Supplementary Material (ESI) for Journal of Materials Chemistry

Synthesis, Structure and Spectroscopic Properties of a New Class of Polymerisable Nickel Dithiolenes

Simon Dalgleish,[a] Carole A. Morrison,[a] Derek S. Middlemiss,[b] Andrew R. Mount,[a] Anna Collins,[a] Luca Pilia,[c] Angela Serpe,[c] M. Laura Mercuri,[c] Susan J. Roberts-Bleming,[d] Adam Charlton,[d] Paola Deplano,*[c] Patrick J. Murphy,[d] Neil Robertson*[a]

[a] *School of Chemistry and EaSTCHEM Research School, University of Edinburgh, West Mains Road, Edinburgh, UK. EH9 3JJ. Email: nrobert1@staffmail.ed.ac.uk*
[b] *Department of Chemistry and WESTCHEM Research School, University of Glasgow, Glasgow. G12 8QQ, UK.*
[c] *Dipartimento di Chimica Inorganica e Analitica,, S.S. 554, Bivio per Sestu, 09042 Monserrato, Cagliari, Italy.*
[d] *Department of Chemistry, University of Wales, Bangor Gwynedd, Wales. LL57 2UW.*

Supplementary Information

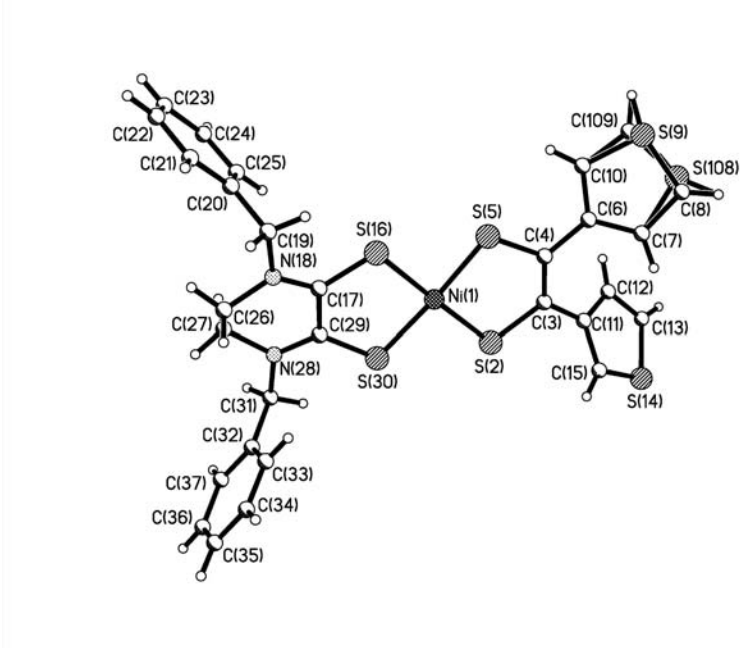

Fig. S1 Crystal structure of **3** showing atom numbering scheme and thermal ellipsoids at 50% probability.

Bond	Bond Length / Å	
	Observed	Calculated
Ni(1)-S(2)	2.1341(9)	2.134811
Ni(1)-S(5)	2.1209(10)	2.134602
Ni(1)-S(16)	2.1593(9)	2.149570
Ni(1)-S(30)	2.1662(10)	2.156362
S(2)-C(3)	1.755(3)	1.753897
S(5)-C(4)	1.755(3)	1.754215
S(16)-C(17)	1.687(3)	1.701575
S(30)-C(29)	1.688(3)	1.705678
C(3)-C(4)	1.357(5)	1.367752
C(17)-C(29)	1.480(5)	1.461147

Angle	Angle Size / °	
	Observed	Calculated
S(2)-C(3)-C(4)-S(5)	-4.10	-2.47
S(16)-C(17)-C(29)-S(30)	14.83	3.27

Table S1a Selected torsion angles of **3** showing an, overall, square planar coordination geometry with a strain away from planarity induced by the R_2pipdt ligand.

Table S1b Selected bond lengths of **3** showing a uniform over-estimation of calculated bond lengths of isolated molecules, but an agreement of the [Ni(dithiolate)(dithione)] nature of the complex.

