Supporting Information for

Interpenetrated metal-organic frameworks of self-catenated four-connected mok nets

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Experimental

Synthesis of N,N'-bis-4-pyridinyl-isophthalamide (4,4'-BPIPA):

Isophthaloyl dichloride (0.1 mol), 4-Aminopyridine (0.25 mol) and 150 mL pyridine were added to a three-necked flask and refluxed for one day. Light-yellow crude product was collected by filtration and washed with DCM (20 mL×4), methanol (40 mL) and water (40 mL), respectively. Purified white powder product was dried at 105 °C for 3 hours. Yield: *ca.* 80%. Anal. Calcd for $C_{18}H_{14}N_4O_2$: C, 67.91; H, 4.43; N, 17.6. Found: C, 67.06; H, 4.01; N, 17.05. IR Characteristics (KBr, cm^{-1}): 1674vs, 1596vs, 1515vs, 1421s, 1301s, 1285s, 1250m, 1229m, 1212m, 1131w, 1105w, 1075w, 994m, 912w, 887w, 823s, 717s, 576m, 537m, 499w.

Syntheses of [Co(4,4'-BPIPA)(2,6-NDC)]·2DMF (1), [Co(4,4'-BPIPA)(4,4'-BPDCA)]·2DMF (2) and [Co(4,4'-BPIPA)(TP)]·2DMF (3) (2,6-NDC=2,6-naphthalenedicarboxylic acid; 4,4'-BPDCA=4,4'-biphenyldicarboxylic acid; TP= terephthalic acid).

A mixture of N,N'-bis-4-pyridinyl-isophthalamide (0.040 g, 0.125 mmol), 2,6-naphthalenedicarboxylic acid (0.027 g, 0.125 mmol), $Co(NO_3)_2·6H_2O$ (0.037 g, 0.125 mmol) was added to 8 mL DMF and stirred for 15 minutes. The reaction mixture was then sealed in a teflon-lined stainless-steel vessel under autogenous pressure at 120 °C for 3 days and cooled to room temperature within a day. Red block crystals of complex **1** suitable for single crystal x-ray crystallography were collected by filtration, washed with cold water and dried in air. Anal. Calcd for $C_{36}H_{34}N_6O_8Co$: C, 58.46; H, 4.65; N, 11.36. Found: C, 58.59; H, 4.48; N, 11.75. IR Characteristics (KBr, cm^{-1}): 1681s, 1658s, 1595s, 1512s, 1424m, 1386m, 1351m, 1331m, 1293m, 1246w, 1211m, 1094w, 1021w, 840w, 802w, 772w, 715w, 598w, 531w.

Complex **2** was synthesized at a higher temperature (150 °C) comparing with **1** and 4,4'-biphenyldicarboxylic acid (0.030 g, 0.125 mmol) was used instead of 2,6-naphthalenedicarboxylic acid. Red purple block crystals of **2** were collected by filtration, washed with cold water and dried in air. Anal. Calcd for $C_{38}H_{36}N_6O_8Co$: C, 59.61; H, 4.75; N, 10.98. Found: C, 59.04; H, 4.31; N, 10.83. IR Characteristics (KBr, cm^{-1}): 1665s, 1604s, 1512s, 1404s, 1332m, 1296m, 1237m, 1208s, 1101m, 1021m, 846m, 774m, 722w, 682w, 658w, 590w, 533w.

Complex **3** was synthesized at a lower temperature (105 °C) comparing with **1** and terephthalic acid (0.020 g, 0.125 mmol) was used instead of 2,6-naphthalenedicarboxylic acid. Red block crystals of **3** suitable for single crystal X-ray diffractions were obtained with some unidentified impurities (very thin pink slides).

Crystallography

Complex **1**, Monoclinic, *C*2/*c*, a = 22.162(2), b = 20.532(2), c = 16.136(2) Å, β = 95.937(2)°, V = 7303.3(1) Å^3, Z = 8, Dx = 1.294 g·cm^{-3}, GooF = 0.993. Final residuals [I>2σ(I)] was R_1 = 0.0808, wR_2 = 0.2389.
Complex **2**, Monoclinic, *C*2/*c*, a = 24.36(4), b = 23.37(7), c = 16.13(3) Å, β = 105.104(2)°, V = 8865(4) Å^3, Z = 8, Dx = 0.925 g·cm^{-3}, GooF = 1.043. Final residuals [I>2σ(I)] was R_1 = 0.0887, wR_2 = 0.2682.
Complex **3**, Monoclinic, *C*2/*c*, a = 7.601(2), b = 29.239(8), c = 14.315(4) Å, β = 96.331(5)°, V = 3162.0(15) Å^3, Z = 4, Dx = 1.444 g·cm^{-3}, GooF = 1.111. Final residuals [I> 2σ(I)] was R_1 = 0.0633, wR_2 = 0.1603.

