Supporting Information

Chemical recycling of imine-linked covalent organic frameworks

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Section S1. General Methods

S1.1 Materials

1,3,5-Tri(4-aminophenyl)benzene (TAPB), *N*,*N*-dimethylformamide (DMF) and anhydrous dimethyl sulfoxide (DMSO) were purchased from Tansoole platform (Adamas/Greagent). Terephthalaldehyde (TPA), 1,4-phenylenediamine (PDA), 1,2-dichlorobenzene, benzaldehyde, *n*-butylamine (BA), 3',5'-diphenylbiphenyl-4-amine, tetrahydrofurfurylamine (THFA), triethylamine, trifluoroacetic acid, scandium triflate ($Sc(OTf)_3$), 1,3,5-trimethylbenzene, acetic acid and benzyl alcohol were purchased from TCI (Shanghai, China). 4,4′,4″,4‴-(Ethene-1,1,2,2-tetrayl)tetraaniline (ETTA), 2,5-bis(2-propyn-1-yloxy)terephthalaldehyde (BPTA), triformylbenzene (TFB), 4,4',4",4'''-methanetetrayltetraaniline (TAM) and 2,5-dimethoxybenzene-1,4-dicarboxaldehyde (DMTA) were purchased from Zhengzhou Alfa Chemical Co., Ltd. (China). *n*-Butanol, hydrazine hydrate ($N_2H_4 \cdot H_2O$, 85%), tetrahydrofuran (THF), acetone and hydrochloric acid (HCl) were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Thieno[3,2-b]thiophene-2,5-dicarbaldehyde (TT) was purchased from Chemsoon Co., Ltd. (Shanghai, China). Methanol (MeOH), 1,4-dioxane and dichloromethane were gotten from Kemao Chemical Reagents Co., Ltd. (Tianjin, China). Ethanol, petroleum ether (PE), and *n*-hexane were obtained from Kainuoke Chemical Co., Ltd. (Xi'an, China). Molecular sieve (type 4A) was purchased from Damao Chemical Reagents Co., Ltd. (Tianjin, China). Dimethyl sulfoxide-d_6 (DMSO-d_6, 99.8% D) was purchased from DSOURCE. Sodium hydroxide (NaOH) was obtained from Tianjin Zhiyuan Chemical Reagent Co., Ltd. (China). All reagents and solvents were used without further purification. The water used was ultrapure water with a conductivity of 18.25 MΩ cm^{-1}.

S1.2 Characterization

Mass spectrometry (MS)

MS spectra were collected on a Bruker MAXIS mass spectrometer using the atmospheric pressure chemical ionization (APCI) method. Samples were introduced into the mass spectrometer with a syringe pump at a flow rate of 160 μL min^{-1}.

Scanning electron microscope (SEM)

The morphology study was performed on a Hitachi TM3030. Samples were fixed with a double-sided

carbon tape to the sample holder, and then coated with gold under vacuum for 120 s at 25 mA using an Au Sputter Coater (BAL-TAC, Baltek) for SEM measurements.

Transmission electron microscope (TEM)

TEM images were obtained on a Talos F200i instrument. A few drops of the depolymerization mixtures were loaded onto a copper mesh by a pipette and dried via natural evaporation for further measurement.

Fourier transform infrared (FT-IR) spectra

FT-IR spectra were collected on a Vertex 70v FT-IR spectrometer with the wavenumber from 4000 to 400 cm^{-1} after samples (~2 mg) were mixed with the dried KBr (100 mg) to form films.

Nuclear magnetic resonance (NMR) measurement

The ^{1}H NMR spectra were recorded at ambient temperature in DMSO-d_6 on a JEOL JMX-GX 400 MHz spectrometer. The residual DMSO-d_5 signal for ^{1}H NMR spectra was referenced at 2.50 ppm.

High-performance liquid chromatography (HPLC)

The liquid chromatogram was recorded on a Shimadzu LC-20AT instrument, which was equipped with a C18 column and a UV detector. The mobile phase was consisted of methanol and water (90:10, v/v), and its flow rate was set at 0.5 mL min^{-1}. The injection volume was 15 μL.

Powder X-ray diffraction (PXRD)

PXRD patterns of all materials were collected at ambient temperature with a Bruker D8 Advance X-ray diffractometer by depositing powder on a glass substrate. The operations were at 40 kV and 100 mA using Cu Kα (λ = 1.54 Å) radiation, with different speeds and a step size of 0.01° in 2θ, and a 2θ range of 2° to 40°.

Nitrogen adsorption/desorption isotherms

Nitrogen adsorption/desorption isotherms were obtained on a Micromeritics ASAP 2460 instrument at 77 K (liquid nitrogen). Samples were outgassed under vacuum at 100 ºC for 8 h before measurements. The surface area was calculated using the Brunauer-Emmett-Teller (BET) method. Micropore and mesopore sizes were determined by a non-local density functional theory (NLDFT) model.

X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) spectra were obtained using an EscaLab Xi+ X-ray photoelectron spectrometer from Thermo Fisher Scientific.

Benzene adsorption isotherms

The benzene isotherms were carried out at 298 K on the ZQ100C vapor adsorption apparatus. The

analyzer was equipped with the benzene steam generation unit and the heating unit. The benzene steam generation unit was used to constantly generate the pure benzene vapor at 318 K. The heating unit was used to maintain the adsorption temperature at 298 K. Before measurements, samples were pretreated at 373 K for 12 h under vacuum to remove water and other gas molecules.

S1.3 Depolymerization and recycling of TAPB-TPA COF

S1.3.1 Model reactions of imine condensation and transimination

Fig. 1b depicts the imine condensation and transamination between benzaldehyde, THFA and 3',5'-diphenylbiphenyl-4-amine. Detailed reaction conditions were as follows:

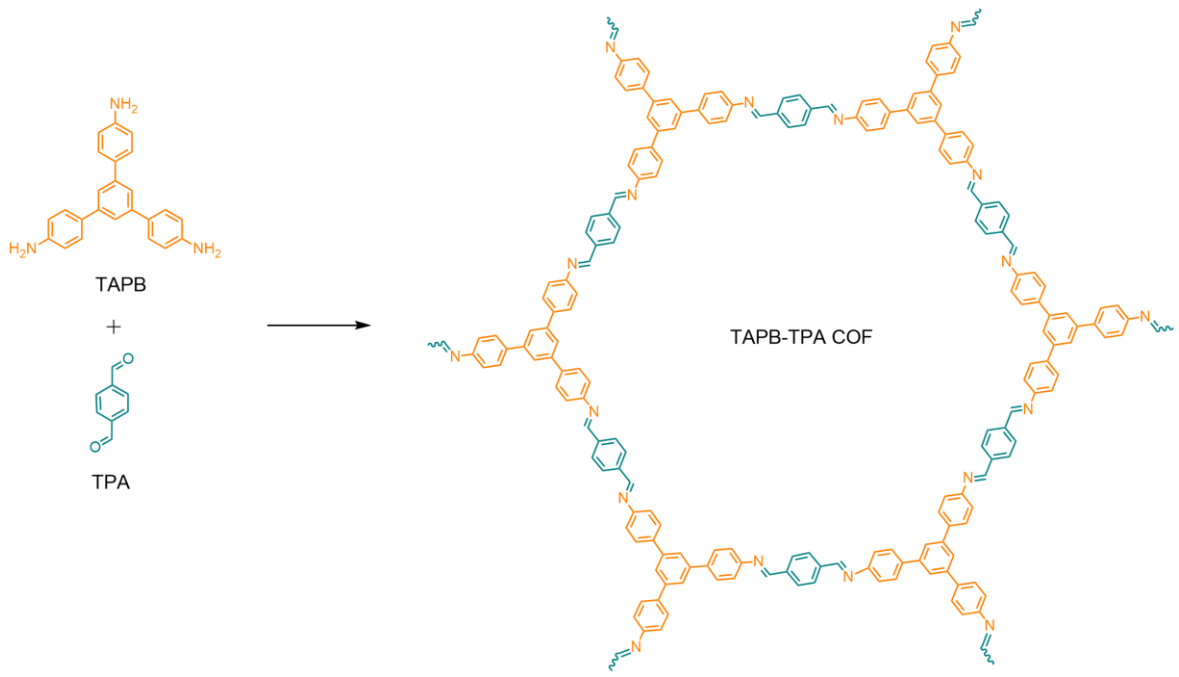
Reaction I: One glass vial was charged with benzaldehyde (10.1 μL, 0.1 mmol) and methanol (5 mL), while the other glass vial was charged with THFA (10.3 μL, 0.1 mmol) and methanol (5 mL). After sonication, the THFA solution and molecular sieve were added to the benzaldehyde-containing glass vial. The mixture reacted under stirring at 50 ºC for 2 days.

Reaction II: One glass vial was charged with benzaldehyde (12.1 μL, 0.12 mmol) and methanol (5 mL), while the other glass vial was charged with 3',5'-diphenylbiphenyl-4-amine (**2**, 32.1 mg, 0.1 mmol) and methanol (5 mL). After sonication, the amine solution and molecular sieve were added to the benzaldehyde-containing glass vial. The mixture reacted under stirring at 50 ºC for 4 days.

Reaction III: The resulting Reaction II mixture (4 mL) mixed with THFA (41.3 μL, 0.4 mmol, 10 equiv. relative to imine bonds), and reacted under stirring at 50 ºC for 4 days.

Reaction IV: To the resulting Reaction III mixture (2 mL), aqueous acetic acid (300 μL, 6 mol L^{-1}) was added, followed by the reaction under stirring at 50 ºC for 1 day.

S1.3.2 Imine condensation for synthesis of TAPB-TPA COF



Scheme S1. Synthesis of TAPB-TPA COF

A reported method with slight modification was used to synthesize TAPB-TPA COF (*Small*, 2022, **19**, 2205501). Briefly, one glass vial was charged with TAPB (89.6 mg, 0.256 mmol), anhydrous DMSO (240 μL) and water (32 μL), while the other glass vial was charged with TPA (51.2 mg, 0.384 mmol) and DMSO (240 μL). After sonication for 3 minutes, the TAPB solution was added to the TPA solution. The mixed homogeneous solution reacted at 40 °C for 4 h. The cured monolith was washed using ethanol (4 × 10 mL) and 1,4-dioxane/1,3,5-trimethylbenzene (4:1, v/v, 4 × 10 mL) in sequence. Then the wet monolith was immersed in a solution comprised of 1,4-dioxane (5.12 mL), 1,3,5-trimethylbenzene (1.28 mL), acetic acid (1.9 mL) and water (1.3 mL), and treated in a 25 mL Teflon-sealed autoclave at 70 °C for 24 h for crystallization. After washing with ethanol (4 × 10 mL) and *n*-hexane (4 × 10 mL), and drying under vacuum at 60 °C for 12 h, the crystalline TAPB-TPA COF was obtained.

Theoretically molar content of imine bonds per gram of TAPB-TPA COF was calculated according to the following equation:

$$n(\text{imine bonds}) = \frac{2 \times n(\text{TPA})}{m(\text{TAPB}) + m(\text{TPA}) - 2 \times n(\text{TPA}) \times M(H_2O)} = 6 \text{ mmol g}^{-1}$$

where *m*(TAPB) and *m*(TPA) represented mass amounts used for TAPB-TPA COF synthesis, and were 89.6 and 51.2 mg, respectively, and the value of *n*(TPA) was 0.384 mmol. *M*(H_2O) is the molar mass of water, 18 g mol^{-1}.

S1.3.3 Transimination for depolymerization of TAPB-TPA COF

In a typical method for depolymerization of TAPB-TPA COF through transamination, TAPB-TPA COF (200 mg, containing 1.2 mmol of imine bonds) was suspended in dichloromethane (100 mL) in a 150 mL round-bottom flask equipped with a stir bar. Then THFA (1242 μL, 12 mmol) was added. The mixture was stirred at room temperature for 4 days. Based on the ratio of imine bonds to THFA, this condition was denoted as 1:10 THFA.

To study the effect of THFA content on depolymerization process, two conditions of 1:5 THFA and 1:3 THFA were conducted similarly. For 1:5 THFA depolymerization, THFA (621 μL, 6 mmol) was added and the mixture was stirred at room temperature for 8 days. For 1:3 THFA depolymerization, THFA (373 μL, 3.6 mmol) was added and the mixture was stirred at room temperature for 16 days.

Besides THFA, another alkylamine, *n*-butylamine (BA, 1190 μL, 12 mmol), was adopted to depolymerize the TAPB-TPA COF (200 mg in 100 mL of dichloromethane) at room temperature for 4 days. This condition was denoted as 1:10 BA. For 1:3 BA depolymerization, BA (357 μL, 3.6 mmol) was added and the mixture was stirred at room temperature for 16 days.

S1.3.4 TAPB monomer recovery through flash column chromatography

The depolymerization mixture obtained using the 1:10 THFA condition was concentrated under the reduced pressure using a rotary evaporator. Crude products were purified by the flash column chromatography (silica gel, 200-300 mesh; PE/MeOH = 200:9, v/v, containing 1% triethylamine). Two chromatographic bands (B1 and B2) were observed, corresponding to compounds of THFA-substituted imine (denoted as alkyl-imine) and TAPB monomer. The recovery efficiency of TAPB was 46% with respect to the mass of pristine TAPB-TPA COF used.

