

Electronic Supplementary Information (ESI)

Two (3,6)-connected porous metal-organic frameworks based on linear trinuclear [Co₃(COO)₆] and paddlewheel dinuclear [Cu₂(COO)₄] SBUs: gas adsorption, photocatalytic behaviour, and magnetic properties

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Table S1 Selected bond lengths [Å] and angles [°] for compound **1** and **2**.

		1	
Co(1)-O(1)	2.076(3)	Co(1)-O(1)#1	2.076(3)
Co(1)-O(3)#2	2.139(3)	Co(1)-O(3)#3	2.139(3)
Co(1)-O(4)#5	2.152(3)	Co(1)-O(4)#4	2.152(3)
Co(2)-O(6)#3	1.978(4)		
Co(2)-O(2)	2.022(4)	Co(2)-O(7')	2.104(10)
Co(2)-O(7)	2.106(5)	Co(2)-N(2)	2.124(6)
Co(2)-N(3)#6	2.14(4)	Co(2)-O(4)#4	2.159(3)
Co(2)-O(5)#4	2.161(4)		
		2	
Cu(1)-O(5)#1	2.005(2)	Cu(1)-O(6)#2	2.004(2)
Cu(1)-O(2)#3	2.017(2)	Cu(1)-O(1)	2.028(2)
Cu(1)-O(4)#4	2.199(2)	Cu(1)-Cu(1)#3	2.7226(7)
O(5)#1-Cu(1)-O(6)#2	166.84(10)	O(5)#1-Cu(1)-O(2)#3	87.78(11)
O(6)#2-Cu(1)-O(2)#3	90.63(10)	O(5)#1-Cu(1)-O(1)	91.69(10)
O(6)#2-Cu(1)-O(1)	86.98(10)	O(2)#3-Cu(1)-O(1)	167.26(9)
O(5)#1-Cu(1)-O(4)#4	99.78(9)	O(6)#2-Cu(1)-O(4)#4	93.36(9)
O(2)#3-Cu(1)-O(4)#4	93.52(9)	O(1)-Cu(1)-O(4)#4	99.11(9)
O(5)#1-Cu(1)-Cu(1)#3	77.45(7)	O(6)#2-Cu(1)-Cu(1)#3	89.38(7)
O(2)#3-Cu(1)-Cu(1)#3	83.53(7)	O(1)-Cu(1)-Cu(1)#3	83.93(7)
O(4)#4-Cu(1)-Cu(1)#3	176.00(7)		

Symmetry transformations used to generate equivalent atoms: For compound **1**: #1 -x+5/3, -y+1/3, -z+4/3; #2: y+1/3, -x+y+2/3, -z+2/3; #3: -y+4/3, x-y-1/3, z+2/3; #4: x-y, x-1, -z+1; #5: -x+y+5/3, -x+4/3, z+1/3; #6: y+1, -x+y+1, -z+2. For compound **2**: #1: -x+y-1/3, -x+1/3, z-2/3; #2: x-y+2/3, x+1/3, -z+1/3; #3: -x+1/3, -y+2/3, -z-1/3; #4: -y+1/3, x-y+2/3, z-1/3.

Table S2 The gas adsorption capacities of MOFs based on H₃BPT ligand.

