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PAPER

Indole-substituted nickel dithiolene complexes in electronic and optoelectronic devices[†]

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The synthesis and full characterisation of a novel indole-substituted nickel dithiolene [Ni(mi-5edt)₂] (3) is reported, and compared to its alkyl-substituted analogue [Ni(mi-5hdt)₂] (4) that has been previously communicated [Dalgleish *et al.*, *Chem. Commun.*, 2009, 5826] [mi-5edt = 1-(*N*-methylindol-5-yl)-ethene-1,2-dithiolate; mi-5hdt = 1-(*N*-methylindol-5-yl)-hex-1-ene-1,2-dithiolate)]. Both complexes are shown to undergo oxidative electropolymerisation, yielding polymer films that retain the redox and optical properties of the monomer. The more soluble analogue **4** is shown to form high quality thin films by spin coating, which have been utilised to fabricate field-effect transistors (FETs) and bulk heterojunction photovoltaic devices (BHJ-PVs). From FET studies, the material shows ambipolar charge transport behaviour, with a maximum carrier mobility of $\sim 10^{-6}$ cm² V⁻¹ s⁻¹ for electrons. By using **4** simultaneously as the electron acceptor as well as a NIR sensitiser in BHJ-PVs, the complex is shown to contribute to the photocurrent, extending light harvesting into the NIR region.

1. Introduction

Organic field-effect transistors have enjoyed considerable attention over the past decade, with confirmed reports of mobilities comparable to those of amorphous silicon.¹ Whilst the initial research into organic semiconductors focussed on purely organic systems, in recent years focus has broadened to look at transition metal complexes.²⁻⁴ Transition metal complexes often display multiple stable redox states, corresponding to electron transfer processes based on the metal or spread over the ligand, and the frontier orbitals are often relatively non-bonding, leading to low reorganisation energies upon electron transfer and, as such, are attractive targets for stable charge transport in organic devices.⁵ In addition to charge-transport properties, transition metal complexes can also display tuneable visible or NIR absorption, leading to applications in optoelectronic devices, such as photovoltaic cells.

Improvements in device efficiencies for organic photovoltaic devices have been realised by increasing the interface between electron donor and acceptor materials.⁶ One common method for achieving this is to form a bulk heterojunction architecture. Bulk heterojunction photovoltaic cells (BHJ-PVs) are most commonly prepared by blending a polymeric electron donor with a substituted fullerene as electron acceptor. To achieve high photocurrents, light absorption over a large part of the solar spectrum is required. This has been achieved for binary systems by replacing PCBM with PC₇₁BM, which has a significantly broader absorption in the visible range than PCBM,⁷ or by developing ternary systems with a sensitiser molecule incorporated to effect light capture at longer wavelengths.⁸⁻¹¹

Nickel-bis-1,2-dithiolenes often show non-innocent character, with multiple redox processes occurring at low potentials due to a low lying LUMO orbital, and efficient delocalisation of the electron density over the ligand.¹² In addition, the narrow HOMO–LUMO gap leads to intense low energy absorption. Despite intensive study over nearly five decades, only a few studies are reported of their incorporation in field-effect transistors. Anthropoulos *et al.* demonstrated ambipolar behaviour for bis-(4-dimethylaminodithiobenzyl)-nickel, with typical hole and electron mobilities (μ) of 10^{-4} cm² V⁻¹ s⁻¹,³ which so far represents the highest reported for a metal dithiolene.^{2,4} A limiting consideration remains the ability of these species to be readily processed into continuous thin films.

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[†] Electronic supplementary information (ESI) available: Table S1: Selected bond lengths and angles of complexes **3** and **4** from geometry optimised structures, compared to the crystal structures of **4** and ligand precursor **1**; Table S2: Calculated energies, intensities and contributions to the NIR absorptions of **3** and **4**; Table S3: Redox processes of **3** and **4**; Fig. S1: Comparison of ¹H NMR of **3** and **1**; Fig. S2: Frontier molecular orbitals of **3** and **4**; Fig. S3: Cyclic voltammetry of **4**; Fig. S4: Electropolymerisation of **3** and **4**; Fig. S5: Cyclic voltammetry of poly **4** on Pt electrode, compared to **4** in solution; Fig. S6: Absorption spectra of P3HT/**4** and PPV/**4** thin films; Fig. S7: Photoluminescence spectra of P3HT/**4** and PPV/**4** thin films. See DOI: 10.1039/c1jm12466h

We previously communicated the preparation of the nickel bis-1,2-dithiolene complex (4) (Scheme 1) and its electropolymerisation to give a NIR electrochromic film.¹³ Due to the propensity of 4 to form uniform thin films by drop or spin coating, it presents an ideal example to further study the application of nickel dithiolene complexes to FETs, and also, for the first time, to explore their potential as the electron acceptor in BHJ-PVs. We report the full synthesis, structural characterisation and study of 4 and the analogous 3, and their application in (opto)electronic materials and devices through both electropolymerisation and solution-coating approaches.

