

## Electronic Supplementary Information

### Stepwise construction of coordinative linkages and dynamic covalent linkages for a porous metal–organic framework

Shuyin Peng, Yuqian Sun, Qingqing Li, Zhongwen Jiang, Yin Rao, Yichen Wu, Qiaowei Li\*

Department of Chemistry, Collaborative Innovation Center of Chemistry for Energy Materials, and Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials, Fudan University, Shanghai 200433, P. R. China.

\*Email: qwli@fudan.edu.cn

### Contents

S1. Materials and Methods.....	1
S2. Single Crystal Structure of $\text{Ag}_3(\text{PyCA})_3$ .....	3
S3. Structural Modeling of FDM-72.....	5
S4. Porosity Characterization of FDM-72.....	8
S5. Physical Characterizations of the MOF.....	9
S6. Oxidative Potential of the Organic Amines.....	12
References.....	12

## S1. Materials and Methods

AgNO<sub>3</sub>, DMSO, dioxane, aqueous acetic acid solution, methanol, ethanol, isopropanol, and *N,N*-dimethylformamide (DMF) are purchased from Sinopharm Chemical Reagent Co., Ltd. 1,3,5-tris(4-aminophenyl)benzene (TAPB) is purchased from Adamas-Beta Reagent Co., Ltd. 1*H*-pyrazole-4-carbaldehyde (HPyCA) is purchased from Bide Pharmatech Co., Ltd. *N,N*-diethylformamide (DEF) and *p*-phenylenediamine (PA) are purchased from TCI (Shanghai) Development Co., Ltd. Mesitylene, anhydrous acetonitrile, and tetrabutylammonium hexafluorophosphate are purchased from InnoChem Science & Technology Co., Ltd. *p*-Toluenesulfonic acid monohydrate (PTSA) is purchased from Shanghai Macklin Biochemical Co., Ltd. Nafion is purchased from Sigma Aldrich Co., Ltd. All solvents and reagents are used without further purification.

Powder X-ray diffraction (PXRD) measurement is conducted by a Bruker AXS D8 Advance diffractometer operated at 1600 W power (40 kV, 40 mA) using Cu *K*α radiation. The simulated PXRD patterns are calculated using Mercury 3.10.3 software from the corresponding single crystal structures. Optical photographs are taken by an AOSVI ASV0870-HK830 optical microscope. <sup>1</sup>H NMR measurements are performed on a Bruker AVANCE III HD NMR analyzer (400 MHz) at 298 K. Before the <sup>1</sup>H NMR measurement, 4.0 mg activated metal–organic framework (MOF) sample is digested in 100 μL DCl (20 wt.% in D<sub>2</sub>O) and 0.5 mL DMSO-*d*<sub>6</sub>, and AgCl is further removed by filtration. Fourier transform infrared (FT-IR) measurements of FDM-72 and its building units (Ag<sub>3</sub>(PyCA)<sub>3</sub> and TAPB) are performed on a ThermoFisher Nicolet iS 10 Spectrometer. X-ray photoelectron spectroscopy (XPS) of FDM-72 is performed on a Kratos Axis Ultra X-ray photoelectron spectrometer (Al *K*α source).

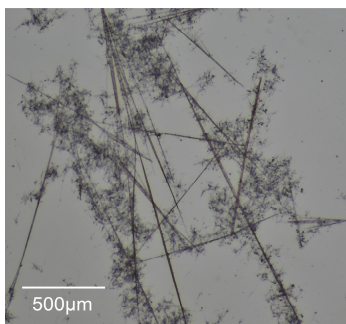
Diffuse reflectance UV-vis spectra of FDM-72 and its building units (Ag<sub>3</sub>(PyCA)<sub>3</sub> and TAPB) are measured on a Lambda 365 UV-vis spectrophotometer. Optical band gap (*E*<sub>g</sub>) of the samples are calculated by the following equation according to the Kubelka–Munk theory:<sup>1</sup>

$$(Ah\nu)^2 = C(h\nu - E_g)$$

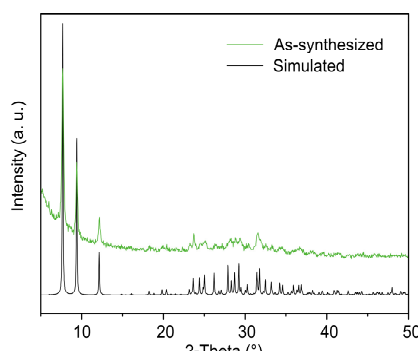
In the equation, *A* refers to the absorbance, *h* is the Planck constant, *ν* refers to the frequency, and *C* is a proportionality constant. *E*<sub>g</sub> is obtained from the extrapolated value of the linear fitting to the curve of (*Ahν*)<sup>2</sup> versus *hν* at *A* = 0.