Crystallographic data were collected on a *Rigaku Mercury CCD/AFC* diffractometer equipped with graphite-monochromated Mo *Kα* radiation with a radiation wavelength of 0.71073 Å by using the *ω*-scan technique. All absorption corrections were performed using the *CrystalClear* program.[S1] Structures were solved by direct methods and refined on F^2 by full matrix least-squares using the *SHELXL-97* program package.[S2] All non-hydrogen atoms were refined anisotropically. CCDC-764789 (**1**), 764788 (**2**) and 772375 (**3**) contain the supplementary crystallographic data. Part of the benzene ring in the asymmetric unit of complex **2** is disordered on two positions C9a C9b C12a C12b C13a C13b C14a C14b with occupancy 50%:50%. In the X-ray structure refinement of complex **2**, guest DMF molecules could not be located because of their high thermal disorder and the final structure model was refined without the solvent molecules by using a SQUEEZE routine of PLATON.[S3] Numbers of DMF molecules were determined mainly by elemental analyisis and TGA analysis

TOPOS calculations

The network simplification of complexes **1** and **2** was performed with *TOPOS* software.[S4] Run *Auto CN* and *Run ADS* commands by choosing metal centers (cobalt in both cases) as nodes gave the simplified nets with 6^5.8-**mok** topologies. Moreover, *TOPOS* indicated three identical **mok** nets related by a single translational vector ([1/2,1/2,0] and the symmetry equivalent [1/2,-1/2,0])

One further note is that **mok** net has transtivity [13], i.e. one node but 3 topologically independent edges: the 3 edges are mapped by the V shaped ligand (BPIPA) and two half bis-carboxylates (L) ligands non equivalent by symmetry. Therefore, the general stoichiometry M(Ligand)$_2$ for a 4-c nodes is actually M(BIPA)(L)$_{0.5}$(L’)$_{0.5}$ resulting in 3 different edges.

Here below is a part of the TOPOS output:

```
Topology for Co1
--------------------
Atom Co1 links by bridge ligands and has
Common vertex with                              R(A-A)
Co 1    0.2868    0.4856    0.2453   ( 0 0 1)    12.907A       1
Co 1   -0.2132   -0.0144    1.2453   ( 0 0 2)    12.954A       1
Co 1   -0.2868   -0.5144    0.2547   (-1-1-1)    16.950A       1
Co 1    0.7132   -0.5144    1.2547   ( 0-1 0)    16.950A       1
-------------------------
Structure consists of 3D framework with Co
There are 3 interpenetrating nets
FIV: Full interpenetration vectors
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[1/2,1/2,0] (15.11A)
[1/2,-1/2,0] (15.11A)
----------------------------------
PIC: [3/2,3/2,0][0,1,0][1,0,1] (PICVR=3)
Zt=3; Zn=1   Class Ia  Z=3

Coordination sequences
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Co1:  1  2  3   4   5   6   7   8    9   10
Num   4 12 30  66 107 154 211 278  353  438
Cum   5 17 47 113 220 374 585 863 1216 1654
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TD10=1654
Vertex symbols for selected sublattice
--------------------------------------
Co1 Point symbol:{6^5.8}
Extended point symbol:[6.6.6.6.6(2).8(4)]
--------------------------------------
Point symbol for net: {6^5.8}
4-c net; uninodal net

Topological type: mok; sev-4-Cccm (uninodal.ttd)
```

Thermal analysis (TG) and X-ray powder diffraction (XRPD)

TGA were carried out on a *NETZSCH STA 449C* instrument. The sample and reference (Al_2O_3) were enclosed in a platinum crucible and heated at a rate of 10 ˚C /min from 30 °C to 800 °C under nitrogen atmosphere. TG plots of complexes **1** and **2** are given in Figure S7. The first weight losses of 21.51 % before 280 ºC (for **1**) and 20.76 % before 200 ºC (for **2**) are assigned to the loss of solvent DMF molecules, which is estimated with two DMF molecules per formula unit (calculated 19.8 % for **1** and 19.1 % for **2**).