2. Results and discussion

We previously reported the synthesis of 4, using the route proposed by Gareau et al. involving synthesis of the dithol-2-one ligand precursor, via the alkyne.14 To prepare 3 containing a terminal alkyne, the Corey-Fuchs procedure provides a cheap, catalyst-free alternative to the Sonogashira reaction used for 2.15 5-bromo-1-methylindole was converted to the aldehyde by a microwave assisted Grignard reaction, in near quantitative yield, by modification of the route described by Mutule et al.¹⁶ This was converted under a modified Corey-Fuchs procedure to the alkyne in good yield (57%).¹⁷ By this method, a cheap, quick and relatively simple procedure has been developed toward a novel dithiolene ligand precursor. Both of these alkyne species could then be converted to the desired dithiol-2-one (Scheme 1). The nickel TBA or TMA salts were synthesised by a route similar to that of Anjos et al.,¹⁸ and oxidation to the neutral complex could be effected using elemental iodine.



The packing structure of **4** showed the complex to crystallise in a columnar stacking arrangement, with an interplanar distance of 3.822 Å, approaching the van der Waals limit for efficient sulfur-nickel overlap (Fig. 1 (lower)). Close contact between the stacks was achieved through the indolyl pyrrole unit (C2) and the dithiolene S (Fig. 1 (upper)). As observed for other pendent aromatic systems,^{24,25} the indolyl groups were twisted out of the molecular plane by some 60°, thus prohibiting a closer packing of the dithiolene cores. This was interesting as the incorporation of a flexible butyl group was included to allow the in-plane twist of the indolyl group, and thus suggested that the origin of this twist perhaps did not lie solely with sterics.²⁶ Compared to the crystal structure of the ligand precursor **2**, which showed classical dithiolate bond lengths for the C–S and C=C bonds (Table S1, ESI†), the complexed ligand showed a shortening of the C–S





Scheme 1 Synthetic routes to 3 and 4. (i) Pd(PPh₃)₂Cl₂, CuI, NEt₃, 1hexyne, DMF; (ii) diisopropyl xanthogen disulfide, AIBN, benzene; (iii) Mg, THF, microwave, DMF; (iv) (Ph₃P*CH₂Br)Br⁻, 'BuOK, THF, -78 °C; (v) [TMA][OH], NiCl₂·6H₂O, MeOH, THF, or NaOMe/MeOH NiCl₂·6H₂O, TBABr; (vi) I₂, MeCN, or [O].

Fig. 1 Single crystal X-ray data for **4** showing (upper) packing in a plan view of the unit cell with close contacts between the molecules through the indolyl pyrrole unit (C2) and the dithiolene S (3.930 Å); (lower) stacking of the dithiolene molecules down the a-axis with short interplanar distance of 3.822 Å.

bonds, and a lengthening of the C=C bond, consistent with a more delocalised aromatic π system over the NiSCCS ring.

No crystals suitable for XRD could be obtained for 3, however, the aromatic nature of the dithiolene core could be observed by ¹H NMR by the large shift to higher frequency for the SCCS ring –H upon complexation, from 6.73 ppm in the ligand precursor (1) to 9.74 ppm in the complex (3) (Fig. S1, ESI[†]). The increase in the aromaticity of this hydrogen has led some groups to investigate the reactivity of such dithiolene complexes,^{24,27} and could be a possible future step for simple tuning of the physical or electronic properties of 3 without the need for a bottom-up synthetic approach.

UV/Vis/NIR spectroscopy of **3** and **4** in DCM show an intense peak in the UV region, and a single peak in the NIR region [910 nm (10,989 cm⁻¹) and 840 nm (11,905 cm⁻¹) for **3** and **4** respectively] (Fig. 2). Neutral nickel dithiolenes characteristically show an intense NIR absorption due to a $\pi \rightarrow \pi^*$ transition between the HOMO and LUMO orbitals.¹² For **3** this transition occurs at ~1,000 cm⁻¹ lower energy than for **4**, indicating a smaller HOMO/LUMO gap, which is in agreement with conclusions drawn from electrochemical studies, and supported by DFT calculations (*vide infra*). For the monoanionic TBA salts, the NIR absorption is preserved as a transition is still possible between the HOMO and the half filled LUMO.²⁸ However, the absorption is shifted to lower energy [960 nm (10,417 cm⁻¹) and 848 nm (11,792 cm⁻¹) for [TBA][**3**] and [TBA][**4**] respectively]. It is not clear why the shift for [TBA][**3**] is 5 times greater than for



Fig. 2 Experimental and calculated UV/Vis/NIR absorbance spectra: (upper) **3** in DCM; (lower) **4** in DCM.

[TBA][4], however this might reflect the increased conformational freedom of the indolyl groups in [TBA][3] having a greater effect on the frontier orbital energies.

