

*Electronic Supplementary Information (ESI)*

**Organic amines as templates: pore imprints with exactly size matching in a series of metal-organic frameworks**

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**Materials:** H-DCI (98%, Sigma-Aldrich), CuI (98%, Sigma-Aldrich), MeCN (98%, Sigma-Aldrich), DEA (98%, Sigma-Aldrich), DPPA (98%, Sigma-Aldrich), DMP (98%, Sigma-Aldrich) and TMHDA (98%, Sigma-Aldrich), HCOOH (98%, Sigma-Aldrich) were all purchased without further purification.

**Synthesis of MCIF-2:** CuI (19 mg, 0.1 mmol), H-DCI (12 mg, 0.1 mmol) were dissolved in 5 ml MeCN with stirring for 10 minutes. Then one drop of DEA was added with stirring carefully. Large amounts of white precipitates were formed and then HCOOH was added drop by drop till the slurry got clear. After staying at room temperature for 3 days, colorless block crystals were collected and washed with MeCN for 3 times and air dried. The yield was about 40% based on CuI. Elemental analysis for  $[\text{Cu}_4\text{I}_4(\text{DCI})(\text{HDEA})] = \text{C}_7\text{H}_8\text{N}_5\text{Cu}_4\text{I}_4$ , calculated (%): C, 9.09; H, 0.86; N, 7.57. Found (%): C, 9.10; H, 0.90; N, 7.50.

**Synthesis of MCIF-3:** CuI (19 mg, 0.1 mmol), H-DCI (12 mg, 0.1 mmol) were dissolved in 5 ml MeCN with stirring for 10 minutes. Then one drop of DPPA was added with stirring carefully. Large amounts of white precipitates were formed and then HCOOH was added drop by drop till the slurry got clear. After staying at room temperature for about 3 days, colorless block crystals were collected and washed with MeCN for 3 times and air dried. The yield was about 35% based on CuI. Elemental analysis for  $[\text{Cu}_4\text{I}_4(\text{DCI})(\text{HDPPA})] = \text{C}_{14}\text{H}_{23}\text{N}_5\text{Cu}_4\text{I}_4$ , calculated (%): C, 16.42; H, 2.25; N, 6.84. Found (%): C, 16.50; H, 2.30; N, 6.80.

**Synthesis of MCIF-4:** CuI (19 mg, 0.1 mmol), H-DCI (12 mg, 0.1 mmol) were dissolved in 5 ml MeCN with stirring for 10 minutes. Then one drop of TMHDA was added with stirring carefully. Large amounts of white precipitates were formed and then HCOOH was added drop by drop till the slurry got clear. After staying at room temperature for 3 days, colorless block crystals were collected and washed with MeCN for 3 times and air dried. The yield was about 35% based on CuI. Elemental analysis for  $[\text{Cu}_{16}\text{I}_{16}(\text{DCI})_4(\text{HTMHDA})_2(\text{H}_2\text{O})] = \text{C}_{40}\text{H}_{56}\text{N}_{20}\text{Cu}_{16}\text{I}_{16}$ , calculated (%): C, 12.42; H, 1.45; N, 7.25. Found (%): C, 16.40; H, 1.50; N, 7.28.

**Single Crystal X-ray Crystallography.** Single Crystal X-ray diffraction data were collected using a Bruker-AXS SMART APEX2 CCD diffractometer ( $\text{Mo K}\alpha$ ,  $\lambda = 0.71073 \text{ \AA}$ ). Indexing was performed using APEX2 (Difference Vectors method). Data integration and reduction were performed using SaintPlus. Absorption correction was performed by multiscan method implemented in SADABS. Space groups were determined using XPREP implemented in APEX2. Structures were solved using SHELXL-2014 (direct methods) and refined using SHELXL-2014 (full-matrix least-squares on  $F^2$ ) with anisotropic displacement contained in APEX2 program packages. Hydrogen atoms on carbon and nitrogen were calculated in ideal positions with isotropic placement parameters set to  $1.2 \times U_{\text{eq}}$  of the attached atoms.

**Theoretical calculation details.** Host-guest interactions were calculated by the Forcite module in the Material Studio software package. The forcefield was chosen as UFF and the Summation method as Ewald. The accuracy was 0.001 kcal/mol. In each MOF, one unit cell was used for calculation. Specially, before the calculation of MCIF-2, the disorder part of HDEA in the structure was omitted, or the calculation would not be converged.

