Supplementary Information

New coordination polymers with extended arm cyclotriguaiacyclene ligands: 1D chains, and interpenetrating or polycatenating 2D $(4^2.6^2)(4.6^2)_2$ networks

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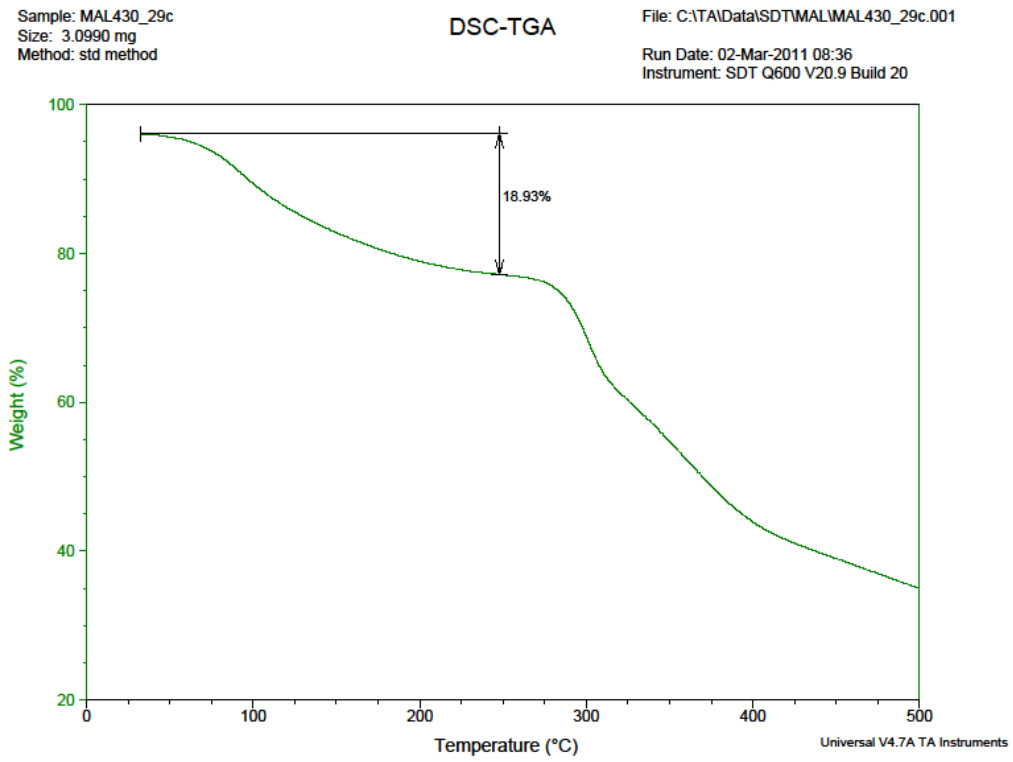
Contents:

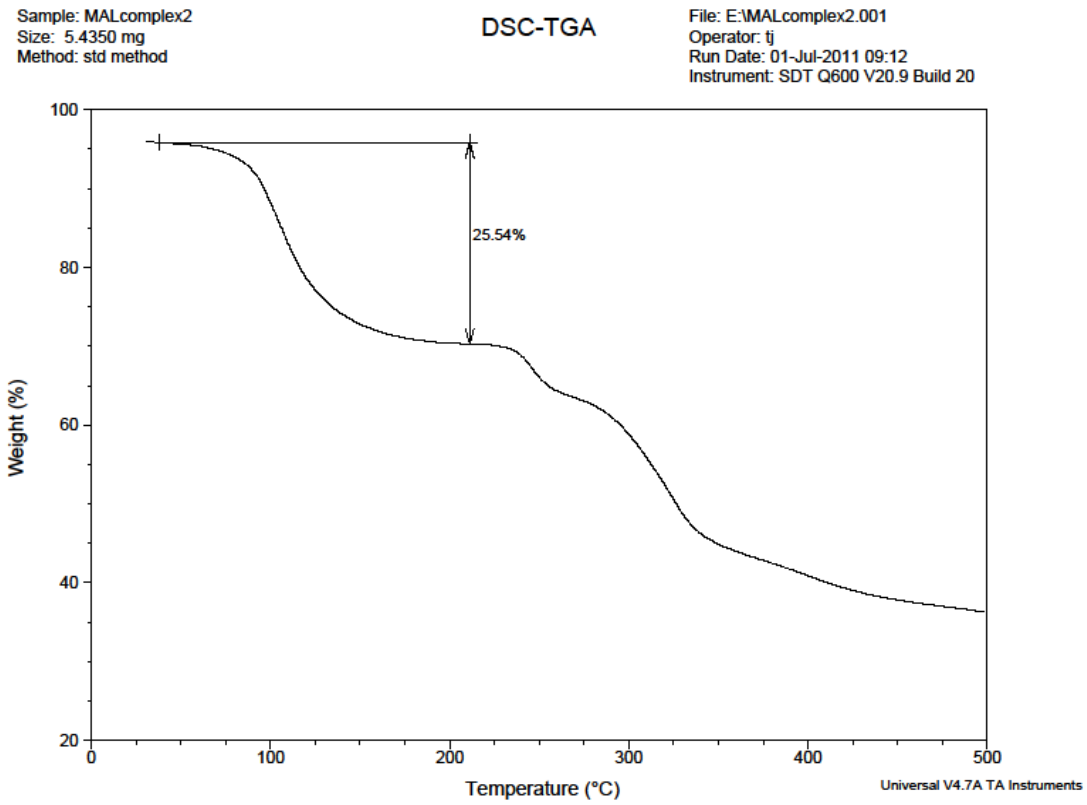
- *Thermogravimetric Analysis (TGA) traces of selected complexes*
- *Additional diagrams of crystal structures for selected complexes*