Hybrid DFT calculations of the electronic structure of 4 were reported previously. To support the experimental results of the electronic absorption behaviour, this has been extended in this work to include the TD-DFT calculated absorption spectra for 4 and 3 (Fig. 2). The calculations were carried out using a polarisable continuum model of DCM ($\varepsilon = 8.93$).²⁹ TD-DFT calculations showed excellent agreement with the experimentally determined absorption spectra, and showed the low energy NIR absorption (910 nm (10,989 cm⁻¹) and 840 nm (11,905 cm⁻¹) for 3 and 4, respectively) to be due to a mixed HOMO and HOMO-2 to LUMO transition. Since the HOMO-2 orbital was predominantly ligand based (pictures of relevant frontier orbitals, energies and contribution to the low-energy absorption are given in Fig. S2, Table S2, ESI[†]), this suggests extensive indole contribution to the electronic properties of the complex.³⁰ The lower energy NIR transition for 3 is suggested to be due to a more extensive contribution from the HOMO-2 orbital, reflecting its increased contribution to the frontier molecular orbitals, due to its more in-plane conformation. For nickel dithiolenes, electron donating groups raise the energy of the HOMO more than that of the LUMO, resulting in a smaller HOMO/LUMO gap, and thus a lower energy absorption in the NIR. Since -Bu is weakly donating, through induction, compared to -H, this suggests that the dominant effect of the -Bu group in 4 is to sterically disfavour a more planar geometry, and thus reduce the extent of donation through resonance from the indole group, compared to 3.

Cyclic voltammetry of **3** and **4** in DCM showed two reversible one-electron processes (at $E_{1/2}^1 = -0.76$ V and -0.90 V, and $E_{1/2}^2$ = +0.07 V and -0.03 V, for **3** and **4**, respectively), as well as two irreversible oxidation processes (at $E_{ox}^3 = +0.92$ V and +1.12 V, and $E_{ox}^4 = +1.46$ V and +1.46 V, for **3** and **4**, respectively) (Fig. 3; Fig S3, Table S3, ESI†). The first two processes correspond to sequential reduction of the neutral complex to a mono ($E_{1/2}^2$) and a dianion ($E_{1/2}^1$), similar to previously reported neutral metal bisdithiolene complexes.¹⁹ The reduction processes of **3** occurred at more positive potentials than for **4**. This suggests that the LUMO orbital, into which the electrons are added, is lower in energy for



Fig. 3 Cyclic voltammetry of **3** in 0.3 M TBABF₄/DCM, starting at 0.5 V, with separate scans to negative and to positive potentials.

3 than **4**. The first oxidation process (E_{ox}^3) occurs at less positive potentials for **3** than **4**, consistent with a greater donor influence from a more in-plane indolyl group in **3** raising the energy of the HOMO more than for **4**. These results are in agreement with the UV/Vis/NIR studies, which showed a NIR absorption at lower energies for **3** than **4**, consistent with a smaller HOMO/LUMO separation in **3**. Additionally, the decreased separation of the reduction processes for **3** than **4** ($\Delta E = +0.83$ V and +0.87 V, respectively) suggest that **3** is better able to stabilise two negative charges developed on the complex, possibly due to increased delocalisation onto the indolyl groups. Such a process is consistent with a more in-plane conformation of the indolyl groups, as suggested by calculations.

2.1 Electropolymerisation studies

For more concentrated solutions of **3** in DCM, cycling the potential into the third (irreversible) process (between -0.3 and +1.0 V) resulted in the deposition of a conducting film on the electrode (Fig. 4 (upper)), analogous to the results previously communicated for **4**.¹³ The increase in peak current indicates the increasing quantities of redox-active material deposited on the electrode. The insolubility of the film in DCM, compared to the monomer, suggested the film to be polymeric in nature.



Fig. 4 Electropolymerisation of **3** to form poly-**3** (upper). Cyclic voltammetry of poly-**3** coated platinum electrode in monomer free electrolyte solution (lower), compared to the redox behaviour of the monomer (middle).

Therefore, it seems that the dithiolene radical, formed upon oxidation, resides, as least partially, on the indolyl group, and results in the oxidative coupling of the indolyl groups. Cycling of poly-3 and poly-4 after transferring to monomer-free electrolyte solution (of the same electrolyte and solvent, as for their formation) showed two chemically reversible processes, corresponding to the sequential reduction of the polymer films (Fig. 4 (middle, lower)), as well as an irreversible oxidation process at a similar potential to the monomers (not shown). For both 3 and 4, films formed at faster scan rates (up to $v = 1.0 \text{ V s}^{-1}$) appeared to show improved film redox behaviour. This was attributed to a shorter residence time at strongly oxidising potentials.

For poly-3, both reduction processes were chemically reversible (Fig. 4 (lower)), however, the second process diminished at faster scan rates ($v > 0.5 \text{ V s}^{-1}$). Additionally, the peak currents of the two reduction processes were rather unbalanced, with the reduction to the monoanion producing a larger current response than the reduction to the dianion. Both these observations suggest that a large steric barrier exists for the incorporation of two molar equivalents of [TBA]⁺ into the film. However, both reduction processes could clearly be observed, with the redox processes for poly-3 at very similar potentials to 3 in solution, suggesting that, contrary to previous results from thienyl containing systems,^{31,32} the dithiolene redox processes were largely unaffected by incorporation into a polymer film.

