

## Electronic Supplementary Information

# Morphological control of covalent organic frameworks in a PEG- H<sub>2</sub>O system

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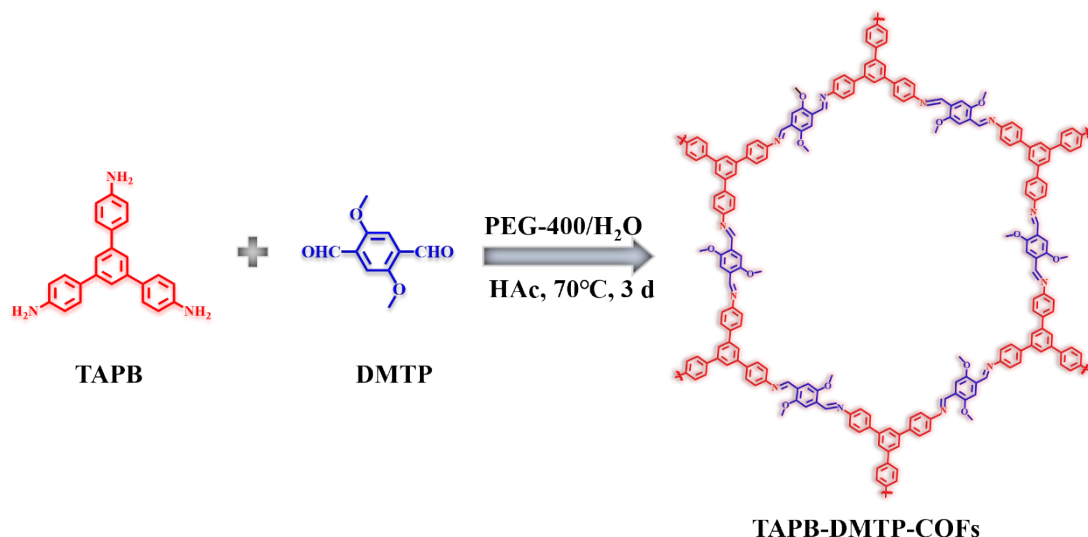
**Section S1. Materials and Methods (pages S2-S7)**

**Section S2. Figures (pages S7-S20)**

## Section S1. Materials and Methods

### Materials and Characterizations.

Unless otherwise specified, all starting materials and reagents are commercially available without any purification process. Among them, the experimental water is 18.2 M $\Omega$ ·cm ultrapure water, prepared by a water purifier. The experiments can be carried out under ambient conditions and do not require any dewatering and deoxygenation processes. Fourier transform infrared (FT-IR) spectra were measured in the range of 600 cm<sup>-1</sup> to 4000 cm<sup>-1</sup> deploying KBr pellets on a Bruker model Nicolet Nexus 870 spectrophotometer. Raman spectra were obtained on a Renishaw InVia Reflex confocal microscope (Renishaw, U.K.) at an excitation wavelength of 523 nm and a scanning range of 100 cm<sup>-1</sup> to 4000 cm<sup>-1</sup>. X-ray photoelectron spectroscopy (XPS) data were obtained by a K-Alpha X-ray photoelectron spectrometer in the range of 600 cm<sup>-1</sup> to 2000 cm<sup>-1</sup>. Power X-ray diffraction (PXRD) data were collected on a PANalytical X'Pert model Pro Multipurpose Diffractometer at 40 kV and 40 mA using Cu K $\alpha$  radiation from  $2\theta = 2^\circ$  to  $45^\circ$  in  $5^\circ$  increments. Field emission scanning electron microscopy images (SEM) were observed on a JOEL model JSM-6701F at an accelerating voltage of 10.0 kV. The synthesized COFs were added to the ethanol solution, dispersed uniformly by ultrasound, and finally dropped onto the scanning sample table. After the ethanol evaporated, the sample was sprayed with gold and finally placed together for measurement. The process is also applicable to TEM measurements. TEM images were obtained on a JOEL model TF20. The thermal stability of the samples was measured via a thermogravimetric analysis (TGA) instrument (STA449C) in the temperature range of 25-800 °C from 25 °C to 800 °C under a N<sub>2</sub> atmosphere with a heating rate of 10 °C/min. Nitrogen adsorption and desorption isotherms were measured at 77 K using an ASiQwin Quantachrome instrument. Specific surface areas were calculated from the adsorption data using Brunauer–Emmett–Teller (BET) methods. Pore size distribution data were calculated based on the nonlocal density functional theory (NLDFT) model.



### Synthesis of nanofibrous TAPB-DMTP COF-1 in PEG-400/H<sub>2</sub>O

In a glass scintillation vial with a volume of 20.0 mL, 1,3,5-tris(4-aminophenyl) benzene (TAPB) (0.04 mmol, 14.0 mg) and 2,5-dimethoxybenzene-1,4-dicarboxaldehyde (DMTP) (0.06 mmol, 11.7 mg) were dissolved in PEG-400/H<sub>2</sub>O (PEG-400/H<sub>2</sub>O=1 mL/1 mL, v/v) under vigorous stirring. After that, 12 M HAc (0.25 mL) was added to each glass scintillation vial. Subsequently, the mixture was vigorously shaken for 10 s on a vortex mixer, placed in an oven, and then incubated at 70 °C for 72 h to obtain yellow precipitates. The precipitate was isolated by centrifugation at 8500 rpm and washed with THF and ethanol (15 mL × 3). Finally, the powders were dried at 70 °C in an oven for 24 h to give a yellow powder (yield of 60%), denoted TAPB-DMTP COF-1.

### Synthesis of flower-like TAPB-DMTP COF-2 in PEG-400/H<sub>2</sub>O

In a glass scintillation vial with a volume of 20.0 mL, TAPB (0.04 mmol, 14.0 mg) and DMTP (0.06 mmol, 11.7 mg) were dissolved in PEG-400/H<sub>2</sub>O (PEG-400/H<sub>2</sub>O=1.5 mL/0.5 mL, v/v) under vigorous stirring. After that, 12 M HAc (0.25 mL) was added to each glass scintillation vial. Subsequently, the mixture was vigorously shaken for 10 s on a vortex mixer, placed in an oven, and then incubated at 70 °C for 72 h to obtain yellow precipitates. The precipitate was isolated by centrifugation at 8500 rpm and washed with THF and ethanol (15 mL × 3). Finally, the powders were dried at 70 °C in an oven for 24 h to give a yellow powder (yield of 90%), denoted TAPB-DMTP COF-2.

### **Synthesis of sea urchin-like TAPB-DMTP COF-3 in PEG-400/H<sub>2</sub>O**

In a glass scintillation vial with a volume of 20.0 mL, TAPB (0.04 mmol, 14.0 mg) and DMTP (0.06 mmol, 11.7 mg) were dissolved in PEG-400/H<sub>2</sub>O (PEG-400/H<sub>2</sub>O=2 mL/1 mL, v/v) under vigorous stirring. After that, 12 M HAc (0.25 mL) was added to each glass scintillation vial. Subsequently, the mixture was vigorously shaken for 10 s on a vortex mixer, placed in an oven, and then incubated at 70 °C for 72 h to obtain yellow precipitates. The precipitate was isolated by centrifugation at 8500 rpm and washed with THF and ethanol (15 mL × 3). Finally, the powders were dried at 70 °C in an oven for 24 h to give a yellow powder (yield of 50%), denoted TAPB-DMTP COF-3.