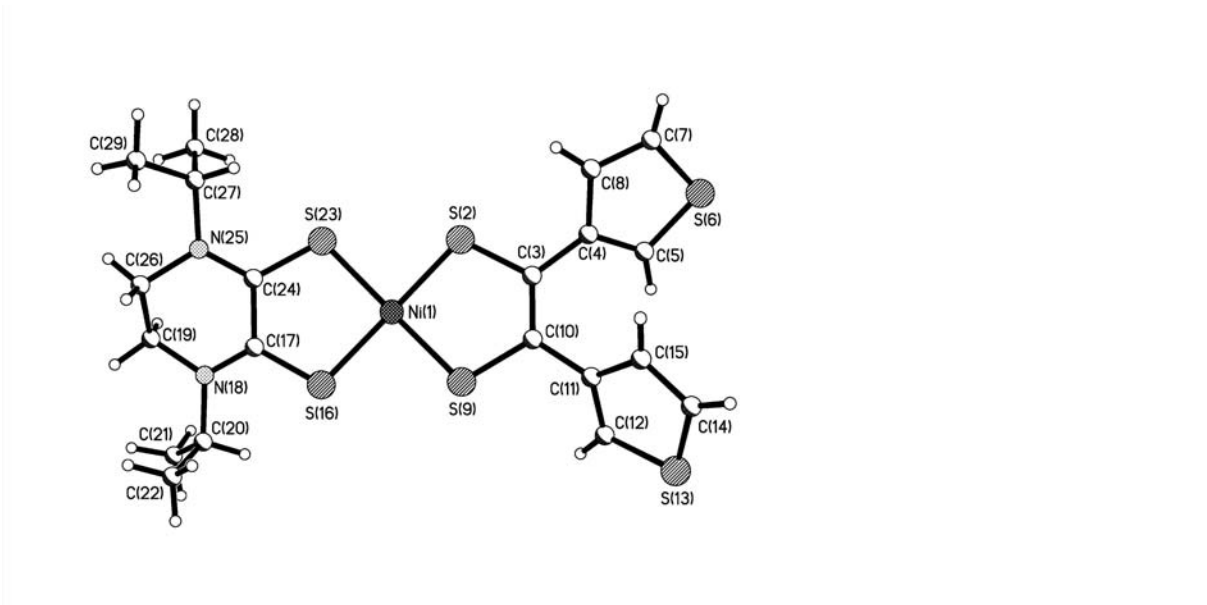

Fig. S2 Crystal structure of **4** showing atom numbering scheme and thermal ellipsoids at 50% probability.

Bond	Bond Length / Å	
	Observed	**Calculated**
Ni(1)-S(2)	2.1404(7)	2.135826
Ni(1)-S(9)	2.1338(7)	2.135628
Ni(1)-S(16)	2.1700(8)	2.149133
Ni(1)-S(23)	2.1604(8)	2.150504
S(2)-C(3)	1.754(3)	1.754347
S(9)-C(10)	1.751(3)	1.754382
S(16)-C(17)	1.694(3)	1.705061
S(24)-C(23)	1.691(3)	1.705139
C(3)-C(10)	1.350(4)	1.367818
C(17)-C(24)	1.479(4)	1.463379

Angle	Angle Size / °	
	Observed	**Calculated**
S(2)-C(3)-C(10)-S(9)	0.62	2.15
S(16)-C(17)-C(24)-S(23)	20.17	0.70

Table S2a Selected torsion angles of **4** showing an, overall, square planar coordination geometry with a strain away from planarity induced by the R_2pipdt ligand.

Table S2b Selected bond lengths of **4** showing a uniform over-estimation of calculated bond lengths of isolated molecules, but an agreement of the [Ni(dithiolate)(dithione)] nature of the complex.

