SUPPLEMENTARY MATERIAL

A Family of Three-Dimensional Molecular Framework Materials Containing the Three-connecting Ligands 2,4,6-tris(n′-pyridyl)-1,3,5-triazine: 3-tpt and 4-tpt

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S1 Single crystal X-ray diffraction

S2 Thermogravimetric analysis

S3 Magnetic susceptiblity

S1 Single crystal X-ray diffraction

S1(a): Fe(4-tpt)$_{4/3}$(NCS)$_2 \cdot n$(Bz,ac) (1a(Bz,ac))

The final refinement indices for **1a(Bz, ac)**, *ca.* 0.20, are large as expected due to more than 50% of the material consisting of unmodelled and disordered solvent. Refinement indices such as these are common in highly porous systems where the solvent molecules are not ordered. Structural solution using a reflection file generated in PLATON SQUEEZE resulted in substantially improved refinement indices of *ca.* 0.11. This strongly suggests that structural solution is indeed correct and that the high residual results from the sea of disordered acetone molecules in the pores.

Synchrotron single crystal data was collected on **1a(Bz,ac)** to assess if higher intensity data may improve the R-factors, **1a(Bz,ac)s**. However, we found little improvement between this and the original data collected with a lab source highlighting that the poor refinement indices are intrinsic to the material rather than any insufficiencies in the data (Table S1).

S1(b): *trans*-[M^{II}(NCS)$_2$(4-tpt)$_{4/3}$]*cis*-[M^{II}(NCS)$_2$(4-tpt)$_2$]$\cdot n$(tce, EtOH) (Fe: 3a(Tce,Et) and Co: 3b(Tce,Et))

In both materials it was unclear if the *b*-axis was *ca.* 23.4 Å or doubled to *ca.* 46.9 Å. Secondly, the β angle is approximately 90° and emulated orthorhombic. Structural solution was successful in the monoclinic space group *P2$_1$/n* with a *b*-axis of 46.966(5) Å, in which merohedral twinning associated with orthorhombic emulation ($\beta \approx 90°$) was observed. All framework atoms, except those which were disordered, were refined anisotropically but constrained to be approximately isotropic using the ISOR command in SHELX.

In addition, a large amount of positional disorder was observed in these materials, such that the layer containing **M$_2$** ions is disordered over two 50% occupied positions. As such, within this layer where the atom potitions of the *cis*-thiocyanate ligands and two-connecting 4-tpt ligands overlap significantly, restraints and constraints were required for stable refinement. In

particular, the pyridyl groups of the tpt ligands were restrained to be optimal and the bond lengths of the thiocyanate ligands were restrained.

For each of these materials PLATON CALC VOID revealed only *ca.* 30% of the crystal volume to consist of the framework structure, the remaining 70% consists of guest molecules comprised of tce and ethanol. Only two tce molecules could be satisfactorily modeled in the refinement process for each material. PLATON SQUEEZE was thus employed to remove the excess electron density resulting from the disordered sea of guest molecules and resulted in greatly improved refinement indices.

As with **1a(Bz,ac)**, synchrotron single crystal data was collected on **3b(Tce,Et)** to assess if stronger intensity data may improve the R-factors, **3b(Tce,Et)s**. However, again we found similar R-factors compared to the original data collected with a lab source highlighting that the majority of the material consists of disordered solvent and that the poor refinement indices are intrinsic to the material rather than any insufficiencies in the data (Table S1).

Table S1. Summary of the single crystal X-ray diffraction data and refinement details for **1a(Bz,ac)s** and **3b(Tce,Et)s**.

Compound	1a(Bz,ac)s	3b(Tce,Et)s
Formula	$Fe(NCS)_2(C_{18}H_{12}N_6)_{4/3}.10(C_3H_6O)$	$Co_2(NCS)_4(C_{18}H_{12}N_6)_3.4(C_2H_2Cl_4)$
FW/gmol-1	1265.37	1954.44
T /°C	123	-100
Crystal System	cubic	monoclinic
Space Group	*Fm-3m*	*P2$_1$/n*
a /Å	38.0830(19)	12.884(3)
b /Å	-	47.182(9)
c /Å	-	22.728(5)
β /°	-	90.180(8)
V /Å^3	55232(5)	13816(5)
ρ_{calc} /Mgm^{-3}	0.913	0.780
μ /mm-1	0.138	0.485
Data/restraints/ Parameters	3486/12/56	27675/329/618
R(F) /% I>2σ (I) {all data}	0.3120{0.3558}	0.1607{0.2162}

