

# Enantiopure vs. Racemic Metalloligands: Impact on Metal-Organic Framework Structure and Synthesis

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## General

All starting materials were obtained from commercial suppliers and used without further purification. Elemental analysis was performed at NuMega Resonance Labs, San Diego, California. Powder X-ray diffraction (PXRD) data were collected on a Rigaku Miniflex II diffractometer at 30kV, 15mA for Cu K $\alpha$  ( $\lambda = 1.5418 \text{ \AA}$ ), with a scan speed of  $5^\circ \text{min}^{-1}$  and a step size of  $0.005^\circ$  in  $3\text{-}40^\circ 2\theta$  at room temperature. The experimental backgrounds were corrected using Jade 5.0. The simulated PXRD patterns were calculated from single-crystal diffraction data using Mercury 1.5. Thermogravimetric analysis (TGA) was performed at a scan speed of  $5^\circ \text{C min}^{-1}$  under nitrogen gas on a TA Instrument Q600 SDT.

## I. Synthesis of [Co(4-cpdpm)<sub>3</sub>]

2,3-dicyano-5,6-dichloro-parabenzoquinone (1.93 g, 8.5 mmol) was dissolved in 30 mL of THF and added drop-wise to a solution of (4-methoxycarbonylphenyl) dipyrromethane (1.98 g, 7.1 mmol) in CHCl<sub>3</sub> (200 mL) cooled under an ice bath. The solution was subsequently stirred under nitrogen gas for 2 h. The chloroform was

removed on a rotary evaporator producing a brown solid, which was used in the next step of the reaction.

$\text{Na}_3\text{Co}(\text{NO}_2)_6$  (0.95 g, 2.4 mmol) was dissolved in a 3:7 acetonitrile: $\text{H}_2\text{O}$  mixture and added to a solution of the crude dipyrromethene (see above) dissolved in acetonitrile (200 mL). An excess of triethylamine (10 mL) was added and the solution was refluxed at 80 °C under nitrogen gas overnight (~14 h). The solution was evaporated and dissolved with dichloromethane and a few drops of methanol. The product was chromatographed on  $\text{SiO}_2$  using dichloromethane as an eluant. The isolated cobalt(III) complex was dried in a vacuum oven overnight. Yield: 1.15 g (1.3 mmol, 55%).

The cobalt(III) complex (1.15 g, 1.3 mmol) was hydrolyzed in a 1:1 THF:4% KOH solution (75 mL). The solution was refluxed at 80 °C under nitrogen gas for 6 h. The solution was allowed to cool to room temperature and the product was precipitated using 6N HCl (~15 mL). The red solid was filtered onto a glass frit and washed several times with cold water. The product was dried in a vacuum oven overnight. Yield: 1.06 g (1.25 mmol, 97%). Spectroscopic data are consistent with those previously reported in the literature.<sup>1, 2</sup>

## II. Resolution of $[\text{Co}(4\text{-cpdpm})_3]$

Resolution was performed with (-)-cinchonidine by a previously reported procedure.<sup>2</sup> Racemic  $\Delta, \Lambda$ - $[\text{Co}(4\text{-cpdpm})_3]$  (805 mg, 0.95 mmol) was dissolved in hot THF (~70 °C, 20 mL) and a solution of (-)-cinchonidine in hot THF (20 mL). The dark-orange solution was allowed to cool and stood covered overnight. An orange precipitate was filtered and chromatographed on  $\text{SiO}_2$  with an ethyl acetate/trifluoroacetic acid (99.7/0.3) solution. The solution was evaporated and dried overnight in a vacuum oven resulting in  $\Lambda$ - $[\text{Co}(4\text{-cpdpm})_3]$ , (443 mg, 0.52 mmol, 55% of starting racemic compound) with an ee of less than 70%. Another subsequent round of resolution of the enriched  $\Lambda$ - $[\text{Co}(4\text{-cpdpm})_3]$  was performed with (-)-cinchonidine (221 mg 0.75 mmol) was performed. The orange precipitate obtained was filtered and washed with hot THF,  $\text{CH}_2\text{Cl}_2$ , and acetone. This precipitate was again purified by chromatography resulting in (286 mg, 0.33 mmol, 64%) of  $\Lambda$ - $[\text{Co}(4\text{-cpdpm})_3]$  with an ee of 97% (as determined by chiral HPLC).<sup>2</sup>

**III. Synthesis of MOF-Co/Zn-5a**

Racemic  $\Delta,\Lambda$ -[Co(4-cpdpm)<sub>3</sub>] (2.1 mg,  $2.48 \times 10^{-6}$  mol) and Zn(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O (6.5 mg,  $2.47 \times 10^{-5}$  mol) were dissolved in DEF/EtOH/H<sub>2</sub>O (1/0.25/0.25 mL) in a 4 mL screw top vial. The mixture was heated to 90 °C at a rate of 2.0 °C min<sup>-1</sup> for 23 h and cooled to room temperature at 0.2 °C min<sup>-1</sup>. The resulting red-green, plate-like crystals were filtered, washed with DEF, and briefly dried in air.