### **Synthesis of spherical TAPB-DMTP COF-4 in PEG-400/H<sub>2</sub>O**

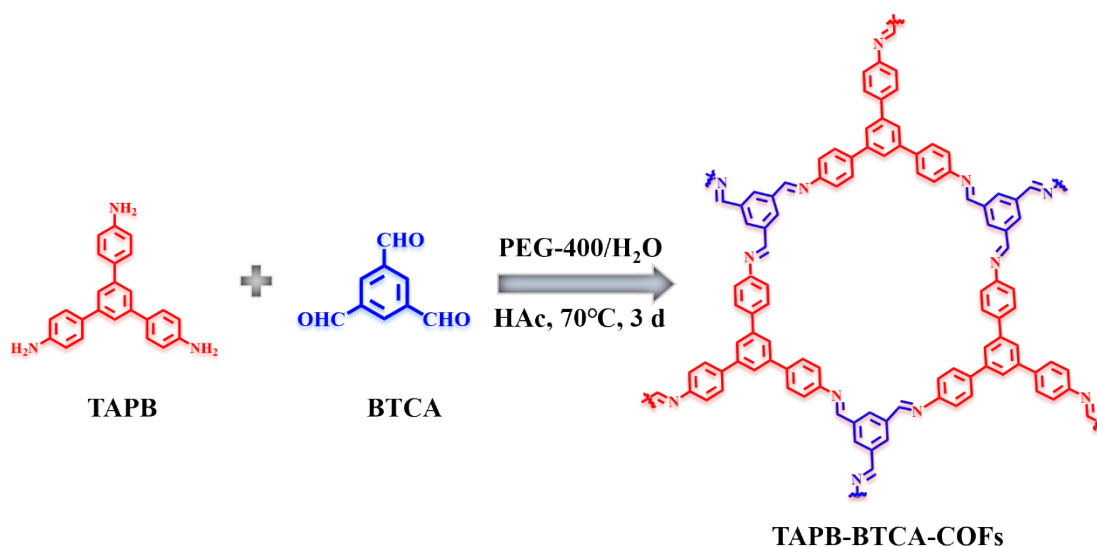
In a glass scintillation vial with a volume of 20.0 mL, on the one hand, TAPB (0.04 mmol, 14.0 mg) was dissolved in PEG-400/H<sub>2</sub>O (PEG-400: H<sub>2</sub>O=0.25 mL: 0.25 mL, v/v) under vigorous stirring, and then benzaldehyde (60.7 μL) was added to generate solution A. On the other hand, DMTP (0.06 mmol, 11.7 mg) was dissolved in PEG-400/H<sub>2</sub>O (PEG-400/H<sub>2</sub>O=0.25 mL/0.25 mL, v/v) under vigorous stirring, after which aniline (54.4 μL) was added to generate solution B. Finally, solution A and solution B were mixed, and 12 M HAc (0.25 mL) was added to the reaction system. In addition, the mixture was vigorously shaken for 10 s on a vortex mixer, placed in an oven, and then incubated at 70 °C for 72 h to obtain yellow precipitates. The precipitate was isolated by centrifugation at 8500 rpm and washed with THF and ethanol (15 mL × 3). Finally, the powders were dried at 70 °C in an oven for 24 h to give a yellow powder, denoted TAPB-DMTP COF-4.

### **Synthesis of TAPB-DMTP COFs with different morphologies via different acids.**

In a glass scintillation vial with a volume of 20.0 mL, TAPB (0.04 mmol, 14.0 mg) and DMTP (0.06 mmol, 11.7 mg) were dissolved in PEG-400/H<sub>2</sub>O (PEG-400/H<sub>2</sub>O=2 mL/1 mL, v/v) under vigorous stirring. After that, 20 mg acid (oxalic acid dihydrate, salicylic acid, benzoic acid) was added to each glass scintillation vial. Subsequently, the mixture was vigorously shaken for 10 s on a vortex mixer, placed in an oven, and then incubated at 70 °C for 72 h to obtain yellow precipitates. The precipitate was isolated by centrifugation at 8500 rpm and washed with THF and ethanol (15 mL × 3). Finally, the powders were dried at 70 °C in an oven for 24 h to give a yellow powder.

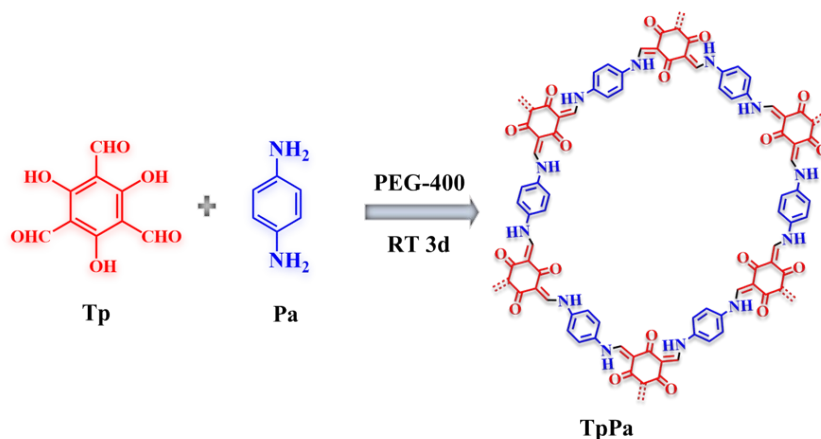


## Synthesis of TAPB-BTCA COFs in PEG-400/H<sub>2</sub>O



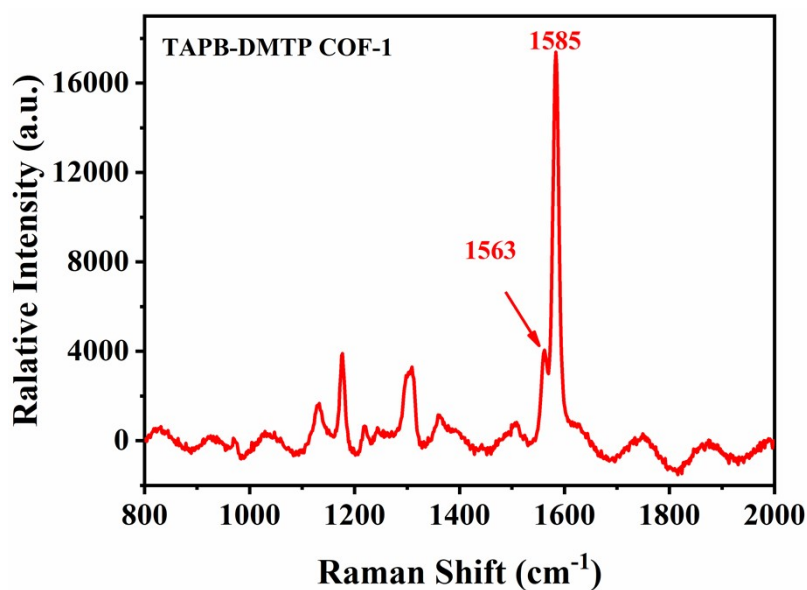
In a glass scintillation vial with a volume of 20.0 mL, TAPB (0.05 mmol, 17.6 mg) and 1,3,5-triformylbenzene (BTCA) (0.05 mmol, 8.1 mg) were dissolved in PEG-400/H<sub>2</sub>O (PEG-400/H<sub>2</sub>O=0.5 mL/4.5 mL, v/v) under vigorous stirring. After that, 12 M HAc (0.25 mL) was added to each glass scintillation vial. Subsequently, the mixture was vigorously shaken for 10 s on a vortex mixer, placed in an oven, and then incubated at 70 °C for 72 h to obtain yellow–brown precipitates. The precipitate was isolated by centrifugation at 8500 rpm and washed with THF and ethanol (15 mL × 3). Finally, the powders were dried at 70 °C in an oven for 24 h to give a yellow–brown powder (yield of 60%).