For poly-4, the redox processes also appeared largely unchanged upon incorporation into a polymer film (Fig. S5, ESI[†]).¹³ However, the current response of the two reduction processes appeared to be more balanced, suggesting improved ion transfer through the film, compared to poly-3. The more balanced reduction processes in poly-4 may be due to the formation of a less dense polymer network, facilitating improved ion transport through the film. This is possibly caused by the steric bulk of the -Bu group on the dithiolene ring, disfavouring close packing of the polymer chains. This is supported by the smaller peak currents for poly-4, than for poly-3, as well as a visibly more coloured film for poly-3, suggesting a smaller dithiolene content in the film of poly-4. To further characterise the polymers, films were grown on a fluorine-doped tin oxide (FTO) coated glass electrodes and were investigated by UV/Vis/NIR spectroscopy (Fig. 5). For poly-3, the absorption spectrum of the formed film showed a broadening of the UV absorption. This is consistent with the linking of the indolyl groups upon polymerisation, as an increase in conjugation would shift the indole-based transitions to lower energy. The absorption spectrum also showed the NIR absorption to be shifted by 1,522 cm⁻¹ to a longer wavelength of 1055 nm. This shift for poly-3 might be due to a number of factors: longer conjugated chain length in the ligand might increase the delocalisation in the polymer backbone, thus reducing the HOMO/LUMO separation; increased planarity upon polymerisation might also raise the HOMO level, resulting in a reduced HOMO/LUMO gap. A third possibility might be that, due to the increased film density (or thickness), some dithiolene species might remain as the monoanion in the film, resulting in a lower energy absorption being observed (vide supra).

For both poly-3 and poly-4, the shift in the NIR absorption was less than that observed for the absorption spectra of the thiophene-substituted complex, poly-Ni(b-2ted)₂,³¹ which showed the NIR absorption to shift by 1896 cm^{-1} further into the



Fig. 5 UV/Vis/NIR spectra of poly-**3** grown by potential cycling on an FTO coated glass electrodes, where the absorption intensity is given as the molar extinction coefficient (ε), and the polymer absorptions are normalised relative to the NIR absorption of the monomer.

NIR upon polymerisation. It also contrasts with the electropolymerised dithiolenes based on a fused thiophene backbone [Ni(b-2tted)₂],³² for which broad redox processes, and a broad absorption across the whole Vis/NIR range were observed, arising from the extensive polyterthiophene component which, in some cases, masked the dithiolene characteristics altogether.

2.2 Solution coated film and FET studies

Deposition of a thin film of **4** on a glass substrate by spin coating led to facile formation of a continuous film, with a shift in the NIR absorption to lower energy [$\lambda_{max} = 915$ nm (1.36 eV), absorption onset = 1323 nm (0.94 eV)]. This suggests some degree of interaction in the solid state, required for good charge transport in a FET. Bottom-gate, bottom-contact (BGBC) organic field-effect transistors were fabricated with gold source and drain electrodes. The Fermi level of gold is approximately 4.8 eV,³³ and lies between the energy levels of the frontier orbitals of **4** (estimated from electrochemical studies),³⁴ giving a barrier to injection of less than 1 eV for both charge carriers (see inset Fig. 6 (a)). Such electrodes are therefore suitable for investigating ambipolar charge transport behaviour in **4**. BGBC OFETs were prepared by spin-casting **4** from chloroform solution.

Fig. 6 shows transfer characteristics (drain current I_D , as a function of gate voltage V_G) of an example BGBC OFET using **4** as the active layer. The channel length and width were in this case $L = 2 \mu m$ and W = 10 mm respectively. Using standard semiconductor models,³⁵ the field-effect mobility of holes and electrons were extracted from Fig. 6 (a) and (b) in the saturation regime to be 10^{-7} cm² V⁻¹ s⁻¹ and 10^{-6} cm² V⁻¹ s⁻¹ respectively.

Whilst hole accumulation (p-type behaviour) has been readily observed in many organic semiconductors, electron accumulation (n-type) has been observed only rarely.³⁶ One reason for this is the poorer environmental stability of the reduced species upon *n*-doping, leading to rapid carrier trapping at the air/semiconductor, or substrate/semiconductor interface.³⁷ Several studies have suggested the limit for ambient stability of n-type semiconductors to be dictated by the oxidation processes with atmospheric water, taking place at E = -0.658 V (*versus*)



Fig. 6 Transfer characteristics of example bottom-gate, bottom-contact (BGBC) organic field-effect transistor (OFET) fabricated from **4**, with (a) negative and (b) positive applied drain voltages (V_D) . The channel length and width are in this case $L = 2 \mu m$ and W = 10 mm respectively. Inset (a): energy levels of **4** relative to Fermi level of gold. Inset (b) architecture of BGBC OFET employed here.

SCE).^{2,4,38} Thus the observation of stable *n*-channel, and ambipolar charge transport for **4**, can be understood in terms of the extensive delocalisation of the frontier orbitals leading to readily accessible redox processes, combined with the ease of formation of a continuous film of **4** from solution. It is notable that **3** did not form continuous films using similar solution processing methods, emphasising the crucial role of molecular substituent groups in determining utility in thin-film devices.

2.3 Photovoltaic devices

Complex 4 shows strong absorption in the NIR, a region poorly covered by other molecular semiconductors. Within the field of organic photovoltaic devices, extending the absorption further into the NIR region is an active area of interest as it would allow for greater harvesting of the solar spectrum. Despite showing a relatively low n-type mobility, the absorption properties of 4 are suited for incorporation into such devices.