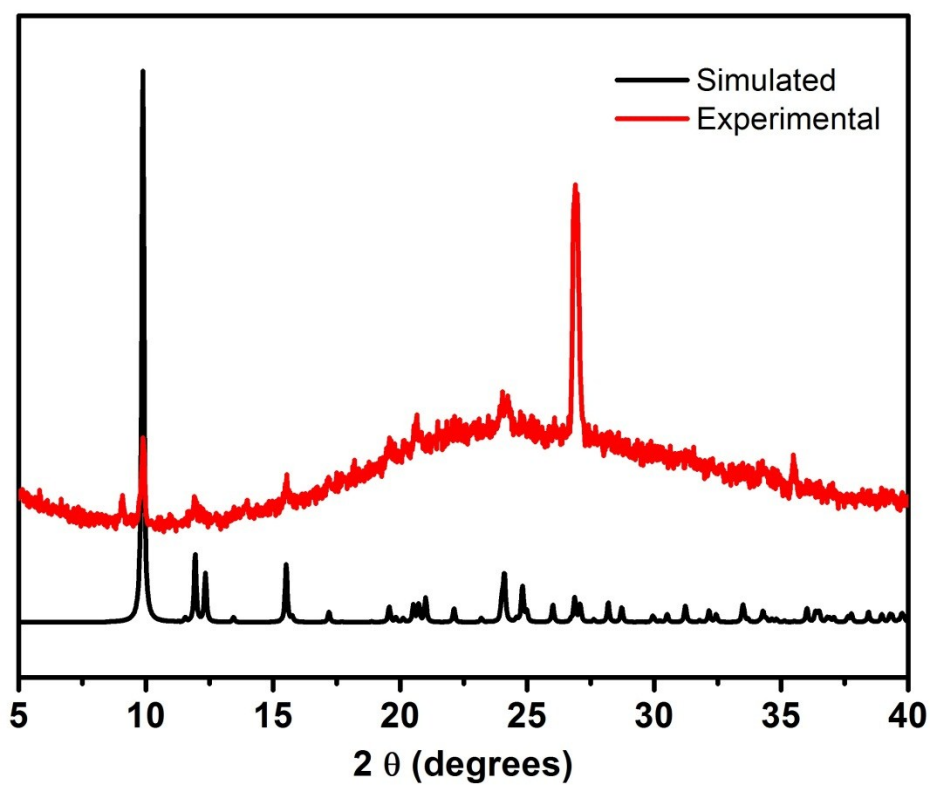


Figure S1. PXRD of MCIF-2.

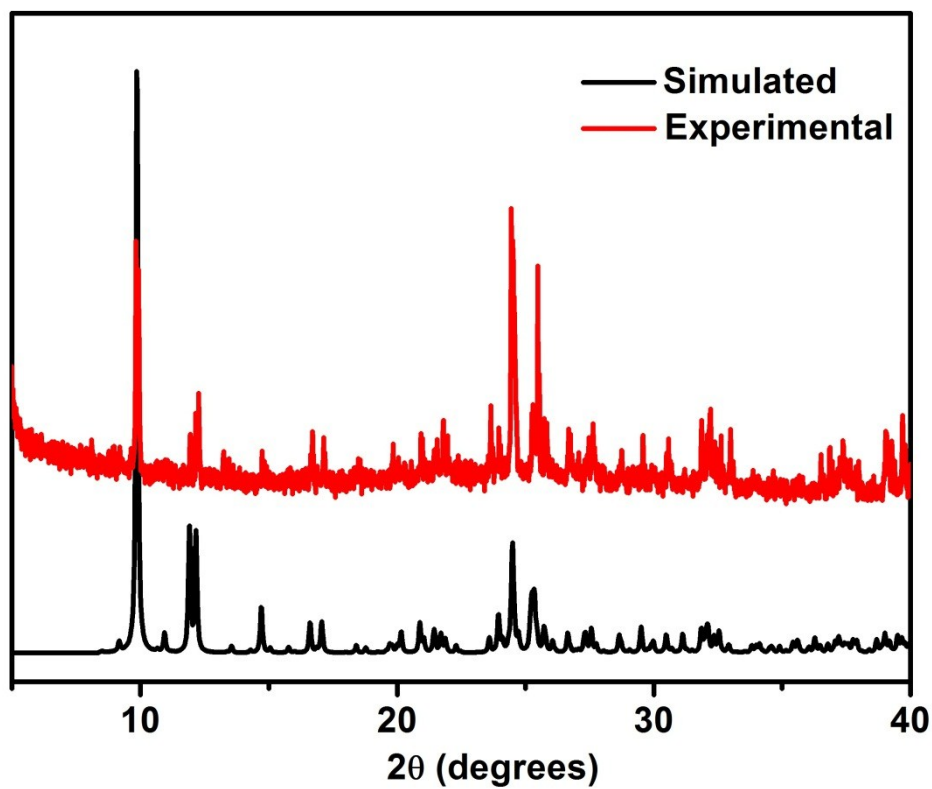


Figure S2. PXRD of MCIF-3.