TGA trace of $[Cd_2(4ph4py)(NO_3)_3(H_2O)_2(DMA)_2].(NO_3).(DMA)_4$ 1



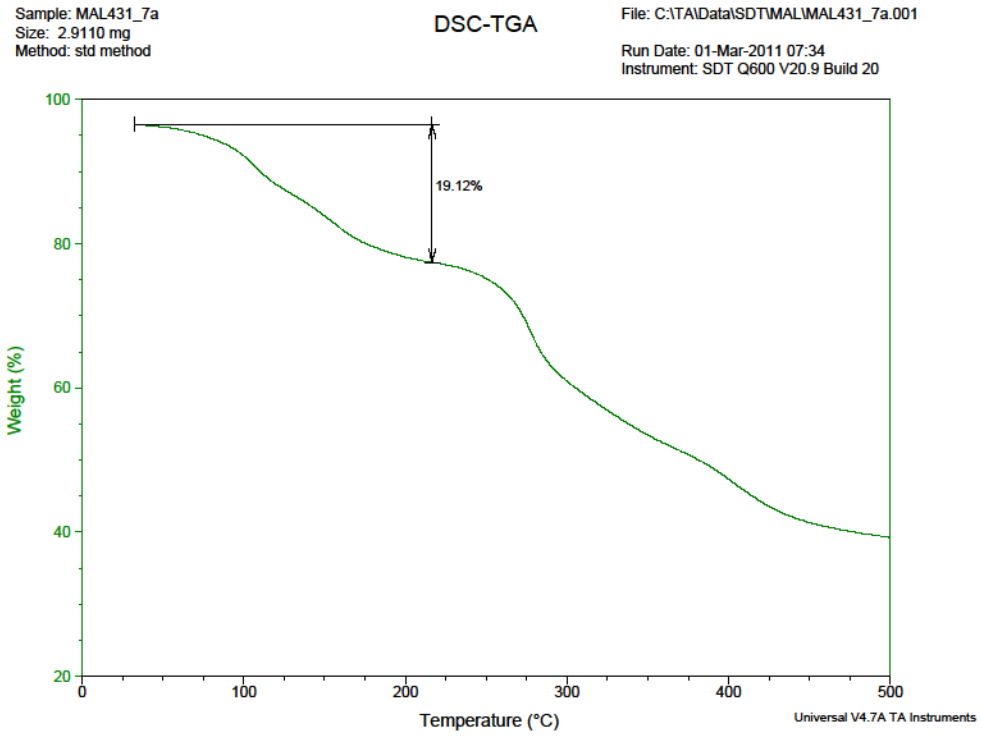
Approximately 18% weight loss is consistent with loss of ~4 molecules of dimethylacetamide (DMA). Only one such molecule was located in the crystal structure, but additional solvation is consistent with void space in the crystal lattice.

TGA trace of $[Zn(4ph4py)_2(CF_3COO)(H_2O)].(CF_3COO)(NMP)_7$ 2



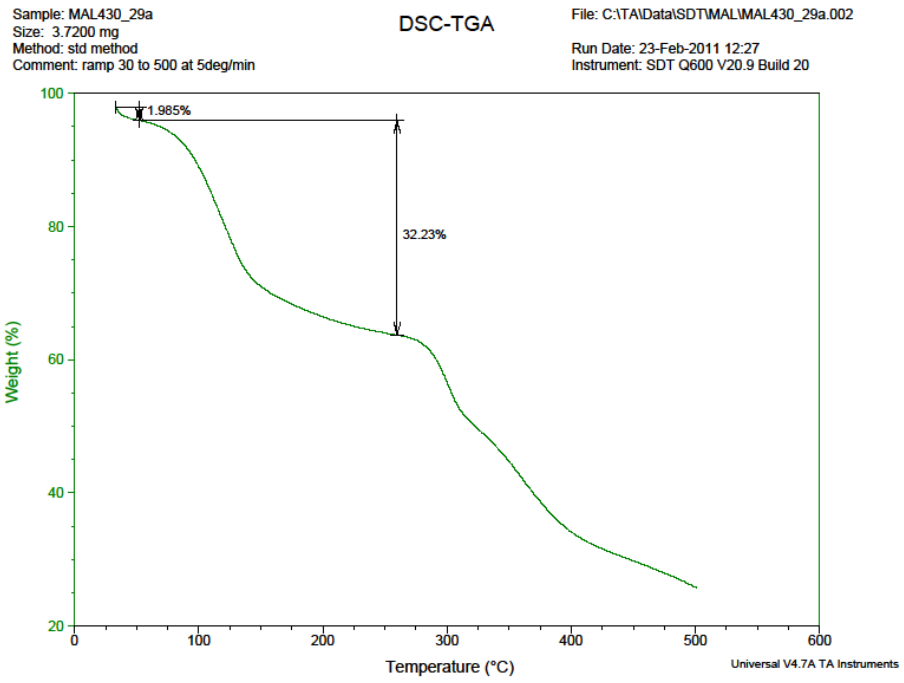
Approximately 25% weight loss is consistent with the loss of ~5 molecules of N-methylpyrrolidone (NMP) and one water. Only the water and two NMP molecules were located in the crystal structure, but additional solvation is consistent with void space in the crystal lattice.