### Synthesis of tris(μ<sub>2</sub>-4-carboxaldehyde-pyrazolato-*N,N*)-tri-silver (Ag<sub>3</sub>(PyCA)<sub>3</sub>)

AgNO<sub>3</sub> (49.0 mg, 0.30 mmol) and HPyCA (27.0 mg, 0.30 mmol) were dissolved in a mixture of 5.0 mL DEF, 4.45 mL methanol and 0.55 mL H<sub>2</sub>O in a 20-mL vial. After the capped vial was placed in an oven at 100 °C for 12 hours, a mixture of colorless single crystals and black powder were obtained (Fig. S1). The mixture was collected and further immersed in DMSO. Methanol was added to the supernatant after centrifugation, and white powder was collected after filtration. The powder was dried in vacuo at 100 °C for 12 h. Yield: 42% based on Ag. Formula: Ag<sub>3</sub>(C<sub>4</sub>H<sub>3</sub>N<sub>2</sub>O)<sub>3</sub>. FT-IR (KBr 4000–400 cm<sup>-1</sup>): *ν* = 3435 (w), 1660 (vs), 1533 (s), 1414 (s), 1385 (w), 1333 (w), 1201 (s), 1031 (s), 863 (w), 764 (s), and 622 (s) (Fig. S3).



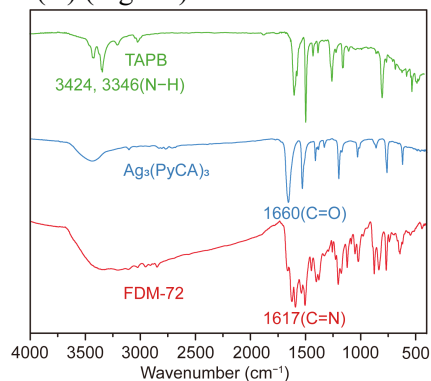
**Fig. S1** Optical image of a mixture of  $\text{Ag}_3(\text{PyCA})_3$  and Ag particles.



**Fig. S2** PXRD pattern of as-synthesized  $\text{Ag}_3(\text{PyCA})_3$ , along with the simulated pattern.

### Synthesis of FDM-72

$\text{Ag}_3(\text{PyCA})_3$  (18.0 mg, 0.03 mmol) and TAPB (21.0 mg, 0.06 mmol) were added to a mixture of 0.5 mL mesitylene, 0.5 mL dioxane, and 0.1 mL aqueous acetic acid solution (9 M) in a 4-mL vial. The capped vial was placed in an oven at 50 °C for 72 h and brown crystalline powder was obtained. The sample was solvent exchanged with DMF 3 times per day for 3 days, followed by solvent exchange with ethanol 3 times per day for 3 days. Activated FDM-72 was obtained by supercritical  $\text{CO}_2$  drying and heating at 100 °C in vacuo for 12 h. Yield: 70% based on Ag. Elemental analysis is carried out by a vario EL cube elemental analyzer. Formula of FDM-72 is proposed to be  $\text{Ag}_{2.73}(\text{C}_{36}\text{H}_{24}\text{N}_9)_{0.91}(\text{C}_{24}\text{H}_{15}\text{N}_3)_{0.09}(\text{H}_2\text{O})_{10}$  (please see the vacancy analysis for more information). Elemental analysis: Calc. (%) C = 40.49, H = 4.20, N = 11.44; Found (%) C = 39.98, H = 3.74, N = 11.22. FT-IR (KBr 4000–400  $\text{cm}^{-1}$ ):  $\nu = 3430$  (w), 1621 (vs), 1589 (vs), 1534 (s), 1501 (vs), 1444 (w), 1399 (w), 1375 (w), 1199 (s), 1171 (w), 1117 (w), 871 (w), 829 (w), and 761 (w) (Fig. S3).



