Electronic Supplementary Material (ESI) for CrystEngComm.

Centric and Acentric Networks Using Low-Symmetry Heterotopic Carboxylate/Pyridyl Ligands

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Supporting Information

Hydrogen Bonding Parameters in Structures of Neutral Ligands

D-H···A	D-H (Å)	H···A (Å) [a]	D···A (Å)	D-H···A (°) [a]	Sym. Op. A
3py3bzH					
O1-H1O···N1	0.8401(10)	1.739(3)	2.5776(15)	175(2)	-x, 1-y, 1-z
N3-H3N···O2	0.8800(10)	2.113(8)	2.9441(15)	157.3(17)	1/2+x, 3/2-y, z-1/2
3py4bzH					
O1A-H14A···N1A	0.8401(15)	1.794(18)	2.580(3)	155(4)	x, y, z-1
O1B-H14B···N1B	0.8400(15)	1.756(7)	2.590(3)	172(4)	x, y, 1+z
O1C-H14C···N1C	0.8401(15)	1.732(5)	2.569(3)	174(4)	x, y, 1+z
O1D-H14D···N1D	0.8402(15)	1.749(5)	2.587(3)	175(4)	x, 1+y, z
O1E-H14E···N1E	0.8400(15)	1.773(10)	2.599(3)	167(4)	x, 1+y, z
O1F-H14F···N1F	0.8401(15)	1.805(12)	2.621(3)	163(4)	x, y-1, z
N3A-H11A···O2D	0.8802(15)	2.119(9)	2.979(3)	165(3)	x, y, z
N3B-H11B···O1D	0.8800(15)	2.275(11)	3.127(3)	163(3)	1+x, y, z
N3C-H11C···O2F	0.8801(15)	2.110(11)	2.966(3)	164(3)	1+x, y, z
N3D-H11D···O2C	0.8800(15)	2.085(14)	2.910(3)	156(3)	x, y, z-1
N3E-H11E···O2B	0.8800(15)	2.065(10)	2.922(3)	165(3)	x, y, z
N3F-H11F···O2A	0.8800(15)	2.073(8)	2.942(3)	169(3)	x-1, y, 1+z
4py3bzH·DMF					
O1-H1O···N1	0.8403(10)	1.719(3)	2.5541(13)	172.6(18)	x-1, 1+y, z
N3-H3N···O3	0.8801(10)	2.112(3)	2.9788(13)	168.0(14)	x, y, z
4py4bzH					
O1-H1O···N1	0.8400(14)	1.753(8)	2.578(2)	167(4)	1/2-x, 3/2+y, 1/2+z
N3-H3N···O2	0.8800(14)	2.033(7)	2.899(2)	168(3)	1/2+x, 3/2-y, z

(a) All O-H and N-H hydrogen atoms were located from the Fourier difference map and distances were refined with distance retraints of 0.84 and 0.88 Å, respectively.

