Supplementary Information

Gentle and Rapid Synthesis of Imine-Linked Covalent Organic Frameworks in Acetic Acid-Based Deep Eutectic Solvents

Quanyuan Qiu[a], Guanwei Li[a], Chenxi Shi[a], Yueren Zeng[a], Kunchi Xie[b], Ke Wang[b], Zhen Song[b], Zhenjie Zhang[c], Xiaoqing Lin[a,*]

[a] School of Chemical Engineering and Light Industry, Guangdong Provincial Key Laboratory of Plant Resources Biorefinery, Guangdong University of Technology, Guangzhou 510006, China

[b] State Key Laboratory of Chemical Engineering, East China University of Science and Technology, Shanghai 200237, China

[c] College of Chemistry, Nankai University, Tianjin 300071, China

[*] Corresponding author: Prof. Xiaoqing Lin (X. Lin)

E-mail: linxiaoqing@gdut.edu.cn

Table of Tables

1. Materials

1,3,5-Tris(4-aminophenyl)benzene (TAPB), 4,4',4''-(1,3,5-Triazine-2,4,6-triyl) trianiline (TAPT), Tris(4-aminophenyl)amine (TAM), 4,4',4'',4'''-(1,8-dihydropyrene-1,3,6,8-tetrayl) tetraaniline (PTTA), Tetrakis (4-aminophenyl) methane (TAFM), 5,10,15,20-Tetrakis (4-aminophenyl)-21h, 23h-porphine (TAPP), Tetrakis(4-aminophenyl)ethene (ETTA), Terephthalaldehyde (PDA), m-Phthalaldehyde (PDE), 2,5-Dihydroxyterephthalaldehyde (DHA), 2,5-Difluoroterephthalaldehyde (DFP), 2,5-Dimethoxy-1,4-benzenedicarboxaldehyde (DMTP), 1,3,5-Benzenetricarboxaldehyde (BTCA), 2,3,5,6-Tetrafluoroterephthalaldehyde (TFP), 4,4'-Biphenyldicarboxaldehyde (BPDA), L-Menthol, Acetic acid (AA), n-Butanol, Acetonitrile (ACN), Polyethylene glycol-400 (PEG-400), Ethyl acetate (EAC), Tetrahydrofuran (THF), Ethanol (EtOH), Methanol (MeOH) , Choline chloride (ChCl), Triethylbenzylammonium chloride (TEBAC) , Glucose, Xylose, Formic acid (FA), Levulinic acid (LA), 5-Hydroxymethylfurfural (5-HMF) , Furfural, Sulfuric acid, and Hexane were all commercially available and used without further purification.

2. Characterizations

Fourier Transform Infrared Spectroscopy (FT-IR) in the region of 4000 cm^{-1} to 650 cm^{-1} was recorded on a Nicolet iS50R FTIR spectrometer. Dispersive Raman spectra were recorded on a Horiba Jobin-Yvon LabRAM HR800 fitted with a 633 nm laser operating at 17 mW in the range 1800-900 cm^{-1}. Nitrogen sorption isotherms were

recorded on a Micromeritics ASAP 2046 unit at 77 K. The NLDFT model was used to analyze the pore size distributions based on the adsorption isotherms. Samples were activated before measurement by heating at 120 °C for 12 h under vacuum. Powder X-ray diffraction (PXRD) patterns were collected on a MiniFlex600-C X-ray diffractometer, operated at 40 kV, 30 mA using Cu-Kα radiation (λ= 1.5406 Å) in Bragg-Brentano geometry. Scanning Electron Microscopy (SEM) was performed on a Zeiss Gemini Sigma 300. Samples were fixed with double-sided carbon tape to the sample holder. The samples were vacuum coated with gold for 45 s at 10 mA using a Quorum SC7620 before measurement. Transmission Electron Microscopy (TEM) imaging was done on a JEOL JEM-F200 at 100 kV without spherical aberration. The ^{13}C solid-state NMR data was acquired using a Bruker Avance Neo 400WB. The ^{1}H NMR data was acquired using a Bruker AVANCE III HD 400 M. Shimadzu high-performance liquid chromatography system (LC-10ATVP) was used to measure the concentration of each component in solution. The system was equipped with a controller (SCL-10AVP), a refractive index detector (RID-10A) and an Aminex HPX-87H anion-exchange column (300 mm×7.8 mm, Bio-Rad, USA). The column temperature was maintained at 55 °C, and the mobile phase was 5 mmol/L H_2SO_4 aqueous solution at a flow rate of 0.5 mL/min. The injection volume was 20 μL, and the analyzing time was 65 min for each sample. The viscosity was measured with an Anton Paar MCR301 Rheometer.

3. Experimental Methods

3.1 Synthesis of DES

3.1.1 Synthesis of Menthol/AA DES

Menthol/AA DES were synthesized with different molar ratios from 6:1 to 1:6. Menthol and AA with a predetermined molar ratio were individually added to reaction reagent bottles and stirred at 70 °C until a transparent liquid was formed.

3.1.2 Synthesis of ChCl/AA DES

ChCl/AA DES were synthesized with different molar ratios from 1:1 to 1:6. ChCl and AA with a predetermined molar ratio were individually added to reaction reagent bottles and stirred at 70 °C until a transparent liquid was formed (6:1 to 2:1 was not available).

3.1.3 Synthesis of TEBAC/AA DES

TEBAC /AA DES were synthesized with different molar ratios from 1:1 to 1:6. TEBAC and AA with a predetermined molar ratio were individually added to reaction reagent bottles and stirred at 70 °C until a transparent liquid was formed (6:1 to 2:1 was not available).

3.1.4 Synthesis of Thymol/AA DES

Thymol and AA with a predetermined molar ratio (1:1) were individually added to reaction reagent bottles and stirred at 70 °C until a transparent liquid was formed.

3.2 Synthesis of model COFs in Menthol/AA DES with different molar ratios

3.2.1 Synthesis of TAPB-PDA COF in Menthol/AA DES with different molar ratios

14.1 mg (0.04 mmol) TAPB and 8.0 mg PDA (0.06 mmol) were added into a 10 mL centrifugal tube. Then, add 2 mL of Menthol/AA DES (6:1 to 1:6) to the centrifuge tube. The mixture was sonicated for 5 min and a homogeneous suspension was formed. Subsequently, the mixture was allowed to stand at 70°C for 24 h to obtain powder product. Powder product was subjected to Soxhlet extraction using THF and EtOH for 24 hours until free of monomer and DES residues, respectively. The powder product was extracted by Soxhlet extraction using THF and EtOH distribution for 24 h. Finally, 3 mL of Hexane would be added and vacuum dried at 50°C under vacuum for 12 h.

3.2.2 Synthesis of TAPB-DHA COF in Menthol/AA DES with different molar ratios

14.1 mg (0.04 mmol) TAPB and 10.0 mg DHA (0.06 mmol) were added into a 10 mL centrifugal tube. The next steps were the same as in 3.2.1.

3.2.3 Synthesis of TAPB-DFP COF in Menthol/AA DES with different molar ratios

14.1 mg (0.04 mmol) TAPB and 10.2 mg DFP (0.06 mmol) were added into a 10 mL centrifugal tube. The next steps were the same as in 3.2.1.

3.3 Synthesis of model COFs in Menthol/AA DES at different temperatures

3.3.1 Synthesis of TAPB-PDA COF in Menthol/AA DES at different temperatures

14.1 mg (0.04 mmol) TAPB and 8.0 mg PDA (0.06 mmol) were added into a 10 mL centrifugal tube. Then, add 2 mL of Menthol/AA DES (1:2) to the centrifuge tube. The mixture was sonicated for 5 min and a homogeneous suspension was formed. Subsequently, the mixture was allowed to stand at different temperatures (25-120°C)

for 24 h to obtain powder product. The next steps were the same as in 3.2.1.

3.3.2 Synthesis of TAPB-DHA COF in Menthol/AA DES at different temperatures

14.1 mg (0.04 mmol) TAPB and 10.0 mg DHA (0.06 mmol) were added into a 10 mL centrifugal tube. Then, add 2 mL of Menthol/AA DES (1:1) to the centrifuge tube. The next steps were the same as in 3.3.1.

3.3.3 Synthesis of TAPB-DFP COF in Menthol/AA DES at different temperatures

14.1 mg (0.04 mmol) TAPB and 10.2 mg DFP (0.06 mmol) were added into a 10 mL centrifugal tube. Then, add 2 mL of Menthol/AA DES (1:6) to the centrifuge tube. The next steps were the same as in 3.3.1.

3.4 Synthesis of model COFs in pure acetic acid

3.4.1 Synthesis of TAPB-PDA COF in pure acetic acid

14.1 mg (0.04 mmol) TAPB and 8.0 mg PDA (0.06 mmol) were added into a 10 mL centrifugal tube. Then, add 2 mL of pure acetic acid to the centrifuge tube. The mixture was sonicated for 5 min and a homogeneous suspension was formed. Subsequently, the mixture was allowed to stand at 70°C for 24 h to obtain powder product. The next steps were the same as in 3.2.1.

3.4.2 Synthesis of TAPB-DHA COF in pure acetic acid

14.1 mg (0.04 mmol) TAPB and 10.0 mg DHA (0.06 mmol) were added into a 10 mL centrifugal tube. Then, add 2 mL of pure acetic acid to the centrifuge tube. The mixture was sonicated for 5 min and a homogeneous suspension was formed. Subsequently, the mixture was allowed to stand at 50°C for 24 h to obtain powder product. The next steps were the same as in 3.2.1.

3.4.3 Synthesis of TAPB-DFP COF in pure acetic acid

14.1 mg (0.04 mmol) TAPB and 10.2 mg DFP (0.06 mmol) were added into a 10 mL centrifugal tube. Then, add 2 mL of pure acetic acid to the centrifuge tube. The mixture was sonicated for 5 min and a homogeneous suspension was formed. Subsequently, the mixture was allowed to stand at 70°C for 24 h to obtain powder product. The next steps were the same as in 3.2.1.

3.5 Scale up synthesis of models COF

3.5.1 Scale up synthesis of TAPB-PDA COF

352.5 mg (1 mmol) TAPB and 200.0 mg PDA (1.5 mmol) were added into a 100 mL glass vial. Then, add 50 mL of Menthol/AA DES (1:2) to the glass vial. The mixture was sonicated for 5 min and a homogeneous suspension was formed. Subsequently, the mixture was allowed to stand at 70°C for 24 h to obtain powder product. The next steps were the same as in 3.2.1.

3.5.2 Scale up synthesis of TAPB-DHA COF

352.5 mg (1 mmol) TAPB and 250.0 mg DHA (1.5 mmol) were added into a 100 mL glass vial. Then, add 50 mL of Menthol/AA DES (1:1) to the glass vial. The mixture was sonicated for 5 min and a homogeneous suspension was formed. Subsequently, the mixture was allowed to stand at 70°C for 24 h to obtain powder product. The next steps were the same as in 3.2.1.

3.5.3 Scale up synthesis of TAPB-DFP COF

352.5 mg (1 mmol) TAPB and 255.0 mg DFP (1.5 mmol) were added into a 100 mL glass vial. Then, add 50 mL of Menthol/AA DES (1:6) to the glass vial. The mixture

was sonicated for 5 min and a homogeneous suspension was formed. Subsequently, the mixture was allowed to stand at 70°C for 24 h to obtain powder product. The next steps were the same as in 3.2.1.

3.5.4 Scale up synthesis of TAPB-TFP COF

1.41 g (4 mmol) TAPB and 1.26 g TFP (6 mmol) were added into a 250 mL glass vial. Then, add 200 mL of Menthol/AA DES (1:6) to the glass vial. The mixture was sonicated for 5 min and a homogeneous suspension was formed. Subsequently, the mixture was allowed to stand at 70°C for 24 h to obtain powder product. The next steps were the same as in 3.2.1.

3.6 Synthesis of model COFs in Menthol/AA DES under different reaction time

3.6.1 Synthesis of TAPB-PDA COF in Menthol/AA DES under different reaction time

14.1 mg (0.06 mmol) TAPB and 8.0 mg PDA (0.04 mmol) were added into a 10 mL centrifuge tube. Then, add 2 mL of Menthol/AA DES (1:2) to the centrifuge tube. The mixture was sonicated for 5 min and a homogeneous suspension was formed. Subsequently, the mixture was allowed to stand at 70°C from 1-48 h to obtain powder product. The next steps were the same as in 3.2.1.

3.6.2 Synthesis of TAPB-DHA COF in Menthol/AA DES under different reaction time

14.1 mg (0.06 mmol) TAPB and 10.0 mg DHA (0.04 mmol) were added into a 10 mL centrifuge tube. Then, add 2 mL of Menthol/AA DES (1:1) to the centrifuge tube.

The mixture was sonicated for 5 min and a homogeneous suspension was formed. Subsequently, the mixture was allowed to stand at 50°C from 1-48 h to obtain powder product. The next steps were the same as in 3.2.1.

3.6.3 Synthesis of TAPB-DFP COF in Menthol/AA DES under different reaction time

14.1 mg (0.06 mmol) TAPB and 10.2 mg DFP (0.04 mmol) were added into a 10 mL centrifuge tube. Then, add 2 mL of Menthol/AA DES (1:6) to the centrifuge tube. The mixture was sonicated for 5 min and a homogeneous suspension was formed. Subsequently, the mixture was allowed to stand at 70°C from 1-48 h to obtain powder product. The next steps were the same as in 3.2.1.

3.7 Synthesis of model COFs in pure acetic acid under different reaction time

Except for changing Menthol/AA DES to pure acetic acid, the other steps were the same as in 3.6.

3.8 Synthesis of TAPB-DHA in organic solvent

14.1 mg (0.04 mmol) TAPB and 10.0 mg DHA (0.06 mmol) were added into a 10 mL centrifuge tube. Then, add 2 mL of organic solvent (acetonitrile, ethyl acetate, polyethylene glycol-400, and n-butanol) and 0.2 mL aqueous solution of acetic acid (3-12M) to the centrifuge tube. The mixture was sonicated for 5 min and a homogeneous suspension was formed. Subsequently, the mixture was allowed to stand at 70°C for 24 h to obtain powder product. The next steps were the same as in 3.2.1.

3.9 Synthesis of TAPB-PDA in different DES

3.9.1 Synthesis of TAPB-PDA COF in ChCl/AA DES

14.1 mg (0.06 mmol) TAPB and 8.0 mg PDA (0.04 mmol) were added into a 10 mL centrifuge tube. Then, add 2 mL of ChCl/AA DES (1:1-1:6) to the centrifuge tube. The mixture was sonicated for 5 min and a homogeneous suspension was formed. Subsequently, the mixture was allowed to stand at 70°C for 24 h to obtain powder product. The next steps were the same as in 3.2.1.

3.9.2 Synthesis of TAPB-PDA COF in TEBAC/AA DES

Except for changing ChCl/AA DES (1:1-1:6) to TEBAC/AA DES (1:1-1:6), the other steps were the same as in 3.9.1.

3.9.3 Synthesis of TAPB-PDA COF in Thymol /AA DES

Except for changing ChCl/AA DES (1:1-1:6) to Thymol /AA DES (1:1), the other steps were the same as in 3.9.1.

3.10 Synthesis of TAPB-PDA in different DES with extra H_2O

Except for changing 2 mL of DES (1:1-1:6) to 1 mL of DES (1:1-1:6) and 1 mL H_2O, the other steps were the same as in 3.9.1.

3.11 General COF synthesis

Weighed an amount of amine monomer and aldehyde monomer with a 10 mL centrifuge tube (see Table 1 for specific amounts). Added 2 mL of DES in the corresponding molar ratio and sonicate for 5 min to obtain the homogeneous suspension. The mixture was allowed to stand at 70°C for 24 h. The next steps were the same as in 3.2.1.