The structure of the devices prepared involved a binary bulk heterojunction architecture, with **4** as the electron transport material, and either P3HT or MDMO-PPV (hereafter PPV) as the hole transport material, since the photophysics of both these polymer systems is well documented.³⁹ In the first instance the optical properties of the blended films were investigated to ensure both components had been incorporated into the film.

The UV/Vis absorption for both P3HT/4 and PPV/4 blends showed incorporation of both species into the film, with the dithiolene component enhancing the absorption in the UV, and extending the absorption properties of the film to lower energies by a discrete absorption in the NIR (Fig. S6, ESI†). Upon blending, the extent of red-shifting of the dithiolene NIR absorption (compared to the solution spectrum) was reduced for both P3HT and PPV blends, when compared to spin coated films of pure 4 (a red-shift of 113 and 278 cm⁻¹ for blends of P3HT and PPV, respectively, compared to a red-shift of 990 cm⁻¹ for pure 4). This suggests less ordering in the dithiolene phase, due to the intermolecular interactions of the dithiolene being broken up by the polymer component.

Film thicknesses of between 60–130 nm were observed, with thicker films formed at slower spin speeds. As devices formed from P3HT have been shown to benefit from an annealing step,⁴⁰ due to the reorganisation of the polymer to form more crystalline

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domains, the effect of annealing on the UV/Vis absorption was also investigated, however these showed negligible change in the intensity or wavelength of maximum absorption (λ_{max}) for the polymer, and no change in the dithiolene absorption. No significant reduction in film thickness (within experimental error), was observed upon annealing, which was consistent with negligible reorganisation taking place.

Photoluminescence (PL) measurements were performed on the deposited films with emission wavelengths between 550 and 950 nm, and excitation at 500 nm. For P3HT, the incorporation of dithiolene (at a ratio of 5:1 of P3HT:4) resulted in a reduction of the intensity of the emission by 95% (at $\lambda_{max} = 718$ nm). The high degree of quenching observed, even at low dithiolene concentration, suggests that efficient charge transfer had occurred. Alternatively, due to the overlap of the P3HT emission and dithiolene absorption bands, energy transfer cannot be discounted. Further increases in dithiolene concentration (for a 2 : 1 and 1:1 P3HT:4) resulted in less marked reductions in the emission intensity, suggesting that, already at a 5:1 (P3HT: dithiolene) ratio, the majority of excitons had been separated, or transferred. For PPV, quenching of the emission at a 5:1 (PPV: 4) ratio was far greater, with quenching of over 99% (at $\lambda_{max} = 591$ nm), again, with little increase in the quenching at higher dithiolene loadings (Fig. S7, ESI[†]). It therefore seems that even at low dithiolene loadings, efficient quenching of the polymer excited state of both P3HT and PPV takes place, consistent with good mixing of the materials upon blending, and efficient electron or energy transfer between the polymer and the dithiolene.

Photovoltaic devices were constructed by a standard procedure, using 1:1 weight ratios of polymer : dithiolene, in chlorobenzene solution. The current response under device illumination was measured, with diode-like behaviour for all devices in the dark, suggesting that the devices were all operating correctly. From the external quantum efficiency (EQE) of each device as a function of wavelength (Fig. 7), it is clear that, for the P3HT devices, the dithiolene contributed to the overall efficiency of the cell, due to a photocurrent generated from an absorption centred around 860 nm, as well as a polymer contribution in the visible range. These data are consistent with charge transfer from 4 to P3HT, however, given the low EQE values, it is unclear whether charge transfer occurs between P3HT and 4, or whether energy transfer occurs, followed by subsequent charge transfer of holes from 4 to P3HT. For the P3HT devices, annealing increased the efficiency of both the dithiolene and polymer contributions. For the PPV devices, negligible photocurrent was generated by the dithiolene, suggesting that no such charge transfer occurs at NIR wavelengths, and the efficiency for the polymer component was far lower than for the P3HT devices. The EQE was low for all regions of the spectra, for all the devices tested (compared with >20% for a reference device of P3HT:PCBM), with maximum external quantum efficiencies for the best performing device of 0.15% and 0.95% for the dithiolene and polymer absorptions, respectively.

Whilst these values were very small, the concept of using a dithiolene moiety as a NIR absorbing species for simultaneous light harvesting and electron transport, was shown for the first time to work in a bulk-heterojunction solar cell. The exact reason



Fig. 7 External quantum efficiencies (EQE) for a 1 : 1 P3HT : 4 blend (annealed and unannealed), as well as a 1 : 1 PPV : 4 blend (unannealed).

for the low EQE values is not known, with either poor electron transport, or rapid charge recombination being the possible reasons. The large structural variety of known Ni-dithiolene complexes, and the observation of higher electron mobility in other examples, suggests these limitations might be overcome in future studies. As expected based on the low EQE values, the devices yielded poor cell efficiencies, with the efficiency of the best performing device (unannealed P3HT : 4) at <0.1%.