1H-NMR Spectra

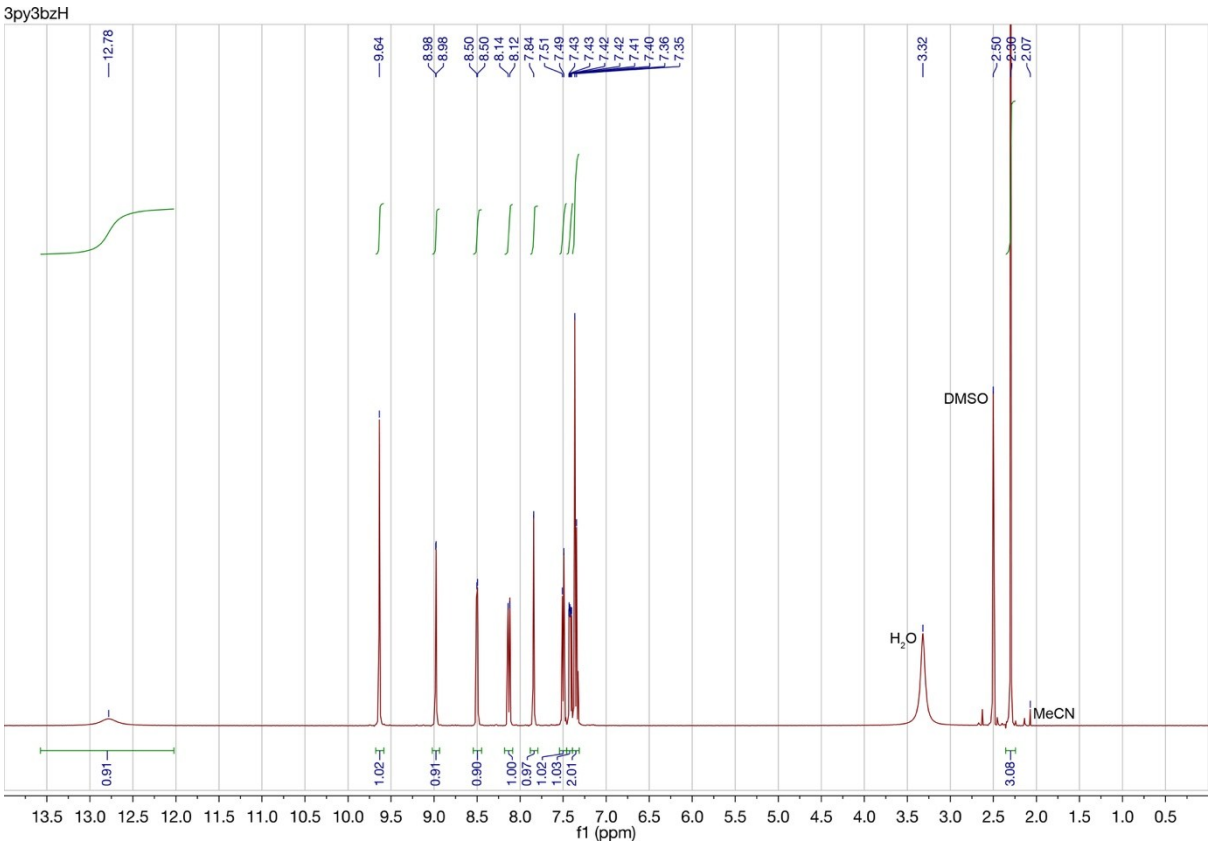

Figure S1: *1H NMR spectrum of 3py3bzH.*

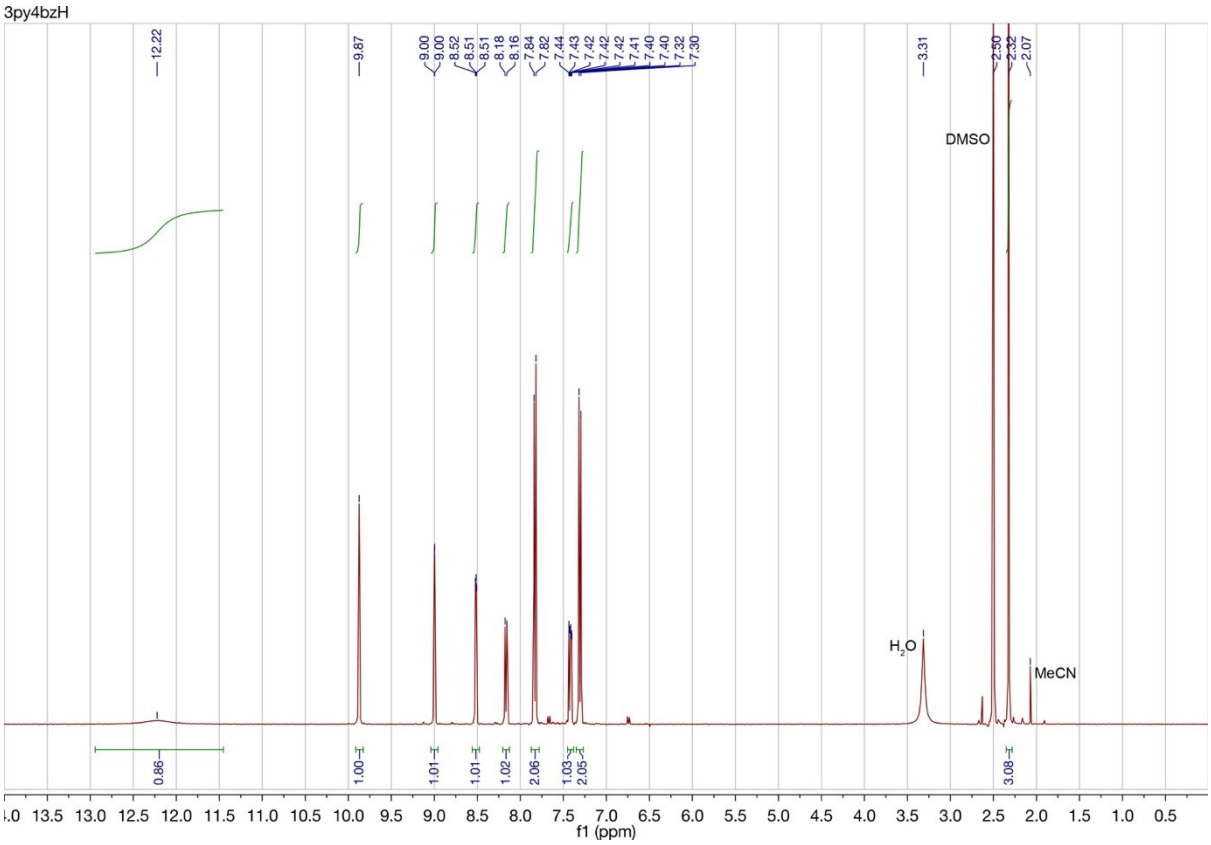

Figure S2: *1H NMR spectrum of 3py4bzH.*

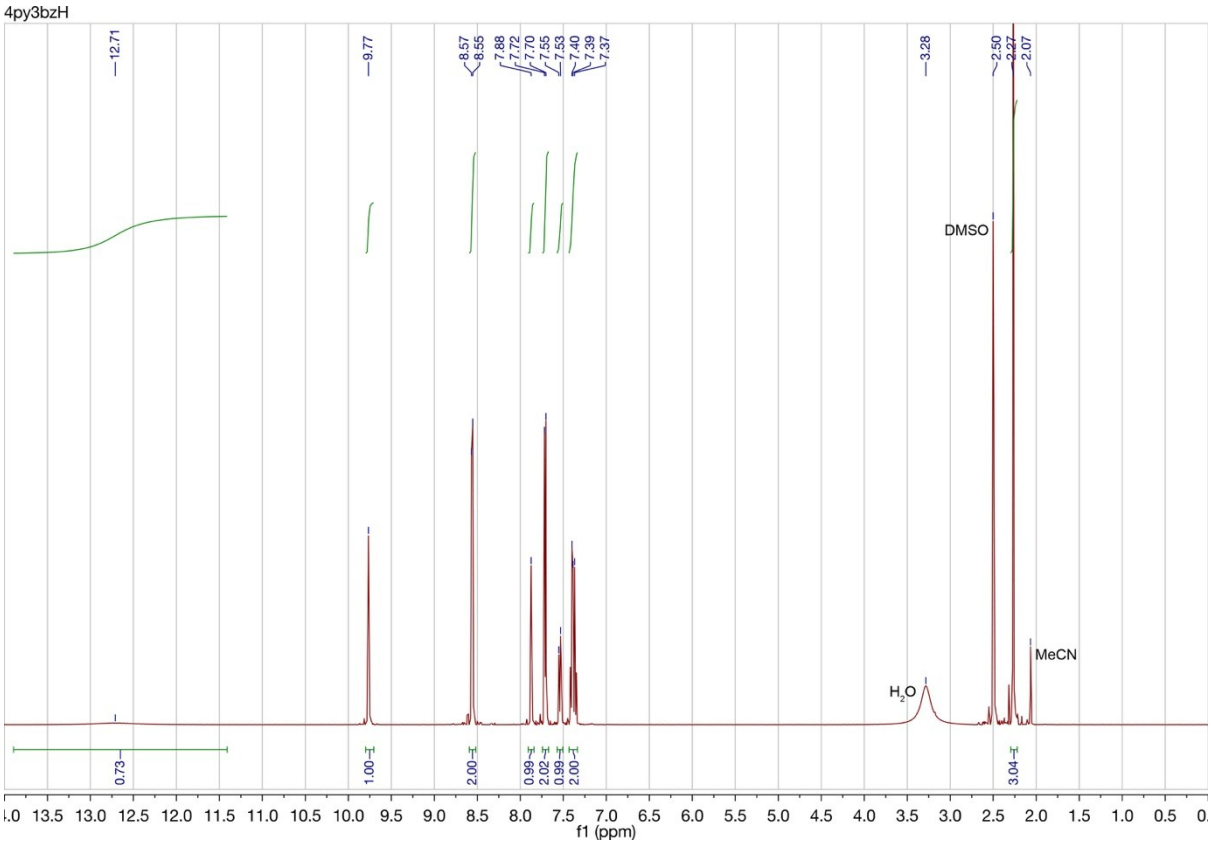

Figure S3: *1H NMR spectrum of 4py3bzH.*

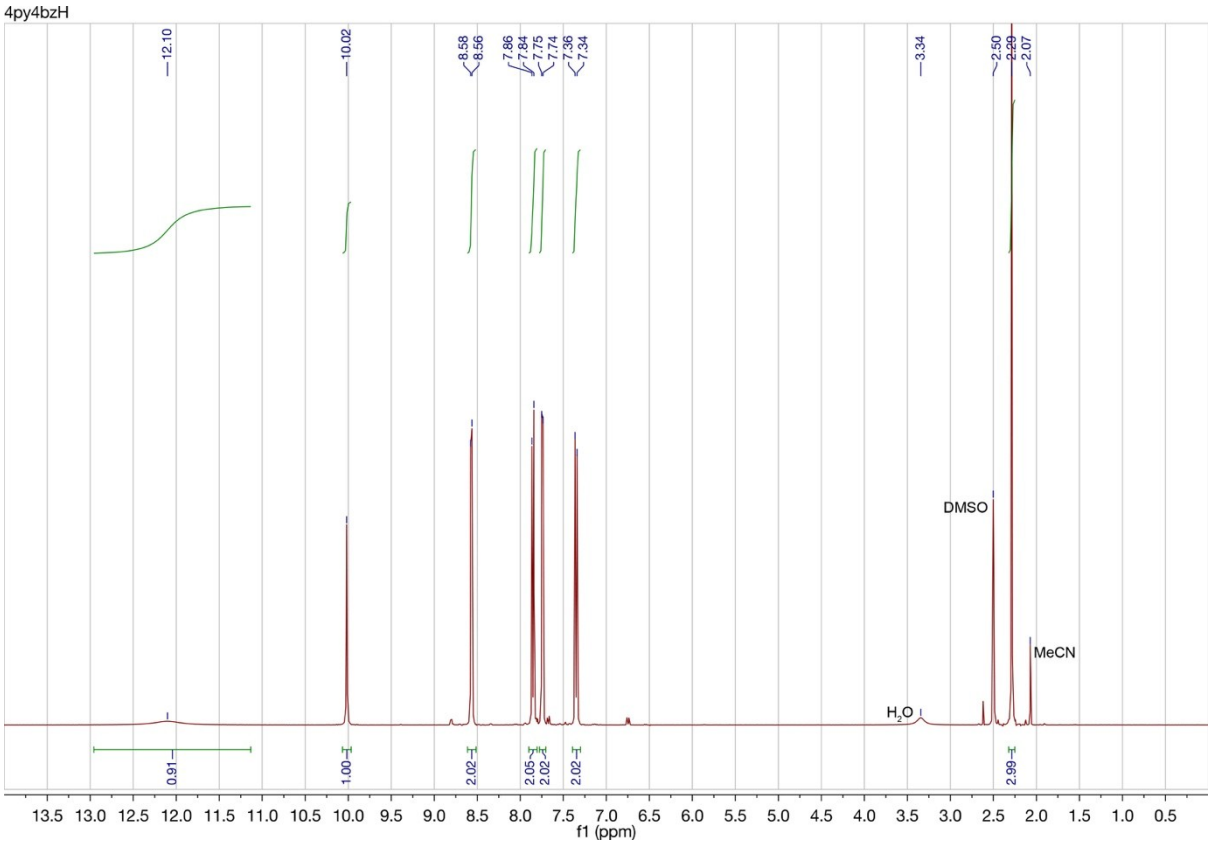

Figure S4: *1H NMR spectrum of 4py4bzH.*

Powder X-Ray Diffraction Data

Power X-ray diffraction (PXRD) measurements were collected using a Bruker X8 diffractometer equipped with Cu-Kα radiation. Data were collected at room temperature and are compared with calculated PXRD traces from low temperature single crystal datasets.