Table S1 Amounts of monomer used and yields for the different COFs

COF	Molar ratio	Aldehyde monomer (mmol)	Amine monomer (mmol)	Yield (%)
TAPB-DMTP	1:1	0.06	0.04	87
TAPB-BTCA	1:4	0.04	0.04	93
TAPT-PDA	1:4	0.06	0.04	71
TAPT-DMTP	1:1	0.06	0.04	81
TAPT-DHA	1:1	0.06	0.04	75
TAPT-DFP	1:6	0.06	0.04	76
TAPT-BTCA	1:6	0.04	0.04	63
PTTA-PDA	1:2	0.08	0.04	90
PTTA-DMTP	1:1	0.08	0.04	84
PTTA-DHA	1:2	0.08	0.04	88
PTTA-DFP	1:6	0.08	0.04	77
PTTA-BTCA	1:2	0.04	0.04	86
TAPB-TFP	1:6	0.06	0.04	81
TAPB-BPDA	1:2	0.06	0.04	78
TPPA-DMTP	1:4	0.08	0.04	72
TAM-BTCA	1:4	0.04	0.04	86
PTTA-PDE	1:2	0.04	0.04	87
TAFM-PDA	1:1	0.08	0.04	80
ETTA-PDA	1:2	0.08	0.16	93
ETTA-BPDA	1:2	0.08	0.16	91

3.12 Experimental procedure for adsorption of COFs in simulated hydrolysates

Adsorption experiments using four COFs, TAPB-PDA, TAPB-DHA, TAPB-DFP, and TAPB-TFP, were carried out in a simulated hydrolysis solution to evaluate their effectiveness in removing inhibitors. The compositions and initial concentrations of the simulated hydrolysate were: glucose, 54.484 g/L; xylose, 4.152 g/L; formic acid, 1.362 g/L; acetic acid, 5.682 g/L; levulinic acid, 0.073 g/L; 5-hydroxymethylfurfural (5-HMF), 0.542 g/L; and furfural, 1.589 g/L. To 5 mL of the simulated hydrolysis solution, 0.05 g of COFs powder was added. After shaking at 120 rpm and 298 K for 4 h, the concentration of each component was determined using high performance liquid chromatography (HPLC) was employed to method was used to determine the experimental results. Adsorption capacity $(q_{i,e})$ was calculated using equation (1) and adsorption selectivity $\left(\alpha_i^{\text{furfural}}\right)$ was calculated using equation (2). $C_{i,0}$ and $C_{i,e}$ are the concentrations of component i before and after adsorption, respectively. *V* is the volume of the aqueous solution (L) and m is the mass of COF (g).

$$q_{i,e} = \frac{\left(C_{i,0} - C_{i,e}\right)V}{m} \tag{1}$$

$$\alpha_i^{\text{furfural}} = \frac{q_{\text{furfural},e} \cdot C_{i,e}}{q_{i,e} \cdot C_{\text{furfural},e}} \tag{2}$$

3.13 Adsorption isotherm experiment

The adsorption isotherms of furfural at different temperatures (288, 298 and 308 K) were investigated. Five mL of furfural solution with different initial concentrations (C_0=0.5, 1.0, 1.5, 2.0, 4.0, 6.0, 8 g/L) were added to a conical flask containing 0.05 g of TAPB-TFP COF. The concentration of furfural was determined using HPLC after

shaking at 120 rpm and 298 K for 4 h. Adsorption capacity (q_e) was calculated using equation (3). C_0 and C_e are the concentrations of furfural before and after adsorption, respectively. *V* is the volume of the aqueous solution (L) and m is the mass of COF (g). In addition, Langmuir and Freundlich adsorption isotherm models (equation (4) and equation (5)) were used to fit static adsorption data for furfural.

$$q_e = \frac{(C_0 - C_e)V}{m} \tag{3}$$

$$q_e = \frac{q_{max} K_L C_e}{1 + K_L C_e} \tag{4}$$

$$q_e = K_F {C_e}^{1/n_F} \tag{5}$$

3.14 Adsorption-desorption cycle experiment

At the end of the adsorption experiments, the TAPB-TFP obtained after adsorption was desorbed with pure ethanol and desorbed in a constant temperature shaker at 120 rpm for 24 h at 45°C. Five adsorption-desorption cycles of TAPB-TFP were carried out under the same experimental conditions to assess the reusability of the TAPB-TFP COF.

3.15 Adsorption kinetic experiments

Adsorption kinetic experiments were conducted using an aqueous furfural solution with an initial concentration of 1.5 g/L at 25°C. The experimental procedure involved preheating 250 mL of the furfural solution in a constant-temperature water bath. Subsequently, 1.0 g of TAPB-TFP COF was added to a three-necked flask, followed by the introduction of the preheated furfural solution. The mixture was continuously stirred at 120 rpm in a thermostatically controlled water bath. Samples were collected at specific time intervals (0, 1, 3, 6, 9, 12, 15, 20, 30, 60, 80, 100, and 120 min), immediately diluted, and analyzed (C_t). The concentration of furfural was

quantitatively determined using High Performance Liquid Chromatography (HPLC). The adsorption capacity (q_t) of TAPB-TFTA at different time points was calculated according to Equation (6).

$$q_t = \frac{(C_0 - C_t)V}{m} \tag{3}$$

4. Figures and Table

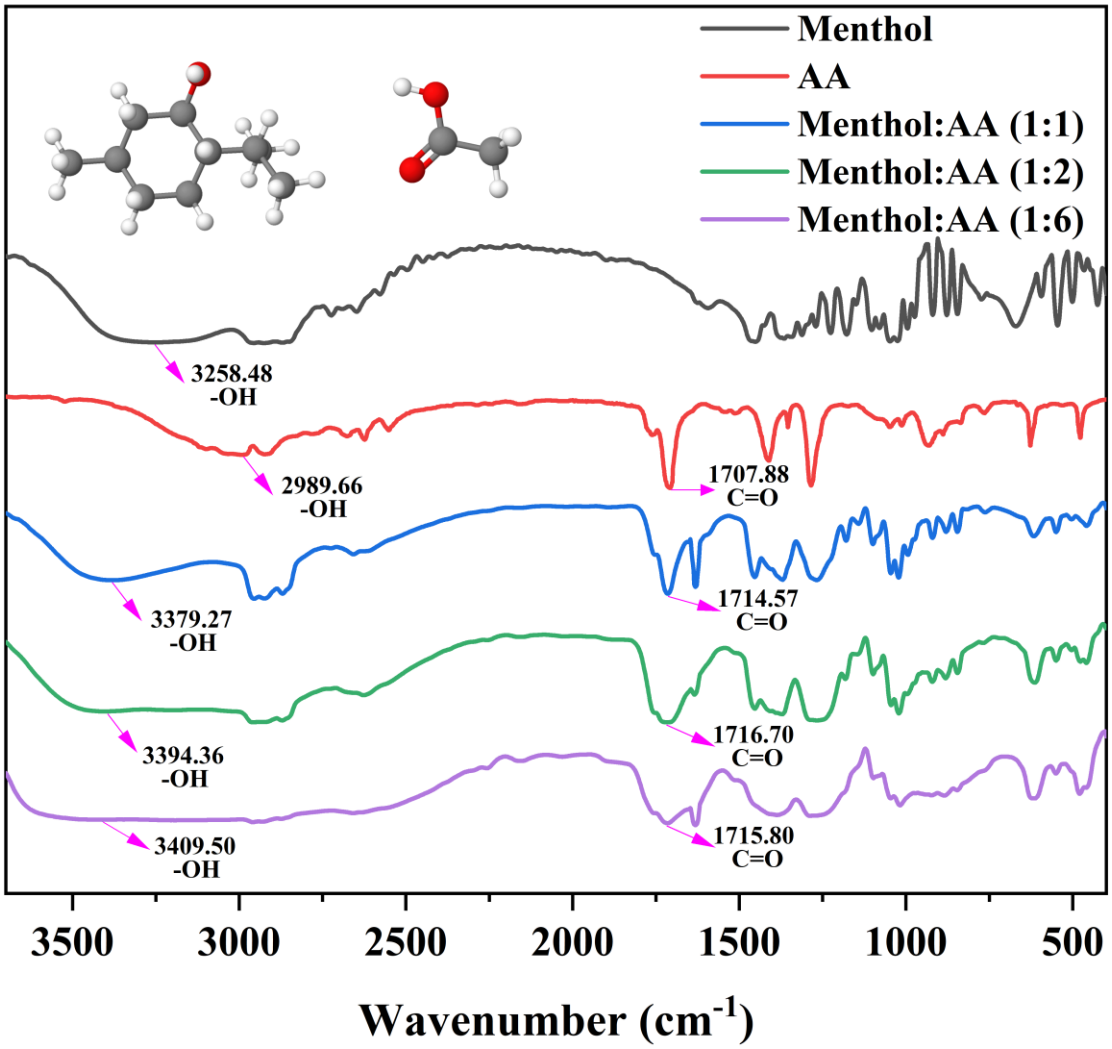

Figure S1 Infrared spectroscopy of DES and pure component.

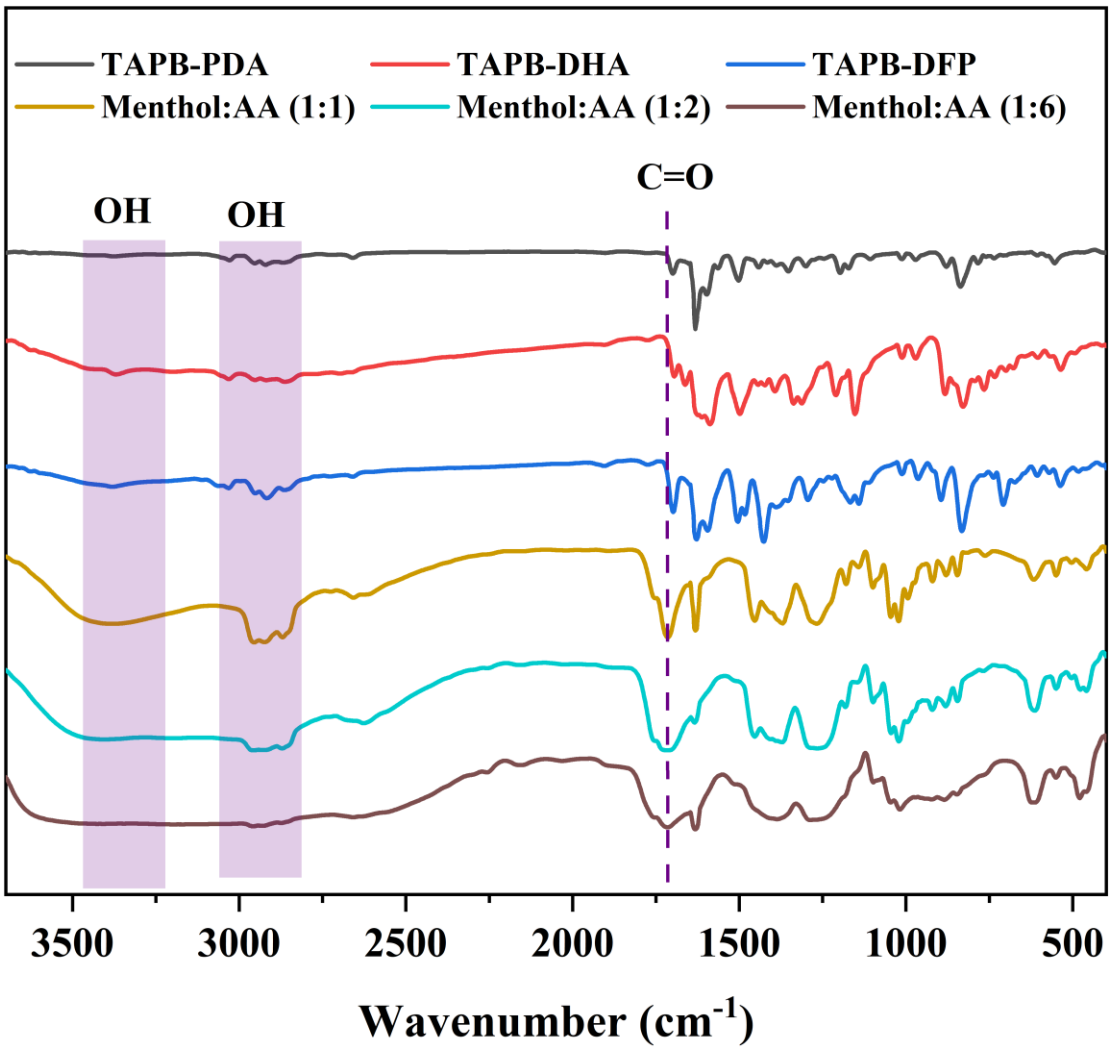

Figure S2 Infrared spectroscopy of DES and model COFs.

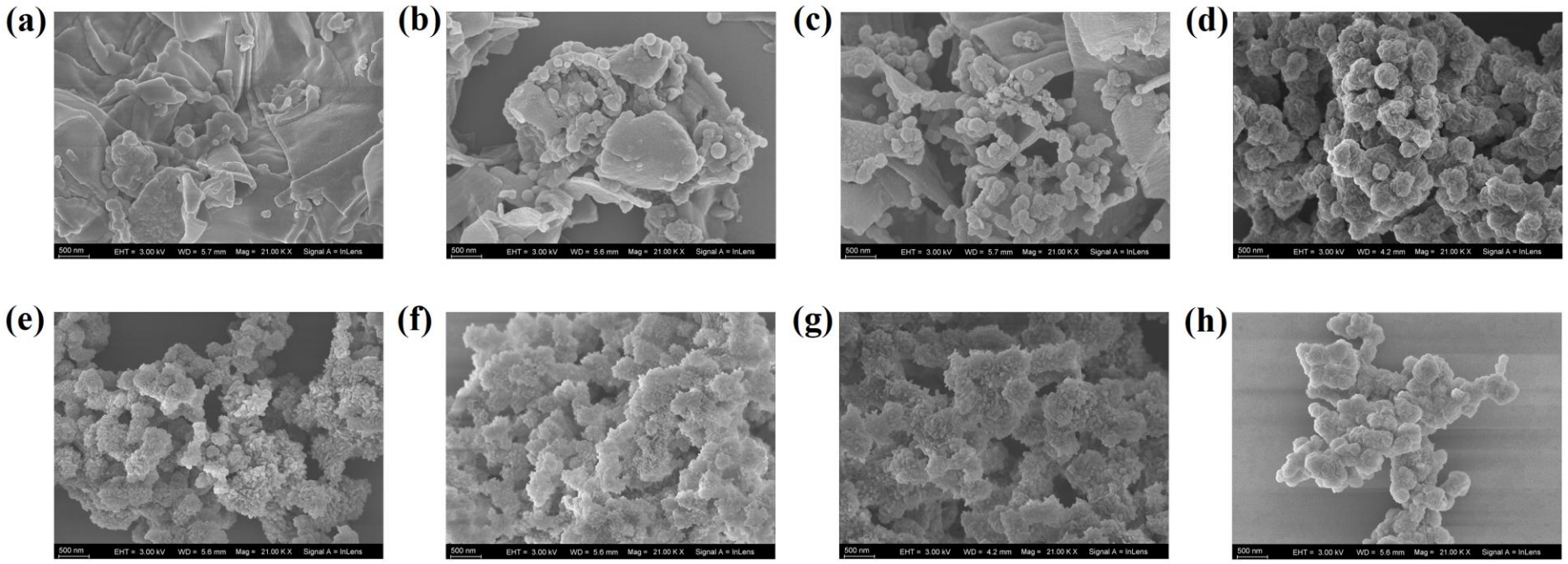

Figure S3 SEM images of the TAPB-PDA COFs that were synthesized in Menthol/AA DES with different molar ratio ((a) 6:1, (b) 4:1, (c) 2:1, (d) 1:1, (e) 1:2, (f) 1:4, (g) 1:6, (h) pure acetic acid).

