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Supplementary Information

Hydrothermal Assembly of Various Dimensional Pure-inorganic Copper-Molybdenum
Frameworks

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Materials and methods

1. Characterization

The crystal data of CMF-1~3 were collected on an Agilent Supernova CCD diffractometer (Mo- $K\alpha$, graphite monochromator, $\lambda = 0.71073 \text{ \AA}$) at 180.0 K. Data reduction was performed using the CryAlisPro program, and Gaussian adsorption correction was applied. The structures were solved by direct methods. Non-hydrogen atoms were located directly from difference Fourier maps. Final structure refinements were performed with SHELX program by minimizing the sum of the squared deviation of F^2 using a full-matrix technique. The PLATON/SQUEEZE program was used to remove scattering contributions from disordered guest molecules and to produce solvent-free diffraction intensities, which were used in the final structure refinement. In these three compounds, the water and ammonia molecules were directly include in the molecular formula based on the elemental analyses and TG analyses.

CCDC-1430700 (CMF-1), CCDC-1430701 (CMF-2), CCDC-1430702 (CMF-3) contain 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.

The purity of the products was examined by power X-ray diffraction (PXRD) on a Rigaku D/Max-2400 diffractometer with a Cu $K\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). The data in the 2θ range of 3–40° were collected in a step of 0.02° with the remaining time 8°/min under the tube conditions 40 kV and 100 mV. The elemental analysis for carbon, nitrogen and hydrogen was carried out with an Elementar Vario EL III microanalyzer. The thermal analysis was done on TGA Q50 V20.6 with a heating rate of 10 °C/min from 40 to 600 °C in air. UV-vis spectra were recorded on a HITACHI U4100 UV-Vis spectrophotometer. X-ray photoelectron spectroscopy analyses (XPS) were done on an Axis Ultra system.

2. Synthesis of CMF-1

The starting materials are all commercially available and were used as purchased without further purification. A typical procedure for the synthesis of CMF-1 was described as follows. $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (1mmol), $(\text{NH}_4)_2\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ (0.6mmol), and $\text{NH}_4\text{B}_5\text{O}_8$ (1.36mmol) was dissolved in 6ml deionized water. 0.5ml acetic acid and a certain amount of ammonia solution were added to the mixture and adjusted the pH value to about 5. After stirring the solution for half an hour, the mixture was sealed in 23ml Teflon-lined autoclaves, and heated at 180°C for 7 days. After being cooled to the room temperature, black rectangle plate-shaped crystals were filtered, washed with distilled water, and dried at room temperature overnight. Yield: 80% based on $(\text{NH}_4)_2\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$. Elemental analysis (wt%) found for CMF-1: C 0.38%, H 2.07%, N 5.31%; calcd. C 0.00%; H 2.08%, N 5.31%.

3. Synthesis of CMF-2

A similar procedure for CMF-1 was used to prepare CMF-2 except that 1.5ml acetic acid were added to 8ml deionized water. After reacting at 220°C for 7 days, crystals of CMF-2 were filtered, washed with distilled water several times, and dried at room temperature overnight. Yield: 70% based on $(\text{NH}_4)_2\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$. Elemental analysis (wt%) found for CMF-2: C 0.12%, H 2.08%, N 5.89%; calcd. C 0.00%, H 2.07%, N 5.53%.

4. Synthesis of CMF-3

A mixture consisting of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (1mmol), $(\text{NH}_4)_2\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ (0.6mmol), $\text{NH}_4\text{B}_5\text{O}_8$

(1.36mmol), 1.5ml acetic acid, and 6ml water were stirred for half an hour. After adjusting the pH value to about 5 by ammonia solution, the resulting mixture was transferred to 23ml Teflon-lined autoclave, and heated at 250°C for 7 days. Black-rod crystals of CMF-3 were obtained and thoroughly washed with distilled water, dried at room temperature. However, it is hard to obtain pure CMF-3 samples to collect powder XRD as some colorless and green powder on the surface of black crystals.