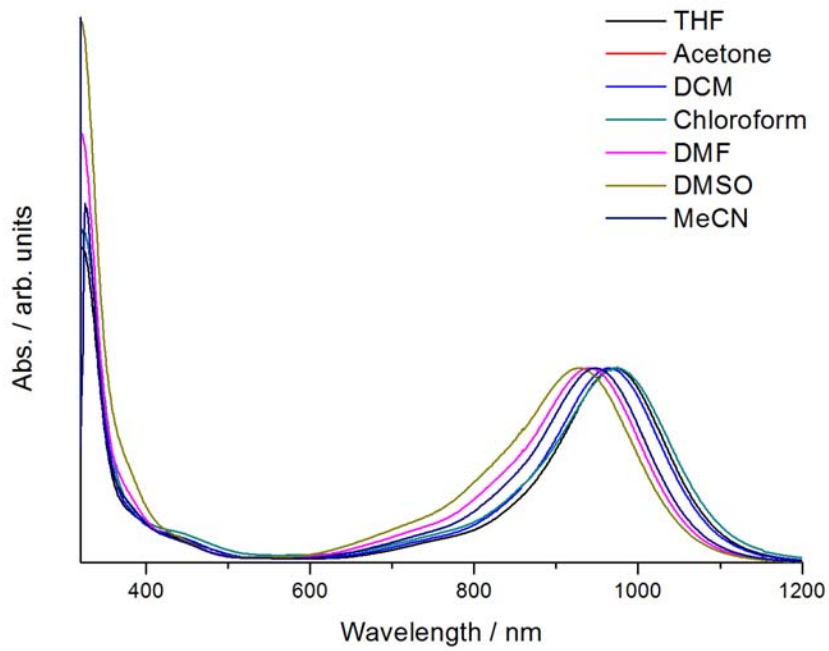

Fig. S3 Solvatochromic studies of **3** showing negative solvatochromism for the NIR absorption.

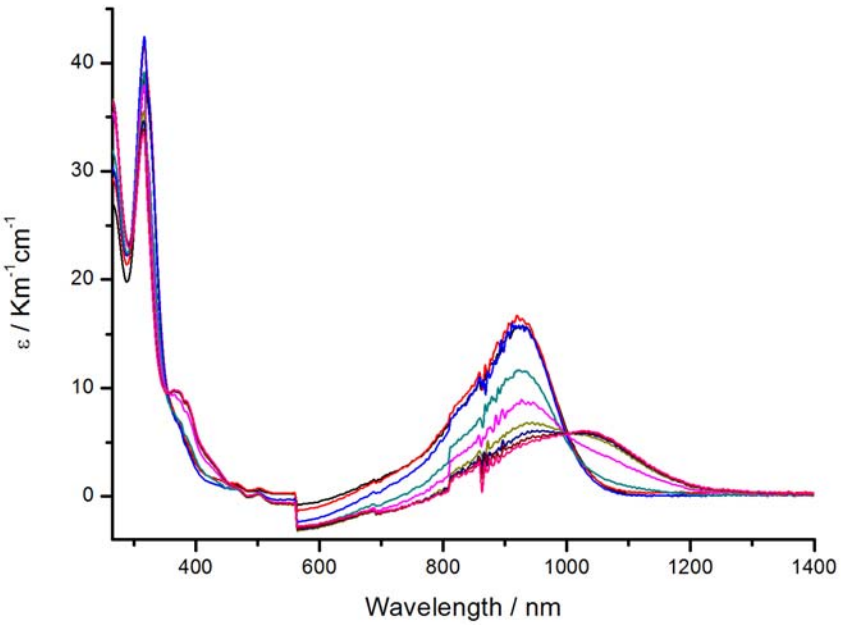

Fig. S4 Optically transparent thin-layer electrochemistry (OTTLE) of the **3** under reductive conditions, showing the formation of a stable anion with a NIR absorption at lower energy than **3**. (Jump at 560 and 805 nm, as well as spike at 880 nm are artefacts of the spectrometer).

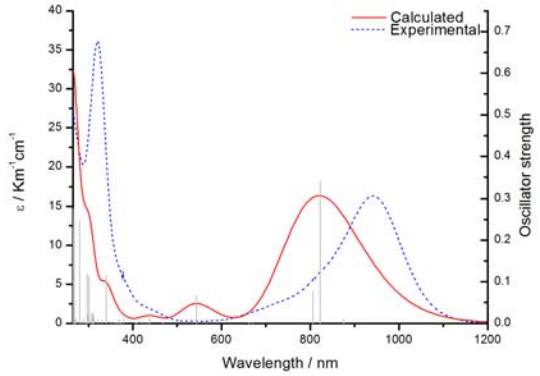

Fig. S5 Experimental and calculated UV/Vis/NIR absorbance spectra of **3** in DCM showing an overestimation of the energy of all the calculated transitions.

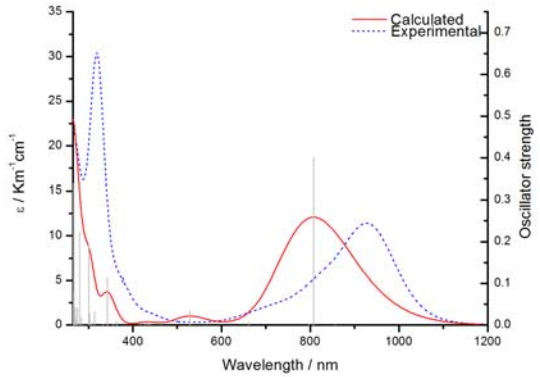

Fig. S6 Experimental and calculated UV/Vis/NIR absorbance spectra of **4** in DCM showing an overestimation of the energy of all the calculated transitions.