## Synthesis of TpPa COFs in PEG-400



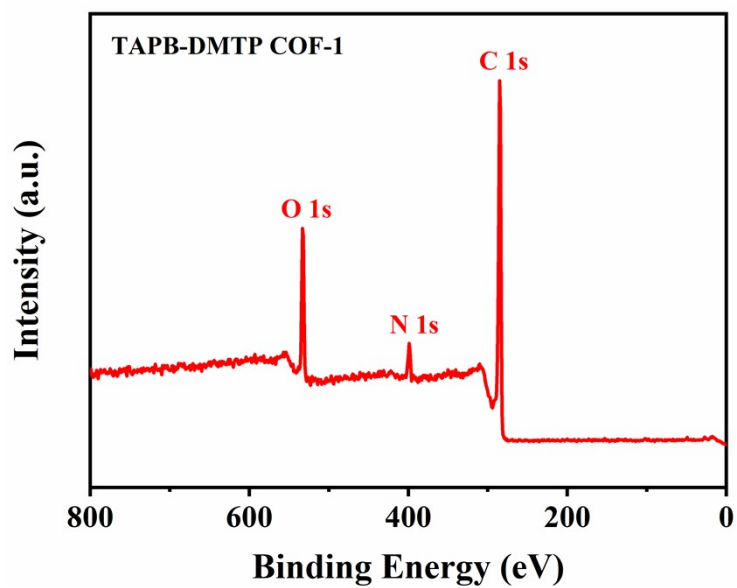
In a plastic centrifuge tube with a volume of 50.0 mL, 1,3,5-triformylphloroglucinol (Tp) (0.10 mmol, 21.0 mg) and p-phenylenediamine (Pa) (0.15 mmol, 16.2 mg) were dissolved in PEG-400 (3 mL) under vigorous stirring. Then, the mixture was kept at 25 °C for 72 h. The precipitate was isolated by centrifugation at 8500 rpm and washed with THF and ethanol (15 mL  $\times$  3), respectively. Finally, the powders were dried at 50 °C in an oven for 24 h to give a red powder (yield of 80%).

## Section S2. Figures

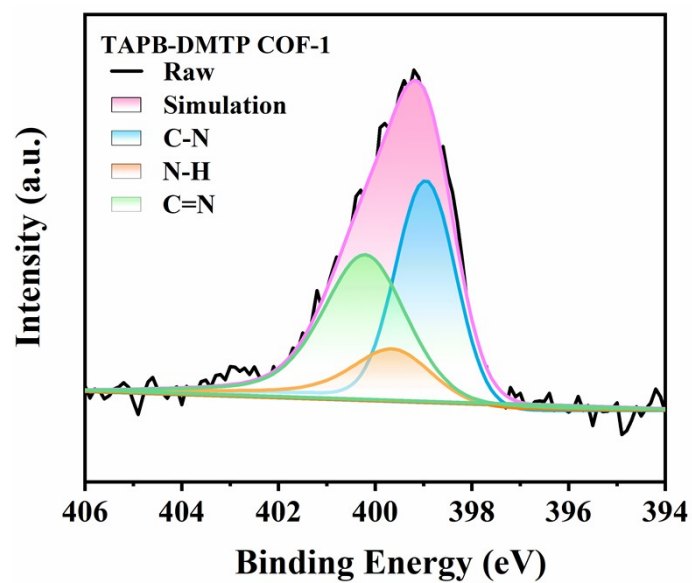


**Fig. S1.** Raman stretches of TAPB-DMTP COF-1 (PEG-400/H<sub>2</sub>O=1 mL/1 mL).

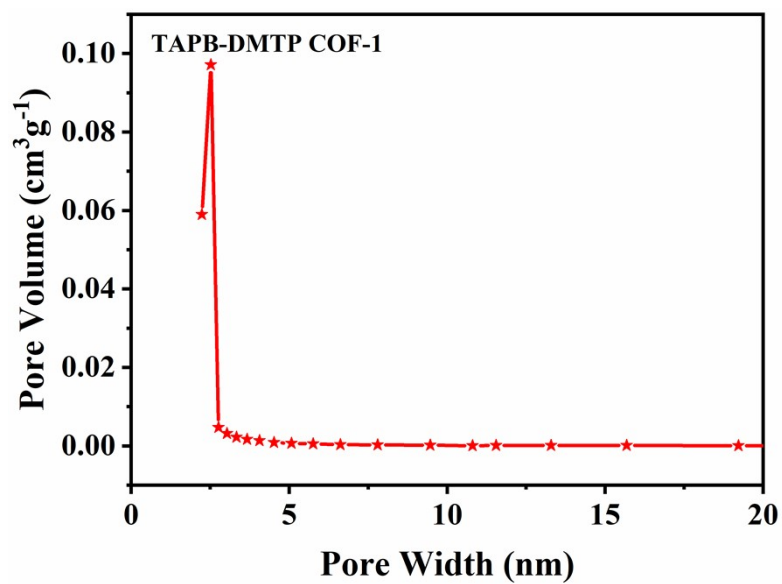




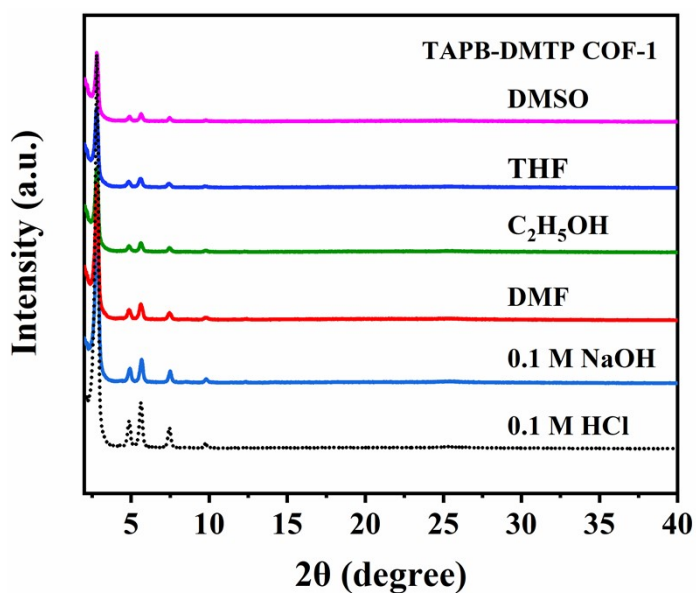
**Fig. S2.** XPS survey spectrum of TAPB-DMTP COF-1 (PEG-400/H<sub>2</sub>O=1 mL/1 mL).