3. Conclusions

We have synthesised two analogous Ni-dithiolene complexes containing indolyl moieties, differing in the presence or absence of a short alkyl chain. The synthetic routes described for each are applicable to a range of related ligand structures with a combination of an aryl and an alkyl (or H) unit attached to each end of the dithiolene core. The X-ray structure of 4 showed stacked metal complexes, which can potentially lead to intermolecular interactions. Indeed upon film formation, intermolecular interactions are evidenced by broadening of the NIR absorption, which may arise due to similar stacking. Complex 3 was shown to undergo similar electropolymerisation to that reported previously for 4, however a significantly more extensive NIR band resulted which, along with poorer counterion penetration upon reduction, suggests a denser film for poly-3, with enhanced interactions between molecules. Extending the NIR absorption to 1400 nm through molecular tuning is highly significant given the technological importance of NIR dyes for applications such as optical communications, and much previous synthetic Nidithiolene work has sought to address this aim.¹²

Due to the excellent film-forming properties of the butylsubstituted **4**, field-effect transistors could be fabricated with the best performing devices showing ambipolar behaviour, with maximum charge carrier mobility of around 10^{-6} cm² V⁻¹ s⁻¹ for electrons, and 10^{-7} cm² V⁻¹ s⁻¹ for holes. BHJ-PV devices were fabricated using for the first time a nickel dithiolene (**4**) as both an electron transport material and a NIR sensitiser. For binary systems with P3HT, we demonstrated the contribution of a dithiolene complex to the efficiency of the cell. Although at present the overall cell efficiencies remain poor, future optimisation of charge mobility or blend morphology could enable this strategy to greatly enhance the NIR light harvesting in BHJ-PVs.

4. Experimental

Electrochemical experiments were performed in dry DCM (stored over KOH, distilled over P_2O_5), or dry MeCN (Sigma-Aldrich), and solutions were degassed with N_2 before use. TBABF₄ was used as supporting electrolyte, which was prepared from tetra-fluoroboric acid and tetrabutyl ammonium hydroxide, and was recrystallised 5 times from water and dried under vacuum at 60 °C for 2 weeks. 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. Electrochemical polymerisation was performed at room temperature on a *ca*. 10 mM monomer solution using the same supporting electrolyte and electrode setup as for the electrochemical experiments.

UV/Vis/NIR measurements were recorded in solution using a quartz cell of path length 10 mm, or as thin films on quartz or FTO substrates fixed perpendicular to the beam on a Perkin-Elmer Lambda 9 spectrophotometer, controlled by a datalink PC, running UV/Winlab software.

Geometry optimisations for isolated molecular units of 3 and 4 were carried out using the Gaussian 03 program,⁴¹ utilising the X-ray crystallographic coordinates of 4 for the starting structures (modified for 3 using ArgusLab 4.0). The wavefunction was expanded using the Pople 6-31G* basis set for all atoms,^{42,43} coupled to the Becke three parameters hybrid exchange and the Perdew-Wang 1991 correlation functionals (B3PW91).44,45 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,46 with the first 70 singlet transitions calculated. Simulated spectra were generated using Gausssum 2.1 freeware program, using a full-width halfmaximum value of 3000 cm⁻¹.

All reagents were used as received, unless otherwise stated. Complex 4, and pro-ligand 2 were synthesised as previously reported.¹³

1-Methylindole-5-carboxaldehyde

To an oven dried microwave vial (25 ml), equipped with a Tefloncoated stirrer bar, was added freshly recrystallised 5-bromo-1methylindole (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 × 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%). $\delta_{\rm H}$ (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) (Scheme 2).



Scheme 2 NMR assignment guide for 5-substituted *N*-methyl indoles synthesised in this work.

5-Ethynyl-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 ylide formed. A solution of 1-methylindole-5-carboxldehyde (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 h, 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 (4×100 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%). $\delta_{\rm H}$ (250 MHz; CDCl₃) 3.00 (s, 1H, CCH), 3.76 (s, 3H, -NMe), 6.47 $(dd, 1H, J = 3.1, 0.8 Hz, H_b), 7.06 (d, 1H, J = 3.1 Hz, H_a), 7.24 (d, J)$ $1H, J = 8.5 Hz, H_e$, 7.35 (dd, $1H, J = 8.5, 1.5 Hz, H_d$), 7.81 (dd, $1H, J = 8.5, 1.5 Hz, H_d$), 7.81 (dd, $1H, J = 8.5, 1.5 Hz, H_d$), 7.81 (dd, $1H, J = 8.5, 1.5 Hz, H_d$), 7.81 (dd, $1H, J = 8.5, 1.5 Hz, H_d$), 7.81 (dd, $1H, J = 8.5, 1.5 Hz, H_d$), 7.81 (dd, $1H, J = 8.5, 1.5 Hz, H_d$), 7.81 (dd, $1H, J = 8.5, 1.5 Hz, H_d$), 7.81 (dd, $1H, J = 8.5, 1.5 Hz, H_d$), 7.81 (dd, $1H, J = 8.5, 1.5 Hz, H_d$), 7.81 (dd, $1H, J = 8.5, 1.5 Hz, H_d$), 7.81 (dd, $1H, J = 8.5, 1.5 Hz, H_d$), 7.81 (dd, $1H, J = 8.5, 1.5 Hz, H_d$), 7.81 (dd, $1H, J = 8.5, 1.5 Hz, H_d$), 7.81 (dd, $1H, J = 8.5, 1.5 Hz, H_d$), 7.81 (dd, $1H, J = 8.5, 1.5 Hz, H_d$), 7.81 (dd, $1H, J = 8.5, 1.5 Hz, H_d$), 7.81 (dd, $1H, J = 8.5, 1.5 Hz, H_d$), 7.81 (dd, $1H, J = 8.5, 1.5 Hz, H_d$), 7.81 (dd, $1H, J = 8.5, 1.5 Hz, H_d$), 7.81 (dd, $1H, J = 8.5, 1.5 Hz, H_d$), 7.81 (dd, $1H, J = 8.5, 1.5 Hz, H_d$), 7.81 (dd, $1H, H_d$), 8.81 (dd, 1H, H_d), 8.81 (dd, $1H, H_d$), 8.81 (dd, 1H, H_d), 8.81 $J = 1.5, 0.8 \text{ Hz}, \text{H}_c$).