**IV. Synthesis of MOF-Co/Zn-5b**

Racemic  $\Delta,\Lambda$ -[Co(4-cpdpm)<sub>3</sub>] (2.1 mg,  $2.48 \times 10^{-6}$  mol) and Zn(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O (1.29 mg,  $4.93 \times 10^{-6}$  mol) were dissolved in DEF/EtOH (1/0.49 mL) in a 4 mL screw top vial. The mixture was heated to 90 °C at a rate of 2.0 °C min<sup>-1</sup> for 23 h and cooled to room temperature at 0.2 °C min<sup>-1</sup>. The resulting red, block-like crystals were filtered, washed with DEF, and briefly dried in air.

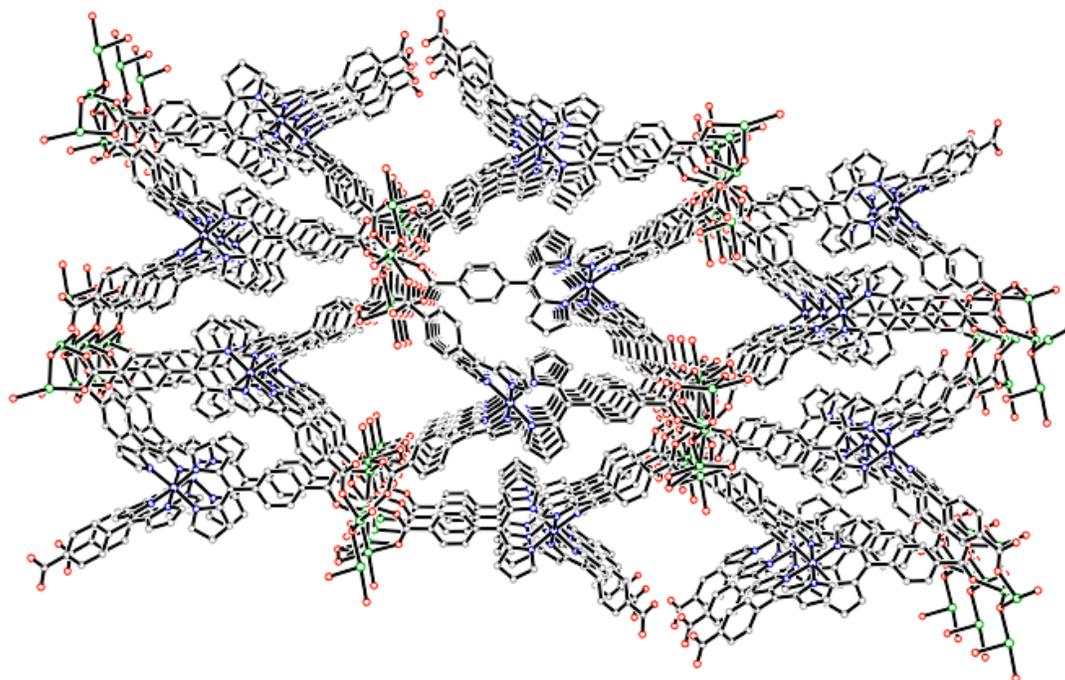
**X-ray Crystallographic Analysis.** Single crystals of each compound suitable for X-ray diffraction structural determination were mounted on nylon loops by using Paratone oil and were cooled in a nitrogen stream on the diffractometer. Data were collected at 100 K on a Bruker APEX diffractometer using an area detector.