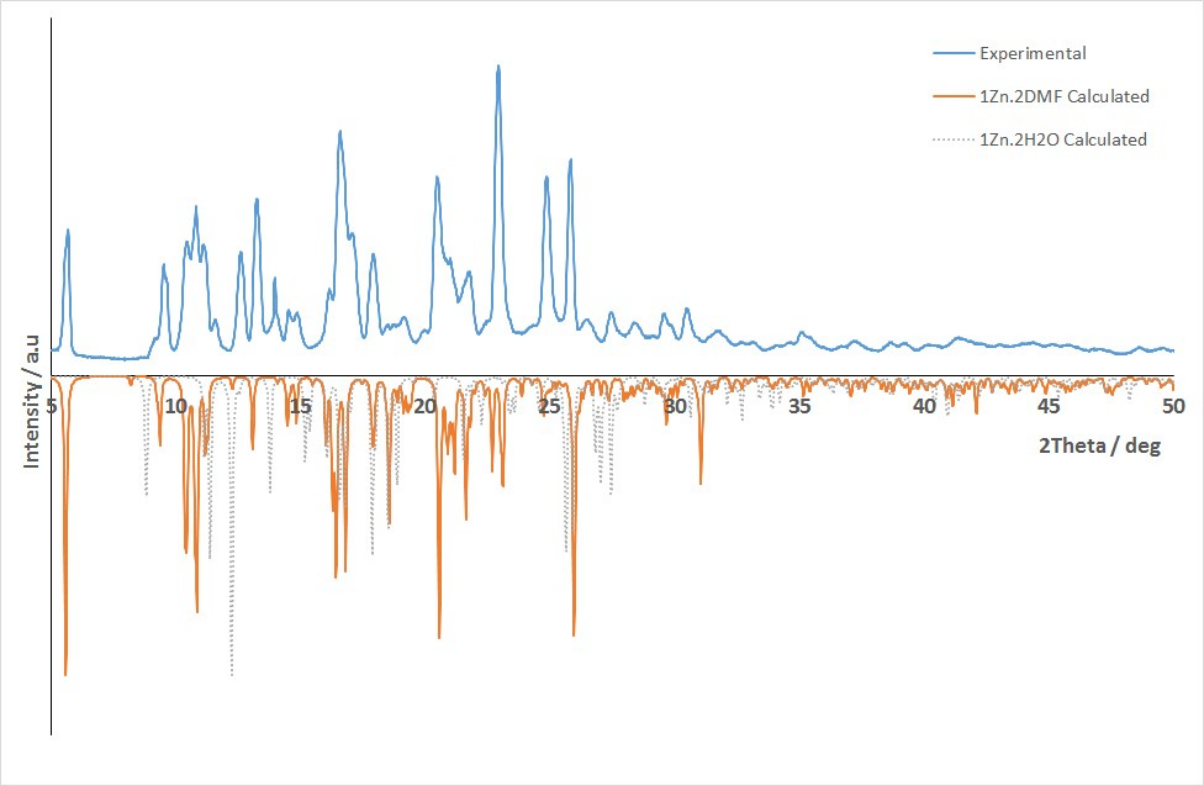

Figure S5: *Comparison of experimental PXRD of bulk* ***1Zn****·2DMF with the calculated patterns for* ***1Zn****·2DMF and* ***1Zn****·2H$_2$O.*