**Fig. S3** FT-IR spectra of FDM-72 and its building units ( $\text{Ag}_3(\text{PyCA})_3$  and TAPB).

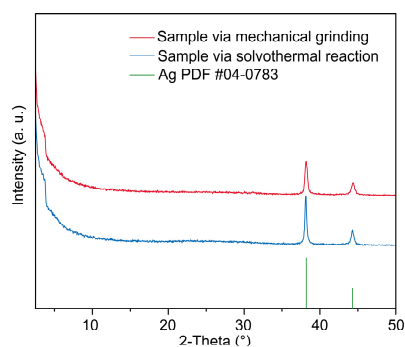
## MOF construction attempts based on $\text{Ag}_3(\text{PyCA})_3$ and PA

The following representative preparation methods were attempted to construct extended structures based on  $\text{Ag}_3(\text{PyCA})_3$  and PA.

(1) Mechanical grinding: PTSA (162 mg, 0.84 mmol) and PA (16.2 mg, 0.15 mmol) mixture were firstly ground for 5 mins.  $\text{Ag}_3(\text{PyCA})_3$  (60.9 mg, 0.10 mmol) was then added, and the mixture was ground for another 10 mins. In addition, 60  $\mu\text{L}$   $\text{H}_2\text{O}$  was added, and the mixture was ground for additional 5 minutes. After standing at room temperature for 1 h, the mixture was transferred to a 20-mL vial and heated at 170  $^\circ\text{C}$  for 15 mins. The powder was then soaked in  $\text{H}_2\text{O}$  for 12 h.

(2) Solvothermal reaction: (a)  $\text{Ag}_3(\text{PyCA})_3$  (18.3 mg, 0.03 mmol) and PA (5.4 mg, 0.05 mmol) were added in a mixture of mesitylene, dioxane, and 0.1 mL aqueous acetic acid solution (6 M) in a 4-mL vial. The total volume of mesitylene and dioxane is 1.0 mL, with the volume ratio between mesitylene and dioxane being from 1:4 to 4:1. The capped vial was placed in an oven at 50  $^\circ\text{C}$  for 72 h. (b)  $\text{Ag}_3(\text{PyCA})_3$  (36.5 mg, 0.06 mmol) and PA (10.8 mg, 0.10 mmol) were added to a mixture of mesitylene, dioxane, and 0.1 mL aqueous acetic acid solution (6 M) in a Schlenk flask. The total volume of mesitylene and dioxane is 1.0 mL, with the volume ratio between mesitylene and dioxane being from 1:4 to 4:1. After flash-frozen at 77 K in a liquid  $\text{N}_2$  bath and degassed with three freeze-pump-thaw cycles, the Schlenk flask was placed in an oven at 120  $^\circ\text{C}$  for 72 h.

All the attempts resulted in formation of Ag particles confirmed by PXRD (Fig. S4).



**Fig. S4** Representative PXRD patterns of products via mechanical grinding and solvothermal reaction.

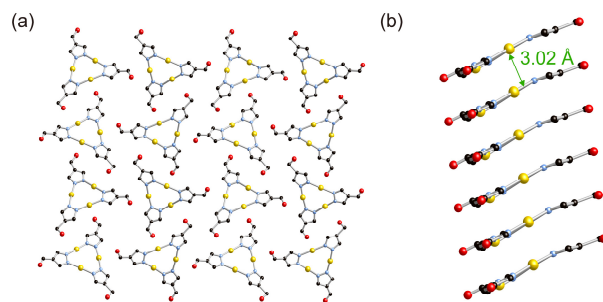
## S2. Single Crystal Structure of $\text{Ag}_3(\text{PyCA})_3$