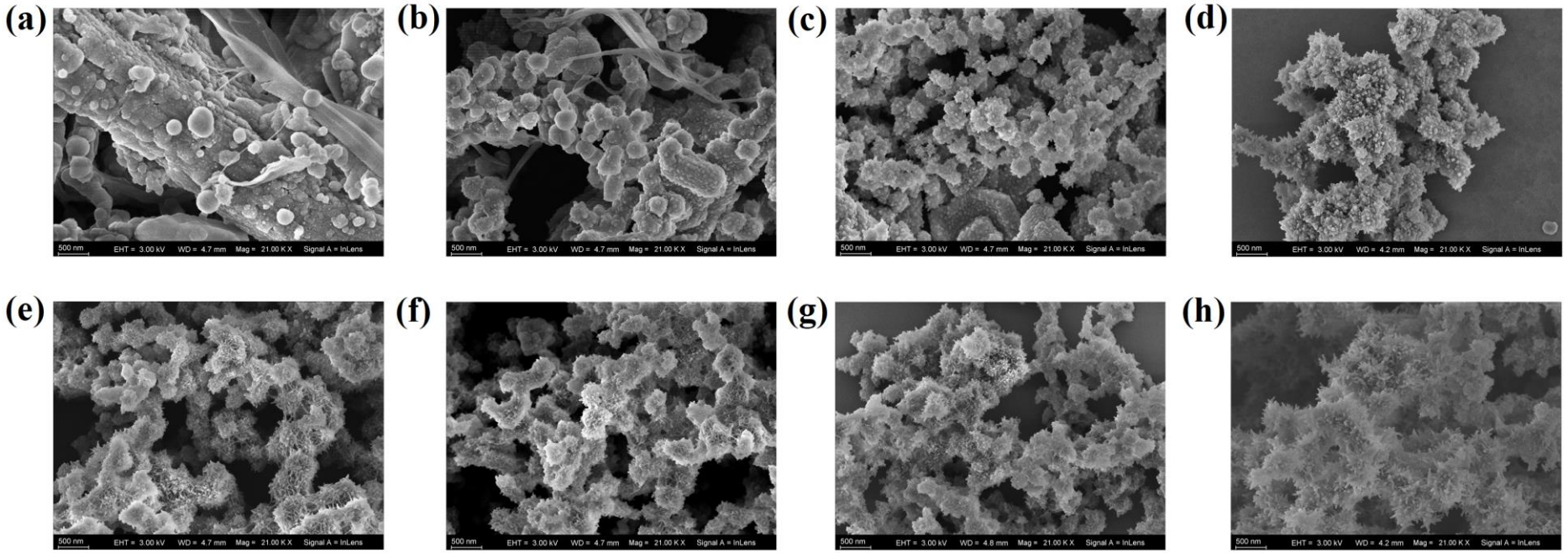

Figure S4 SEM images of the TAPB-DHA COFs that were synthesized in Menthol/AA DES with different molar ratio ((a) 6:1, (b) 4:1, (c) 2:1, (d) 1:1, (e) 1:2, (f) 1:4, (g) 1:6, (h) pure acetic acid).

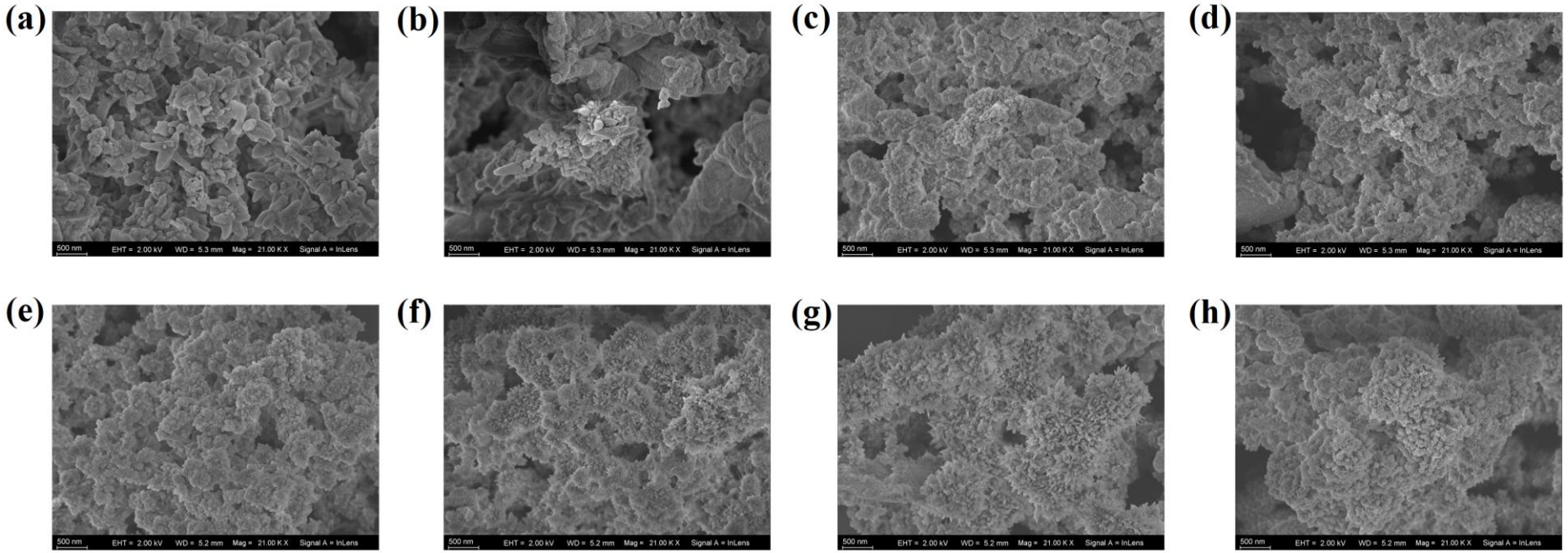

Figure S5 SEM images of the TAPB-DFP COFs that were synthesized in Menthol/AA DES with different molar ratio ((a) 6:1, (b) 4:1, (c) 2:1, (d) 1:1, (e) 1:2, (f) 1:4, (g) 1:6, (h) pure acetic acid).

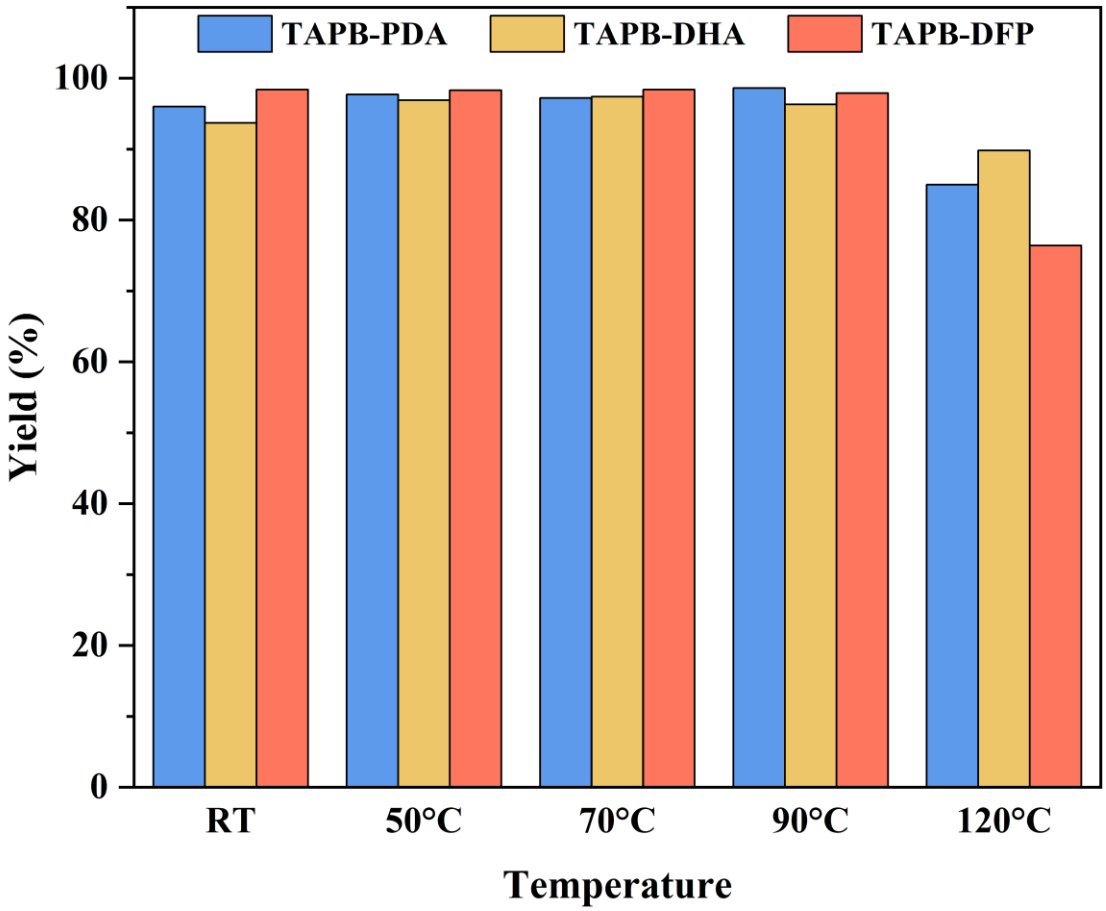

Figure S6 The yields of the three model COFs synthesized in Menthol/AA DES at different temperatures.

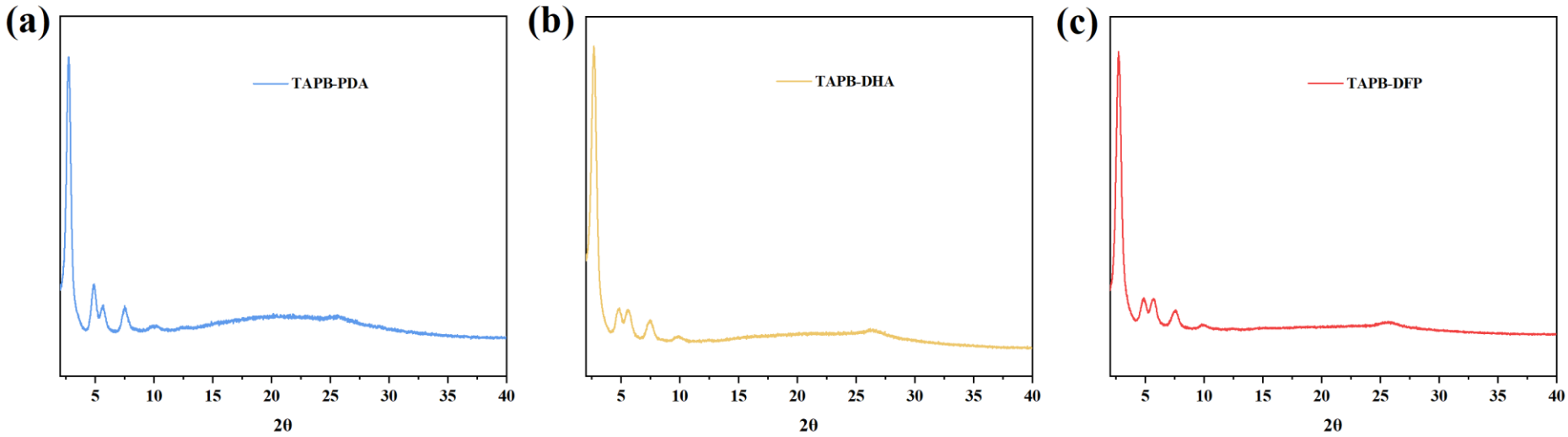

Figure S7 PXRD patterns of three models COFs synthesized in Menthol/AA DES at room temperature.

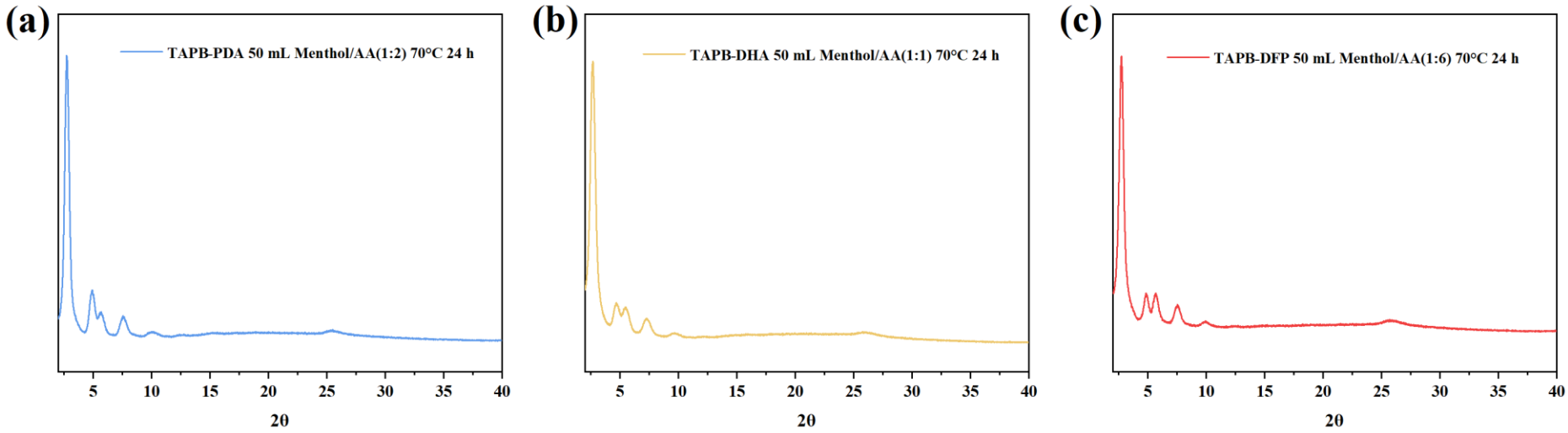

Figure S8 PXRD patterns of the large-scale synthesis of three model COFs synthesized in Menthol/AA DES.

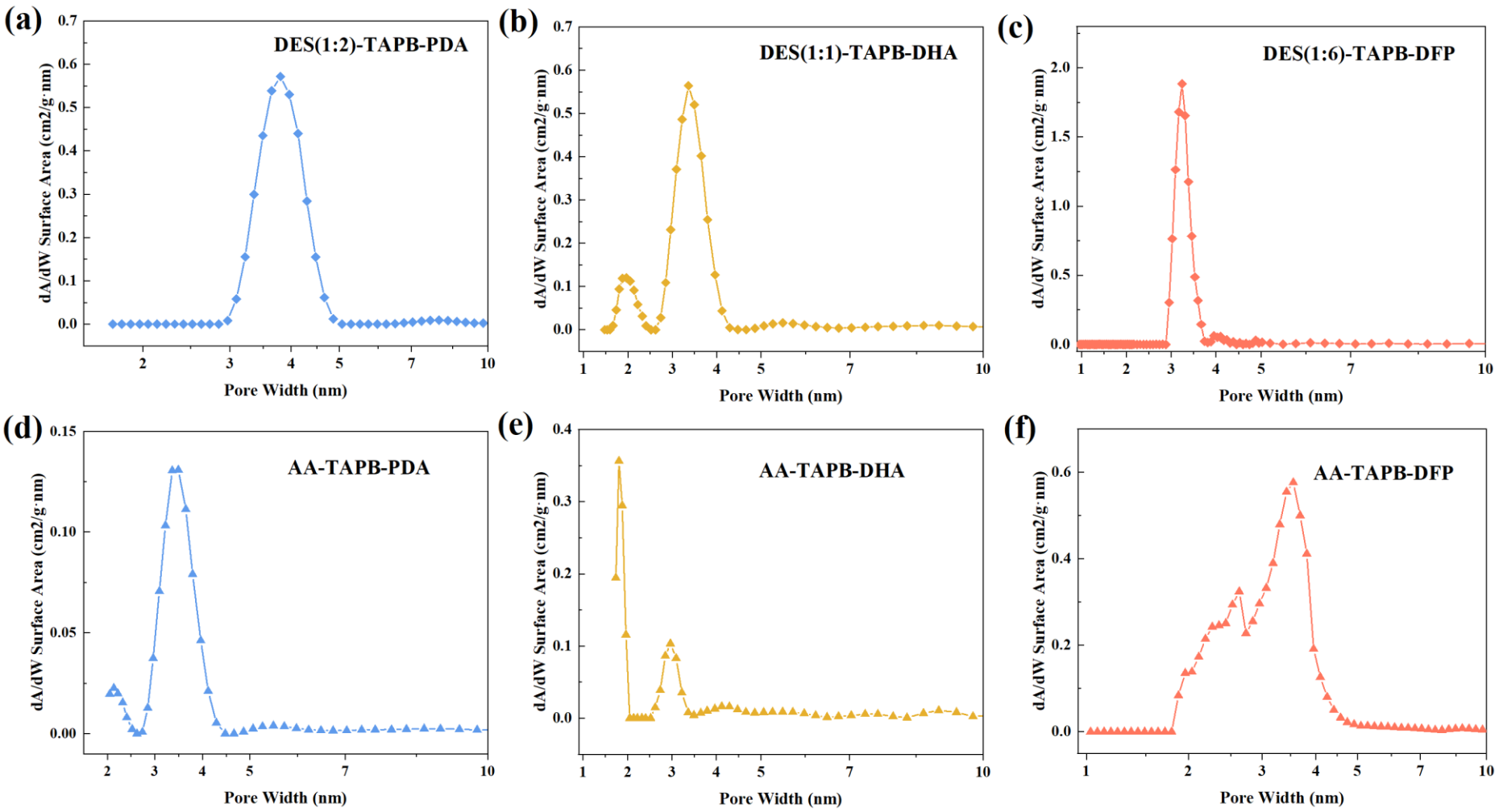

Figure S9 The pore size distributions of the COF synthesized in Menthol/AA DES and pure acetic acid.