X-ray powder diffraction (XRPD) was performed with a *Rigaku DMAX 2500* diffractometer. Samples of complexes **1** and **2** were grounded finely with an agate mortar before measurements. Partially amorphization has been observed for the samples (especially with complex **2**) because of the loss of crystalline solvents during the preparation of the samples. Complex **2** has a larger solvent accessible void of 44.1 % and likely loses solvent molecules more easily.

References

(S1) Molecular Structure Corporation & Rigaku, 2000. CrystalClear, Version 1.36. MSC, 9009 New Trails Drive, The Woodlands, TX 77381-5209, USA, and Rigaku Corporation, 3-9-12 Akishima, Tokyo, Japan.
(S2) G. M. Sheldrick, SHELXS-97, Program for Crystal Structure Solution and Refinement; University of Göttingen, 1997.
(S3) A. L. Spek, J. Appl. Crystallogr., 2003, **36**, 7.
(S4) V. A. Blatov, IUCr CompComm. Newsletter 2006, **7**, 4;
see also http://www.topos.ssu.samara.ru.

Scheme S1 View of the different conformation of 4,4'-BPIPA in complexes **1** and **2** (*trans* - left) and **3** (*cis* - right).

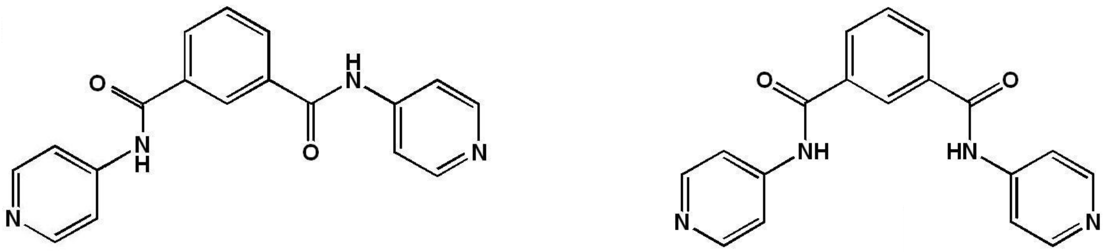


Fig. S1 A view of the basic building block of complexes **1-3** (from left to right).

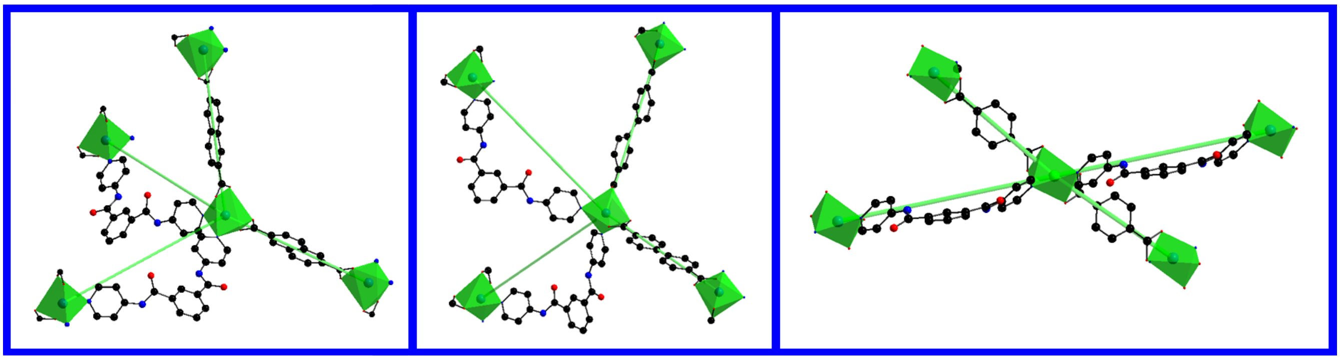


Fig. S2 A view of the basic six-membered ring (top-left) and doubly interpenetrated **hcb** nets (top-right and bottom) in complex **2**.