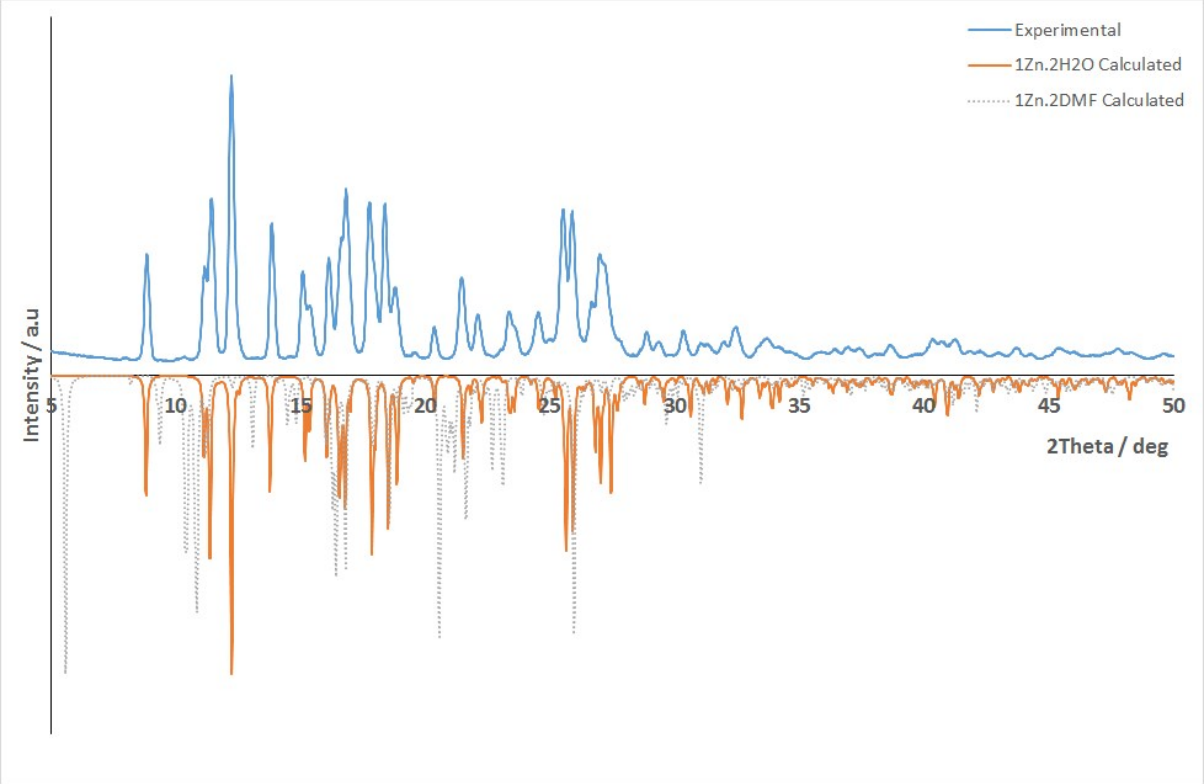

Figure S6: *Comparison of experimental PXRD of bulk* ***1Zn****·2H$_2$O with the calculated patterns for* ***1Zn****·2H$_2$O and* ***1Zn****·2DMF.*

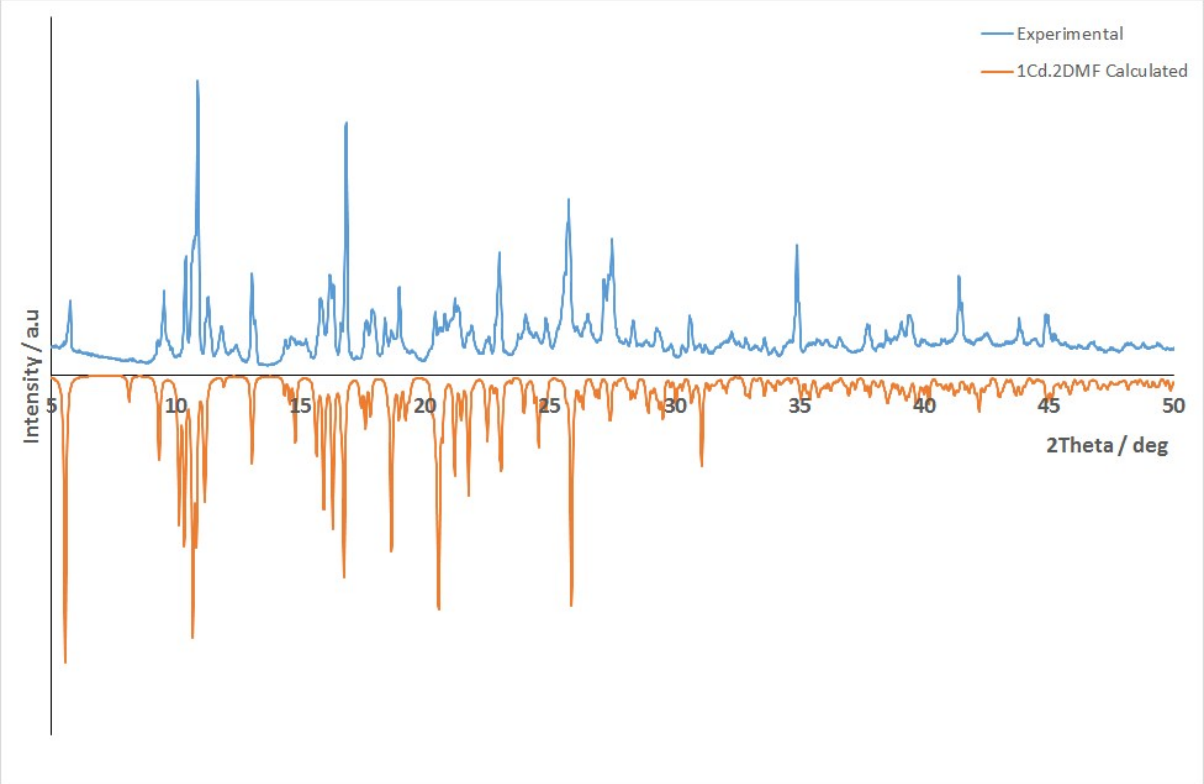

Figure S7: *Comparison of experimental PXRD of bulk* ***1Cd*** *with the calculated pattern for* ***1Cd****·2DMF.*