TGA trace of $[Co(3ph3py)(NO_3)_2].(NMP)_4$ 3



Approximately 19% weight loss is consistent with loss of 3 molecules of N-methylpyrrolidone (NMP).

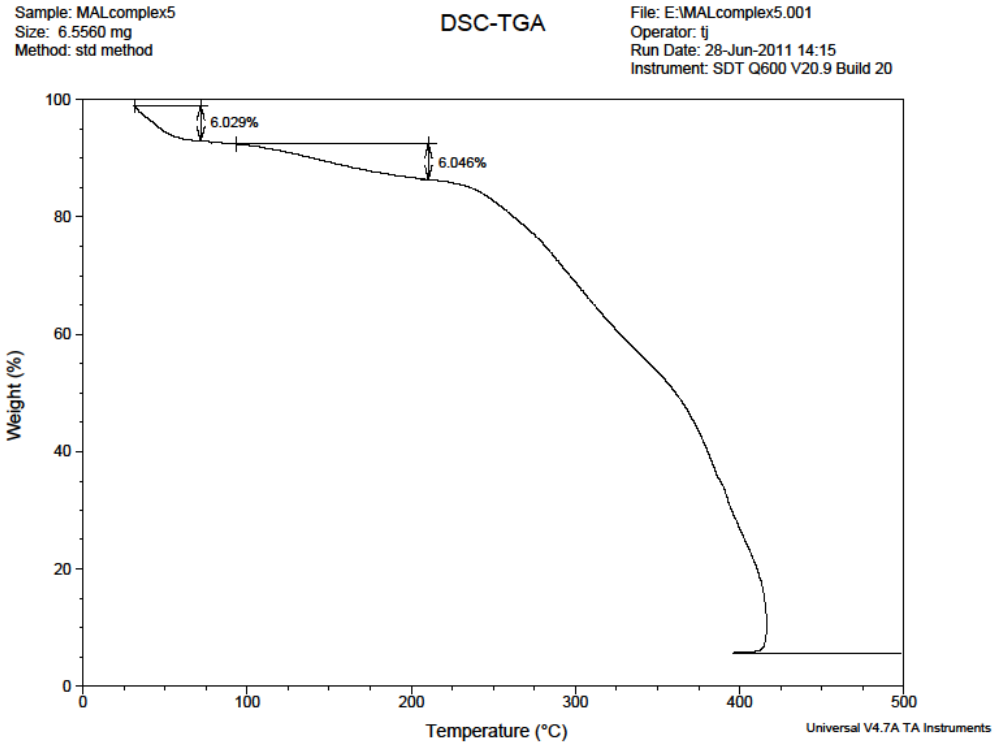
TGA trace of $[Cd_2(4ph4py)_2(NO_3)_4(NMP)].(NMP)_9(H_2O)_4$ 4



Approximately 2% weight loss is consistent with loss of 4 molecules of water, while subsequent weight loss is consistent with loss of ~ 10 molecules of NMP. Only two NMP molecules and no water positions were refined