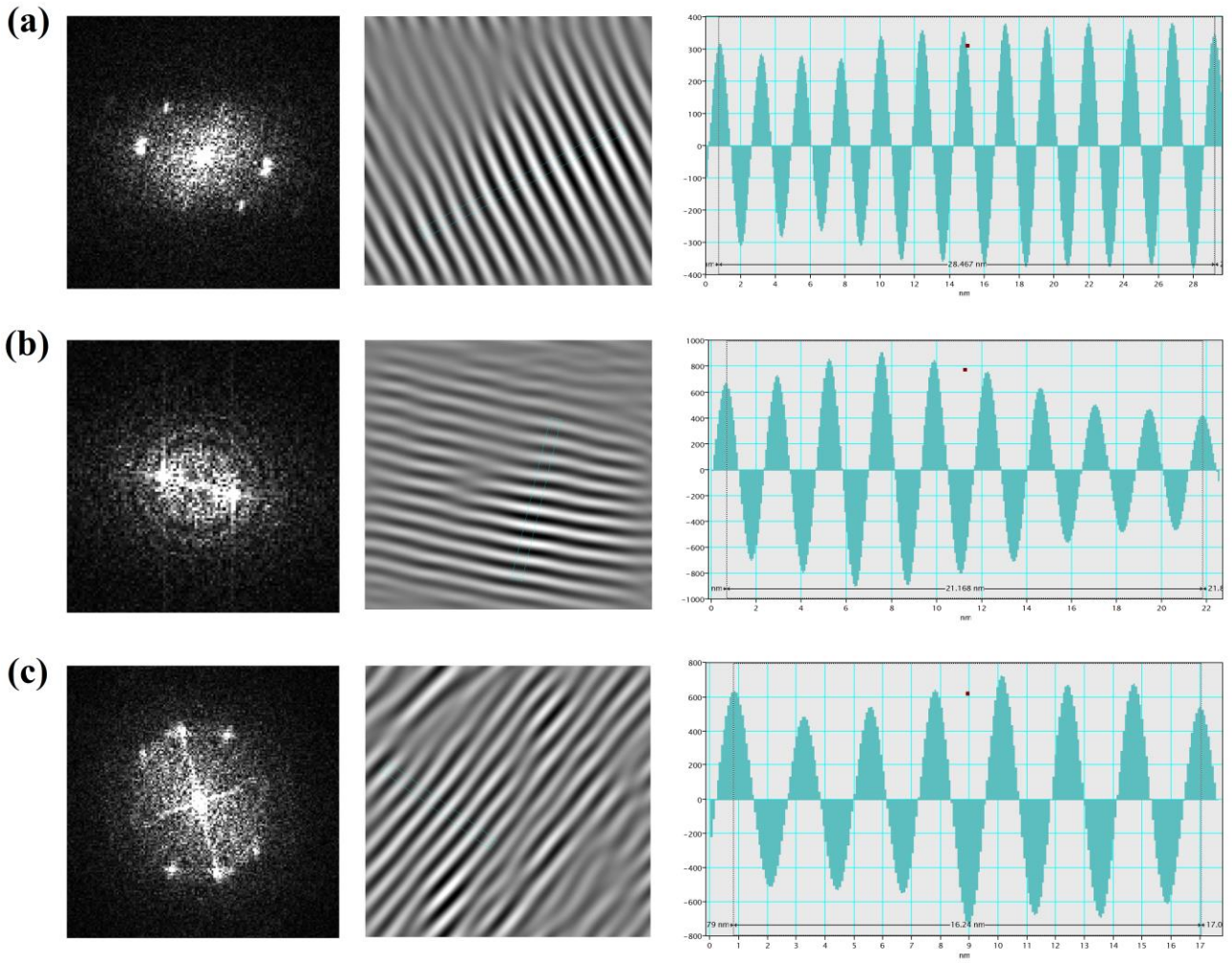

Figure S10 FFT and IFFT patterns of three models COFs synthesized in Menthol/AA DES ((a) TAPB-PDA, (b) TAPB-DHA, (c) TAPB-DFP).

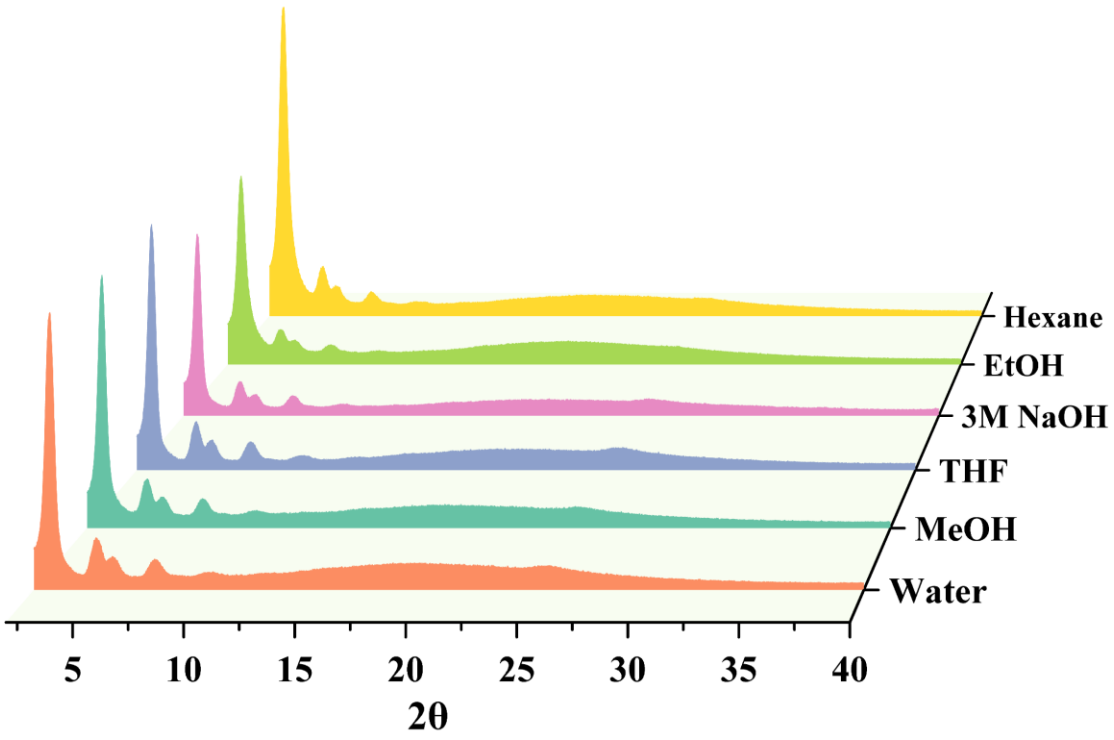

Figure S11 PXRD patterns of TAPB-PDA COF after 1 day immersion in different solvents.

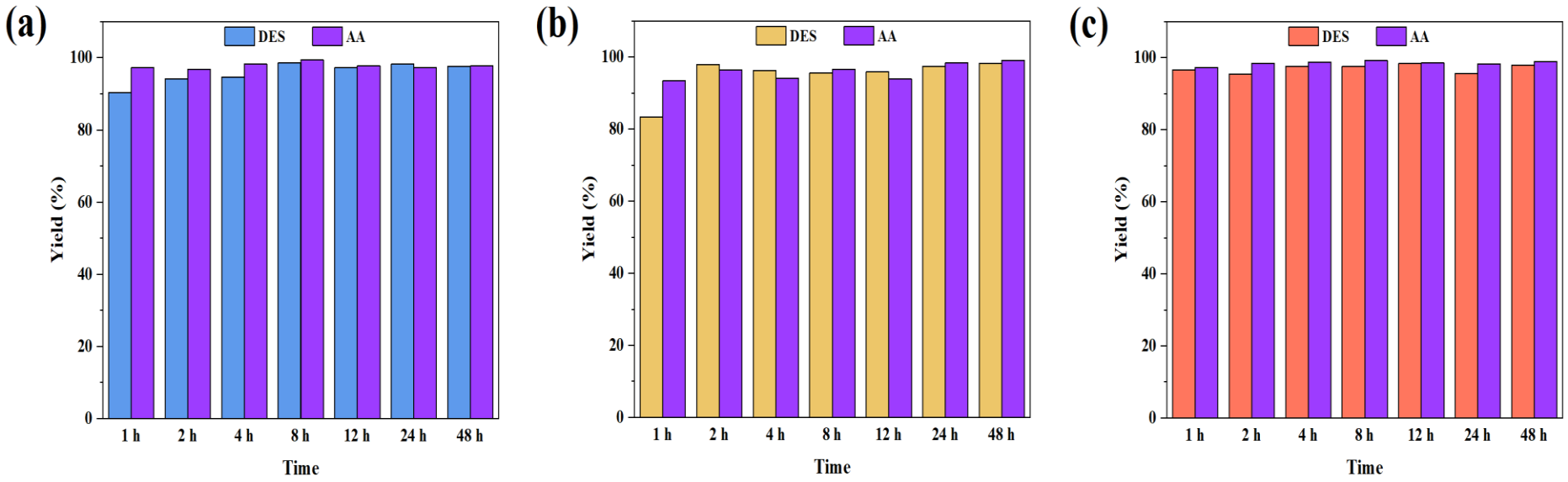

Figure S12 The yields of the three model COFs synthesized in Menthol/AA DES and pure acetic acid with reaction times ranging from 1 to 48 h ((a) TAPB-PDA, (b)TAPB-DHA, (c)TAPB-DFP).

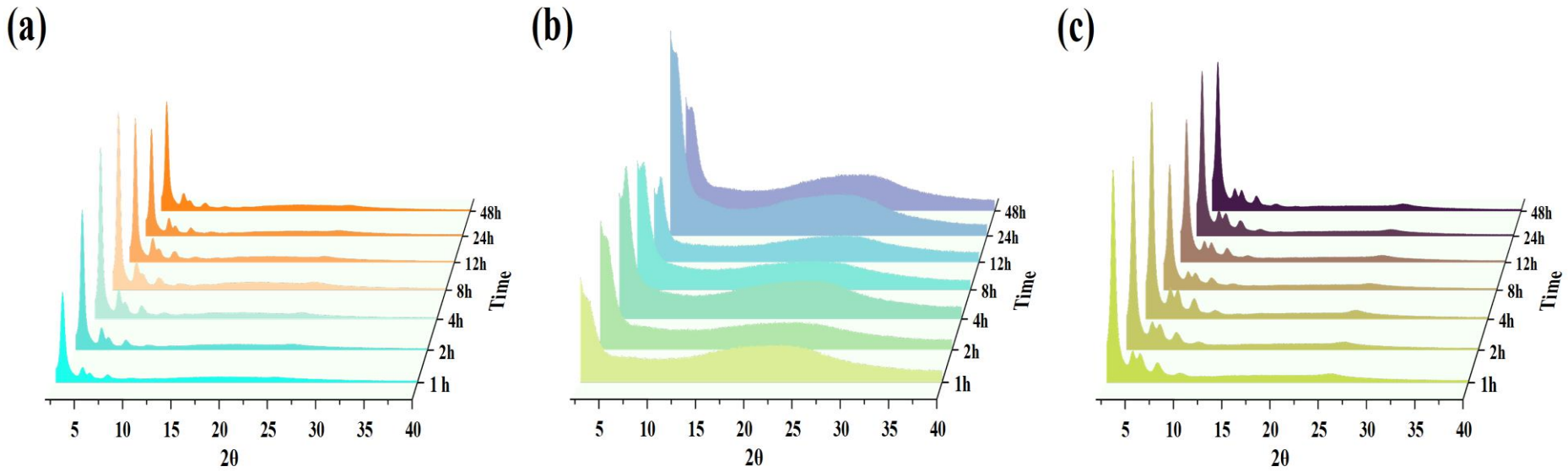

Figure S13 PXRD patterns of the three model COFs synthesized in pure acetic acid with reaction times ranging from 1 to 48 h ((a) TAPB-PDA, (b)TAPB-DHA, (c)TAPB-DFP).

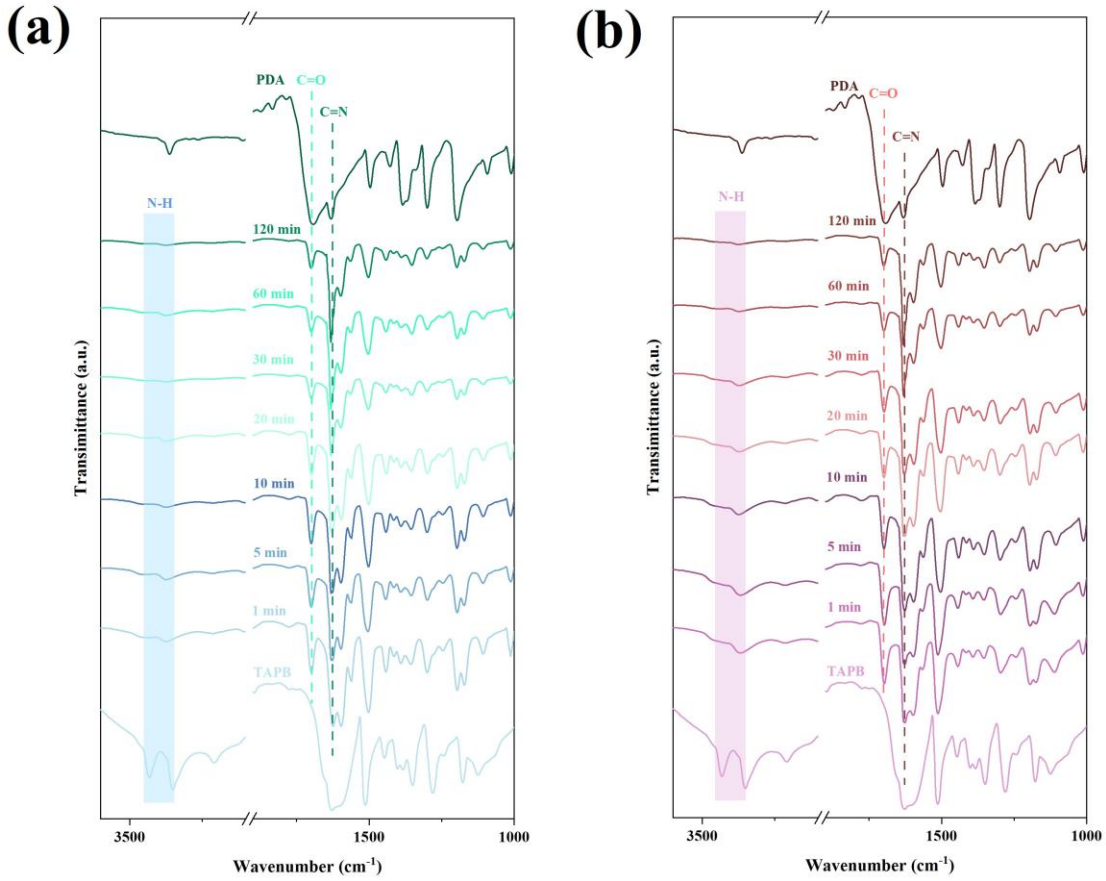

Figure S14 Infrared Spectrometer of TAPB-PDA COF ((a) Menthol/AA DES, (b) pure acetic acid).