Rw(F^2) /% I>2σ (I) {all data}	0.7079{0.7266}	0.3819{0.4200}
GoF	1.719	1.169

S2 Thermogravimetric analysis

Thermogravimetric analysis on **1a(Bz,ac)** revealed a two-step desolvation process where below 40 °C the pore acetone is removed and by 100 °C the pore benzyl alcohol is removed. The framework is then stable until *ca.* 175 °C after which decomposition occurs (Figure S1).
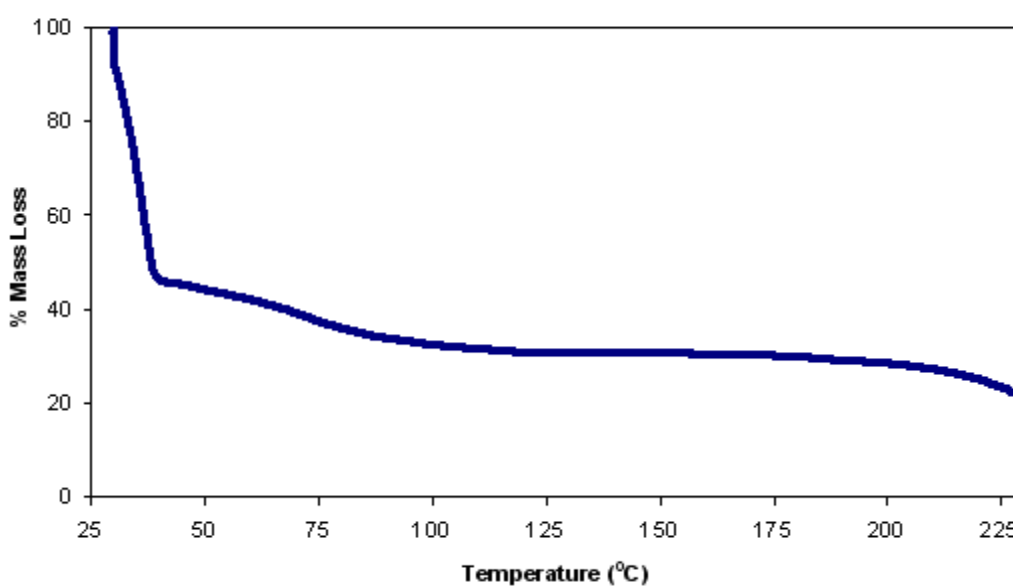

Figure S1- Thermogravimetry of the desolvation/decomposition process of **1a(Bz,ac)**.

For the resorption experiment a sample of **1a(Bz,ac)** was heated at 0.50 °C.min^{-1} to 100 ºC and held for 1 h before cooling to room temperature under a dinitrogen atmosphere. This revealed an approximately 80% weight loss which is consistent with that expected for the removal of both acetone and benzyl alcohol. The desolvated sample was then emersed in liquid benzyl alcohol and held at room temperature for 1 h before heating at 0.5 ºC.min^{-1} to 100 ºC (Figure S2). This revealed an approximately 50% weight loss which is consistent with that expected for the removal of benzyl alcohol only.
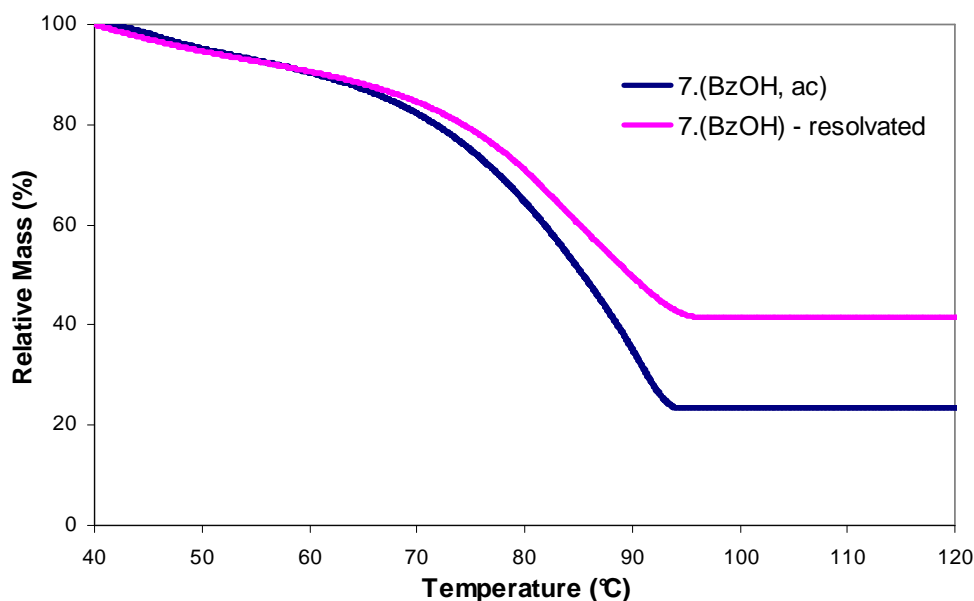
Figure S2 - Thermogravimetry of the desolvation (blue) and subsequent resolvation (red) with benzyl alcohol of **1a(Bz,ac)**.

