Electronic Supplementary Material (ESI) for CrystEngComm.

A robust metallomacrocyclic motif for the formation interpenetrated coordination polymers

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Supporting Information

1. X-Ray crystallography refinement details

***Poly*-[Cd_2(AlaNDI)$_2$(bipy)(DMF)$_4$][Cd_2(AlaNDI)$_2$(bipy)(DMF)$_2$(OH_2)$_2$], 1**

The DMF molecules each exhibited signs of disorder and so were modelled with a combination of SHELX DFIX, DANG, FLAT, RIGU and ISOR restraints to give these molecules a chemically sensible model. The two solvents positions in the coordination sphere of Cd(2) both appear to be disordered between a water molecule and a DMF molecule, so each was modelled at 50% occupancy.

***Poly*-[Cd_4(AlaNDI)$_4$(bipy*)*(DMF)$_4$(OH_2)$_2$]·5H_2O·4DMF, 2**

The bipy ligand has rotational disorder and was modelled over two positions (fixed occupancies of 70:30) with SHELX DFIX, FLAT, DELU and ISOR restraints. The DMF molecules were also refined with SHELX DFIX and ISOR restraints. The structure of **2** contains solvent accessible voids in which no solvent could be modelled. The data was processed with SQUEEZE, showing two voids each of 785 Å^3 containing 211 e^- (*i.e.* 211 per formula unit).

***Poly*-[Mn_4(AlaNDI)$_4$(bipy)(DMF)$_4$(OH_2)$_2$]·2DMF·5.5H_2O, 3**

The solvent coordinated to one of the axial positions of both Mn(1) and Mn(2) were disordered between a DMF and H_2O molecule (fixed 50:50 occupancies). In the case of Mn(1) the molecules share an oxygen atom position, while for Mn(2) the oxygen atoms are spatially separated. The partial occupancy DMF coordinated to Mn(2) was refined using SHELX DELU restraints. The lattice DMF in close proximity to the disordered solvent coordinated to Mn(2) was modelled as the same PART and occupancy as the coordinated water molecule and was refined with SHELX DELU and DFIX restraints. The remaining axial solvent position on Mn(1) was occupied by a DMF molecule which was modelled with SHELX DELU, ISOR, FLAT and DFIX restraints in order to model a chemically sensible molecule. The data was processed with SQUEEZE, showing voids totalling 430 Å^3 containing 95 e^- per formula unit.

***Poly*-[Cd(AlaNDI)(bipy)(OH_2)]·3.5H_2O·0.5DMF, 4**

The crystals did not diffract well at high resolution, even using synchrotron radiation, with a very poor R_{int} past 0.9 Å, therefore the SHEL command was used to restrict data used in the refinement to this limit. The structure of **3** contains solvent accessible voids in which no solvent could be modelled. The data was processed with SQUEEZE, showing one void per unit cell of 1856 Å^3 containing 588 e^-.

***Poly*-[Zn_2(AlaNDI)$_2$(bipy)$_2$]·0.3MeOH·0.7H_2O, 5**

The uncoordinated solvent was disordered between a methanol and a water molecule (fixed 30:70 occupancies). The methanol was refined with SHELX ISOR and DFIX restraints to model a chemically sensible molecule.

***Poly*-[Mn(HAlaNDI)$_2$(dpe)], 6**

No restraints used in refinement.

***Poly*-[Cd$_2$(AlaNDI)$_2$(4PyNDI)$_2$]·4DMF, 7**

The 4PyNDI coligands showed signs of rotational disorder associated with the pyridyl rings which could not be modelled over two positions. These were refined using SHELX ISOR and DELU restraints, with somewhat elongated displacement parameters being an accurate depiction of this disorder. The AlaNDI ligands were also refined with some SHELX DELU, ISOR and FIX restraints to give a chemically sensible model. The structure contained solvent accessible voids in which no solvent could be accurately modelled. The data was processed with SQUEEZE, showing voids of 720 Å^3 containing 163 e$^-$ per asymmetric unit.

***Poly*-[Cd$_2$(AlaNDI)$_2$(OH$_2$)$_2$(4PyNDI)$_2$]·DMF·H$_2$O, 8**

The sample diffracted poorly with particularly R_{int} values past 0.88 Å, therefore the SHEL command was used to exclude this data from the refinement. The poor data quality also led to a small, non-zero flack parameter.

The non-coordinated DMF molecule was refined with SHELX DFIX, DANG and DELU restraints to give a chemically sensible molecular geometry. Numerous bond lengths in the NDI ligands were also refined using SHELX DFIX restraints to give chemically sensible distances. Three of the pyridyl groups were refined with DELU restraints.

***Poly*-[Cd$_2$(AlaNDI)$_2$(DMF)$_2$(OH$_2$)$_2$(4PyNDI)]·DMF·4H$_2$O, 9**

The crystals were of poor quality and did not diffract well, despite employing synchrotron radiation. A SHEL command was used to exclude data beyond 0.85 Å from the refinement. The solvent molecules showed signs of disorder which could not be modelled, so the model of these molecules was refined with SHELX DFIX, DELU, RIGU and ISOR restraints.