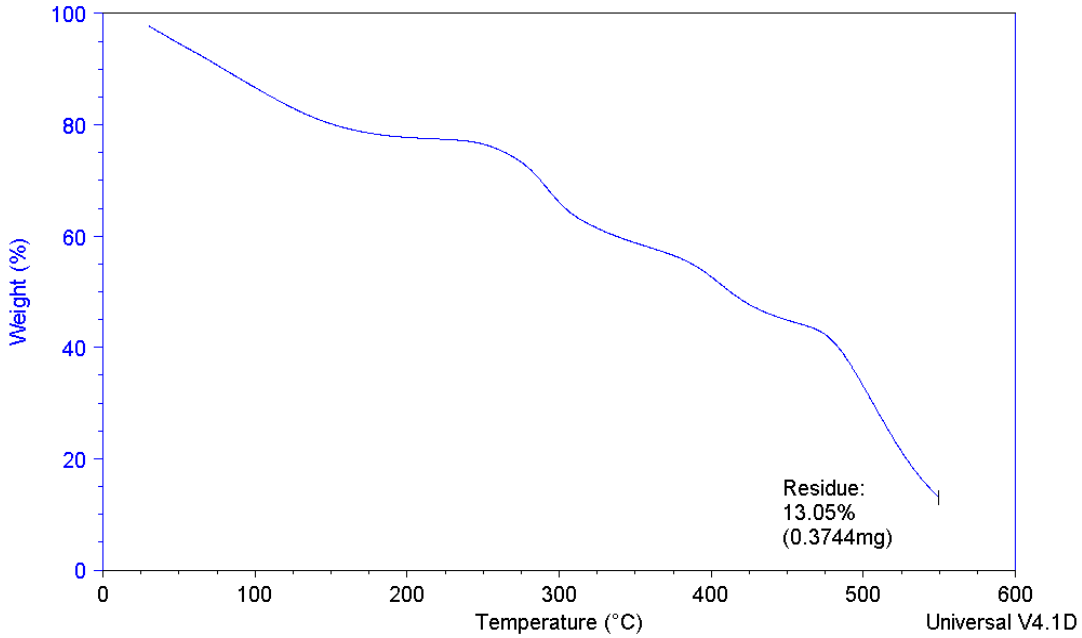
in the crystal structure, however the presence of additional solvent molecules is approximately consistent with the size of the voids in the crystal lattice.

TGA trace of $[Co(4ph4py)(H_2O)_2].(NO_3)_2.(DMF)_2$ complex 5:



Each approximately 6% weight loss is consistent with loss of a dimethylformamide and water (= 6.9%). DMF molecules were not located in the crystal structure however the presence of additional solvent molecules is consistent with voids in the crystal lattice. Voids are sufficiently large to contain more solvent molecules however TGA did not give evidence of these

TGA trace of $[Co_2(3ph4py)_2(NO_3)(H_2O)_5].(NO_3)_3.(DMF)_8$ 6:



Approximately 20% weight loss is consistent with loss nine moelcules of DMF. DMF molecules were not located in the crystal structure, however the presence of these additional solvent molecules is consistent with the size of the voids in the crystal lattice.

Additional Diagrams of Crystal Structures

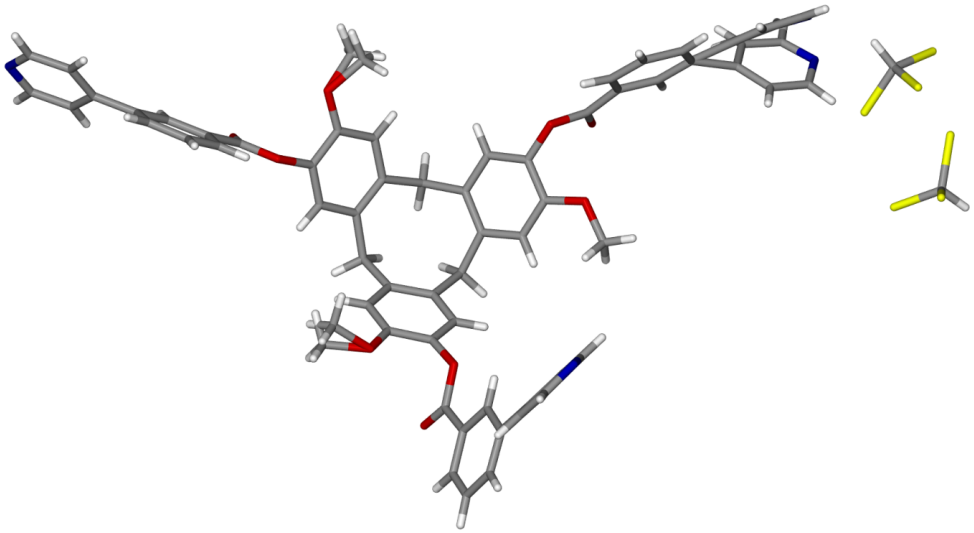


Fig. S1. Asymmetric unit of crystalline clathrate complex 3ph4py.$(CHCl_3)_{1.5}$ showing the disorder model for methyl and pyridyl groups.

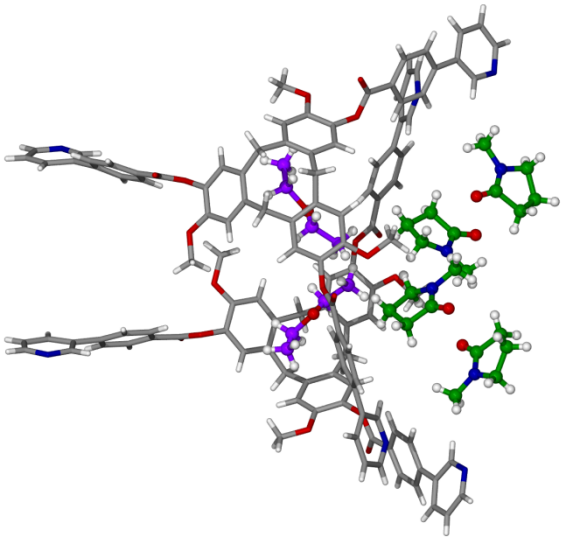


Fig. S2. Asymmetric unit of inclusion complex 4ph3py.(Et_2O).$(NMP)_2$ with NMP shown as ball-and-stick.