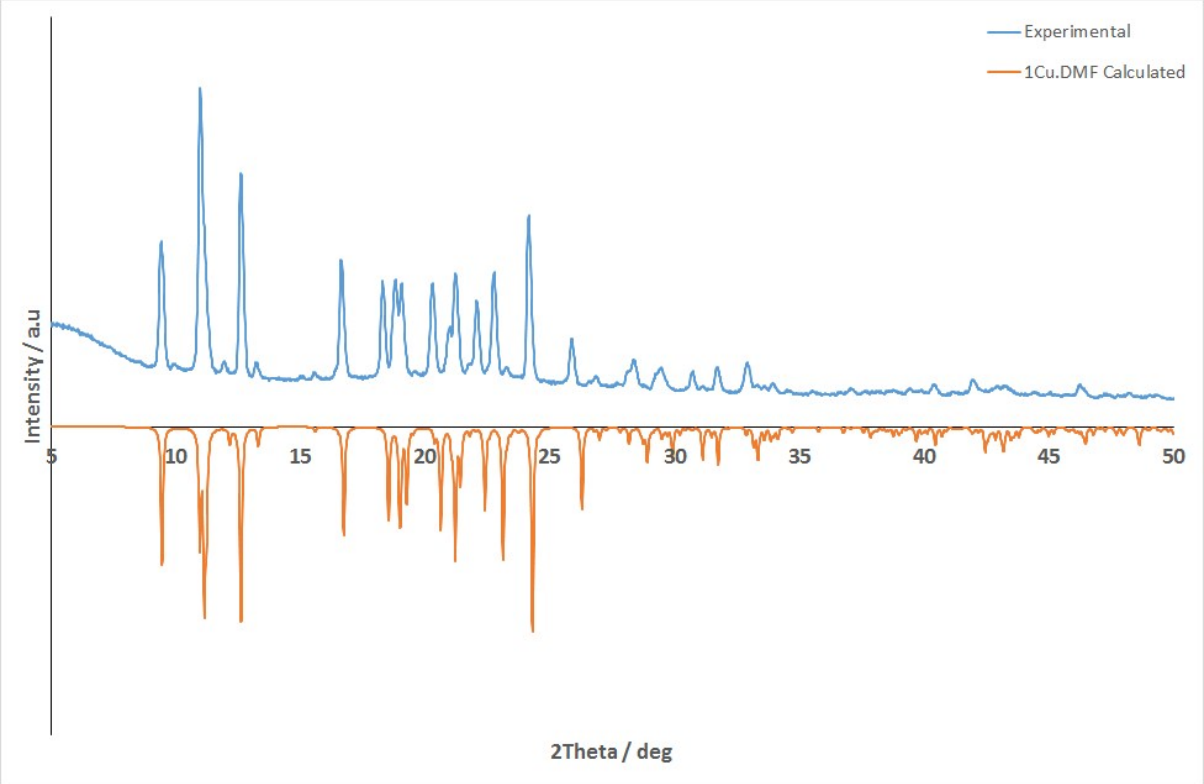

Figure S8: *Comparison of experimental PXRD of bulk* ***1Cu*** *with the calculated pattern for* ***1Cu****·DMF.*

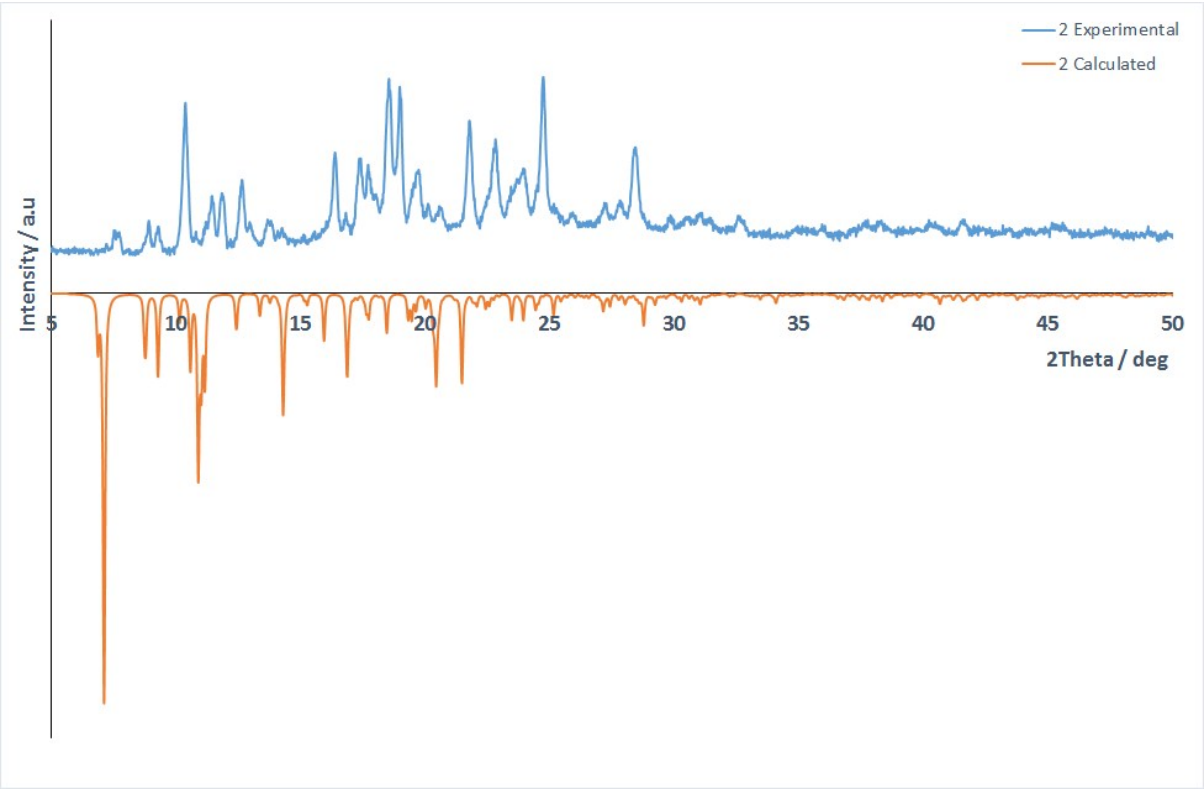

Figure S9: *Comparison of experimental PXRD of bulk* ***2*** *with the calculated pattern for* ***2****. The sample experiences rapid collapse of crystallinity upon standing in air and possible impurities in the bulk.*