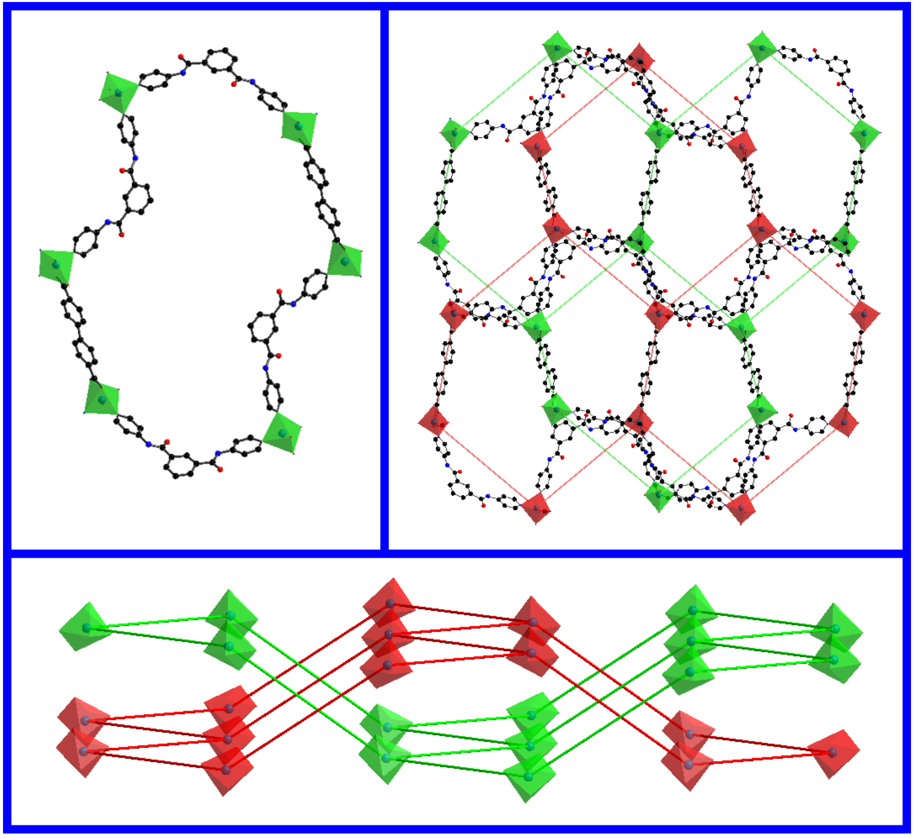
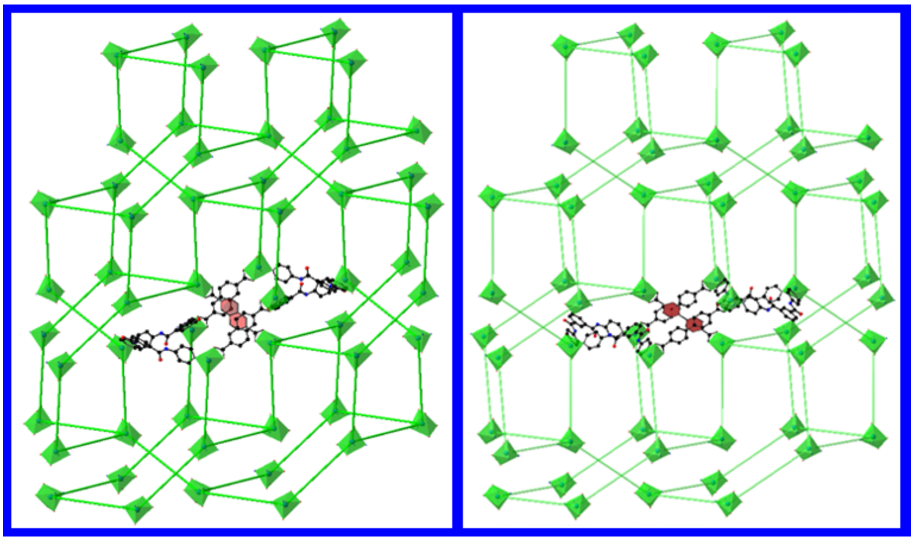


Fig. S3 Topological presentation the 3-D nets of complexes **1** (left) and **2** (right) simplified by showing organic linkers as bold lines. The self-catenation pattern is highlighted.



A single net of **1** and the packing of 3 interpenetrated nets, showing the voids left after the removal of solvents.