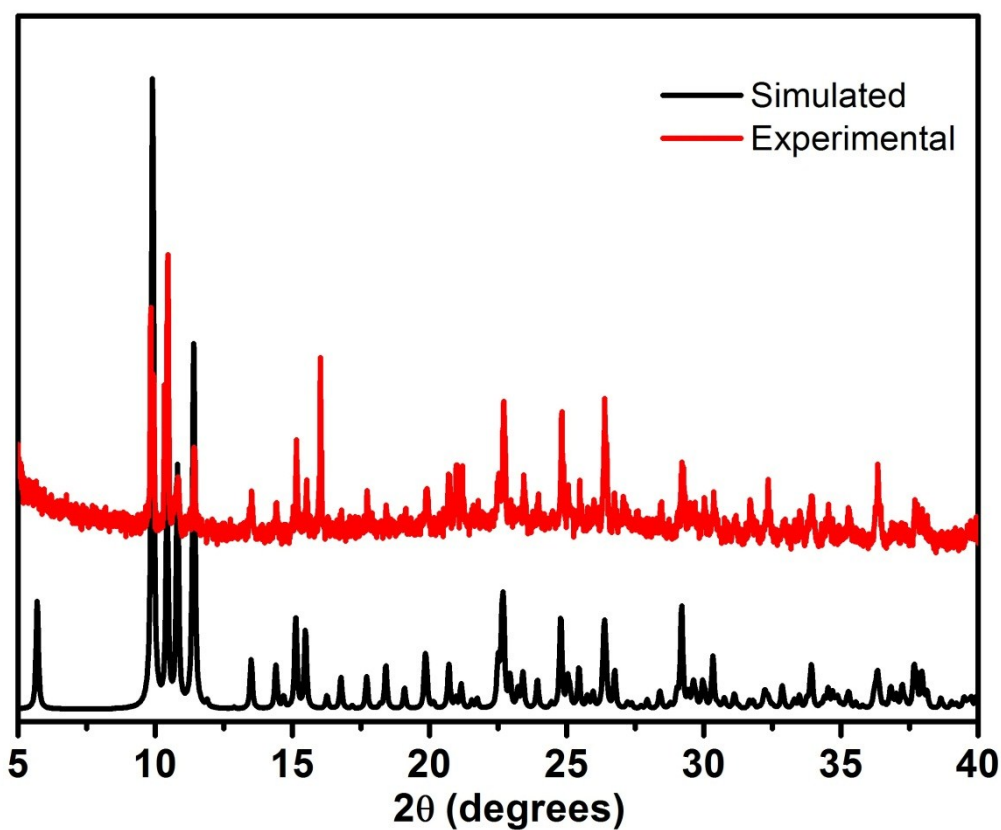


Figure S3. PXRD of MCIF-4.

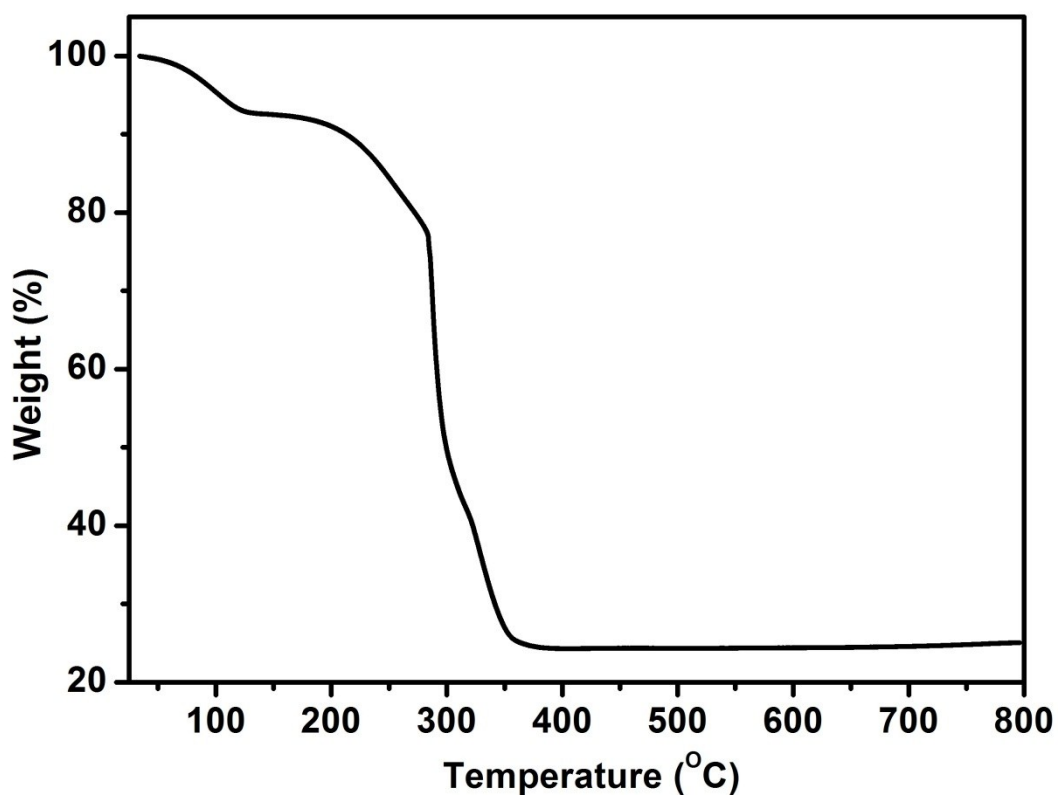


Figure S4. TG analysis of MCIF-2.

