# Influence of the R-substituents on the properties of [Ni(R<sub>2</sub>pipdt)(dmit)] complexes and crystal structure where $R = CH_2C_6H_5$ †‡§

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 $[Ni(R_2pipdt)(dmit)], (R_2pipdt = 1,4-disubstituted-piperazine-3,2-dithione, R = CH_2C_6H_5; dmit = 1,4-disubstituted-piperazine-3,2-disubstituted-piperazine-3,2-disubstituted-piperazine-3,2-disubstituted-piperazine-3,2-disubstituted-piperazine-3,2-disubstituted$ 1,3-dithiole-2-thione-4,5-dithiolate) (1b) has been prepared and characterised and the properties compared with those of the known complex 2b belonging to the same class where  $R = Pr^{i}$ . Cyclic voltammetry of 1b and 2b was carried out and compared with that of the respective  $R_2$  pipdt ligand precursors (1a and 2a). The nature of the R-groups of the pipdt ligand exerts an effect on the redox potentials and confirmed the position of the LUMO as mainly on the R<sub>2</sub>pipdt part of the complex. Accordingly the low frequency absorption, assigned to the HOMO-LUMO transition which has inter-ligand charge-transfer character, is found for 1b at lower frequency when compared to the corresponding transition of **2b**. In situ EPR was carried out on electroreduced radical species of the  $R_2$  pipdt ligand precursors (1a, 2a) and corresponding complexes (1b, 2b). This revealed considerable delocalisation of the unpaired electron on the R2pipdt ligand in 1b and 2b with coupling constants to N and H comparable with those of 1a and 2a. Complex 1b crystallised in the space group Pnma and shows an essentially planar complex (with out-of-plane R groups)  $\pi$  stacked at a distance of 3.65(1) Å. Such a one-dimensional structure is not achieved in the case of 2b, where the complex units are almost parallel and head-to-tail with each other forming dimers and this difference in solid-state packing is apparent in the diffuse reflectance spectrum of each. Plane-wave DFT calculations for 1b revealed a highly one-dimensional band structure with considerable band dispersion along the direction of greatest molecular interaction via  $\pi$ -stacking.

## Introduction

Metal dithiolenes have been intensely studied since the 1960s for their novel properties that lead to many applications in the fields of conducting and magnetic materials, dyes, non-linear optics and catalysis.<sup>1,2,3</sup> Metal dithiolene complexes possess highly delocalised frontier orbitals and this results in properties including redox activity with one or more reversible redox processes (depending on the metal), low energy absorption in the visible/NIR region and strong intermolecular interactions through the S atoms in the delocalised core. The electronic and photophysical properties of dithiolene complexes can be tuned by variation of the attached ligand set<sup>4</sup> and of particular interest, the ligand 1,3-dithiole-2thione-4,5-dithiolate (dmit)<sup>5</sup> has been widely used in the field of conducting materials.<sup>6,7</sup>

Unsymmetrical [Ni(II)(dithione)(dithiolate)] complexes, where the dithione is formally a neutral donor ligand and the dithiolate is formally a dianionic species, are of interest as NIR dyes and NLO materials due to the intense LLCT transition that these display.<sup>8,9,4</sup> These have been assigned as "push-pull" complexes where the "push" is due to the electron donating dithione ligand and the "pull" is due to the electron withdrawing dithiolate ligand.9 In the case of  $[Ni(R_2pipdt)(dithiolate)]$  complexes  $(R_2pipdt = 1,4$ disubstituted-piperazine-3,2-dithione) (Fig. 1, with dithiolate = dmit), this was illustrated through DFT calculations,9 wherein the HOMO in these complexes was assigned as based mostly on the dithiolate ligand and the LUMO based mostly on the dithione, although both have components over the entire molecule. This results in a highly delocalised structure with a small HOMO-LUMO gap and therefore an intense NIR band in their absorption spectrum. Changing the characteristics of the R groups may be expected to change the electronic characteristics of a "push-pull" complex, resulting in a redistribution of the electron density and greater emphasis being placed on one of the resonance forms.



Fig. 1 Structure of complexes studied in this work.  $R = CH_2C_6H_5$  (Bz), 1b;  $R = Pr^i$ , 2b.

