

Electronic Supporting Information

Thermo-regulating Mesoporous Semi-rigid Metal-organic-polymer Frameworks for Controllable Adsorption and Confinement

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Experimental Section

Synthesis of 1,4-phenylenebis(methylene)-bis(2-hydroxyethyl)-bis(carbonotrithioate) (d-CTA-OH).

d-CTA-OH was successfully synthesized according to the previously reported method.¹ As shown in **Figure S1A**, 2.0 g of $K_3PO_4 \cdot H_2O$ (8.685 mmol) and 0.600 mL of 2-mercaptoethanol (8.562 mmol) were mixed in 15 mL of THF and magnetically stirred for 10 minutes. Next, 1.36 mL of carbon disulfide (CS_2 ; 22.61 mmol) was added dropwise into the mixture and kept being stirred for 2 hours. Subsequently, 15 mL of THF solution of 1,4-bis(bromomethyl)benzene (0.993 g; 3.76 mmol) was slowly dripped into the mixed solution and fully stirred for 4 hours. Finally, the solution was filtrated for the removal of insolubles, and further concentrated by rotary evaporation. The products were obtained by thin-layer chromatography (petroleum ether : ethyl acetate = 1 : 2). Yield: 0.832 g (53.4%). 1H -NMR (600 MHz, d_6 -DMSO; see **Figure S2A**): δ =7.35 ppm (s, 4H, $-CH_2C_6H_4CH_2-$), 4.66 ppm (s, 4H, $-CH_2C_6H_4CH_2-$), 5.09~5.11 ppm (t, 2H, $-CH_2OH$), 3.63~3.66 ppm (m, 4H, SCH_2CH_2OH), 3.49~3.51 ppm (t, 4H, $-SCH_2CH_2-$). ^{13}C -NMR (600 MHz, d_6 -DMSO; see **Figure S2B**): δ =224.14 ppm ($-SCS-S$), 135.23 ppm ($CH_2CC_6H_4CCH_2-$), 129.96 ppm ($-CC_6H_4C-$), 58.86 ppm ($-CCH_2S-$), 40.54 ppm ($-SCH_2CH_2-$), 40.06 ppm ($-CH_2CH_2OH$). m/z : 432.95 ($C_{14}H_{18}O_2S_6^+$) (see **Figure S2C**).

ppm (t, 6H), 2.68-2.70 ppm (t, 6H), 12.51 ppm (s, 3H). ^{13}C -NMR (600 MHz, d_6 -DMSO; see **Figure S2H**): δ =172.91, 136.72, 129.77, 40.52, 40.18, 32.79, and 32.26 ppm. m/z : 682.89 ($C_{21}H_{24}O_6S_9^+$) (see **Figure S2I**).

Synthesis of 1,4-benzylbis(methylene)-bis(hydroxyethyl)-bis(thiocarbonate) (d-CTA-COOH).

As shown in **Figure S1A**, 2.0 g of $K_3PO_4 \cdot H_2O$ (8.685 mmol) and 0.7899 g of 3-mercaptopropionic acid (9.42 mmol) were added into 15 mL of acetone and magnetically stirred for 20 minutes. Subsequently, 1.36 mL of CS_2 (22.51 mmol) was added dropwise and then stirred for 2 hours at room temperature. Next, 10 mL of acetone solution of α, α' -dibromo-p-xylene (0.993g; 3.76 mmol) was dripped slowly,

and then stirred for another 2 hours. Afterwards, the yellow insolubles were filtered out and dissolved in deionized water again. After recrystallization by mild acidification of diluted hydrochloric acid (HCl), the solid precipitates was obtained again by filtration and redissolved in 50 mL of the mixed solvent of dichloromethane and isopropanol (volume ratio=9 : 1). And then the resulting yellow solution was extracted three times with deionized water, and added with 2.0 g of anhydrous magnesium sulfate (MgSO₄). Finally, the solution was collected through filtration and further concentrated by rotary evaporation. The products were obtained via vacuum drying at 60 °C overnight. Yield: 0.740 g (42.24%). ¹H-NMR (600 MHz, d₆-DMSO; see **Figure S2D**): δ=7.34 ppm (s, 4H, -CH₂C₆H₄CH₂-), 4.64 ppm (s, 4H, -CH₂C₆H₄CH₂-), 12.39 ppm (t, 2H, -CH₂COOH), 3.53~3.56 ppm (m, 4H, -SCH₂CH₂-), 2.67-2.69 ppm (t, 4H, -CH₂CH₂COOH-). ¹³C-NMR (600 MHz, d₆-DMSO; see **Figure S2E**): δ=223.73 ppm (-SCS-S), 172.5 ppm (-CH₂COOH)135.17 (CH₂CC₄H₄CCH₂-), 129.96 ppm (-CC₄H₄C-), 40.45 ppm (-CCH₂S-), 32.80 ppm (-SCH₂CH₂-), 32.20 ppm (-CH₂CH₂COOH). m/z: 488.94 (C₁₄H₁₈O₂S₆⁺) (see **Figure S2F**).

Synthesis of 1,3,5-benzyltri(methylene)-tri(hydroxyethyl)-tri(thiocarbonate) (t-CTA-COOH).

As shown in **Figure S1A**, t-CTA-COOH was synthesized using the same method. Typically, 2.0 g of K₃PO₄·H₂O (8.685 mmol) and 1.000 g of 3-mercaptopropionic acid (9.42 mmol) were uniformly mixed in 15 mL of acetone. Subsequently, 1.00 mL of CS₂ (16.55 mmol) was added dropwise into the mixture and magnetically stirred for 2 hours. And 5 mL of acetone solution of 1,3,5-tris(bromomethyl)benzene (0.660 g; 1.85 mmol) was slowly dripped and stirred for 2 hours at room temperature. Subsequently, the yellow insolubles was filtered out, dissolved in deionized water again, and recrystallized by mild acidification of diluted HCl in turn. Next, the resulting solid was collected again by filtration, redissolved in ethyl acetate, and extracted three times with deionized water. Afterwards, 2.0 g of anhydrous MgSO₄ was added into the yellow solution to absorb remaining water, and filtered out. Finally, the solution was further concentrated by rotary evaporation, and then thoroughly dried in vacuum at 60 °C

overnight to obtain the products. Yield: 0.653 g (51.93%). ¹H-NMR (600 MHz, d₆-DMSO; see **Figure S2G**): δ=7.33 ppm (s, 3H), 4.64 ppm (s, 6H), 3.53-3.56.

Synthesis of multi-armed P(AAm-co-AN)s using different CTAs.

All the random copolymer P(AAm-co-AN)s were prepared via addition fragmentation chain transfer polymerization (RAFT) using the above synthesized CTAs. Take d-UCSTP-COOH as an example. As shown in **Figure 1B**, 2.310 g of AAm (32.50 mmol), 0.954 g of AN (17.70 mmol), 78 mg of d-CTA-COOH (0.170 mmol), and 8.9 mg of AIBN (0.054 mmol) were dissolved in 12.5 mL of DMF inside a 50 mL Schlenk flask in turn. After three freeze-thaw cycles, the mixed solution was thoroughly degassed and preheated to 62 °C. The polymerization was allowed to proceed for 7 hours under magnetic stirring. Afterwards, the products were obtained by reprecipitation of the reaction liquid into methanol, and filtration. Finally, the resulting precipitates were re-dissolved in deionized water to be dialyzed against deionized water for 3 days, and then recovered by lyophilization. In the other two similar polymerizations of d-UCSTP-OH and t-UCSTP-COOH, the CTA usages were 78 mg of d-CTA-OH (0.176 mmol) and 78 mg of t-CTA-COOH (0.118 mmol), respectively. All the operations followed the same post-processing protocol.

