

Supporting Information

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Porous Metal Carboxylate Boron Imidazolate Frameworks**

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Synthesis of MC-BIF-1S: NaB(im)₄ (0.036 g), Zn(AC)₂·2H₂O (0.043 g), 1,4-Benzenedicarboxylic (1,4-BDC, 0.032 g), imidazole (im, 0.016 g) and 1,3-dimethyl-propyleneurea (p-murea, 2.12 g) were placed in a 20 ml vial. The sample was heated at 120 °C for 5 days, and then cooled to room-temperature. After washed by ethanol, the colorless crystals were obtained (yield: 0.056 g, 52.8% based on B).

Synthesis of MC-BIF-2H: MC-BIF-2H (yield: 0.101 g, 64.5% based on B) was obtained by the similar method as described for MC-BIF-1S except for using water instead of p-murea and increasing the quantity of im from 0.016 g to 0.024 g.

Synthesis of MC-BIF-3H: MC-BIF-3H (yield: 0.048 g, 51.6% based on B) was obtained by the similar method as described for MC-BIF-1S except for using 1,3,5-BTC and H₂O instead of 1,4-BDC and p-murea.

Synthesis of MC-BIF-4S: MC-BIF-4S (yield: 0.078 g, 52.6% based on B) was obtained by the similar method as described for MC-BIF-1S except for using Cd(AC)₂·2H₂O instead of Zn(AC)₂·4H₂O.

Synthesis of MC-BIF-5H: MC-BIF-5H (yield: 0.096 g, 82.7% based on B) was obtained by the similar method as described for MC-BIF-4S except for using water instead of p-murea.

Synthesis of MC-BIF-6S: MC-BIF-5H (yield: 0.018 g, 33.3% based on B) was obtained by the similar method as described for MC-BIF-1S just without using 1,4-Benzenedicarboxylic.

Single-crystal structure analysis: Each crystal was glued to a glass fiber with epoxy resin and mounted on a Bruker APEX II diffractometer equipped with a fine focus, 2.0 kW sealed tube X-ray source (MoK radiation, $\lambda = 0.71073 \text{ \AA}$) operating at 50 kV and 30 mA. The empirical absorption correction was based on equivalent reflections. Each structure was solved by direct methods followed by successive difference Fourier methods. All non-hydrogen atoms were refined anisotropically. Computations were performed using SHELXTL and final full-matrix refinements were against F². CCDC-764367-764372 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

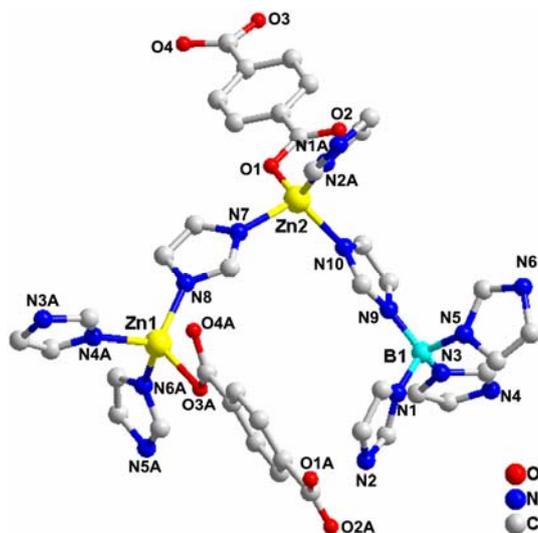


Figure S1. View of the coordination environments of boron and zinc ions in MC-BIF-1S.

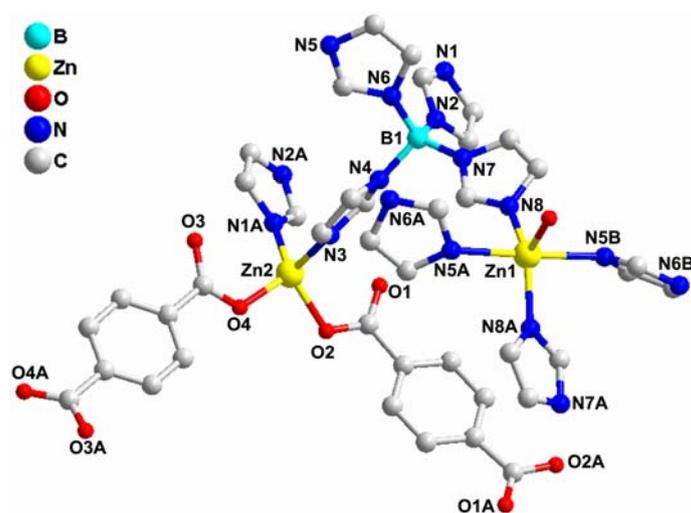


Figure S2. View of the coordination environments of boron and zinc ions in MC-BIF-2H.