S1.3.5 Two recycling routes for TAPB-TPA COF

Route I: Room-temperature recycling (RTR)

The room-temperature recycling was carried out at ambient pressure. After complete depolymerization

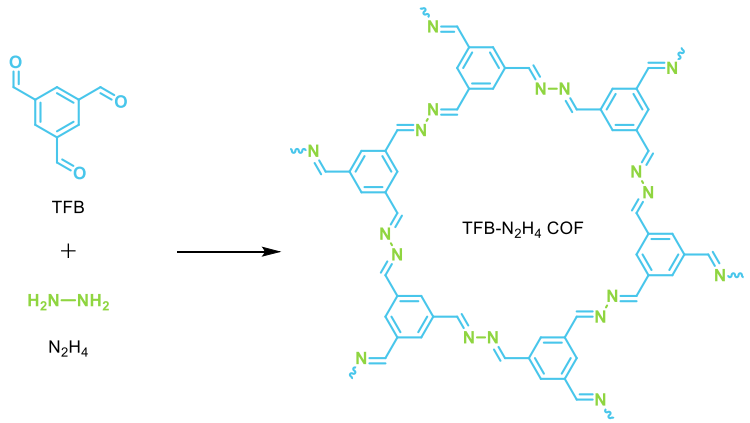
with conditions as described in **S1.3.3** section (1:3 THFA, 1:5 THFA, and 1:10 THFA), aqueous acetic acid (18 mL, 6 mol L^{-1}) was directly added to depolymerization mixtures without any purification. The mixture was stirred at room temperature and ambient pressure for 24 h, generating a yellow solid. After washing with ethanol (4 ×10 mL) and *n*-hexane (4 ×10 mL), and drying at 60 °C under vacuum, the crystalline TAPB-TPA COF was regenerated. Recycling conditions were denoted as 1:3 THFA-RTR, 1:5 THFA-RTR, and 1:10 THFA-RTR, respectively.

Route II: Solvothermal recycling (STR)

The solvothermal recycling of TAPB-TPA COF was performed in a 25 mL Teflon-sealed autoclave. Depolymerization mixtures obtained through methods described in **S1.3.3** section (1:3 THFA, 1:5 THFA, 1:10 THFA, 1:3 BA, and 1:10 BA) were evaporated and dried to remove dichloromethane. Note that excess THFA or BA may be removed during the evaporation treatment. Concentrated mixtures were transferred to a 25 mL Teflon, to which glacial acetic acid (equimolar to the THFA or BA added), water and 1,4-dioxane/1,3,5-trimethylbenzene solution (4:1, v/v) were added, accounting for 20%, 13% and 67% of the total solution volume, respectively. The sealed autoclave was treated at 70 °C for 24 h. The as-synthesized solid was washed with ethanol (4 ×10 mL) and *n*-hexane (4 ×10 mL), and dried at 60 °C under vacuum to regenerate crystalline TAPB-TPA COF. Recycling conditions were denoted as 1:3 THFA-STR, 1:5 THFA-STR, 1:10 THFA-STR, 1:3 BA-STR, and 1:10 BA-STR.

S1.4 Depolymerization of other imine-linked COFs

S1.4.1 Synthesis and depolymerization of TFB-N_2H_4 COF



Scheme S2. Synthesis of TFB-N_2H_4 COF

A reported method with slight modification was used to synthesize TFB-N_2H_4 COF (*Chem. Commun.*, 2025, **61**, 19465-19468). Briefly, a 2-ml centrifuge tube was charged with TFB (60.0 mg, 0.37 mmol) and anhydrous DMSO (169.8 μL). The mixture and sonicated to form a suspension liquid, to which the hydrazine hydrate (38.0 μL) was added. After sonication, the mixed homogeneous solution reacted at 40 ºC for 4 h. The cured monolith was washed using ethanol (4 × 10 mL) and *n*-butanol (4 × 10 mL) in sequence. Then the wet monolith was immersed in a solution comprised of 1,3,5-trimethylbenzene (4.0 mL), *n*-butanol (2.0 mL) and aqueous acetic acid (4.0 mL, 6 mol L^{-1}), and treated in a 25 mL Teflon-sealed autoclave at 120 ºC for 4.5 days for crystallization. After washing with ethanol (4 × 10 mL) and *n*-hexane (4 × 10 mL), and drying under vacuum at 60 ºC for 12 h, the crystalline TFB-N_2H_4 COF was obtained.

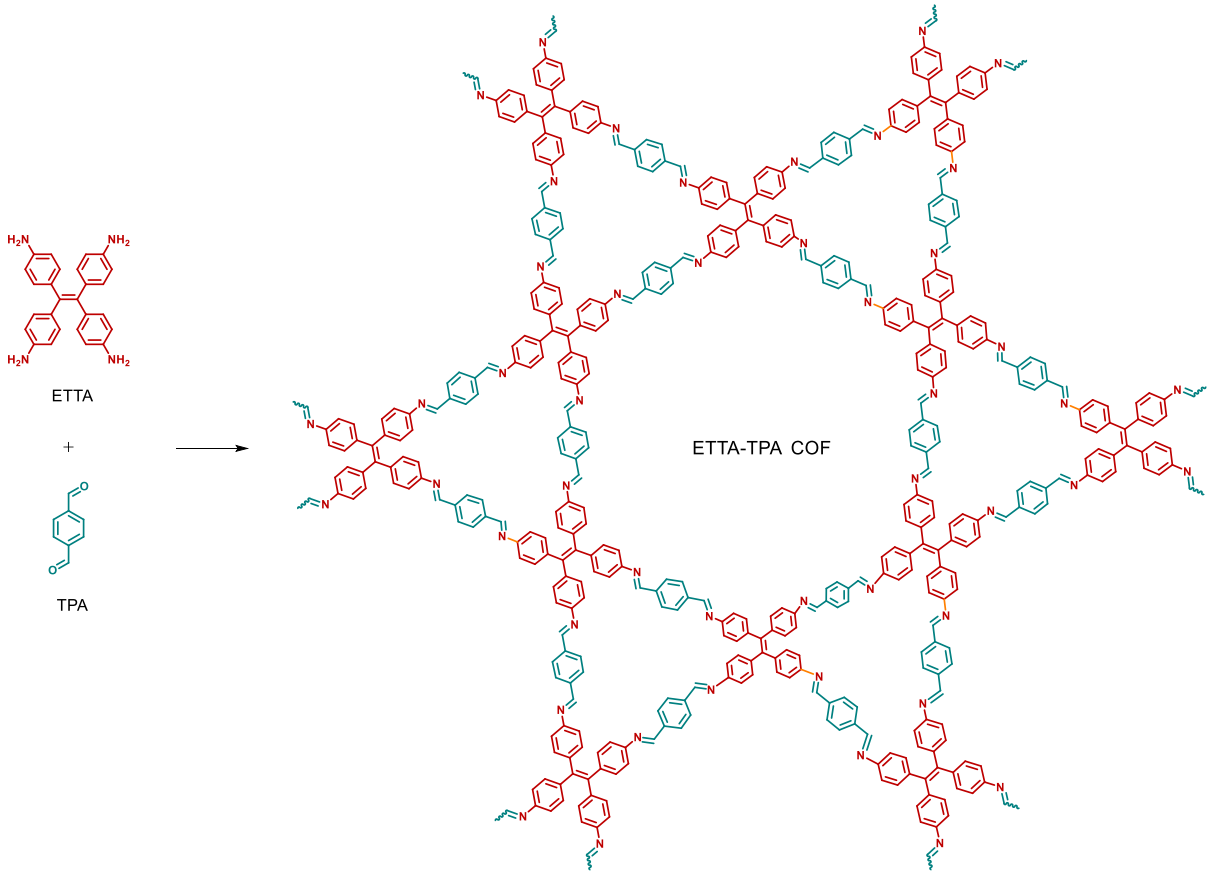
Theoretically molar content of imine bonds per gram of TFB-N_2H_4 COF was calculated according to the following equation:

$$n(\text{imine bonds}) = \frac{3 \times n(\text{TFB})}{m(\text{TFB}) + 1.5 \times n(\text{TFB}) \times M(N_2H_4) - 3 \times n(\text{TFB}) \times M(H_2O)} = 19.2 \text{ mmol g}^{-1}$$

where m(TFB) represented mass amounts used for TFB-N_2H_4 COF synthesis, 60.0 mg, and the value of n(TFB) was 0.37 mmol. $M(N_2H_4)$ is the molar mass of hydrazine, 32 g mol^{-1}. $M(H_2O)$ is the molar mass of water, 18 g mol^{-1}. It is noteworthy that an excess of hydrazine hydrate was introduced during the synthesis of TFB-N_2H_4 COF.

The depolymerization of TFB-N_2H_4 COF was carried out with a molar ratio of imine bonds to THFA at 1:10. TFB-N_2H_4 COF (40 mg, containing 0.768 mmol of imine bonds) was suspended in dichloromethane (20 mL) in a 30 mL glass vial equipped with a stir bar. Then THFA (792.8 μL, 7.68 mmol) was added. The mixture was stirred at 30 ºC. The depolymerization process was shown in Fig. S21 and no depolymerization of TFB-N_2H_4 COF was observed.

S1.4.2 Synthesis and depolymerization of ETTA-TPA COF



Scheme S3. Synthesis of ETTA-TPA COF

A reported method with slight modification was used to synthesize ETTA-TPA COF (*Adv. Funct. Mater.*, 2024, **34**, 2400433). Briefly, one glass vial was charged with ETTA (180 mg, 0.459 mmol), 1,4-dioxane (550 μL) and water (75 μL), while the other glass vial was charged with TPA (123 mg, 0.917 mmol) and 1,4-dioxane (550 μL). After sonication for 3 minutes, the ETTA solution was added to the TPA solution. The mixed homogeneous solution reacted at 80 °C for 4 h. The cured monolith was obtained. Then the monolith was immersed in a solution comprised of 1,4-dioxane (4.90 mL), acetic acid (206 μL) and water (319 μL), and treated in a 25 mL Teflon-sealed autoclave at 120 °C for 4 days for crystallization. After washing with ethanol (4 × 10 mL) and *n*-hexane (4 × 10 mL), and drying under vacuum at 60 °C for 12 h, the crystalline ETTA-TPA COF was obtained.

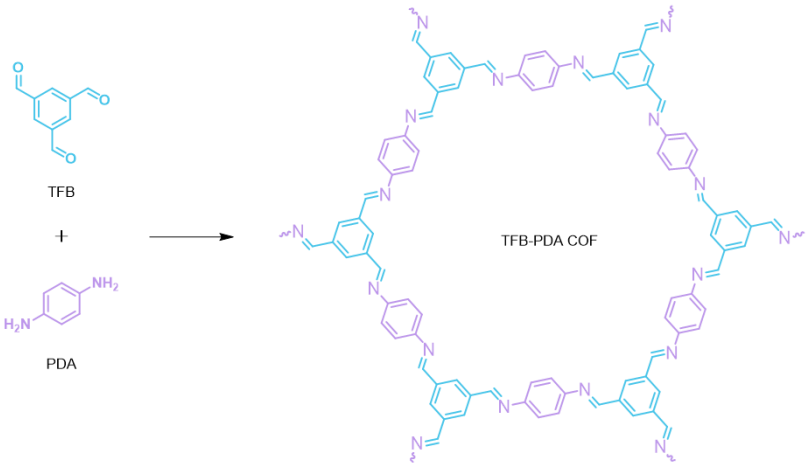
Theoretically molar content of imine bonds per gram of ETTA-TPA COF was calculated according to the following equation:

$$n(\text{imine bonds}) = \frac{2 \times n(\text{TPA})}{m(\text{ETTA}) + m(\text{TPA}) - 2 \times n(\text{TPA}) \times M(H_2O)} = 6.79 \text{ mmol g}^{-1}$$

where *m*(ETTA) and *m*(TPA) represented mass amounts used for ETTA-TPA COF synthesis, and were 180 and 123 mg, respectively, and the value of *n*(TPA) was 0.917 mmol. *M*(H_2O) is the molar mass of water, 18 g mol^{-1}.

The depolymerization of ETTA-TPA COF was carried out with a molar ratio of imine bonds to THFA at 1:10. ETTA-TPA COF (40 mg, containing 0.272 mmol of imine bonds) was suspended in dichloromethane (20 mL) in a 30 mL glass vial equipped with a stir bar. Then THFA (281 μL, 2.72 mmol) was added. The mixture was stirred at 30 °C for 6 days. The depolymerization process was shown and percentages of residual solids regarding to the mass of pristine ETTA-TPA COF were calculated (Fig. S24).

S1.4.3 Synthesis and depolymerization of COF-LZU1



Scheme S4. Synthesis of COF-LZU1

A reported method with slight modification was used to synthesize COF-LZU1 (*Small*, 2022, **19**, 2205501). Briefly, one glass vial was charged with PDA (80.0 mg, 0.740 mmol), anhydrous DMSO (175 μL) and water (25 μL), while the other glass vial was charged with TFB (80.0 mg, 0.493 mmol) and DMSO (200 μL). After sonication for 3 minutes, the PDA solution was added to the TFB solution. The mixed homogeneous solution reacted at 40 °C for 4 h. The cured monolith was washed using ethanol (4 × 10 mL) and 1,4-dioxane/1,3,5-trimethylbenzene (4:1, v/v, 4 × 10 mL) in sequence. Then the wet monolith was immersed in a solution comprised of 1,4-dioxane (5.12 mL), 1,3,5-trimethylbenzene (1.28 mL), acetic acid (1.9 mL) and water (1.3 mL), and treated in a 25 mL Teflon-sealed autoclave at 70 °C for 24 h for crystallization. After washing with ethanol (4 × 10 mL) and *n*-

hexane (4 × 10 mL), and drying under vacuum at 60 °C for 12 h, the crystalline COF-LZU1 was obtained.