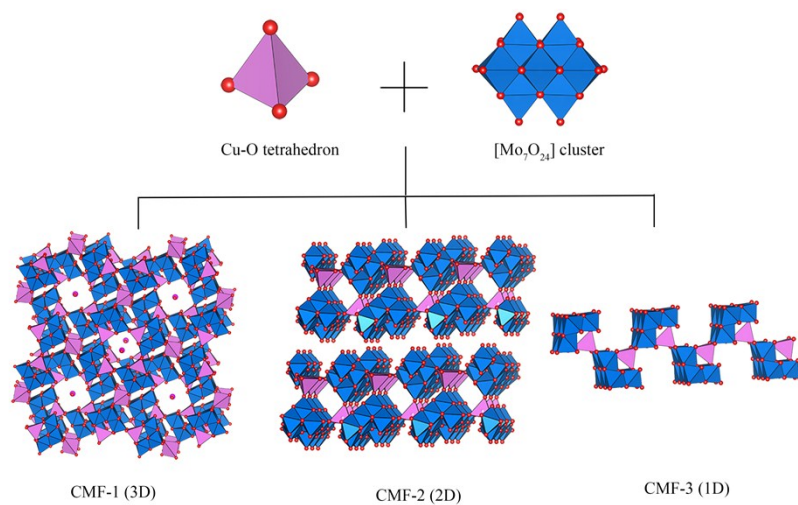
5. Catalysis experiments of CMF-1~3

Here, we select methylene blue (MB) as a representative of the dye pollutant in water to investigate the catalytic activity of CMF-1~3. In a typical procedure for catalytic reactions, 0.0412g of CMF-1 were suspended in a fresh aqueous dye solution ($C_0= 3\text{mg}/100\text{ml}$, 50ml) in a conical flask and the suspension was stirred for a certain time at room temperature. The degradation experiments with increasing time were performed by adding 0.08g CMF-1 to 100ml solution and took 1ml per minute. The catalysts were reused by centrifuging and heated at 160°C for 2h. The solution samples were withdrawn for UV-vis analysis to investigate the degradation ratio of the dye at 664nm. The degradation ratio of MB was then calculated with the following equation:

$$D (\%) = [(A_0 - A)/A_0] \times 100 = [(C_0 - C)/C_0] \times 100 \quad (1)$$

Where D is degradation ratio, C_0 , A_0 and C, A are the concentration and absorbance values of the MB solution at the peak of 664nm before and after reactions, respectively.

Figures



FigureS1. A series of various dimensional frameworks, CMF-1~3, self-assembling by Cu-O tetrahedra and $[\text{Mo}_7\text{O}_{24}]$ clusters.

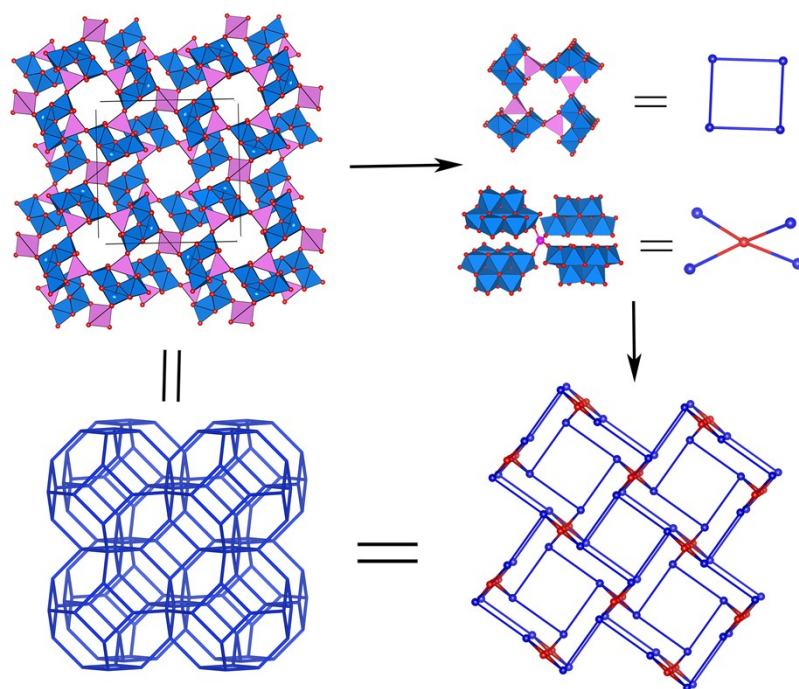


Figure S2. Polyhedral and topological representation of CMF-1 along the c -axis. The topological structure of CMF-1 is SOD.

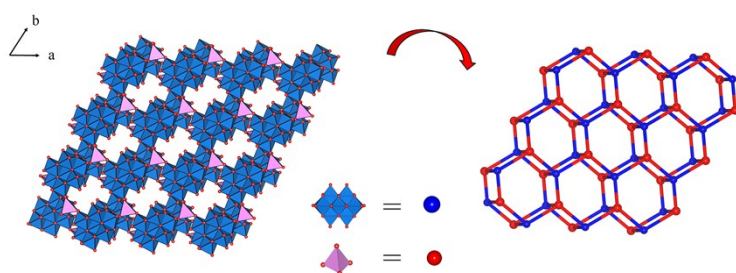


Figure S3. The 3D polyhedral and topological representation of CMF-2 in the c -axis, which could be described as a net type SP 2-periodic net (6,3)Ia with point symbol $(4^3.6^3)$ (TOPOS)^{S1}.