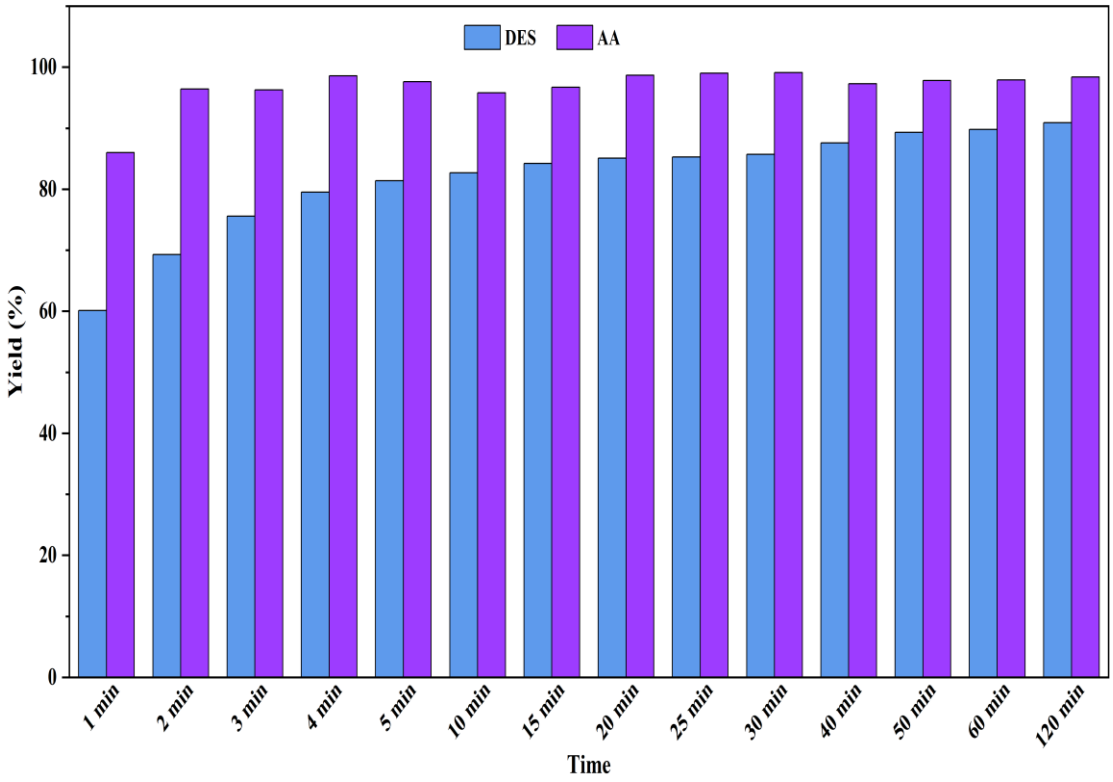

Figure S15 The yields of TAPB-PDA COF synthesized in Menthol/AA DES and pure acetic acid at room temperature with reaction times ranging from 1 to 120 min.

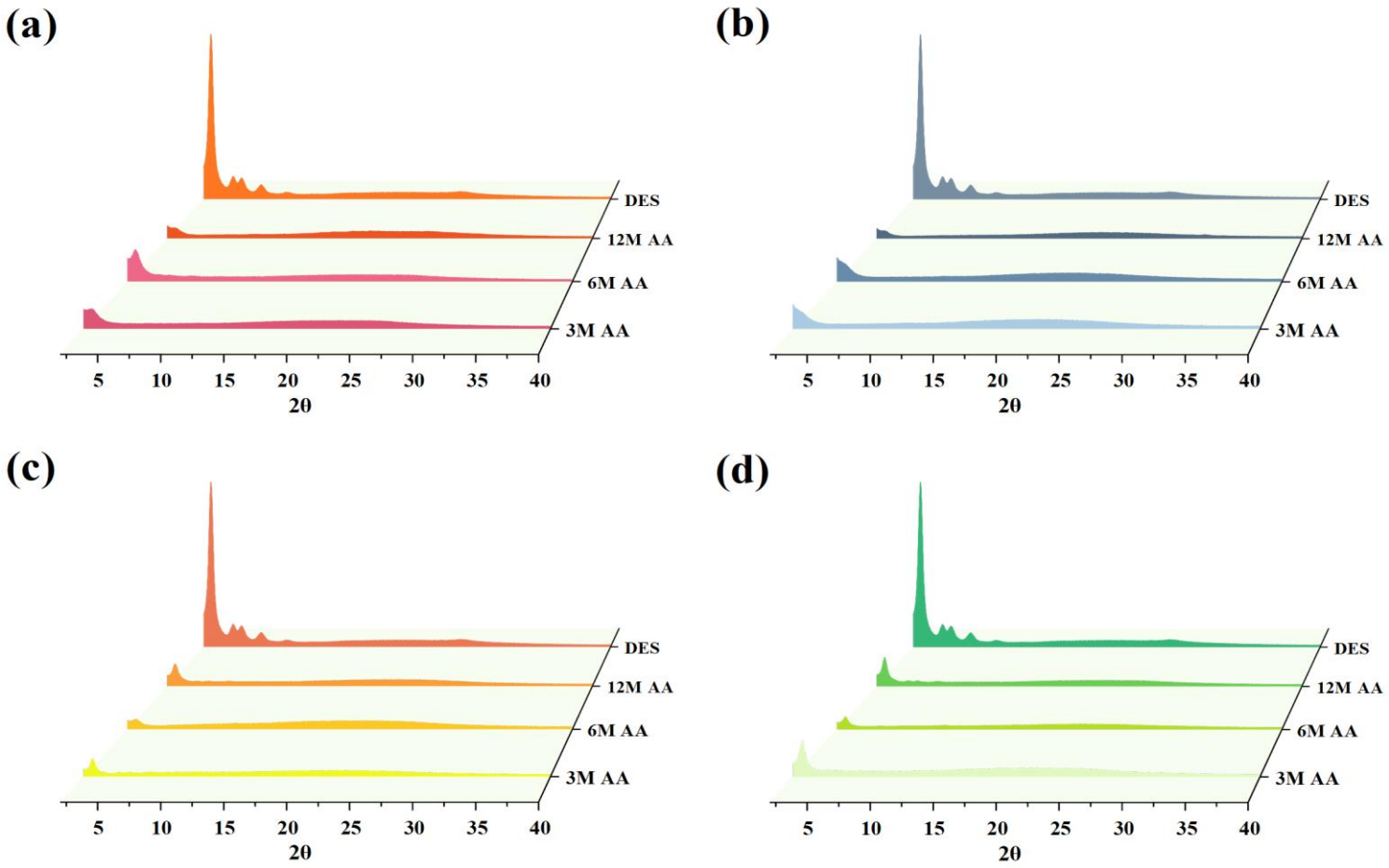

Figure S16 PXRD patterns of TAPB-DHA COF synthesized using different solvents and different concentrations of AA((a) n-Butanol, (b) Polyethylene glycol-400, (c) Acetonitrile, (d) Ethyl acetate).

Table S2 Synthesis conditions and results of TAPB-DHA COF.

Entry	Solvent	Catalyst	Temperature (°C)	Time (h)	Yield (%)	Crystallinity
1	n-Butanol	3M AA	70	24	91.8	No
2	n-Butanol	6M AA	70	24	95.3	Low
3	n-Butanol	12M AA	70	24	95.7	No
4	PEG-400	3M AA	70	24	93.3	No
5	PEG-400	6M AA	70	24	94.6	No
6	PEG-400	12M AA	70	24	94.1	No
7	ACN	3M AA	70	24	87.5	No
8	ACN	6M AA	70	24	89.3	No
9	ACN	12M AA	70	24	90.7	Low
10	EAC	3M AA	70	24	93.2	Moderate
11	EAC	6M AA	70	24	95.5	Low
12	EAC	12M AA	70	24	96.1	Moderate
13	Menthol/AA (1:1)	Menthol/AA (1:1)	70	24	94.9	Outstanding

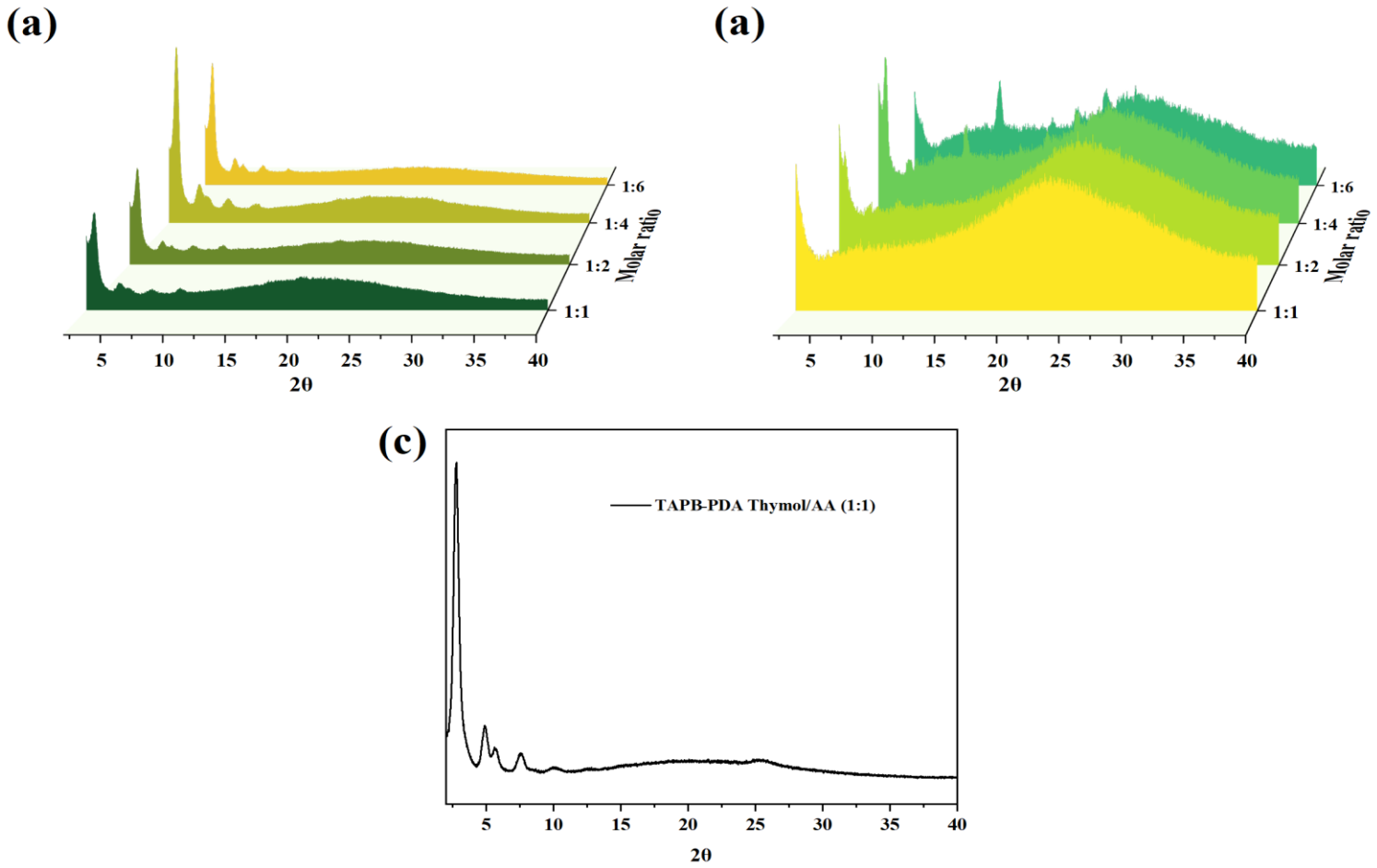

Figure S17 PXRD patterns of TAPB-PDA COF synthesized using different DES ((a) ChCl/AA DES, (b) TEBAC/AA DES, (c) Thymol/AA DES).

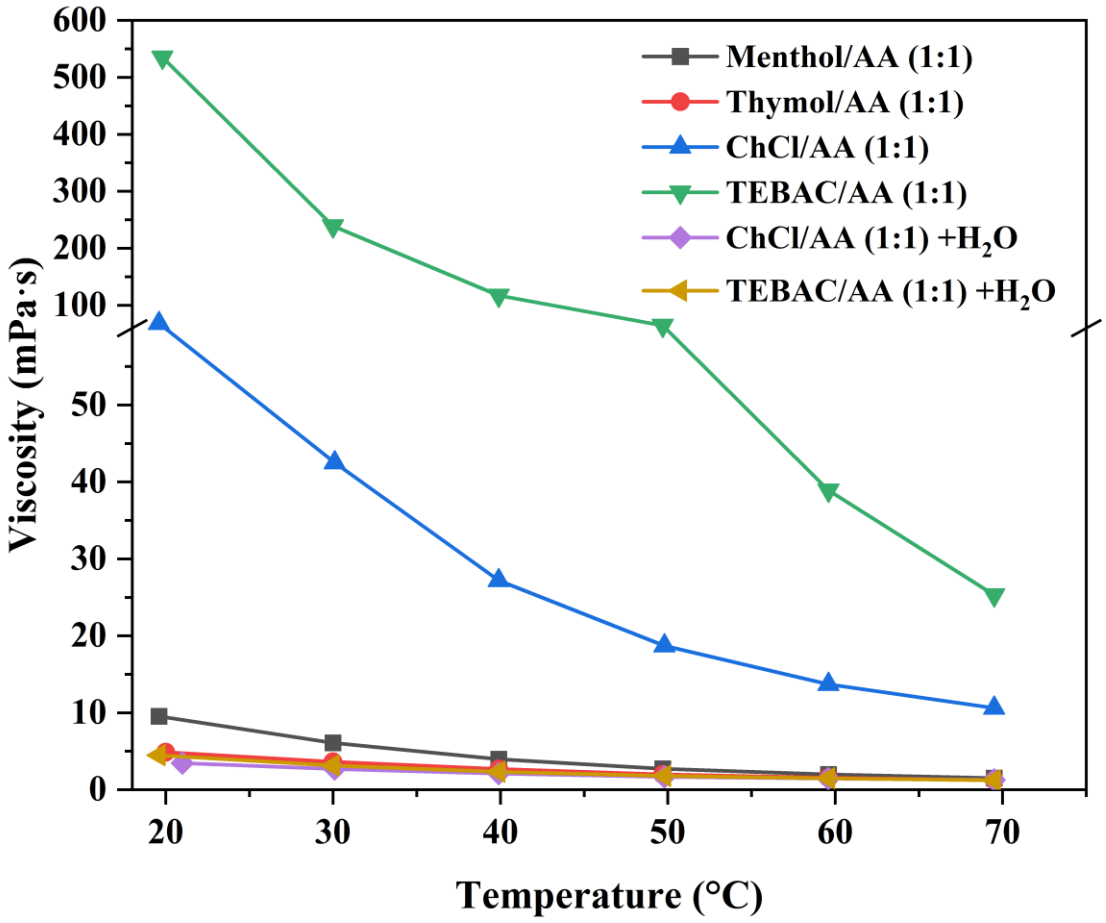

Figure S18 The viscosity of DES at different temperatures.

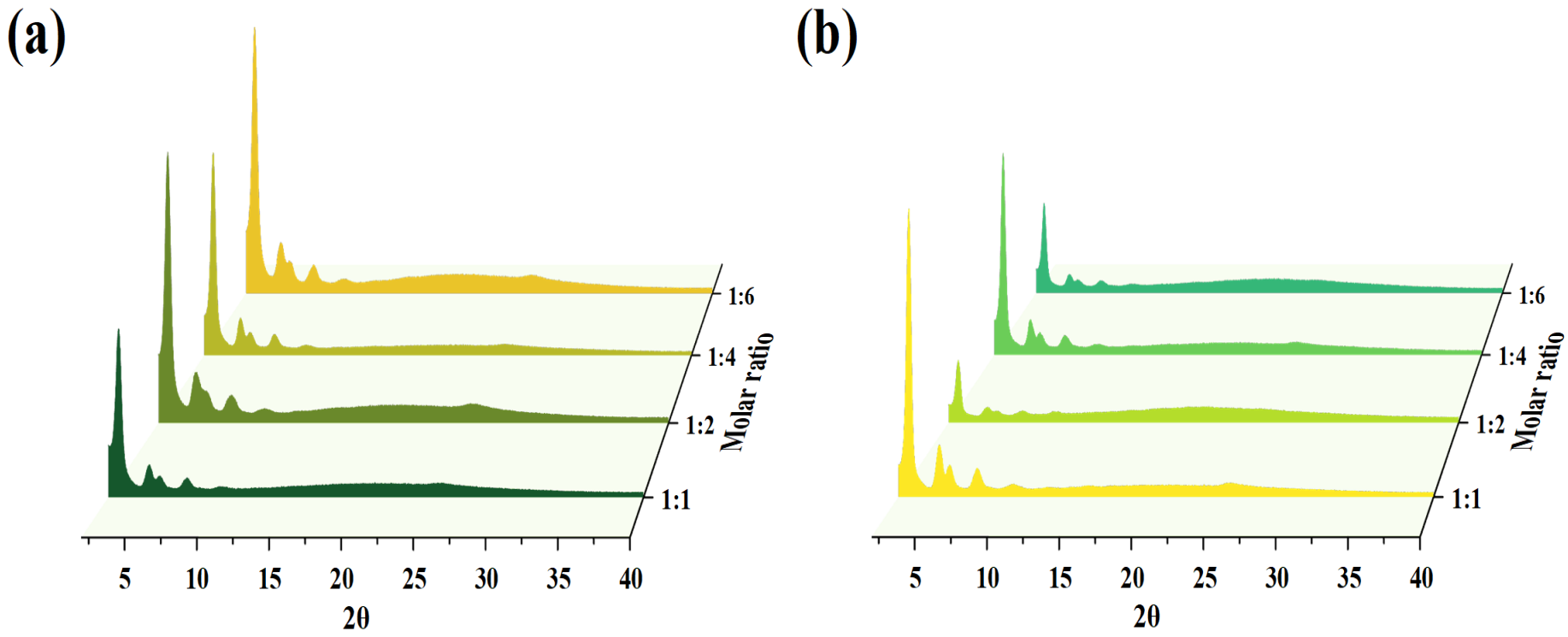

Figure S19 PXRD patterns of TAPB-PDA COF synthesized using different DES with 50% (v/v) H_2O ((a) ChCl/AA DES, (b) TEBAC/AA DES).