### Crystallographic Data for MOF-Co/Zn-5

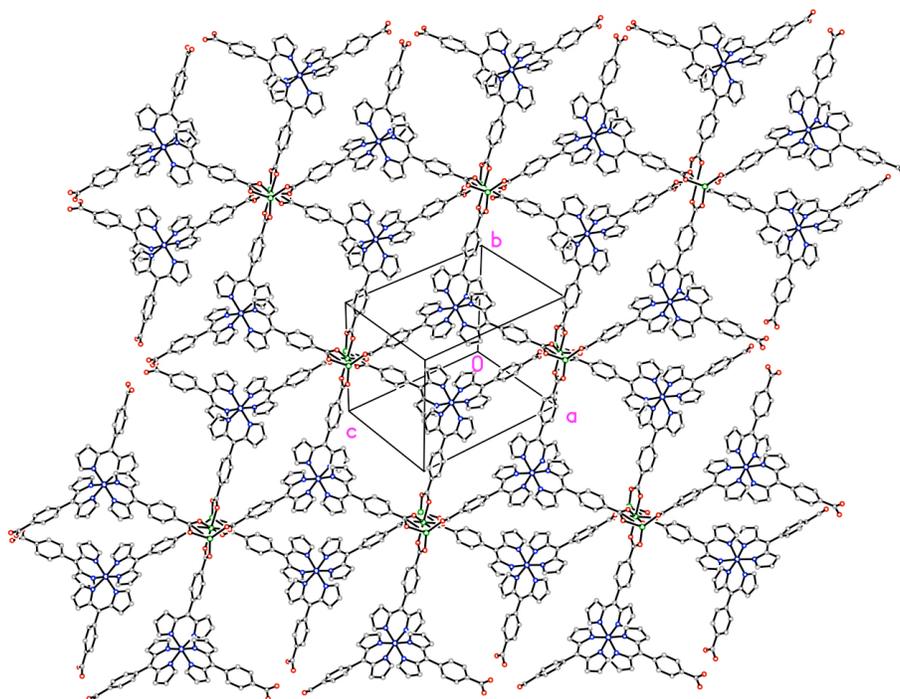
Empirical formula	C <sub>53</sub> H <sub>41.5</sub> Co N <sub>7</sub> O <sub>9.5</sub> Zn <sub>2</sub>	
Formula weight	1118.10	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2 <sub>1</sub> /n	
Unit cell dimensions	a = 15.229(4) Å	α = 90°.
	b = 8.796(2) Å	β = 89.977(5)°.
	c = 38.650(11) Å	γ = 90°.
Volume	5177(2) Å <sup>3</sup>	
Z	4	
Density (calculated)	1.434 Mg/m <sup>3</sup>	
Absorption coefficient	1.299 mm <sup>-1</sup>	
F(000)	2286	
Crystal size	0.27 x 0.23 x 0.04 mm <sup>3</sup>	
Crystal color and habit	red plate	
Theta range for data collection	1.34 to 26.37°.	
Index ranges	-19 ≤ h ≤ 19, -10 ≤ k ≤ 10, -48 ≤ l ≤ 48	
Reflections collected	43650	
Independent reflections	10531 [R(int) = 0.0841]	
Observed reflections (I > 2σ(I))	7689	
Completeness to theta = 25.00°	99.8 %	
Max. and min. transmission	0.96078 and 0.74449	
Data / restraints / parameters	10531 / 0 / 690	
Goodness-of-fit on F <sup>2</sup>	1.042	
Final R indices [I > 2σ(I)]	R1 = 0.0787, wR2 = 0.2051	
R indices (all data)	R1 = 0.1109, wR2 = 0.2285	
Largest diff. peak and hole	1.369 and -0.634 e.Å <sup>-3</sup>	