Crystal of  $\text{Ag}_3(\text{PyCA})_3$  coated with Paratone oil on a Cryoloop pin at 173 K under  $\text{N}_2$  flow was mounted on a Bruker D8 Venture MetalJet X-ray diffractometer equipped with a Photon II detector and operated at 200 W (70 kV, 2.86 mA) to generate gallium  $K\alpha$  radiation ( $\lambda = 1.34138$  Å). The crystal structure was solved by Direct Methods and refined on  $F^2$  by full-matrix least squares using SHELX-2018<sup>2</sup> program in Olex2.<sup>3</sup> Details of the crystal data collection, structure solution, and refinement are given in Table S1. Deposition number 2307737 contains the

supplementary crystallographic data for Ag<sub>3</sub>(PyCA)<sub>3</sub>. The data is provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

**Table S1** Crystal data and structure refinement for the Ag<sub>3</sub>(PyCA)<sub>3</sub> complex.

Name	Ag <sub>3</sub> (PyCA) <sub>3</sub>
Empirical formula	Ag <sub>24</sub> C <sub>96</sub> H <sub>72</sub> N <sub>48</sub> O <sub>24</sub>
Formula weight	4870.89
Temperature	173.15 K
Wavelength	1.34138 Å
Crystal system	Orthorhombic
Space group	<i>Fdd2</i>
Unit cell dimensions	$a = 45.975(3)$ Å, $b = 37.787(3)$ Å, $c = 3.7540(3)$ Å
Volume	6521.7(8) Å <sup>3</sup>
Z	2
Density (calculated)	2.480 Mg/m <sup>3</sup>
Absorption coefficient	19.676 mm <sup>-1</sup>
<i>F</i> (000)	4608
Crystal size	0.12 × 0.11 × 0.10 mm <sup>3</sup>
Theta range for data collection	3.916 to 52.377°
Index ranges	-54 ≤ <i>h</i> ≤ 54, -44 ≤ <i>k</i> ≤ 44, -4 ≤ <i>l</i> ≤ 4
Reflections collected	24166
Independent reflections	2751 [ <i>R</i> (int) = 0.0785]
Completeness to theta = 52.377 °	99.0 %
Absorption correction	None
Max. and min. transmission	0.7503 and 0.3975
Refinement method	Full-matrix least-squares on <i>F</i> <sup>2</sup>
Data / restraints / parameters	2751 / 6 / 218
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.160
Final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0395, w <i>R</i> <sub>2</sub> = 0.1097
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.0495, w <i>R</i> <sub>2</sub> = 0.1117
Absolute structure parameter	0.06(4)
Extinction coefficient	n/a
Largest diff. peak and hole	1.868 and -0.923 e.Å <sup>-3</sup>



**Fig. S5** (a) Ball-and-stick illustration of  $\text{Ag}_3(\text{PyCA})_3$  single crystal structure. (b) Side view showing the packing of  $\text{Ag}_3(\text{PyCA})_3$  with an intermolecular distance of 3.02 Å. Ag, yellow; C, black; N, blue; O, red.

### S3. Structural Modeling of FDM-72

Considering that both  $\text{Ag}_3(\text{PyCA})_3$  and TAPB can serve as  $C_3$  building units, we modeled FDM-72 as a two-dimensional (2D) structure of honeycomb layers with hexagonal crystal system. We first conducted geometry optimization to yield the unit cell parameters of the eclipsed model:  $a = 24.6101 \text{ \AA}$ ,  $c = 3.7033 \text{ \AA}$ , with the space group of  $P\bar{6}$ . Based on the simulated and the experimental PXRD pattern, Pawley method was applied to further refine the eclipsed model:  $a = 24.0661 \text{ \AA}$ ,  $c = 4.2981 \text{ \AA}$ ,  $R_{\text{wp}} = 7.29\%$ , and  $R_{\text{p}} = 5.85\%$ . It should be noted that the modeled  $c$  value is larger than the expected  $\pi$ - $\pi$  interaction distance, indicating unsatisfied quality of the PXRD data, although similar values in isostructural MOFs was reported.<sup>4</sup>

A staggered packing model of FDM-72 was also constructed by operating an additional translation between neighboring layers by  $a/2$  and  $b/2$ . After geometry optimization, the model yielded the unit cell parameters of  $a = 24.5076 \text{ \AA}$ ,  $c = 6.8237 \text{ \AA}$ , with the space group of  $P6_3$ . Pawley refinement resulted in a refined unit cell of  $a = 23.7252 \text{ \AA}$ ,  $c = 6.5299 \text{ \AA}$ ,  $R_{\text{wp}} = 8.15\%$ ,  $R_{\text{p}} = 6.44\%$ .