compounds	BET / Langmuir surface area [m ² g ⁻¹]	CO ₂ uptake at [cm ³ g ⁻¹]	H ₂ uptake at 77K	Refs
Mg ₃ (BPT) ₂ (H ₂ O) ₄	714/837	—	1.3 wt%	26a
porph@MOM-11	997/1096	90.2/273K	1.40 wt%	26b
Porph(Cl⁻)@MOM-11-(Na⁺)	965/1077	96.9/273K	1.46 wt%	26b
Porph(Cl⁻)@MOM-11-(Ba²⁺)	919/1020	92.5/273K	1.38 wt%	26b
Porph(Cl⁻)@MOM-11-(Cd²⁺)	893/995	84.5/273K	1.33 wt%	26b
Porph(Cl⁻)@MOM-11-(Mn²⁺)	995/1077	96.4/273K	1.58 wt%	26b
Yb(BPT)(H ₂ O)·(DMF) _{1.5} (H ₂ O) _{1.25}	515.6	16.7/296K	—	26c
Cu ₃ (C ₁₅ H ₇ O ₆) ₂ (UMCM-150)	2300/3100	—	2.1 wt%	26d
porph@MOM-10	1158/1309	—	1.30 wt%	26e
Mnporph@MOM-10-Mn	1140/1282	—	1.58 wt%	26e
Cuporph@MOM-10-CdCu	290/332	—	0.42 wt%	26e
porph@MOM-11 (P11)	997/1096	93/273K	—	26f
P11-Cu	1251/1406	92/273K	—	26f

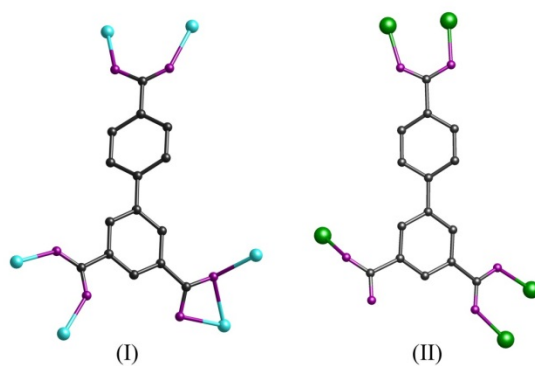


Fig. S1 The two coordination modes of BPT³⁻ligand in **1** and **2**.

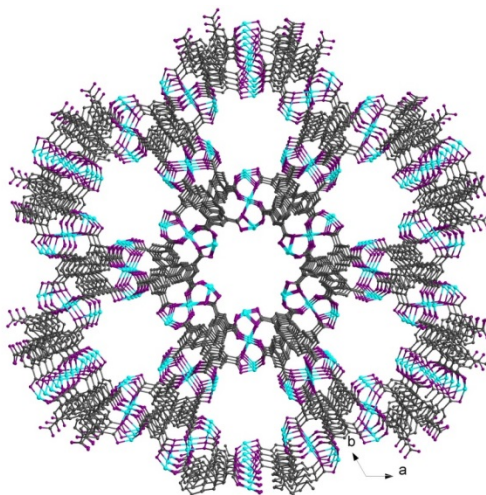


Fig. S2 View of the 3D framework constructed by [Co₃(BPT)₂] units with showing the 1D hexagonal channels.

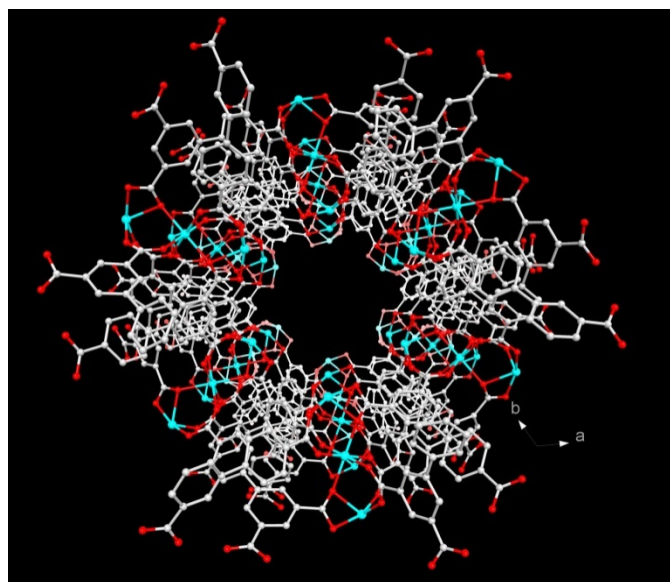


Fig. S3 Projection view of the 1D pore in **1**.