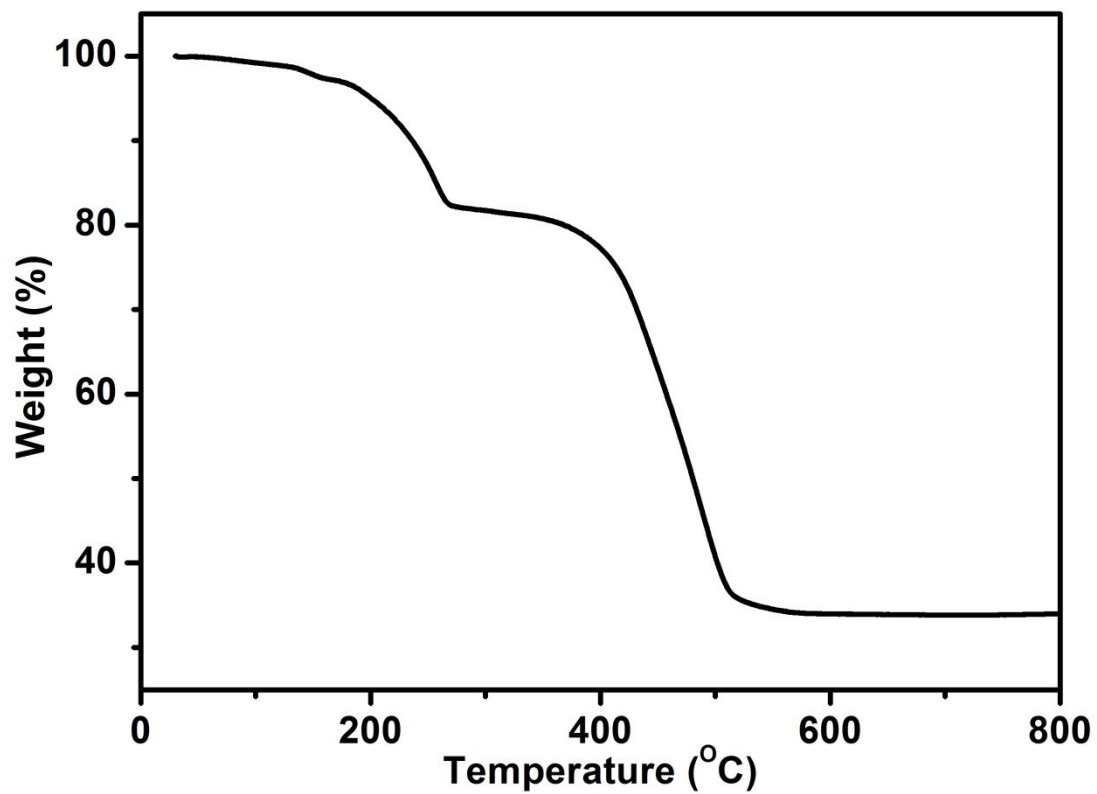


Figure S5. TG analysis of MCIF-3.

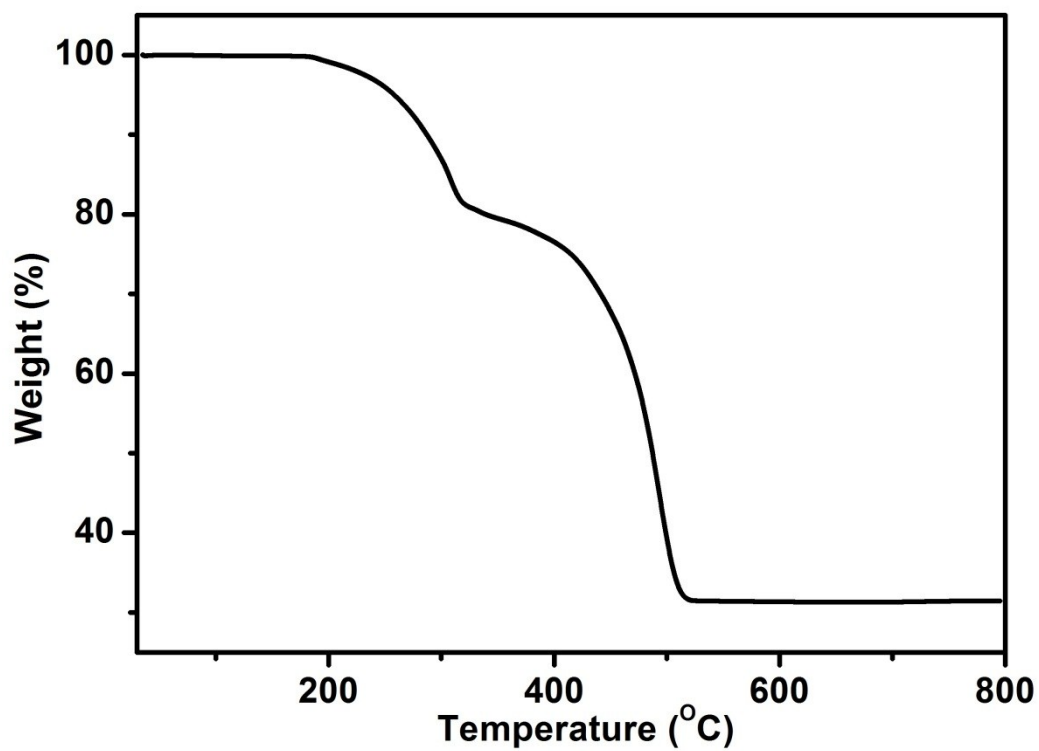


Figure S6. TG analysis of MCIF-4.