Empirical formula of MOPFs.

Rietveld refinement result was obtained according to the following formula²:

$$S = \sum_i W_i (y_i - y_{ci})^2$$

Here S , W_i and y_i is standard deviation, weight factor and experimental value. y_{ci} was obtained using equation:

$$y_{ci} = S \sum_K |F_K|^2 L_K \phi(2\theta_i - 2\theta_K) P_K A S_r E + y_{bi}$$

Here S is scale factor; K represents the Millker index of Bragg reflection h, k, l ; F_K is the K_{th} Bragg reflection structure factor; L_K is the Lorentz polarization factor and multiplicity factor; $\phi(2\theta_i - 2\theta_K)$ represents the area-normalized peak function; P_K is

the preferred orientation factor; A is the absorption factor, S_r is the surface roughness factor, E is the extinction factor; y_{bi} is the background intensity at point i .

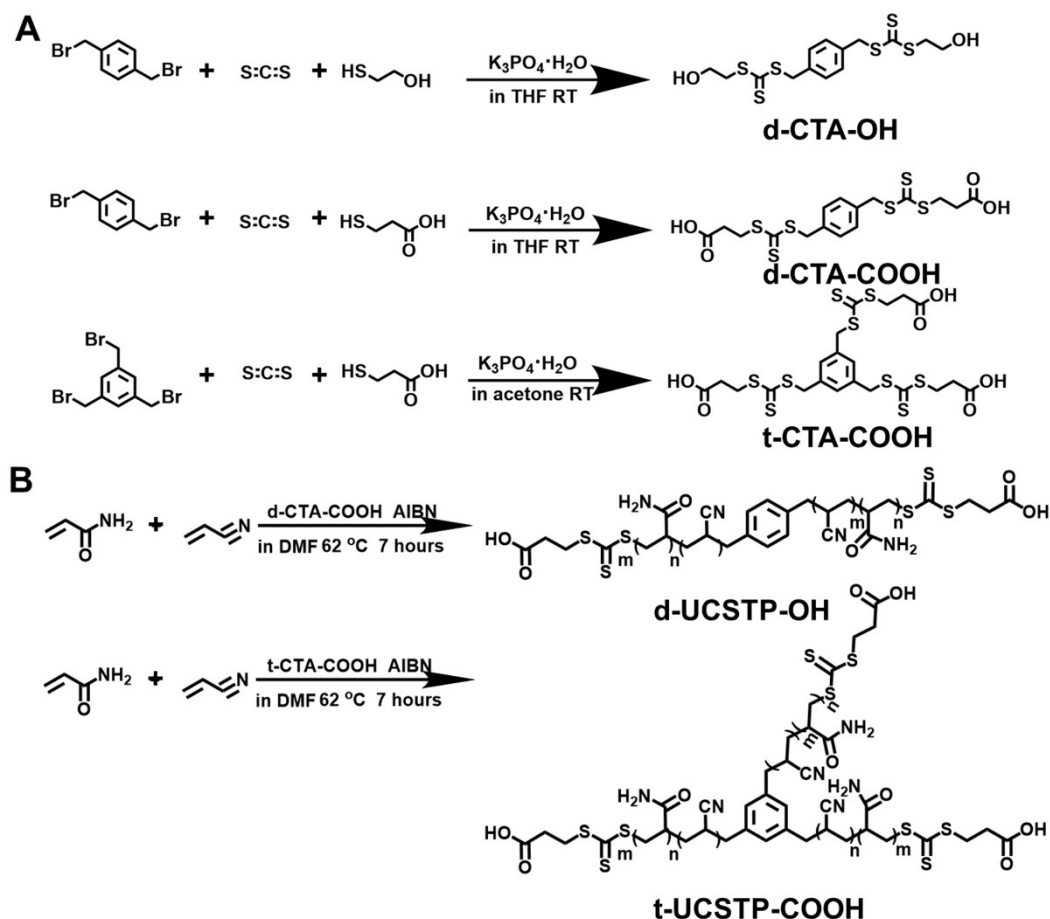


Figure S1. Synthetic routes of 1,4-Phenylenebis(methylene)-bis(2-hydroxyethyl)-bis(carbonotrithioate) (*d*-CTA-OH), 1,4-Benzylbis(methylene)-bis(hydroxyethyl)-bis(thiocarbonate) (*d*-CTA-COOH), and 1,3,5-Benzyltri(methylene)-tri(hydroxyethyl)-tri(thiocarbonate) (*t*-CTA-COOH) as chain transfer agents (CTA; A), and two corresponding poly(acrylamide-co-acrylonitrile)s [P(AAm-co-AN)s] with upper critical solution temperature (UCST; *d*-UCSTP-OH and *t*-UCSTP-COOH) (B).

