Metal Ion Attachment in Cavities of Metal Organic Polyhedra to Enhance Framework Robustness and Catalytic Performance

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Experimental Section

Chemicals

All reagents and solvents used in synthetic studies are commercially available and were used as supplied without further purification. Styrene oxide (Tansoole), Copper nitrate trihydrate, Hydrochloric acid, N,N-dimethylacetamide (DMA), Methanol, Toluene, Ethanol, Propanol, Isopropanol, N-butanol, Propylene oxide, Cyclohexene oxide, Carbazole, Concentrated sulfuric acid were purchased from Sinopharm Chemical Reagent limited corporation, Epichlorohydrin, Butadiene monoxide, Anhydrous aluminium chloride, Aminopyrazine (Apz), Pyrazine (Pz) were obtained from Aladdin Chemicals.

Materials Synthesis

Synthesis of 9H-carbazole-3,6-dicarboxylic acid (H$_2$CDC): The ligand 9H-carbazole-3,6-dicarboxylic acid (H$_2$CDC) was synthesized according to the literature[1].

compound 1

[Cu$_{12}$(CDC)$_{12}$(DMA)$_6$(H$_2$O)]$_6$·xS (1) was synthesized as blue-green crystals under solvothermal conditions: 13 mg of H$_2$CDC and 24 mg of Cu (NO$_3$)$_2$·3H$_2$O in 3 mL of DMA/EtOH (V:V= 5:1) mixed solvent were placed in a capped vial (20 mL). The vial was heated at 100°C for 2 days. Cyan green block crystals were formed and isolated by washing with 5:1 EtOH/DMA (2 × 3 mL) dried in air. Yield:31%

compound 2

[Cu$_{12}$(CDC)$_{12}$(Apz)$_2$(DMA)$_4$(H$_2$O)]$_6$·xS (2) was synthesized as cyan green rhombic crystals under solvothermal conditions: 5 mg of Apz and compound **1** in 3 mL of DM-A/EtOH (V:V = 5:1) mixed solvent were placed in a capped vial (20 mL).The solution stood at 100°C for 1 day and gave cyan green rhombic crystals and isolated by washing with 5:1 EtOH/DMA (2 × 3 mL) dried in air. Yield:18%

compound 3

① [Cu$_{12}$(CDC)$_{12}$(Pz)$_2$(DMA)$_6$(H$_2$O)]$_4$·xS (3) was synthesized as cyan green rhombic crystals under solvothermal conditions: 13 mg of H$_2$CDC and 24 mg of

Cu(NO$_3$)$_2$·6H$_2$O and 4 mg of Pz in 3 mL of DMA/EtOH (V:V = 5:1) mixed solvent were placed in a capped vial (20 mL). The vial was heated at 100℃ for 2 days. Cyan green rhombic crystals were formed and isolated by washing with 5:1 EtOH/DMA (2×3 mL) dried in air. Yield:32.5%

② [Cu$_{12}$(CDC)$_{12}$(Pz)$_2$(DMA)$_6$(H$_2$O)]$_4$·xS (3) was synthesized as cyan green rhombic crystals under solvothermal conditions: 5 mg of Pz and 24 mg of Cu(NO$_3$)$_2$·6H$_2$O and compound 1 in 3 mL of DMA/EtOH (V:V = 5:1) mixed solvent were placed in a capped vial (20 mL). The solution stood at 100℃ for 1 day and gave cyan green rhombic crystals as compound 3, [Cu$_{12}$(CDC)$_{12}$(Pz)$_2$(DMA)$_6$(H$_2$O)]$_4$·xS were isolated by washing with 5:1 EtOH/DMA (2 × 3 mL) dried in air. Yield:27%

compound 4

① [Cu$_{12}$(CDC)$_{12}$(Apz)$_2$(DMA)$_4$(H$_2$O)]$_6$·xS (4) was synthesized as cyan green rhombic crystals under solvothermal conditions: 13 mg of H$_2$CDC and 24 mg of Cu(NO$_3$)$_2$·6H$_2$O and 5 mg of Apz in 3 mL of DMA/EtOH (V:V = 5:1) mixed solvent were placed in a capped vial (20 mL). The vial was heated at 100 °C for 2 days. Cyan green rhombic crystals were formed and isolated by washing with 5:1 EtOH/DMA (2×3mL) dried in air. Yield:30%

② [Cu$_{12}$(CDC)$_{12}$(Apz)$_2$(DMA)$_6$(H$_2$O)]$_4$·xS (3) was synthesized as cyan green rhombic crystals rystals under solvothermal conditions: 5 mg of Apz and 24 mg of Cu(NO$_3$)$_2$·6H$_2$O and compound 1 in 3 mL of DMA/EtOH (V:V = 5:1) mixed solvent were placed in a capped vial (20 mL). The solution stood at 100℃ for 1 day and gave cyan green rhombic crystals as compound 3, [Cu$_{12}$(CDC)$_{12}$(Apz)$_2$(DMA)$_4$(H$_2$O)]$_6$·xS (4) were isolated by washing with 5:1 EtOH/DMA (2 × 3 mL) dried in air. Yeild:24%

compound 5

[Cu$_{12}$(CDC)$_{12}$(Apz)$_2$(DMA)$_4$(H$_2$O)$_6$Ni$_{0.5}$(H$_2$O)$_6$]·xS (5) was synthesized as cyan green rhombic crystals under solvothermal conditions: 5 mg of Apz and 30 mg of Ni(NO$_3$)$_2$·6H$_2$O and compound 1 in 3 mL of DMA/EtOH (V:V = 5:1) mixed solvent were placed in a capped vial (20 mL).The solution stood at 100℃ for 1 day and gave

cyan green rhombic crystals as compound 5, which were isolated by washing with 5:1 EtOH/DMA (2 × 3 mL) dried in air. Yeild:15%

compound 6

$[Cu_{12}(CDC)_{12}(Apz)_2(DMA)_4(H_2O)_6Zn_{0.5}(H_2O)_6]\cdot xS$ (6) was synthesized as cyan green rhombic crystals under solvothermal conditions: 5 mg of Apz and 30 mg of $Zn(NO_3)_2\cdot 6H_2O$ and compound 1 in 3 mL of DMA/EtOH (V:V = 5:1) mixed solvent were placed in a capped vial (20 mL).

The solution stood at 100℃ for 1 day and gave cyan green rhombic crystals as compound 6, $[Cu_{12}(CDC)_{12}(Apz)_2(DMA)_4(H_2O)_6Zn_{0.5}(H_2O)_6]\cdot xS$ (6) which were isolated by washing with 5:1 EtOH/DMA (2 × 3 mL) dried in air. Yelid:14.8%

Characterization

All starting chemicals and solvents were commercially available and were directly used without further purification. Thermogravimetric analyses (TGA) were performed on a Mettler-Toledo Model SDTA851e analyzer under a nitrogen atmosphere with a rate of 10 °C min^{-1}. Powder X-ray diffraction (PXRD) patterns were recorded using Cu *Kα* radiation (λ = 1.5418 Å) on a PANalytical X'Pert[3] powder diffractometer with a vacuum apparatus at 40 kV and 40 mA. Inductively coupled plasma optical emission spectroscopy (ICP-OES) to determine the elemental composition and content of Zn and Ni catalyst. The instrument used was the Ultima 2 model from HORIBA Jobin Yvon. Energy-dispersive X-ray spectroscopy (EDS, Bruker QUANTAX, Germany) linked-up with cold field emission scanning electron microscope (FESEM, Regulus 8100, Japan). The morphologies of the samples were characterized by Scanning Electron Microscope (SEM, Hitachi S-4800 scanning electron microscope). X-ray photoelectron spectroscopy (XPS) measurements were conducted on a VG Scientific ESCA Lab Mark II spectrometer using Al Kα as the X-ray source. All binding energies were referenced to the C1s peak of the surface adventitious carbon at 284.8 eV. Fourier transform infrared spectra (FT-IR) were measured in the range of 500-4000 cm^{-1} by a Nicolet 5700 FT-IR.

Single-Component Gas sorption measurements.

The gas adsorption test was performed using the Micromeritics ASAP 2020 HD88 analyzer. Before the measurement, the samples were evacuated and activated at RT condition in vacuum for 12 hours. Adsorption-desorption isotherms was examined at 77K. The Brunauer-Emmett-Teller (BET) surface area was calculated using adsorption data in a relative pressure ranging from 0.04 to 0.20. The total pore volume was determined from the amount adsorbed at a relative pressure of about 0.99. The pore diameter was calculated from the adsorption branch by using the nonlocal density functional theory (NLDFT) methods.