2. Powder X-Ray diffraction

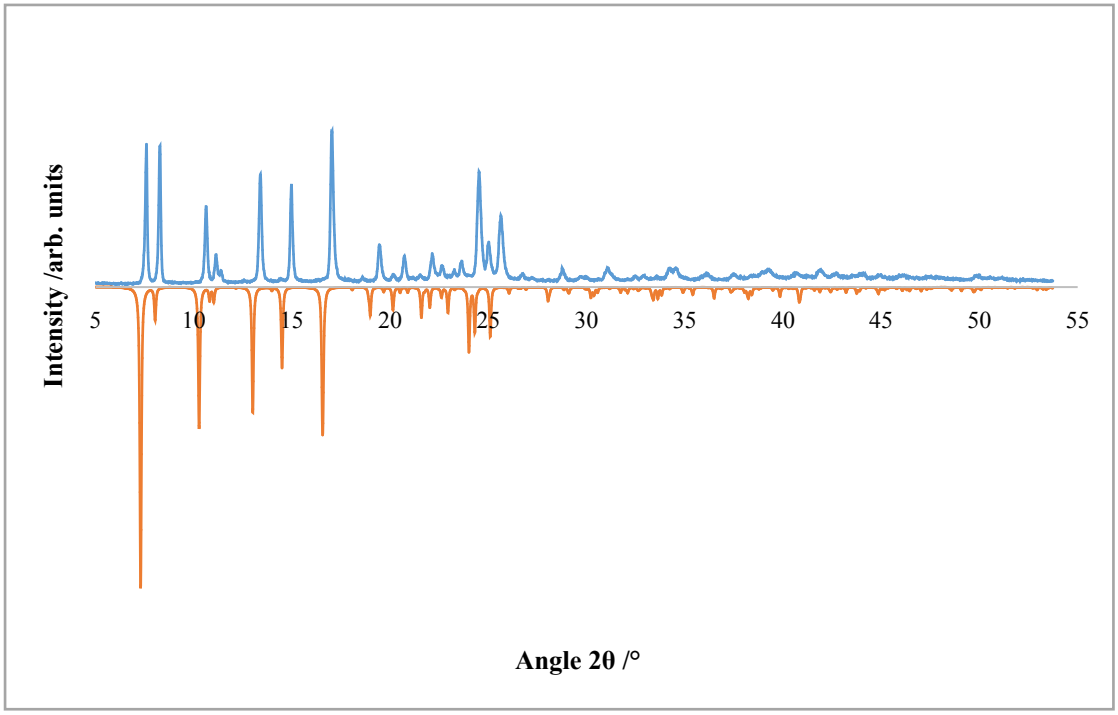

Figure S1: Comparison of experimental (298 K, blue) and calculated (100 K, orange) PXRD of *poly*-$[Cd_2(AlaNDI)_2(bipy)(DMF)_4][Cd_2(AlaNDI)_2(bipy)(DMF)_2(OH_2)_2]$, **1**.