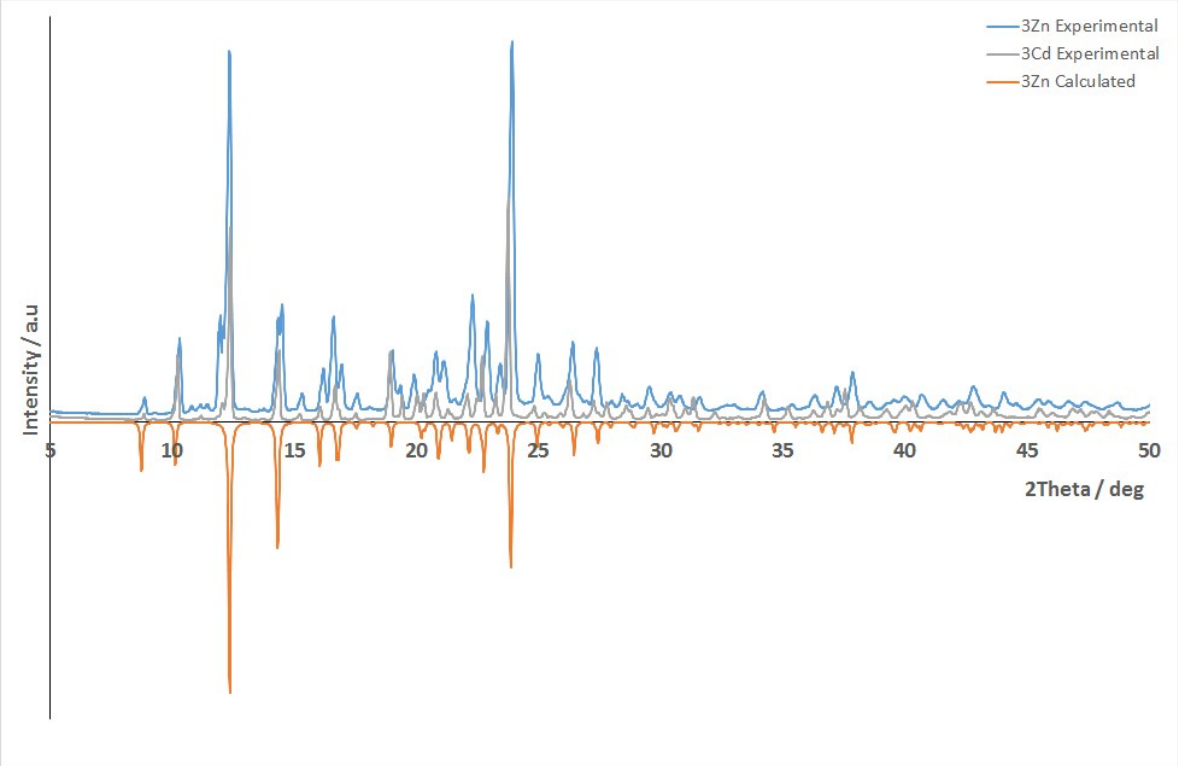

Figure S10: *Comparison of experimental PXRD of bulk* ***3Zn*** *and* ***3Cd*** *with the calculated pattern for* ***3Zn****·1.5H_2O.*