Table S3 Synthesis conditions and results of TAPB-PDA COF.

Entry	DES	Temperature (°C)	Time (h)	Yield (%)	Crystallinity
1	ChCl/AA (1:1)	70	24	26.1	Low
2	ChCl/AA (1:2)	70	24	28.2	Low
3	ChCl/AA (1:4)	70	24	30.2	Moderate
4	ChCl/AA (1:6)	70	24	40.0	Moderate
5	ChCl/AA (1:1) 50% (v/v) H_2O	70	24	53.2	Outstanding
6	ChCl/AA (1:2) 50% (v/v) H_2O	70	24	55.6	Outstanding
7	ChCl/AA (1:4) 50% (v/v) H_2O	70	24	61.1	Outstanding

8	ChCl/AA (1:6) 50% (v/v) H_2O	70	24	66.7	Outstanding
9	TEBAC/AA (1:1)	70	24	6.8	No
10	TEBAC/AA (1:2)	70	24	11.4	No
11	TEBAC/AA (1:4)	70	24	15.8	Low
12	TEBAC/AA (1:6)	70	24	27.0	No
13	TEBAC/AA (1:1) 50% (v/v) H_2O	70	24	33.9	Outstanding
14	TEBAC/AA (1:2) 50% (v/v) H_2O	70	24	38.5	Moderate
15	TEBAC/AA (1:4) 50% (v/v) H_2O	70	24	40.4	Outstanding
16	TEBAC/AA (1:6)	70	24	40.9	Moderate

	50% (v/v) H_2O				
17	Thymol/AA (1:1)	70	24	95.8	Outstanding
18	Menthol/AA (1:1)	70	24	93.6	Outstanding


(a)
TAPB-DMTP
P6
a=37.5969 Å
b=37.5969 Å
c=3.82834 Å
R_{wp}=3.49%
R_p=2.74%
(b)
TAPB-BTCA
P-6
a=18.6610 Å
b=18.6610 Å
c=3.51374 Å
R_{wp}=4.06%
R_p=3.13%
(c)
TAPT-PDA
P6
a=37.4425 Å
b=37.4425 Å
c=3.46913 Å
R_{wp}=3.20%
R_p=2.51%
(d)
TAPT-DMTP
P6
a=37.1306 Å
b=37.1306 Å
c=3.50221 Å
R_{wp}=4.35%
R_p=3.59%
(e)
TAPT-DHA
P6
a=37.3781 Å
b=37.3781 Å
c=3.47681 Å
R_{wp}=2.95%
R_p=2.19%
(f)
TAPT-DFP
P6
a=37.0948 Å
b=37.0948 Å
c=3.91877 Å
R_{wp}=4.66%
R_p=3.45%
(g)
TAPT-BTCA
P-6
a=18.5567 Å
b=18.5567 Å
c=3.57658 Å
R_{wp}=3.52%
R_p=2.78%
(h)
PTTA-PDA
P1
a=24.4840 Å
b=24.4840 Å
c=3.69680 Å
R_{wp}=4.13%
R_p=3.00%
(i)
PTTA-DMTP
P1
a=24.4809 Å
b=24.4809 Å
c=3.67168 Å
R_{wp}=3.08%
R_p=2.36%
(j)
PTTA-DHA
P1
a=24.3472 Å
b=24.3333 Å
c=3.96863 Å
R_{wp}=5.55%
R_p=3.59%
(k)
PTTA-DFP
P1
a=24.3670 Å
b=24.3665 Å
c=4.00806 Å
R_{wp}=4.49%
R_p=3.34%
(l)
PTTA-BTCA
P1
a=41.7280 Å
b=16.2229 Å
c=3.85008 Å
R_{wp}=9.33%
R_p=5.15%
(m)
TAPB-TFP
P6/M
a=36.7714 Å
b=36.7714 Å
c=3.83679 Å
R_{wp}=2.84%
R_p=2.22%
(n)
TAPB-BPDA
P6/M
a=45.5478 Å
b=45.5478 Å
c=3.45017 Å
R_{wp}=3.22%
R_p=2.48%
(o)
TAPP-DMTP
P1
a=25.6854 Å
b=25.6854 Å
c=4.21108 Å
R_{wp}=3.36%
R_p=2.62%
(p)
TAM-BTCA
P1
a=17.0629 Å
b=16.3921 Å
c=3.37242 Å
R_{wp}=8.89%
R_p=4.97%
(q)
PTTA-PDE
P1
a=54.4841 Å
b=24.1799 Å
c=4.00716 Å
R_{wp}=2.95%
R_p=2.31%
(r)
TAFM-PDA
I41/A
a=28.1270 Å
b=28.1270 Å
c=8.87900 Å
R_{wp}=7.21%
R_p=4.86%
(s)
ETTA-PDA
P6
a=38.7034 Å
b=38.7034 Å
c=5.54756 Å
R_{wp}=3.22%
R_p=2.43%
(t)
ETTA-BPDA
P6
a=47.4523 Å
b=47.4523 Å
c=5.14280 Å
R_{wp}=3.14%
R_p=2.26%
Refined
Experimental
Difference
Simulated
Background
Braggposition
2θ

Figure S20 Pawley refinements of PXRD patterns ((a) TAPB-DMTP, (b) TAPB-BTCA, (c) TAPT-PDA, (d) TAPT-DMTP, (e) TAPT-DHA, (f) TAPT-DFP, (g) TAPT-BTCA, (h) PTTA-PDA, (i) PTTA-DMTP, (j) PTTA-DHA, (k) PTTA-DFP, (l) PTTA-BTCA, (m) TAPB-TFP, (n) TAPB-BPDA, (o) TPPA-DMTP, (p) PTTA-PDE, (q) TAM-BTCA, (r) TAFM-PDA, (s) ETTA-PDA, (t) ETTA-BPDA).

Table S4 Pawley refinement parameters.

Entry	COF	Space Group	R_{WP} (%)	R_P (%)
1	TAPB-DMTP	P6	3.49	2.74
2	TAPB-BTCA	P-6	4.06	3.13
3	TAPT-PDA	P6	3.20	2.51
4	TAPT-DMTP	P6	4.35	3.59
5	TAPT-DHA	P6	2.95	2.19
6	TAPT-DFP	P6	4.66	3.45
7	TAPT-BTCA	P-6	3.52	2.78
8	PTTA-PDA	P1	4.13	3.00
9	PTTA-DMTP	P1	3.08	2.36
10	PTTA-DHA	P1	5.55	3.59
11	PTTA-DFP	P1	4.49	3.34
12	PTTA-BTCA	P1	9.33	5.15
13	TAPB-TFP	P6/M	2.84	2.22
14	TAPB-BPDA	P6/M	3.22	2.48
15	TAPP-DMTP	P1	3.36	2.62
16	TAM-BTCA	P1	8.89	4.97
17	PTTA-PDE	P1	2.95	2.31
18	TAFM-PDA	I41/A	7.21	4.86
19	ETTA-PDA	P6	3.22	2.43
20	ETTA-BPDA	P6	3.14	2.26

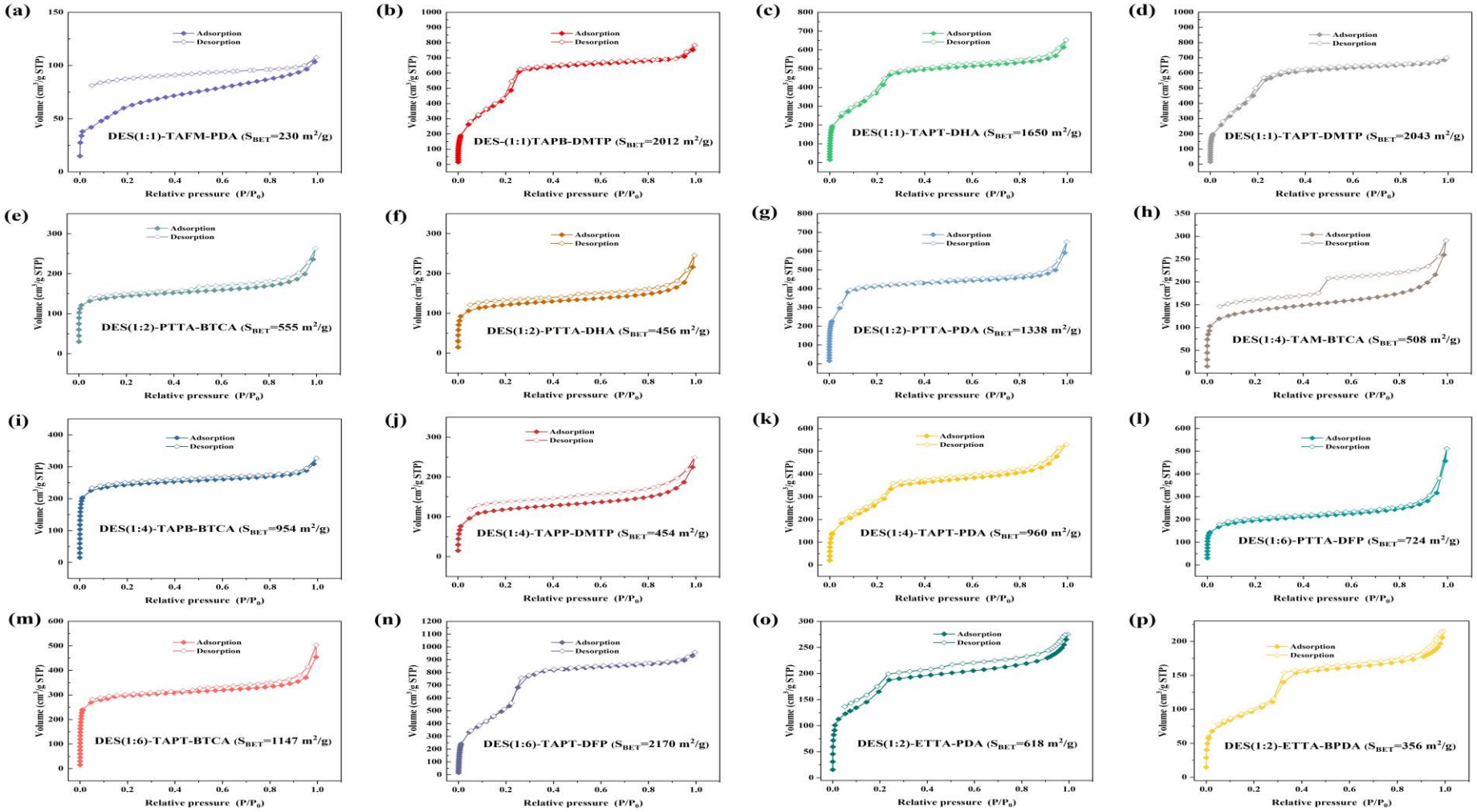

Figure S21 N_2 adsorption-desorption isotherms of different COF.

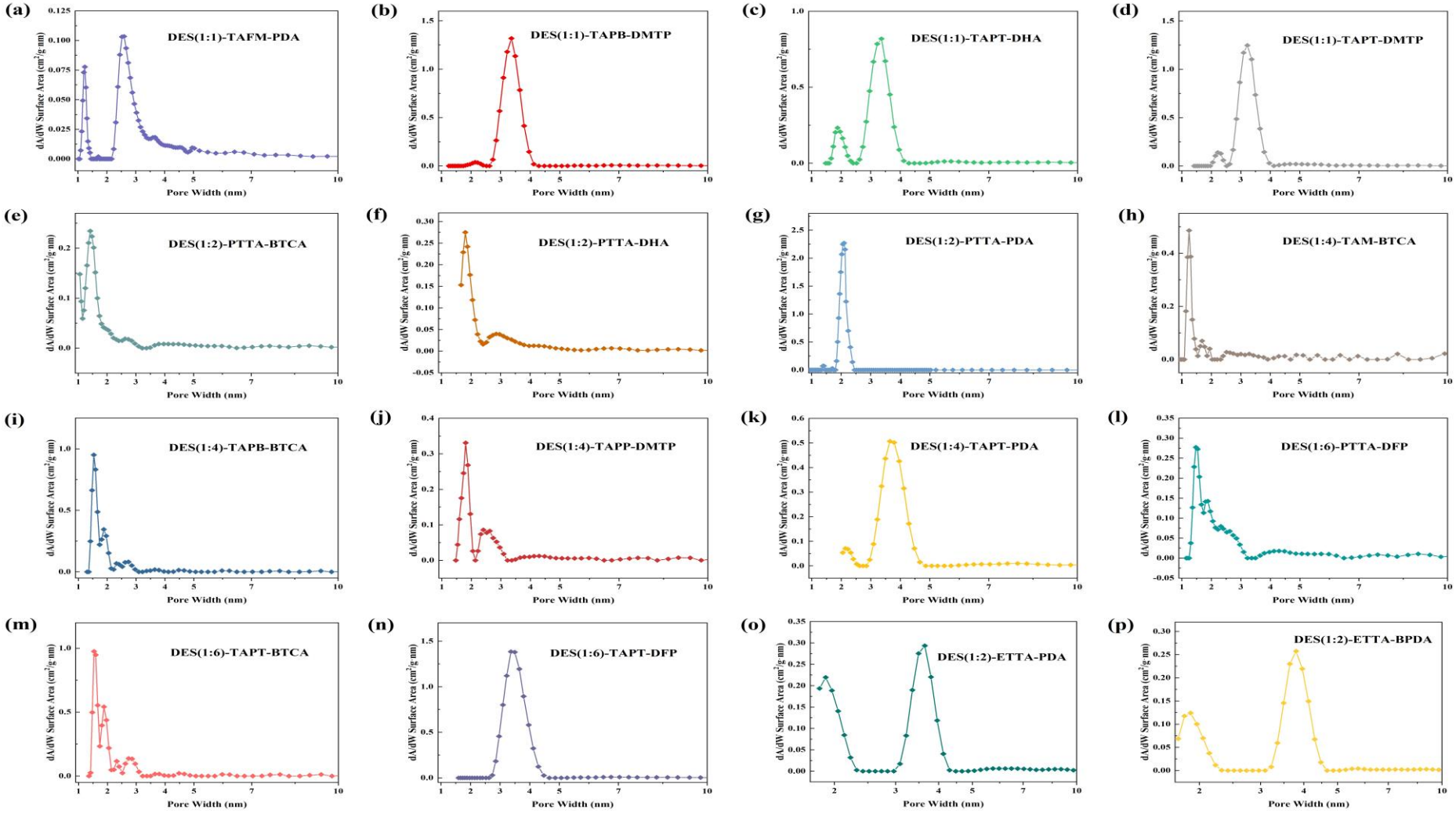

Figure S22 The pore size distributions of different COFs.