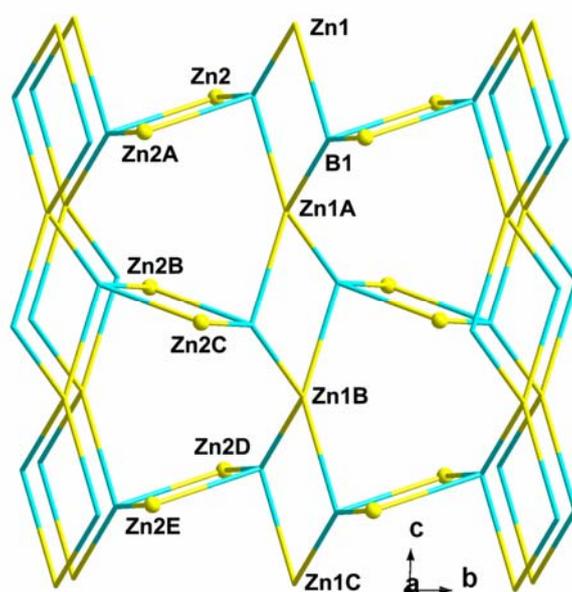


Figure S3. View of 3D B/im/Zn framework in MC-BIF-2H. All the 2-connected im ligands were simplified as lines.

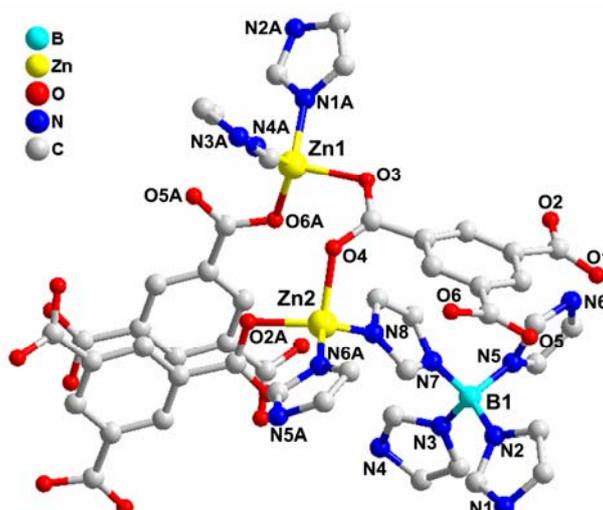


Figure S4. View of the coordination environments of boron and zinc ions in MC-BIF-3H. The asymmetric unit of MC-BIF-3H contains one crystallographic independent $[B(im)_4]^-$ group, two Zn^{2+} ions and one 1,3,5-BTC ligand. The coordination mode of BTC is that two BTC carboxyl groups adopt $\eta^1:\eta^0:\mu_1$ fashion to bond to two Zn^{2+} ions from the same B/im/Zn layer, while the third BTC carboxyl groups adopt $\eta^1:\eta^1:\mu_2$ fashion to link two Zn^{2+} ions from two neighboring layers.