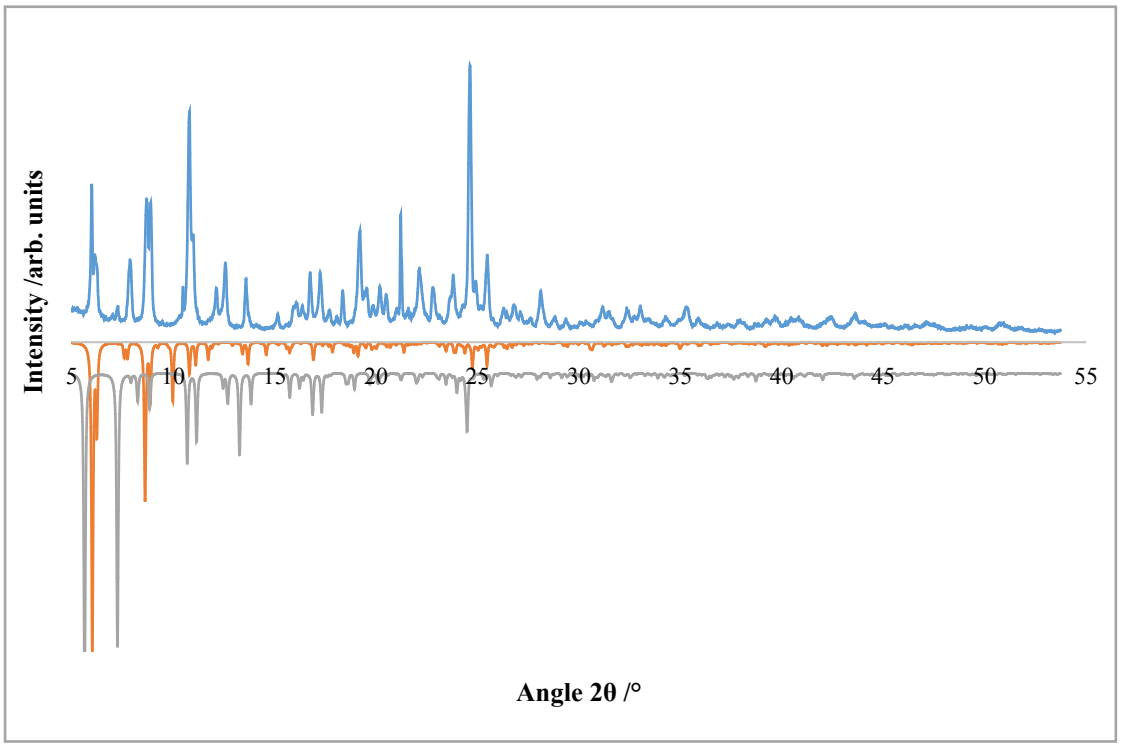

Figure S2: Comparison of experimental (298 K, blue) and calculated (100 K) PXRD of *poly*-$[Cd_4(AlaNDI)_4(bipy)(DMF)_4(OH_2)_2]\cdot 5H_2O\cdot 4DMF$, **2** (orange) and *poly*-$[Cd(AlaNDI)(bipy)(OH_2)]\cdot 3.5H_2O\cdot 0.5DMF$, **4** (grey).

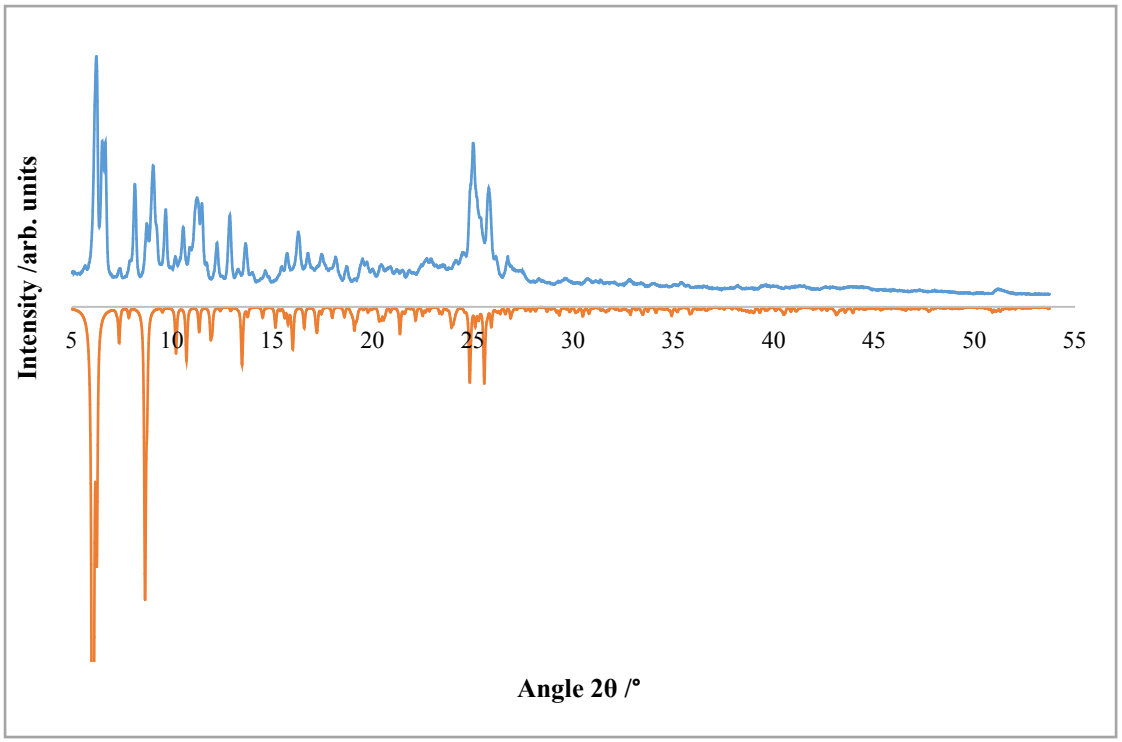

Figure S3: Comparison of experimental (298 K, blue) and calculated (100 K, orange) PXRD of *poly*-$[Mn_4(AlaNDI)_4(bipy)(DMF)_4(OH_2)_2]\cdot 2DMF\cdot 5.5H_2O$, **3**.