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 $<sup>\</sup>S$  Electronic supplementary information (ESI) available: UV/Vis and EPR spectra of compounds  $1a^-, 1b^-, 2a^-$  and  $2b^-;$  Fig. S1–S6 and Table S1. See DOI: 10.1039/b712243h

Studies of the [Ni(R<sub>2</sub>pipdt)(dithiolate)] series of complexes to date have focussed largely on their optical properties in the context of NLO and NIR dyes. Ni-bis(dithiolene) complexes, however, often show attractive superconducting, metallic and photoconducting properties,<sup>6.7,10</sup> that depend crucially on the solid-state packing of the complexes as well as the intrinsic molecular characteristics. We present in this paper spectroscopic, structural and computational results that compare the influence of the R-substituents of the R<sub>2</sub>pipdt ligand on the solid-state as well as the molecular properties of [Ni(R<sub>2</sub>pipdt)(dmit)], **1b** (R = CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>), and **2b** (R = Pr<sup>i</sup>).

#### **Results and discussion**

The novel mixed dithiolene complex **1b** (Fig. 1) was prepared by an analogous method to  $[Ni(Pr_{2}^{i}pipdt)(dmit)]$  **2b** which, despite the interesting nature of these complexes and the general importance of the dmit ligand, is the only previously structurally characterised example of the series shown in Fig. 1.<sup>4,9</sup> (Other examples, not structurally characterised, have been reported previously in a PhD thesis.) Synthesis involved reaction of  $[TBA]_2[Ni(dmit)_2]$  with the dicationic symmetric Ni dithione molecules,  $[Ni(R_2pipdt)_2][BF_4]_2$ .

Crystals of **1b** were grown by slow diffusion of diethyl ether into a saturated solution of 1b in DMF. For 1b the central Ni atom is coordinated by four S atoms in a square planar environment with Ni–S bonds ranging from 2.1477(5)–2.1628(4) Å (Fig. 2). The molecule is essentially planar except for the Bz substituents at the R<sub>2</sub>pipdt N and the torsion angle of only 5.88° around S12, C22, N32, C62 suggests that the Np<sub> $\pi$ </sub>-lone pair is almost parallel to the  $C_2S_2$   $\pi$ -system as previously reported for **2b**. The Ni–S bond lengths are similar in value to those previously published for other "push-pull" coordination complexes9 (and references therein) which suggests that the Ni–S  $\sigma$  bonds are more or less equivalent irrespective of the nature of the ligand and that the Ni-S  $\pi$  interactions have only minor importance or none at all.<sup>9</sup> The C-S bond lengths are shorter (ca. 0.04 Å) in the R<sub>2</sub>pipdt ligand than in dmit (since it has  $\pi$  donors adjacent to the C<sub>2</sub>S<sub>2</sub> core). The C–C bond is significantly longer in the  $R_2$  pipdt (1.477(3) Å) than



Fig. 2 X-Ray crystal structure of 1b showing the atom labeling scheme. Selected bond lengths (Å) and angles (°): Ni–S(12) 2.1477(5), Ni–S(11) 2.1627(4), S(11)–C(21) 1.7306(16), S(12)–C(22) 1.6908(16), C(22)–C(22') 1.477(3), C(21)–C(21') 1.349(3), S(12)–Ni–S(11) 87.544(16), S(11)–Ni–S(11') 94.07(2), S(11')–Ni–S(12') 87.541(16), S(12')–Ni–S(12) 90.84(3).

the dmit (1.349(3) Å) corresponding to the electron poor nature of the pipdt and electron rich dmit ligand. The crystal lattice shows the complex forms stacks (Fig. 3) with an interplanar distance of 3.65(1) Å, which is typical of  $\pi$ -stacked metal dithiolene complexes. In contrast, such a one-dimensional structure is not observed in the case of **2b**. In this case the complex units are almost parallel and head-to-tail with each other forming dimers through short contacts between the S-atoms of dmit and the two carbon atoms of the C<sub>2</sub>S<sub>2</sub> moiety of Pr<sub>2</sub><sup>i</sup>pipdt (3.42 and 3.34 Å) (Fig. 4).<sup>9</sup>



Fig. 3 View along the *b*-axis showing packing motif of 1b.