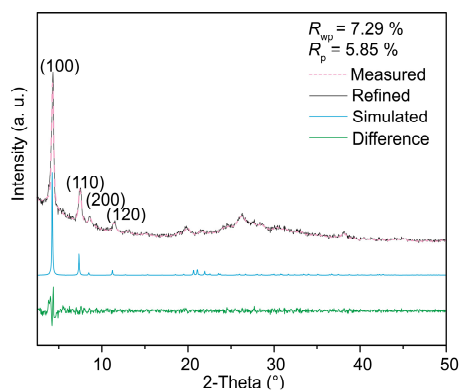
**Table S2** Unit cell parameters and atomic coordinates of the eclipsed model of FDM-72 after the Pawley refinement.

FDM-72 with eclipsed packing: $P\bar{6}$ , $a = 24.0661 \text{ \AA}$ , $c = 4.2981 \text{ \AA}$ , $V = 2155.85 \text{ \AA}^3$			
Atom Name	x	y	z
Ag1	0.56976	0.26185	0.5000
C1	0.56619	0.42810	0.5000
C2	0.50082	0.38638	0.5000
C3	0.45394	0.40725	0.5000
C4	0.49095	0.32473	0.5000
C5	0.29408	0.60073	0.5000
C6	0.36066	0.62624	0.5000
C7	0.38967	0.58332	0.5000
C8	0.35118	0.51539	0.5000
C9	0.37880	0.47653	0.5000
C10	0.44535	0.50444	0.5000
C11	0.48389	0.57036	0.5000
C12	0.45711	0.60959	0.5000
H1	0.59061	0.48001	0.5000
H2	0.40311	0.37311	0.5000
H3	0.44546	0.28031	0.5000
H4	0.26454	0.55051	0.5000
H5	0.29968	0.48992	0.5000
H6	0.34798	0.42514	0.5000
H7	0.53552	0.59130	0.5000
H8	0.49139	0.65996	0.5000
N1	0.47724	0.46860	0.5000
N2	0.54887	0.32918	0.5000
N3	0.59565	0.39390	0.5000

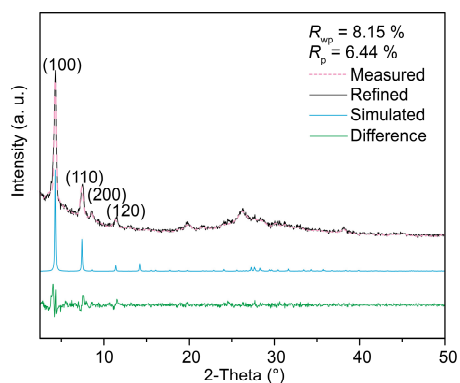
**Table S3** Unit cell parameters and atomic coordinates of the staggered model of FDM-72 after the Pawley refinement.

FDM-72 with staggered packing: $P6_3$ , $a = 23.7252 \text{ \AA}$ , $c = 6.5299 \text{ \AA}$ , $V = 3549.38 \text{ \AA}^3$			
Atom Name	x	y	z
Ag1	0.89979	-0.05982	0
C1	0.92583	0.11919	0
C2	0.86062	0.08537	0
C3	0.81827	0.11132	0
C4	0.84295	0.02222	0
C5	0.63444	0.26747	0
C6	0.70057	0.30084	0
C7	0.73623	0.26665	0
C8	0.70494	0.19993	0
C9	0.73791	0.16798	0
C10	0.80404	0.20172	0
C11	0.8325	0.26796	-0.00002
C12	0.79814	0.29582	0
H1	0.96155	0.17382	0
H2	0.76331	0.07724	0
H3	0.79296	-0.02362	0
H4	0.60695	0.21199	0
H5	0.64949	0.17049	0
H6	0.7106	0.1125	0
H7	0.88781	0.29949	-0.00005
H8	0.82747	0.35127	0.00002
N1	0.84061	0.17085	0
N2	0.89527	0.01748	0
N3	0.9474	0.07843	0