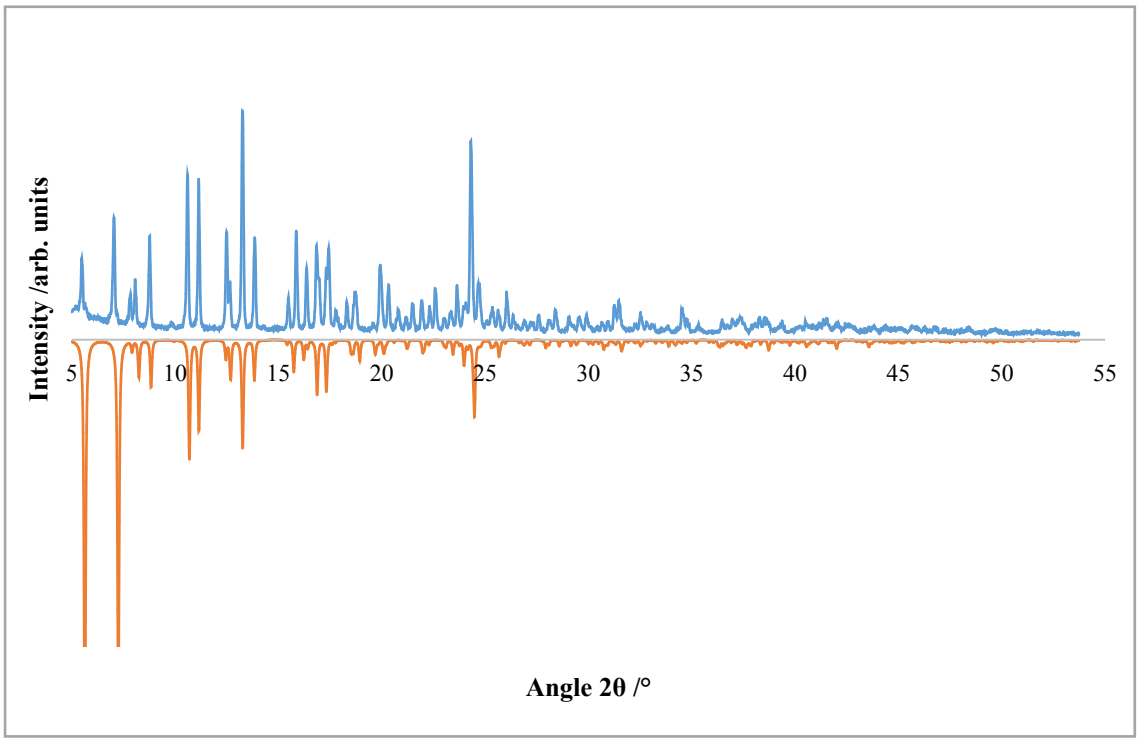

Figure S4: Comparison of experimental (298 K, blue) and calculated (100 K, orange) PXRD of *poly*-$[Cd(AlaNDI)(bipy)(OH_2)]\cdot 3.5H_2O\cdot 0.5DMF$, **4**.

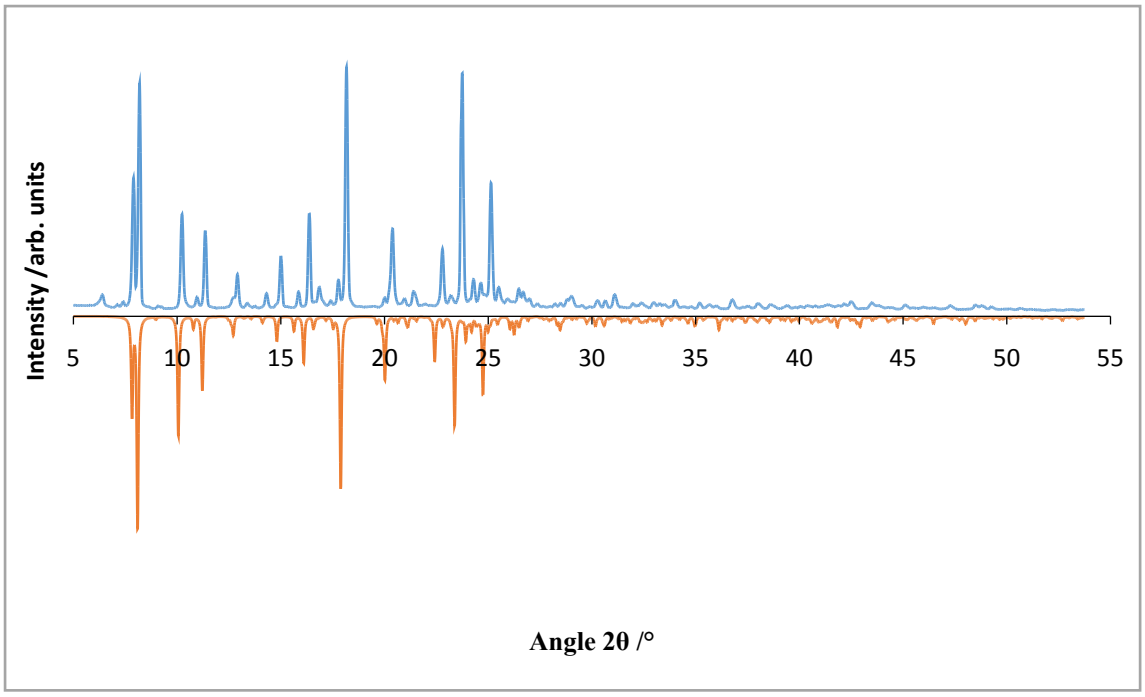

Figure S5: Comparison of experimental (298 K, blue) and calculated (100 K, orange) PXRD of *poly*-$[Zn_2(AlaNDI)_2(bipy)_2]\cdot 0.3MeOH\cdot 0.7H_2O$, **5**.