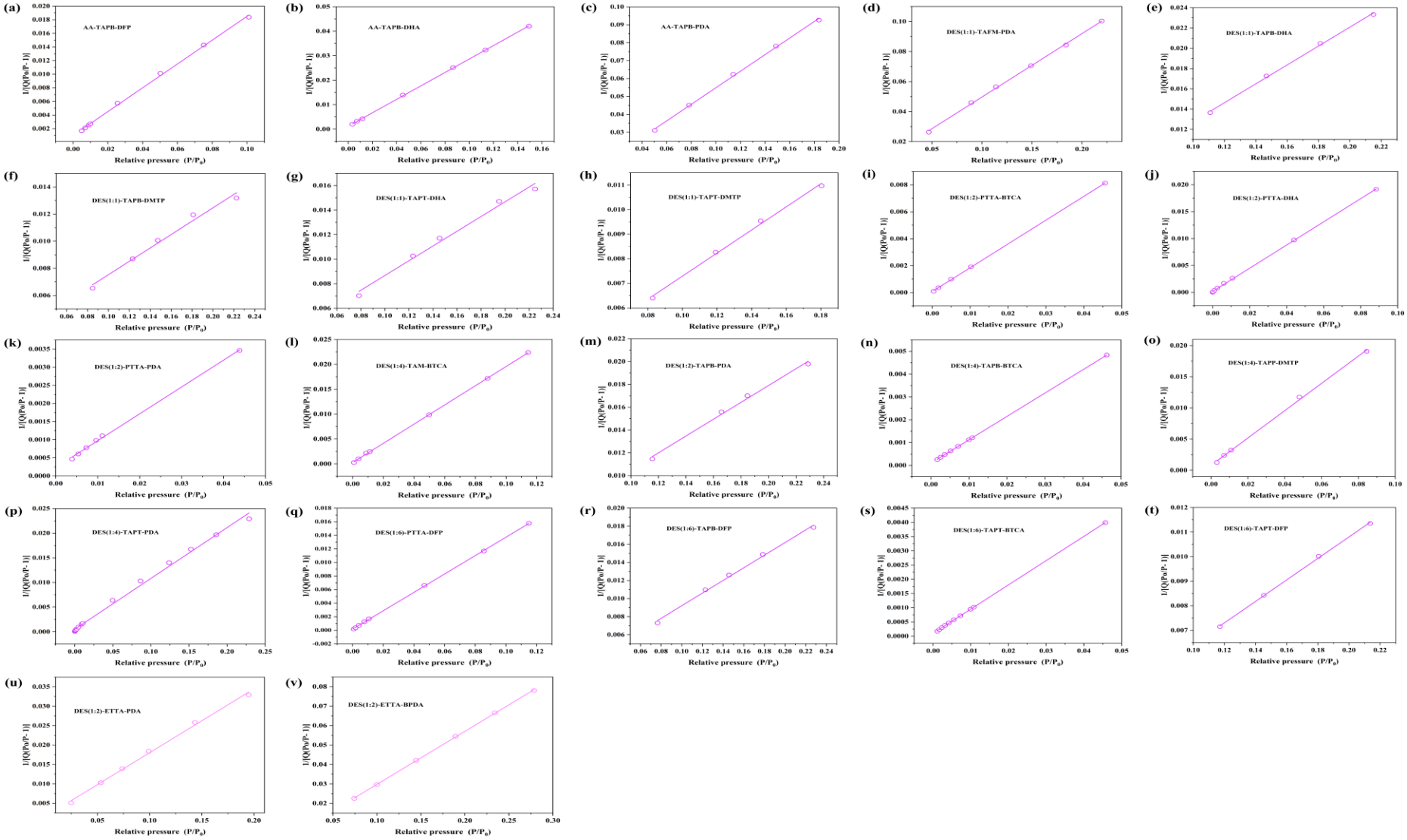
(a)
AA-TAPB-DFP
(b)
AA-TAPB-DHA
(c)
AA-TAPB-PDA
(d)
DES(1:1)-TAFM-PDA
(e)
DES(1:1)-TAPB-DHA
(f)
DES(1:1)-TAPB-DMTP
(g)
DES(1:1)-TAPT-DHA
(h)
DES(1:1)-TAPT-DMTP
(i)
DES(1:2)-PTTA-BTCA
(j)
DES(1:2)-PTTA-DHA
(k)
DES(1:2)-PTTA-PDA
(l)
DES(1:4)-TAM-BTCA
(m)
DES(1:2)-TAPB-PDA
(n)
DES(1:4)-TAPB-BTCA
(o)
DES(1:4)-TAPP-DMTP
(p)
DES(1:4)-TAPT-PDA
(q)
DES(1:6)-PTTA-DFP
(r)
DES(1:6)-TAPB-DFP
(s)
DES(1:6)-TAPT-BTCA
(t)
DES(1:6)-TAPT-DFP
(u)
DES(1:2)-ETTA-PDA
(v)
DES(1:2)-ETTA-BPDA
1/[Q(Po/P- 1)]
Relative pressure (P/P0)

Figure S23 BET plot of different COFs.

Table S5 Comparison of synthesis conditions and properties between Imine-linked COFs in this study and in the literature.

COF	Time (h)	Temperature (°C)	S_{BET} (m^2/g)	Yield (%)	Solvent	Catalyst	Reference
TAPB-PDA	24	70	1333	98	Menthol/AA	Menthol/AA	This work
	2	25	1397	88	o-DCB: n-Butanol	$Fe(NO_3)_3$	[1]
	72	70	610	85	Dioxane: Mesitylene	AA	[2]
	72	120	377.29	86	ChCl/HFIP	ChCl/HFIP	[3]
	4	70	2400	90	Dioxane: Mesitylene	AA	[4]
TAPB-DHA	24	70	1038	98	Menthol/AA	Menthol/AA	This work
	48	80	444.56	79	ChCl/HFIP	ChCl/HFIP	[5]
	96	25	790	-	Ethyl acetate	$Sc(CF_3SO_3)_3$	[6]
	72	120	1480	80	Dioxane: Mesitylene	AA	[7]
	72	120	26.4	-	Dioxane/THF/n-Butanol	AA	[8]

TAPB-DFP	24	70	1401	96	Menthol/AA	Menthol/AA	This work
	72	120	1720	89	o-DCB: n-Butanol	AA	[9]
TAFM-PDA	24	70	230	80	Menthol/AA	Menthol/AA	This work
	16	70	50	84	n-Butanol	AA	[10]
	48	90	20	84	Dioxane	AA	[11]
TAPB-DMTP	24	70	2012	88	Menthol/AA	Menthol/AA	This work
	16	70	2329	90	n-Butanol	AA	[10]
	72	120	1027	82	o-DCB: n-Butanol	$Sc(OTf)_3$	[12]
	72	120	-	85	ChCl/HFIP	ChCl/HFIP	[3]
TAPT-DHA	24	70	1650	75	Menthol/AA	Menthol/AA	This work
	72	120	709	88	DMAC: o-DCB	AA	[13]
	96	120	1130	85	o-DCB: n-Butanol: DMSO	AA	[14]
TAPT-DMTP	24	70	2043	88	Menthol/AA	Menthol/AA	This work

	16	70	2161	90	n-Butanol	AA	[10]
	24	65	1228	65	Dioxane: Mesitylene	AA	[15]
PTTA-BTCA	24	70	555	80	Menthol/AA	Menthol/AA	This work
PTTA-DHA	24	70	456	88	Menthol/AA	Menthol/AA	This work
	72	120	1062	78	Dioxane: Mesitylene	AA	[16]
PTTA-PDA	24	70	1338	90	Menthol/AA	Menthol/AA	This work
	72	120	2093	69	Dioxane	AA	[17]
TAM-BTCA	24	70	508	86	Menthol/AA	Menthol/AA	This work
	120	25	555	-	Dioxane	AA	[18]
TAPB-BTCA	24	70	954	93	Menthol/AA	Menthol/AA	This work
	16	70	1057	94	n-Butanol	AA	[10]
	72	120	810	-	Dioxane	AA	[19]
	72	25	962	-	Acetonitrile	AA	[20]

TAPP-DMTP	24	70	454	72	Menthol/AA	Menthol/AA	This work
	168	120	1178	82	o-DCB: n-Butanol	AA	[21]
TAPT-PDA	24	70	960	71	Menthol/AA	Menthol/AA	This work
	2	25	937	62	o-DCB: n-Butanol	$Fe(NO_3)_3$	[1]
PTTA-DFP	24	70	724	77	Menthol/AA	Menthol/AA	This work
	72	120	1435	85	o-DCB: n-Butanol	AA	[22]
TAPT-BTCA	24	70	1147	63	Menthol/AA	Menthol/AA	This work
	24	120	1443	-	Dioxane: Mesitylene	AA	[23]
	3	25	217	90	AA	AA	[24]
TAPT-DFP	24	70	2170	76	Menthol/AA	Menthol/AA	This work
	72	120	963	85	o-DCB: n-Butanol	AA	[9]

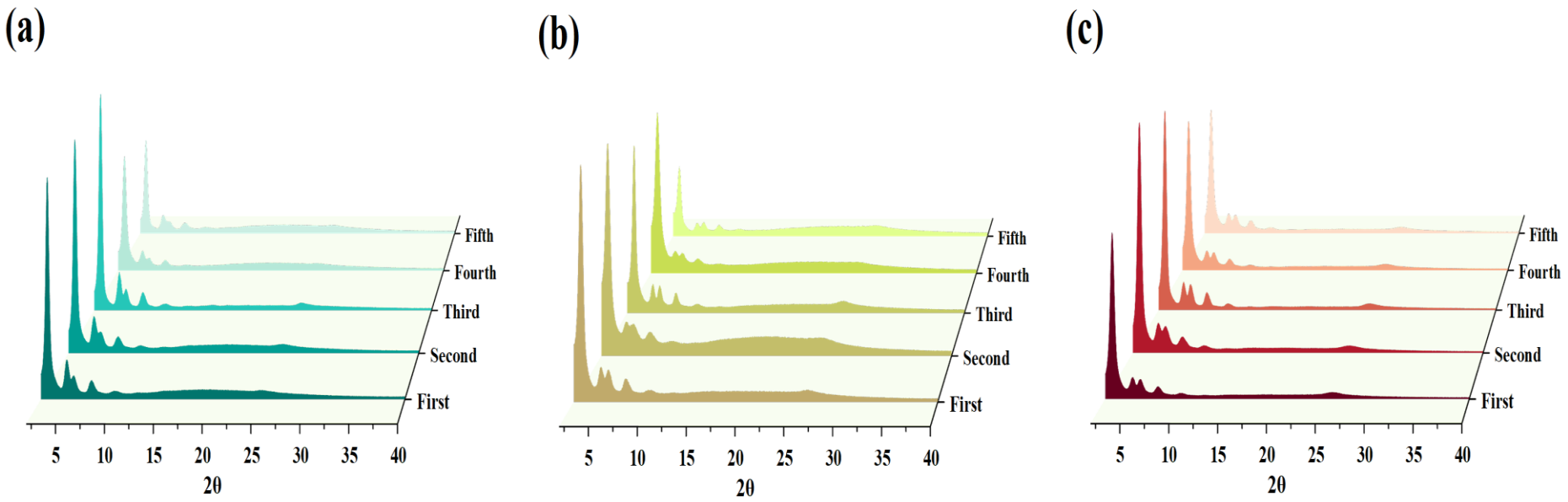

Figure S24 PXRD patterns of the model COFs synthesized using recycle DES ((a) TAPB-PDA, (b)TAPB-DHA, (c)TAPB-DFP).

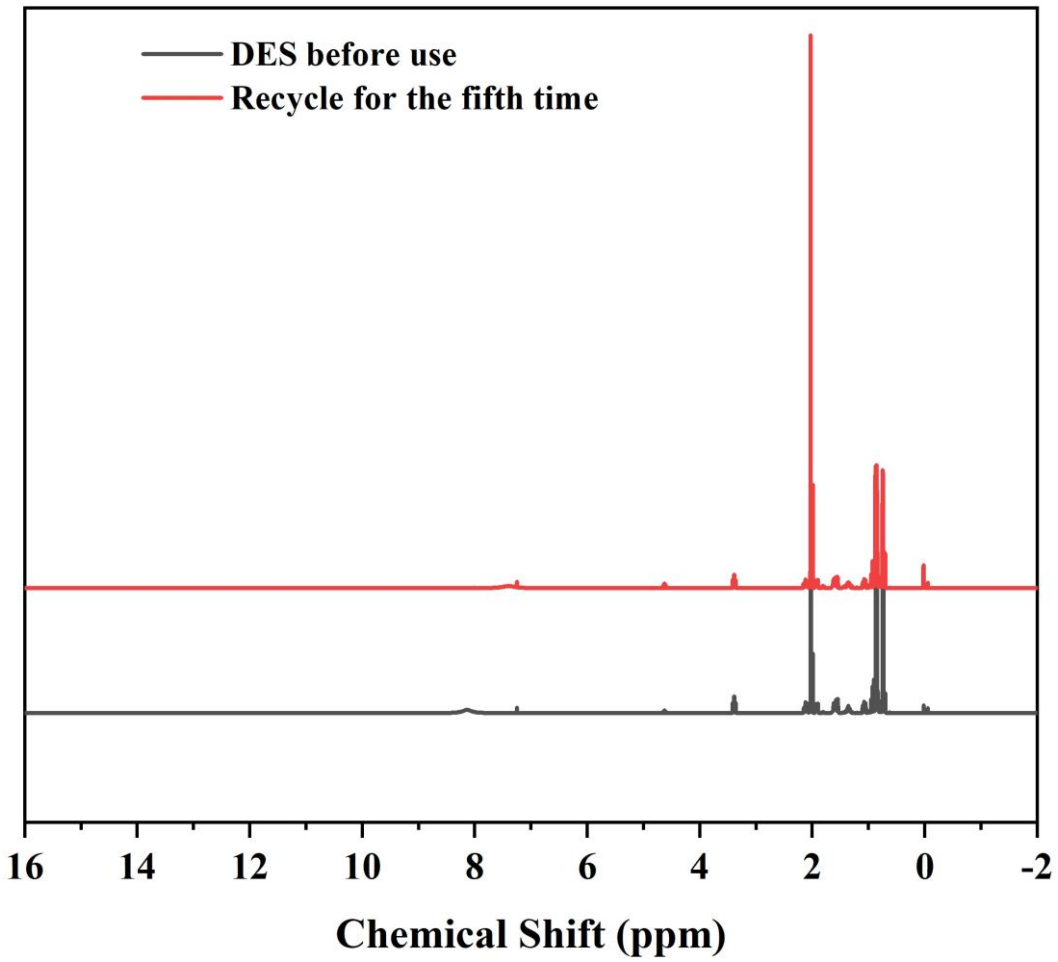

Figure S25 ^{1}H NMR spectra of Menthol/AA DES (1:2) before use and after recycle for five times.

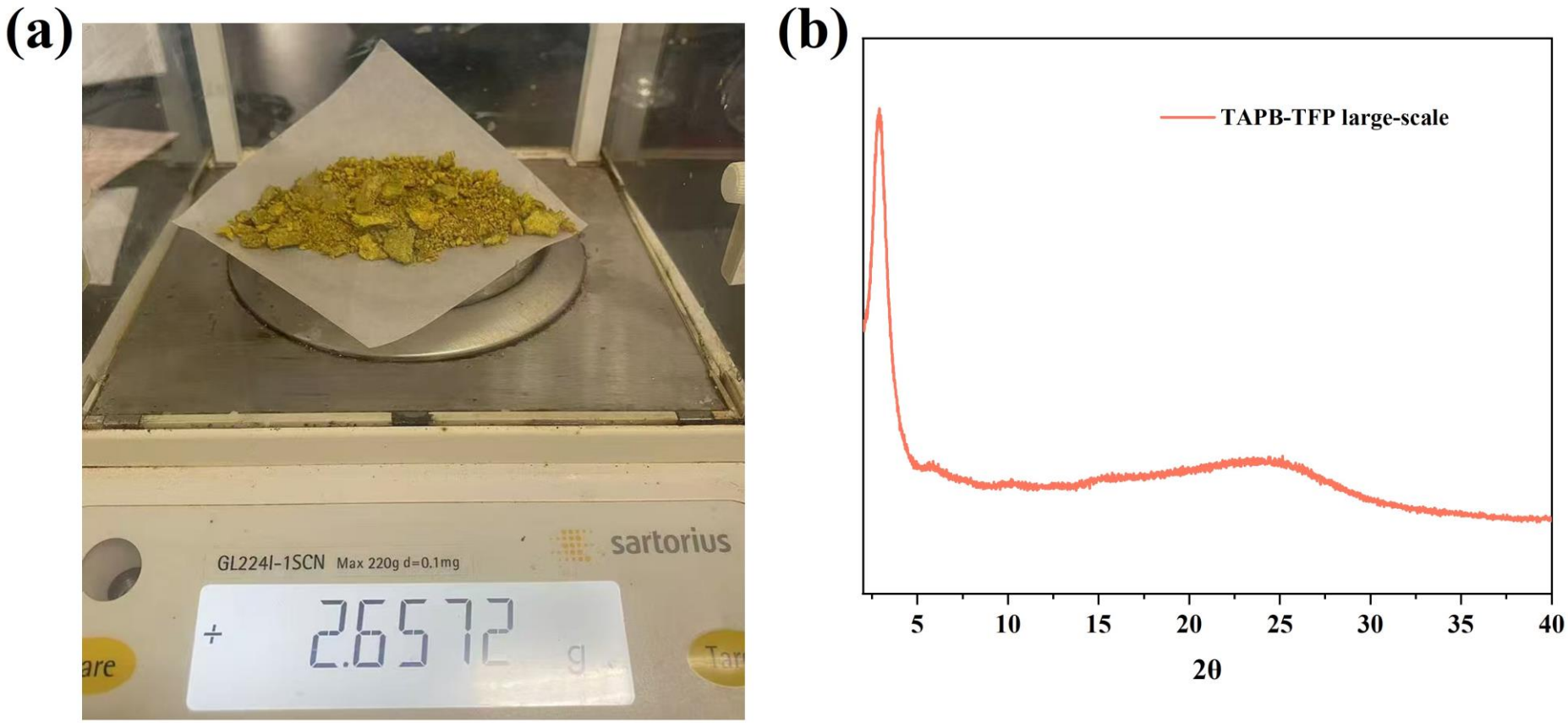

Figure S26 (a) Large scale synthesis of TAPB-TFP COF, (b) PXRD pattern of TAPB-TFP COF (large scale).