**Crystallographic Data for MOF-Co/Zn-5b**

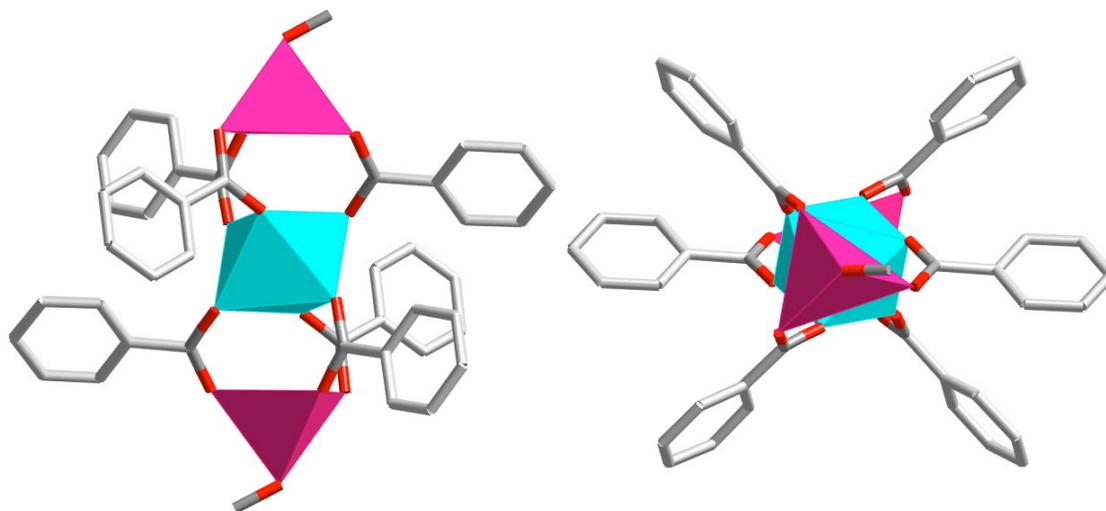
Empirical formula	C <sub>55.5</sub> H <sub>46</sub> Co N <sub>7.5</sub> O <sub>7.5</sub> Zn <sub>1.5</sub>	
Formula weight	1094.98	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 13.626(3) Å	α = 81.062(4)°.
	b = 14.766(3) Å	β = 81.660(4)°.
	c = 17.357(4) Å	γ = 75.534(4)°.
Volume	3319.8(12) Å <sup>3</sup>	
Z	2	
Density (calculated)	1.095 Mg/m <sup>3</sup>	
Absorption coefficient	0.835 mm <sup>-1</sup>	
F(000)	1127	
Crystal size	0.15 x 0.15 x 0.05 mm <sup>3</sup>	
Theta range for data collection	1.19 to 26.37°.	
Index ranges	-16 ≤ h ≤ 17, -18 ≤ k ≤ 18, -21 ≤ l ≤ 21	
Reflections collected	36922	
Independent reflections	13380 [R(int) = 0.0800]	
Completeness to theta = 25.00°	98.9 %	
Max. and min. transmission	0.9594 and 0.8850	
Refinement method	Full-matrix least-squares on F <sup>2</sup>	
Data / restraints / parameters	13380 / 0 / 736	
Goodness-of-fit on F <sup>2</sup>	0.906	
Final R indices [I > 2σ(I)]	R1 = 0.0605, wR2 = 0.1507	
R indices (all data)	R1 = 0.0905, wR2 = 0.1642	
Largest diff. peak and hole	0.811 and -0.413 e.Å <sup>-3</sup>	



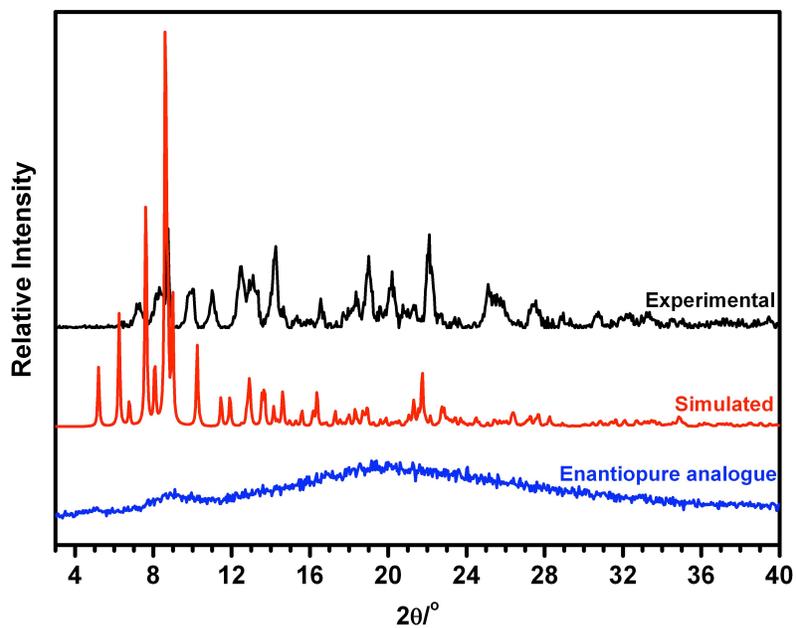
**Fig. S1** Packing diagram of MOF-Co/Zn-5a. Solvent molecules and hydrogen atoms omitted for clarity.