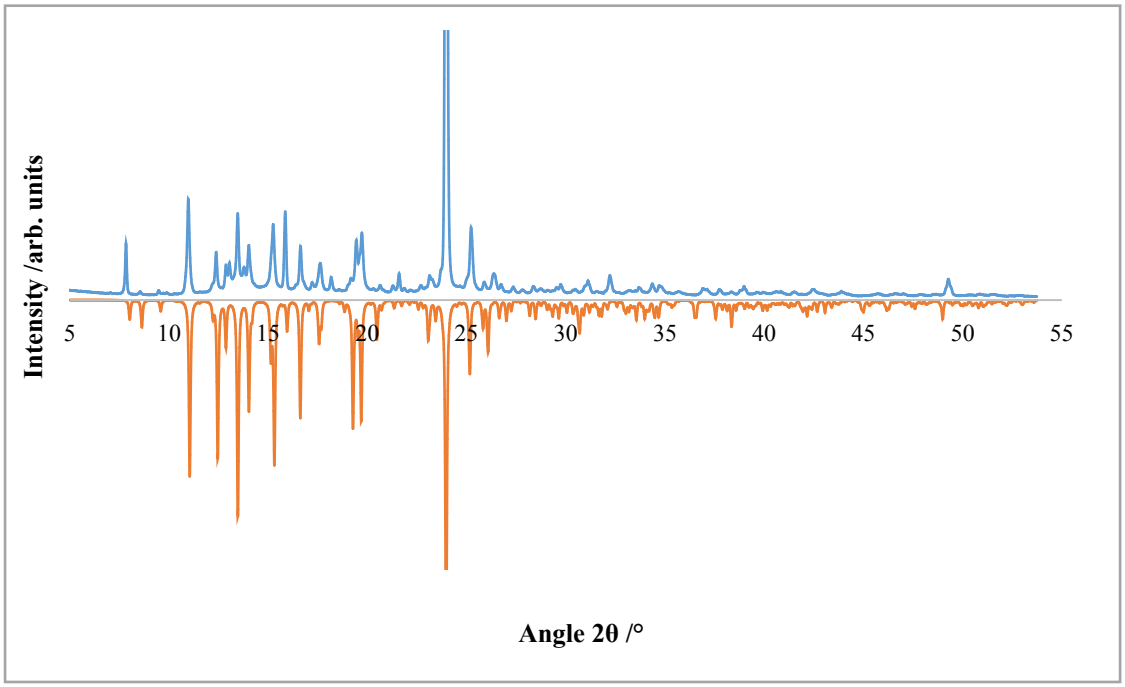

Figure S6: Comparison of experimental (298 K, blue) and calculated (100 K, orange) PXRD of *poly*-$[Mn(HAlaNDI)_2(dpe)]$, **6**.

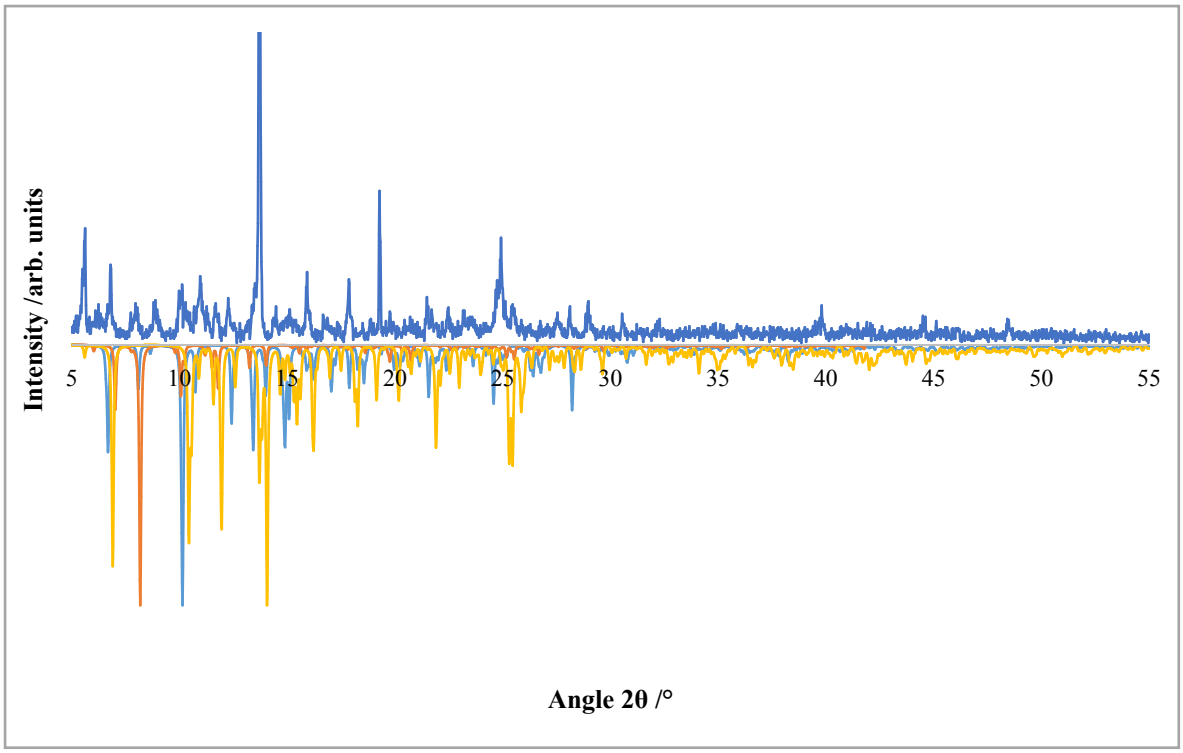

Figure S7: Comparison of experimental (298 K, blue) and calculated (100 K) PXRD of *poly*-[$Cd_2(AlaNDI)_2(4PyNDI)_2$]·4DMF, **7** (orange), *poly*-[$Cd_2(AlaNDI)_2(OH_2)_2(4PyNDI)_2$]·DMF·$H_2O$, **8** (light blue) and *poly*-[$Cd_2(AlaNDI)_2(DMF)_2(OH_2)_2(4PyNDI)$]·DMF·$4H_2O$, **9** (yellow).