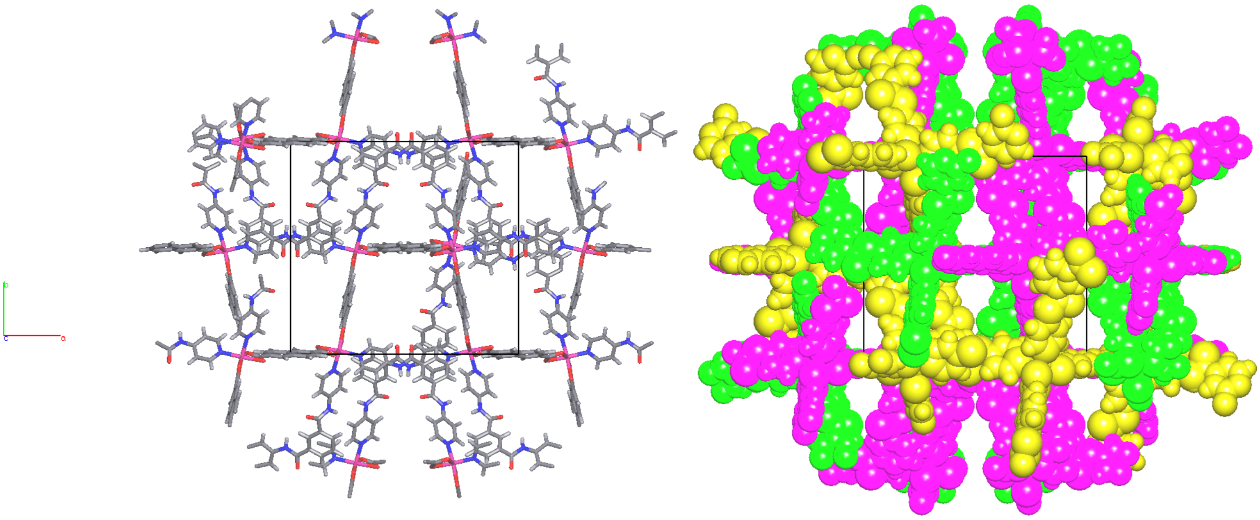


Fig. S4 Adsorption and desorption isotherms of complex **1** for the N_2 uptake at 77 K.

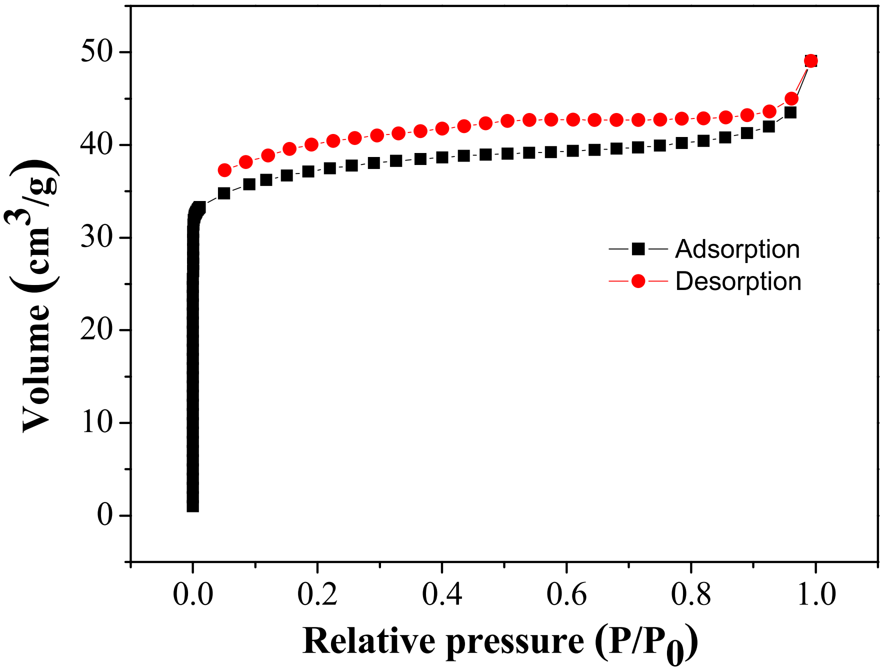


Fig. S5 A view of the basic **sql** layer (top) and the 2-fold interpenetration in complex **3** (middle and bottom).