Fig. 4 X-Ray structure showing head-to-tail dimer packing for 2b.9

The electrochemistry of **1b** and **2b**, along with the corresponding  $R_2$ pipdt ligand precursors (**1a** and **2a**) was studied by cyclic voltammetry in a solution of 0.1 M TBABF<sub>4</sub> in DMF at 293 K. Redox potentials for the processes are listed in Table 1. Each of the two pipdt ligand precursors, **1a** and **2a** shows one reduction process within the solvent window (Fig. 5), chemically reversible for **1a** and quasireversible for **2a**. Reduction of the ligands is noticeably easier for **1a** than **2a**, indicating that the substituent on the N of the pipdt ligand influences the reduction potential of the ligand. Both ligands show one chemically irreversible

 Table 1
 Redox potentials,  $E_{1/2}$ , of the (R<sub>2</sub>pipdt) ligand precursors and [Ni(R<sub>2</sub>pipdt)(dmit)] complexes in DMF solution. All processes are chemically reversible unless otherwise indicated: \*irreversible, <sup>§</sup>quasi reversible

		$E_1/V$	$E_2/V$	$E_3/V$
1a	Bz2pipdt		-1.24	1.13*
1b	[Ni(Bz2pipdt)(dmit)]		-0.41	0.69*
2a	Pr <sup>i</sup> 2pipdt		-1.40 <sup>§</sup>	1.01*
2b	[Ni(Pr <sup>i</sup> 2pipdt)(dmit)]		-0.49	0.65*



Fig. 5 Cyclic voltammogram of the reduction (left) and oxidation (right) of 1a (solid line) and 2a (broken line) in a solution of  $0.1 \text{ M TBABF}_4$  in DMF at 293 K.

oxidation within the solvent window and the ease of oxidation is approximately converse to that of the ease of reduction of the ligands, with oxidation easier for **2a** than **1a** (Fig. 5). After coordination of each ligand to a metal centre the reduction potentials of the resulting complexes is shifted to a less negative potential (Fig. 6). Both complexes **1b** and **2b** show two chemically reversible or quasireversible reductions within the solvent window. The electrochemistry of **2b** shows similar results to the previously reported data in acetonitrile.<sup>9</sup> The ease of reduction for the complexes follows the order **1b** > **2b**, analogous to the ligand precursors, and the reduction potentials of the [Ni(R<sub>2</sub>pipdt)(dmit)] complexes are again shown to be dependant on the R substituent on the pipdt ligand. This can be seen more clearly in the second reduction of the complexes, where the second reduction potential of **2b** is significantly more negative than that of **1b**.



Fig. 6 Cyclic voltammogram of the reductions (left) and oxidation (right) of 1b (solid line) and 2b (broken line) in a solution of  $0.1 \text{ M TBABF}_4$  in DMF at 293 K.

Both complexes **1b** and **2b** show one chemically irreversible oxidation process, and **2b** is easier to oxidise (Fig. 6). Previous DFT calculations on [Ni(H<sub>2</sub>pipdt)(dithiolate)]<sup>9</sup> and consideration of the bond lengths in **1b** and **2b**<sup>9</sup> suggest that although the frontier orbitals are spread over the entire molecule, the LUMO has a greater component on the R<sub>2</sub>pipdt ligand and the HOMO has a greater component on the dithiolate ligand (dmit). Our results with varying R indicate a greater variation in the reduction potential (0.13 V for  $E_1$ , 0.08 V for  $E_2$ ) than the variation in the oxidation potential (0.04 V for  $E_3$ ) and this adds experimental evidence to support the calculated locations of the frontier orbitals. In all the electrochemical results **1a/1b** is more electron rich than **2a/2b** and it might be envisaged that even larger changes could be engineered by using a wider variety of R groups.