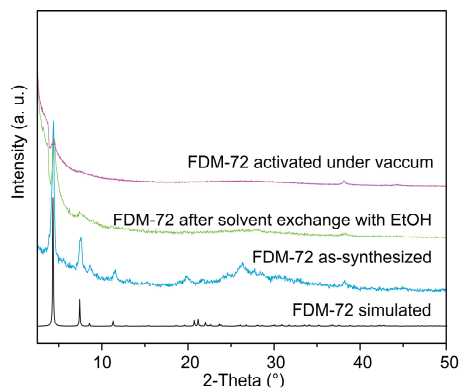
**Fig. S6** Refinement of the eclipsed structural model based on the measured PXRD pattern using the Pawley method. The difference plot is indicated in green.



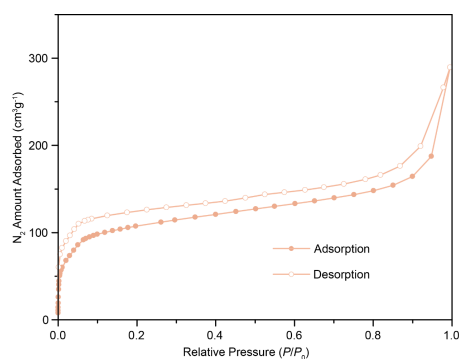
**Fig. S7** Refinement of the staggered structural model based on the measured PXRD pattern using the Pawley method. The difference plot is indicated in green.

#### S4. Porosity Characterization of FDM-72

N<sub>2</sub> adsorption measurements are performed on a Micromeritics ASAP2020 gas adsorption analyzer at 77 K. FDM-72 sample was degassed at 100 °C in vacuo for 12 h before measurement.



**Fig. S8** PXRD patterns of FDM-72 through different stages of activation.

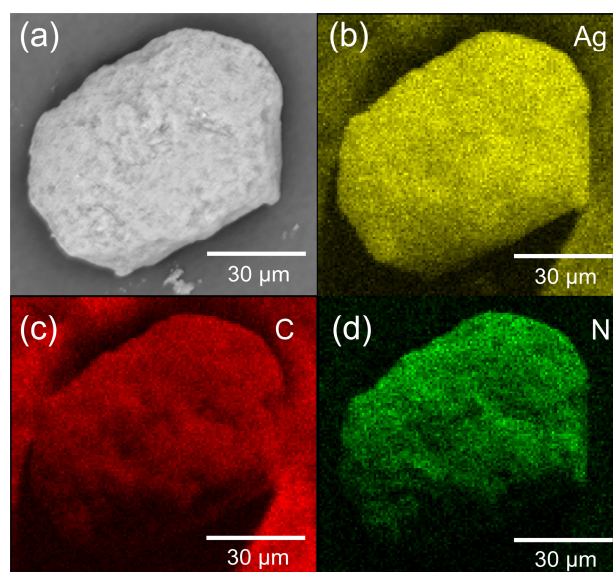


**Fig. S9** 77 K N<sub>2</sub> adsorption (filled symbol) and desorption (open symbol) isotherms for FDM-72. 42 adsorption data points ( $P/P_0$  from  $3.93 \times 10^{-5}$  to 0.99) and 31 desorption data points were collected. Five continual points at the  $P/P_0$  range from  $7.01 \times 10^{-2}$  to  $1.18 \times 10^{-1}$  were used for Brunauer–Emmett–Teller (BET) surface area calculation. The specific BET surface area of FDM-72 is  $395 \text{ m}^2 \text{ g}^{-1}$ , with a correlation coefficient  $R$  being 0.999900. The  $C$  constant in the BET equation is 294.879.

Pore distribution of FDM-72 is analyzed using the nonlocal density functional theory (NLDFT) adsorption model from the N<sub>2</sub> adsorption data ( $P/P_0 = 10^{-5}$ –0.99) at 77 K (calculation model: N<sub>2</sub> at 77 K on silica (cylinder pore, NLDFT adsorption branch model)). The fitting error between the experimental isotherm and that based on NLDFT model is 0.982%.