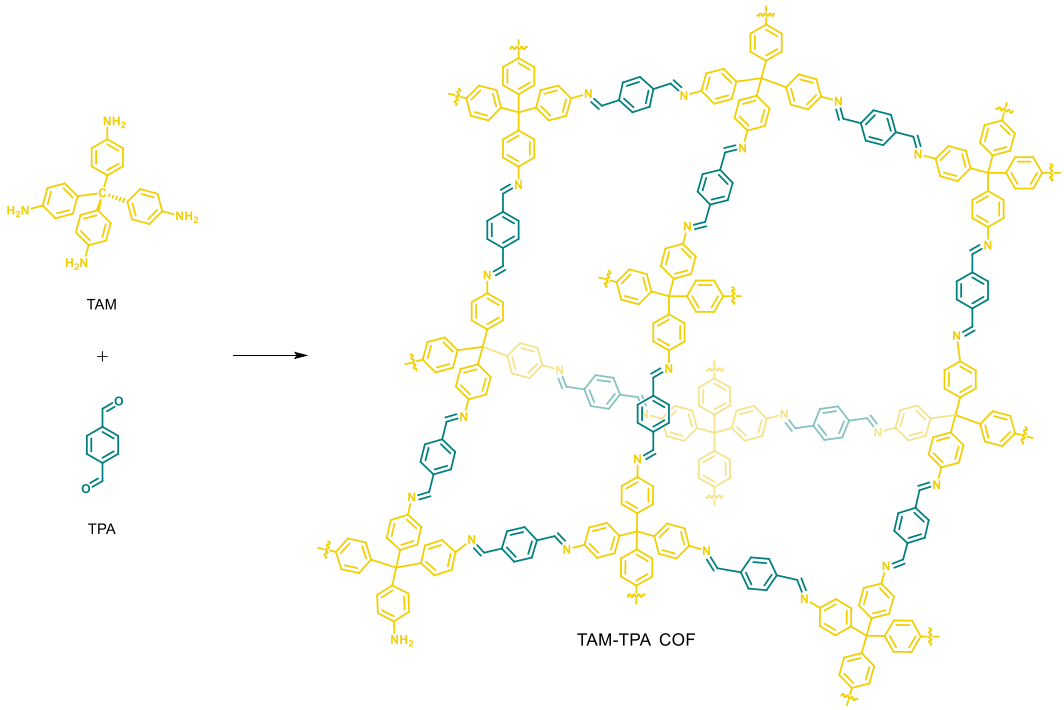
Theoretically molar content of imine bonds per gram of COF-LZU1 was calculated according to the following equation:

$$n(\text{imine bonds}) = \frac{2 \times n(\text{PDA})}{m(\text{TFB}) + m(\text{PDA}) - 2 \times n(\text{PDA}) \times M(H_2O)} = 11.1 \text{ mmol g}^{-1}$$

where m(TFB) and m(PDA) represented mass amounts used for COF-LZU1 synthesis, and were 80.0 and 80.0 mg, respectively, and the value of n(PDA) was 0.740 mmol. $M(H_2O)$ is the molar mass of water, 18 g mol^{-1}.

The depolymerization of COF-LZU1 was carried out with a molar ratio of imine bonds to THFA at 1:10. COF-LZU1 (40 mg, containing 0.444 mmol of imine bonds) was suspended in dichloromethane (20 mL) in a 30 mL glass vial equipped with a stir bar. Then THFA (458 μL, 4.44 mmol) was added. The mixture was stirred at 30 °C for 2 days. The depolymerization process was shown and percentages of residual solids regarding to the mass of pristine COF-LZU1 were calculated (Fig. S27).

S1.4.4 Synthesis and depolymerization of COF-300



Scheme S5. Synthesis of COF-300

One glass vial was charged with TAM (38.0 mg, 0.1 mmol), 1,4-dioxane (891.3 μL) and aqueous trifluoroacetic acid (57.6 μL, 6 mol L^{-1}), while the other glass vial was charged with TPA (26.8 mg, 0.2 mmol) and 1,4-dioxane (300 μL). After sonication for 3 minutes, the TPA solution was added to the TAM solution. The mixed homogeneous solution reacted at 30 °C for 24 h. After washing with ethanol (4 × 10 mL) and *n*-hexane (4 × 10 mL), and drying under vacuum at 60 °C for 12 h, the crystalline COF-300 was obtained.

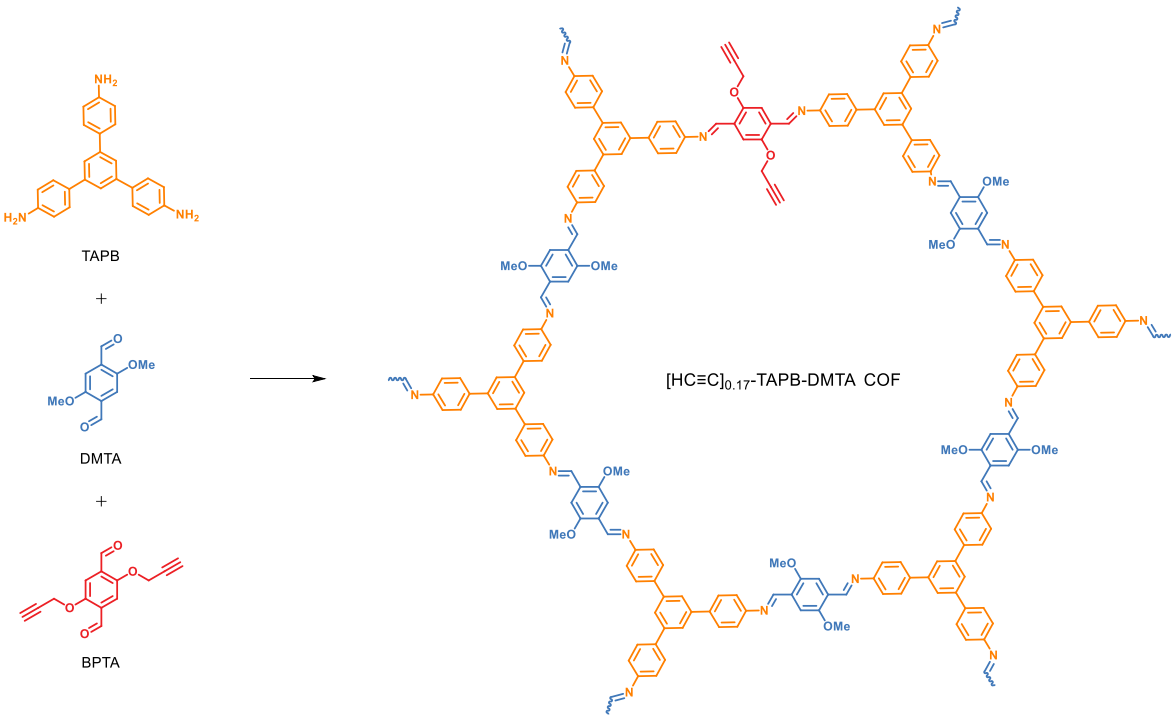
Theoretically molar content of imine bonds per gram of COF-300 was calculated according to the following equation:

$$n(\text{imine bonds}) = \frac{2 \times n(\text{TPA})}{m(\text{TAM}) + m(\text{TPA}) - 2 \times n(\text{TPA}) \times M(H_2O)} = 6.94 \text{ mmol g}^{-1}$$

where m(TAM) and m(TPA) represented mass amounts used for COF-300 synthesis, and were 38.0 and 26.8 mg, respectively, and the value of n(TPA) was 0.2 mmol. $M(H_2O)$ is the molar mass of water, 18 g mol^{-1}.

The depolymerization of COF-300 was carried out with a molar ratio of imine bonds to THFA at 1:10. COF-300 (40 mg, containing 0.278 mmol of imine bonds) was suspended in dichloromethane (20 mL) in a 30 mL glass vial equipped with a stir bar. Then THFA (287 μL, 2.78 mmol) was added. The mixture was stirred at 30 °C for 6 days. The depolymerization process was shown and percentages of residual solids regarding to the mass of pristine COF-300 were calculated (Fig. S30).

S1.4.5 Synthesis and depolymerization of $[HC\equiv C]_{0.17}$-TAPB-DMTA COF



Scheme S6. Synthesis of $[HC\equiv C]_{0.17}$-TAPB-DMTA COF

A reported method with slight modification was used to synthesize $[HC\equiv C]_{0.17}$-TAPB-DMTA COF (*Nat. Chem.*, 2015, **7**, 905-912). Briefly, *n*-butanol/1,2-dichlorobenzene (1/1 mL) mixtures of TAPB (56.2 mg, 0.16 mmol), DMTA (38.8 mg, 0.20 mmol) and BPTA (9.7 mg, 0.04 mmol) in the presence of an acetic acid catalyst (0.2 ml, 6 mol L^{-1}) in a 25 mL Teflon-sealed autoclave at 120 ºC for 3 days. After washing with THF (6 × 10 mL) and drying under vacuum at 120 ºC for 12 h, the crystalline $[HC\equiv C]_{0.17}$-TAPB-DMTA COF was obtained.

Theoretically molar content of imine bonds per gram of $[HC\equiv C]_{0.17}$-TAPB-DMTA COF was calculated according to the following equation:

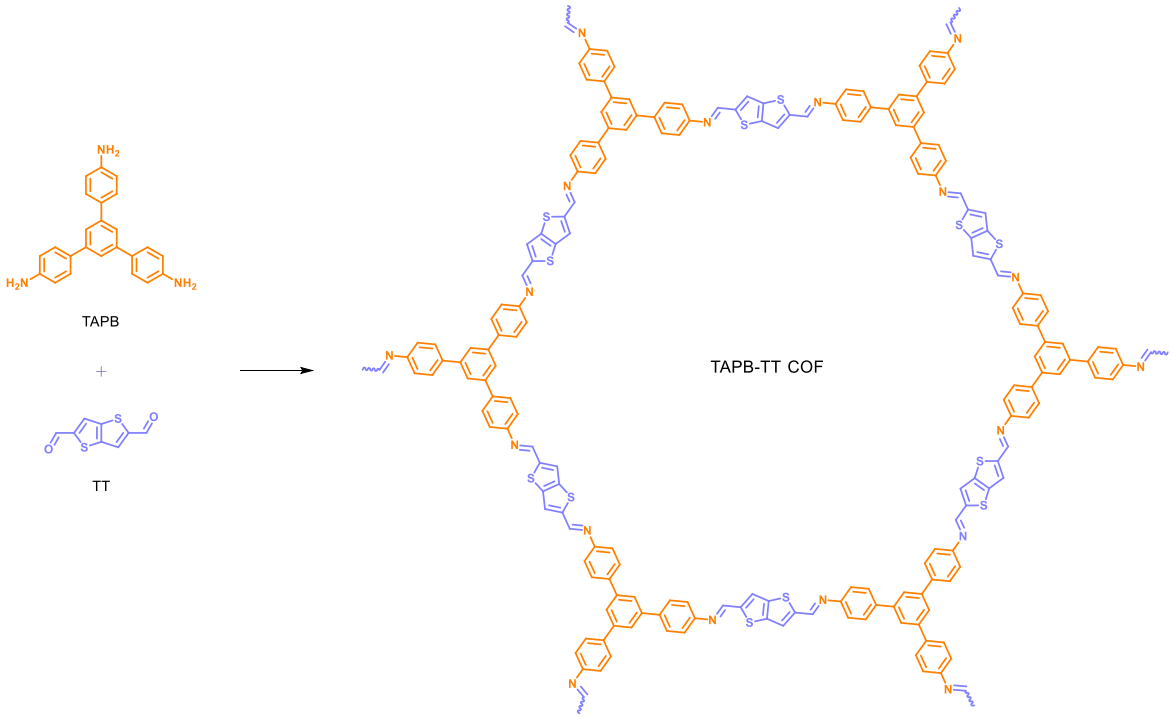
$$n(\text{imine bonds}) = \frac{3 \times n(\text{TAPB})}{m(\text{TAPB}) + m(\text{DMTA}) + m(\text{BPTA}) - 3 \times n(\text{TAPB}) \times M(H_2O)} = 5 \text{ mmol g}^{-1}$$

where *m*(TAPB), *m*(DMTA) and *m*(BPTA) represented mass amounts used for $[HC\equiv C]_{0.17}$-TAPB-DMTA COF synthesis, and were 56.2, 38.8 and 9.7 mg, respectively, and the value of *n*(TAPB) was 0.16 mmol. $M(H_2O)$ is the molar mass of water, 18 g mol^{-1}.

The depolymerization of $[HC\equiv C]_{0.17}$-TAPB-DMTA COF was carried out with a molar ratio of imine

bonds to THFA at 1:10. $[HC{\equiv}C]_{0.17}$-TAPB-DMTA COF (40 mg, containing 0.2 mmol of imine bonds) was suspended in dichloromethane (20 mL) in a 30 mL glass vial equipped with a stir bar. Then THFA (206.4 μL, 2 mmol) was added. The mixture was stirred at 30 °C for 4 days. The depolymerization process was shown and percentages of residual solids regarding to the mass of pristine $[HC{\equiv}C]_{0.17}$-TAPB-DMTA COF were calculated (Fig. S33).