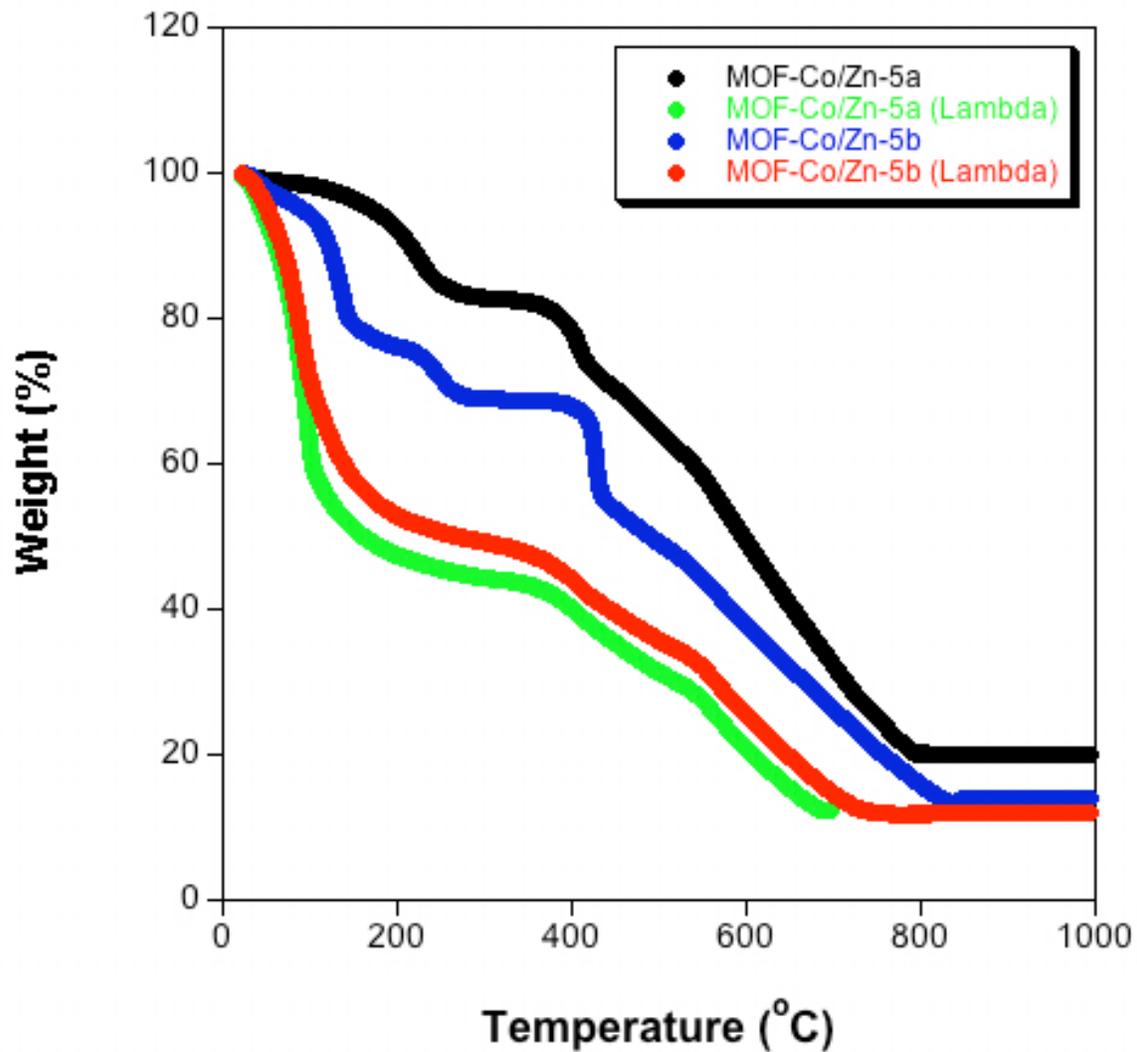
**Fig. S2** Packing diagram of MOF-Co/Zn-5b. Solvent molecules and hydrogen atoms omitted for clarity.