Crystallographic Studies

Data collection and structural analysis of crystal **1**, **2**, **3** ,**4** ,**5** and **6** ware collected on the Rigaku Oxford single-crystal diffractometer equipped with graphite monochromatic Cu *Kα* radiation (*λ* = 1.54184 Å). The crystal was kept at constant temperature during data collection. Using Olex2[2], the structure was solved with the Superflip[3] structure solution program using charge flipping and refined with the ShelXL[4] refinement package using least-squares minimization. All nonhydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms on the ligands were placed in idealized positions and refined using a riding model. We employed PLATON[5] and SQUEEZE[6] to calculate the diffraction contribution of the solvent molecules and thereby produce a set of solvent-free diffraction intensities. The detailed crystallographic data and structure refinement parameters are summarized in Table S1. (CCDC: 2328856-2328861)

Table S1 Crystal data and structure refinements for 1 to 6.

compounds	1	2	3
No. CCDC	2328856	2328857	2328858
Empirical formula	$C_{96}H_{75}Cu_6N_9O_{30}$	$C_{96}H_{65}Cu_6N_{11}O_{29}$	$C_{96}H_{71}Cu_6N_{10}O_{32}$
Formula weight	2215.89	2217.83	2217.83
Temperature/K	293(2)	100.01(10)	292.93(10)
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$
a/Å	20.4272(2)	19.9879(3)	19.6648(2)
b/Å	23.7472(3)	24.0664(3)	23.7626(3)
c/Å	36.3951(3)	36.0958(4)	35.7591(4)
α/°	90	90	90
β/°	90.6280(10)	91.8020(10)	92.4590(10)
γ/°	90	90	90
V/Å^3	17653.8(3)	17354.8(4)	16694.4(3)
Z	4	4	4
ρ_{calc}g/cm^3	0.834	0.849	2.459
μ/mm^{-1}	1.182	1.203	8.390
F(000)	4512.0	4496.0	11832.0
Radiation	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)
Rint	0.0476	0.0788	0.0505
Independent reflections	35046	30422	32987
Reflections collected	154130	110406	112029
Data/restraints/parameters	35046/71/1282	30422/0/1288	32987/84/1279
Goodness-of-fit on F^2	1.022	1.194	1.051
Final R indexes [I>=2σ (I)][a]	R_1 = 0.0741 wR$_2$ = 0.2213	R_1 = 0.1063 wR$_2$ =0.3016	R_1 = 0.0640 wR$_2$ = 0.1952
Final R indexes[all data][a]	R_1 = 0.0993 wR$_2$ = 0.2482	R_1 = 0.1369 wR$_2$ = 0.3270	R_1 = 0.0869 wR$_2$ = 0.2158

Compounds	4	5	6
No. CCDC	2328856	2328857	2328861
Empirical formula	$C_{96}H_{76}Cu_{6.5}N_{11}O_{32}$	$C_{96}H_{71}Cu_6N_{11}Ni_{0.5}O_{32}$	$C_{96}H_{65}Cu_5N_{11}O_{32}Zn_{0.5}$
Formula weight	2308.68	2301.23	2300.34
Temperature/K	293	297	293.47（10）
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$
a/Å	20.0729(2)	20.0194(6)	20.0469(2)
b/Å	24.2132(3)	24.0786(8)	24.2099(3)
c/Å	36.0451(4)	36.0357(11)	35.9724(4)
α/°	90	90	90
β/°	91.8860(10)	91.700(3)	91.7560(10)
γ/°	90	90	90
V/Å^3	17509.5(3)	17363.0(9)	17450.4(3)
Z	4	4	4
ρ_{calc}g/cm^3	0.876	0.880	0.876
μ/mm^{-1}	1.276	1.279	1.309
F(000)	4694.0	4672.0	4656.0
Radiation	Cu $K\alpha$ ($\lambda = 1.54184$)	Cu $K\alpha$ ($\lambda = 1.54184$)	Cu $K\alpha$ ($\lambda = 1.54184$)
Rint	0.0498	0.0916	0.0372
Independent reflections	34503	34397	30729
Reflections collected	99797	114338	118023
Data/restraints/parameters	34503/6/1324	34397/0/1323	30729/0/1319
Goodness-of-fit on F^2	1.050	0.948	1.021
Final R indexes [I>=2σ(I)][a]	$R_1 = 0.0770$ wR$_2$ = 0.2340	$R_1 = 0.0835$, wR$_2$ = 0.2263	$R_1 = 0.0941$ wR$_2$ = 0.2609
Final R indexes [all data][a]	$R_1 = 0.1011$ wR$_2$ = 0.2566	$R_1 = 0.1383$ wR$_2$ = 0.2674	$R_1 = 0.1116$ wR$_2$ = 0.2843