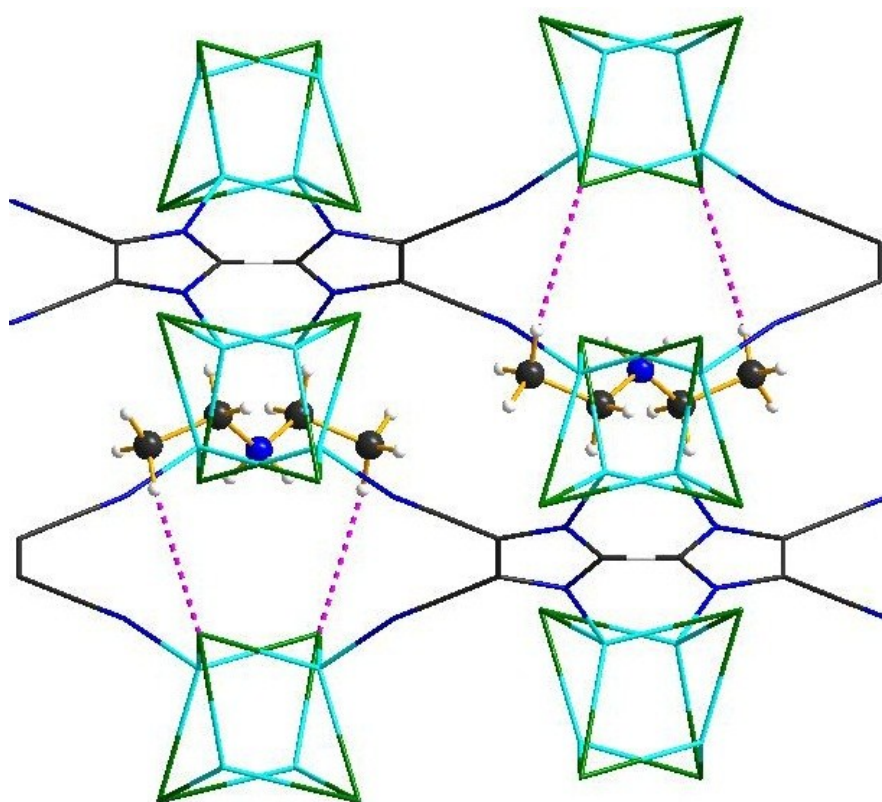


Figure S7. The host-guest interactions in MCIF-2.

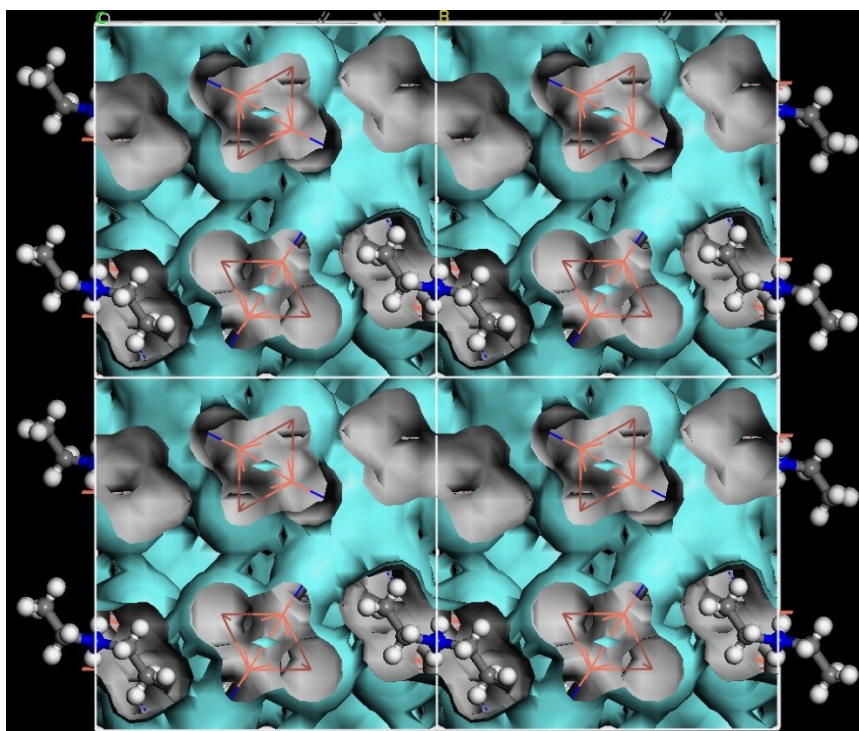


Figure S8. The connolly surface of MCIF-2.

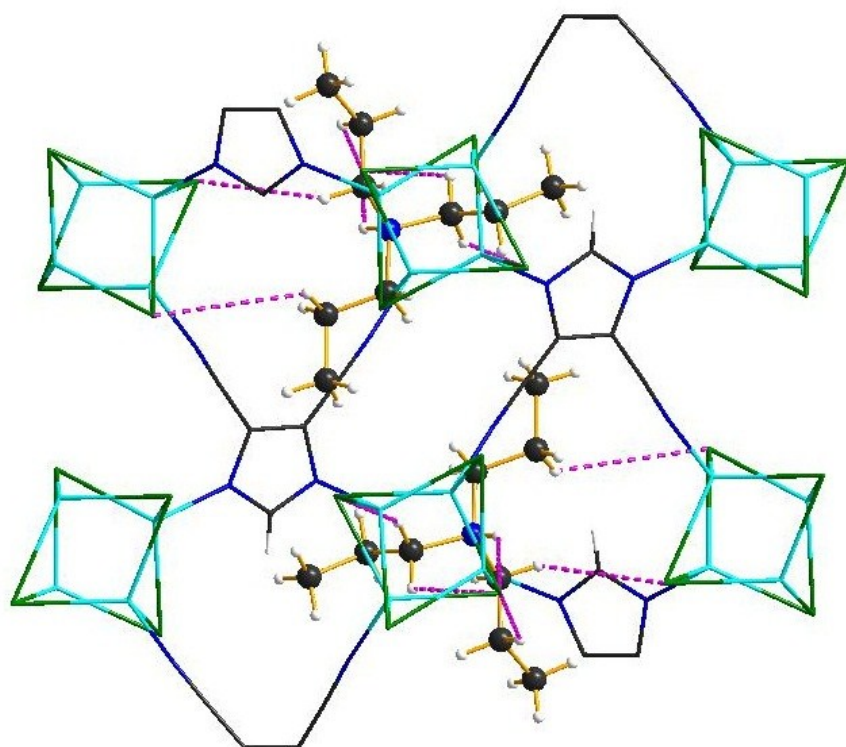


Figure S9. The host-guest interactions in MCIF-3.