3. Thermogravimetric analysis

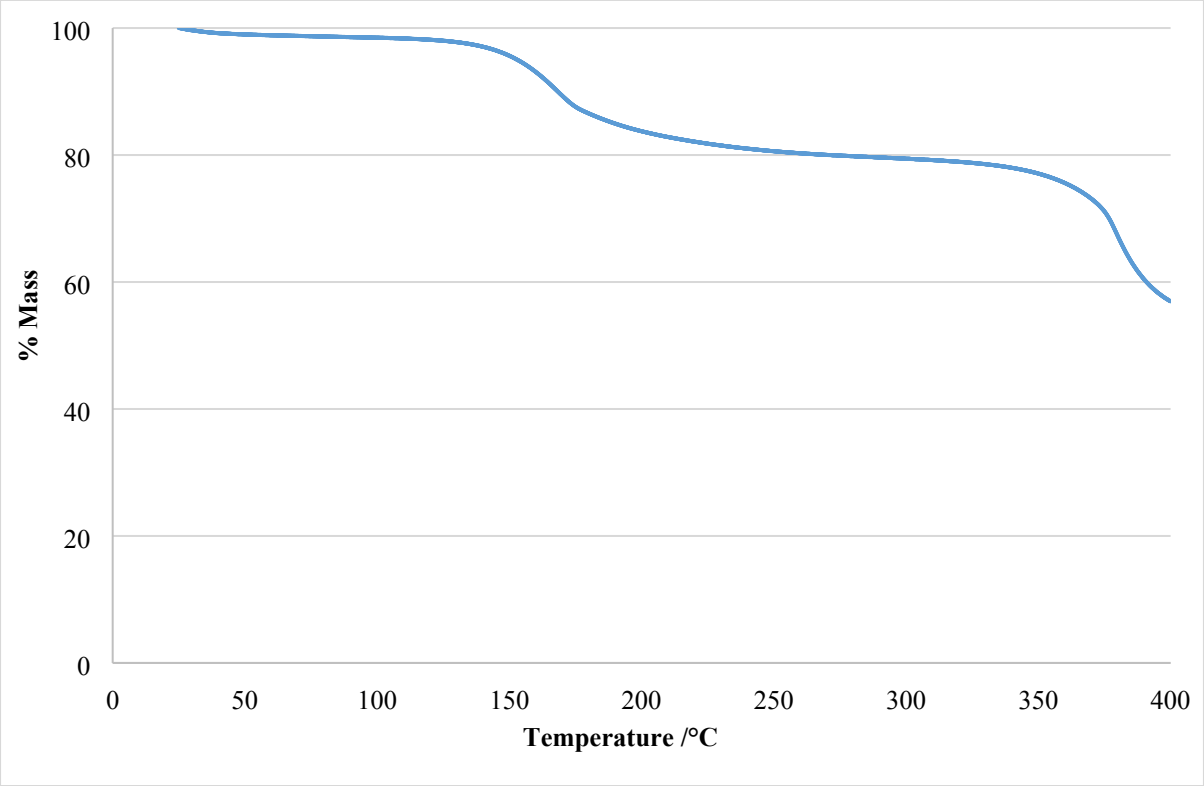

Figure S8: Thermogravimetric analysis trace for *poly*-$[Cd_2(AlaNDI)_2(bipy)(DMF)_4][Cd_2(AlaNDI)_2(bipy)(DMF)_2(OH_2)_2]$, **1**.