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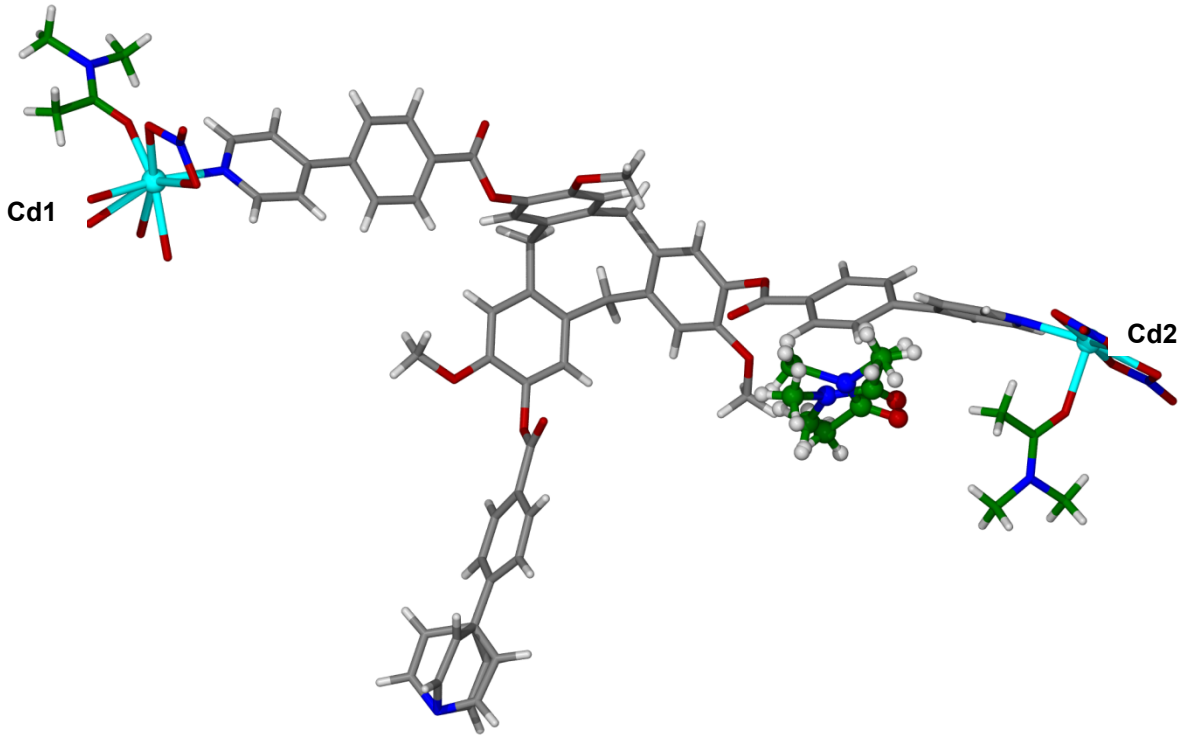
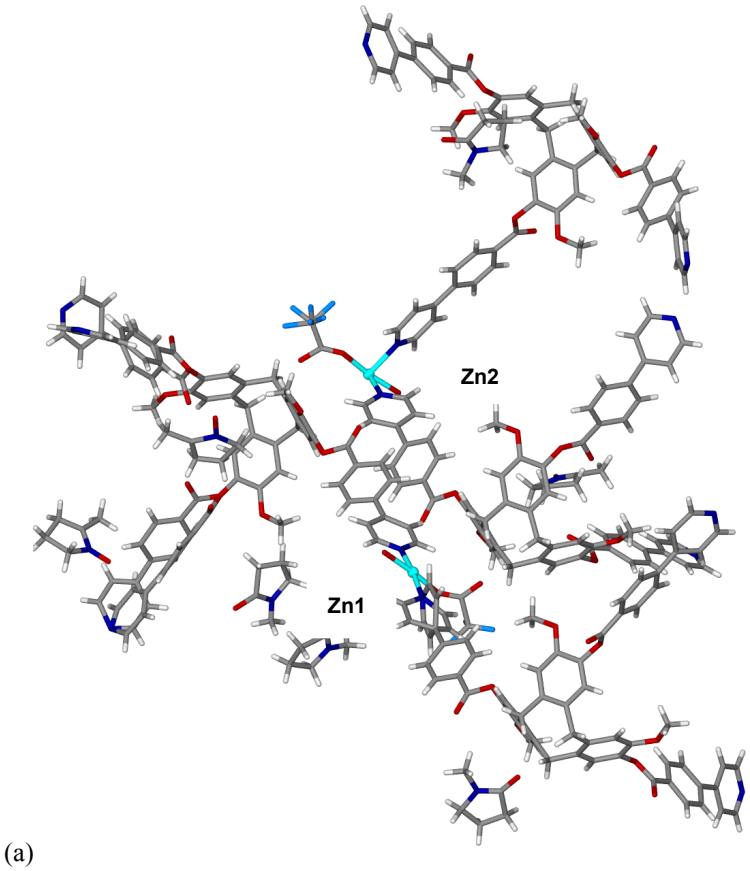
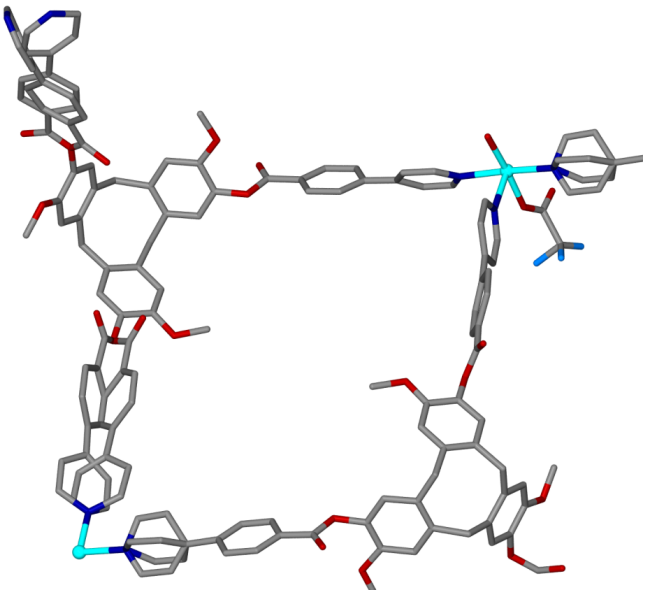