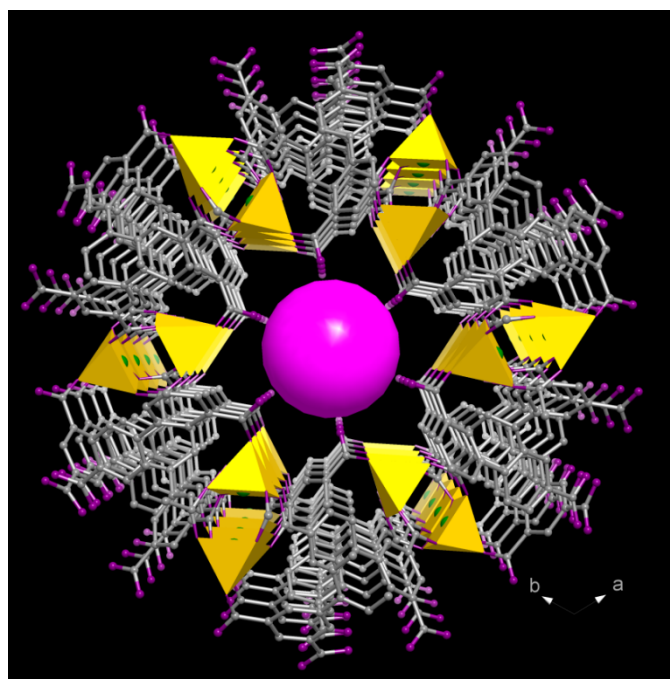


Fig. S4 View of 1D hydrophilic channel in **2** along the *c*-direction.

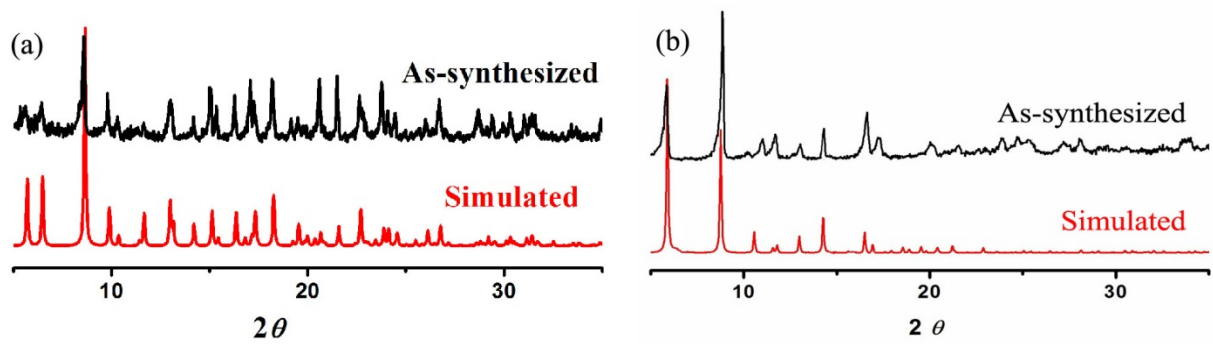


Fig. S5 The PXRD patterns of compound 1 and 2 (a for 1, b for 2).