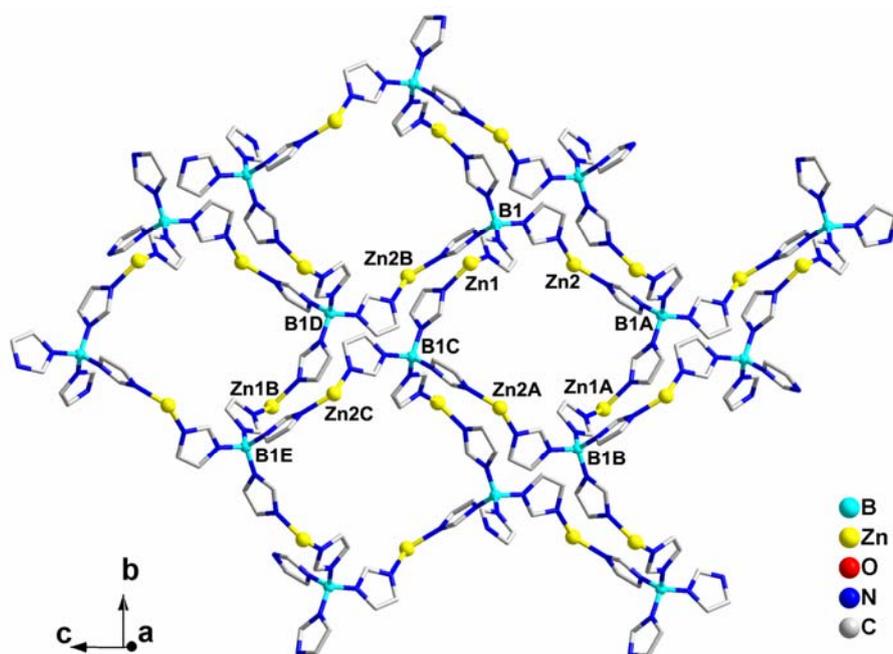


Figure S5. View of 2-D B/im/Zn layer of MC-BIF-3H, constructing from two kinds of $B_4Zn_4(im)_8$ eight-rings.

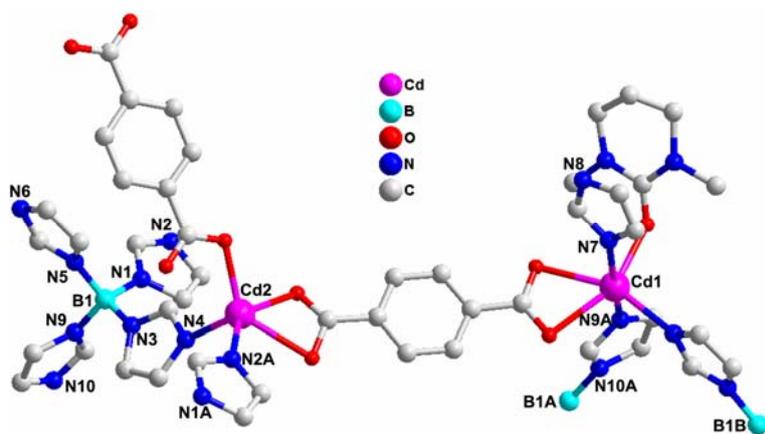


Figure S6. View of the coordination environments of boron and cadmium ions in MC-BIF-4S.

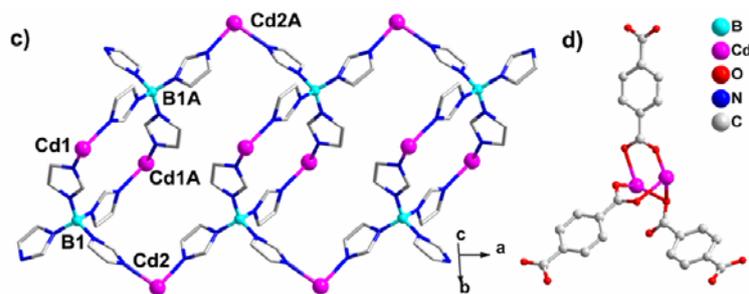


Figure S7. a) and b) View of 1-D B/im/Cd tube and coordination mode of 1,4-bdc in MC-BIF-5H, respectively.

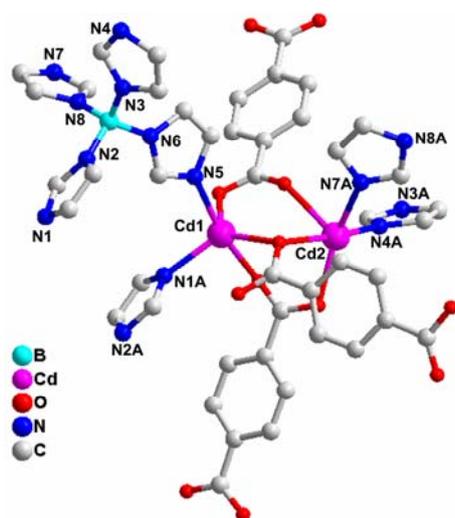


Figure S8. View of the coordination environments of boron and cadmium ions in MC-BIF-5H.