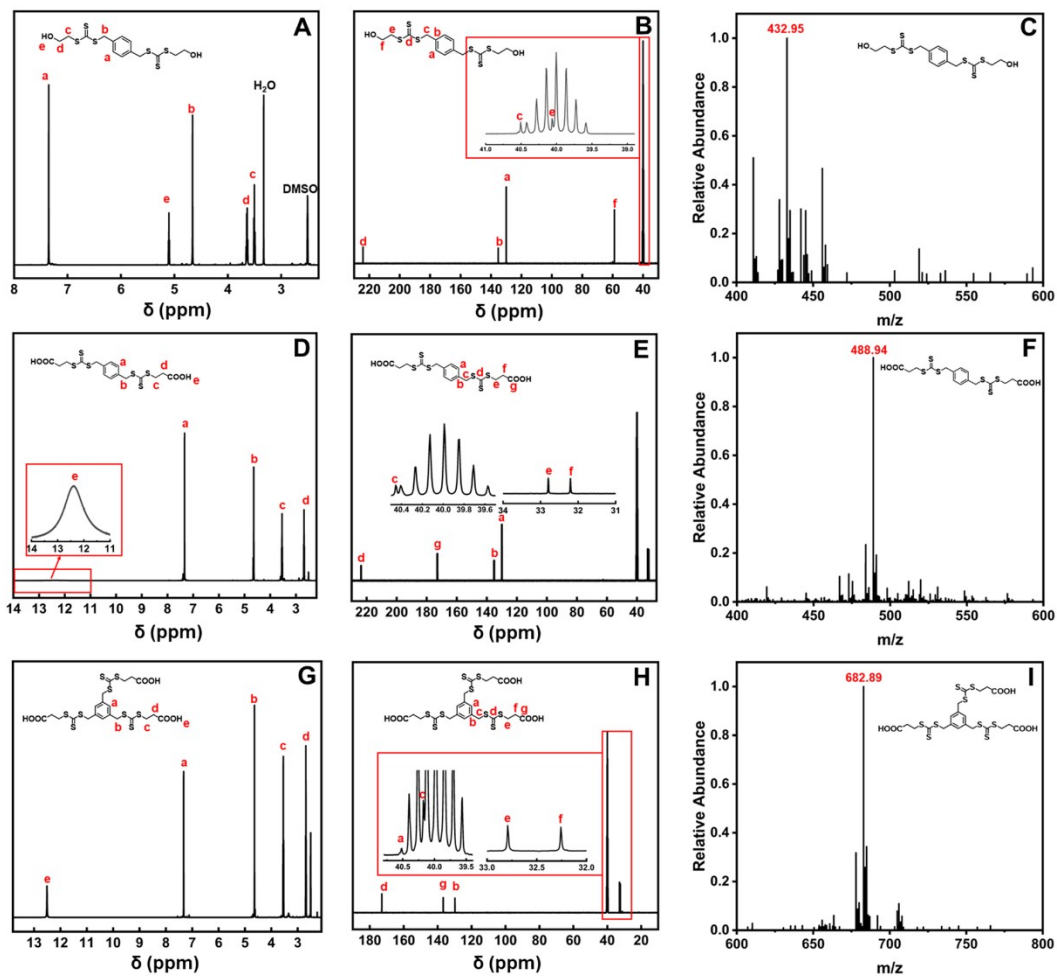


Figure S2. ^1H -nuclear magnetic resonance (NMR; A, D, G), ^{13}C -NMR (B, E, H) and mass spectra (MS) of *d*-CTA-OH, *d*-CTA-COOH, and *t*-CTA-COOH, respectively (C, F, I).

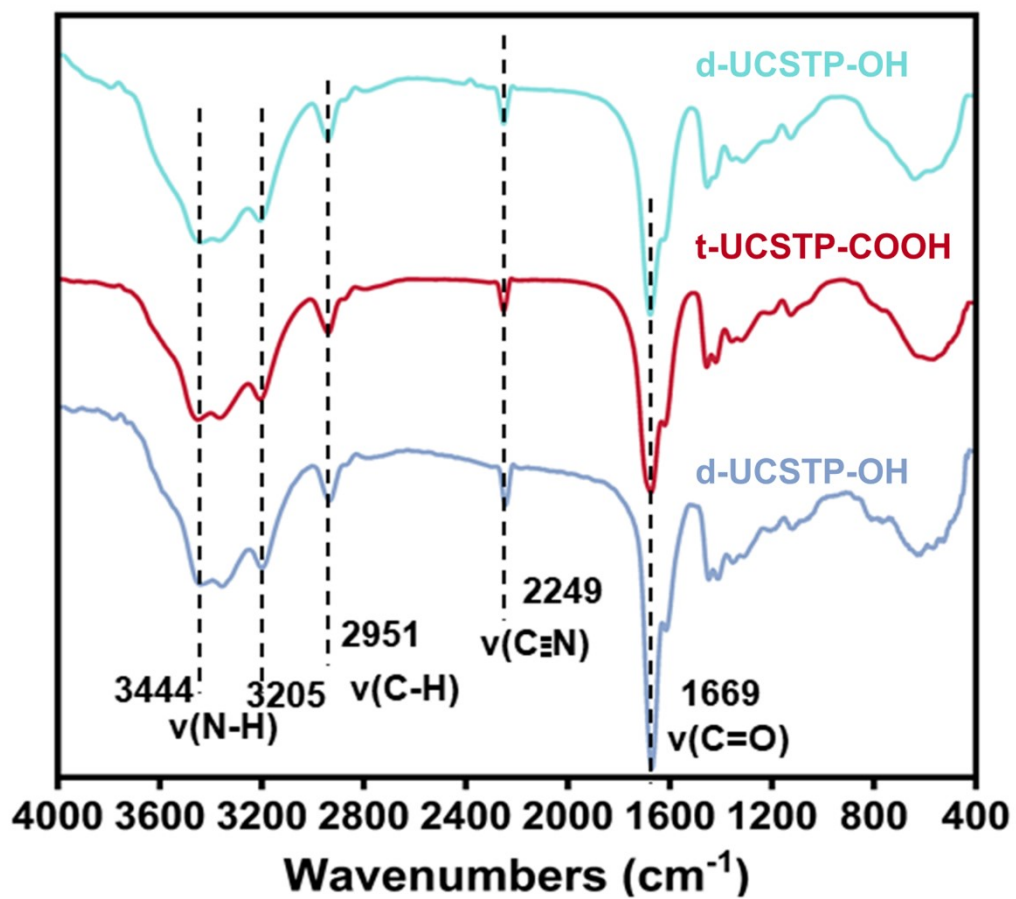


Figure S3. Fourier transform infrared (FT-IR) spectra of *d*-UCSTP-OH, *d*-UCSTP-COOH and *t*-UCSTP-COOH, respectively.

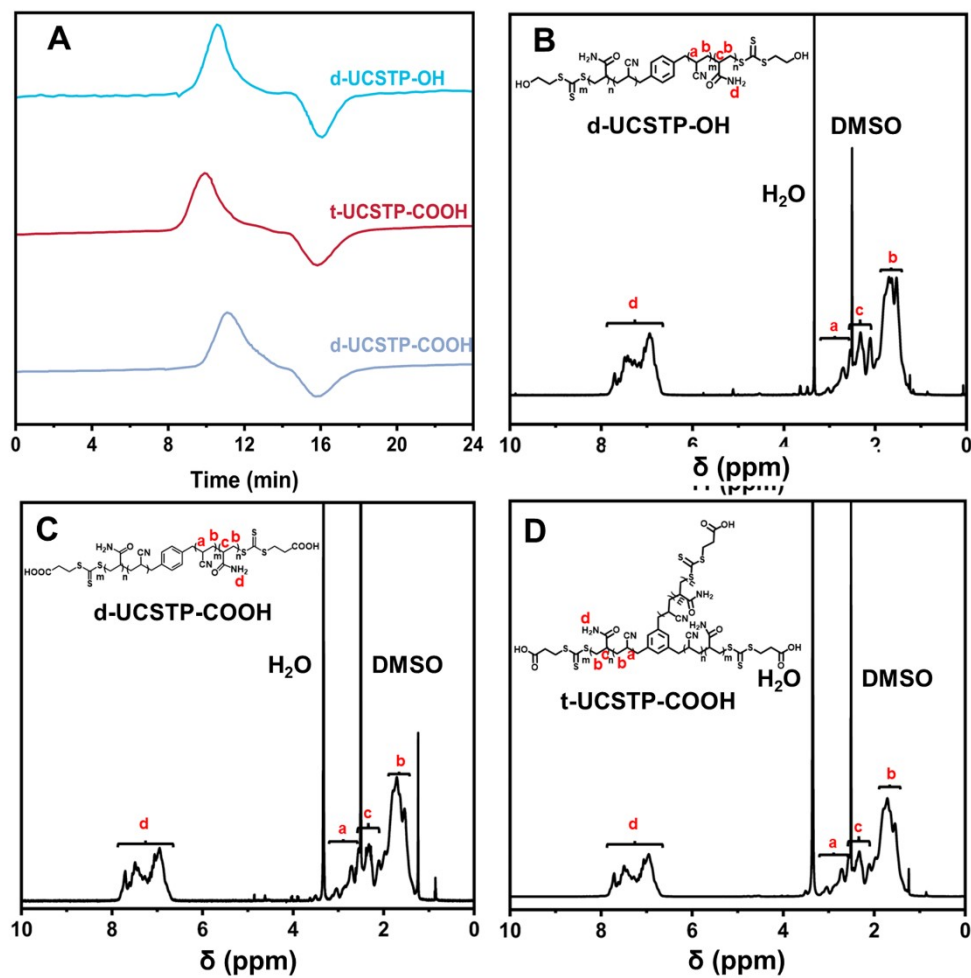


Figure S4. Gel permeation chromatography (GPC) and ¹H-NMR spectra of three UCST-type P(AAm-co-AN)s using *d*-CTA-OH, *d*-CTA-COOH, *t*-CTA-COOH as CTA, respectively (i.e. *d*-UCSTP-OH, *d*-UCSTP-COOH and *t*-UCSTP-COOH).