Complex	Energy / nm		Osc. Strength	Composition
	Calculated	Observed		
3	822.17	940	0.3406	HOMO→LUMO 54% (LL'CT)
				HOMO-3→LUMO 16% (MLCT)
	543.31		0.0655	HOMO-2→LUMO 78% (MMLL′CT)
	265.14	320	0.2754	HOMO-7→LUMO+1 31% (LMCT)
4	807.55	928	0.4017	HOMO→LUMO 65% (LL'CT)
	528.33		0.034	HOMO-2→LUMO 81% (MMLL′CT)
	264.80	319	0.3382	HOMO-7→LUMO+1 54% (LMCT)

Table S3 A comparison of selected transitions in the calculated UV/Vis/NIR spectra from TD-DFT calculations on **3** and **4** with experimental data. The data confirms the low energy absorption is due to ligand to ligand charge-transfer. Highlighted data represents a transition calculated but not observed.

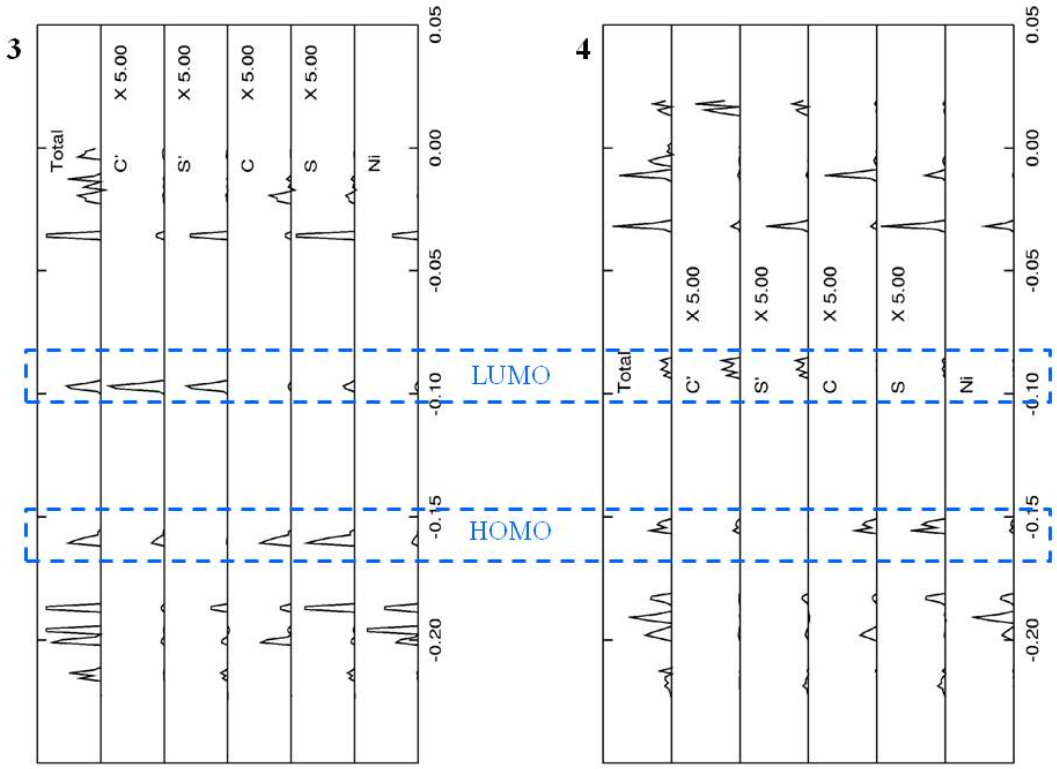

Fig. S7 Densities-of-states plots of **3** and **4** showing contributions for the NiS_4C_4 to the frontier orbitals, where C and S relate to the b-3ted and C′ and S′ relate to the R_2pipdt.