Raman spectra have previously been collected to provide information on the electron distribution in related dithiolene complexes.<sup>9</sup> Typically, the C=C stretch shows a shift to higher frequency as the negative charge on the complex increases: this peak is found at 1435 cm<sup>-1</sup> in  $[Ni(dmit)_2]^{2-}$  and at 1390 cm<sup>-1</sup> in

 $[Ni(dmit)_2]^{1-}$ . Complex **1b** shows a peak at 1430 cm<sup>-1</sup>, in agreement with the assignment of a -2 formal charge to the dmit ligand. These results are indicative of "pull" character (dithiolate) for the dmit ligand and hence "push" character (dithione) for the Bz<sub>2</sub>pipdt ligand, with significant separation of charges in the resulting complex.<sup>4,9</sup>

The UV/Vis spectra of compounds 1b and 2b (Fig. 7, Table 2) show an intense peak in the UV, a visible peak near 490 nm and two peaks which partially overlap in the 700-850 nm region. Table 2 shows the  $\lambda_{max}$  values and molar extinction coefficients. According to previous assignments, the lowest energy band is due to a HOMO-LUMO transition. This transition has a certain LLCT character due to the unbalanced contribution to the frontier  $\pi$ -orbitals of the two ligands: a greater weight of the R<sub>2</sub>pipdt to the LUMO (dithione) and a greater weight of dmit to the HOMO (dithiolate) and its nature is consistent with the predicted and observed negative solvatochromism and molecular first hyperpolarisability.<sup>4,8,9</sup> The value of  $\lambda_{max}$  follows the order 1b > 2b (858 nm vs. 829 nm) indicating that the HOMO-LUMO gap is smaller for 1b in agreement with electrochemical results which showed that  $E_3-E_2$  is smaller for 1b (Table 1) and in keeping with the more electron rich Pr<sup>i</sup> groups raising the energy of the LUMO more than that of the HOMO. An inspection of the frontier orbitals, based on approximate Extended Hückel methods,11 allows assignment of the peak (shoulder) which appears near 700 nm. This absorption, which is particular to the dmit class of the [Ni(R<sub>2</sub>pipdt)(dithiolate)] family, may be assigned to the HOMO  $\rightarrow$  LUMO + 5 transition which involves  $\pi$  orbitals with a predominant contribution of the dmit ligand (see Fig. 8). Note that in this complex due to the presence of four additional closely-spaced  $\pi$ -orbitals of the benzyl substituents the LUMO + 5 orbital is the next highest orbital based on the dmit moiety.



Fig. 7 UV/Vis/NIR spectra of **1b** (solid red line) and **2b** (broken black line) in DMF solution at 293 K.

To gain insight into the influence of the solid-state structure on the electronic characteristics, the diffuse reflectance spectra of **1b** and **2b** were recorded (Table 2, Fig. 9). At higher energies, the bands observed corresponded to equivalent absorptions for the solution species and the principal differences from the solution spectra occurred for the lower energy bands. For both **1b** and **2b**, the band arising from the HOMO–LUMO transition was shifted to  $\lambda_{max} = 960$  nm in the solid state, indicative of the interaction with neighbouring molecules. For **2b**, however, an additional shoulder at 1450 nm was evident. The presence of this

	$\lambda_{ m max}/ m nm\left(\lambda_{ m max}/ m cm^{-1} ight)\left(arepsilon/M^{-1} ight. m cm^{-1} ight)$	$\lambda_{ m max}/ m nm~(\lambda_{ m max}/ m cm^{-1})~(\epsilon/M^{-1}~ m cm^{-1})$	$\lambda_{ m max}/ m nm~(\lambda_{ m max}/ m cm^{-1})~(e/M^{-1}~ m cm^{-1})$	$\lambda_{ m max}/ m nm~(\lambda_{ m max}/ m cm^{-1})~(arepsilon/ m M^{-1}~ m cm^{-1})$	$\lambda_{ m max}/ m nm~(\lambda_{ m max}/ m cm^{-1})$
1b	$326.5 \\ (30.600) \\ (33 \times 10^3)$	$ \begin{array}{c} 487 \\ (20500) \\ (9.7 \times 10^3) \end{array} $	750* (13300)	$858 (11 650) (10.6 \times 10^3)$	
2b	$\begin{array}{c} 3.19\\(31 \ 350)\\(30 \times 10^3)\end{array}$	$\begin{array}{c} 490.5 \\ (20400) \\ (9.0 \times 10^3) \end{array}$	720* (13 900) —	$\begin{array}{c} 829\\ (12\ 100)\\ (8.2\ \times\ 10^3)\end{array}$	
1b DR	340 (29 400)	500 (20 <i>00</i> 0)	780 (12800)	960 (10 400)	
2b DR	340 (29 400)	500 ( <i>20 000</i> )	780 (12800)	960 (10 400)	1450* ( <i>6900</i> )