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

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 h. The solvent was removed under reduced pressure and the crude product purified by trituration in warm methanol (6 h), yielding pure product after filtration (1.26 g, 68%). $\delta_{\rm H}$ (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).

[TBA][Ni(mi-5edt)₂] ([TBA][3])

To a stirred solution of freshly cut sodium (117 mg, 5.10 mmol) in dry degassed MeOH (35 ml) under nitrogen was added **1** (600 mg, 2.43 mmol), and the solution stirred with gentle warming for 1 h until complete dissolution. [TBA]Br was added

and allowed to dissolve, whereafter a solution of NiCl₂·6H₂O (289 mg, 1.22 mmol) in MeOH (25 ml) was added dropwise over 45 mins. The flask was opened to air and stirring was continued for one hour before cooling in the freezer for one hour. The crude product was filtered, and washed with cold MeOH and purified by recrystallisation from DCM/EtOH, affording the title compound as a brown precipitate (480 mg, 53%). Anal calcd for $C_{38}H_{54}N_3S_4Ni$: C, 61.69; H, 7.36; N, 5.68; S, 17.34; found C, 61.73; H, 7.43; N, 5.57; S, 17.45, $\lambda_{max} = 960$ nm.

[Ni(mi-5edt)₂] (3)

Route 1. Complex [TBA][**3**] (300 mg, 0.405 mmol) was dissolved in MeCN (20 ml) and I₂ (206 mg, 0.810 mmol) was added in MeCN (10 ml). A green precipitate formed immediately, and was filtered and washed with EtOH. The crude product was recrystallised from DCM/EtOH to yield **3** as a dark green precipitate (121 mg, 60%). $\delta_{\rm H}$ (500 MHz; CDCl₃) 3.83 (s, 6H, -NMe), 6.60 (d, 2H, J = 3.1 Hz, H_b), 7.11 (d, 2H, J = 3.1 Hz, H_a), 7.37 (d, 2H, J = 8.7 Hz, H_e) 7.90 (d, 2H, J = 8.7, 1.7 Hz, H_d), 8.33 (d, 2H, J = 1.7 Hz, H_c), 9.75 (s, 2H, C(S)H).

Route 2. To a stirred solution of 1 (594 mg, 2.40 mmol) in THF (24 ml) was added [TMA][OH] \cdot 5H₂O (958 mg, 5.29 mmol) in MeOH (2 ml). After 5 mins, NiCl₂ \cdot 6H₂O (286 mg, 0.515 mmol) in MeOH (2 ml) was added and the reaction mixture stirred at room temperature overnight. [TMA][**3**] was filtered off as a brown precipitate. [TMA][**3**] was dissolved in MeCN (40 ml), and I₂ (974 mg, 3.84 mmol) was added in MeCN (20 ml). A green precipitate formed immediately, and was filtered and washed with EtOH. Recrystallisation in DCM/Et₂O yielded pure **3** as a dark green precipitate (736 mg, 63%). $\delta_{\rm H}$ (500 MHz; CDCl₃) 3.83 (s, 6H, -NMe), 6.60 (d, 2H, J = 3.1 Hz, H_b), 7.11 (d, 2H, J = 3.1 Hz, H_a), 7.37 (d, 2H, J = 8.7 Hz, H_e) 7.90 (d, 2H, J = 8.7, 1.7 Hz, H_d), 8.33 (d, 2H, J = 1.7 Hz, H_c), 9.75 (s, 2H, C(S)H). Anal calcd for C₂₂H₁₈N₂S₄Ni: C, 53.13; H, 3.65; N, 5.63; found C, 53.06; H, 3.53; N, 5.56, $\lambda_{max} = 910$ nm ($\epsilon = 25.6 \times 10^3$ M⁻¹cm⁻¹).