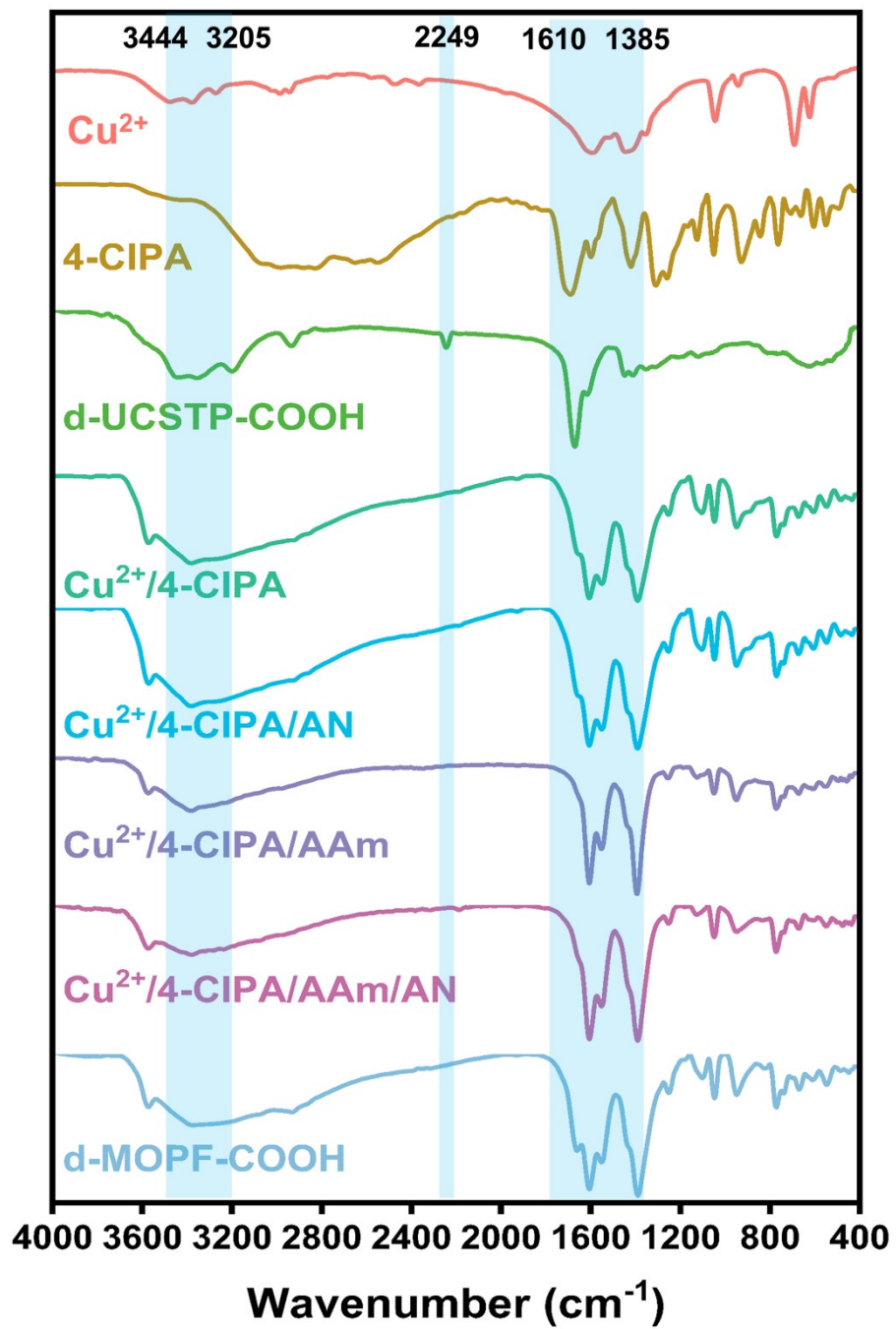


Figure S5. FT-IR spectra of all the raw materials and products.