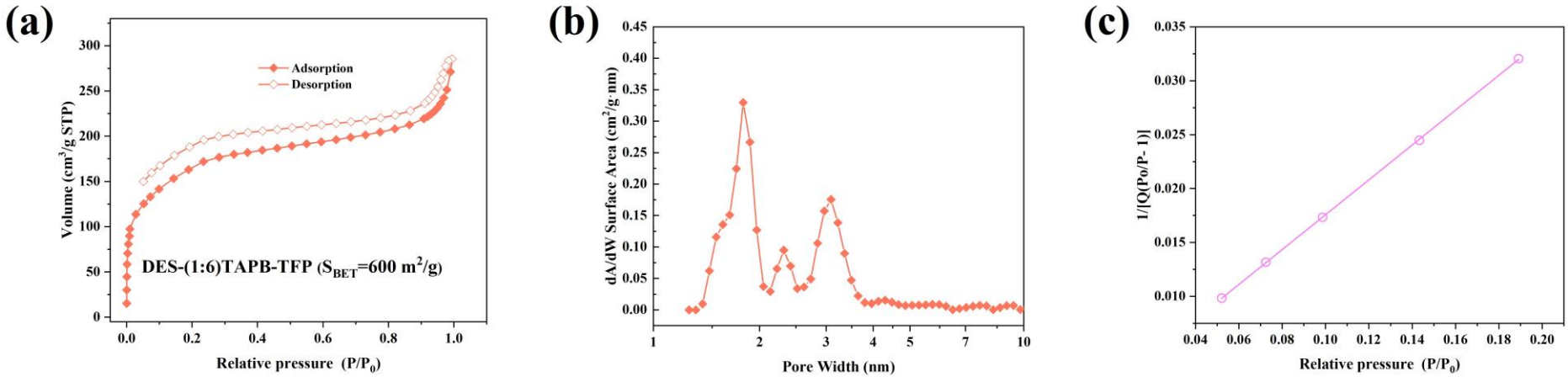

Figure S27 (a) N_2 adsorption-desorption isotherms of TAPB-TFP COF (large scale), (b) The pore size distributions of TAPB-TFP COF (large scale), (c) BET plot of TAPB-TFP COF (large scale).

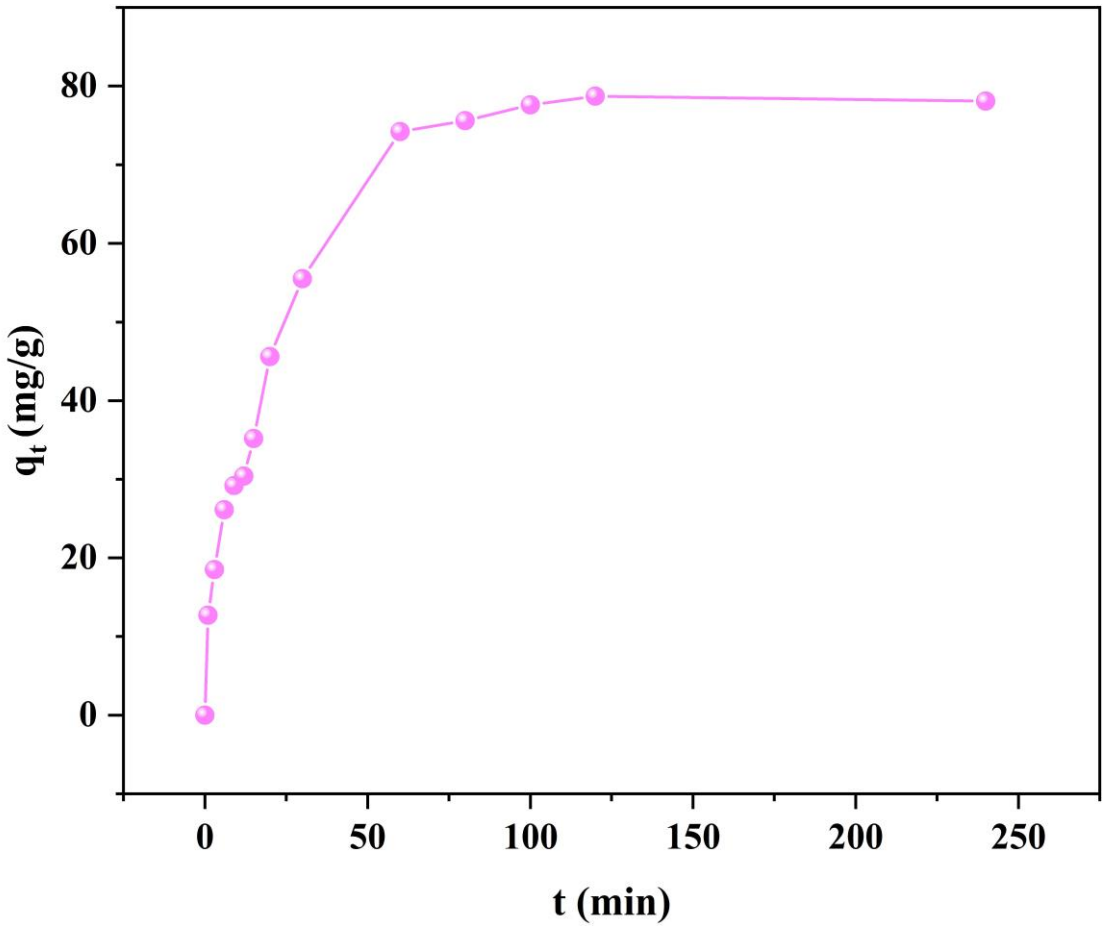

Figure S28 Kinetics of furfural adsorption by TAPB-TFP COF.

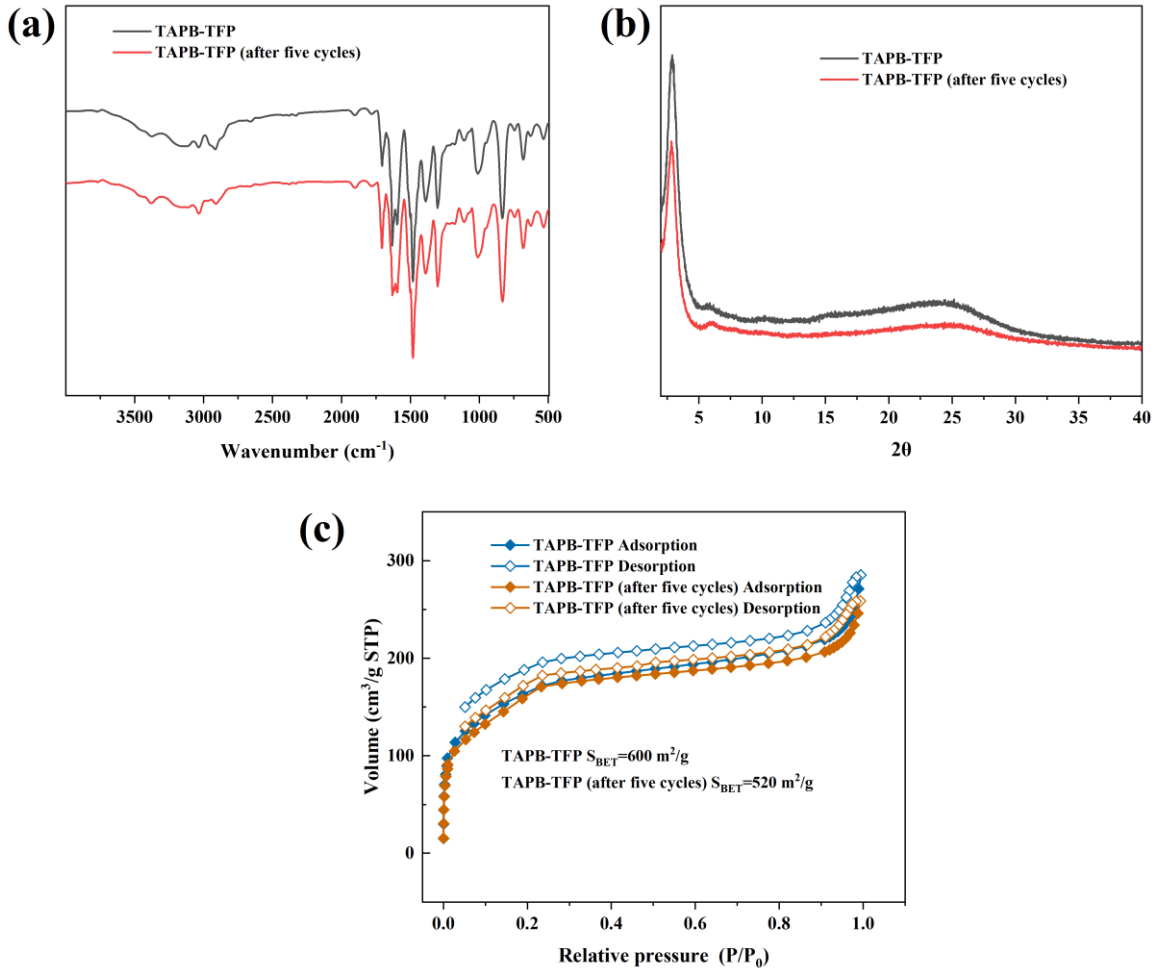

Figure S29 (a) Infrared spectrometer; (b) PXRD pattern; (c) N_2 adsorption-desorption isotherm.

Table S6 Langmuir and Freundlich isotherm parameters for the adsorption of furfural onto NKCOF-41 at 25-45°C.

T/ °C	Langmuir			Freundlich		
	q_{max} (mg/g)	K_L (L/g)	R^2	K_F (mg/(g×(L/g)$^{1/n}$))	1/n	R^2
25	233.4	0.49	0.972	75.30	0.495	0.994
35	210.8	0.44	0.990	62.50	0.527	0.989
45	193.2	0.43	0.987	56.39	0.537	0.986

5. References

1. D. Zhu, Z. Zhang, L. B. Alemany, Y. Li, N. Nnorom, M. Barnes, S. Khalil, M. M. Rahman, P. M. Ajayan and R. Verduzco, *Chem. Mater.*, 2021, **33**, 3394-3400.
2. B. J. Smith, A. C. Overholts, N. Hwang and W. R. Dichtel, *Chem. Commun.*, 2016, **52**, 3690-3693.
3. L. Deng, L. Wang, S. Liu, Q. Liu, J. Wang, Y. Tao, M. Tian, Y. Yang, Y. Zou, H. Niu, D. Wang and D. Gao, *Macromolecules*, 2023, **56**, 7707-7720.
4. C. Feriante, A. M. Evans, S. Jhulki, I. Castano, M. J. Strauss, S. Barlow, W. R. Dichtel and S. R. Marder, *J. Am. Chem. Soc.*, 2020, **142**, 18637-18644.
5. M. Gao, D. Wang, L. Deng, S. Liu, K. Zhang, T. Quan, L. Yang, X. Kang, Z. Xia and D. Gao, *Chem. Mater.*, 2021, **33**, 8036-8051.
6. S. Zhao, C. Jiang, J. Fan, S. Hong, P. Mei, R. Yao, Y. Liu, S. Zhang, H. Li, H. Zhang, C. Sun, Z. Guo, P. Shao, Y. Zhu, J. Zhang, L. Guo, Y. Ma, J. Zhang, X. Feng, F. Wang, H. Wu and B. Wang, *Nat. Mater.*, 2021, **20**, 1551-1558.
7. S. Kandambeth, V. Venkatesh, D. B. Shinde, S. Kumari, A. Halder, S. Verma and R. Banerjee, *Nat. Commun*, 2015, **6**, 6786.
8. D. Zhu, S. Zhou, Z. Zhou, R. Li, J. Ye, X. Ziyu, S. Lan, Y. Zhang, S. Miao and W. Wang, *Colloid. Surface. A*, 2020, **600**, 124910.
9. B. Ma, Y. Xu, F. Hu, L. Zhai, Y. Huang, H. Qiao, J. Xiong, D. Yang, Z. Ni, X. Zheng and L. Mi, *RSC Adv.*, 2022, **12**, 31276-31281.
10. A. Laemont, G. Matthys, R. Lavendomme and P. van der Voort, *Angew. Chem. Int. Ed.*, 2024, **63**, e202412420.

11. D. M. Fischbach, G. Rhoades, C. Espy, F. Goldberg and B. J. Smith, *Chem. Commun.*, 2019, **55**, 3594-3597.

12. Y. Zhu, D. Zhu, Q. Yan, G. Gao, J. Xu, Y. Liu, S. B. Alahakoon, M. M. Rahman, P. M. Ajayan, E. Egap and R. Verduzco, *Chem. Mater.*, 2021, **33**, 6158-6165.

13. H.-L. Qian, C. Dai, C.-X. Yang and X.-P. Yan, ACS App. Mater. Interfaces., 2017, **9**, 24999-25005.

14. Y. Zhao, X. Tao, B. Xu, W. Liu and S. Lin, *Adv. Funct. Mater.*, 2024, **34**, 2401895.

15. C. Kang, Z. Zhang, A. K. Usadi, D. C. Calabro, L. S. Baugh, K. Yu, Y. Wang and D. Zhao, *J. Am. Chem. Soc.*, 2022, **144**, 3192-3199.

16. B. Ma, Y. Xu, F. Hu, G. Zhang, X. Zheng, Z. Wang, H. Qiao, D. Yang and L. Mi, *Macromol. Chem. Phys.*, 2022, **223**, 2100462.

17. Y. Meng, G. Lin, H. Ding, H. Liao and C. Wang, *J. Mater. Chem. A*, 2018, **6**, 17186-17191.

18. Y. Zhang, Y. Wu, Y. Liu and J. Feng, *Chem. Eng. J.*, 2022, **428**, 131040.

19. D. Zhu and R. Verduzco, *ACS Appl. Mater. Interfaces*, 2020, **12**, 33121-33127.

20. W. Li, Z. Bie, C. Zhang, X. Xu, S. Wang, Y. Yang, Z. Zhang, X. Yang, K. H. Lim, Q. Wang, W.-J. Wang, B.-G. Li and P. Liu, *J. Am. Chem. Soc.*, 2023, **145**, 19283-19292.

21. H. Yang, Z. Lu, X. Fu, Q. Li, L. Xiao, R. Zhao, Y. Zhao and L. Hou, *Polym. Chem.*, 2021, **12**, 6998-7004.

22. B. Ma, F. Hu, X. Yang, Y. Huang, X. Yang, H. Qiao, Z. Wang, D. Yang, W. Ai and L. Mi, *Appl. Catal. A: Gen.*, 2023, **662**, 119269.

23. Y. Wu, P. Li, L. Chen, A. Li, C. Li, J. Chen, F. Zhai, D. Xu, Y. Song, D. Cao, J. Sun, K. Hu, S. Wang and M. V. Sheridan, *ACS Sustainable Chem. Eng.*, 2024, **12**, 6659-6665.

24. J.-G. Fu, L.-X. Xie, J. Du, Z. Xu, Z.-Q. Shi, L.-F. Hou and G. Li, *ACS Sustainable Chem. Eng.*,

2024, **12**, 13873-13884.