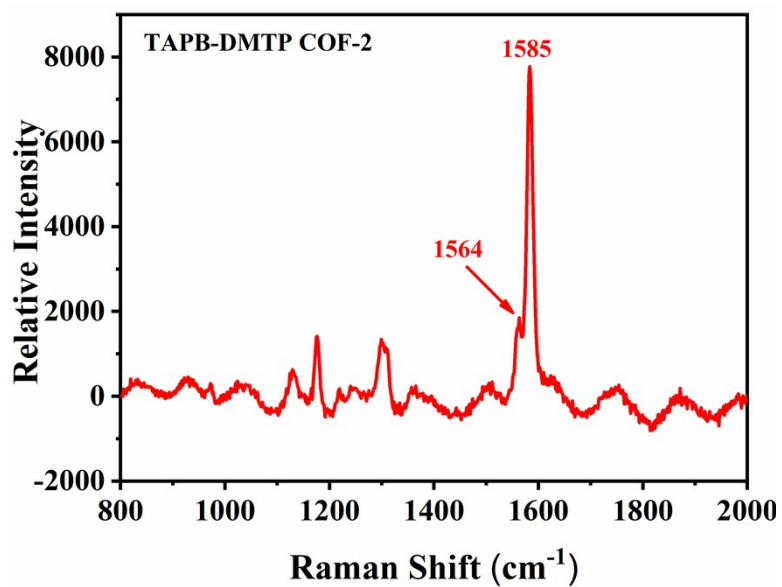
**Fig. S3.** N 1s region in the XPS of TAPB-DMTP COF-1 (PEG-400/H<sub>2</sub>O=1 mL/1 mL).



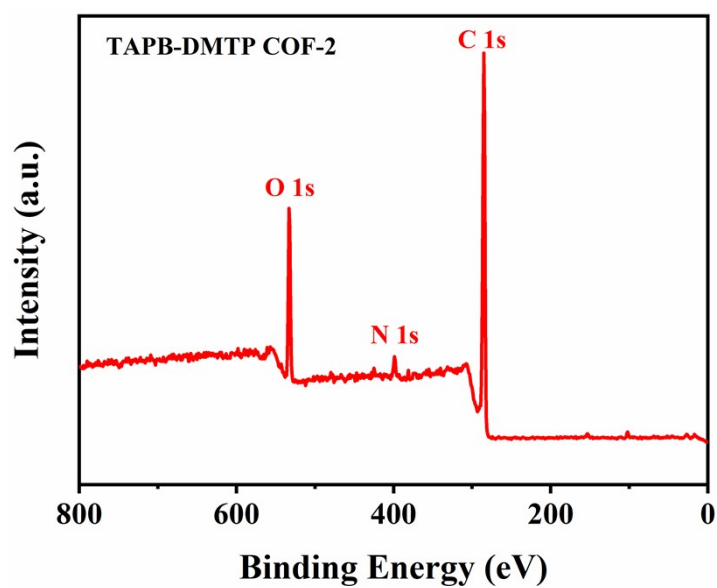
**Fig. S4.** DFT pore size distribution for the TAPB-DMTP COF-1 (PEG-400/H<sub>2</sub>O=1 mL/1 mL).



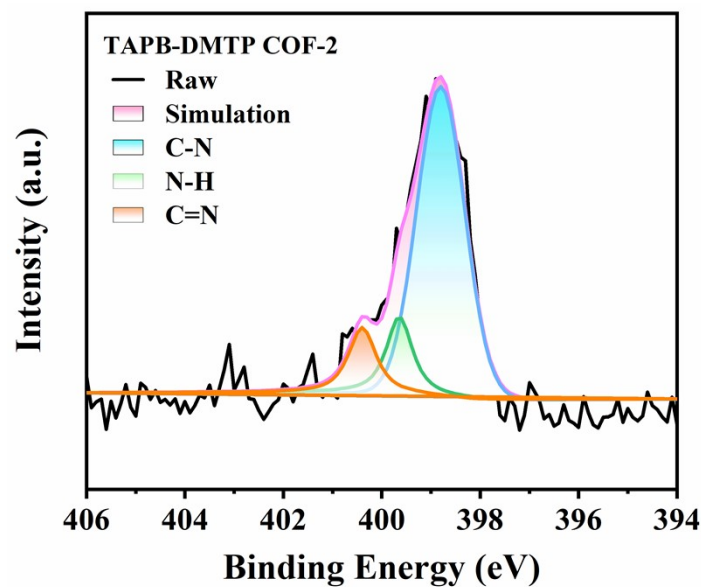
**Fig. S5.** Chemical stability test of TAPB-DMTP COF-1 (PEG-400/H<sub>2</sub>O=1 mL/1 mL)



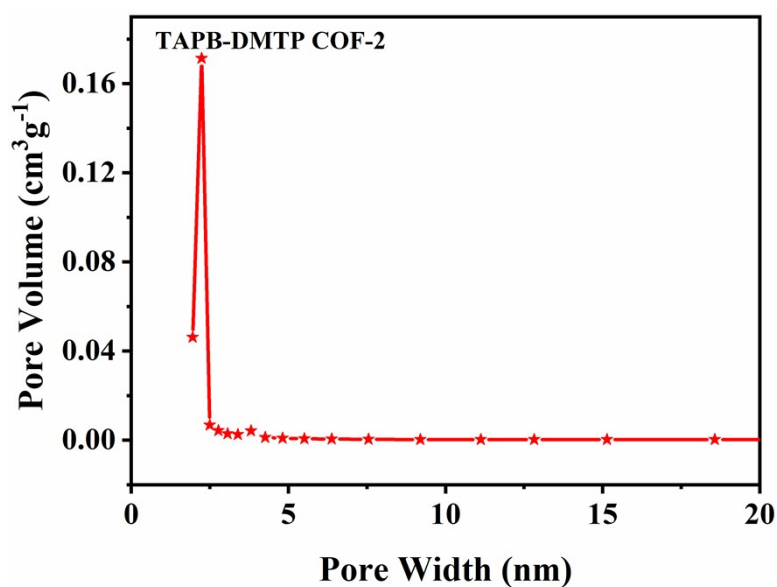
**Fig. S6.** Raman stretches of TAPB-DMTPCOF-2 (PEG-400/H<sub>2</sub>O=1.5 mL/0.5 mL).