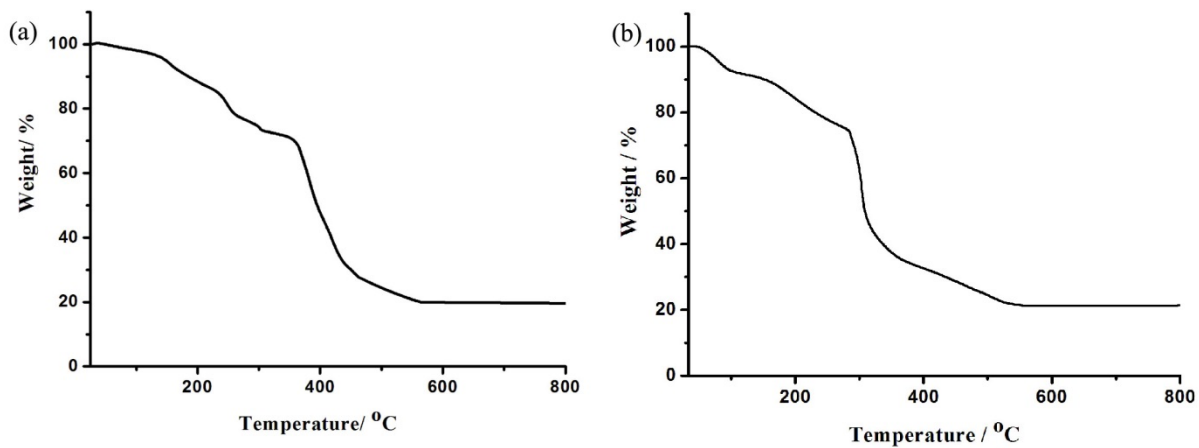


Fig. S6 Thermogravimetric curve of compound 1 and 2 (a for 1, b for 2).

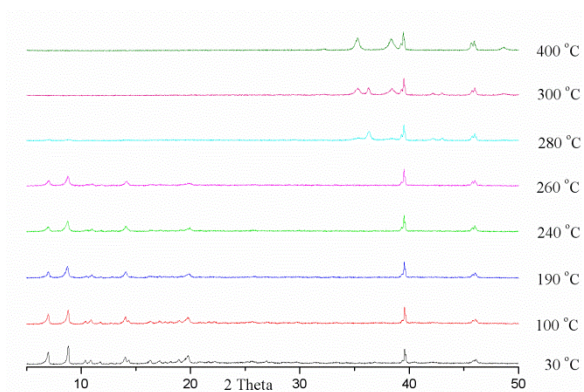


Fig. S7 The temperature-dependent PXRD patterns of 2.

Photocatalytic experiments

The band gap sizes of polymer were investigated by UV-vis diffuse reflection measurement method at room temperature. The results give an E_g (band gap energy) value of 2.10 eV (Fig. S8, ESI†). The photocatalytic activities of compound **1** were further studied. The $\alpha h\nu^2$ vs $h\nu$ curves for products are shown in Figure S. According to the equation $(\alpha h\nu)^2 = K(h\nu - E_g)$ (where α is the absorption coefficient, $h\nu$ is the discrete photo energy, K is a constant, and E_g is the band gap energy), the extrapolated value (the straight lines to the x axis) of $h\nu$ at $\alpha = 0$ give absorption edge energies corresponding to $E_g = 2.10$ eV for the compound.^{1,2}

Possible photocatalytic reaction mechanism

As mentioned in the literature, the photocatalytic mechanism is deduced as follows: because the HOMO is mainly contributed by oxygen and (or) nitrogen 2p bonding orbitals (valence band, VB) and the LUMO by empty transition metal orbitals (conduction band, CB). Under visible light irradiation, the electrons (e^-) were excited from the valence band (VB) to the conduction band (CB). The same number of holes (h^+) that have oxidation remained in the valence band. Furthermore, O_2 or hydroxyl (OH^-) adsorbed on the surfaces of complexes could interact with the electrons (e^-) on the CB or the hole (h^+) on the VB, respectively, which probably formed the hydroxyl radicals ($\cdot OH$). Later on, the $\cdot OH$ radicals could degrade the organic dye effectively to accomplish the photocatalytic process.³⁻⁵

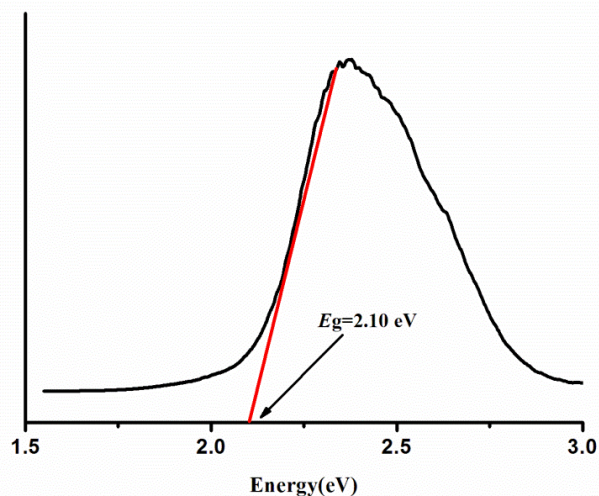


Fig. S8 The $\alpha h\nu^2$ vs $h\nu$ curve of **1**.