[a]$R_1 = \sum(|F_o| - |F_c|) / \sum|F_o|$, [b]wR$_2 = [\sum w(F_o^2 - F_c^2)^2/ \sum w(F_o^2)^2]^{0.5}$
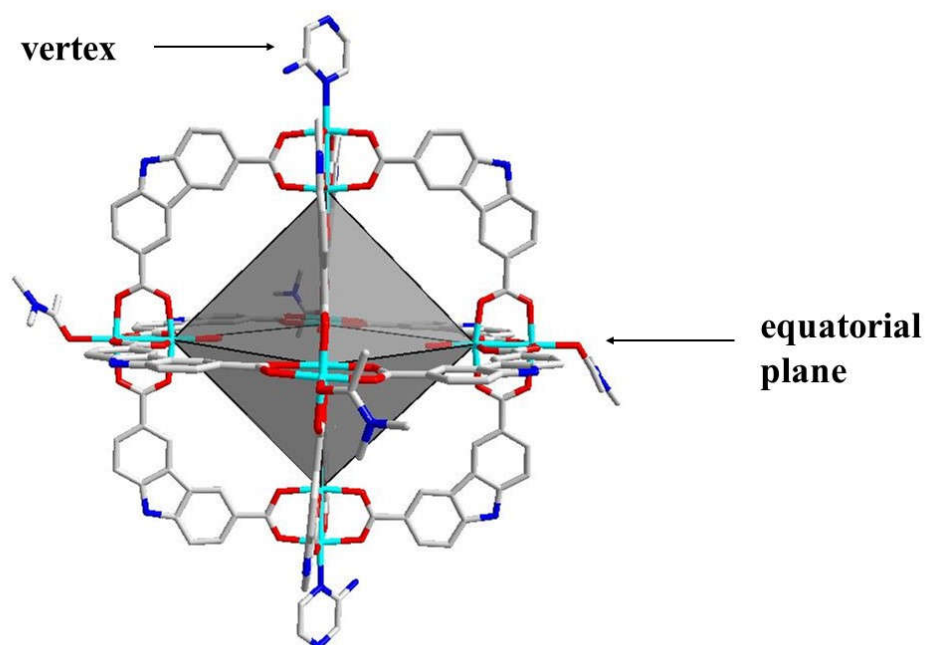
Figure.S1 the vertex and equatorial plane of compound **2**
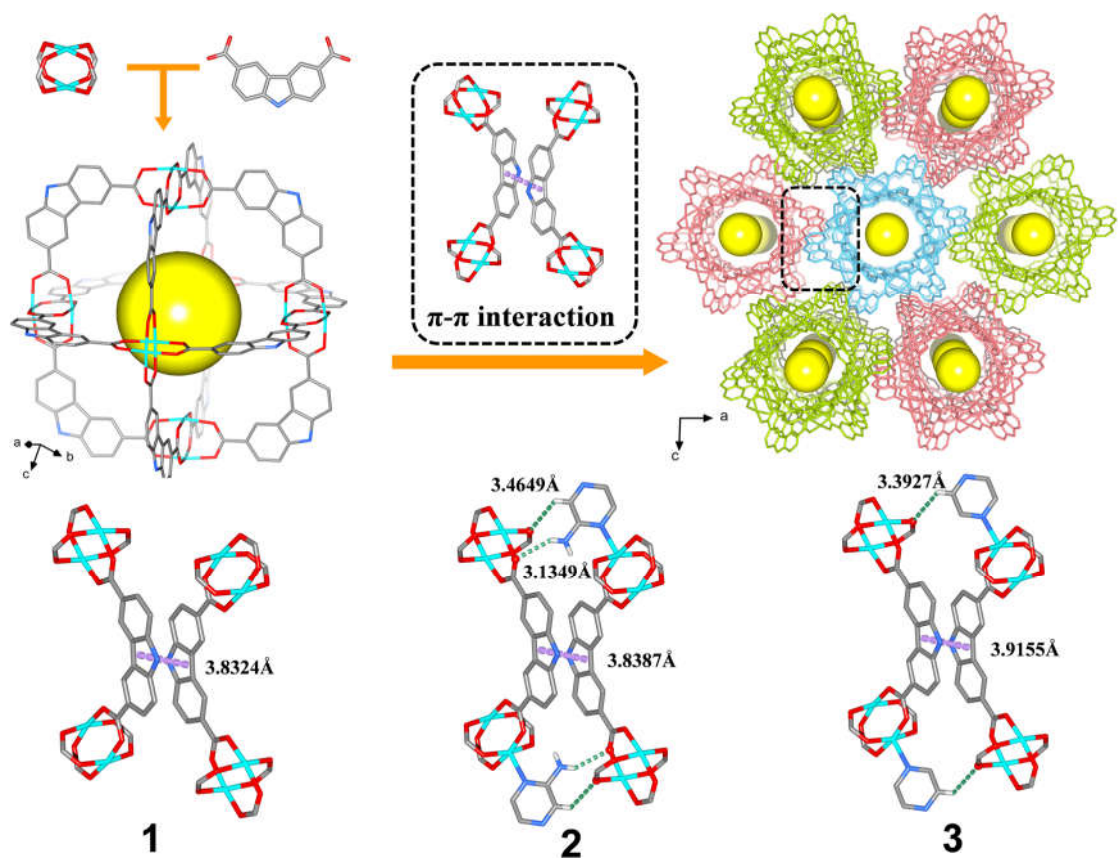
Figure.S2 π-π interaction of compound **1**, **2**, **3** and hydrogen bonding interaction (DA distance**)** of compound **2, 3**
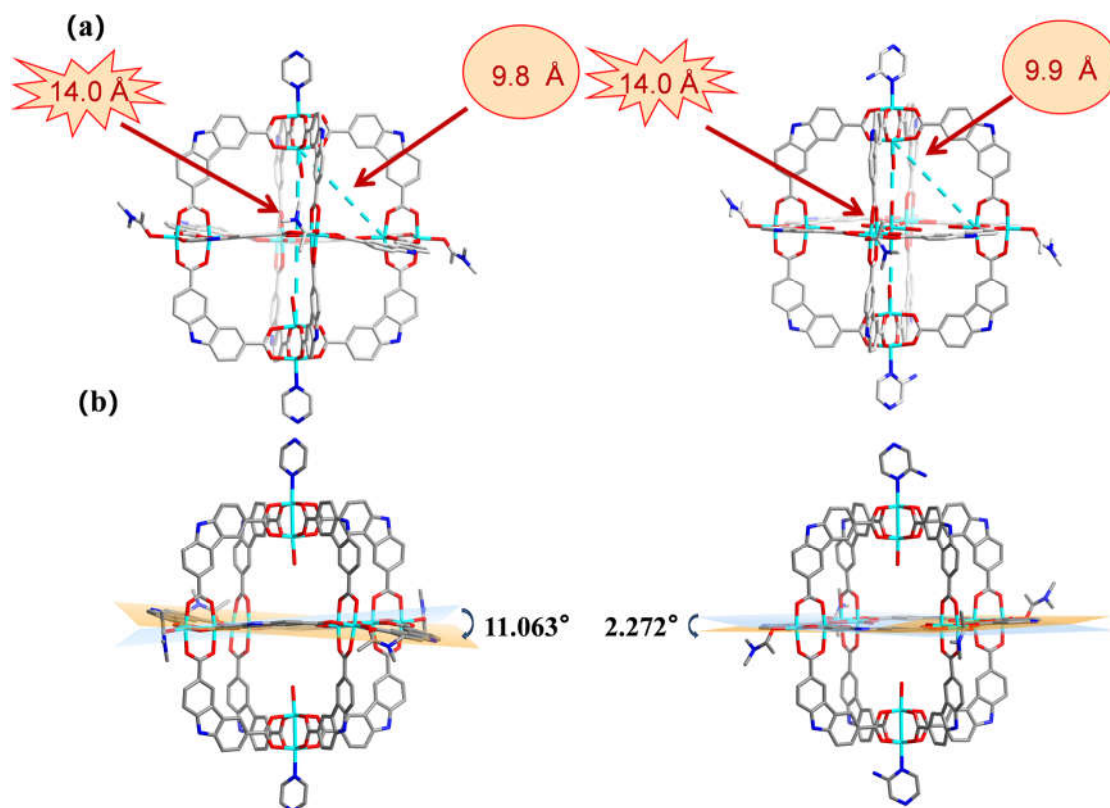