[TBA][Ni(mi-5hdt)₂] ([TBA][4])

A solution of freshly cut sodium (68.5 mg, 2.98 mmol) in dry degassed MeOH (20 ml) was added under nitrogen to **5** (430 mg, 1.42 mmol), and the solution stirred for 1 h until homogeneous. [TBA]Br (914 mg, 2.84 mmol) was added and allowed to dissolve, whereafter a solution of NiCl₂·6H₂O (168 mg, 0.709 mmol) in MeOH (10 ml) was added dropwise over 45 mins. The flask was opened to air and stirring was continued for one hour before cooling in the freezer for one hour. The crude product was filtered and washed with cold MeOH, and purified by recrystallisation from DCM/EtOH, affording the title compound as a brown precipitate (297 mg, 49%). Anal calcd for C₄₆H₇₀N₃S₄Ni: C, 64.84; H, 8.28; N, 4.93; found C, 64.96; H, 8.15; N, 4.84, $\lambda_{max} = 848$ nm.

X-Ray crystallography

4-(1-Methyl-5-indol-5yl)-[1,3]dithiol-2-one (1). Colourless shard (dimensions $0.17 \times 0.14 \times 0.06 \text{ mm}^3$) $C_{12}H_9NOS_2$, T = 100 K, space group $P2_1/c$, $M_r = 247.32$, monoclinic, a = 6.6997 (3) Å, b = 7.3685(4) Å, c = 22.4087(12) Å, $\beta = 93.852(5)^\circ$,

V = 1103.74(10) Å³, $D_c = 1.488$ Mg m⁻³, $\mu = 4.168$ mm⁻¹, no. of reflections for cell = 1937, $\Theta_{max} = 72.6537^{\circ}$, Z = 4, 3096 reflections collected, unique $[R_{int}] = 2124$ [0.0350], $T_{min}/T_{max} = 0.3299/0.7900$, parameters 146, R_1 [$F > 4\sigma(F)$] = 0.0674, wR = 0.1751.

[Ni(mi-5hdt)_2] (4). Dark green plate (dimensions $0.25 \times 0.19 \times 0.06 \text{ mm}^3) \text{ C}_{30}\text{H}_{34}\text{N}_2\text{Ni}_1\text{S}_4$, T = 100 K, space group $P2_1/c$, $M_r = 609.59$, monoclinic, a = 4.31010(13) Å, b = 15.6910(4) Å, c = 21.4795(7) Å, $\beta = 91.526(3)^\circ$, V = 1452.14(8) Å³, $D_c = 1.394 \text{ Mg}$ m⁻³, $\mu = 0.978 \text{ mm}^{-1}$, no. of reflections for cell = 5598, $\Theta_{max} = 28.478^\circ$, Z = 2, 8971 reflections collected, unique $[R_{int}] = 3166$ [0.046], $T_{min}/T_{max} = 0.62/0.94$, parameters 169, R_1 [$F > 4\sigma(F)$] = 0.0458, wR = 0.1299, $\Delta \rho_{max}/e$ Å⁻³ = 0.67, $\Delta \rho_{min}/e$ Å⁻³ = -1.01.

Device fabrication and testing

For organic field-effect transistor (OFET) measurements, a bottom-contact, bottom-gate architecture was employed. A heavily doped silicon wafer served as both the substrate and global gate electrode, with a 200 nm thermally grown SiO₂ layer (capacitance (C_i) of 17 nF cm⁻²) as the gate dielectric. Gold source and drain electrodes were defined using standard photolithographic techniques. The SiO₂ surface was then passivated with a layer of hexamethyldisilane (HMDS). Material **4** was then deposited onto the samples *via* spin-casting from solution, using the solvent chloroform. Finally the OFETs were annealed at 50 °C for 30 min to evaporate any residual solvent. A schematic representation of the OFET structure is shown in the inset to Fig. 6(b).

For blended films of polymer/4, these were spin coated at a range of speeds onto quartz substrates, and the UV/Vis spectra measured. For P3HT, a 1 : 1 weight ratio of dithiolene to polymer was dissolved in chlorobenzene (at 70 °C), giving a total dissolved content of 40 mg ml⁻¹. This blend was spin coated at 2000, 2500, 3000 and 3500 rpm. For PPV, due to its reduced solubility in chlorobenzene compared to P3HT, a 1 : 1 weight ratio of dithiolene to polymer, with a total dissolved content of 10 mg ml⁻¹, was used. The blend was spin at 1500, 2000, 2500 and 3000 rpm. The thickness of these films was analysed using a Dektak surface profiler.

EQE measurements were performed using a 100 W tungsten halogen lamp dispersed through a monochromator as the light source and a Keithley 237 source meter unit (SMU) to measure the short circuit current at various wavelengths. Incident light intensity was continuously monitored during measurement by a reference photodiode calibrated by a Hamamatsu S8746-01 calibrated photodiode.

For photovoltaic devices, the substrates used were ITO coated glass, cleaned in an ultrasonic bath (10 mins IPA, 10 mins acetone), and oxygen plasma etched (250 W, 10 mins) before use. An anodic buffer layer of poly(3,4-ethylene-dioxythiophene): poly(styrene sulfonate) (PEDOT:PSS)⁴⁷ was first spin coated (6000 rpm, 60 s), and annealed (250 °C, 10 mins) under N₂. Under air free conditions, the active layers were then spin coated at 2000 rpm for 60 s for both polymers, affording films of thickness ~100 nm. In order to assess whether an annealing step resulted in better performance for the P3HT devices, half of the P3HT substrates were annealed at 70 °C for 10 mins. Aluminium

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