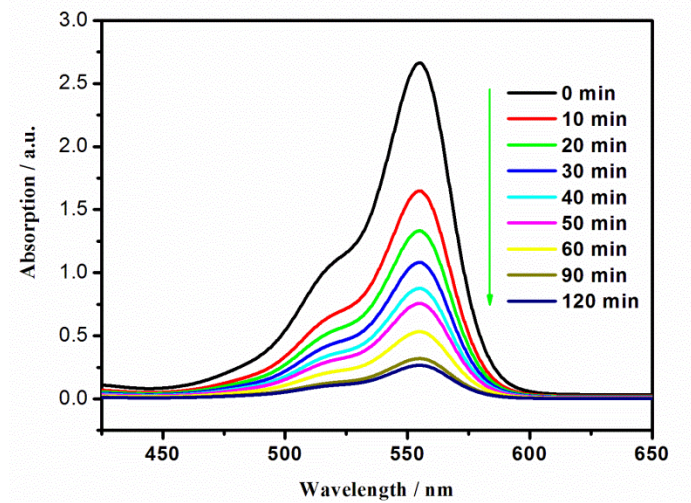


Fig. S9 Absorption spectra of the RhB solution during the decomposition reaction under visible-light irradiation with the use of compound **1** and H_2O_2 .

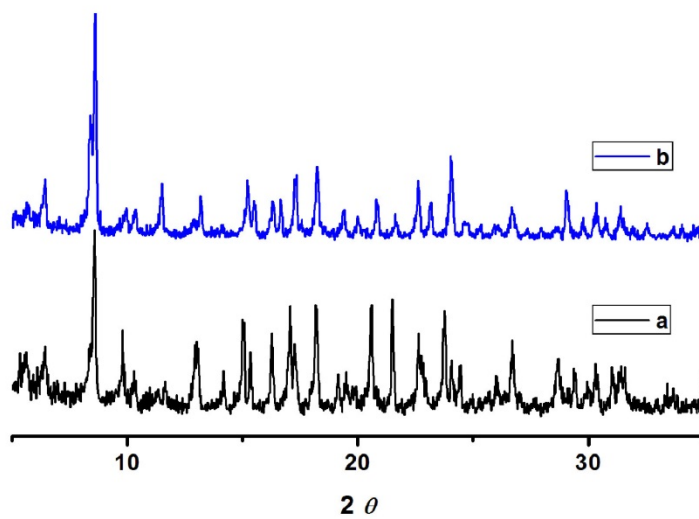


Fig. S10 The PXRD patterns of **1** (a for as-synthesized, b for after the photocatalytic experiment).

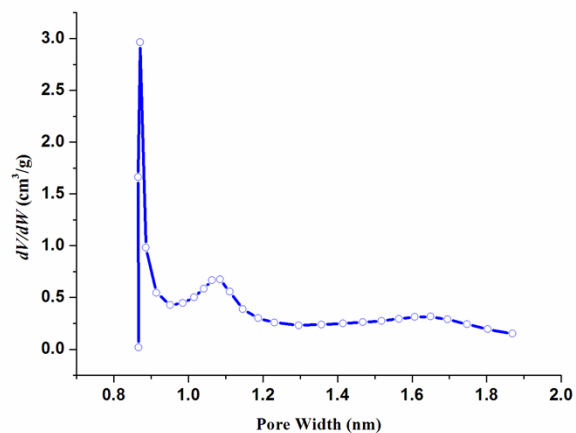


Fig.S11 Pore size distribution based on Horvath-Kawazoe (H-K) model in **2**.

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