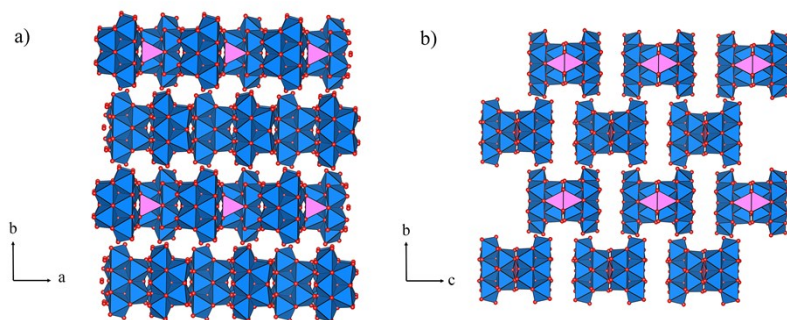


Figure S4. Structures of CMF-3 viewing in the c -axis and a -axis.

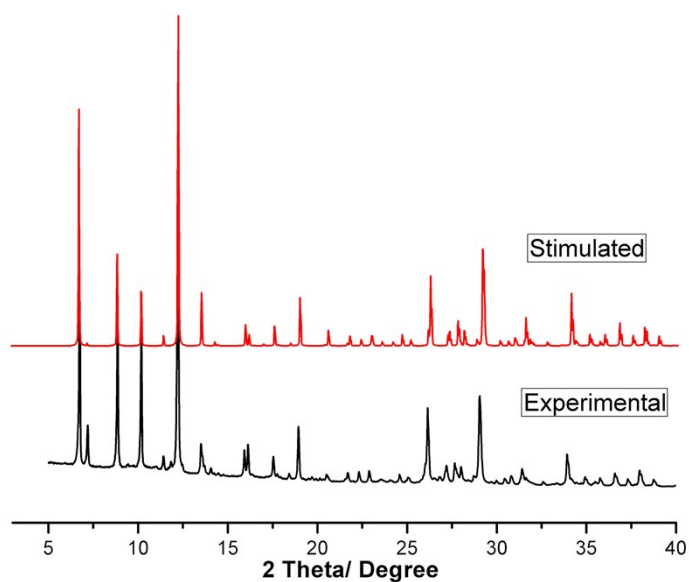


Figure S5. The stimulated and experimental powder X-ray diffraction patterns of CMF-1. The experimental data was obtained in a transmission mode because of strong preferred orientation.

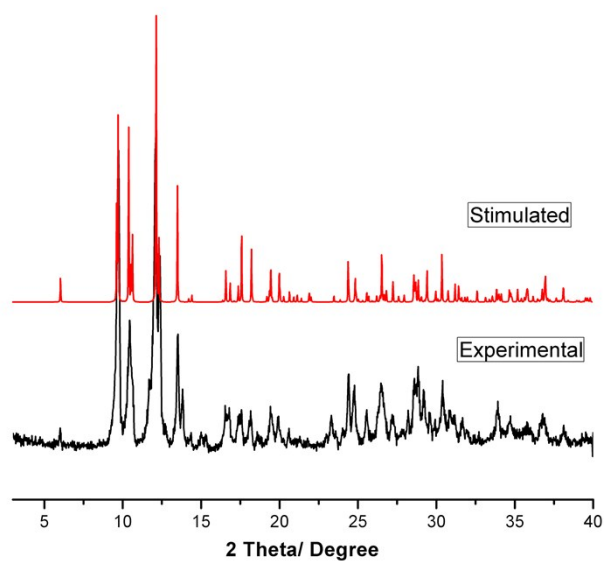


Figure S6. The stimulated and experimental powder X-ray diffraction patterns of CMF-2.

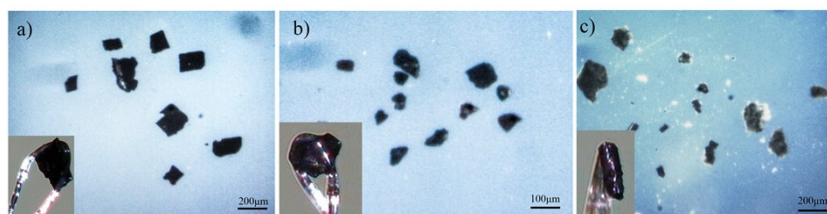


Figure S7. The micrographs of CMF-1 (a) crystals, CMF-2 (b) crystals, and CMF-3 (c) crystals, all of which are black. CMF-1 crystals are rectangle-like plate particles, while the morphologies of CMF-2 are not regular. The crystals of CMF-3 are surrounded by some white powder, so the SXRD data were collected by cutting a crystal carefully.