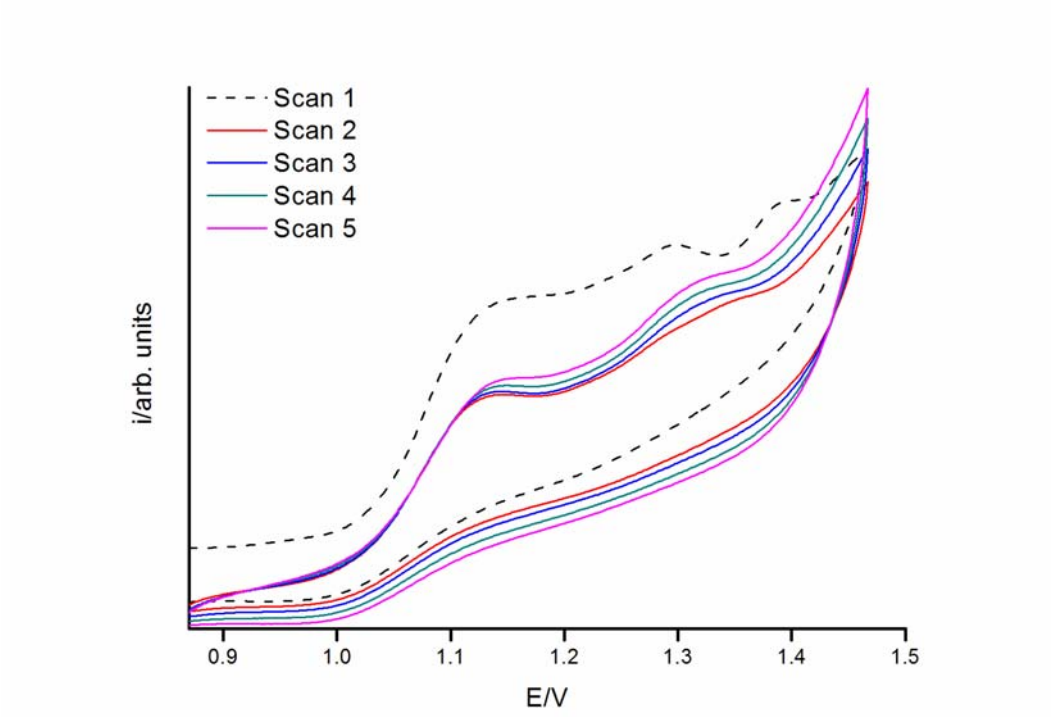

Fig. S8 Cyclic voltammetry (100 mVs^{-1}) of **3** <1.5 V in DCM containing 0.3 M $TBABF_4$. Currents at all potentials increase with potential cycling after the first scan for <1.5 V showing depositing of a conducting film.

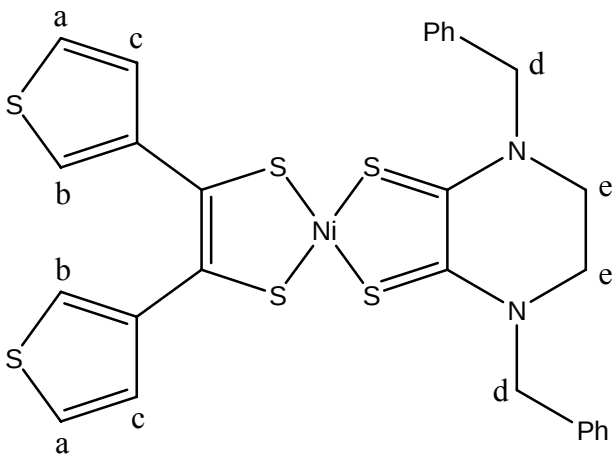

Fig. S9 [1]HNMR labelling scheme for **3**.

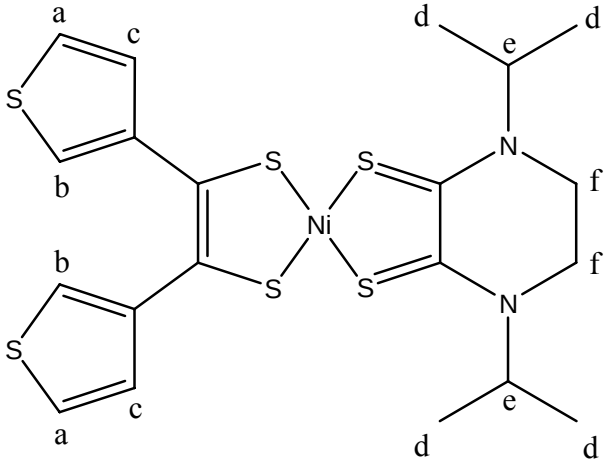

Fig. S10 [1]HNMR labelling scheme for **4**.