Figure.S3 (a) The angle of the equatorial plane of compound **3** and compound **4**; (b) The cavity dimension and the trigonal windows dimension of compound **3** and compound **4**, green short dashes represent the distance between the atoms
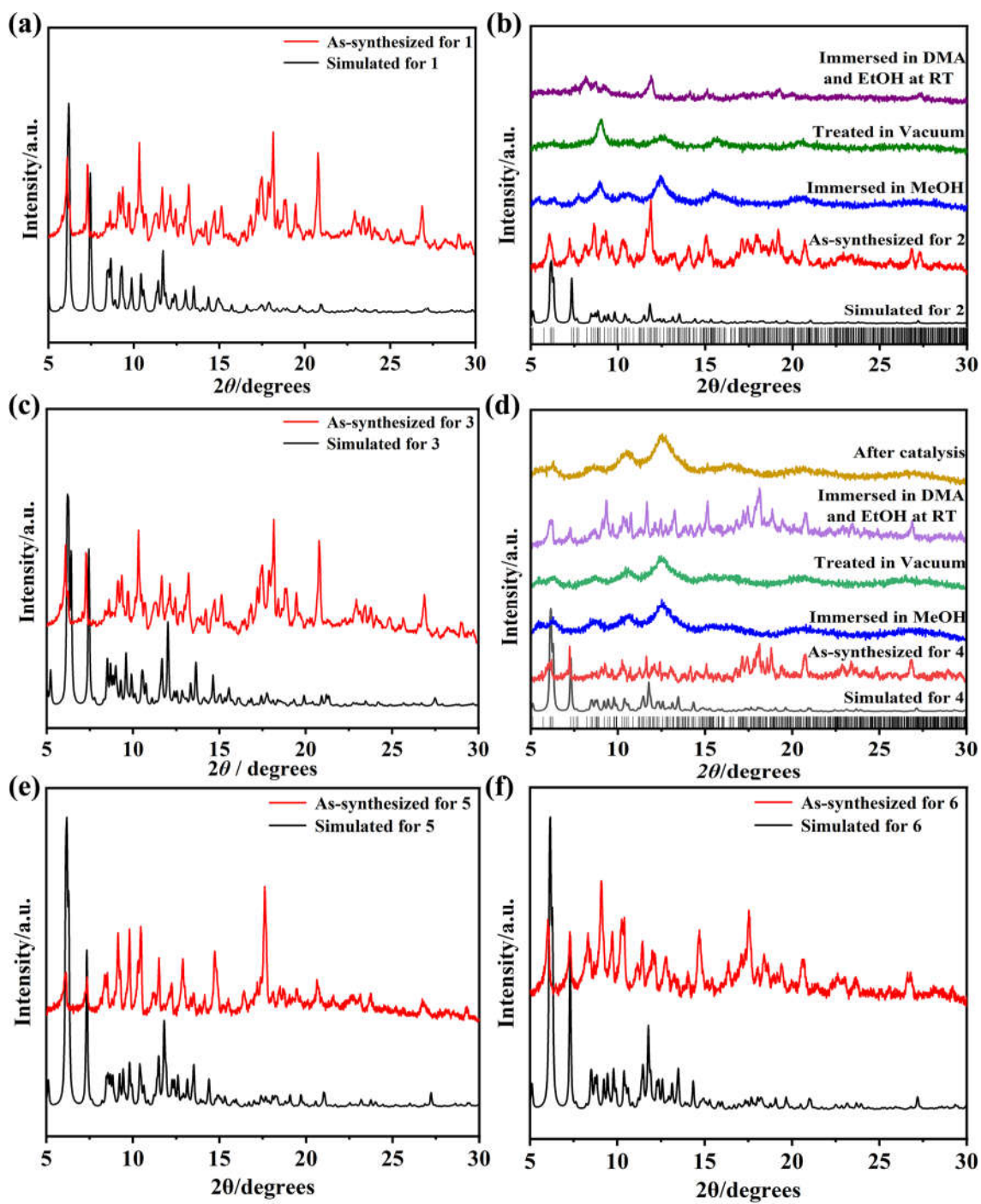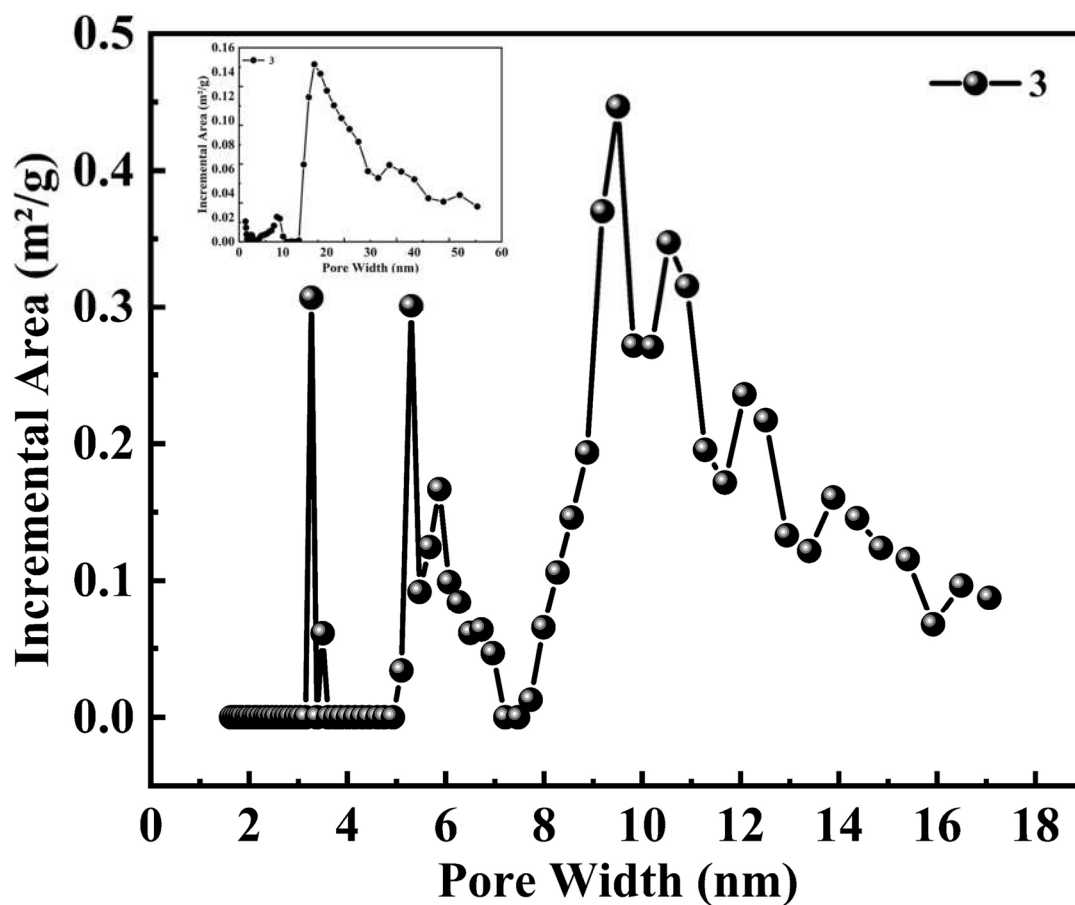
Figure.S4 The powder X-ray diffraction patterns of six compounds.