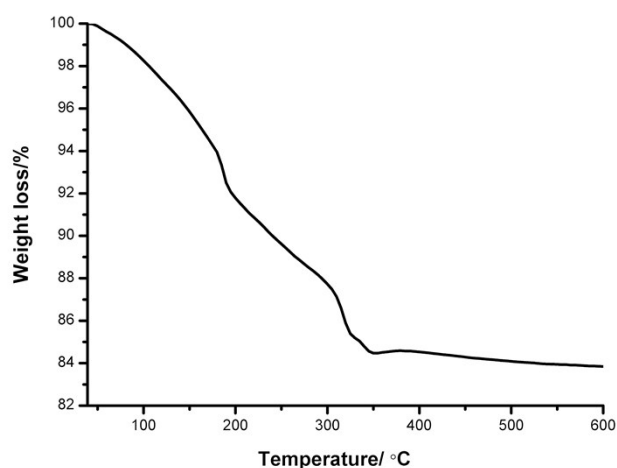


Figure S8. TG curve of CMF-1 in air. From room temperature to 240°C, a weight loss of 10.07% corresponding to the loss of H₂O and NH₃ in the channel; at the range of 240°C to 400°C, a weight loss of 5.14% corresponding to the loss of H₂O from terminal hydroxyl groups.

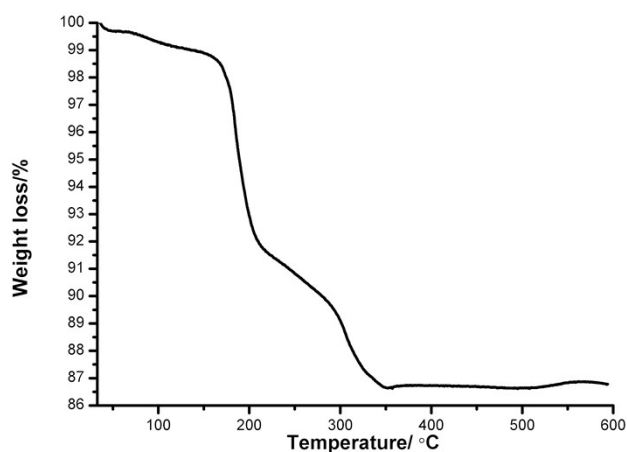


Figure S9. TG curve of CMF-2 in air. From room temperature to 220°C, a weight loss of 7.33% corresponding to the loss of H₂O and NH₃ in the channel; at the range of 220°C to 390°C, a weight loss of 3.53% corresponding to the loss of H₂O from terminal hydroxyl groups.

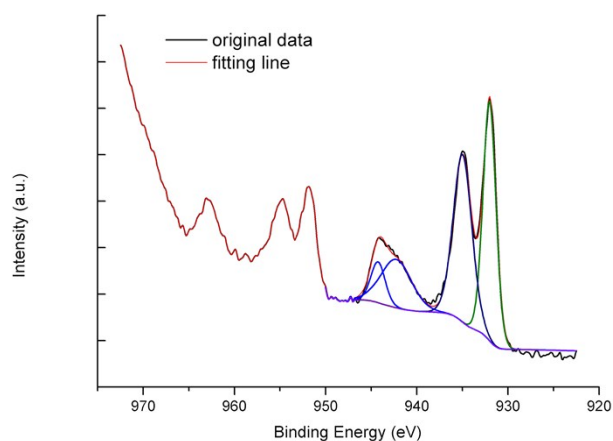


Figure S10. XPS of copper ions in CMF-1^{S2}. The black line and red line show the original data and fitting data, respectively. In order to have a better base line, only Cu-2p_{3/2} were fitting to calculate the probable ratio of Cu⁺/Cu²⁺ in CMF-1. The green fitting peaks at 932.0eV represent 2p_{3/2} of Cu⁺, and royal peaks at 935.0eV are Cu²⁺. The blue lines are shake-up lines of Cu²⁺, which is a signal of the existence of Cu²⁺. Based on the analysis of Cu-2p_{3/2}, the area ratio of Cu⁺/Cu²⁺ in CMF-1 is about 1.0:1.7.