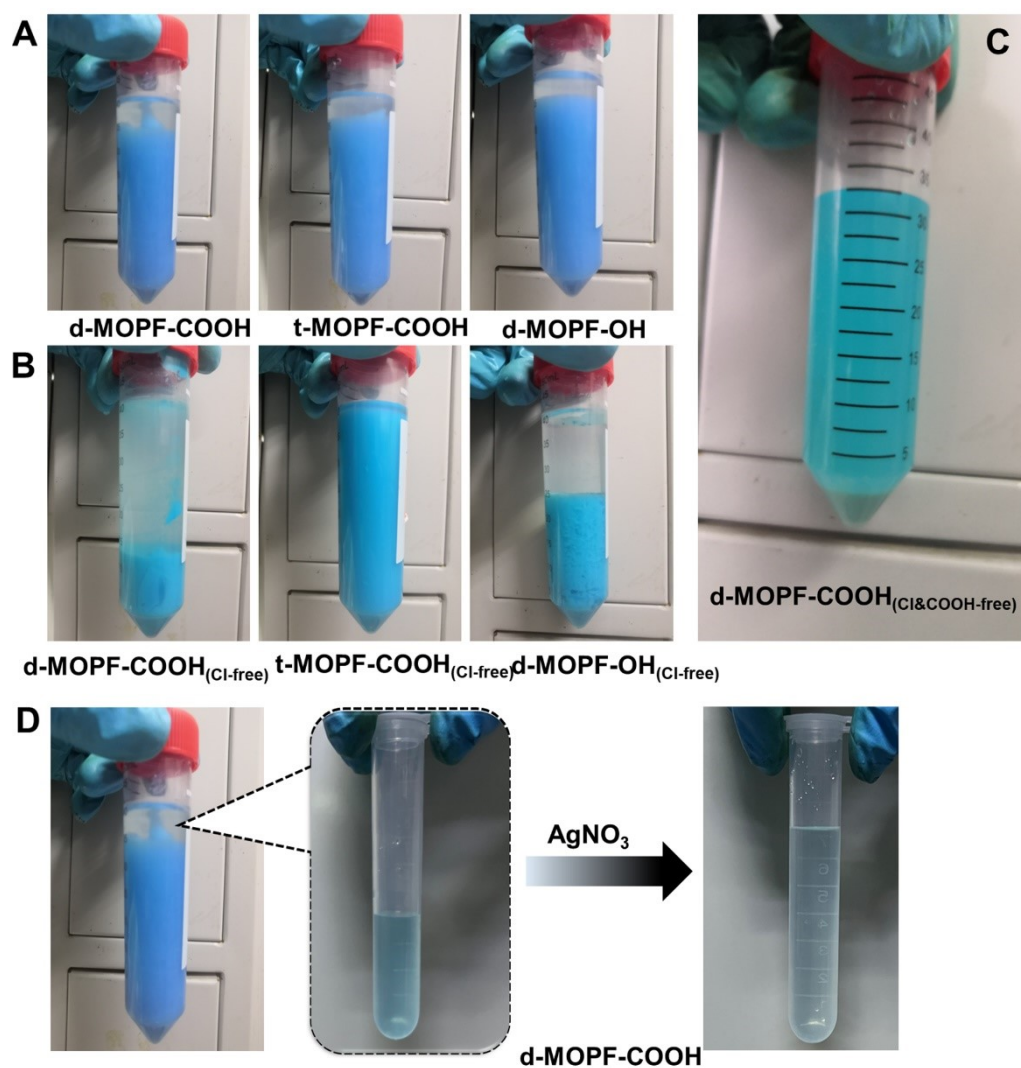


Figure S6. Object pictures of precipitation tests in acetone-water mixed solution: (A) the resulting Metal-organic-polymer frameworks (MOPFs) using 4-chloroisophthalic acid (4-CIPA) with chlorine substituent and two adjacent carboxy groups as small organic linker; (B) the resulting MOPFs using isophthalic acid with only two adjacent carboxy groups (-COOH) as small organic linker; (C) the resulting *d*-MOPF-OH using 1,3-benzenedimethanol without any chlorine substituent and carboxy group as small organic linker; (D) the supernatant of the *d*-MOPF-COOH mixed solution after the addition of aqueous silver nitrate (AgNO₃) solution. **Note:** *d*-MOPF-OH, *d*-MOPF-COOH and *t*-MOPF-COOH denoted the resulting MOPFs using *d*-UCSTP-OH, *d*-UCSTP-COOH and *t*-UCSTP-COOH as flexible polymeric linkers, respectively

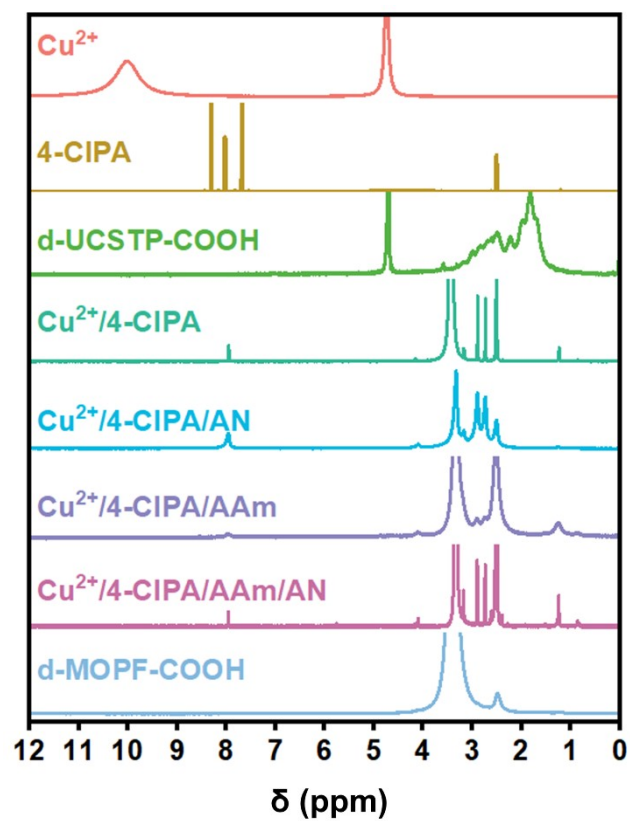


Figure S7. ¹H-NMR spectra of all the raw materials and products.

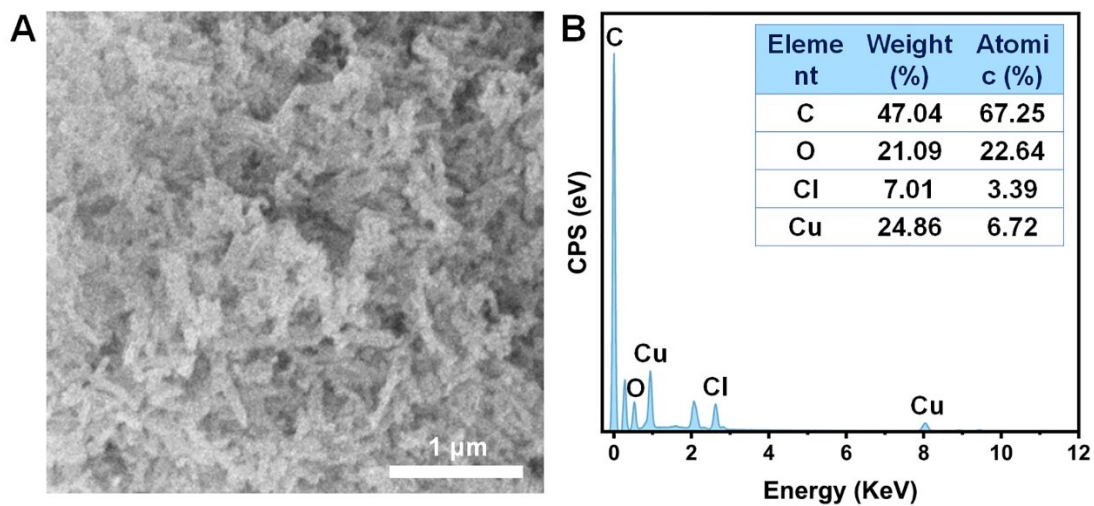


Figure S8 Scanning electron microscope image (A) and corresponding energy disperse spectroscopy analysis of the crude metal-organic framework (MOF) only prepared by cupric acetate and 4-chloroisophthalic acid (4-CIPA) as control (B).