Thermogravimetric analysis on **3a(Tce,Et)** revealed a two-step desolvation process where below 50 °C the pore ethanol is removed and below 100 °C the Tce is removed. The framework is then stable until *ca.* 200 °C after which decomposition occurs (Figure S3).
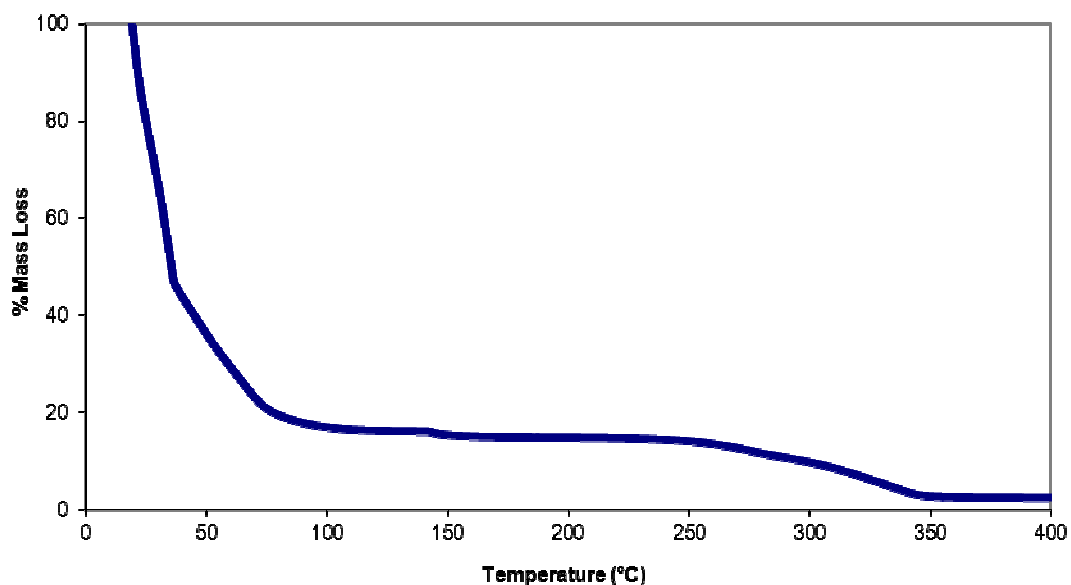

Figure S3. Thermogravimetry of the desolvation/decomposition process of **3a(Tce,Et)**.