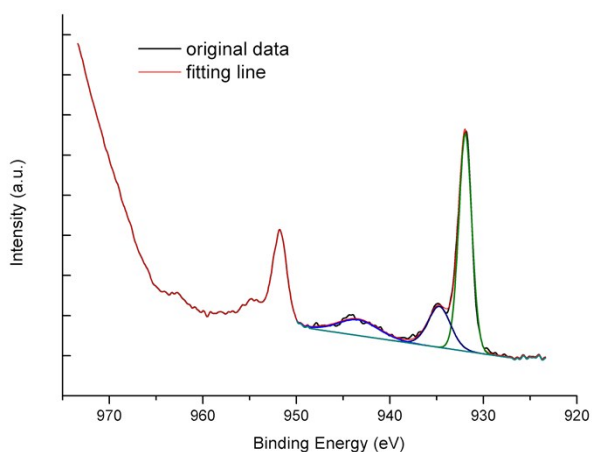


Figure S11. XPS of copper ions in CMF-2. Similar analysis to XPS of CMF-1, the ratio of $\text{Cu}^+/\text{Cu}^{2+}$ in CMF-2 is about 1.9:1.0.

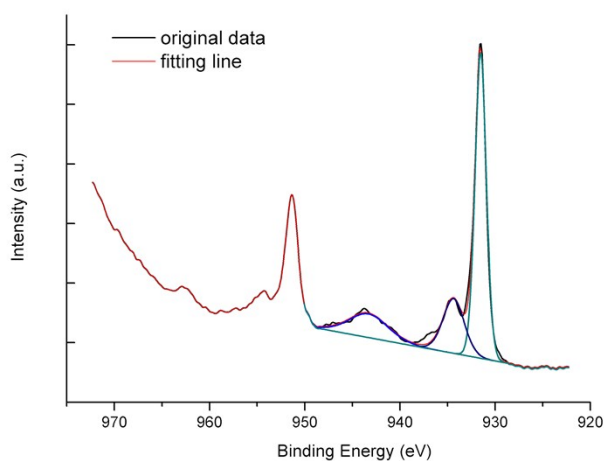


Figure S12. XPS of copper in CMF-3. Similar analysis to XPS of CMF-1, the ratio of $\text{Cu}^+/\text{Cu}^{2+}$ in CMF-2 is about 1.7:1.0.

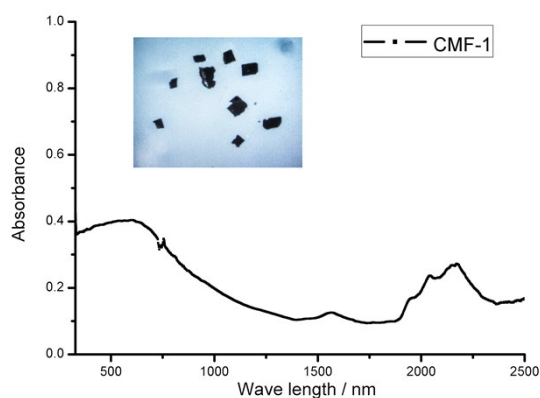


Figure S13. UV-vis-NIR spectrum of CMF-1 from 328nm to 2500nm. CMF-1 can absorb lights from UV to infrared light as CMF-1 are black.

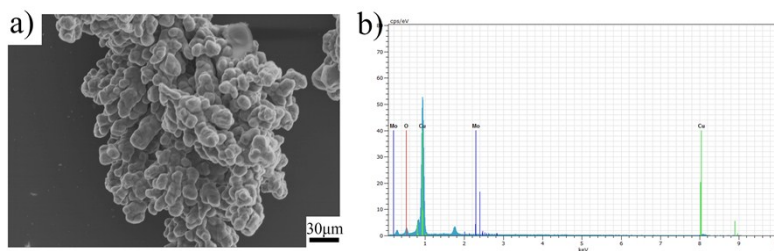


Figure S14. SEM image and EDX pattern of Cu power, obtained at 250°C. As shown in EDX, the ratio of Cu/Mo/O is 96.7/0.3/2.9.