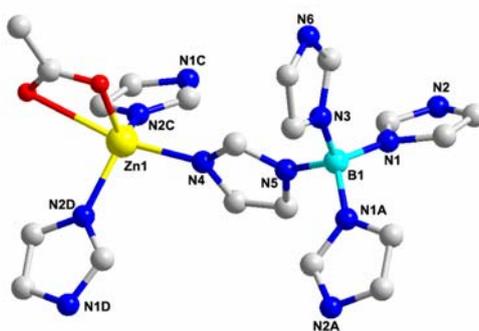


Figure S9 View of the coordination environments of boron and zinc ions in MC-BIF-6S.

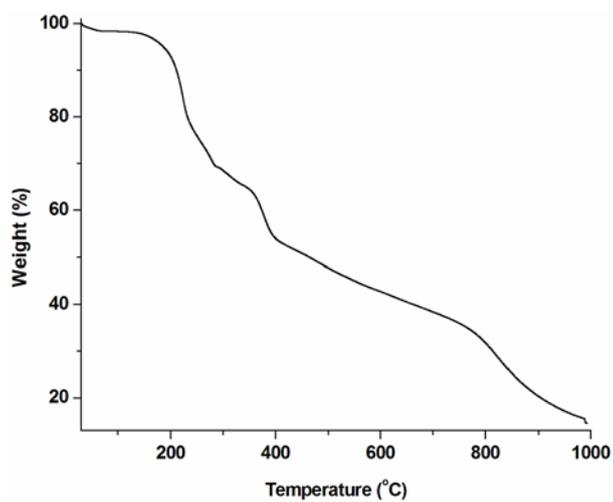


Figure S10. TGA curve of MC-BIF-1S.

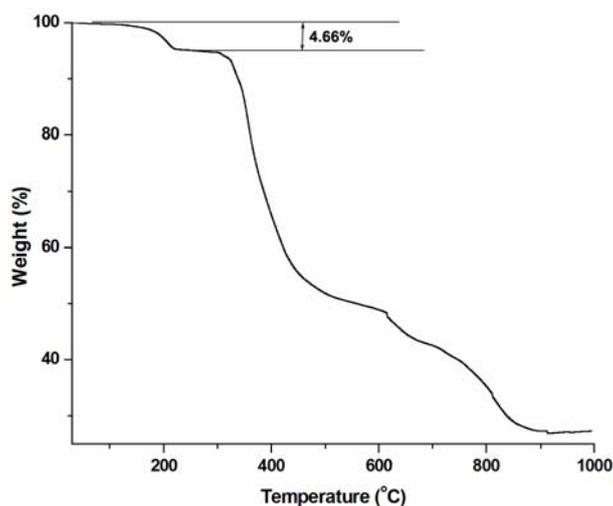


Figure S11. TGA curve of MC-BIF-2H.

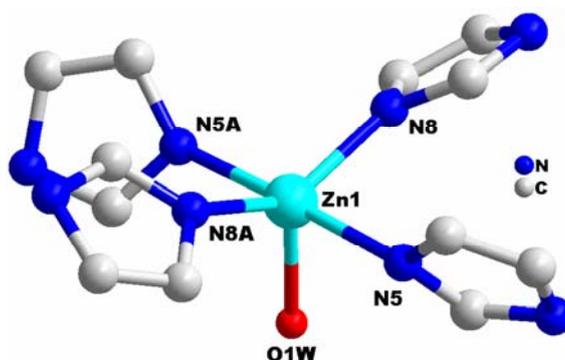


Figure S12. View of the coordination configuration of Zn1 in MC-BIF-2H.

Table S1. Comparison of some structural parameters of MC-BIF-2H before and after heating at 220°C for 2 hours.^a

	MC-BIF-2H	
	before heating	after heating
Site occupation factor of O1W	0.5	0.25
Site occupation factor of O2W	1.0	0.35
U(eq) of O1W	0.045(2)	0.054(7)
U(eq) of O2W	0.076(2)	0.067(8)
Bond length of Zn1-O1W	2.020(9) Å	2.290(20) Å
Bond length of Zn1-N5/N5A	2.205(6) Å	2.110(10) Å
Bond length of Zn1-N8/N8A	2.044(6) Å	2.002(9) Å
Largest diff. peak/hole	0.830/-0.704	0.644/-0.617
Final <i>R</i> [<i>I</i> >2σ(<i>I</i>)]	0.0517	0.0669

a: O1W is the terminal water ligand of Zn1 and located at a crystallographic special position with original site occupation factor 0.5; O2W is the extraframework water; U(eq) is equivalent isotropic displacement parameter.