Fig. 9 The diffuse reflectance spectra of [Ni(Bz<sub>2</sub>pipdt)(dmit)] (dotted line) and [Ni(Pr<sup>i</sup>pipdt)(dmit)] (continuous line). The absorbances are reported in arbitrary units.

additional band presumably arises from a new absorption within the dimer units due to the particularly strong dimerisation present in 2b (Fig. 4) with short  $S \cdots C$  interactions between molecules of 3.42 and 3.34 Å, compared with the regular stacks of weaker interacting molecules for 1b (interplanar separation of 3.65 Å). Thus, the diffuse reflectance spectra reflect the differences in solidstate electronic characteristics that arise from the different packing of 1b and 2b.

UV/Vis/NIR spectroelectrochemistry was performed on ligands 1a and 2a (Table S1, Fig. S1 and S2§) for comparison with complexes 1b and 2b, but poor solubility of the latter upon reduction at the low temperatures required for chemical stability precluded measurement of these so no further interpretations could be made. In situ EPR spectroelectrochemistry was performed on 1a, 1b, 2a and 2b (Fig. 10 and Fig. S3-S6§). The distribution of the unpaired electron density on the reduced species was studied by analysing the couplings to compare the location of the first reduction electron in 1b and 2b to its location on the corresponding uncoordinated ligand precursor, 1a and 2a. Each species was reduced in a solution of 0.1 M TBABF<sub>4</sub> in DMF at 233 K to give an EPR active solution and at a higher temperature (293 K) the spectra were more resolved (Tables 3 and 4). Simulation of the spectra in terms of the g-factor, coupling constants and line width was achieved for each. In every case, on introduction of a second electron to form the dianionic species the signal collapsed

**Table 3** EPR coupling constants for  $1a^-$  and  $1b^-$  in 0.1 M TBABF<sub>4</sub>– DMF at 293 K. All hyperfine coupling constants are given in G.  $\Delta$  = linewidth

Paran	neter 1a-	1b-	
$\begin{array}{c} A (\mathrm{H} \\ A (\mathrm{H} \\ A (\mathrm{N} \\ \Delta \\ g \end{array}$	$\begin{array}{c} \times \ 4) & 2.211 \\ \times \ 4) & 2.211 \\ \times \ 2) & 2.82 \\ & 0.8 \\ & 1.9987 \end{array}$	3.68 2.211 2.722 1.4 2.0013	

**Table 4** EPR coupling constants for  $2a^-$  and  $2b^-$  in 0.1 M TBABF<sub>4</sub>– DMF at 233 K. All hyperfine coupling constants are given in G.  $\Delta =$  linewidth

Parameter	2a <sup>-</sup>	2b <sup>-</sup>
$a (H \times 2)$	0.619	0.619
$a (H \times 4)$	3.05	4.206
$a (N \times 2)$	2.392	4.206
$\Delta$	0.5	3.0
g	1.9982	1.9988



**Fig. 10** EPR spectrum of  $1a^{1-}$  in solution of 0.1 M TBABF<sub>4</sub> in DMF at 293 K. Egen = -1.70 V.

as the second electron enters the same orbital as the first to give a diamagnetic ion.