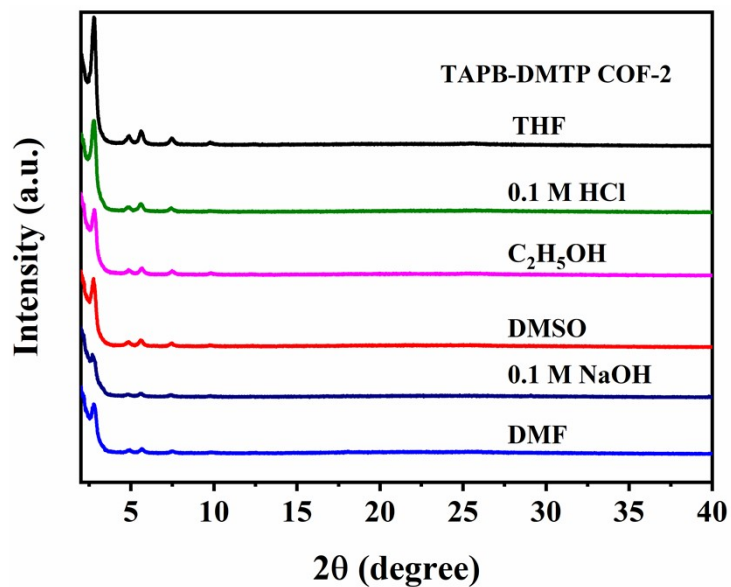
**Fig. S7.** XPS survey spectrum of TAPB-DMTP COF-2 (PEG-400/H<sub>2</sub>O=1.5 mL/0.5 mL).



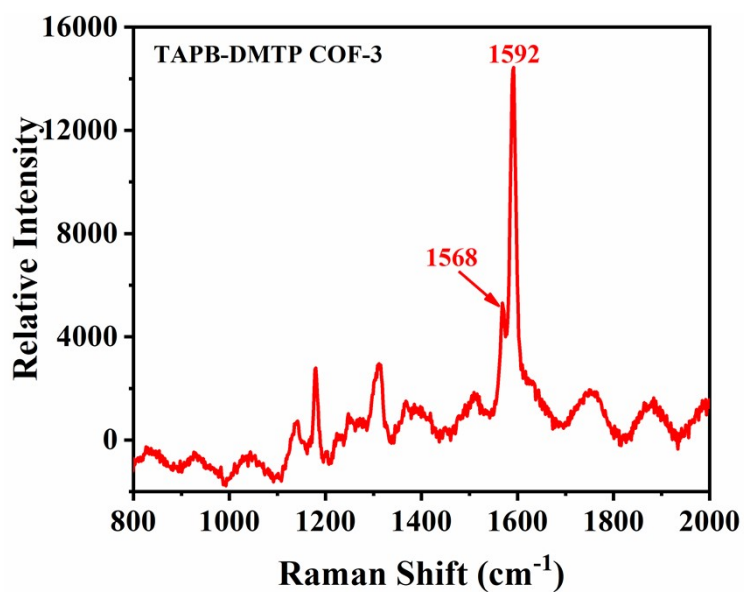
**Fig. S8.** N 1s region in the XPS of TAPB-DMTP COF-2 (PEG-400/H<sub>2</sub>O=1.5 mL/0.5 mL).



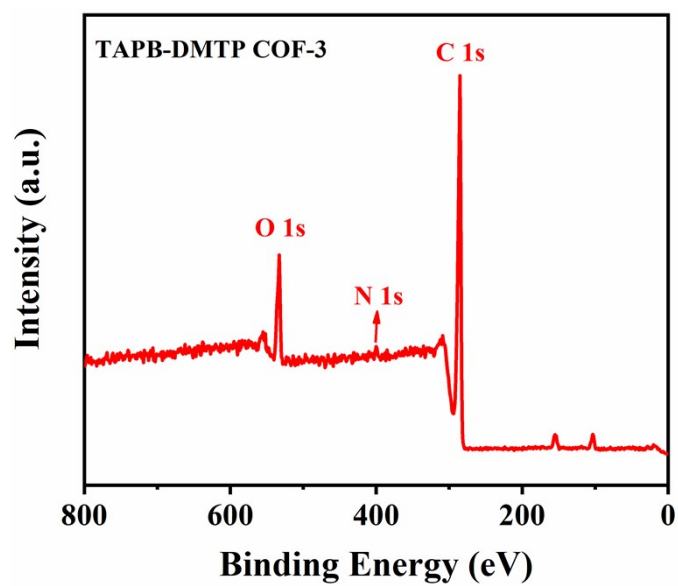
**Fig. S9.** DFT pore size distribution for the TAPB-DMTP COF-2 (PEG-400/H<sub>2</sub>O=1.5 mL/0.5 mL).



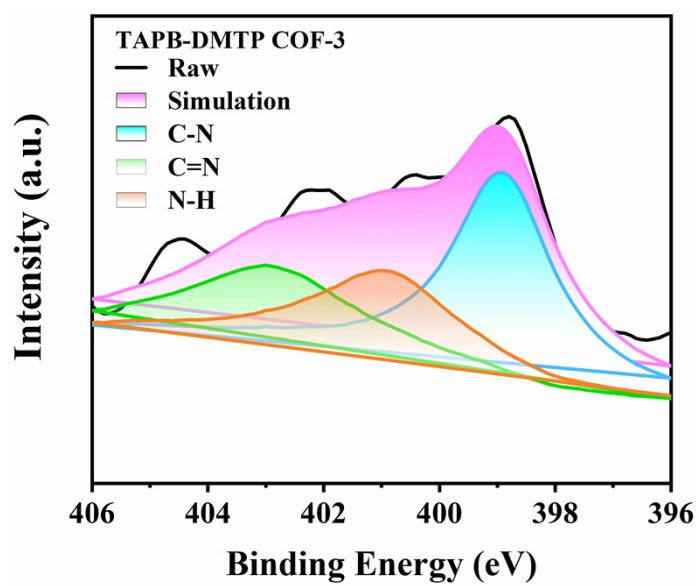
**Fig. S10.** Chemical stability test of TAPB-DMTP COF-2 (PEG-400/H<sub>2</sub>O=1.5 mL/0.5 mL).



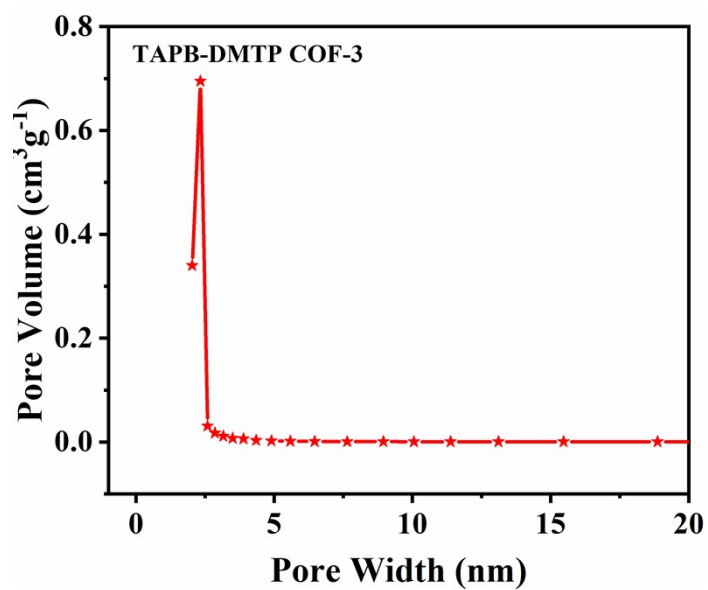
**Fig. S11.** Raman stretches of TAPB-DMTP COF-3 (PEG-400/H<sub>2</sub>O=2 mL/1 mL).