When MC-BIF-2H was heated at 150 °C under vacuum for 24 h, the coordinated water molecules as well as the extraframework water molecules were removed (water can be found on the wall of the sample tube). TG analysis indicates the observed first weight loss is 4.66% in the range 120 ~ 220 °C (Figure S11), in good agreement with the removal of both extraframework and coordinated water of MC-BIF-2H (4.75%). So the extraframework and coordinated water of MC-BIF-2H are removed in the same temperature range. Further, the PXRD patterns of MC-BIF-2H before and after gas adsorption measurement, and the simulated pattern derived from the X-ray single crystal data of MC-BIF-2H also match well. All these data confirm that dehydrated MC-BIF-2H possesses open metal sites. Finally, a single crystal of MC-BIF-2H was heated at 220 °C for 2 hours, and then used for data collection. By comparing crystal structural data of MC-BIF-2H before and after heating at 220 °C for 2 h, we confirmed again that structure of dehydrated MC-BIF-2H is stable and possesses open metal sites. As shown in Figure S12, the coordinated water of MC-BIF-2H is bonded to Zn1 atom. Each 5-coordinated Zn1 atom is defined by four N atoms from four im ligands and one terminal H₂O ligand. Table S1 shows the site occupation of O1W and O2W of heated MC-BIF-2H decreased from original 0.5 and 1.0 to 0.25 and 0.35, respectively, which indicates more than half of water has been removed. The refined occupancies of O1W and

O2W are 0.2532 and 0.3533, respectively. Further, compared with the bond lengths of Zn1-O1W and Zn1-N before heating, the bond length of Zn1-O1W after heating is remarkably lengthened, and at the same time, the bond lengths of Zn1-N after heating are all shortened. These changes of bond lengths support the fact that coordinated water ligands have been partially removed. The partial removal is likely due to the kinetics, because the crystal was heated for only 2 hours. So the above X-ray single crystal experiment also confirms that dehydrated MC-BIF-2H has open metal sites. It is noteworthy that when the same crystal was heated at 250 °C for 2 hours and then used for indexing, the indexing result showed it was still a single crystal with the same unit cell but its reflection intensity became very weak and there was nearly no reflection spots in the high angle area ($2\theta > 30^\circ$).

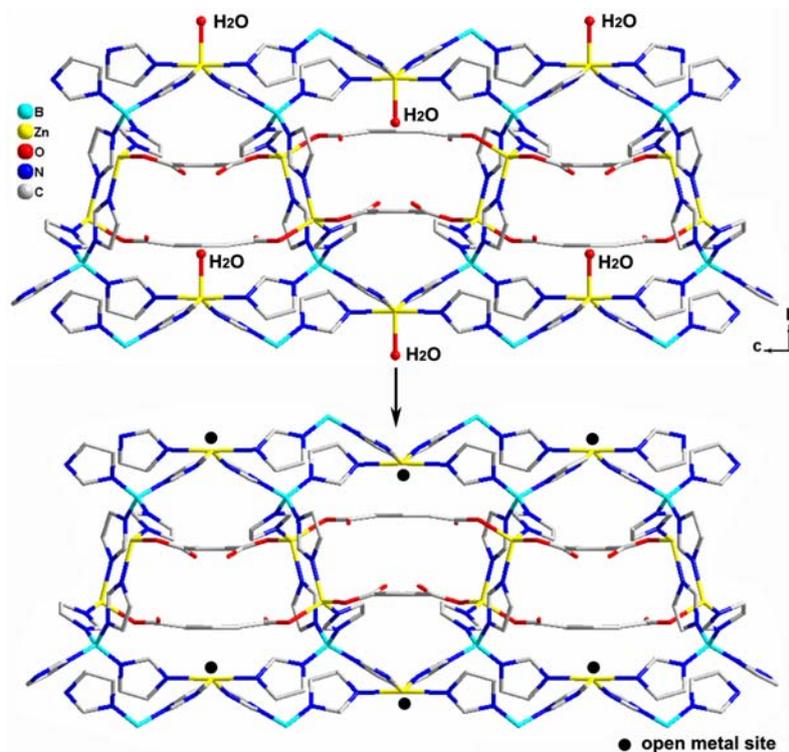


Figure S13. View of the open metal sites of MC-BIF-2H after removal of the coordinated water molecules.