Fig. S3. Asymmetric unit of $Cd_2(4ph4py)(NO_3)_3(H_2O)_2(DMF)_2].(NO_3).(DMF)$ **1** showing disorder model for aquo ligands and DMF solvent (ball-and-stick)



(a)



(b)

Fig. S4 Complex $[Zn(4ph4py)_2(CF_3COO)(H_2O)].(CF_3COO)(NMP)_2$ **2** (a) asymmetric unit; (b) highlight of disorder of phenyl-pyridine side arms for chain containing Zn1

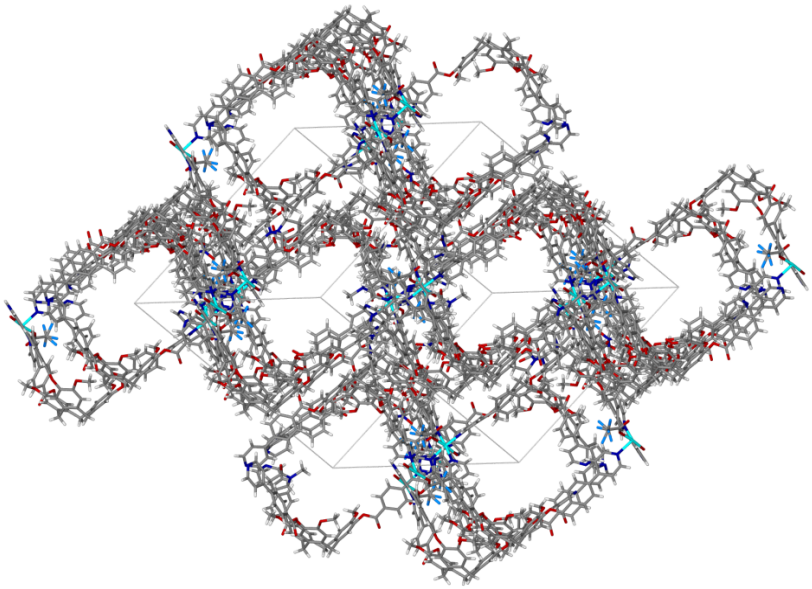


Fig. S5 Packing diagram of complex $[Zn(4ph4py)_2(CF_3COO)(H_2O)].(CF_3COO)(NMP)_2$ **2**.