S1.4.6 Synthesis and depolymerization of TAPB-TT COF



Scheme S7. Synthesis of TAPB-TT COF

A reported method with slight modification was used to synthesize TAPB-TT COF (*Chin. Chem. Lett.*, 2023, **34**, 107201). Briefly, a 25 mL Teflon-sealed autoclave was charged with TAPB (56.2 mg, 0.16 mmol), TT (47.1 mg, 0.24 mmol), 1,3,5-trimethylbenzene (2.4 mL) and benzyl alcohol (0.26 mL). After sonication for 20 minutes, aqueous acetic acid (0.2 mL, 6 mol L^{-1}) was added to the mixture. The mixed homogeneous dispersion reacted at 120 °C for 3 days. After washing with acetone (4 × 10 mL) and ethanol (4 × 10 mL), and drying under vacuum at 60 °C for 12 h, the crystalline TAPB-TT COF was obtained.

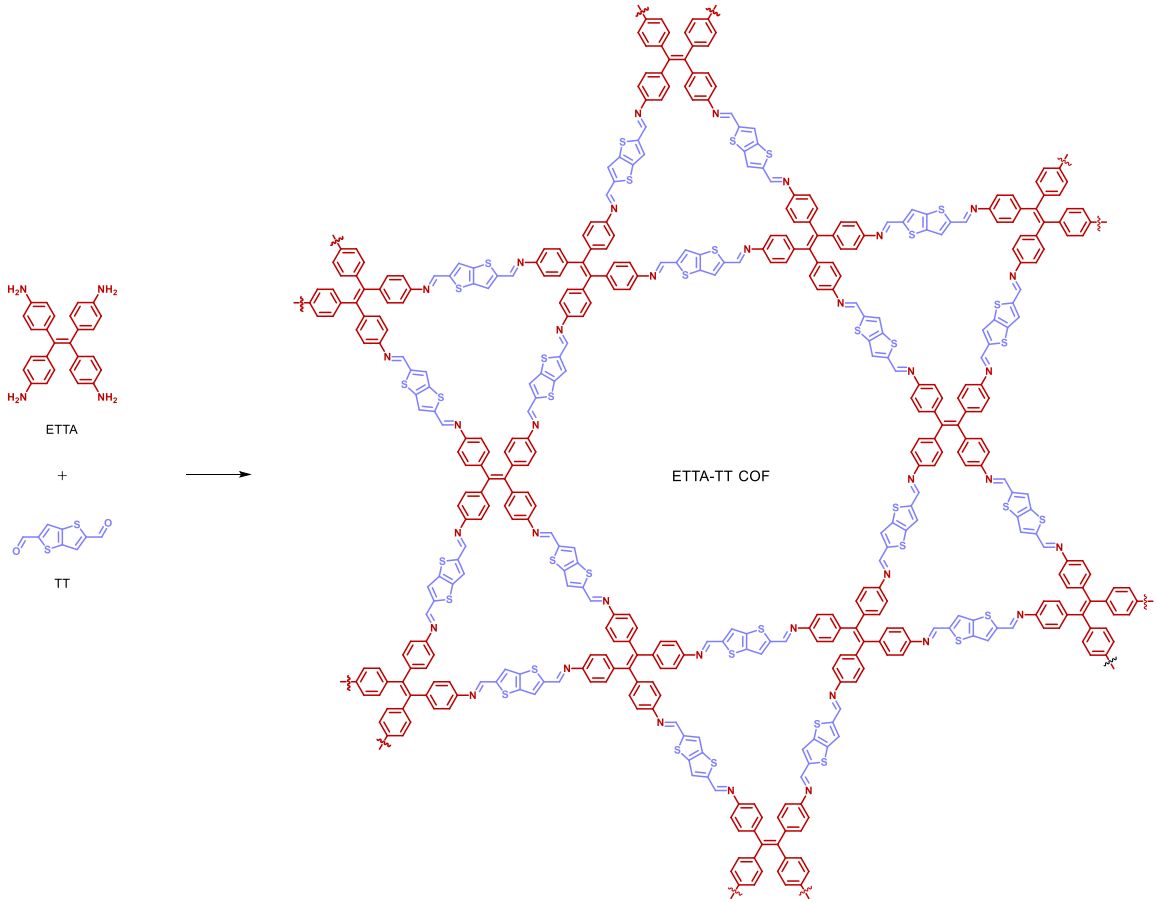
Theoretically molar content of imine bonds per gram of TAPB-TT COF was calculated according to the following equation:

$$n(\text{imine bonds}) = \frac{3 \times n(\text{TAPB})}{m(\text{TAPB}) + m(\text{TT}) - 3 \times n(\text{TAPB}) \times M(H_2O)} = 5.07 \text{ mmol g}^{-1}$$

where m(TAPB) and m(TT) represented mass amounts used for TAPB-TT COF synthesis, and were 56.2 and 47.1 mg, respectively, and the value of n(TAPB) was 0.16 mmol. $M(H_2O)$ is the molar mass of water, 18 g mol^{-1}.

The depolymerization of TAPB-TT COF was carried out with a molar ratio of imine bonds to THFA at 1:10. TAPB-TT COF (40 mg, containing 0.2028 mmol of imine bonds) was suspended in dichloromethane (20 mL) in a 30 mL glass vial equipped with a stir bar. Then THFA (209.3 μL, 2.028 mmol) was added. The mixture was stirred at 30 °C for 6 days. The depolymerization process was shown and percentages of residual solids regarding to the mass of pristine TAPB-TT COF were calculated (Fig. S36).

S1.4.7 Synthesis and depolymerization of ETTA-TT COF



Scheme S8. Synthesis of ETTA-TT COF

A reported method with slight modification was used to synthesize ETTA-TT COF (*Nat. Chem.*, 2016, **8**, 310-316). Briefly, a 25 mL Teflon-sealed autoclave was charged with ETTA (58.9 mg, 0.15 mmol), TT (58.9 mg, 0.30 mmol), 1,3,5-trimethylbenzene (0.5 mL) and benzyl alcohol (4.5 mL). After sonication for 20 minutes, aqueous acetic acid (0.5 mL, 6 mol L^{-1}) was added to the mixture. The mixed homogeneous dispersion reacted at 120 ºC for 3 days. After washing with DMF (6 × 10 mL), and drying under vacuum at 120 ºC for 12 h, the crystalline ETTA-TT COF was obtained.

Theoretically molar content of imine bonds per gram of ETTA-TT COF was calculated according to the following equation:

$$n(\text{imine bonds}) = \frac{2 \times n(\text{TT})}{m(\text{ETTA}) + m(\text{TT}) - 2 \times n(\text{TT}) \times M(H_2O)} = 5.6 \text{ mmol g}^{-1}$$

where m(ETTA) and m(TT) represented mass amounts used for ETTA-TT COF synthesis, and were 59.8 and 58.9 mg, respectively, and the value of n(TT) was 0.30 mmol. $M(H_2O)$ is the molar mass of water, 18 g mol^{-1}.

The depolymerization of ETTA-TT COF was carried out with a molar ratio of imine bonds to THFA at 1:10. ETTA-TT COF (40 mg, containing 0.224 mmol of imine bonds) was suspended in dichloromethane (20 mL) in a 30 mL glass vial equipped with a stir bar. Then THFA (231.6 μL, 2.24 mmol) was added. The mixture was stirred at 30 ºC for 6 days. The depolymerization process was shown and percentages of residual solids regarding to the mass of pristine ETTA-TT COF were calculated (Fig. S39).

S1.5 $Sc(OTf)_3$-catalyzed depolymerization process and recycling

S1.5.1 $Sc(OTf)_3$-catalyzed transimination for depolymerization of TAPB-TPA COF

In a typical $Sc(OTf)_3$-catalyzed depolymerization of TAPB-TPA COF, with conditions as described in **S1.3.3** section (1:3 THFA), TAPB-TPA COF (200 mg, containing 1.2 mmol of imine bonds) was suspended in dichloromethane (100 mL) in a 150 mL round-bottom flask equipped with a stir bar. Then THFA (373 μL, 3.6 mmol) was added. Finally, $Sc(OTf)_3$ (71 mg, 0.144 mmol) was added under stirring conditions. The mixture was stirred at 30 ºC for 48 hours. Based on the ratio of $Sc(OTf)_3$ to THFA, this depolymerization condition was denoted as 1:3 THFA-4% Sc^{III}.

To study the effect of THFA and $Sc(OTf)_3$ contents on the depolymerization process, five conditions of 1:2 THFA-4% Sc^{III}, 1:1.5 THFA-4% Sc^{III}, 1:3 THFA-0.5% Sc^{III}, 1:2 THFA-0.5% Sc^{III} and 1:1.5 THFA-0.5% Sc^{III} were conducted similarly. For 1:2 THFA-4% Sc^{III} depolymerization, THFA (248.4 μL, 2.4 mmol) and $Sc(OTf)_3$ (47.4 mg, 0.096 mmol) were added, then the mixture was stirred at 30 °C for 48 hours. For 1:1.5 THFA-4% Sc^{III} depolymerization, THFA (186.3 μL, 1.8 mmol) and $Sc(OTf)_3$ (35.5 mg, 0.072 mmol) were added, then the mixture was stirred at 30 °C for 144 hours. For 1:3 THFA-0.5% Sc^{III} depolymerization, THFA (373 μL, 3.6 mmol) and $Sc(OTf)_3$ (6.7 mg, 0.018 mmol) were added, then the mixture was stirred at 30 °C for 96 hours. For 1:2 THFA-0.5% Sc^{III} depolymerization, THFA (248.4 μL, 2.4 mmol) and $Sc(OTf)_3$ (5.9 mg, 0.012 mmol) were added, then the mixture was stirred at 30 °C for 228 hours. For 1:1.5 THFA-0.5% Sc^{III} depolymerization, THFA (186.3 μL, 1.8 mmol) and $Sc(OTf)_3$ (4.4 mg, 0.009 mmol) were added, then the mixture was stirred at 30 °C. The depolymerization processes were shown in Fig. S39.

S1.5.2 RTR method for TAPB-TPA COF

After complete depolymerization, a filtration step was performed before the RTR to remove excess $Sc(OTf)_3$ using a 0.1 μm filter. The recycling was conducted as described in **S1.3.5** section (Route I, Room-temperature recycling). The aqueous acetic acid (18 mL, 6 mol L^{-1}) was added to the filtrate. Recycling conditions were denoted as 1:1.5 THFA-0.5% Sc^{III}-RTR, 1:2 THFA-0.5% Sc^{III}-RTR, 1:3 THFA-0.5% Sc^{III}-RTR, 1:1.5 THFA-4% Sc^{III}-RTR, 1:2 THFA-4% Sc^{III}-RTR, and 1:3 THFA-4% Sc^{III}-RTR, respectively.

Section S2. Supplementary Figures

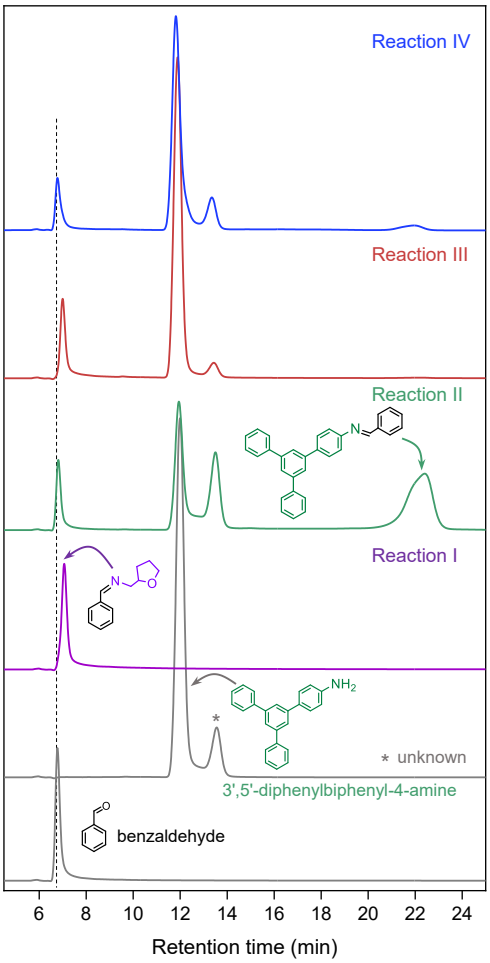


Fig. S1 Chromatograms of monomers and model reaction mixtures. Note that all reaction mixtures after only simple filtration were loaded into the liquid chromatography instrument. Imine condensation and reversible transimination have been confirmed, although the conversions may be below 100%. The Reaction III was carried out by adding THFA to the mixture resulted from Reaction II. The strong nucleophilicity of THFA enabled the transformation of aromatic imine to a THFA-substituted imine. After continuous addition of acetic acid to the Reaction III, the regeneration of aromatic imine was observed as evidenced in MS spectrum (Fig. 1c) and chromatograms.