Figure.S5 Incremental area distribution obtained from N_2 sorption isotherms (N_2 at 77 K NLDFT) for compound **3** (Embedding figures show the pore size distribution analysis of CO_2 adsorption data at 273 K using the NLDFT model.)
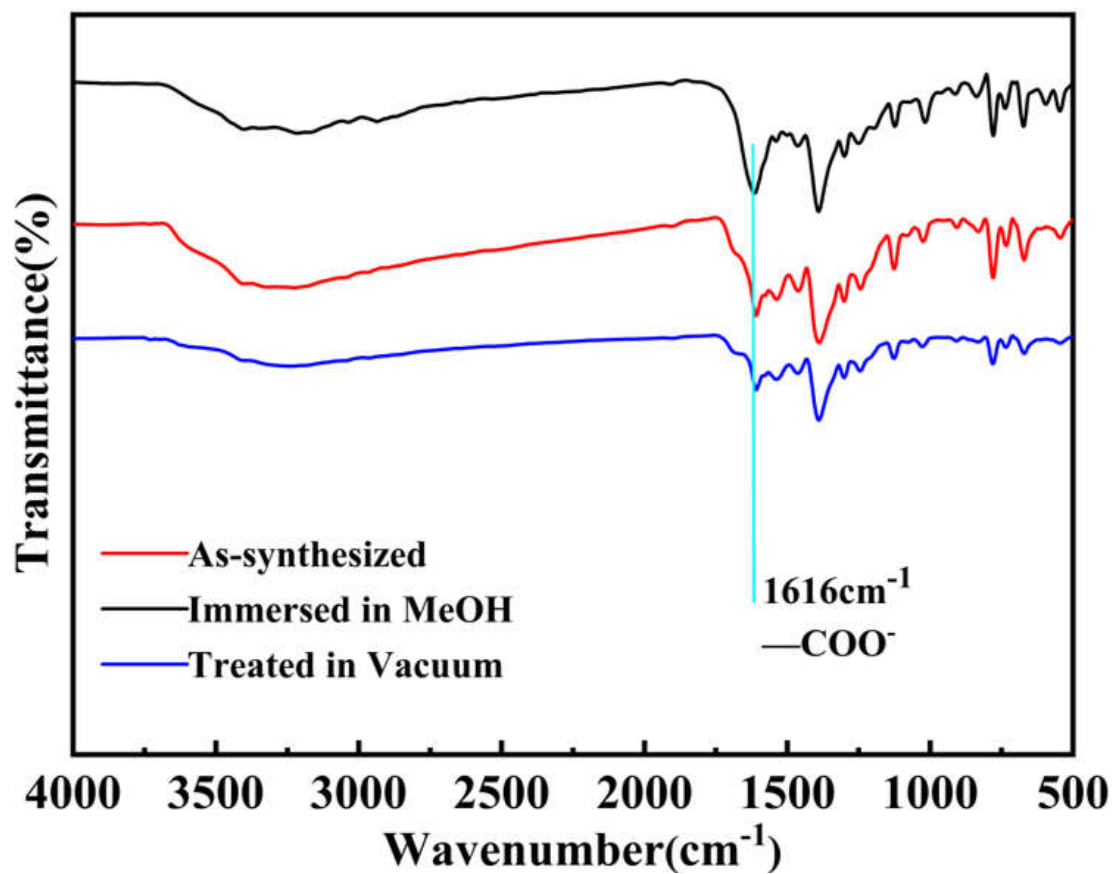
Figure.S6 The infrared spectra of compound **4**
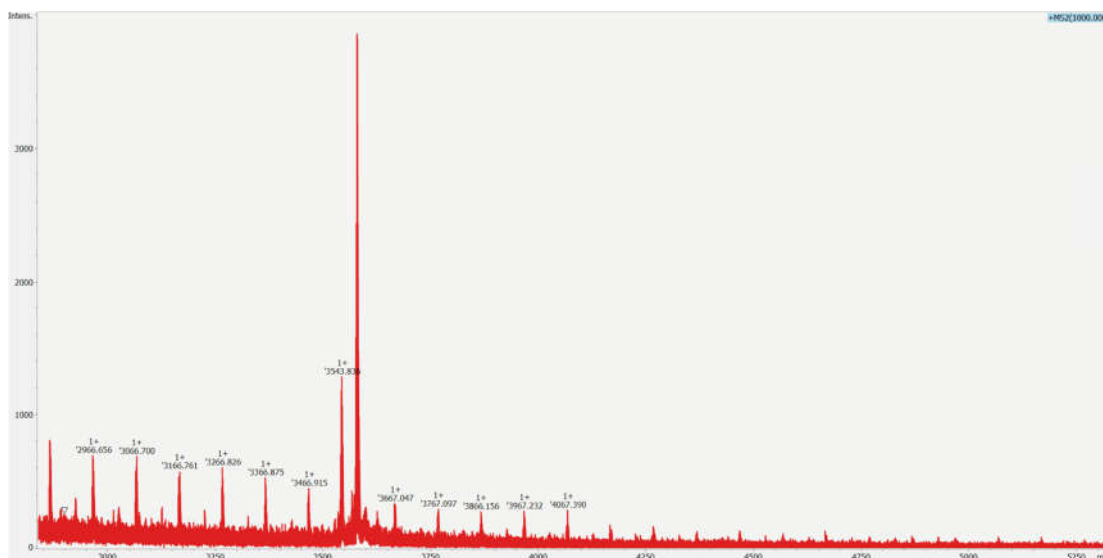
Figure.S7 The mass spectrometry of activated compound **4a**
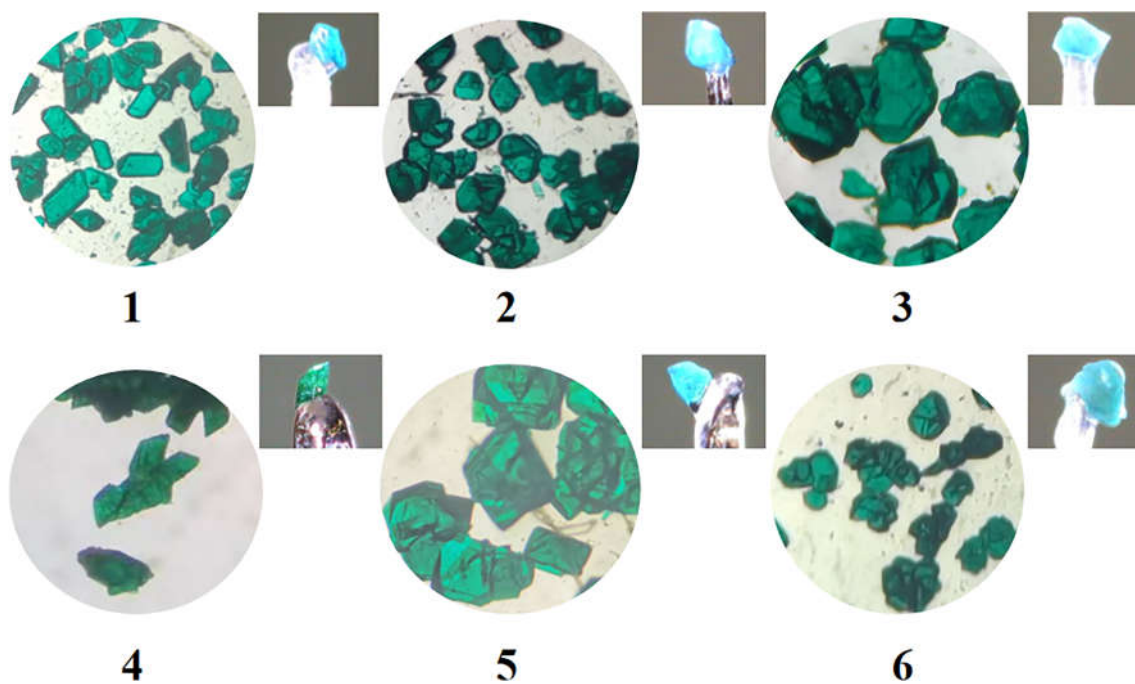
Figure.S8 The single crystal images of compound **1-6**
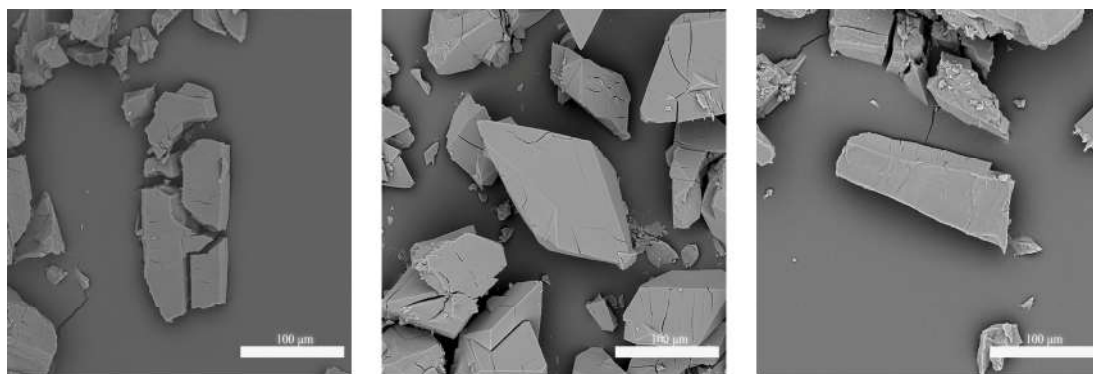
Figure.S9 SEM images of compounds **2**, **4** and **5**