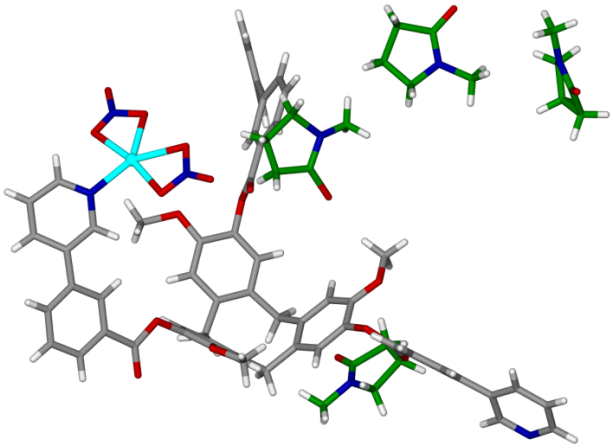


Fig. S6 Asymmetric unit of complex $[Co(3ph3py)(NO_3)_2].(NMP)_4$ **3**

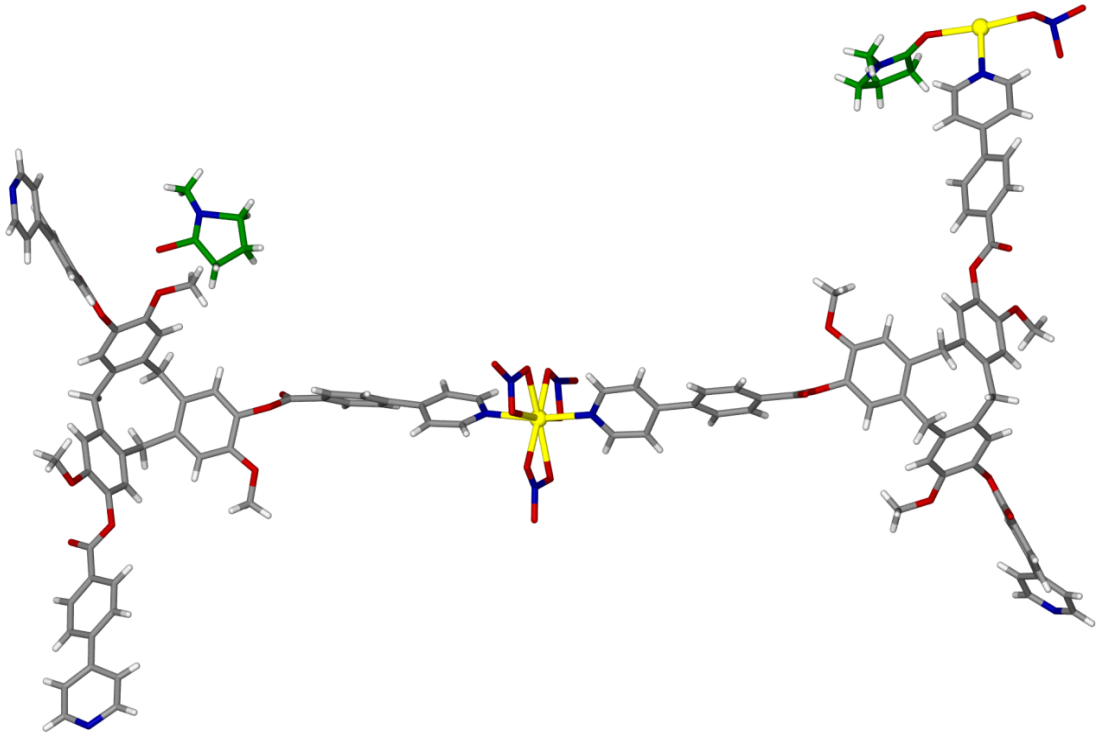


Fig S7 Asymmetric unit of complex $[Cd_2(4ph4py)_2(NO_3)_4(NMP)].(NMP)$ **4**.