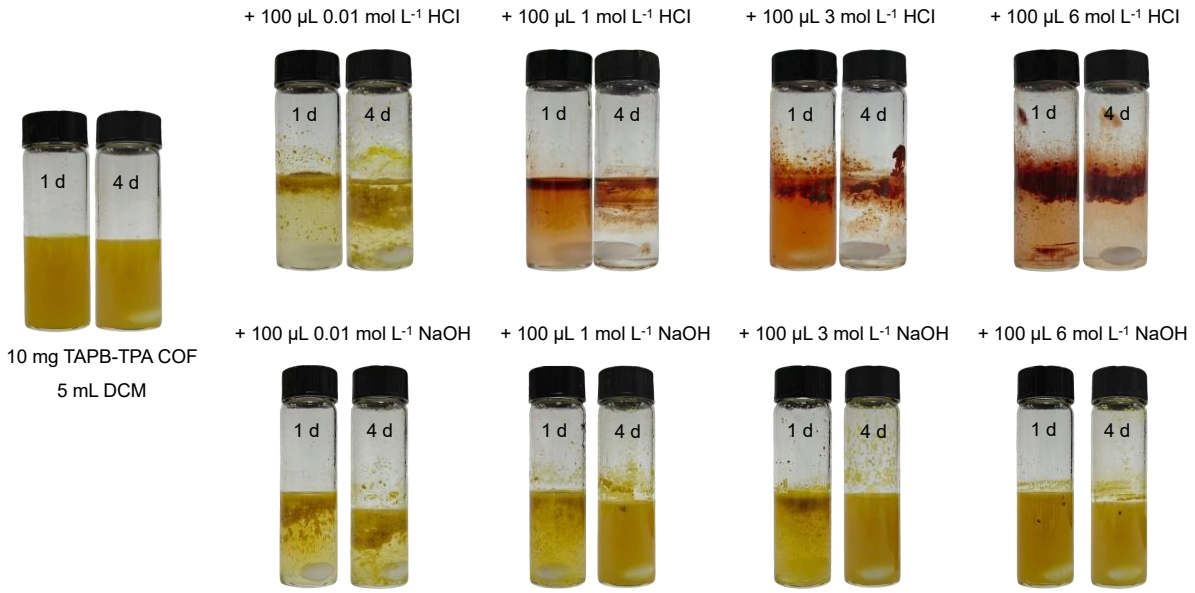


Fig. S2 Using an aqueous solution of HCl or NaOH to depolymerize TAPB-TPA COF. 10 mg of TAPB-TPA COF was dispersed in 5 mL of dichloromethane (DCM), followed by the addition of 100 µL of HCl or NaOH solutions at varying concentrations (0.01 mol L^{-1}, 1 mol L^{-1}, 3 mol L^{-1} and 6 mol L^{-1}) under stirring. The COFs remain stable without obvious depolymerization after 1 day and 4 days under all tested acidic and basic conditions.

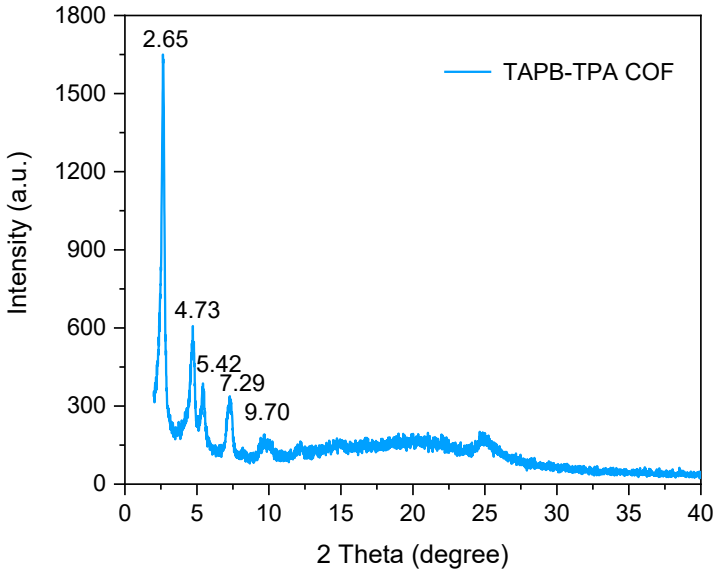


Fig. S3 PXRD pattern of the pristine TAPB-TPA COF.

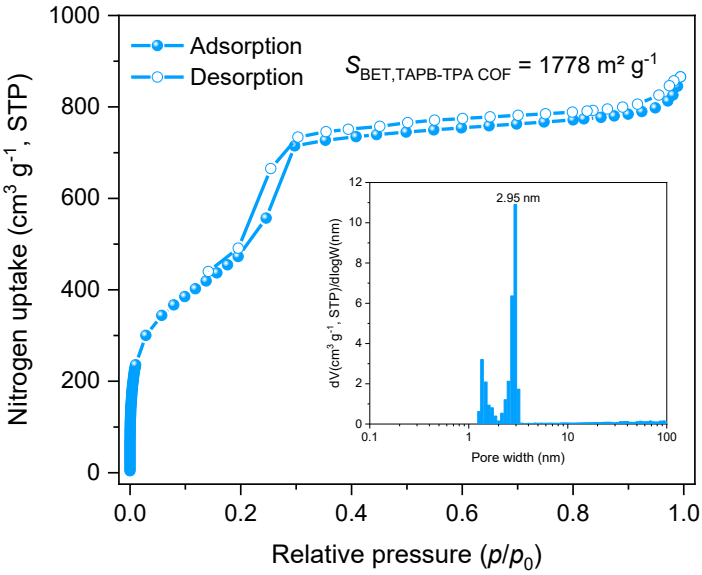


Fig. S4 Nitrogen adsorption/desorption isotherm and pore width of the pristine TAPB-TPA COF.

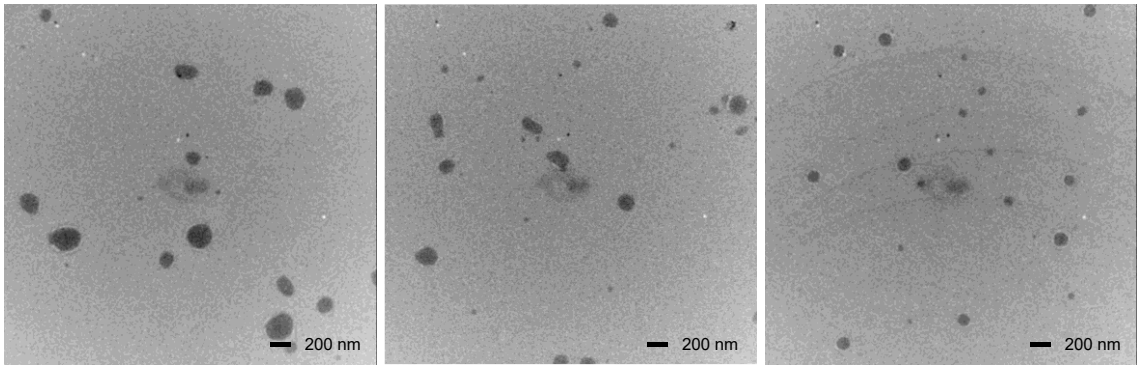


Fig. S5 TEM images (different views selected) of residual solid in the 1:10 THFA depolymerization mixture after 4 days. The depolymerization mixture was directly used for sample preparation without filtration (see also Fig. 2b).

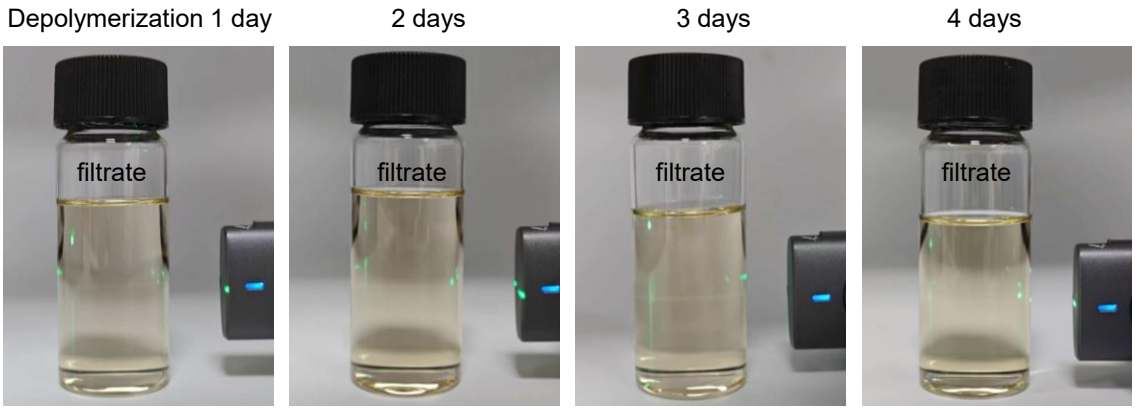


Fig. S6 Photographs of filtrates at different depolymerization times. The condition of 1:10 THFA was used to depolymerize the TAPB-TPA COF, and the resulting depolymerization mixtures were filtered using 0.1 μm filter. None Tyndall effect indicated that residual solids in depolymerization mixtures were removed (see also Fig. 2b).

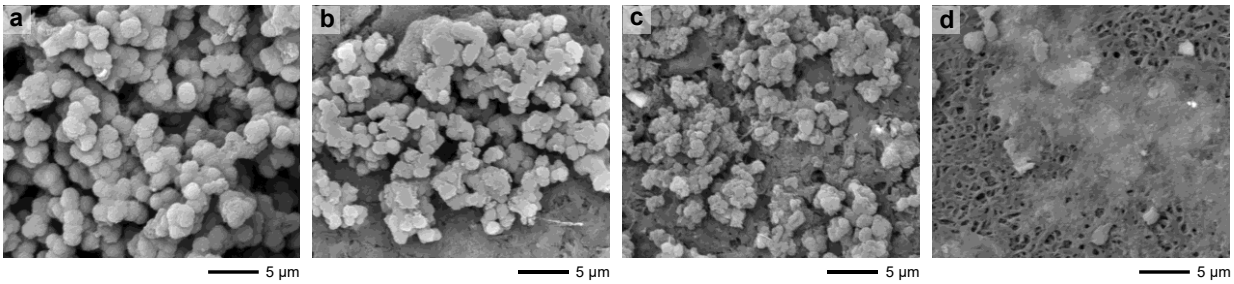


Fig. S7 SEM images of residual solids in depolymerization mixtures. (a) 1 day. (b) 2 days. (c) 3 days. (d) 4 days. The 1:10 THFA condition was adopted to depolymerize the TAPB-TPA COF. Residual solids were collected by filtration of depolymerization mixtures with 0.1 μm filter (see also Fig. 2b).

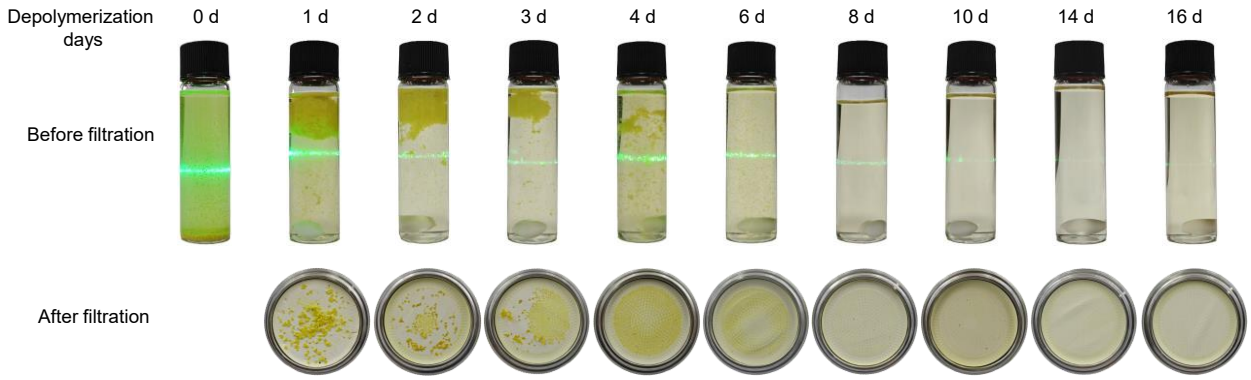


Fig. S8 Photographs of 1:3 THFA depolymerization mixtures and residual solids collected using 0.1 μm filter.

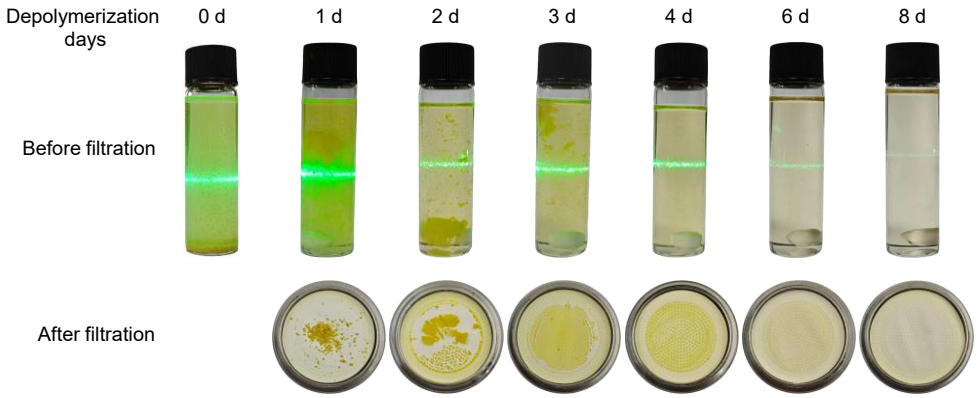


Fig. S9 Photographs of 1:5 THFA depolymerization mixtures and residual solids collected using 0.1 μm filter.