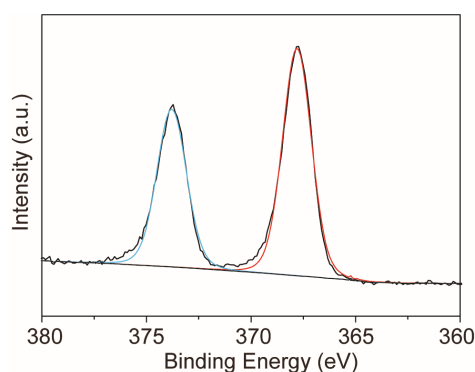
## S5. Physical Characterizations of the MOF

Scanning electronic microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX) mapping images of FDM-72 are collected using a Phenom ProX scanning electronic microscope. ~2 mg MOF sample is immersed in 5 mL MeOH and then drop-casted at the SEM stage.



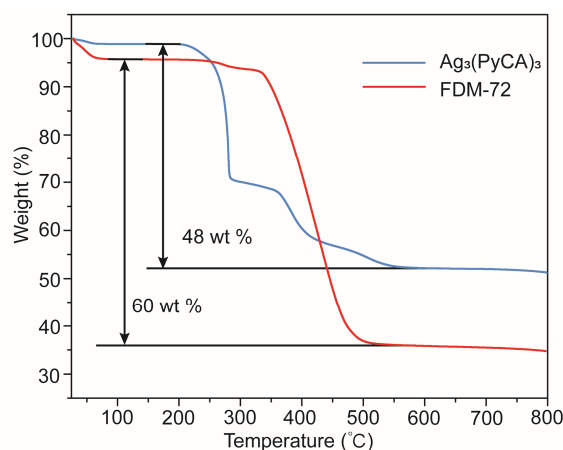
**Fig. S10** (a) Representative SEM image and (b–d) corresponding EDX mapping of FDM-72 on carbon-coated grid.

Before the XPS measurement, FDM-72 sample is degassed at 100 °C in vacuo for 12 h. The binding energy is internal referenced by the aliphatic C (1s) (284.8 eV).



**Fig. S11** High-resolution XPS profile of Ag 3d. The Ag 3d<sub>5/2</sub> and Ag 3d<sub>3/2</sub> sharp peaks at 367.8 and 373.9 eV suggest the oxidation state of Ag in FDM-72 is +1.

Thermogravimetric analysis (TGA) was performed on a TA Discovery SDT 650 from 25 to 800 °C with a heating rate of 10 °C min<sup>-1</sup> under air flow.

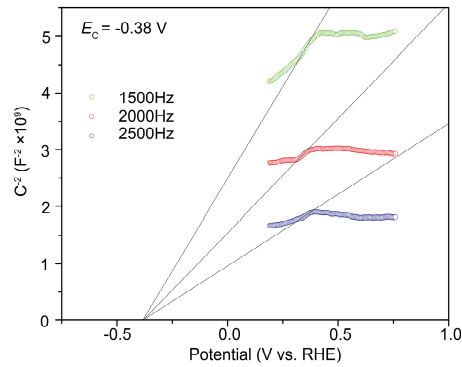


**Fig. S12** TGA curves of FDM-72 and Ag<sub>3</sub>(PyCA)<sub>3</sub> under air flow. For FDM-72, no obvious weight loss is observed between 80 and 330 °C. The material loses 60 wt% from 330 to 510 °C due to the MOF decomposition. The residual weight (35 wt%) is close to the theoretical value (36 wt% for Ag<sub>2</sub>O as the residue). For Ag<sub>3</sub>(PyCA)<sub>3</sub>, 48 wt% is lost at 200–560 °C, and the residual 52 wt% corresponds to the theoretical value (55 wt% for Ag<sub>2</sub>O).