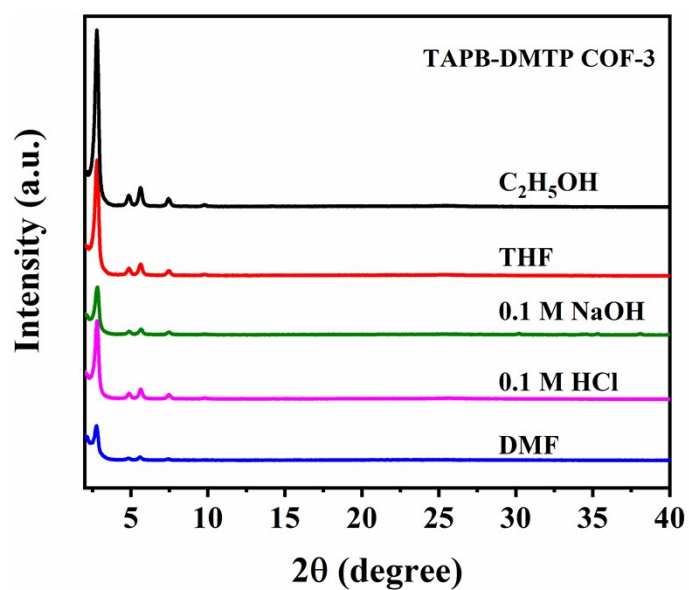
**Fig. S12.** XPS survey spectrum of TAPB-DMTP COF-3 (PEG-400/H<sub>2</sub>O=2 mL/1 mL).



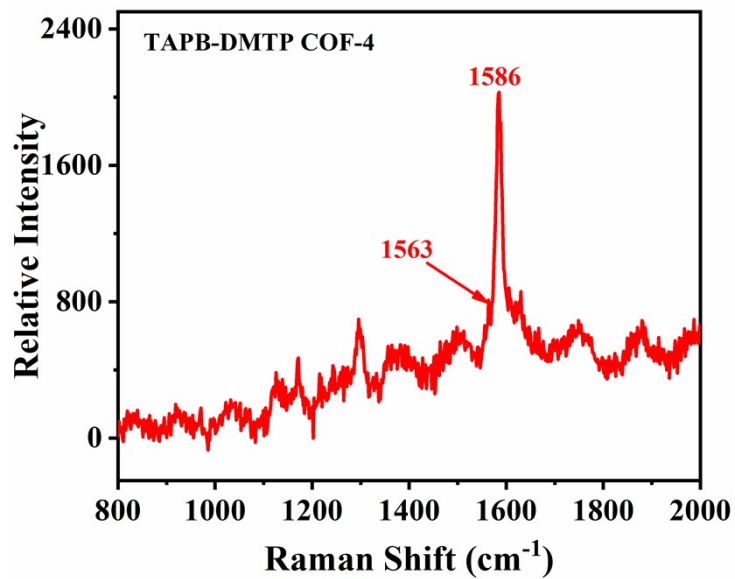
**Fig. S13.** N 1s region in the XPS of TAPB-DMTP COF-3 (PEG-400/H<sub>2</sub>O=2 mL/1 mL).



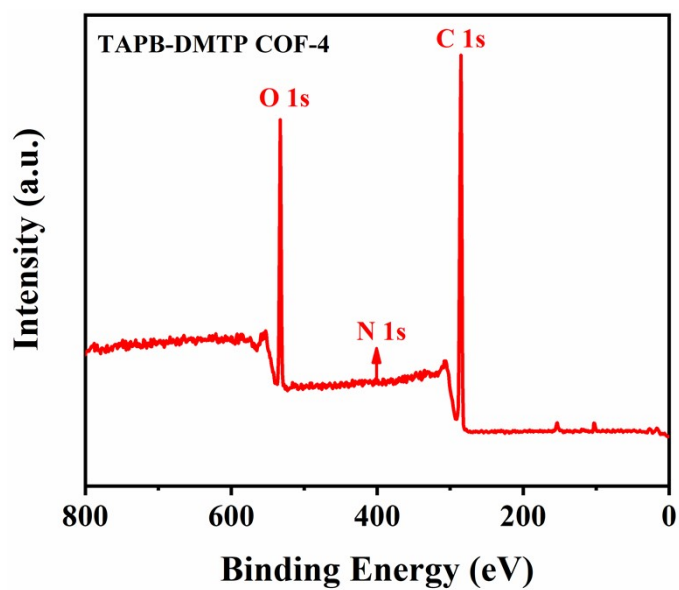
**Fig. S14.** DFT pore size distribution for the TAPB-DMTP COF-3 (PEG-400/H<sub>2</sub>O=2 mL/1 mL).