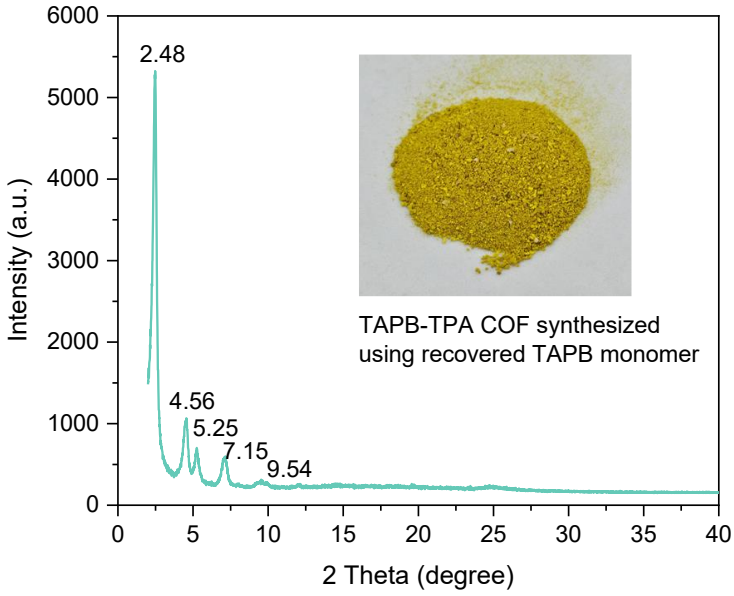


Fig. S10 PXRD pattern of the fresh TAPB-TPA COF synthesized using recovered TAPB monomer.

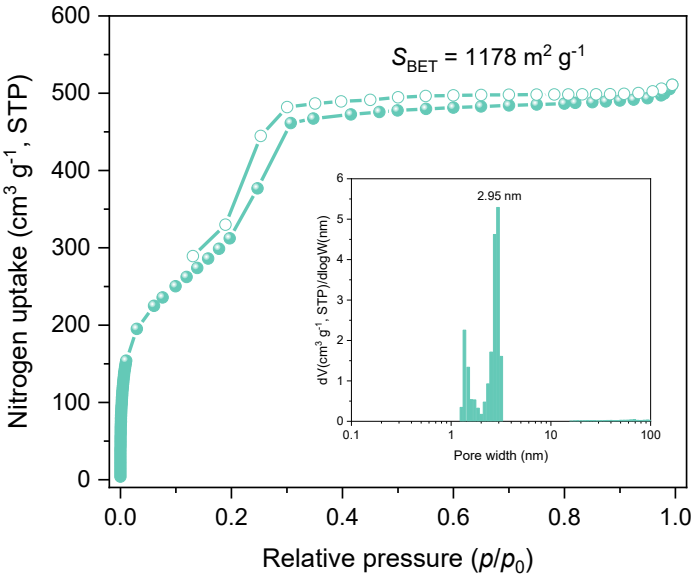


Fig. S11 Nitrogen adsorption/desorption isotherm and pore width of the fresh TAPB-TPA COF synthesized using recovered TAPB monomer.

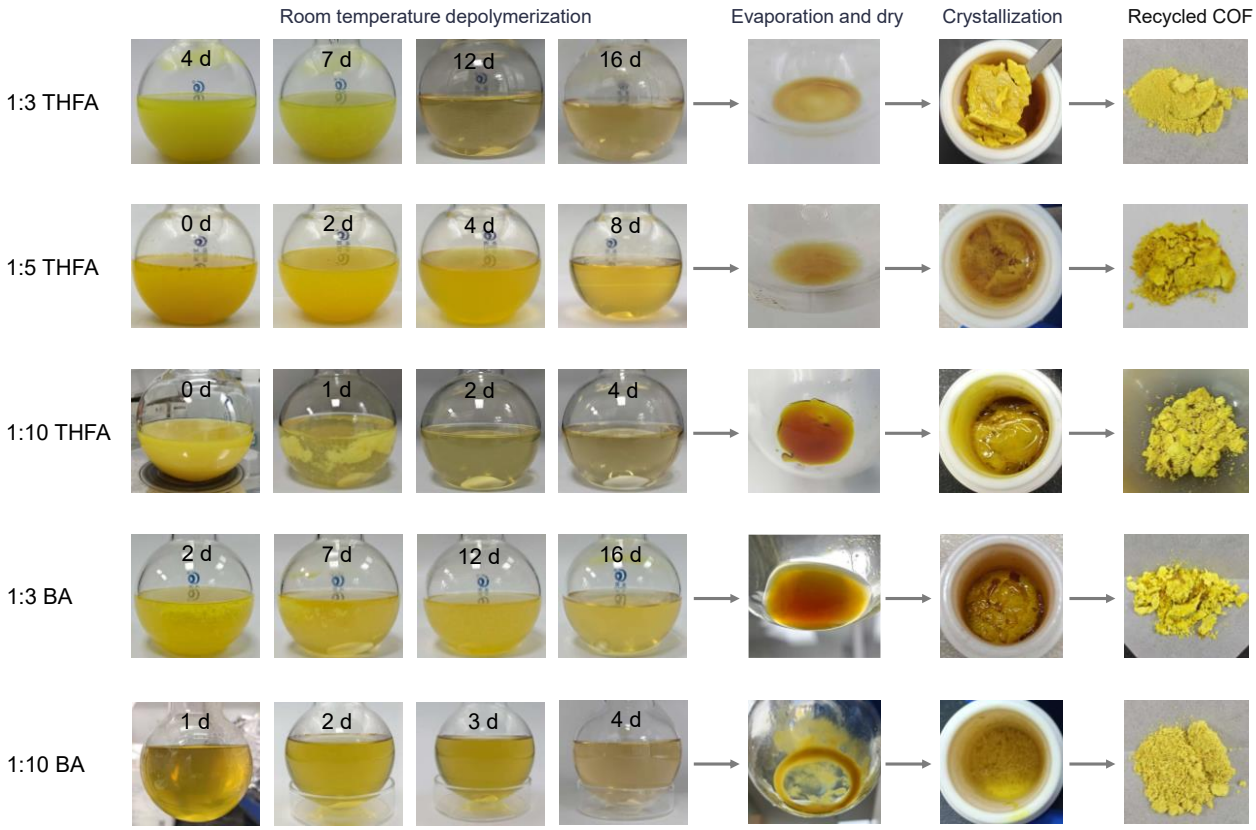


Fig. S12 Photographs of depolymerization mixtures and recycled TAPB-TPA COFs. TAPB-TPA COFs were recycled through the solvothermal method (Route II, see also Fig. 3b). Note that in order to compare different depolymerization conditions, some photographs for 1:10 THFA are the same as Fig. 3b.

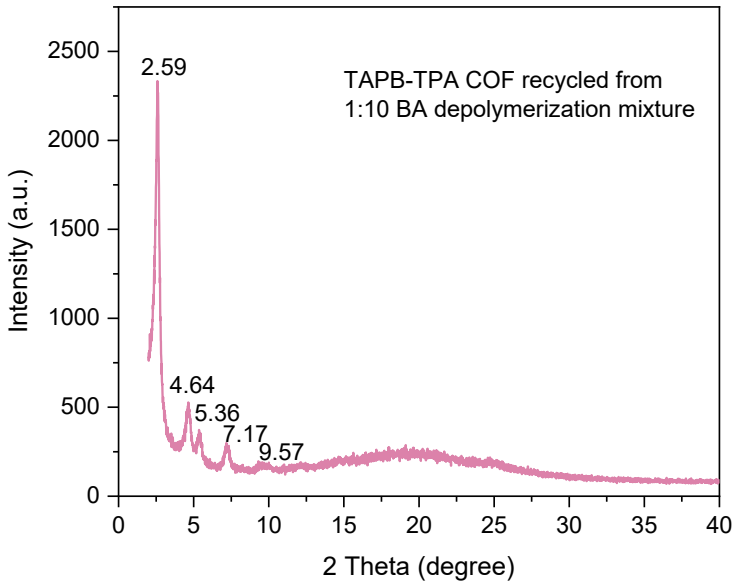


Fig. S13 PXRD pattern of the TAPB-TPA COF recycled from 1:10 BA depolymerization mixture and using the solvothermal recycling method (1:10 BA-STR, Route II, see also Fig. 3b).

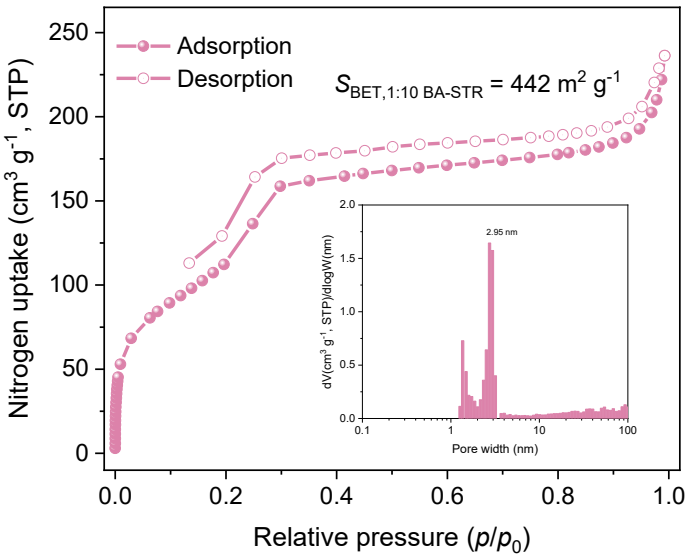


Fig. S14 Nitrogen adsorption/desorption isotherm and pore width of the TAPB-TPA COF recycled from 1:10 BA depolymerization mixture and using solvothermal recycling method (1:10 BA-STR, Route II, see also Fig. 3b).

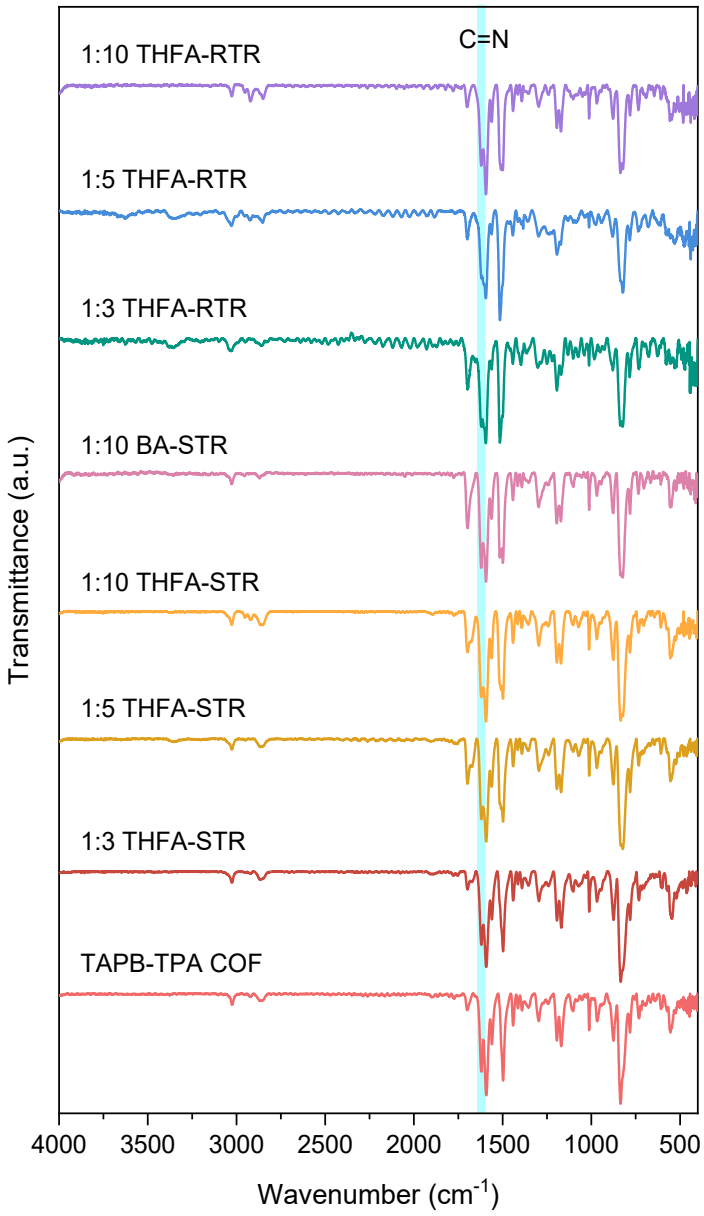


Fig. S15 FI-IR spectra of the pristine and recovered TAPB-TPA COFs. The peak at 1620 cm^{-1} was assigned to the C=N stretching vibration. Notes of 1:3 THFA-RTR, 1:5 THFA-RTR, and 1:10 THFA-RTR represented that corresponding depolymerization mixtures were treated by adding aqueous acetic acid for the room-temperature recycling of TAPB-TPA COF (Route I, see also Fig. 3a). Notes of 1:3 THFA-STR, 1:5 THFA-STR, 1:10 THFA-STR, and 1:10 BA-STR represented that TAPB-TPA COFs were recycled from corresponding depolymerization mixtures by the solvothermal method (Route II, see also Fig. 3b).