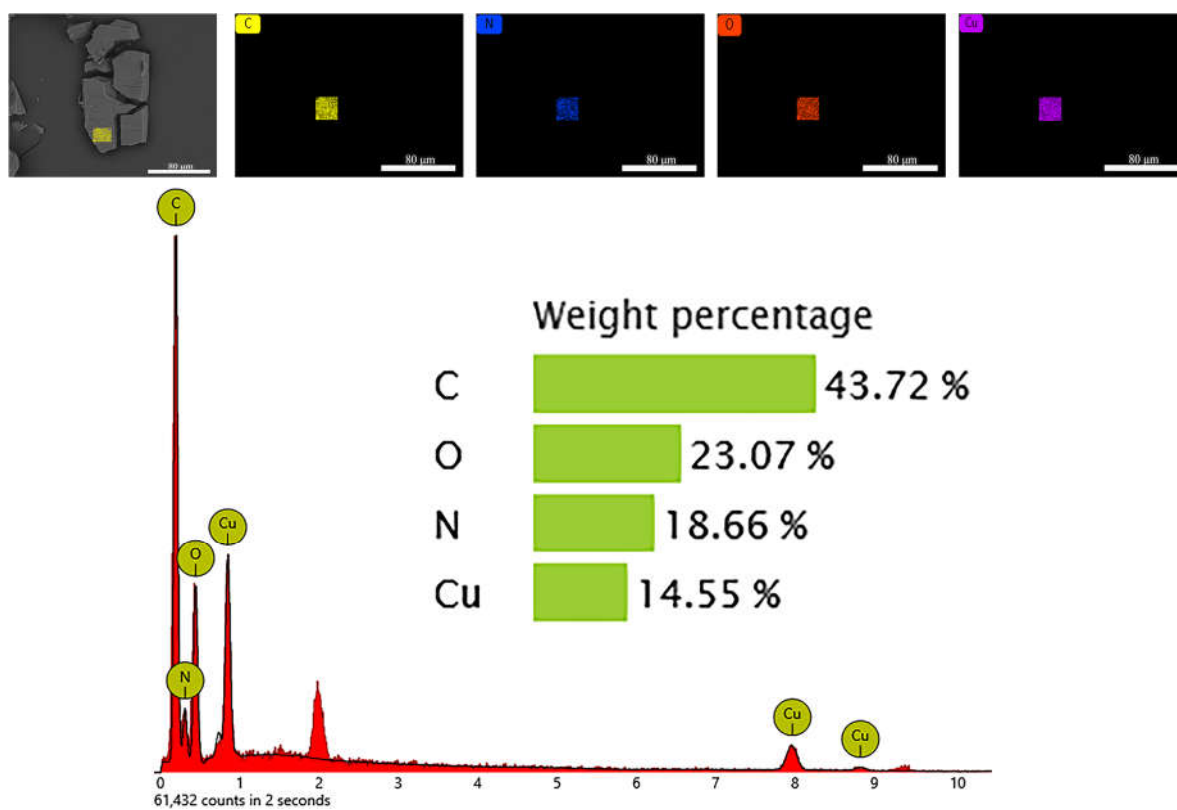
Figure.S10 EDS of compound **2**
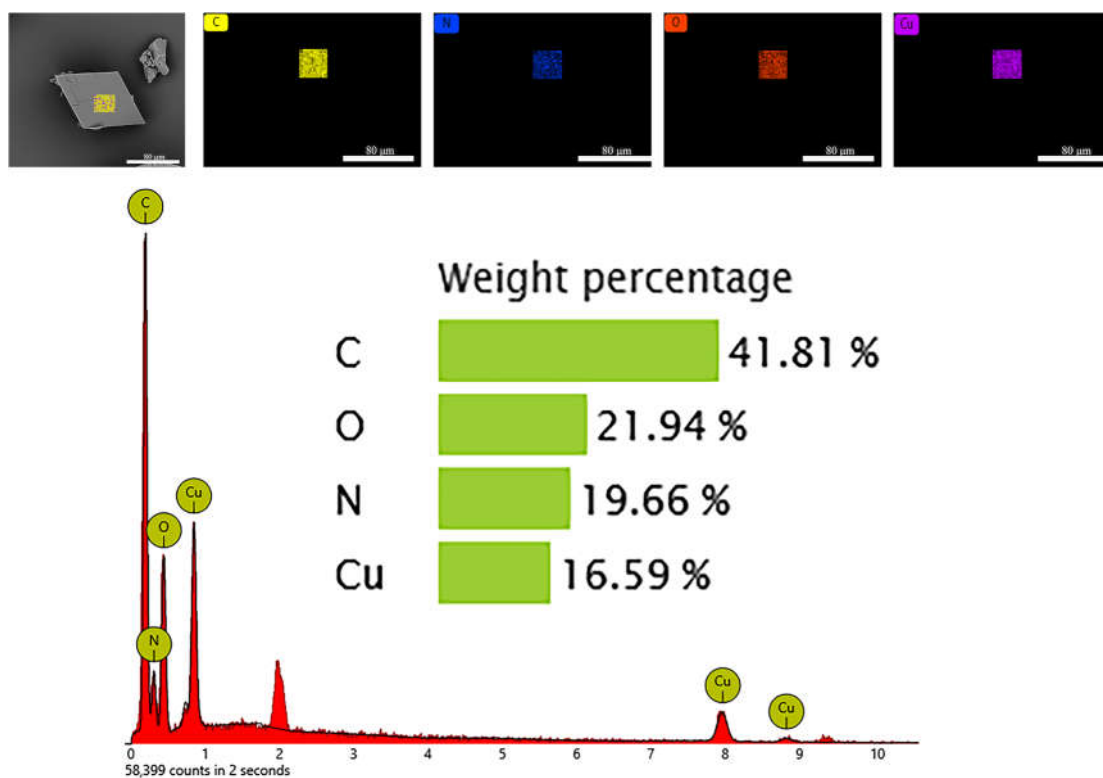
Figure.S11 EDS of compound **4**
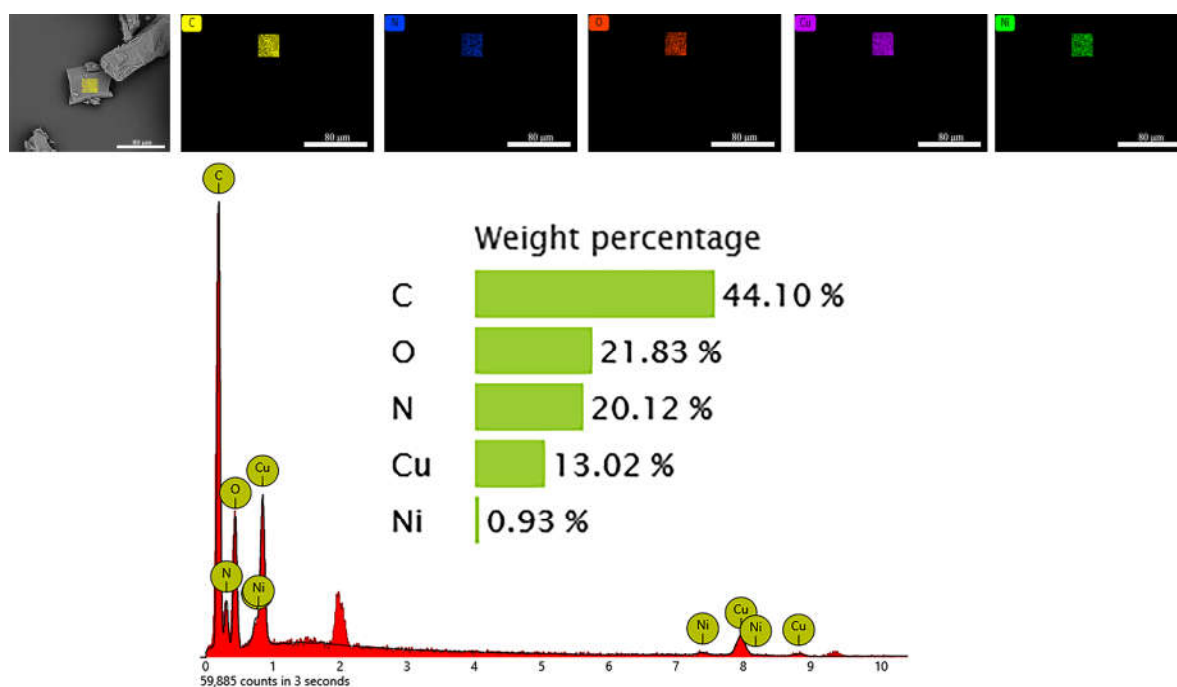
Figure.S12 EDS of compound **5**
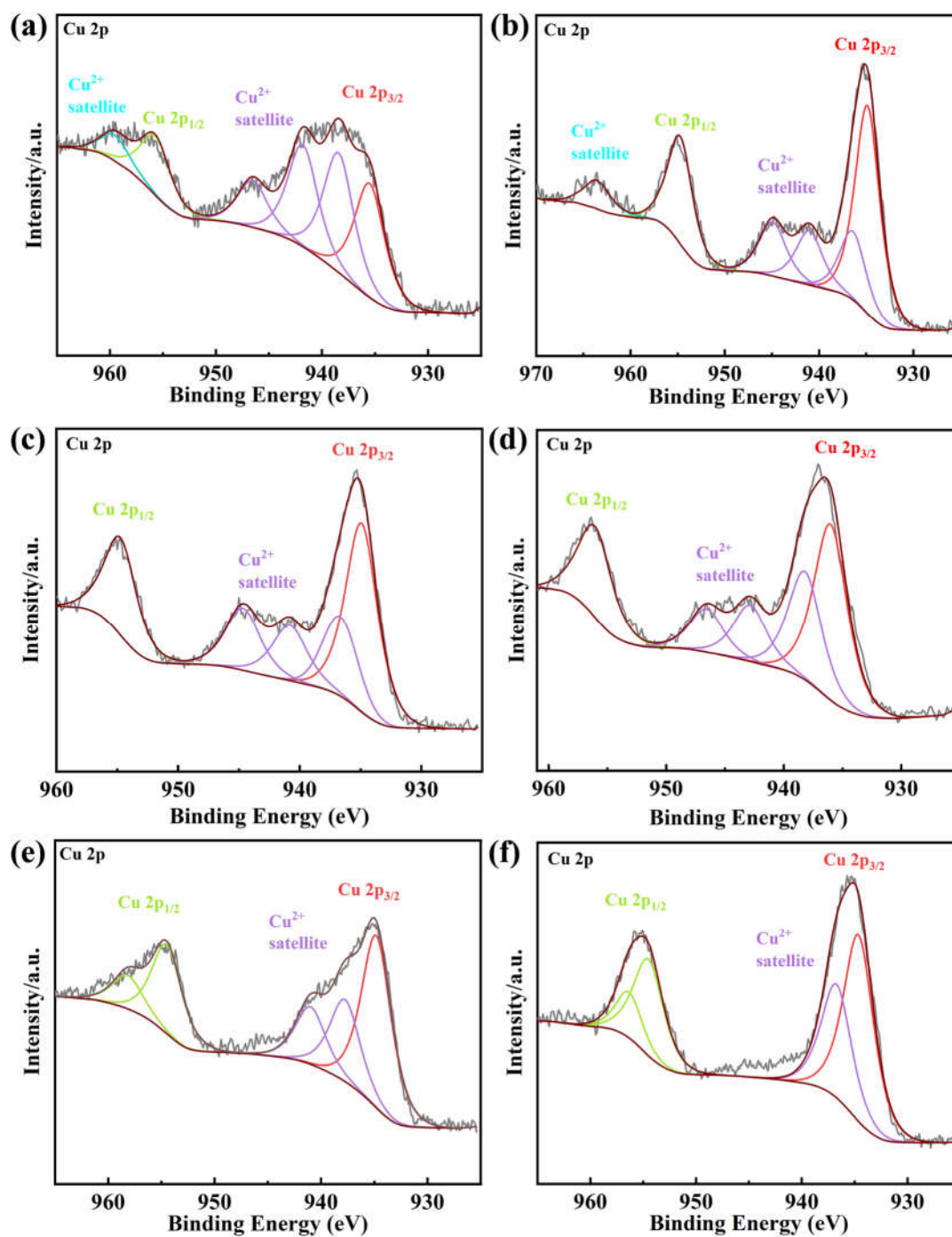
Figure.S13 The XPS of compound **2a, 4a** and **5a.** (a), (c) and (e) are the XPS spectra of compounds **2a**, **4a** and **5a** before catalysis, respectively. (b), (d) and (f) are the XPS spectra of compounds **2a**, **4a** and **5a** after catalysis, respectively.
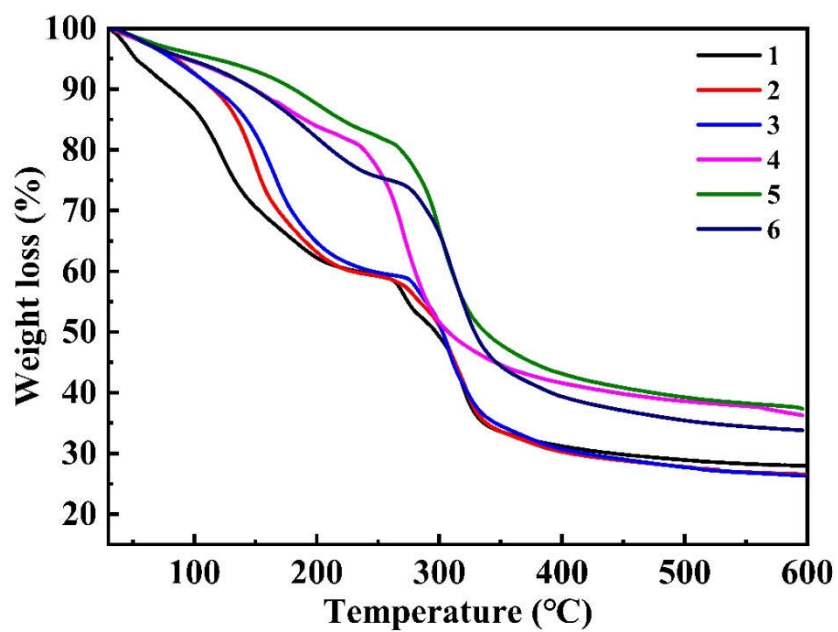
Figure.S14 TGA patterns of compound **1-6**

