents increase with cycling indicating deposition of a conducting film.

This conclusion is further supported by the absorption spectrum of poly-**1** grown on a fluorine-doped tin oxide (FTO) coated glass electrode (Fig. 4). The absorption spectrum of the neutral film confirms indole linkage by a broadening of the UV absorption, however, the negligible shift of the NIR absorption suggests limited delocalisation of the dithiolenic core into the polymer network [862 nm ( $11,601$   $\text{cm}^{-1}$ )].

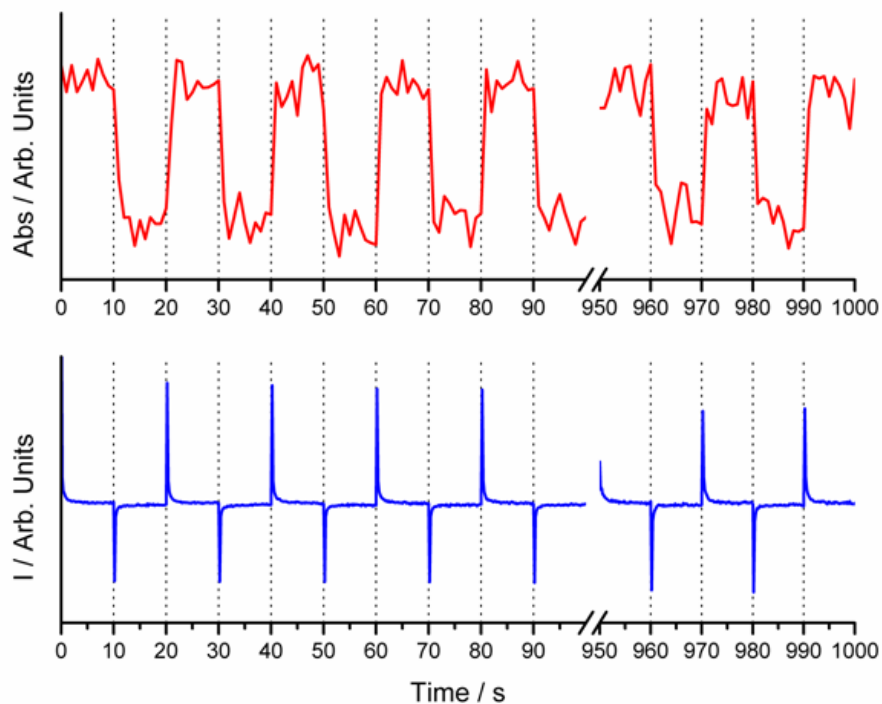


**Figure 4.** UV/Vis/NIR spectra of **1** and normalised spectra of poly-**1** under an applied potential of 0.3 V (neutral) -0.4 V (mono-reduced) and -1.0 V (di-reduced).

This contrasts sharply with other electropolymerised dithiolenes based on thiophenes, where broad redox processes and broad visible absorption processes arose from the polythiophene component, in some cases masking the dithiolenes characteristics.

The clean, reversible nature of the redox processes in poly-1 suggested that the film might be reversibly reduced under an applied potential. The absorption spectra of the FTO film of poly-1 was recorded at different potentials<sup>‡</sup> and showed that the NIR absorption profile could be reversibly varied under an applied potential (Fig. 4). At an applied potential of -0.4 V, the polymer was reduced, resulting in a decrease in the intensity and a red-shift of the NIR absorption. At an applied potential of -1.0 V, the absorption in the whole NIR range was switched off completely. This transformation corresponds to the sequential filling of the LUMO orbital. Addition of one electron to the LUMO orbital perturbs the transitions across a reduced HOMO-LUMO gap, whilst a complete filling of the LUMO orbital removes such a transition altogether. At a wavelength of ~800 nm, the absorption could be switched off by an applied potential of -0.4 V, whilst at ~900 nm, the absorption could be effectively halved at the same potential, or switched off at -1.0 V. As such, a three way optical switch, effective in the NIR region, has been developed.

Such a switchable system might find application in the telecommunications field as a variable optical attenuator (VOA).<sup>17</sup> Switching of signal transmission intensity in the NIR region (800-2000 nm) is useful in signal modulation for silica fibre-optics as they are most transparent in the NIR region.<sup>18</sup> For such a system to be useful, fast switching and good stability are prerequisites.<sup>19</sup> Reversible switching of the absorption intensity of the film at 860 nm was observed by switching the applied potential between 0.3 V and -0.4 V and showed the absorption to vary with only minimal loss in peak absorption over 100 cycles (Fig. 5). Cycling to the dianionic state was slower, possibly due to the steric difficulty associated with the incorporation of two molar equivalents of bulky [TBA]<sup>+</sup> counterions through the film, however the process was shown to be chemically reversible by the regeneration of the peak at 860 nm upon holding an applied potential of 0.3 V.



**Figure 5.** Switching of the absorption properties of poly-1 at 860 nm under an oscillating potential of 0.3 V and -0.4 V. Film shows good stability over 100 cycles.

In conclusion, we have stabilised a novel nickel dithiolene by oxidative electropolymerisation and shown the absorption spectrum of the resultant film to be reversibly switched between three absorption states within the NIR region.

Future work will focus on the use of gel electrolytes with less bulky cations to enhance device stability and improve the switching speed of the second reduction. Additionally, by increasing the donating contribution of the alkyl substituent, it is hoped that we may raise the HOMO level sufficiently to reduce the energy of the NIR transition into the most transparent silica fibre-optic window of 1300-1550 nm.<sup>20</sup>



## Notes and references

[‡] All electrochemical experiments were performed at room temperature in dry MeCN using 0.1 M TBABF<sub>4</sub> supporting electrolyte in a three electrode cell against a Ag/AgCl (sat. KCl) reference electrode, calibrated at +0.55 V against Ferrocene/Ferrocenium in the background electrolyte.

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