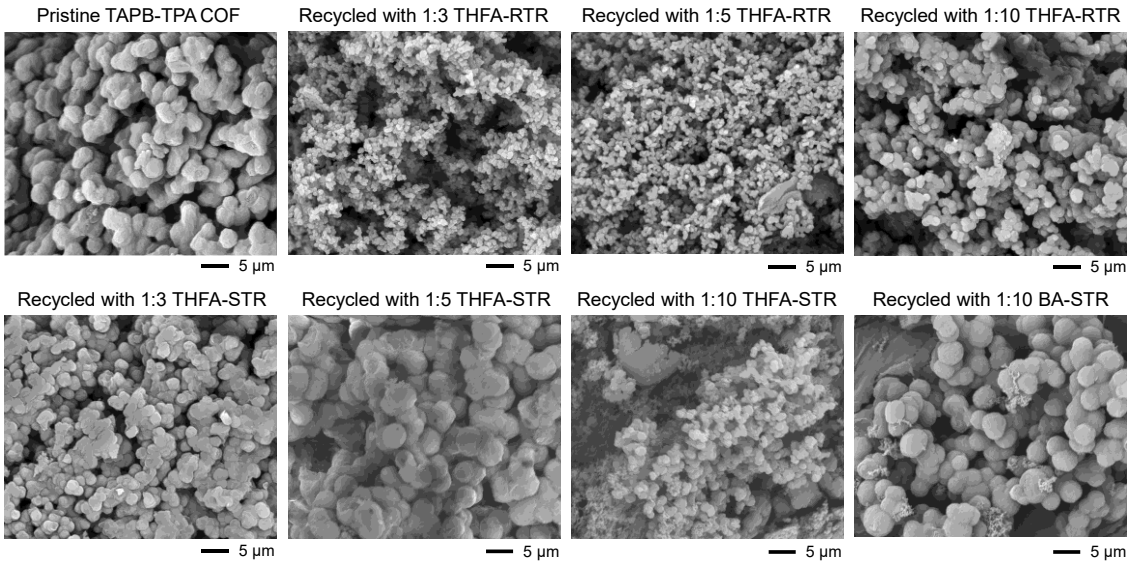


Fig. S16 SEM images of the pristine and recycled TAPB-TPA COFs. Notes of 1:3 THFA-RTR, 1:5 THFA-RTR, and 1:10 THFA-RTR represented that corresponding depolymerization mixtures were treated by adding aqueous acetic acid for the room-temperature recycling of TAPB-TPA COF (Route I, see also Fig. 3a). Notes of 1:3 THFA-STR, 1:5 THFA-STR, 1:10 THFA-STR, and 1:10 BA-STR represented that TAPB-TPA COFs were recycled from corresponding depolymerization mixtures by the solvothermal method (Route II, see also Fig. 3b).

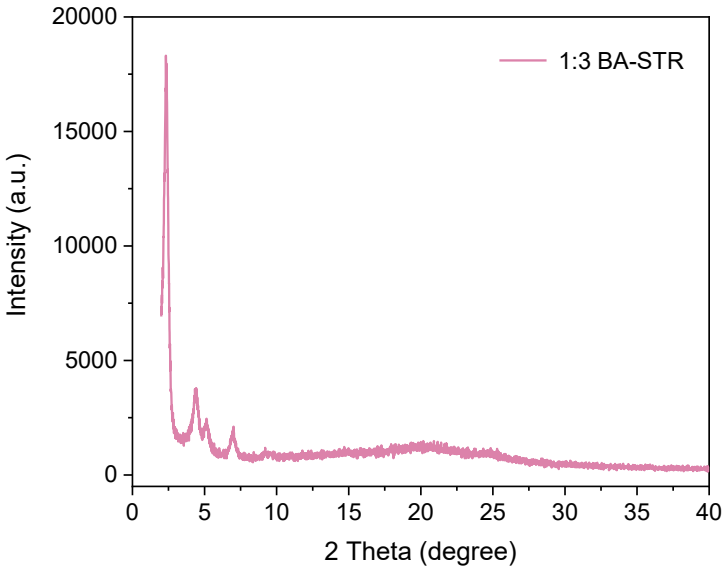


Fig. S17 PXRD pattern of the TAPB-TPA COF recycled from 1:3 BA depolymerization mixture and using the solvothermal recycling method (1:3 BA-STR, Route II, see also Fig. 3b).

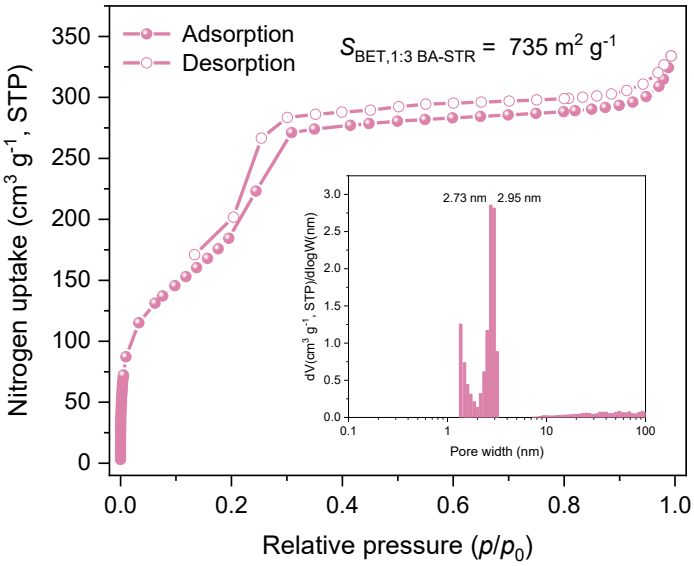


Fig. S18 Nitrogen adsorption/desorption isotherm and pore width of the TAPB-TPA COF recycled from 1:3 BA depolymerization mixture and using solvothermal recycling method (1:3 BA-STR, Route II, see also Fig. 3b).

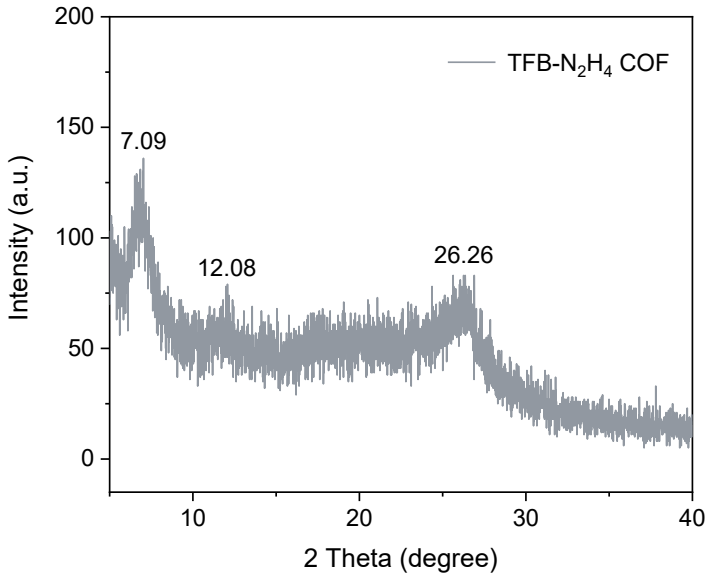


Fig. S19 PXRD pattern of TFB-N_2H_4 COF.

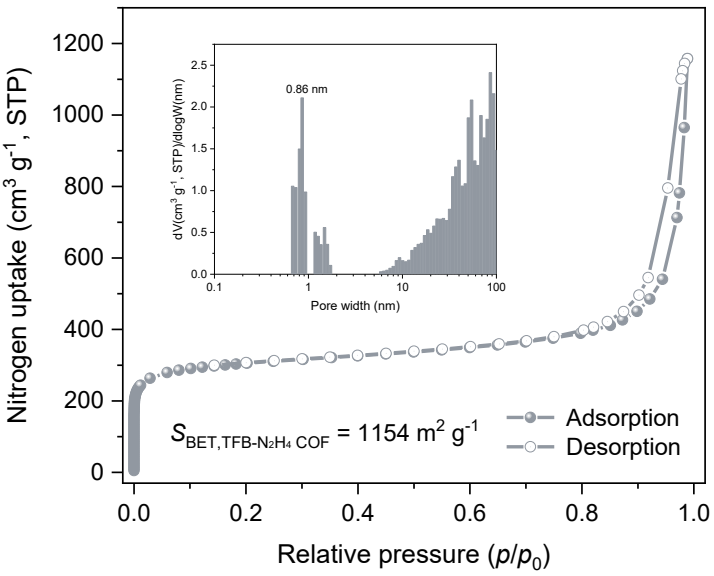


Fig. S20 Nitrogen adsorption/desorption isotherm and pore width of TFB-N_2H_4 COF.

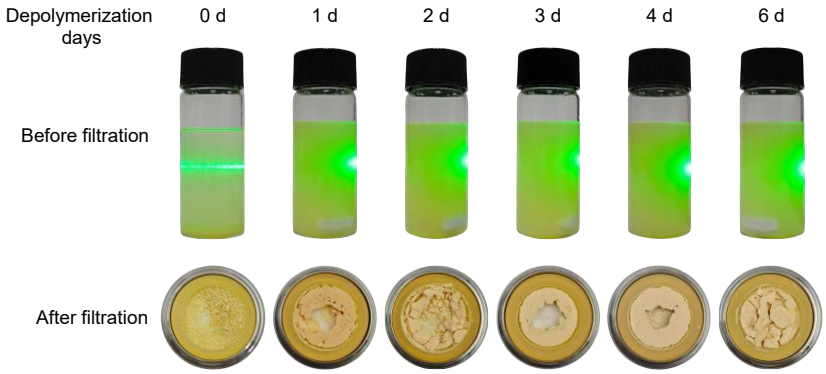


Fig. S21 Depolymerization of TFB-N_2H_4 COF and photographs of 1:10 THFA depolymerization mixtures and residual solids collected using 0.1 μm filter.

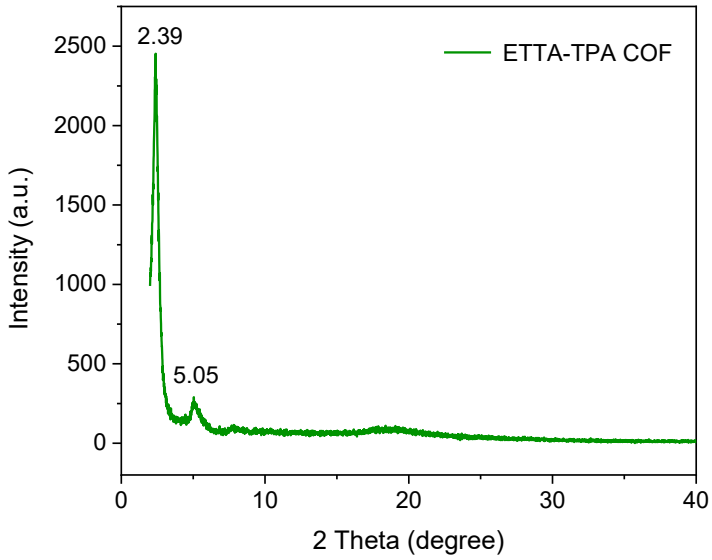


Fig. S22 PXRD pattern of ETTA-TPA COF.

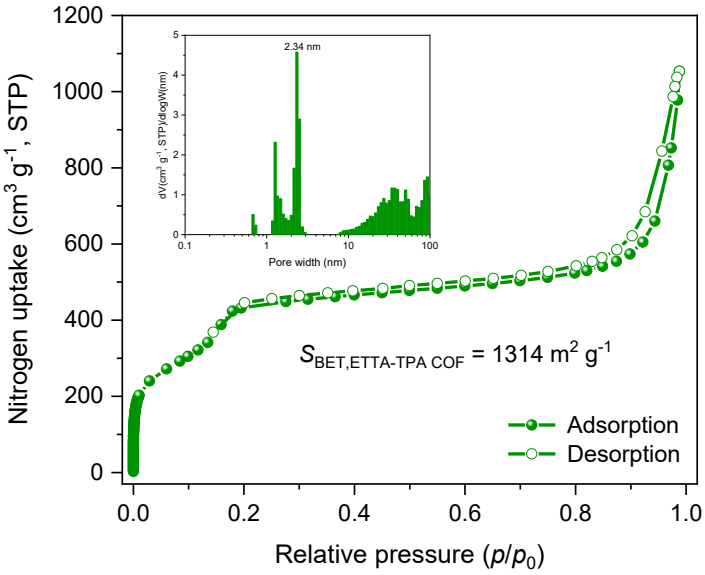


Fig. S23 Nitrogen adsorption/desorption isotherm and pore width of ETTA-TPA COF.