In each case for a ligand, and its corresponding [Ni(R<sub>2</sub>pipdt)(dmit)] complex, it can be seen that the reduction electron couples to the ring N atoms, ring H atoms and the H atoms on the N-substituent, illustrating the considerable electron delocalisation in all cases. The comparable magnitude of the coupling constants in the free ligands and in the complexed ligands strongly suggest that for the [Ni(R<sub>2</sub>pipdt)(dmit)] complexes (1b and 2b) the reduction electron locates itself primarily on the dithione ligand. Indeed, in the case of 2b<sup>-</sup>, coupling to the R<sub>2</sub>pipdt N-atoms and H-atoms is increased in comparison with  $2a^{-}$ . In addition, the g-factor in the complexes 1b and 2b are very close to the free electron value typical of organic radicals, suggesting that the LUMO has little contribution from the Ni atom and is largely ligand based. The results of this EPR study therefore support assignment of the LUMO of these complexes as highly delocalised and R<sub>2</sub>pipdt ligand based, consistent with the findings of the previous theoretical studies.<sup>4,9</sup>

Due to the extended intermolecular interactions *via*  $\pi$ -stacking shown by **1b** in the X-ray structure, we sought to further explore the bulk material properties of this solid. Accordingly plane-wave DFT calculations were carried out to investigate the molecular overlap and resulting band structure. The result obtained for the distribution of the frontier orbitals on individual molecules was consistent with those of previous calculations on isolated molecules using localised basis functions.<sup>9</sup> The band structure is shown along the principle reciprocal-space axes (Fig. 11) (for a tetragonal unit cell, these are parallel to the direction of the corresponding real axes).



**Fig. 11** Band structure calculation for **1b** through plane-wave DFT calculations showing bands around the Fermi level (dotted line).

There are four molecules per unit cell and this is reflected in the presence of four HOMO bands around 1.5–2 eV and four LUMO bands around 2.5 eV. For such DFT calculations, the gap between filled and vacant orbitals is typically underestimated and this is the case here, as shown by the diffuse reflectance spectrum for **1b** where the low-energy tail extending to around 1 eV gives an experimental estimate of the gap.

Relevant to the potential conductivity properties, we observe significant band dispersion along the (0, 0, 0.5) direction which corresponds to the direction of greatest molecular overlap as shown in the X-ray structure (Fig. 3, *c*-axis direction). The band dispersion of around 0.25 eV for both HOMO and LUMO bands is comparable to that observed in many  $[Ni(dmit)_2]^{x-}$  salts<sup>12</sup> which suggests that  $[Ni(R_2pipdt)(dmit)]$  complexes, when the R substituents have the suitable steric and electronic features (*e.g.* **1b**), may be able to show electro-conductivity when suitably doped. Almost no intermolecular interaction is determined for **1b** along the (0, 0.5, 0) direction, however, consistent with the separation of the molecular units caused by the benzyl groups along the *b*-direction of the crystal. Thus, **1b** forms an essentially one-dimensional material in contrast with the typical two-dimensional characteristics of many  $[Ni(dmit)_2]^{x-}$  salts.

## Conclusions

The work reported has provided the first insight into the role of the R-groups in controlling the molecular and solid-state electronic and structural properties of the complexes  $[Ni(R_2pipdt)(dmit)]$ . Electrochemical, spectroscopic and spectroelectrochemical evidence for the isolated molecules has confirmed that the LUMO is

primarily based on the  $R_2$ pipdt ligand and that the LUMO energy (and to a lesser extent the HOMO energy) can be varied by the choice of suitable R. Structural, spectroscopic and computational work has shown the influence of the R-groups on the solid state structure and properties of the materials. Variation of the R-group from  $Pr^i$  (2b) to benzyl (1b) leads to a uniform one-dimensional stack rather than the strongly dimerised motif of the former. This is reflected in the diffuse reflectance spectra of the complexes and in the similar band dispersion for 1b to that observed for example in [Ni(dmit)<sub>2</sub>]. This suggests potential for these complexes as conducting materials when suitably doped. Future work will include study of the conductivity properties of 1b in crystalline and thin film form when doped chemically or in a field-effect transistor.

#### Experimental

Electrochemical studies were carried out using a DELL GX110 PC with General Purpose Electrochemical System (GPES), version 4.8 software connected to an autolab system containing a PGSTAT 20 potentiostat. The techniques used a three electrode configuration, with a 0.5 mm diameter Pt disc working electrode, a Pt rod counter electrode and an Ag/AgCl (saturated KCl) reference electrode against which the ferrocenium/ferrocene couple was measured to be +0.55 V. The supporting electrolyte was 0.1 M tetrabutylammonium tetrafluoroborate (TBABF<sub>4</sub>).