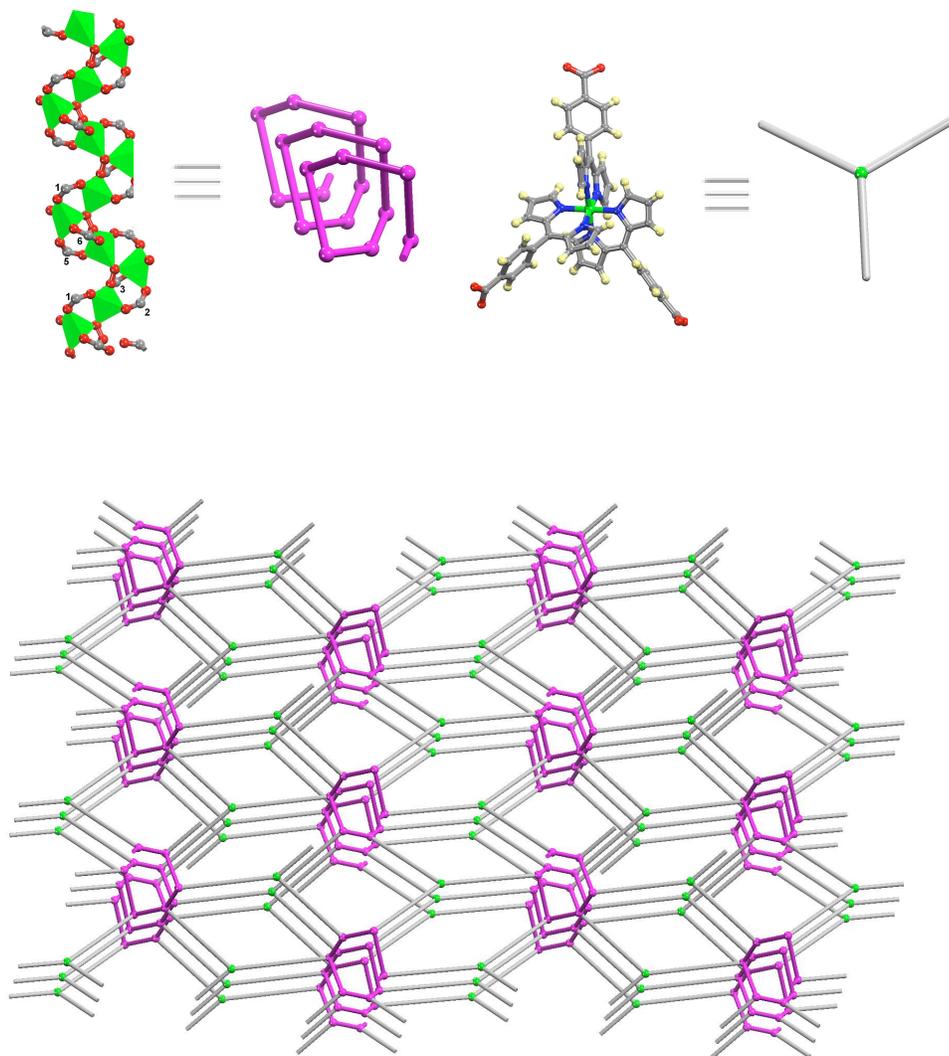
**Fig. S3** Two perspectives on the trinuclear SBU in MOF-Co/Zn-5b. Hydrogen atoms and solvent molecules have been omitted (or partially omitted) for clarity. Cobalt (green), tetrahedral zinc (pink), octahedral zinc (cyan), oxygen (red), and carbon (gray).



**Fig. S4** Simulated (red) and experimental (black) PXRd pattern for MOF-Co/Zn-5b. The pattern obtained from the reaction product using  $\Lambda$ -[Co(4-cpdpm)<sub>3</sub>] is shown in blue, indicating an amorphous material. Differences in the experimental and simulated patterns suggest a phase change in the crystal.



**Fig. S5** TGA traces of MOF-Co/Zn-5a (black) and MOF-Co/Zn-5b (blue). TGA traces of the amorphous products obtained with  $\Lambda$ -[Co(4-cpdpm)<sub>3</sub>] and Zn(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O under identical conditions used to prepare MOF-Co/Zn-5a (green) and MOF-Co/Zn-5b (red).



**Fig. S6** An alternative interpretation of the topology of MOF-Co/Zn-5a. The iSBUs are simplified as 6-fold helices (top left), which are cross-linked by the trigonal metalloligands (top right), giving rise to a binodal 3-connected net (bottom). This new topology has been identified by the EPINET database as sqc946 (<http://epinet.anu.edu.au/>). Some topological parameters for this net include:  $(6 \cdot 6 \cdot 12_2)(6 \cdot 12_2 \cdot 12_2)$  (vertex symbols); 3, 6, 10, 18, 32, 52, 73, 98, 125, 156 and 3, 6, 11, 18, 31, 52, 73, 98, 125, 156 (coordination sequences).

## References

- 1) C. Brückner, Y. Zhang, S. J. Rettig and D. Dolphin, *Inorg. Chim. Acta*, 1997, 263, 279-286.
- 2) S. G. Telfer, and J. Wuest, *Chem. Commun*, 2007, 3166-3168.