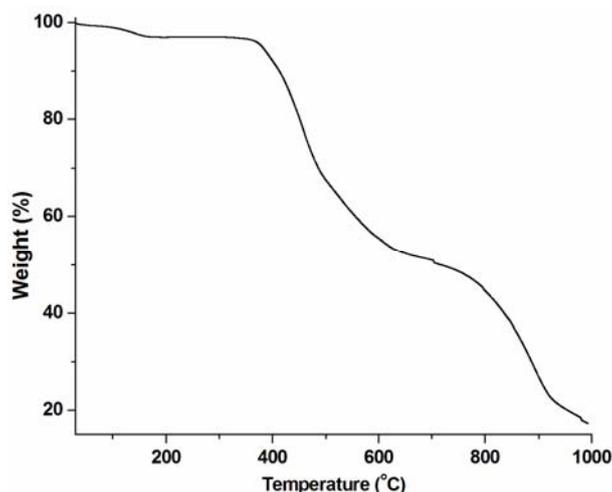


Figure S14. TGA curve of MC-BIF-3H.

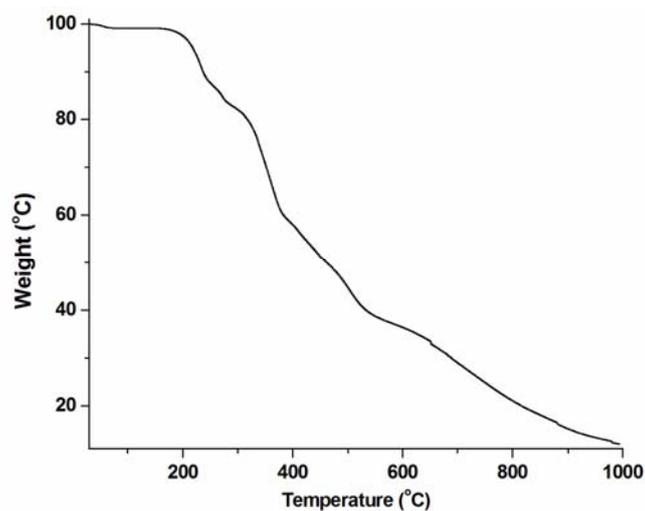


Figure S15. TGA curve of MC-BIF-4S.

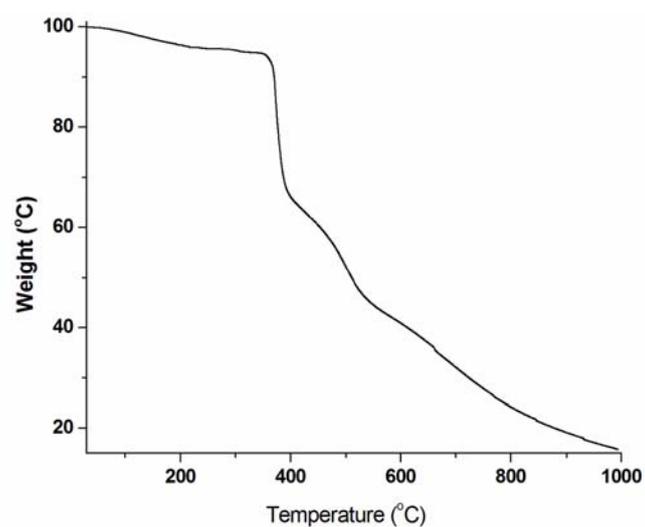


Figure S16. TGA curve of MC-BIF-5H.

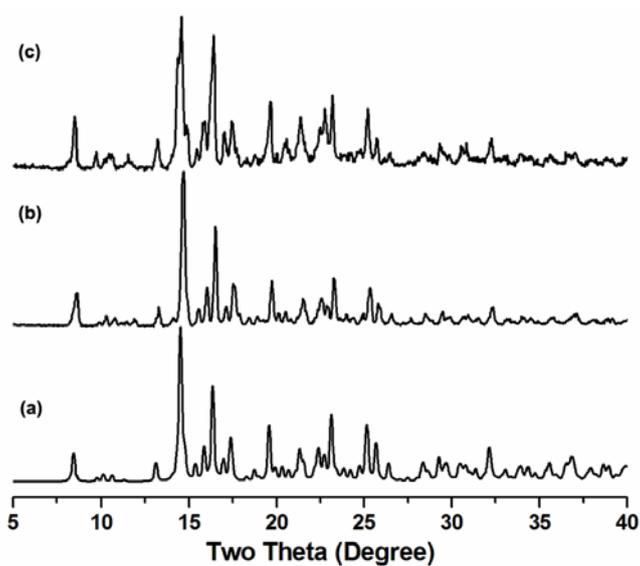


Figure S17. XPRD patterns for MC-BIF-2H: (a) calculated on the basis of the structure determined by single-crystal X-ray diffraction; (b) and (c) before and after heating MC-BIF-2H at 150 °C for 24 h, respectively.