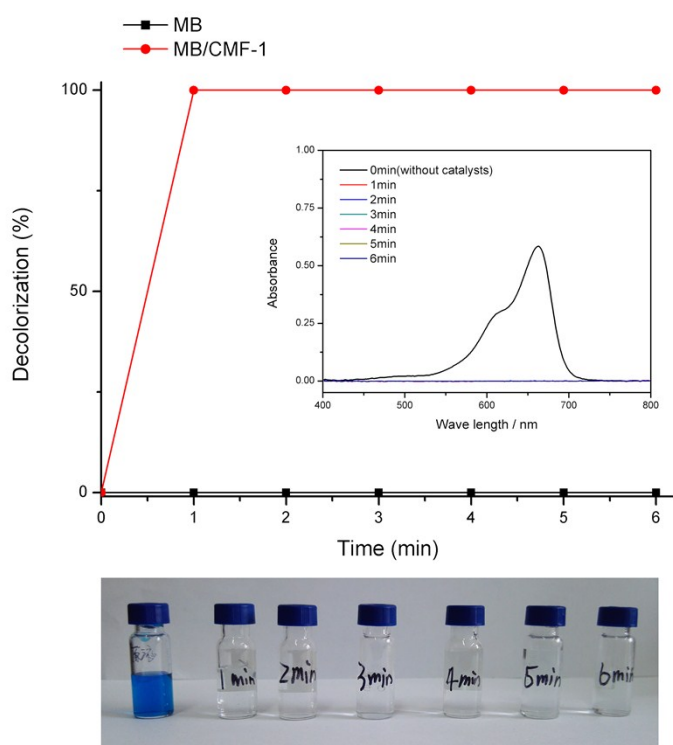


Figure S15. Degradation of MB in reaction systems. 0.0823g CMF-1 for the red curve, 0g for the black curve; the inset shows UV-vis spectral changes of MB solution corresponding to the red curve. It can be clearly seen that the absorption peak of MB almost disappear after reaction for about 1min, both from UV-vis spectral and photographs.

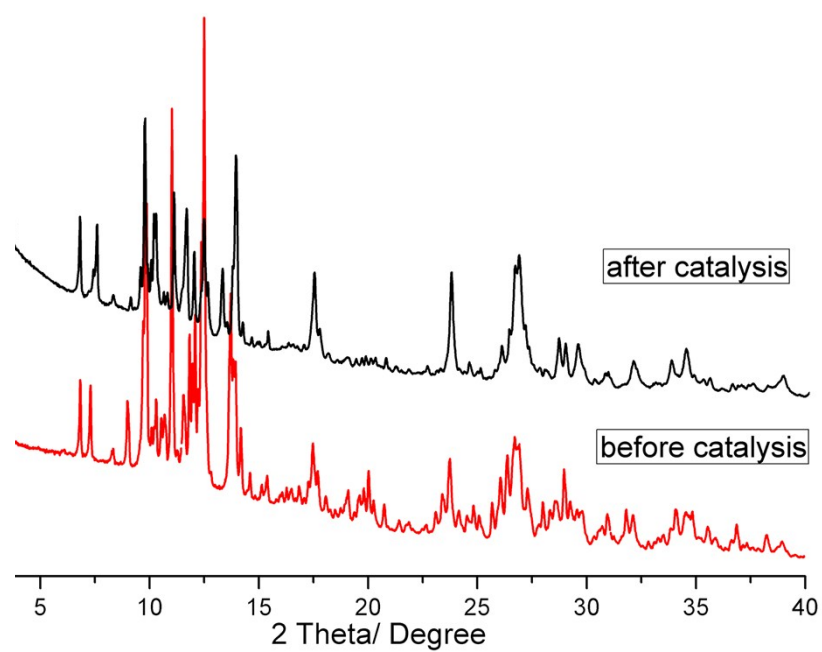


Figure S16. XRD patterns of CMF-1 as-synthesized and recovered after degradation of MB. CMF-1 can be reused with decreasing crystallinity and appearance of impurities, while the feature peaks of CMF-1 at low angles can be observed in XRD patterns.

