Supplementary Information

Highly unusual interpenetration isomers of electroactive nickel bis(dithiolene) coordination frameworks

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1 Ligand Synthesis

 $[Ni(pedt)_2][Et_4N]$, (pedt = 1-(pyridine-4-yl)ethylene-1,2-dithiolate): 4-Pyridyl-1,3-diol-2-one (1.28 g, 6.40 mmol) was dissolved in methanol (180 mL) and the solution degassed (dinitrogen). To this was added sodium methoxide in methanol (30%, 3.20 mL) followed by a solution of NiCl₂.6H₂O (0.768 g, 3.20 mmol) in methanol (20 mL) and the reaction mixture was stirred for 1 h. This solution was then filtered through paper and tetraethylammonium bromide (1.36 g, 6.40 mmol) added. The reaction was stirred in an open container for 1 h after which the stirrer bar was removed and the open container left in the freezer for 16 h. The solution was filtered on a sinter 'S4' to yield a microcrystalline product which was washed with cold methanol and air dried. 59.1% yield (0.990 g, 1.89 mmol); ES-MS -ve (m/z): 392 [Ni(pedt)₂]⁻. The phase purity of the bulk product was checked with powder X-ray diffraction.

2 Powder X-ray diffraction

Powder X-ray diffraction (PXRD) data were obtained using a PANalytical X'Pert PRO Diffractometer with Cu-K α ($\lambda = 1.5406$ Å) radiation, which was equipped with a solid-state PIXcel detector. For **1** and the ligand, the microcrystalline powders was spread as synthesised over a silicon crystal plate and rotated within the beam. The mixed phase product obtained from the 'DMF only' synthesis was measured in a sealed capillary containing the mother liquor as desolvation of **2** led to its gradual disappearance from the powder pattern. The sample was packed wet and capillary rotated within the X-ray beam.



Figure S1. Powder X-ray diffraction pattern of **1** (above blue) and pattern predicted from the single crystal X-ray diffraction data of the same (below red).



Figure S2. Powder X-ray diffraction pattern of [Ni(pedt)₂][Et₄N] (above orange) and pattern predicted from the single crystal X-ray diffraction data of the same (from Dai *et al.*, *Phys. Chem. Chem. Phys.*, 2013, **15**, 4016-4023) (below green).



Figure S3. PXRD of the mixed phases obtained when the reaction is performed in only DMF.

3 Single Crystal X-Ray Diffraction

Single-crystal data of **1** were collected on a Bruker-Nonius FR591 Kappa Apex II diffractometer using Mo K α radiation ($\lambda = 0.71073$ Å). A dark purple prismatic crystal was attached with ParatoneN oil to a short fibre. The crystal was cooled to 150 K with a stream of dinitrogen from an Oxford Cryosystems Cryostream. Empirical absorption corrections were applied using SADABS. The initial structure solution was obtained using SHELXS and refined with SHELXL.

Single-crystal data of **2** were collected on the MX2 beamline at the Australian Synchrotron, Victoria, Australia ($\lambda = 0.71085$ Å). A dark purple prismatic crystal was attached with ParatoneN oil to a fibre loop. The crystal was cooled to 100 K with a stream of dinitrogen from an Oxford Cryosystems Cryostream. Empirical absorption corrections were applied using SADABS. The initial structure solution was obtained using SHELXS and refined with SHELXL.

1 crystallised in the monoclinic space group C2/c (#15) with cell parameters a = 15.350(2), b = 22.346(2), c = 15.4685(17) Å and $\beta = 107.2669(7)^{\circ}$. Each octahedral zinc ion is bound axially by dmf molecules and equatorially by the pyridyl nitrogen of the [Ni(pedt)₂]. The metalloligands consists of two pedt moieties, each bound bidentate (κ^2 S,S') to a central square planar nickel. The pyridyl groups are distal, i.e. the metalloligand is in a *trans* configuration. All four metalloligands extend within the plane to ligate to another Zn centre. In this way a two dimensional network is formed. The network consists of a (4,4) grid, having Zn-Zn distances 18.640(2) (edge λ through Ni1) and 18.765(2) Å (edge γ through Ni2) with Zn-Zn-Zn angles of 107.15 ($\lambda \lambda$), 73.37($\lambda \gamma$) and 106.12° ($\gamma \gamma$). All of the metals within a layer lie within a single plane.

The metalloligands along λ and γ each contain an inversion centre at the Ni but are structurally unique from one another. As well as spanning different distances, they also vary in the torsion angles between the pyridyl rings and the Ni(edt)₂ core, 29.04 (λ) and 23.71° (γ). The 2D layers are described by the miller indicex (2 0 -4) and are separated by a distance of 3.779 Å, with the layers stacking in the *c* direction. The bound dmf molecules are disordered over two positions, the major component having 82% occupancy. Two free DMF molecules lie within voids.

2 crystallised in the trigonal space group $C3_1/c$ (#159) with cell parameters a = b = 27.525(4), c = 24.215(5) Å and $\alpha = \beta = 90$, $\gamma = 120^{\circ}$. The connectivity of **2** is identical to **1** though the network now consists of a more regular grid, having Zn-Zn distances 18.546(2) and (edge ζ through Ni1) and 18.545(3) Å (edge ξ through Ni2) with Zn-Zn-Zn angles of 94.42 and 81.51°. The layers corrugate slightly about a mean plane with ridges running along *c*.

The metalloligands along ζ and ξ are both fully contained within the asymmetric unit. To a first approximation the ligands can be considered planar (all [Ni(edt)₂]-pyridyl torsion angles < 15°). The layers are described by the miller indices (0 2 0), (2 0 0) and (2 -2 0). The axial positions of the zinc appear to be bound by solvent but could not be refined crystallographically (modelled as a single oxygen). We might assume that the solvent is either dmf (as in 1) or else simply water from either wet solvent or the hydrated zinc salt.