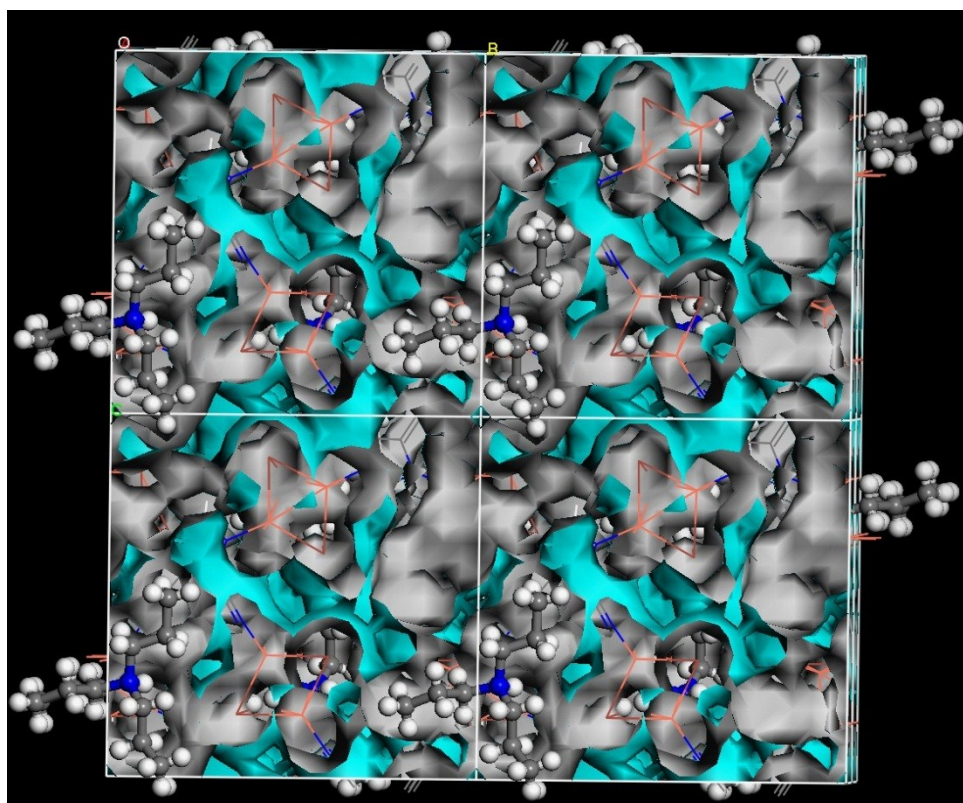


Figure S10. The connolly surface of MCIF-3.

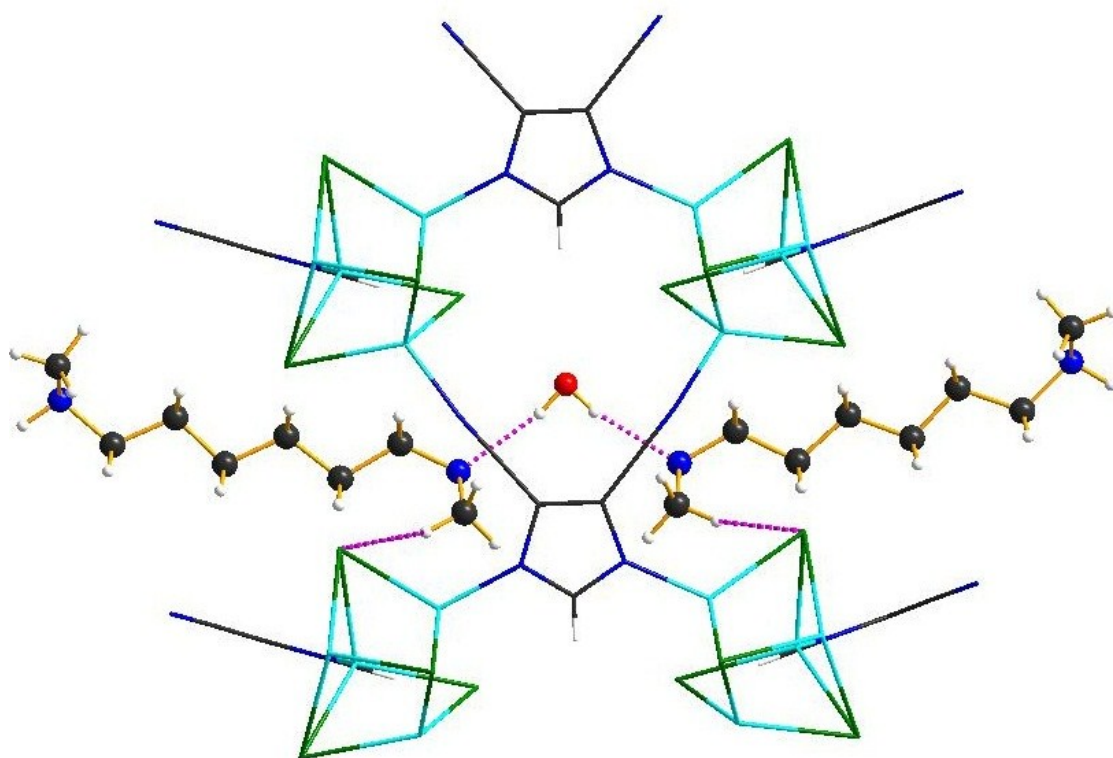


Figure S11. The host-guest interactions in MCIF-4.