**Fig. S15.** Chemical stability test of TAPB-DMTP COF-3 (PEG-400/H<sub>2</sub>O=2 mL/1 mL).

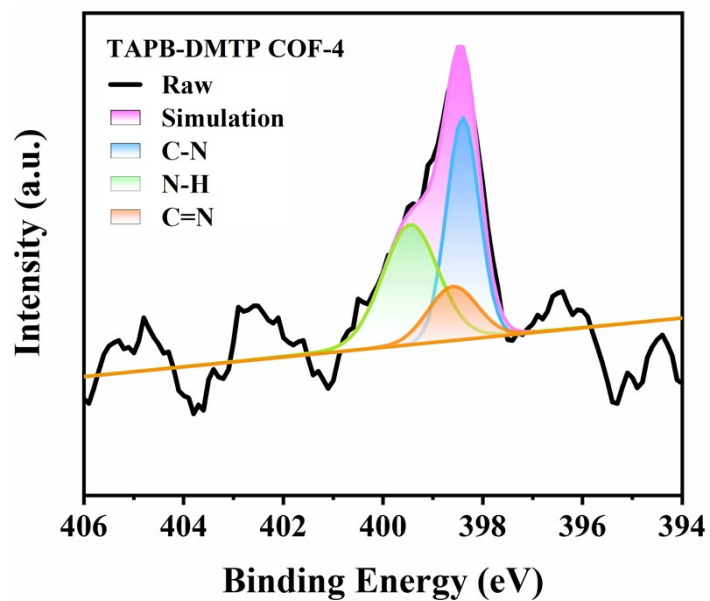


**Fig. S16.** Raman stretches of TAPB-DMTPCOF-4 (PEG-400/ $\text{H}_2\text{O}$ =0.5 mL/0.5 mL).

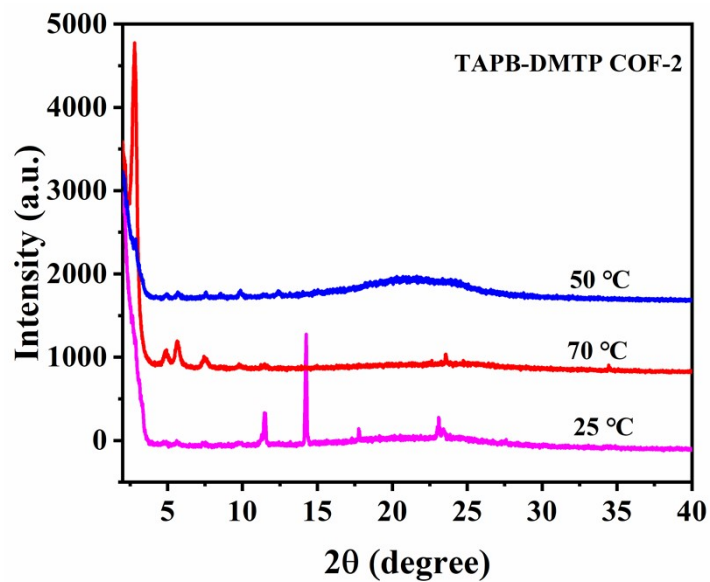


**Fig. S17.** XPS survey spectrum of TAPB-DMTP COF-4 (PEG-400/ $\text{H}_2\text{O}$ =0.5 mL/0.5 mL).

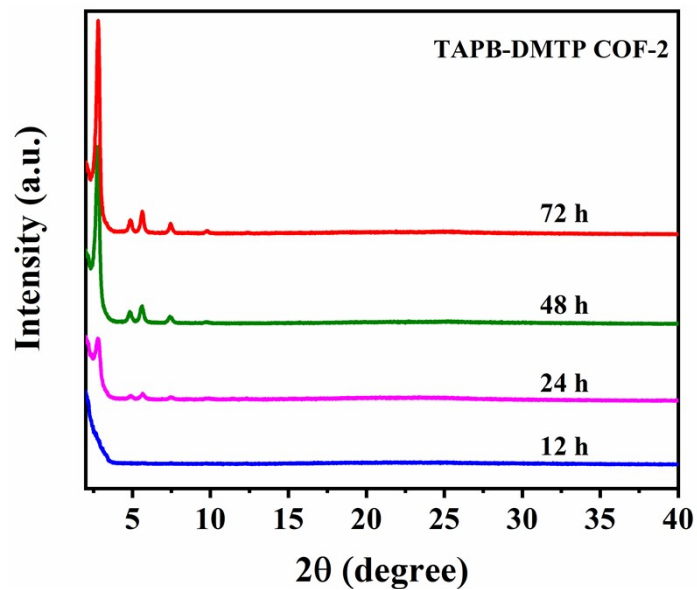




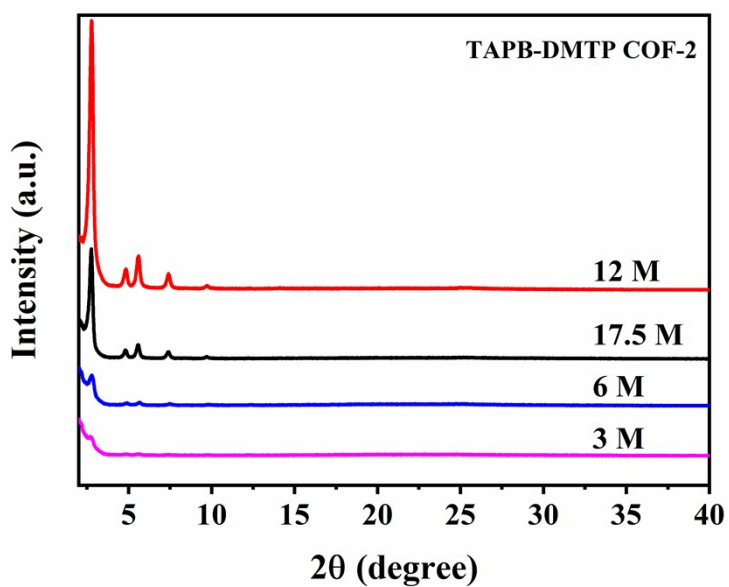
**Fig. S18.** N 1s region in the XPS of TAPB-DMTP COF-4 (PEG-400/H<sub>2</sub>O=0.5 mL/0.5 mL).



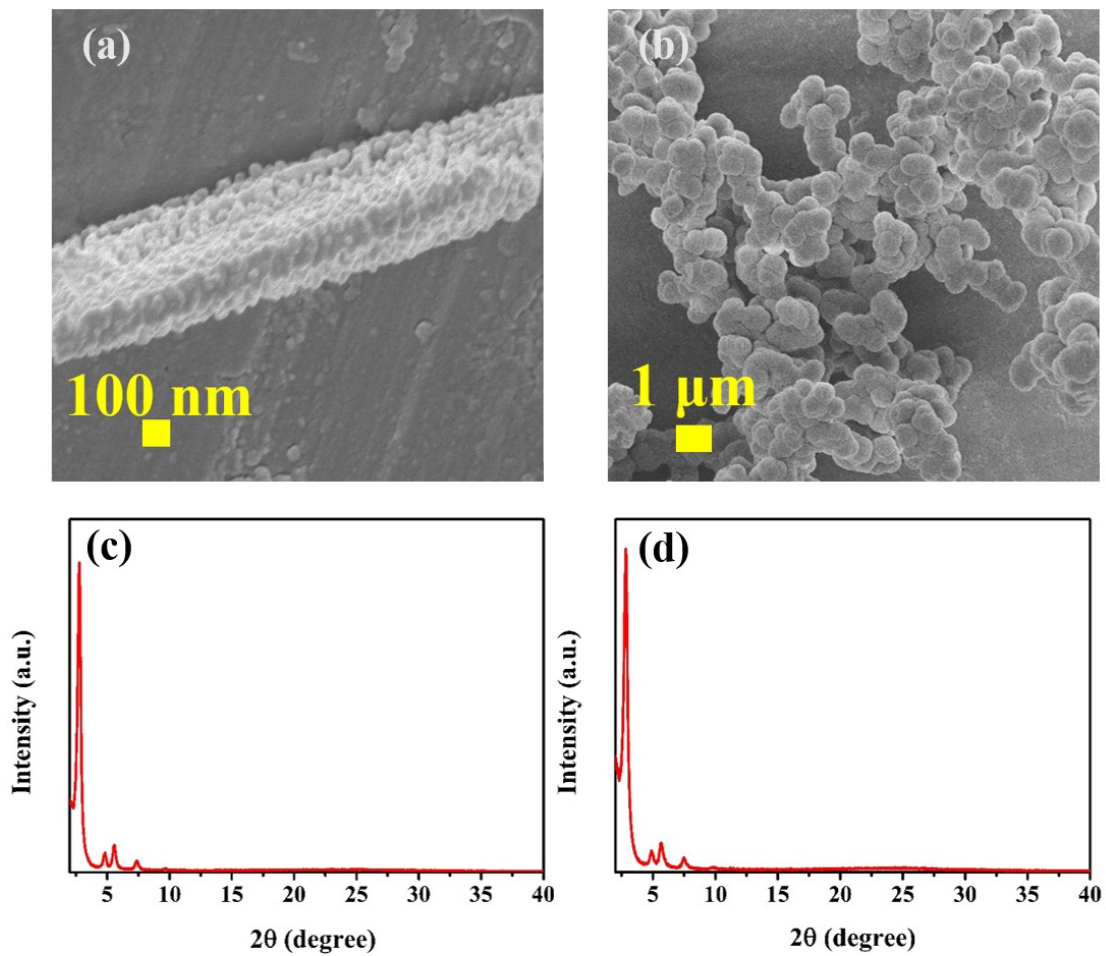
**Fig. S19.** Investigation on the influence of temperature on the preparation of TAPB-DMTP COF-2 (PEG-400/H<sub>2</sub>O=1.5 mL/0.5 mL).