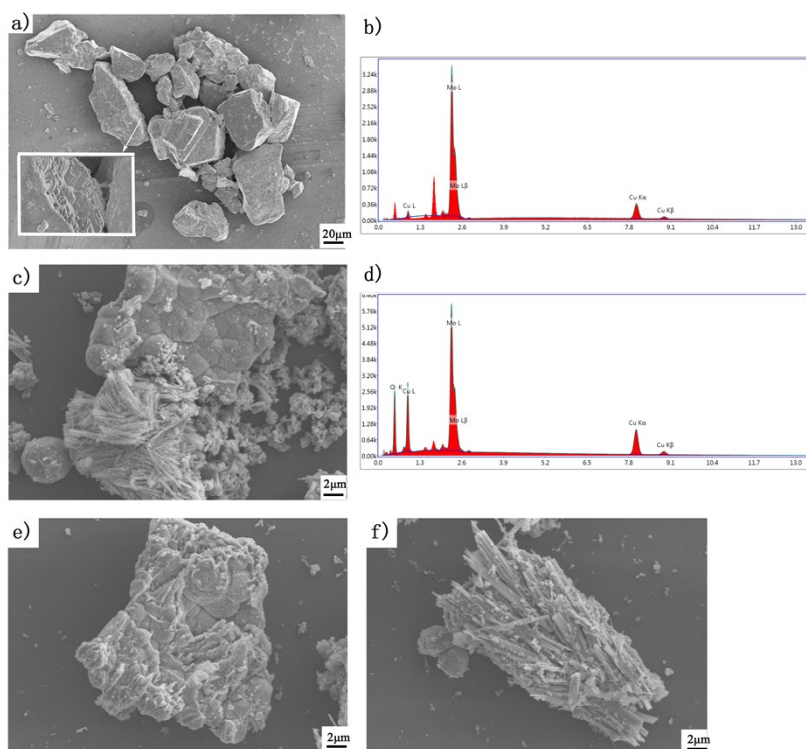


Figure S17. SEM images and EDX patterns of catalysts before and after reactions. a), b) SEM image and EDX pattern of CMF-1 before reaction, which are block-like; c), d) CMF-1 stirred with 10ml water for 5min. Two morphologies appears, globular and rodlike, while the EDX patterns are similar to b); e), f) SEM images of CMF-1 after catalytic reactions. The morphologies are similar to that of c), which was only stirred with water.

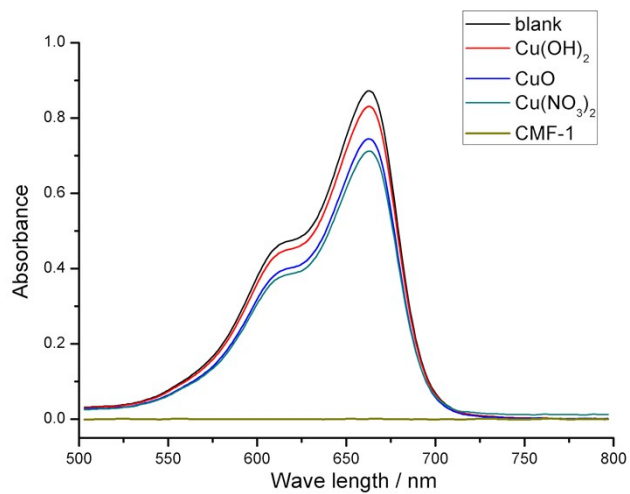


Figure S18. UV-vis spectra of the dye solution after 30min in the presence of different catalysts including Cu(OH)₂, CuO, Cu(NO₃)₂, and CMF-1. In contrast to CMF-1, the degradation ratio of Cu(OH)₂, CuO, Cu(NO₃)₂ are 18%, 15%, 4.8%, respectively.

Tables

Table S1. Crystal data and structure refinements for compounds CMF-1~3.

Compound	CMF-1	CMF-2	CMF-3
Empirical fomula	Cu ₁₀ Mo ₅₆ O ₁₉₂ ·2[Cu(NH ₃) ₂]·36 (NH ₄)·7.6(OH)·27.2(H ₂ O)	CuMo ₇ O ₂₄ ·5(NH ₄)·2 .83(H ₂ O)·0.34(OH)	CuMo ₇ O ₂₄ H _{4.6}
<i>M_r</i>	10538.51	1266.07	1123.75
Temperature(K)	180.0(10)	180.0(10)	180.0(10)
Crystal size(mm)	0.20×0.18×0.08	0.07×0.06×0.02	0.18×0.08×0.06
Crystal system	Tetragonal	Triclinic	Orthorhombic
Space group	<i>I4/m</i>	<i>P</i> -1	<i>Pnma</i>
<i>a</i>/Å	17.2929(7)	10.3503(4)	10.4495(7)
<i>b</i>/Å	17.2929(7)	10.3933(4)	19.2758(9)
<i>c</i>/Å	19.8829(12)	15.1733(6)	13.2417(8)
<i>α</i>°	90	76.113(4)	90
<i>β</i>°	90	75.040(4)	90
<i>γ</i>°	90	62.687(4)	90
<i>V</i>/Å³	5945.9(6)	1387.00(9)	2667.2(3)
<i>Z</i>	1	2	4
<i>F</i>(000)	4264.0	1040.0	2060.0
Reflection collected	3014	5559	2763
Independent reflections	2199	4478	2110
GOF on <i>F</i>²	1.030	1.018	1.049
Final <i>R</i> indexes [<i>I</i>>=4σ(<i>I</i>)]	0.0402	0.0362	0.0532
Final <i>R</i> indexes [all data]	0.0586	0.0478	0.0719
<i>wR</i>₂	0.1081	0.0876	0.1347
Largest diff. peak and hole (e.Å⁻³)	0.967/-0.859	1.177/-0.931	1.483/-1.356

Table S2. Design of orthogonal experiments.