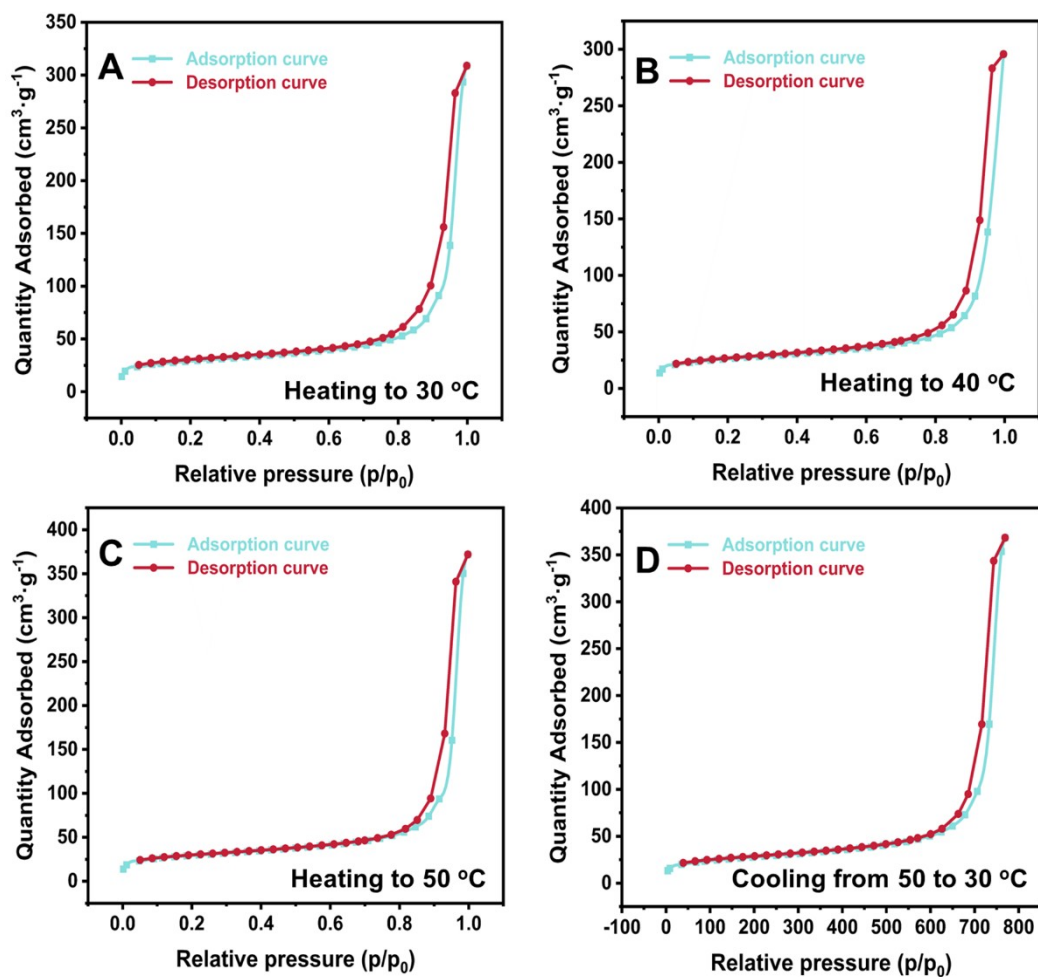


Figure S9. N_2 adsorption-desorption isotherm lines of *d*-MOPF-COOH at 30 °C (A), 40 °C (B), 50 °C (C) and after cooled to 30 °C (D).

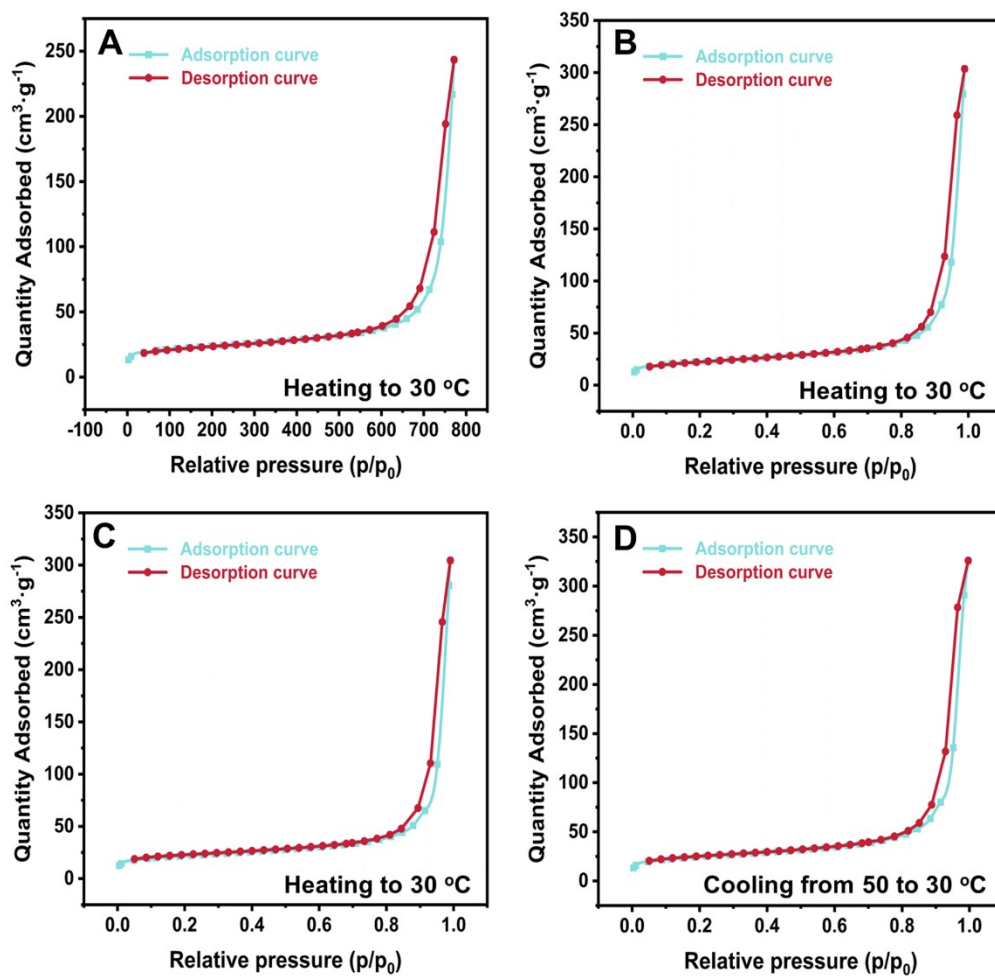


Figure S10. N₂ adsorption-desorption isotherm lines of *t*-MOPF-COOH at 30 °C (A), 40 °C (B), 50 °C (C) and after cooled to 30 °C (D).

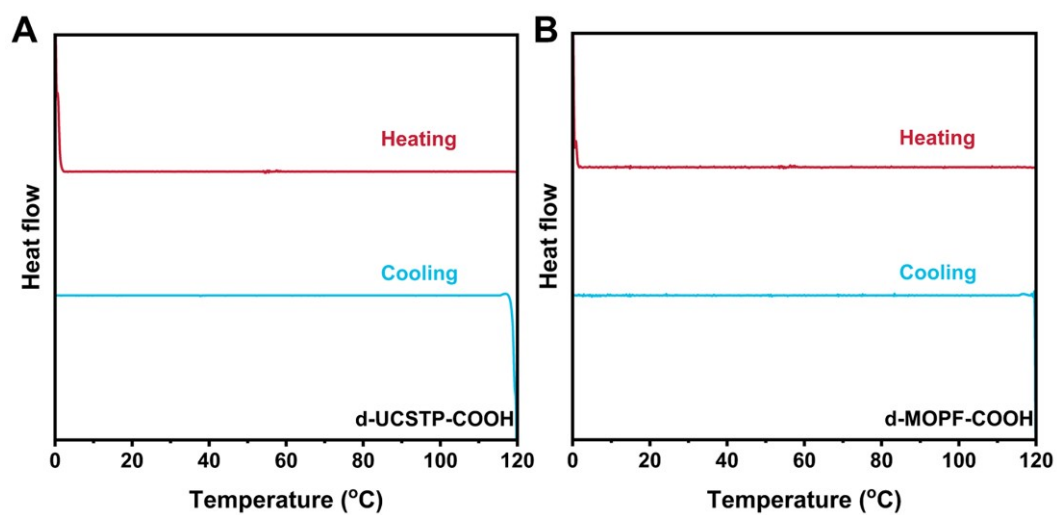


Figure S11. Differential scanning calorimetric (DSC) curves of *d*-UCSTP-COOH (A) and *d*-MOPF-COOH (B) within the temperature range between 0 and 120 °C.