S3 Magnetic susceptiblity

The $\chi_M T$ values for **1a(Bz,ac)** remain approximately constant at 3.4 cm^3 K mol^{-1} between 300 and 20 K, which is in the range of expected values for high spin iron(II). The subsequent drop in $\chi_M T$ below 20 K corresponds, most probably, to the occurrence of spin-orbit coupling of the high spin ions (Figure S4).
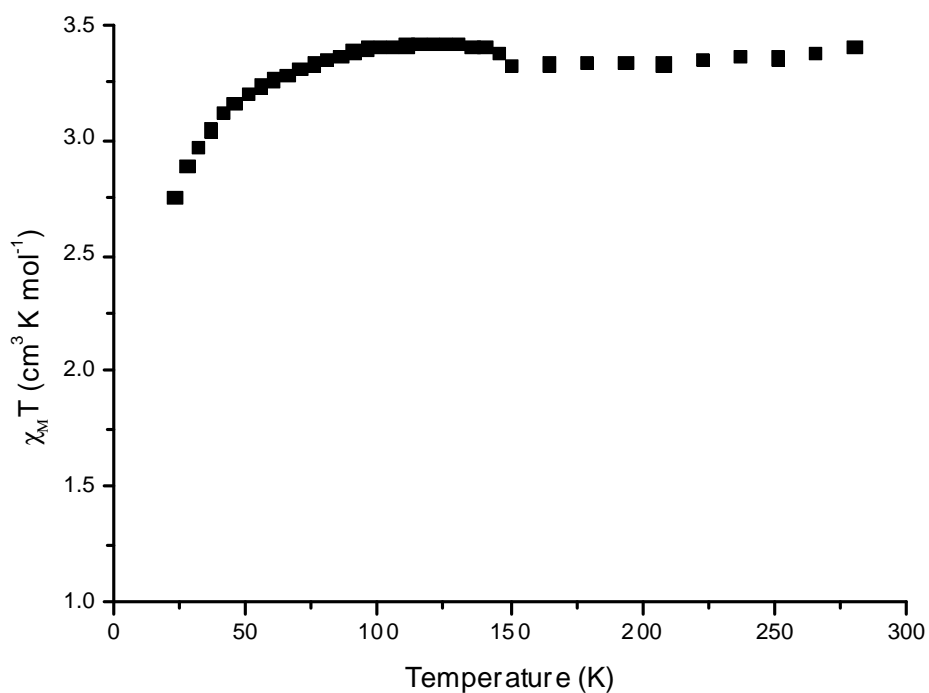

Figure S4 - Magnetic data for **1a(Bz,ac)**.

The $\chi_M T$ values of **3a(Tce,Et)** remain approximately constant at 3.65 cm^3 K mol^{-1} between 300 and 20 K consistent with the presence of high spin iron(II) sites only. Below 20 K $\chi_M T$ values decrease slightly due to spin-orbit coupling and zero-field splitting effects.
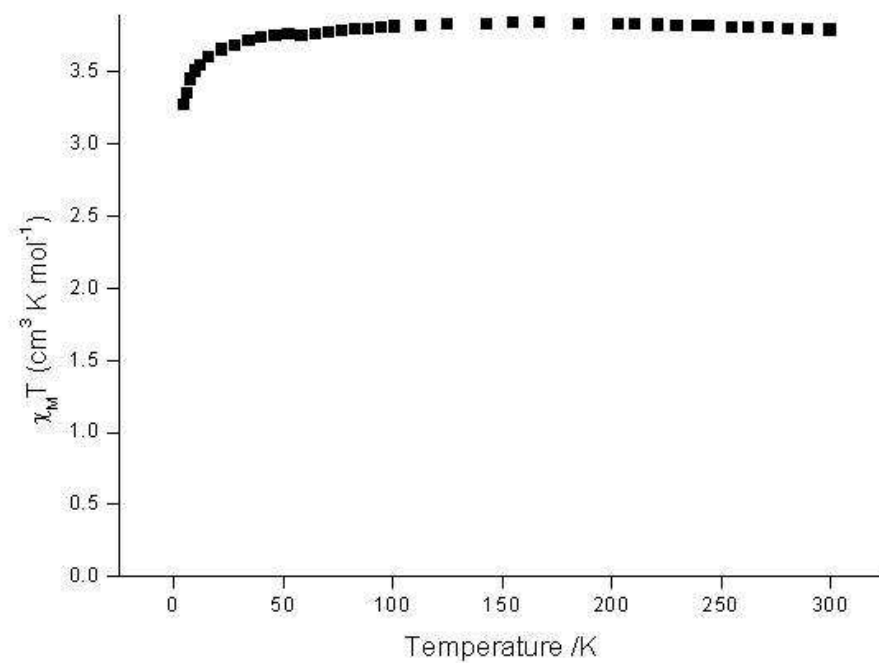

Figure S5. Magnetic data for **3a(Tce,Et)**.