	Cu source /mmol	Mo source /mmol	NH ₄ B ₅ O ₈ /mmol	H ₂ O /ml	CH ₃ COOH /ml	pH
1	1	0.3	0	2	0.5	4
2	1	0.6	1	4	1.0	5
3	1	0.9	2	6	1.5	6
4	1	1.2	4	8	2.0	7
5	1	0.3	1	4	1.5	7
6	1	0.6	0	2	2.0	6
7	1	0.9	4	8	0.5	5
8	1	1.2	2	6	1.0	4
9	1	0.3	2	6	2.0	5
10	1	0.6	4	8	1.5	4
11	1	0.9	0	2	1.0	7
12	1	1.2	1	4	0.5	6
13	1	0.3	4	8	1.0	6
14	1	0.6	2	6	0.5	7
15	1	0.9	1	4	2.0	4
16	1	1.2	0	2	1.5	5

Table S3. Design of systematic experiments.

	Cu(NO ₃) ₂ /mmol	(NH ₄) ₂ Mo ₇ O ₂₄ /mmol	NH ₄ B ₅ O ₈ /mmol	H ₂ O /ml	CH ₃ COOH /ml	Temperature /°C	
1	1	0.3	1	2	0.5	180	
2		0.6		2			1.5
3		0.9		2			
4		1.2		2			
5		0.3		4	4		
6		0.6		4			
7		0.9		4			
8		1.2		4			
9		0.3		6		6	
10		0.6		6			
11		0.9		6			
12		1.2		6			
13		0.3		8	8		
14		0.6		8			
15		0.9		8			
16		1.2		8			

Table S4. Bond lengths of Cu ions in CMF-1~3.

Bond lengths of Cu ions in CMF-1

Cu(1)-N(1)	1.890(16)	Cu(1)-N(1)#3	1.890(16)	Cu(1)-O(11)	3.179(3)
Cu(1)-O(11)#2	3.179(3)	Cu(1)-O(11)#7	3.179(3)	Cu(1)-O(11)#8	3.179(3)
Cu(2)-O(4)	1.979(4)	Cu(2)-O(4)#4	1.979(4)	Cu(2)-O(11)#2	2.065(6)
Cu(2)-O(5)#2	2.060(6)	Cu(3)-O(8)	1.997(5)	Cu(3)-O(8)#1	1.997(5)
Cu(3)-O(8)#5	1.997(5)	Cu(3)-O(8)#6	1.997(5)		

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y,z #2 -y,x,z #3 -x,-y,-z #4 x,y,-z #5 y+1/2,-x+1/2,-z+1/2 #6 -y+1/2,x+1/2,-z+1/2
#7 y,-x,z #8 -x,-y,z

Bond lengths of Cu ions in CMF-2

Cu(1)-O(5)#1	1.953(4)	Cu(1)-O(10)	2.065(4)	Cu(1)-O(11)	1.953(4)
Cu(1)-O(15)	1.947(4)				

#1 -x,-y,-z

Bond lengths of Cu ions in CMF-3

Cu(1)-O(12)	1.978(6)	Cu(1)-O(12)#1	1.978(6)	Cu(1)-O(11)	2.044(8)
Cu(1)-O(10)	2.047(9)				

#1 x, -y-1/2, z

Table S5. Bond valence sum (BVS) analysis of valence states of copper ions in CMF-1~3.

CMF	Cu sites	Cu ⁺	Cu ²⁺	Cu ⁺ /Cu ²⁺ (XPS)
CMF-1	Cu1	0.906		1.0:1.7
	Cu2	1.291	1.597	
	Cu3	1.368	1.692	
CMF-2	Cu1	1.414	1.751	1.9:1.0
CMF-3	Cu1	1.322	1.638	1.7:1.0

References

- S1. TOPOS program. Blatov, V. A.; Shevchenko, A. P. V4.0 ed.; Samara State University: Samara, Russia, 2010.
- S2. P. Steiner, V. Kinsinger, I. Sander, B. Siegwart, S. Hufner, C. Politis, R. Hoppe and H. P. Müller, *Zeitschrift für Physik B Condensed Matter*, 1987, **67**, 497.