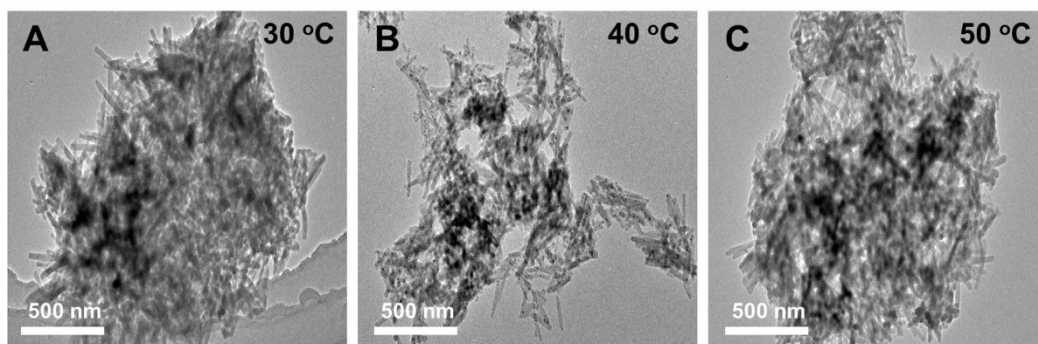


Figure S12. Transmission electron microscope (TEM) images of *d*-MOPF-COOH at 30 °C (A), 40 °C (B) and 50 °C (C).

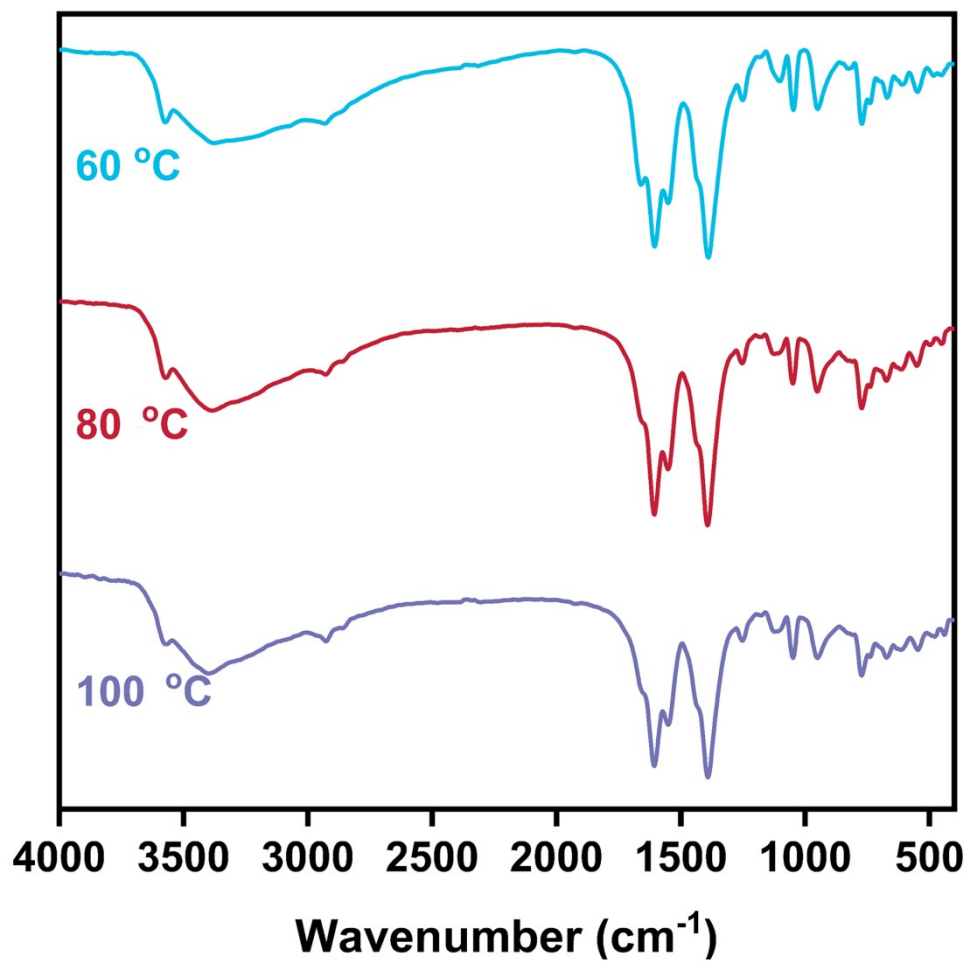


Figure S13. FT-IR spectra of *d*-MOPF-COOH at 60, 80, and 100 °C.

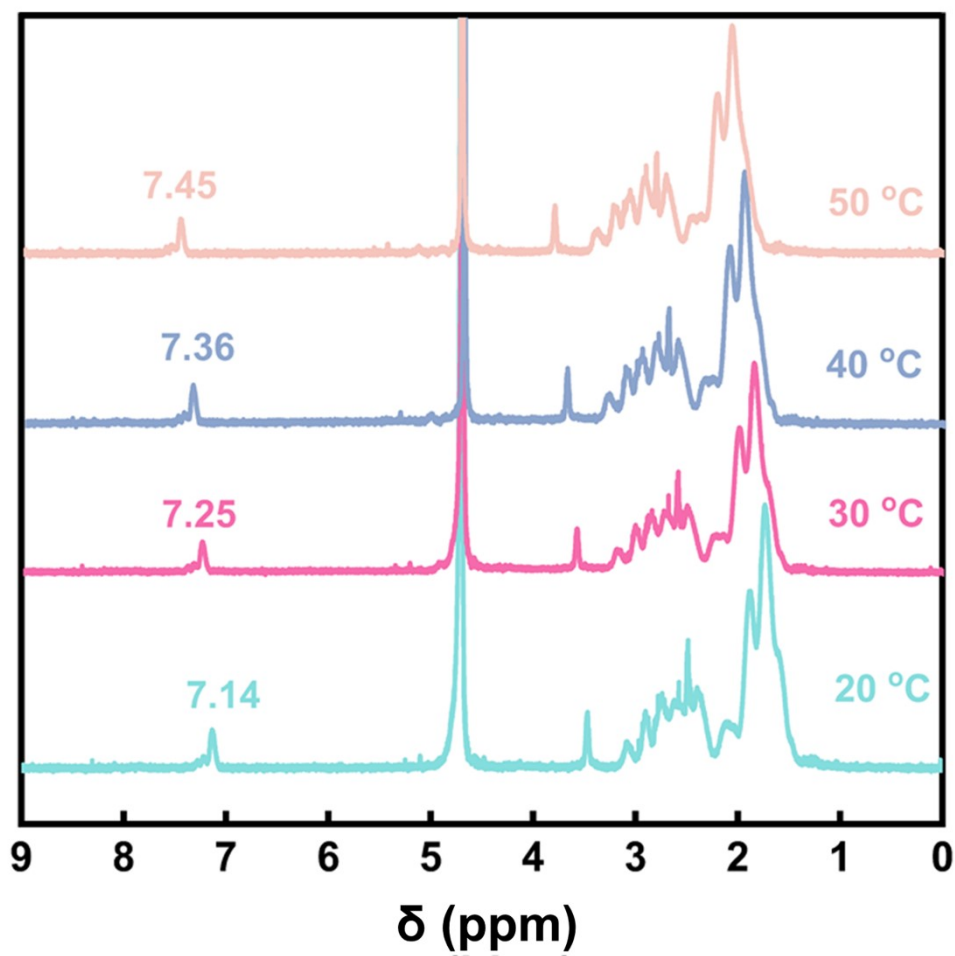


Figure S14. Variable-temperature ¹H-NMR spectra of *d*-UCSTP-COOH in D₂O.