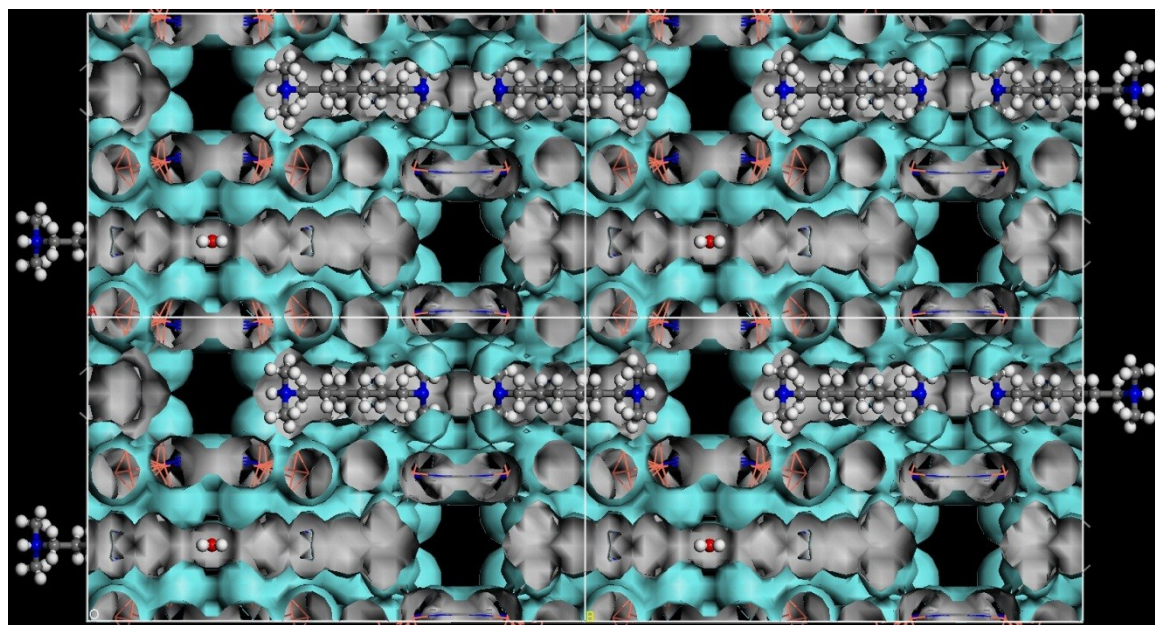


Figure S12. The connolly surface of MCIF-4.



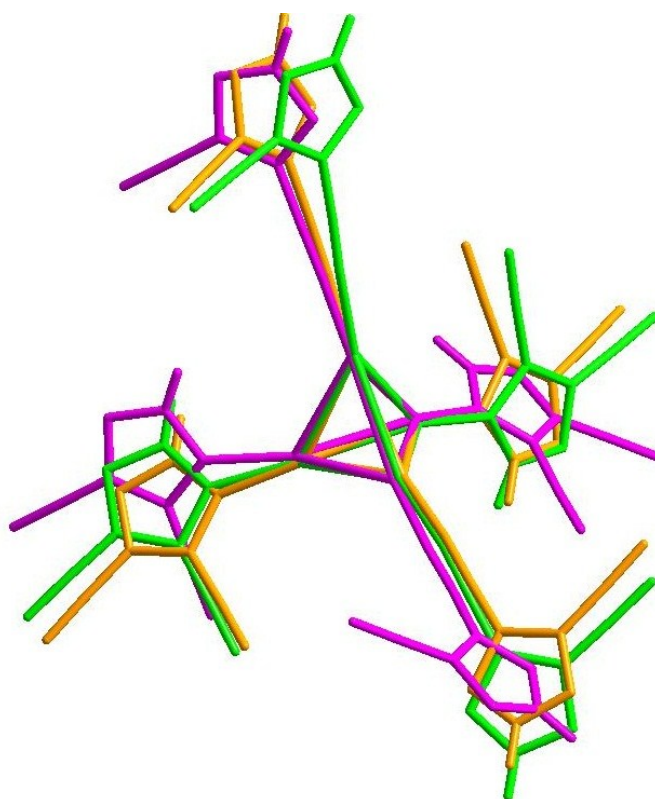


Figure S13. The conformation overlap of MCIFs. Orange: MCIF-2; Green: MCIF-3; Purple: MCIF-4.