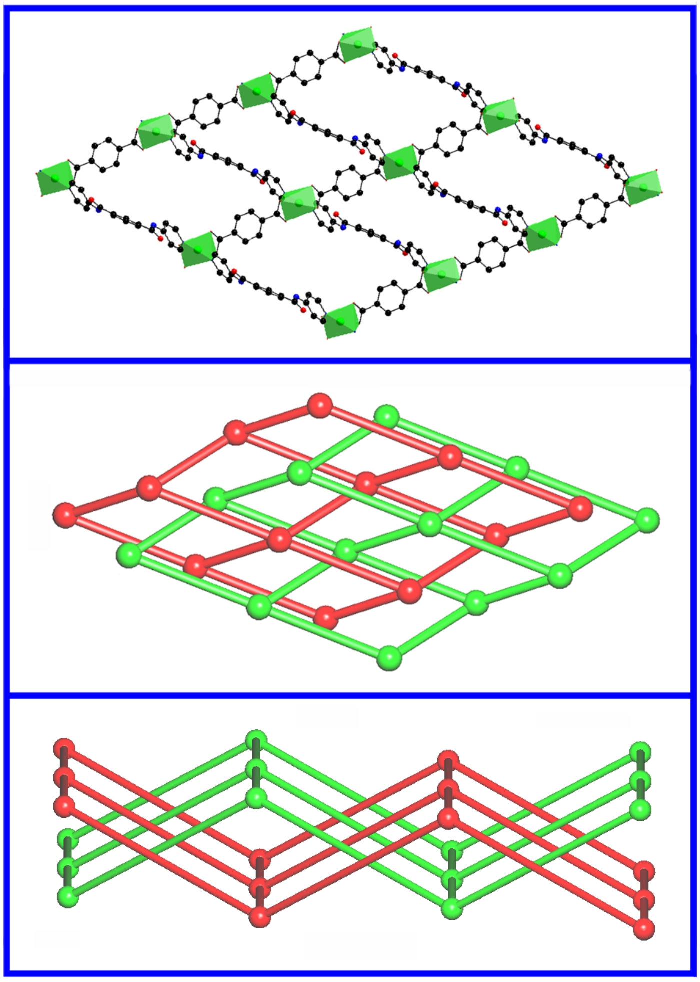


Fig. S6 A view of the 3D packing of complex **3**, showing the interdigitation of the interpenetrated bilayers.

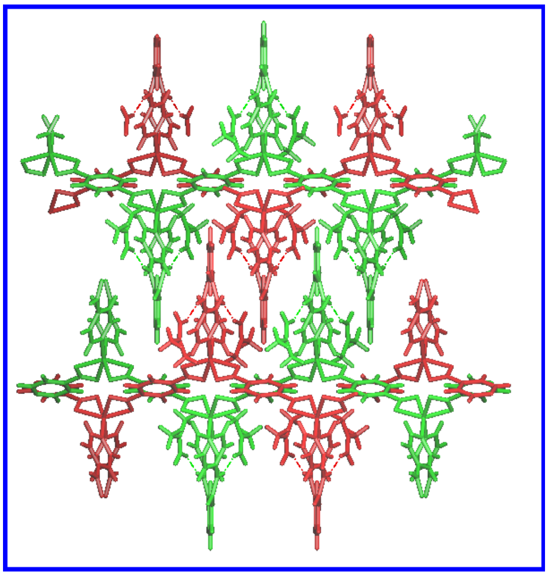


Fig. S7 TG curves for complexes **1** (left) and **2** (right).

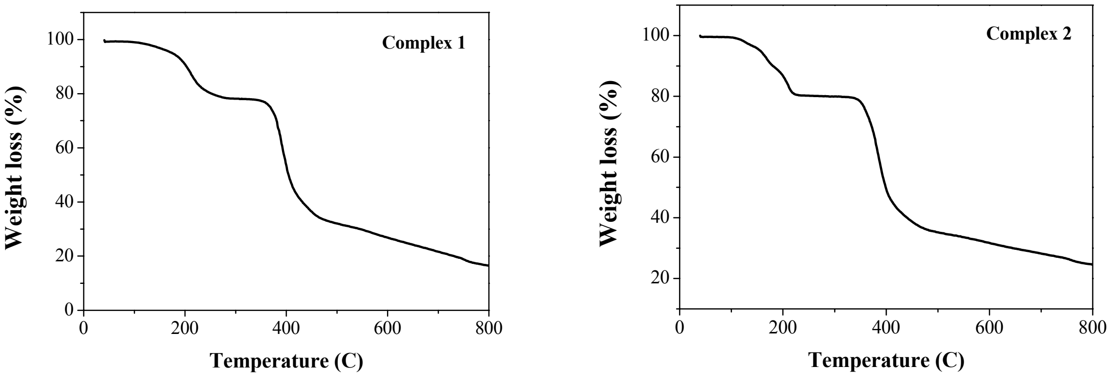


Fig. S8 PXRD spectra of complexes **1** (top) and **2** (bottom).