Additional Results and Discussion

Compounds **5** and **6** have the same structure as compound **4**, with the presence of hydrated ions of nickel hexahydrate in the cavities of compound **5**. After filtering the compound **5** and **6** from the solvent, it was placed in a 65°C oven for drying. Analysed by inductively coupled plasma emission spectroscopy (ICP-OES), we found that the metal ion mass ratio in the structure of compound **5** is 13.1:1, which is consistent with the results of the single-crystal structure analysis. In the cavity of compound **6**, there are hydrated ions of zinc hexahydrate, also analysed by inductively coupled plasma emission spectroscopy (ICP-OES), we found that the mass ratio of metal ions in the structure of compound **6** is 14.6:1, which is in line with the results of single-crystal structural analysis, indicating that there are metal ions in the structure. This is consistent with the results of single crystal structure analysis, indicating the presence of metal hydration ions in the structure.

Table S2: The theoretical and actual values of compounds **5** and **6** in inductively coupled plasma optical emission spectroscopy (ICP-OES).

	Cu:Ni	Cu:Zn
Theoretical value	13:1	12:1
Experimental value	13.1:1	14.6:1

Catalytic Reactions

The ring-opening reactions of styrene oxide with methanol were performed in sealed glassware. The solid catalysts were vacuumed at RT condition. The whole reaction process was conducted under a nitrogen atmosphere. For a typical reaction, the reactant styrene oxide (2 mmol) and a solid catalyst (2-3 mmol%) were stirred in methanol (10 mL) at 328K, respectively. The reaction mixtures were periodically withdrawn at the intervals of 3.5h throughout the reaction. The obtained upper liquid was analyzed by using an Agilent Technologies gas chromatograph (GC-126) equipped with a flame ionization detector (FID) and 0.25mmx30m capillary column. The used catalyst was isolated from reaction mixture by centrifugation. After being washed with methanol for three times, isolated by centrifugation and dried in vacuum, the recovered catalyst was used in the next cycle of reaction.

Some conventional ring-opening catalysts were employed to compare with the Pore-functionalised MOPs. Because the reaction conditions vary from one report to another, it is hard to compare the activity of catalysts directly. On the basis of table S3, nevertheless, it can be tentatively concluded that the compound 5 shows catalytic activity higher than typical MOFs while comparable to some conventional catalysts.

The conversion of the product is calculated as follows:

$$\text{Conversion of styrene oxide } (C_{\text{styrene oxide}}) = \frac{\text{moles of styrene oxide converted}}{\text{moles of styrene oxide in feed}} \times 100\%$$

$$\text{Selectivity of product } (S) = \frac{\text{moles of product}}{\text{moles of styrene oxide converted}} \times 100\%$$
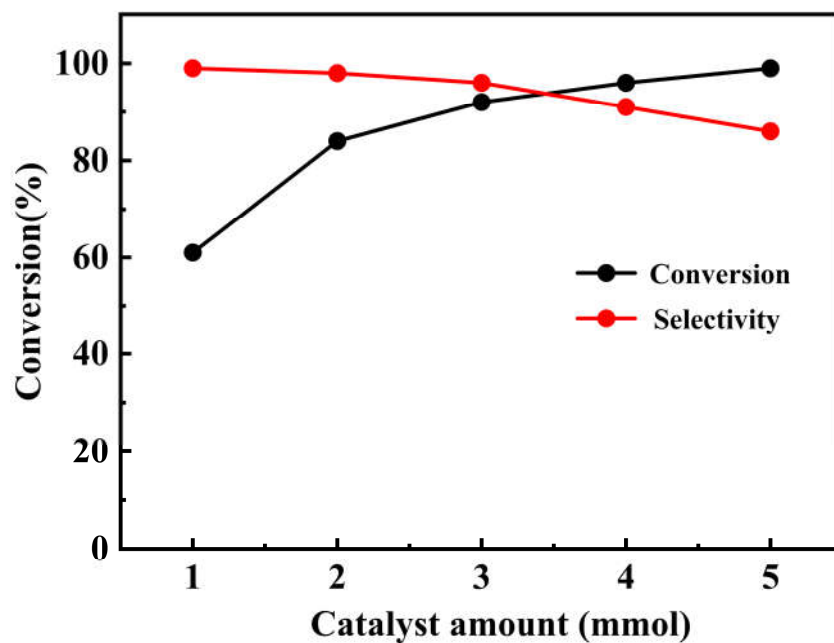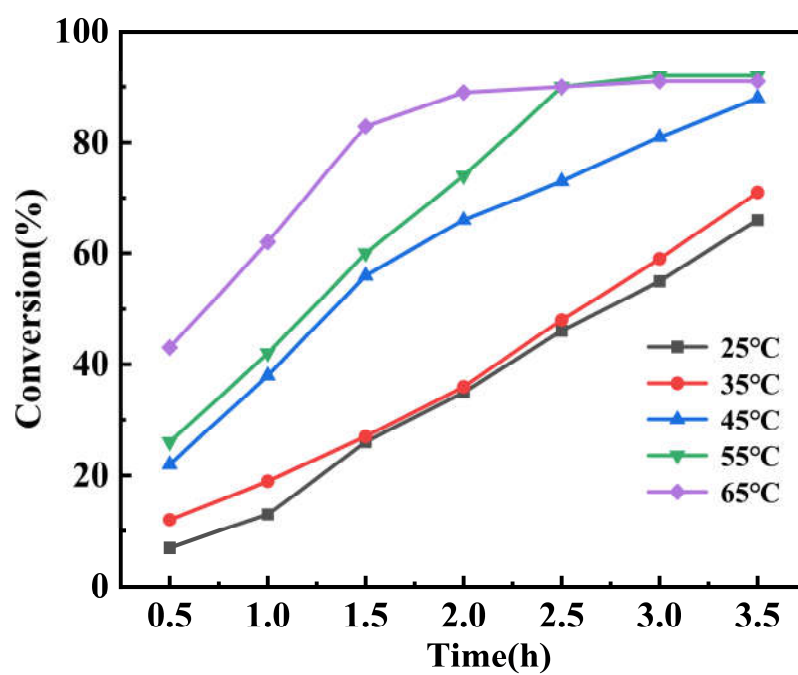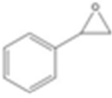
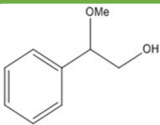**Figure.S15** Effect of amount of catalyst on the reaction

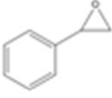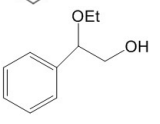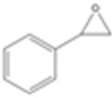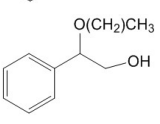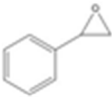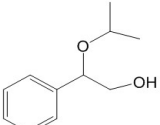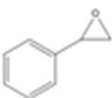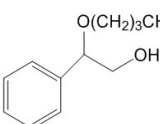**Figure.S16** Effect of different temperature on catalytic reaction