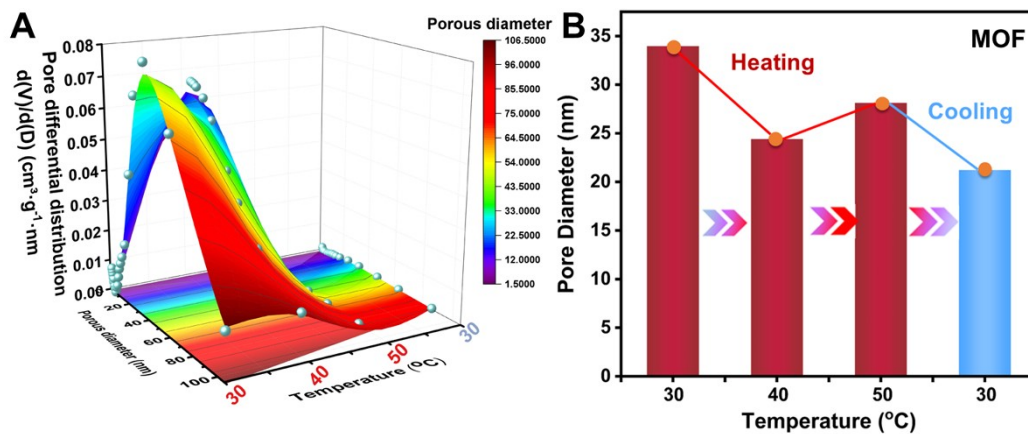


Figure S15. Pore differential distributions of the crude MOF at 30, 40, and 50 °C (A), and average pore diameters of the crude MOF at 30, 40, and 50 °C and after cooled to 30 °C (B).

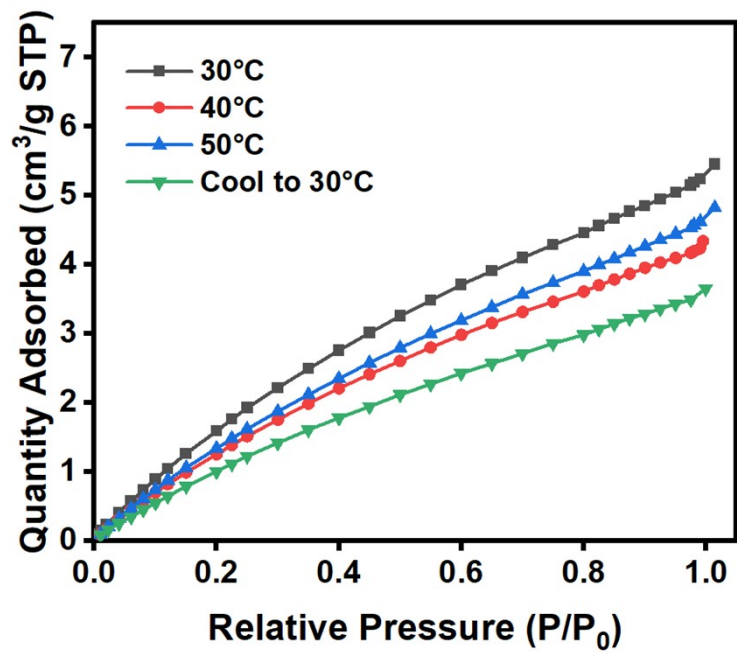


Figure S16. CO₂ absorption isotherms of the crude MOF at different temperatures.

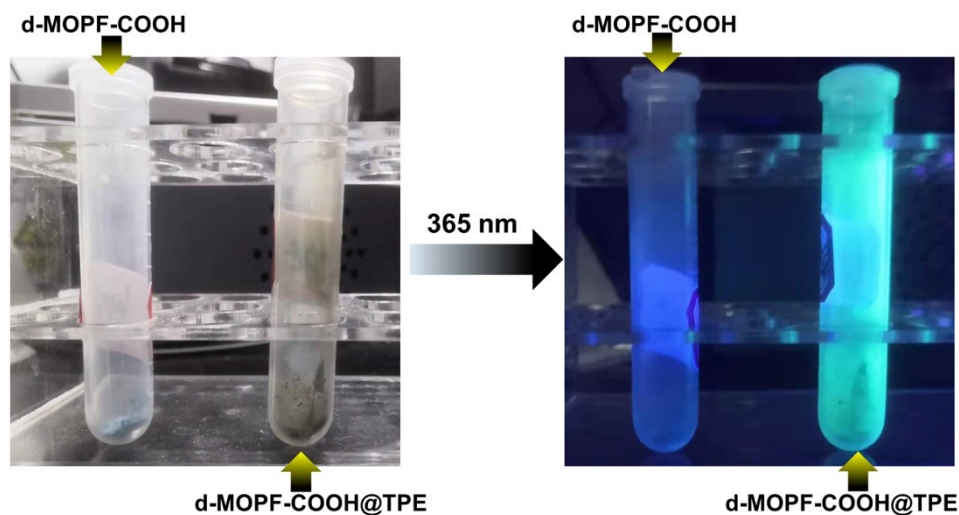


Figure S17. Object pictures of the aqueous solution of 1,1,2,2-tetra(4-carboxylphenyl)ethylene (TPE)-loaded *d*-MOPF-COOH before and after ultraviolet (UV; wavelength: 365 nm) irradiation (crude *d*-MOPF-COOH as control).

Table S1. Physicochemical properties of the resulting UCST-type P(AAm-*co*-AN) copolymers (i.e. *d*-UCSTP-OH, *d*-UCSTP-COOH, and *t*-UCSTP-COOH).

Sample		<i>d</i> -UCSTP- OH	<i>d</i> -UCSTP- COOH	<i>t</i> -UCSTP- COOH
AN units (mol%)	In feed	35	35	35
	In product ^a	26.04	28.49	28.40
AAm units (mol%)	In feed	65	65	65
	In product ^a	73.96	71.51	71.60
Number-average Molecular Weight ^b (g/mol)		6.90×10 ⁴	3.77×10 ⁴	9.63×10 ⁴
Weight-average Molecular Weight ^b (g/mol)		8.80×10 ⁴	5.59×10 ⁴	13.86×10 ⁴
Polydispersity Index ^b		1.275	1.483	1.439

Notes: the superscript “a” denotes the results determined by GPC (see **Figure S4A**); the superscript “b” denotes the results determined by ¹H-NMR spectra (see **Figure S4B, S4C, and S4D**).

Table S2 Comparison between superficial and intrinsic element analyses of the resulting MOPFs.

Sample	XPS (atom ratio)				EA (mass ratio)		
	C 1s (%)	Cu 2p (%)	Cl 2p (%)	N 1s (%)	Cl:N	C (wt.%)	N (wt.%)
MOF* (Cu ²⁺ /4-CIPA*)	59.25	7.61	5.68	~	~	~	~
<i>d</i> -MOPF-OH	68.59	3.06	3.00	1.77	1.69	27.14	1.19
<i>d</i> -MOPF-COOH	72.00	2.48	2.26	1.24	1.82	28.25	0.68
<i>t</i> -MOPF-COOH	60.68	6.22	4.11	2.24	1.83	28.33	0.97

Note: MOF* denotes the crude MOF without any polymeric linker as control.

Reference

1. R. Wang, C. L. McCormick and A. B. Lowe, *Macromolecules*, 2005, **38**, 9518-9525.
2. H. M. Rietveld. *Acta Cryst.* 1967, **22**, 151-152.