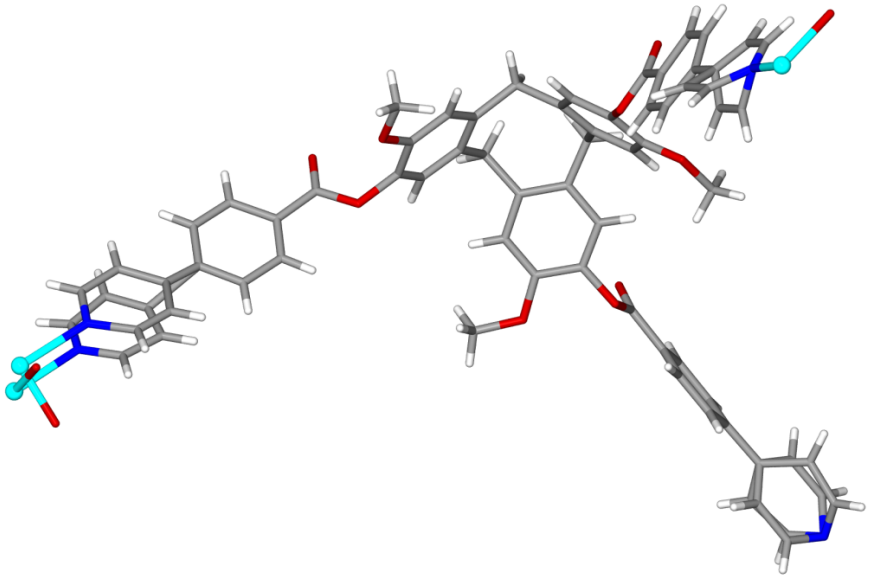
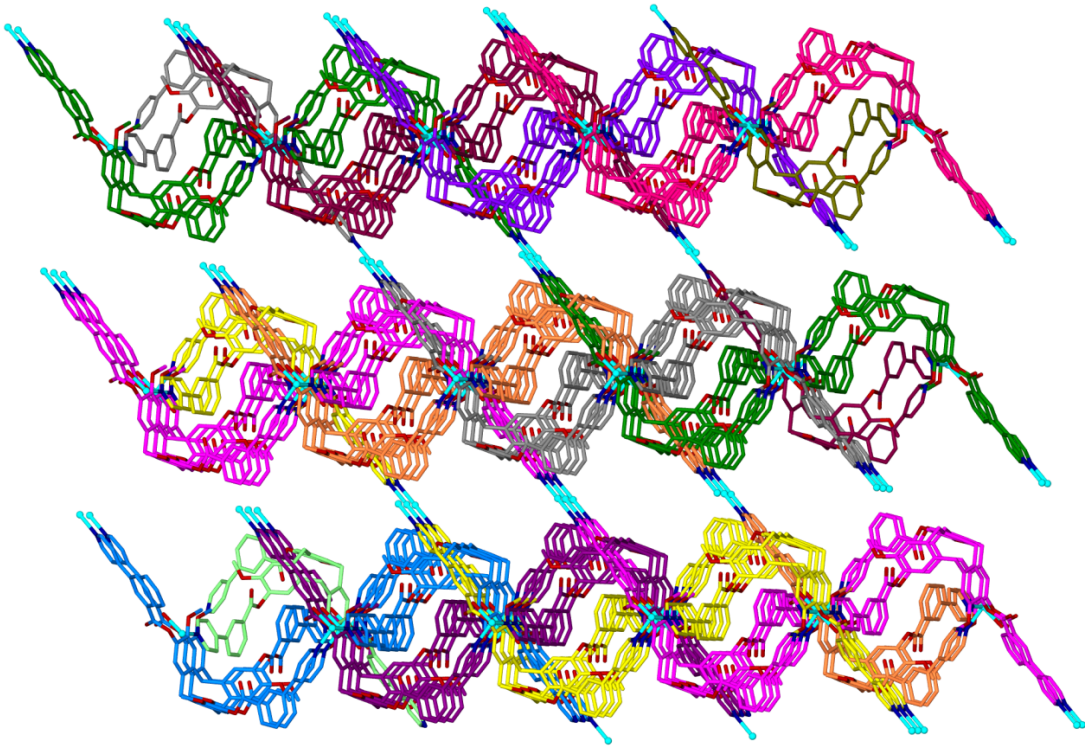
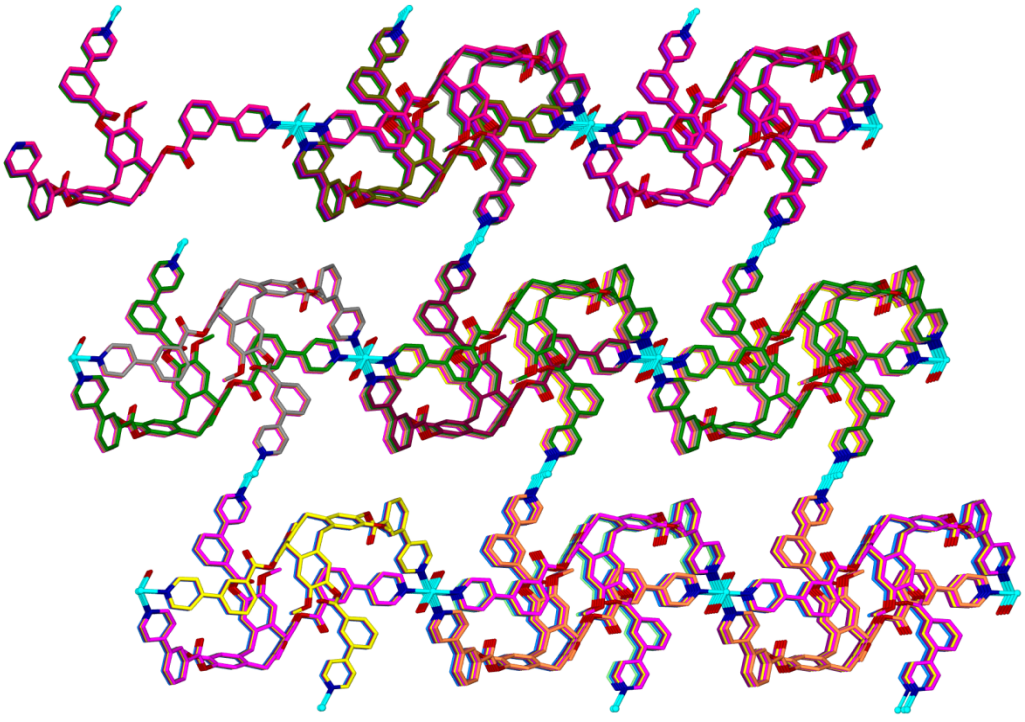


Fig S8 Asymmetric unit of the structure of $[Co(4ph4py)(H_2O)_2].(NO_3)_2$ **5** illustrating the severe disorder of the structure with pyridyl and $Co(H_2O)$ groups disordered.



(a)



(b)

Fig S9 (a) and (b) Packing diagrams for complex $[Co_2(3ph4py)_2(NO_3)(H_2O)_5].(NO_3)_3$ **6**, with different 2D polymers shown in different colours.