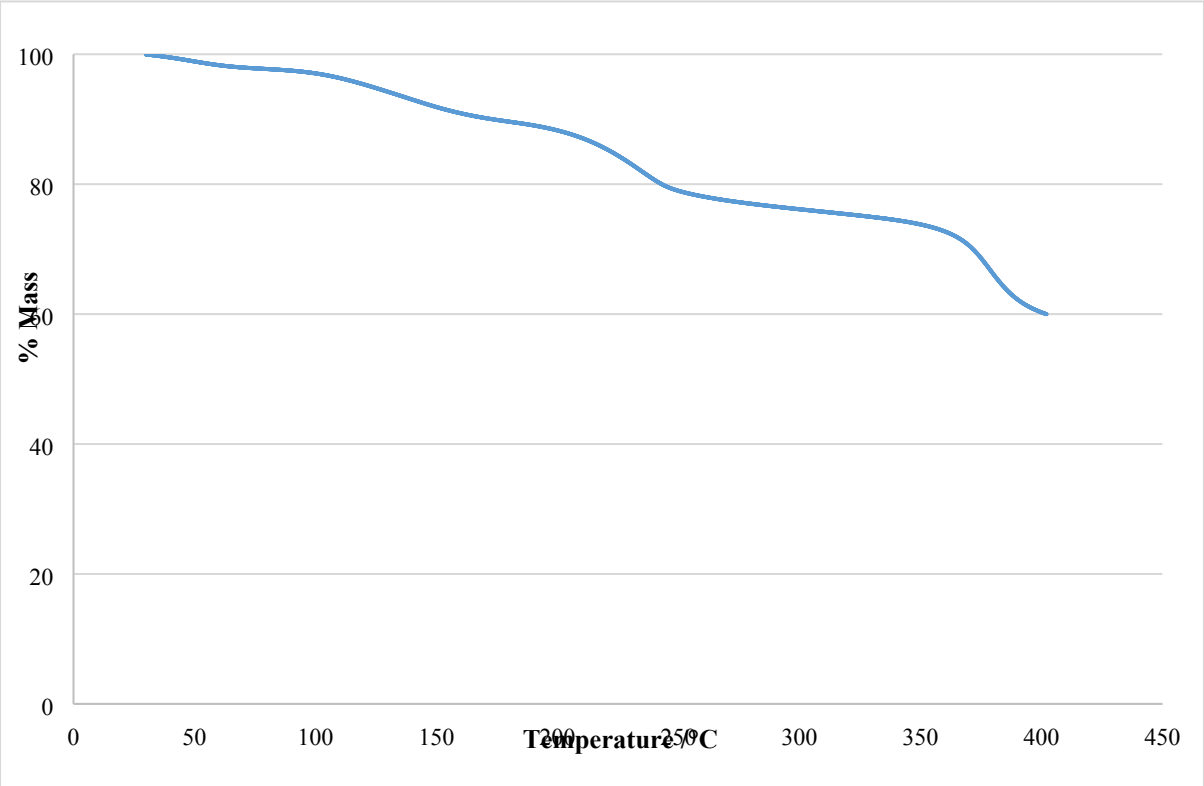

Figure S9: Thermogravimetric analysis trace for *poly*-$[Mn_4(AlaNDI)_4(bipy)(DMF)_4(OH_2)_2]\cdot 2DMF\cdot 5.5H_2O$, **3**.

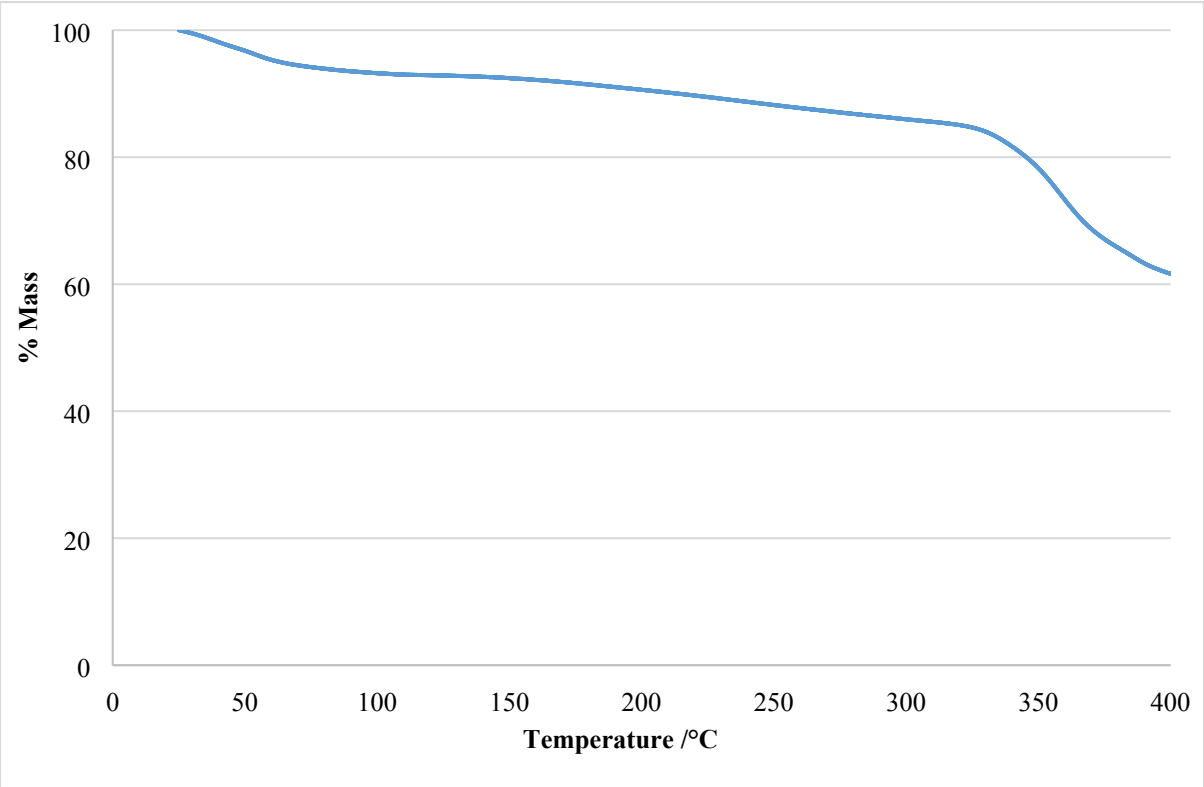

Figure S10: Thermogravimetric analysis trace for of *poly*-[Cd(AlaNDI)(bipy)(OH_2)]·3.5H_2O·0.5DMF, **4**.