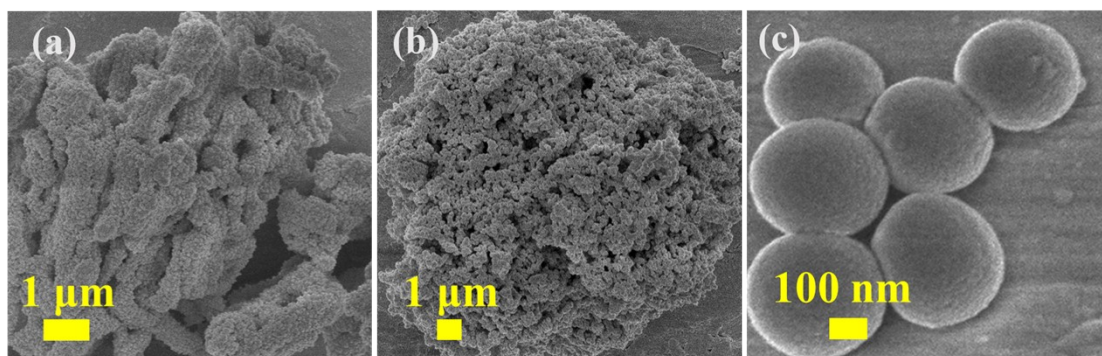
**Fig. S20.** Investigation on the influence of time on the preparation of TAPB-DMTP COF-2 (PEG-400/H<sub>2</sub>O=1.5 mL/0.5 mL).



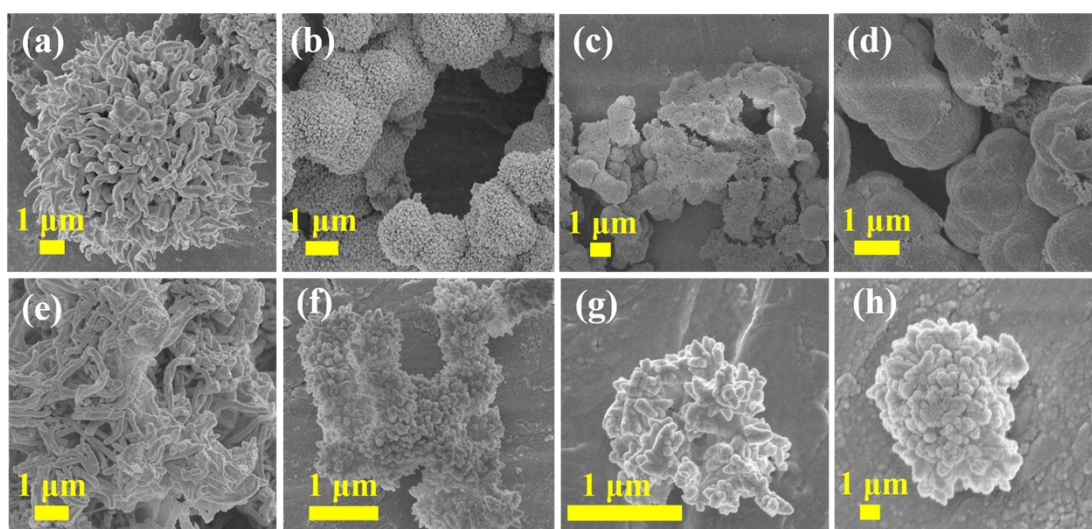
**Fig. S21.** Investigation on the influence of acetic acid concentration on the preparation of TAPB-DMTP COF-2 (PEG-400/H<sub>2</sub>O=1.5 mL/0.5 mL).



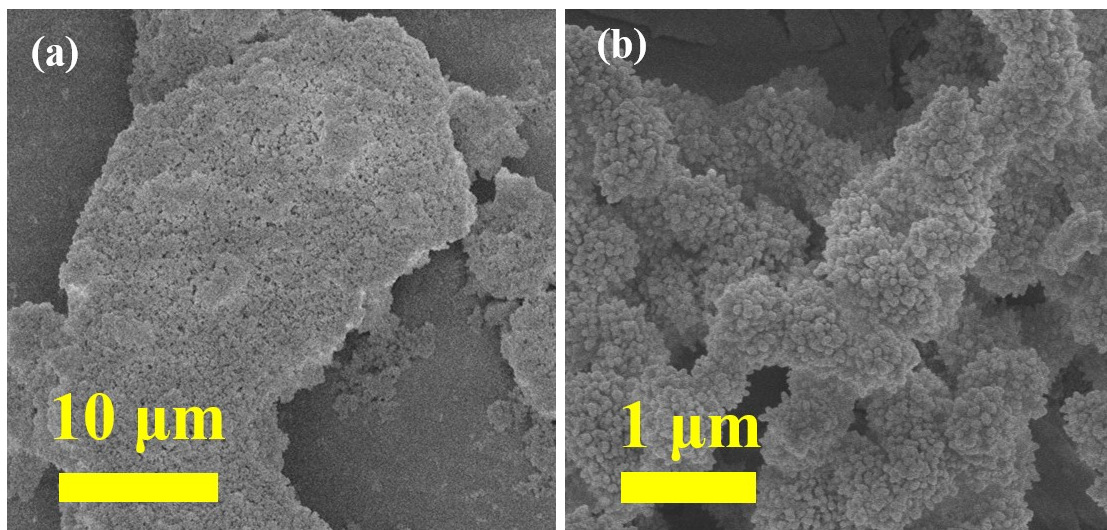
**Fig. S22.** SEM images and PXRD patterns of TAPB-DMTP COFs only using H<sub>2</sub>O and PEG-400 as reaction medium, respectively. (a, c) H<sub>2</sub>O as reaction medium, (b, d) PEG-400 as reaction medium.



**Fig. S23.** Investigation on the influence of modifiers on the morphology of TAPB-DMTP COF-4, (a) benzaldehyde, (b) aniline, (c) benzaldehyde and aniline.



**Fig. S24.** SEM images of TAPB-DMTP COFs prepared with 20 mg of different acids and different PEG; (a)  $\text{H}_2\text{O}$  /PEG-400=1 mL/1 mL, salicylic acid; (b)  $\text{H}_2\text{O}$ /PEG-400=1 mL/1.5 mL, salicylic acid; (c)  $\text{H}_2\text{O}$ /PEG-400=1 mL/1.5 mL, oxalic acid dihydrate; (d)  $\text{H}_2\text{O}$ /PEG-400=1 mL/1.5 mL, benzoic acid; (e)  $\text{H}_2\text{O}$ /PEG-200=0.5 mL/0.5 mL, 12 M HAc; (f)  $\text{H}_2\text{O}$ /PEG-200=0.5 mL/2 mL, 12 M HAc; (g)  $\text{H}_2\text{O}$ /PEG-600=0.5 mL/1 mL, 12 M HAc; (h)  $\text{H}_2\text{O}$ /PEG-600=0.5 mL/1.5 mL, 12 M HAc.



**Fig. S25.** SEM images of the TAPB-BTCA COFs (a) and TrPa (b).