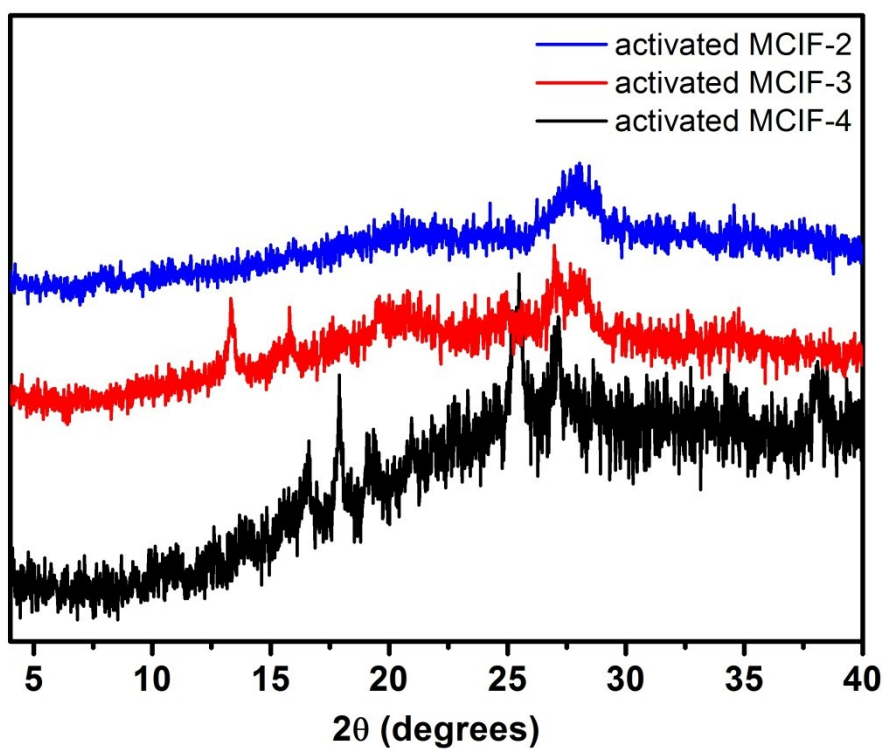


Figure S14. The XRD patterns of activated MCIFs.

Table S1. Crystal data and structure refinement for MCIF-2.

Identification code	1	
Empirical formula	C7 H8 Cu4 I4 N5	
Formula weight	923.94	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pnna	
Unit cell dimensions	a = 14.8153(12) Å	a = 90°.
	b = 14.3340(12) Å	b = 90°.
	c = 11.4471(10) Å	g = 90°.
Volume	2430.9(4) Å <sup>3</sup>	
Z	4	
Density (calculated)	2.525 Mg/m <sup>3</sup>	
Absorption coefficient	8.527 mm <sup>-1</sup>	
F(000)	1652	
Crystal size	0.150 x 0.150 x 0.100 mm <sup>3</sup>	
Theta range for data collection	2.277 to 28.708°.	
Index ranges	-15 ≤ h ≤ 19, -19 ≤ k ≤ 18, -13 ≤ l ≤ 15	
Reflections collected	19213	
Independent reflections	3084 [R(int) = 0.0288]	
Completeness to theta = 25.242°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Refinement method	Full-matrix least-squares on F <sup>2</sup>	
Data / restraints / parameters	3084 / 41 / 120	
Goodness-of-fit on F <sup>2</sup>	1.086	
Final R indices [I > 2σ(I)]	R1 = 0.0369, wR2 = 0.1005	
R indices (all data)	R1 = 0.0522, wR2 = 0.1094	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.322 and -0.798 e.Å <sup>-3</sup>	

Table S2. Crystal data and structure refinement for MCIF-3.

Identification code	1	
Empirical formula	C <sub>14</sub> H <sub>23</sub> Cu <sub>4</sub> I <sub>4</sub> N <sub>5</sub>	
Formula weight	1023.13	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2 <sub>1</sub> /n	
Unit cell dimensions	a = 11.3646(11) Å	a = 90°.
	b = 14.8491(12) Å	b = 98.850(2)°.
	c = 14.7153(13) Å	g = 90°.
Volume	2453.7(4) Å <sup>3</sup>	
Z	4	
Density (calculated)	2.770 Mg/m <sup>3</sup>	
Absorption coefficient	8.463 mm <sup>-1</sup>	
F(000)	1880	
Crystal size	0.220 x 0.200 x 0.180 mm <sup>3</sup>	
Theta range for data collection	1.960 to 25.267°.	
Index ranges	-11 ≤ h ≤ 13, -17 ≤ k ≤ 15, -17 ≤ l ≤ 16	
Reflections collected	15126	
Independent reflections	4369 [R(int) = 0.0294]	
Completeness to theta = 25.242°	98.4 %	
Absorption correction	Semi-empirical from equivalents	
Refinement method	Full-matrix least-squares on F <sup>2</sup>	
Data / restraints / parameters	4369 / 0 / 247	
Goodness-of-fit on F <sup>2</sup>	1.041	
Final R indices [I > 2σ(I)]	R <sub>1</sub> = 0.0353, wR <sub>2</sub> = 0.0830	
R indices (all data)	R <sub>1</sub> = 0.0400, wR <sub>2</sub> = 0.0849	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.390 and -0.848 e.Å <sup>-3</sup>	

Table S3. Crystal data and structure refinement for MCIF-4.

Identification code	1_sq	
Empirical formula	C <sub>40</sub> H <sub>56</sub> Cu <sub>16</sub> I <sub>16</sub> N <sub>20</sub> O	
Formula weight	3880.08	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pmmn	
Unit cell dimensions	a = 17.840(2) Å	a = 90°.
	b = 31.000(4) Å	b = 90°.
	c = 8.4707(11) Å	g = 90°.
Volume	4684.6(11) Å <sup>3</sup>	
Z	2	
Density (calculated)	2.751 Mg/m <sup>3</sup>	
Absorption coefficient	8.858 mm <sup>-1</sup>	
F(000)	3512	
Crystal size	0.220 x 0.200 x 0.180 mm <sup>3</sup>	
Theta range for data collection	1.314 to 25.135°.	
Index ranges	-21 ≤ h ≤ 21, -32 ≤ k ≤ 36, -10 ≤ l ≤ 10	
Reflections collected	29028	
Independent reflections	4402 [R(int) = 0.0478]	
Completeness to theta = 25.135°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Refinement method	Full-matrix least-squares on F <sup>2</sup>	
Data / restraints / parameters	4402 / 17 / 230	
Goodness-of-fit on F <sup>2</sup>	1.103	
Final R indices [I > 2σ(I)]	R1 = 0.0360, wR2 = 0.0842	
R indices (all data)	R1 = 0.0444, wR2 = 0.0880	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.709 and -0.934 e.Å <sup>-3</sup>	