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 C₁₈H₁₄N₄O₂: 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'-BPDC)]·2DMF (2) and [Co(4,4'-BPIPA)(TP)]·2DMF (3) (2,6-NDC=2,6-naphthalenedicarboxylic acid; 4,4'-BPDC=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(NO₃)₂·6H₂O (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 C₃₆H₃₄N₆O₈Co: 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 C₃₈H₃₆N₆O₈Co: 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, C2/c, a = 22.162(2), b = 20.532(2), c = 16.136(2) Å, β = 95.937(2)°, V = 7303.3(1) Å³, Z = 8, Dx = 1.294 g·cm⁻³, Goof = 0.993. Final residuals [I>2σ(I)] was R₁ = 0.0808, wR₂ = 0.2389.

Complex 2, Monoclinic, C2/c, a = 24.36(4), b = 23.37(7), c = 16.13(3) Å, β = 105.104(2)°, V = 8865(4) Å³, Z = 8, Dx = 0.925 g·cm⁻³, Goof = 1.043. Final residuals [I>2σ(I)] was R₁ = 0.0887, wR₂ = 0.2682.

Complex 3, Monoclinic, C2/c, a = 7.601(2), b = 29.239(8), c = 14.315(4) Å, β = 96.331(5)°, V = 3162.0(15) Å³, Z = 4, Dx = 1.444 g·cm⁻³, Goof = 1.111. Final residuals [I>2σ(I)] was R₁ = 0.0633, wR₂ = 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. Structures were solved by direct methods and refined on F² by full matrix least-squares using the SHELXL-97 program package. 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. Numbers of DMF molecules were determined mainly by elemental analysis and TGA analysis.
TOPOS calculations

The network simplification of complexes 1 and 2 was performed with TOPOS software. 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 transitivity [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 $M(\text{Ligand})_2$ for a 4-c nodes is actually $M(\text{BIPA})(L)_{0.5}(L')_{0.5}$ resulting in 3 different edges.

Here below is a part of the TOPOS output:

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**Topology for Co1**

Atom Co1 links by bridge ligands and has

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Structure consists of 3D framework with Co

**There are 3 interpenetrating nets**

FIV: Full interpenetration vectors

- $[1/2,1/2,0]$ (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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**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 (Al₂O₃) 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 °C (for 1) and 20.76 % before 200 °C (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
(S2) G. M. Sheldrick, SHELXS-97, Program for Crystal Structure Solution and Refinement; University of Göttingen, 1997.
(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).