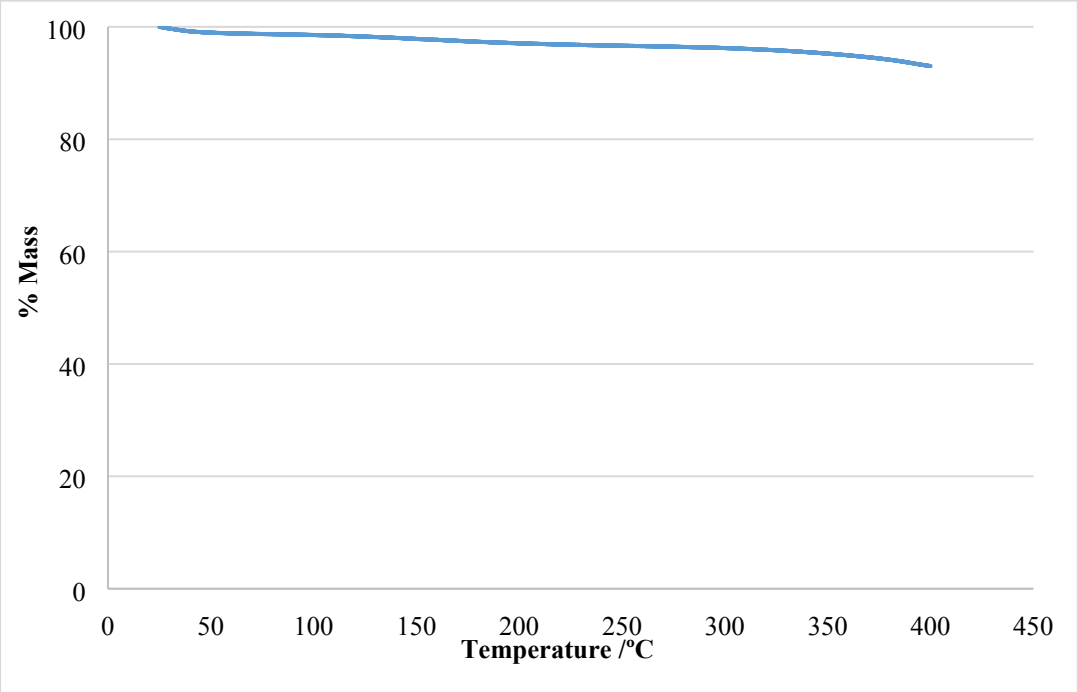

Figure S11: Thermogravimetric analysis trace for *poly*-[Zn_2($AlaNDI)_2$($bipy)_2$]·0.3MeOH·0.7H_2O, **5**.

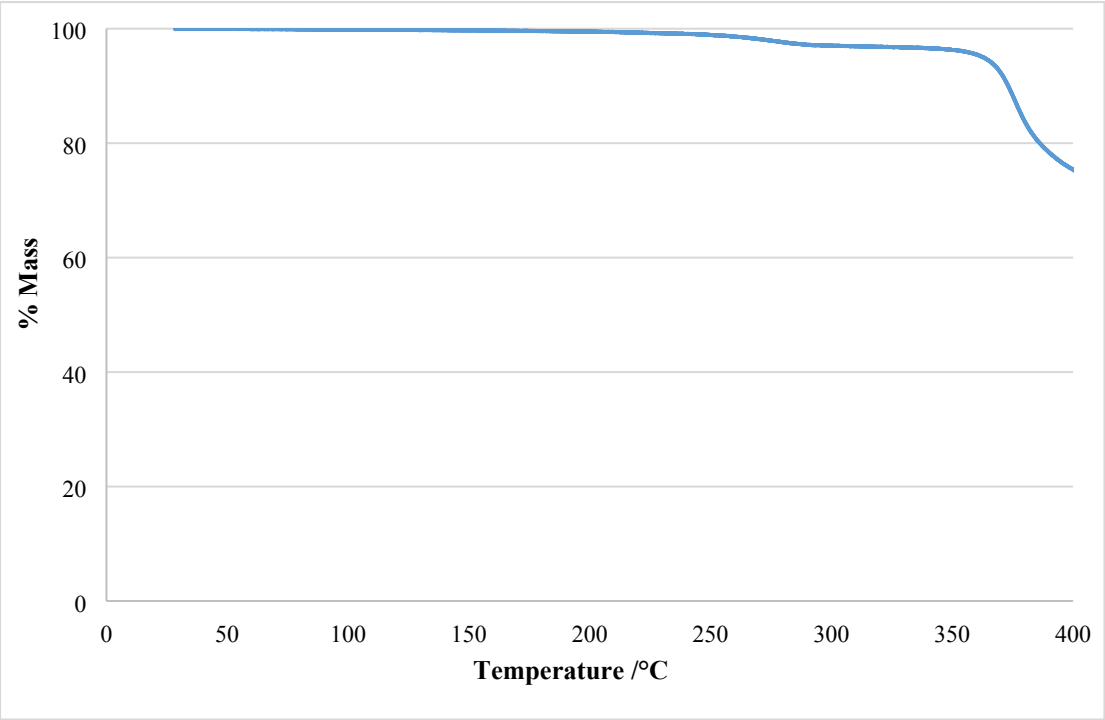

Figure S12: Thermogravimetric analysis trace for *poly*-[Mn(HAlaNDI)$_2$(dpe)], **6**.