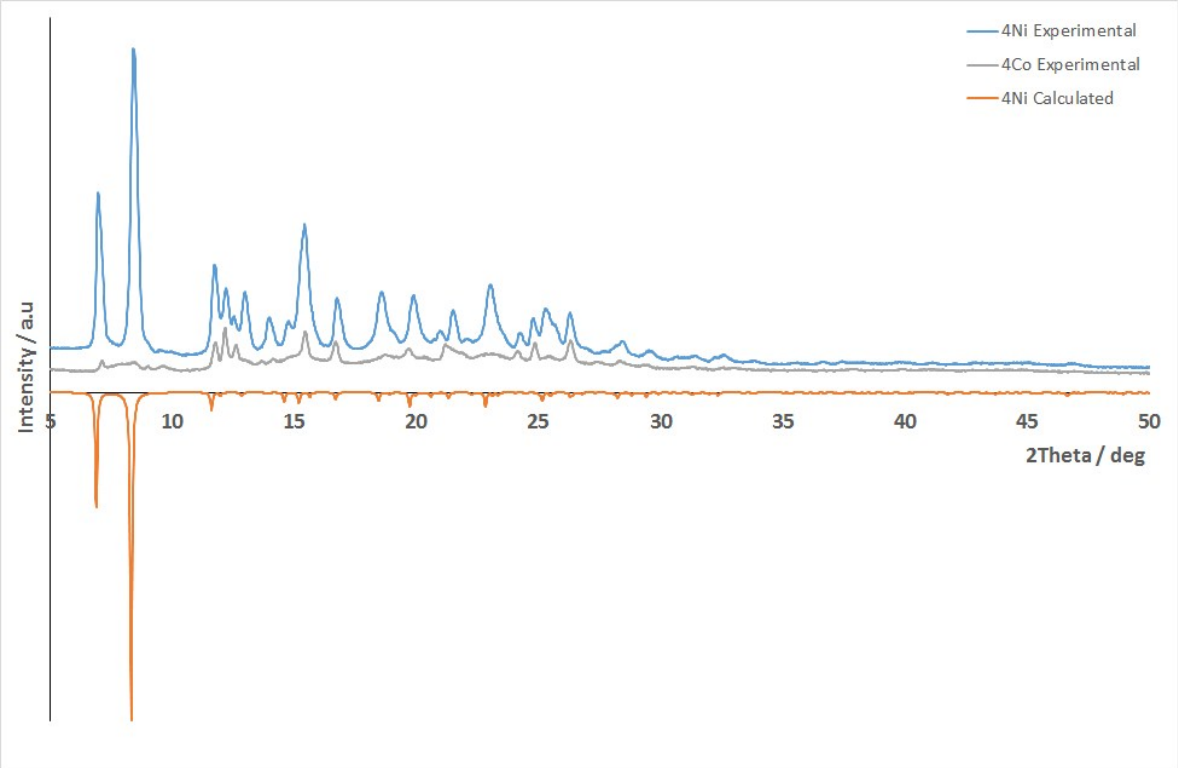

Figure S11: *Comparison of experimental PXRD of bulk* ***4Ni*** *and* ***4Co*** *with the calculated pattern for* ***4Ni****·7H_2O.*

Additional Crystallographic Refinement Details

1Cu·DMF: The DMF molecule in the lattice is disordered over a symmetry site. The molecule was therefore refined as fixed at ½ occupancy using an anisotropic model.

1Zn·H2O: The hydrogen atoms of the lattice water molecule were located from the Fourier difference map and refined using DFIX restraints with riding displacement parameters (d = 0.88 Å; μ_H = 1.5 x μ_O). The H···H distance (and thus H-O-H angle) was not restrained.

2: One of the ligands is partially disordered (except for the pyridyl ring and the carboxylate group). These two positions were refined with fixed 50:50 occupancy using an anisotropic model. One DMF molecule in the lattice is disordered over two over-lapping positions whose occupancies were freely refined (52:48) using an isotropic model. One further DMF was located at 50% occupancy and refined using an isotropic model with no restraints. SQUEEZE was applied locating a total void volume of 500 $Å^3$ per cell (154 e^-). This equates to one DMF per formula unit and was incorporated into the UNIT card prior to final refinement. Microanalysis suggests a hydrated material, with rapid loss of crystallinity observed upon standing in air.

3Zn: SQUEEZE was applied locating a total void volume of 275 $Å^3$ per cell (57 e^-). This equates to 1.5 water molecules per formula unit and was incorporated into the UNIT card prior to final refinement. Microanalysis suggests a similarly hydrated formula.

3Cd: SQUEEZE was applied locating a total void volume of 275 $Å^3$ per cell (64 e^-). This equates to 1.5 water molecules per formula unit and was incorporated into the UNIT card prior to final refinement. Microanalysis suggests a similarly hydrated formula.

4Ni: SQUEEZE was applied locating a total void volume of 1977 $Å^3$ per cell (208 e^-). This equates to 7 per formula unit and was incorporated into the UNIT card prior to final refinement. Microanalysis suggests a less hydrated material, likely due to solvent loss in transfer.

4Co: SQUEEZE was applied locating a total void volume of 2014 $Å^3$ per cell (501 e^-). This equates to 16 per formula unit and was incorporated into the UNIT card prior to final refinement. Microanalysis suggests a less hydrated material, likely due to solvent loss in transfer.

Additional Diagrams

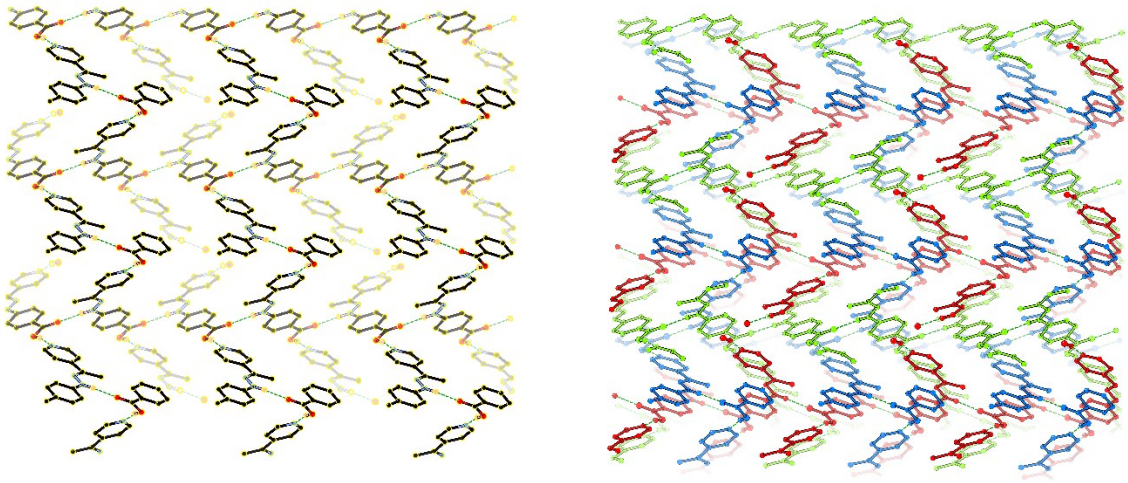

Figure S8: *One 3D hydrogen-bonded network in the structure of* ***4py4bzH*** *(left) and the interpenetration of three such networks to form the overall structure with pi-stacking between the molecules (right).*