Figure S4. Structure of the 2D grids in the solid state of **1** (left) and **2** (right), solvent removed for clarity. The asymmetric unit only is labelled. Colours: Zn, pink; Ni, green; C, grey; N, blue; S, yellow; H, white.



Figure S5. Side on view of the layers of the 2D grids in the solid state of planar 1, viewed along b (top) and corrugated 2, viewed along c (bottom).

Identification code	1	2
Empirical formula	$C_{40}H_{48}N_8Ni_2O_4S_8Zn$	$C_{28}H_{20}N_4Ni_2O_2S_8Zn$
Formula weight	1144.13	883.75
Temperature/K	150(2)	100(2)
Crystal system	monoclinic	trigonal
Space group	C2/c	P31c
a/Å	15.350(2)	27.525(4)
b/Å	22.346(2)	27.525(4)
c/Å	15.4658(17)	24.215(5)
α/°	90	90
β/°	107.269(7)	90
γ/°	90	120
Volume/Å ³	5065.8(10)	15889(5)
Ζ	4	6
$\rho_{calc}mg/mm^3$	1.500	0.554
m/mm ⁻¹	1.582	0.745
F(000)	2360	2676.0
Crystal size/mm ³	$0.8\times0.35\times0.25$	$0.1\times0.025\times0.025$
Radiation	MoKa ($\lambda = 0.71073$)	Synchrotron ($\lambda = 0.71085$)
2Θ range for data collection	3.32 to 70.28°	6.946 to 52.752°
Index ranges	$-24 \le h \le 24, -36 \le k \le 36, -24 \le l \le$	$-34 \le h \le 34, -34 \le k \le 34, -30 \le l \le 30$
Reflections collected	24 143043	230737
Independent reflections	11255 [R _{int} = 0.0426, R _{sigma} = 0.0190] 11255/185/340	21594 [$R_{int} = 0.1082, R_{sigma} = 0.0475$]
Data/restraints/parameters		21594/585/406
Goodness-of-fit on F ²	1.134	2.695
Final R indexes [I>= 2σ (I)]	$R_1 = 0.0355, wR_2 = 0.0884$	$R_1 = 0.1182, wR_2 = 0.2825$
Final R indexes [all data]	$R_1 = 0.0533, wR_2 = 0.1034$	$R_1 = 0.1734, wR_2 = 0.2922$

4 Discussion of kinetic and thermodynamic products

The cause of the interpenetration isomerism is not immediately apparent, but of the possible explanations one may consider the rate of crystallisation as the most compelling. By this argument **1** is a highly kinetically stable product which is isolated in DMF/EtOH solution. This mother liquor is very poor at solubilising early growth fragments, causing exclusive growth of the fast-forming product. When performed in DMF one may suppose that nascent fragments exist for longer and reach a larger size whilst still in solution. It is thus possible for coordination, rearrangement, and catenation to occur before precipitation, allowing growth of the thermodynamic product, **2**. Once precipitation has begun the topology is locked in and epitaxial growth leads to microcrystalline products.

From careful study of the crystal structure of **2**, we can identify a number of sulfur to pyridyl hydrogen bonds as shown in Figure S6. We may conclude that these interactions lower overall the energy of the system more than the entropic penalty associated solvent in with large cavities.



Figure S6. Three asymmetric units of 2 from different sheets, indicating the hydrogen bonding present in the atom pairsC8 - S8 and C9 - S5. Colours as described previously

5 Electrochemistry

Cyclic voltammetry (CV) was performed using a BASi Epsilon Electrochemical Analyser with a standard three-electrode set up under an argon atmosphere. The working electrode was \emptyset 1 mm glassy carbon disk with a high surface area Pt coil counter electrode. All the measurements were performed at 50 mV/s scan rate.

Solution state CV was performed with an Ag wire as a reference electrode and ferrocene (Fc) was added as an internal reference. A small amount of $[Ni(pedt)_2][Et_4N]$ was dissolved in 0.1 M $[(n-C_4H_9)_4N](PF_6)$ in anhydrous MeCN which was used as supporting electrolyte.

For solid state CV, a single junction Ag/AgCl reference electrode was used with aqueous KCl (0.1 M) as supporting electrolyte. **1** was mounted onto the working electrode using mechanical immobilisation: the electrode was pressed against the powder forming a weakly bound layer on its surface.



Figure S7. Cyclic voltammogram of $[Ni(pedt)_2][Et_4N]$ in solution. The arrow indicates the direction of the forward scan.

6 UV/Vis/NIR Spectroscopy

UV/Vis/NIR Spectroscopy was performed on a CARY5000 spectrophotometer equipped with a Praying Mantis attachment against a BaSO₄ background. Samples were ground in a pestle and mortar BaSO₄ before measurement.

Spectra were collected as the Kebulka-Munk function and normalised such that the near-IR transition equalled 1.

7 IR Spectroscopy

FT-IR spectroscopy was performed on a Bruker Tensor 27 System. Samples were ground in a KBr matrix and data were collected in the region 4000 - 400 cm⁻¹ over 32 scans.



Figure S8. IR spectra of 1 (above, blue) and [Ni(pedt)₂][Et₄N] (below, orange).

8 Thermogravimetric Analysis (TGA)

TGA was performed under a flow of nitrogen (0.1 L/min) on a TA Instruments Hi-Res Thermogravimetric Analyser from 30-600 °C at 1 °C/min.



Figure S9. TGA plot for 1.