Table S3: Effect of different alcohols on the reaction

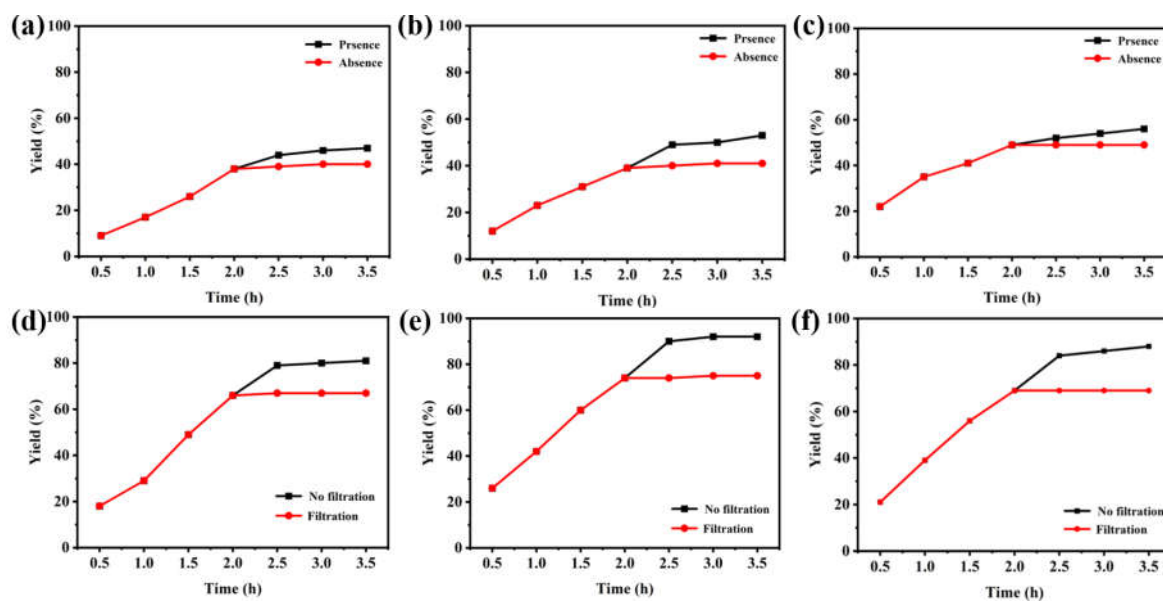| Entry	Reactants Epoxide	Alcohol	Time(h)	Products	Conversion (%)	Selectivity (%)
1		MeOH	3.5		92	99
2		EtOH	3.5		86	99
3		Propanol	3.5		73	98
4		Isopropanol	3.5		54	96
5		n-Butanol	3.5		66	98

Figure.S17 (a)-(f) Time-conversion plot for the filtration test of the ring opening styrene oxide with MeOH catalyzed by compound **1-6**

Table S4: Ring opening styrene oxide with MeOH catalyzed by different catalysts

Entry	Catalyst	Atm	Time	Conversion (%)	Ref
1	MIL-101	N_2	48h	44	7
2	MIL-101-SO_3H	N_2	10min	99	8
3	$Cu(BF_4)_2 \cdot H_2O$	N_2	120min	33	9
4	Eu-MOF	N_2	48h	11	10
5	$[Cu_3(BTC)_2]$	N_2	10min	25	11
6	Cu-MOF	N_2	120min	21	9, 12
7	compound **5**	N_2	3.5h	92	This work

Scheme 1. Proposed Mechanism for Methanolysis of Styrene Oxide in the Presence of compound **4** Catalysts
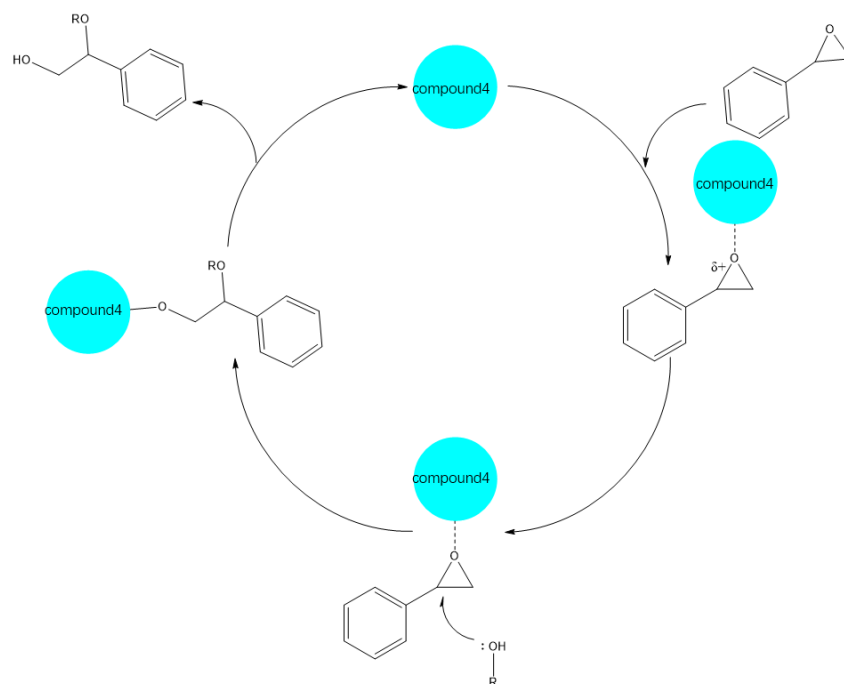
References

1.   D. J. T. Jian-Rong Li, Hong-Cai Zhou, Interconversion between Molecular Polyhedra and Metal-Organic Frameworks, *J. Am. Chem. Soc.*, 2009, 131, 6368–6369.

2.   O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, OLEX2: a complete structure solution, refinement and analysis program, *J. Appl. Crystallogr.*, 2009, 42, 339-341.

3.   L. Palatinus and G. Chapuis, SUPERFLIP– a computer program for the solution of crystal structures by charge flipping in arbitrary dimensions, *J. Appl. Crystallogr.*, 2007, 40, 786-790.

4.   G. M. Sheldrick, A short history of SHELX, *Acta. Crystallographica.*, 2007, 64, 112-122.

5.   A. L. Spek, Single-crystal structure validation with the program PLATON, *J.Appl. Crystallogr.*, 2003, 36, 7-13.

6.   L. Sarkisov and A. Harrison, Computational structure characterisation tools in application to ordered and disordered porous materials, *Mol. Simul.*, 2011, 37, 1248-1257.

7.   L. H. Wee, F. Bonino, C. Lamberti, S. Bordiga and J. A. Martens, Cr-MIL-101 encapsulated Keggin phosphotungstic acid as active nanomaterial for catalysing the alcoholysis of styrene oxide, *Green Chem.*, 2014, 16, 1351-1357.

8.   Y. X. Zhou, Y. Z. Chen, Y. Hu, G. Huang, S. H. Yu and H. L. Jiang, MIL-101-SO$_3$H: A Highly Efficient Brønsted Acid Catalyst for Heterogeneous Alcoholysis of Epoxides under Ambient Conditions, *Chem. Eur. J.*, 2014, 20, 14976-14980.

9.   D. Jiang, A. Urakawa, M. Yulikov, T. Mallat, G. Jeschke and A. Baiker, Size Selectivity of a Copper Metal–Organic Framework and Origin of Catalytic Activity in Epoxide Alcoholysis, *Chem. Eur. J.*, 2009, 15, 12255-12262.

10. S. M. F. Vilela, D. Ananias, J. A. Fernandes, P. Silva, A. C. Gomes, N. J. O. Silva, M. O. Rodrigues, J. P. C. Tomé, A. A. Valente, P. Ribeiro-Claro, L. D. Carlos, J. Rocha and F. A. Almeida

Paz, Multifunctional micro- and nanosized metal–organic frameworks assembled from bisphosphonates and lanthanides, *J. Mater. Chem. C.*, 2014, 2.

11. L. H. Wee, M. R. Lohe, N. Janssens, S. Kaskel and J. A. Martens, Fine tuning of the metal–organic framework $Cu_3(BTC)_2$ HKUST-1 crystal size in the 100 nm to 5 micron range, *J. Mater.*, 2012, 22.

12. D. Jiang, T. Mallat, F. Krumeich and A. Baiker, Copper-based metal-organic framework for the facile ring-opening of epoxides, *J. Catal.*, 2008, 257, 390-395.