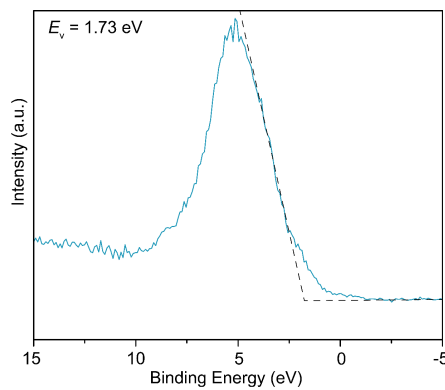
FDM-72 (10.0 mg) was ground and then dispersed in a mixture of 1.5 mL isopropanol, 0.5 mL H<sub>2</sub>O, and 40 μL Nafion in a 4-mL vial. After 1 h sonication, the dispersion was drop-casted onto a glassy carbon electrode. A Pt plate (counter electrode), an Ag/AgCl electrode (reference electrode), and a coated glassy carbon electrode (working electrode) were assembled into a three-electrode system with 0.2 M Na<sub>2</sub>SO<sub>4</sub> aqueous solution as the electrolyte. The Mott-Schottky plots were collected at different frequencies and were performed on a CH Instrument CHI660E electrochemical workstation. The conduction band edge potential ( $E_C$ ) of the sample was calculated by the following equation:<sup>5</sup>

$$\frac{1}{C^2} = \frac{2}{\varepsilon\varepsilon_0eN_D} \left( V - E_C - \frac{k_B T}{e} \right)$$

$C$  refers to the interfacial capacitance,  $\varepsilon$  and  $\varepsilon_0$  refer to the relative permittivity of the semiconductor and the permittivity of vacuum,  $e$  refers to the elementary charge,  $N_D$  refers to the carrier concentration,  $k_B$  is the Boltzmann constant, and  $T$  refers to temperature.  $E_C$  was obtained from the extrapolated value of the linear fitting to the curve of  $\frac{1}{C^2}$  versus potential at  $\frac{1}{C^2} = 0$ .



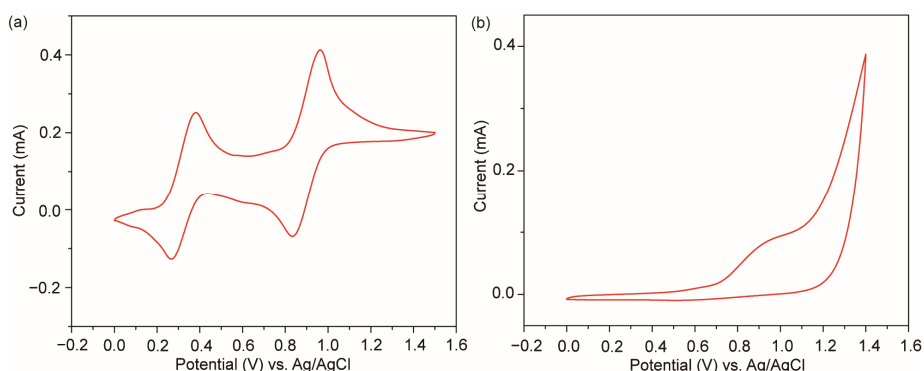
**Fig. S13** Mott-Schottky plots of FDM-72.



**Fig. S14** Valence-band X-ray photoelectron spectroscopy (VB-XPS) profile of FDM-72.

## S6. Oxidative Potential of the Organic Amines

Cyclic voltammetry (CV) measurements were carried out in anhydrous acetonitrile using BioLogic SP-300 electrochemical station. For measurements of PA and TAPB, both solutions contained 0.10 M tetrabutylammonium hexafluorophosphate and 0.054 M analyte. Measurements were performed in a glass reservoir equipped with glassy carbon electrode (working electrode), a Pt plate (counter electrode), and an Ag/AgCl electrode (reference electrode). CV scans were collected from 0 to 1.5 V (for PA) and from 0 to 1.4 V (for TAPB) at  $100 \text{ mV s}^{-1}$ .



**Fig. S15** CV curves of (a) PA and (b) TAPB. The amine concentration (0.054 M) is the same with the concentration used for the MOF synthesis.

## References

1. P. Kubelka and F. Munk, *Z. Tech. Physical*, 1931, **12**, 593–609.
2. G. Sheldrick, *Acta Crystallogr., Sect. A*, 2008, **64**, 112–122.
3. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr.*, 2009, **42**, 339–341.
4. R.-J. Wei, H.-G. Zhou, Z.-Y. Zhang, G.-H. Ning and D. Li, *CCS Chem.*, 2021, **3**, 2045–2053.
5. R. Beranek, *Adv. Phys. Chem.*, 2011, **2011**, 786759.