*In situ* EPR spectra were recorded on an X-Band Bruker ER200D-SCR spectrometer, connected to PC running EPR Acquisition System, version 2.42 software. Species were electrogenerated using a BAS CV-27 Voltammograph and temperature controlled using a Bruker ER111VT unit.

Diffuse reflectance spectra (2000–300 nm) were recorded on KBr pellets by using a Cary 5 spectrophotometer equipped with a diffuse reflectance accessory.

Raman spectra were taken at room temperature on a single crystal by using a Raman microscope (BX 40, Olimpus) spectrometer (ISA xy 800) equipped with an Ar<sup>+</sup> laser ( $\lambda = 514.15$  nm). A 180° reflective geometry was adopted. The samples were mounted on a glass microscope slide and the scattering peaks were calibrated against a Si standard ( $\lambda = 520$  cm<sup>-1</sup>). A typical spectrum was collected with a 300 s time constant at a 1 cm<sup>-1</sup> resolution and was averaged over 2 scans. No sample decomposition was observed during the experiments.

For the UV/Vis spectroelectrochemistry study, the quartz cell used was 0.5 mm thick, the working electrode a Pt/Rh gauze, the counter electrode a Pt wire and the reference electrode Ag/AgCl. A Perkin-Elmer Lambda 9 spectrophotometer, linked to a PC running UV/Winlab software was used to record the spectra. In every case after recording the final spectrum the potential was adjusted so that the neutral starting material was regenerated and each absorption spectrum was observed to return exactly to that of the starting species, thus the monoreduced species  $1a^-$  and  $2a^-$  are all stable at 213 K.

DFT plane wave calculations were performed using the density functional formalism within the generalized gradient approximation using the CASTEP code.<sup>13,14</sup> The electronic wavefunctions are expanded in a plane wave basis set up to a kinetic energy cut off of 380 eV which converges the total energy of the system to better than 1 meV atom<sup>-1</sup>. The valence electron and ion interactions

are described using ultrasoft pseudo potentials. Integrations over the Brillouin zone are performed on a grid which also converges the total energy of the system to 1 meV atom<sup>-1</sup>. Geometry optimizations are performed by relaxing the positions and unit cell parameters under the influence of the Hellmann–Feynman forces and stresses respectively.

All chemicals were used as supplied by Sigma-Aldrich. [TBA]<sub>2</sub>[Ni(dmit)<sub>2</sub>] was synthesised by a previously published method.<sup>5</sup>

Bz<sub>2</sub>pipdt (1,4-dibenzyl-piperazine-2,3-dithione) (1a) was synthesised as previously reported.<sup>15</sup> The synthesis departed from that of the original synthesis for the conversion of the diketone product to the dithione. Lawessons reagent was used for this conversion as previously described for a related ligand.<sup>16</sup> Yield 51.0%. MS (FABMS) m/z: 327 (M<sup>+</sup>). Anal calcd for C<sub>18</sub>H<sub>18</sub>N<sub>2</sub>S<sub>2</sub>: C, 66.2; H, 5.6; N, 8.6. Found C, 66.7; H, 6.1; N, 9.3.

[Ni(Bz<sub>2</sub>pipdt)<sub>2</sub>][BF<sub>4</sub>]<sub>2</sub> was synthesised by a similar method to that previously reported for Pt analogues of the complex.<sup>17</sup> NiCl<sub>2</sub>·6(H<sub>2</sub>O) (0.2 g, 0.84 mmol) was dissolved in *ca*. 50 mL EtOH and **1a** (0.55 g, 1.68 mmol) was dissolved in 50 mL DCM and the two solutions were added together and stirred at RT for 30 min. The solvent was removed and the crude product was dissolved in EtOH before filtering to remove excess ligand. NaBF<sub>4</sub> (0.184 g, 1.68 mmol) was added as a solid to the solution and the mixture was stirred at RT until a solid product precipitated. The product was recrystallised by dropwise addition of diethyl ether to a hot solution of the product in MeCN. Yield 57.4% MS (FABMS) m/z: 797 ([{Ni(Bz<sub>2</sub>pipdt)<sub>2</sub>}(BF<sub>4</sub>)]<sup>+</sup>). Anal calcd for C<sub>36</sub>H<sub>36</sub>N<sub>4</sub>S<sub>1b2</sub>F<sub>8</sub>Ni: C, 48.8; H, 4.1; N, 6.3. Found C, 48.6; H, 4.1; N, 6.2.