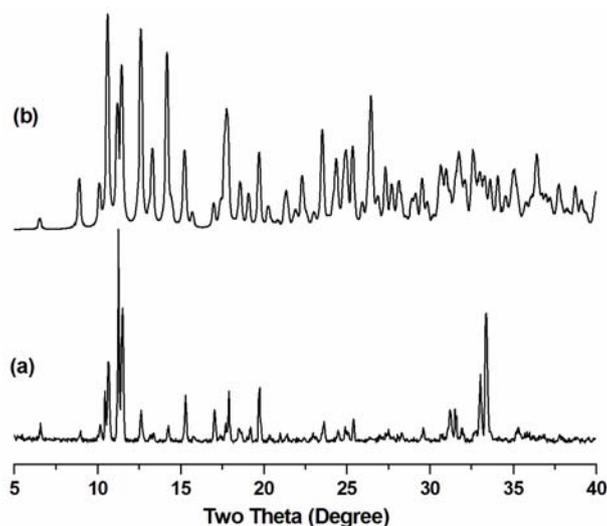


Figure S18. XPRD patterns for MC-BIF-3H: (a) after heating MC-BIF-3H at 150 °C for 24 h; (b) calculated on the basis of the structure determined by single-crystal X-ray diffraction.

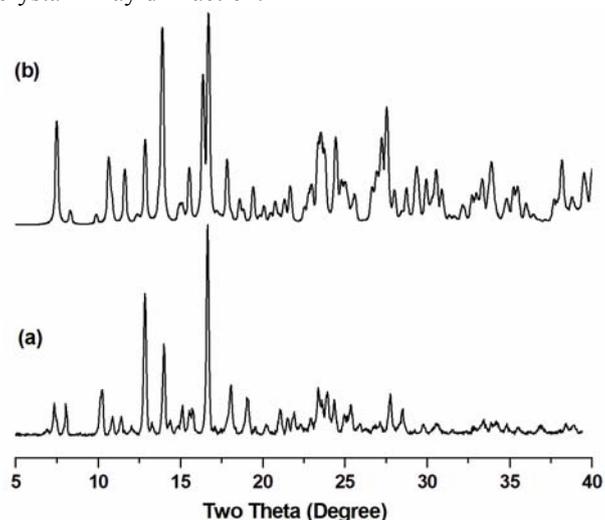


Figure S19. XPRD patterns for MC-BIF-5H: (a) after heating MC-BIF-5H at 150 °C for 24 h; (b) calculated on the basis of the structure determined by single-crystal X-ray diffraction.

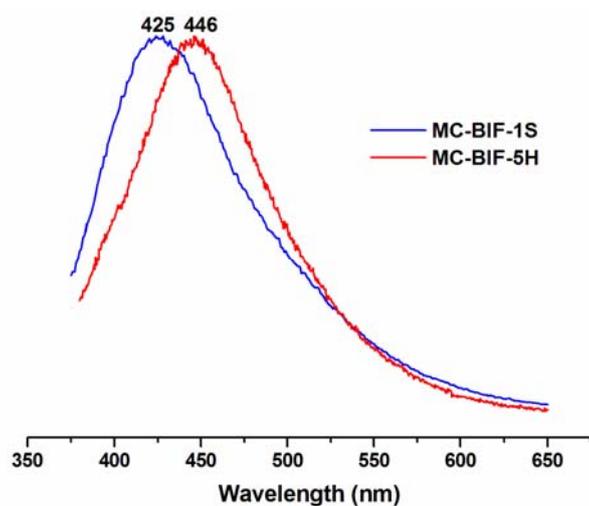


Figure S20. Solid room temperature photoluminescent spectra of MC-BIF-1S and MC-BIF-5H excitation at 340 nm.

MC-BIF-1S and MC-BIF-5H were selected for photoluminescent characterization, an intense emission at 425 nm for MC-BIF-1S and 446 nm for MC-BIF-5H are observed, respectively, which are attributed to LMCT (*Inorg. Chem.*, **2003**, *42*, 944; *CrystEngComm*, **2008**, *10*, 158).