[Ni(Bz<sub>2</sub>pipdt)(dmit)] (**1b**) was synthesised by modifying the previously reported method for **2b**.<sup>4</sup> Yield 92.0% MS (FABMS) m/z: 581 (M<sup>+</sup>). Anal calcd for C<sub>21</sub>H<sub>18</sub>N<sub>2</sub>S<sub>7</sub>Ni: C, 43.4; H, 3.1; N, 4.8. Found C, 43.6; H, 1.6; N, 4.7.

 $[Ni(Pr^{i}pipdt)_{2}][BF_{4}]_{2}$  was synthesised as described previously.<sup>4</sup> MS (FABMS) m/z: 259 ( $[Ni(Pr^{i}pipdt)_{2}]^{2+}$ ), 605 ( $[{Ni(Pr^{i}pipdt)_{2}}(BF_{4})]^{+}$ ). Yield 66.0%. Anal calcd for  $C_{20}H_{36}N_{4}S_{4}B_{2}F_{8}Ni$ : C, 34.7; H, 5.2; N, 8.1. Found C, 34.5; H, 5.2; N, 7.7.

[Ni(Pr<sup>i</sup>pipdt)(dmit)] (**2b**) was synthesised according to the literature method.<sup>4</sup> Yield 71.4%. MS (FABMS) m/z: 484 (M<sup>+</sup>). Anal calcd for C<sub>13</sub>H<sub>18</sub>N<sub>2</sub>S<sub>7</sub>Ni: C, 32.2; H, 3.7; N, 5.8. Found C, 32.3; H, 3.65; N, 5.3.

X-Ray crystallography: \$\$ Green lath-like needles of 1b (dimensions  $0.58 \times 0.19 \times 0.07 \text{ mm}^3$ ) were grown by slow diffusion of diethyl ether into a saturated solution of 1b in DMF. Single crystal X-ray diffraction data were collected using Mo-Ka radiation on a Smart APEX CCD diffractometer equipped with an Oxford Cryosystems low-temperature device operating at 150 K. An absorption correction was applied using the multi-scan procedure SADABS.<sup>18</sup> The structure was solved by Patterson methods  $(DIRDIF)^{19}$  and refined by full-matrix least squares against  $|F|^2$ using all data (SHELXL-97).<sup>20</sup> Figures were prepared using the programme Mercury.<sup>21</sup> The molecule lies with its long axis in a crystallographic mirror plane. C42/C52 are disordered about the mirror, with occupancies both equal to 0.5. N-C and C-C were lightly restrained to 1.45 and 1.52 Å. The part-weight atoms were refined with isotropic displacement parameters, all other non-H atoms were refined with anisotropic displacement parameters. H-atoms were placed in idealized positions. C<sub>21</sub>H<sub>18</sub>N<sub>2</sub>S<sub>7</sub>Ni, T/K = 150, space group *Pnma*, a = 19.1586(6), b = 19.5819(5), c = 6.1048(2) Å, V = 2290.29(12) Å<sup>3</sup>, no. reflections for cell = 7912,  $\theta_{\text{max}}(^{\circ}) = 28.75$ , Z = 4,  $D_c = 1.686$  Mg m<sup>-3</sup>,  $\mu = 1.500$  mm<sup>-1</sup>, reflections collected = 25 384, unique [ $R_{\text{int}}$ ] = 2941 [0.0376], no.  $I > 2\sigma = 2487$ ,  $T_{\text{min}}/T_{\text{max}} = 0.684/0.900$ , parameters = 144,  $R_1$ [ $F > 4\sigma(F)$ ] = 0.0298, wR = 0.0758, S = 1.046,  $\Delta\rho_{\text{max}}/e$  Å<sup>-3</sup> = 0.50,  $\Delta\rho_{\text{min}}/e$  Å<sup>-3</sup> = -0.55.

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