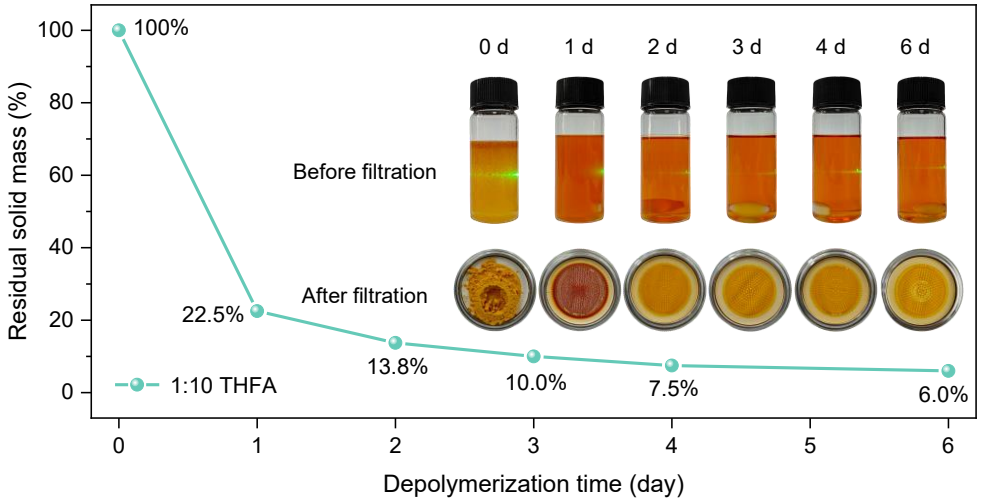


Fig. S24 Depolymerization of ETTA-TPA COF and time-dependent residual solid mass under 1:10 THFA condition. Insert: photographs of 1:10 THFA depolymerization mixtures and residual solids collected using 0.1 μm filter.

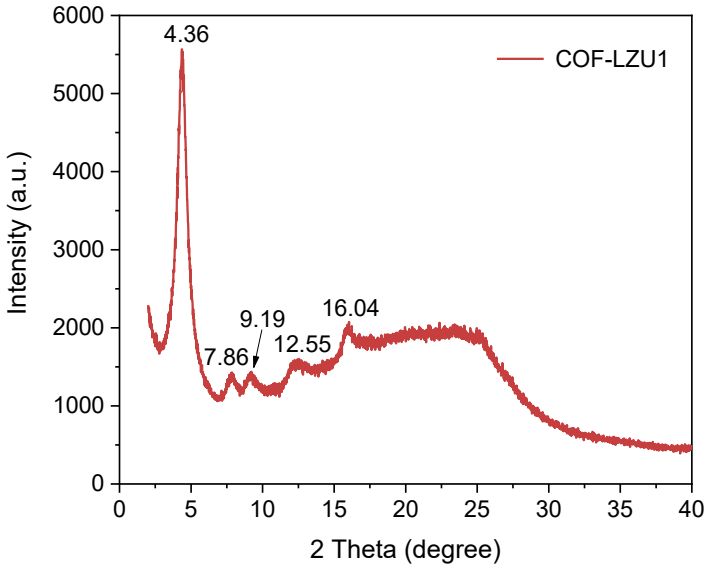


Fig. S25 PXRD pattern of COF-LZU1.

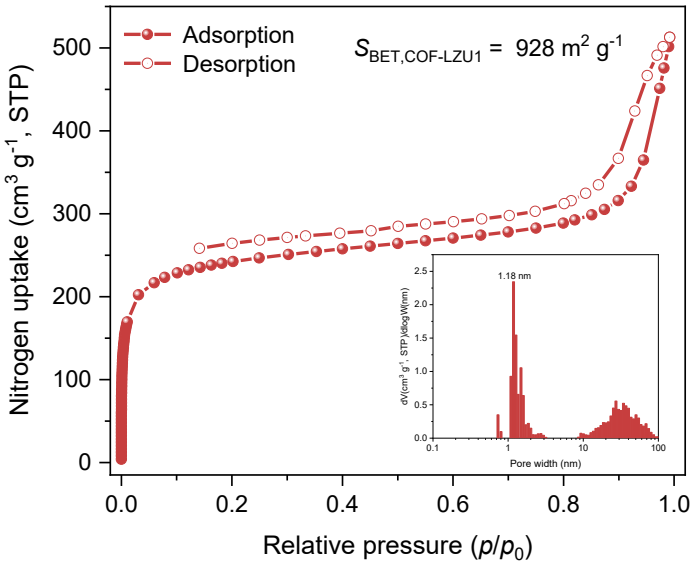


Fig. S26 Nitrogen adsorption/desorption isotherm and pore width of COF-LZU1.

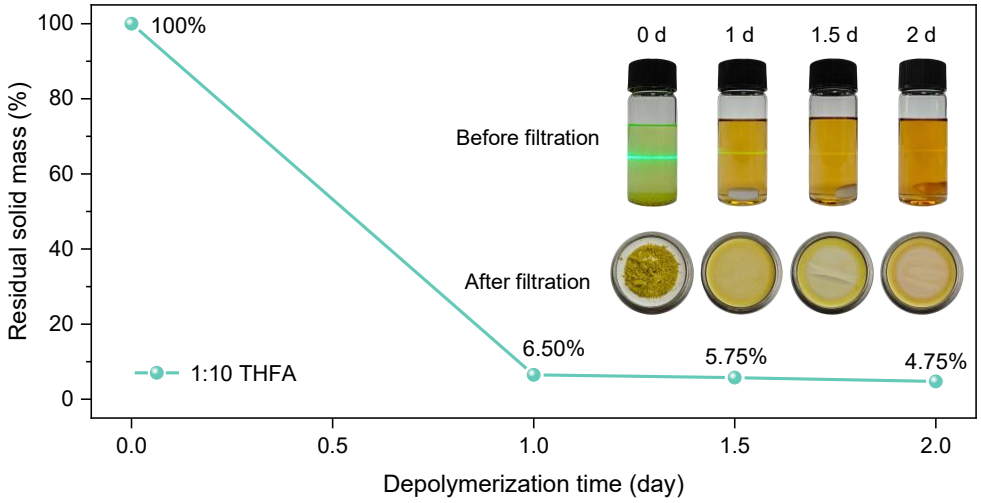


Fig. S27 Depolymerization of COF-LZU1 and time-dependent residual solid mass under 1:10 THFA condition. Insert: photographs of 1:10 THFA depolymerization mixtures and residual solids collected using 0.1 μm filter.

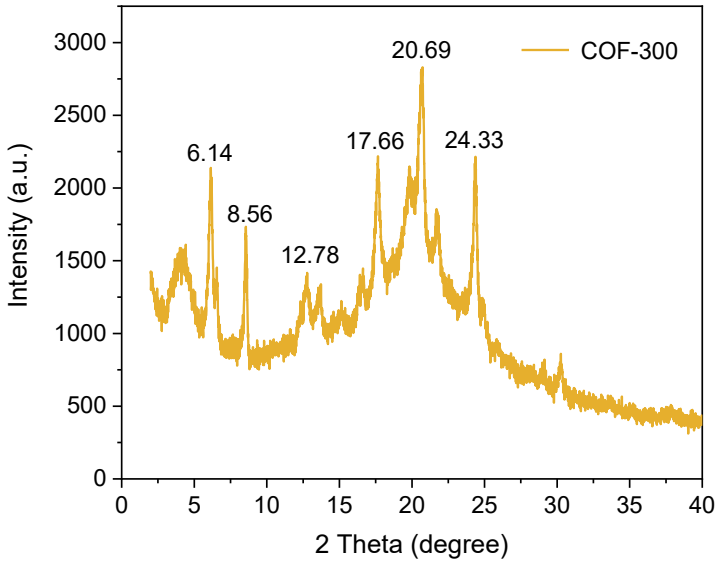


Fig. S28 PXRD pattern of COF-300.

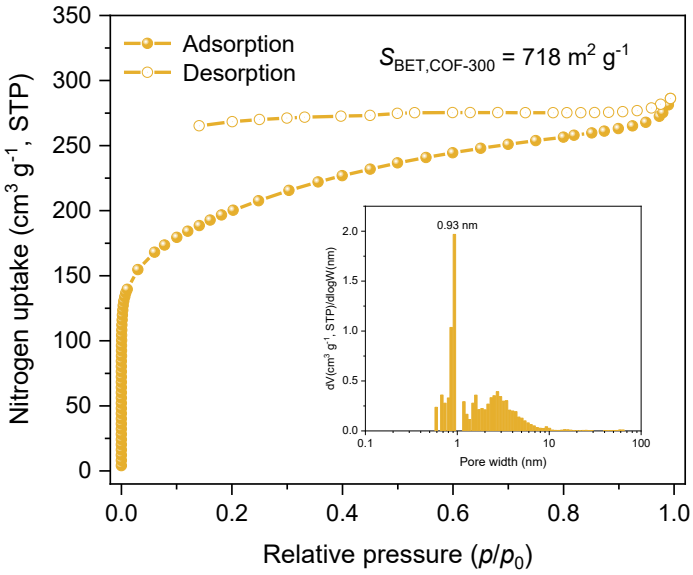


Fig. S29 Nitrogen adsorption/desorption isotherm and pore width of COF-300.

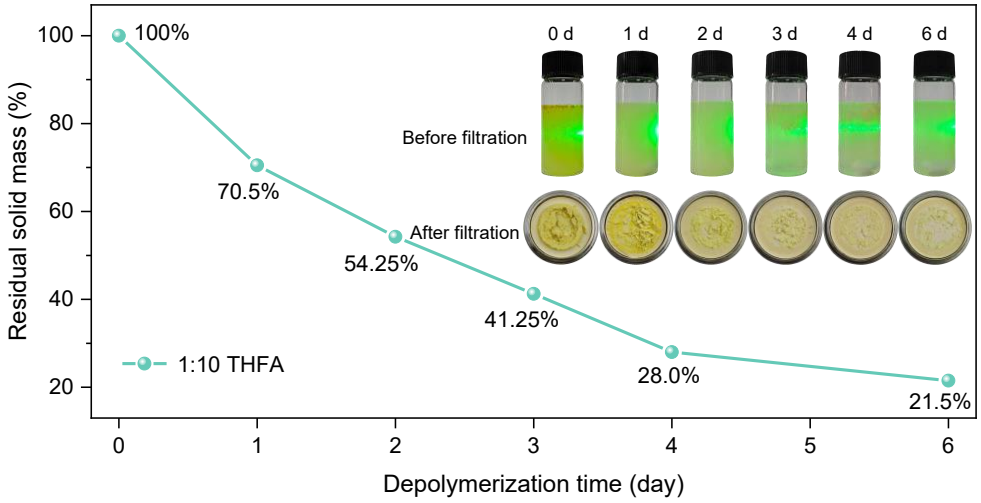


Fig. S30 Depolymerization of COF-300 and time-dependent residual solid mass under 1:10 THFA condition. Insert: photographs of 1:10 THFA depolymerization mixtures and residual solids collected using 0.1 μm filter.

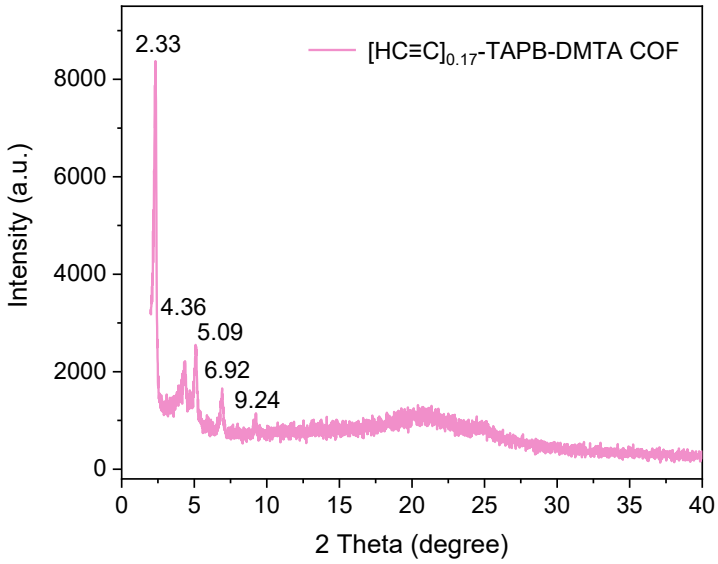


Fig. S31 PXRD pattern of $[HC{\equiv}C]_{0.17}$-TAPB-DMTA COF.

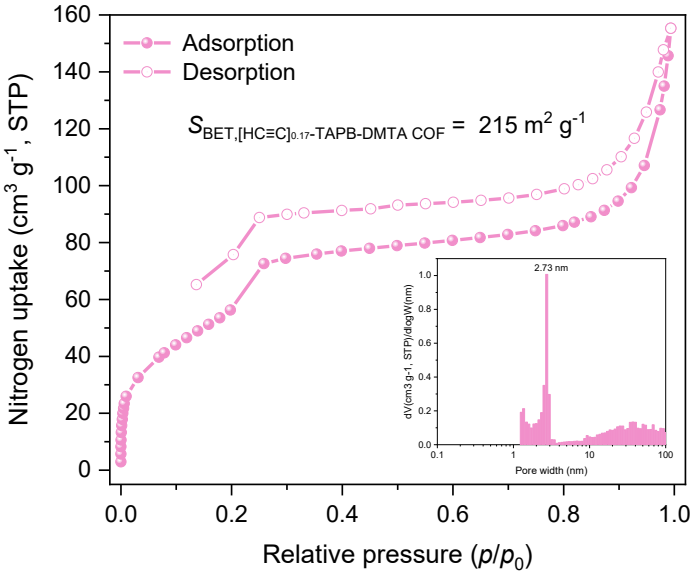


Fig. S32 Nitrogen adsorption/desorption isotherm and pore width of $[HC\equiv C]_{0.17}$-TAPB-DMTA COF.

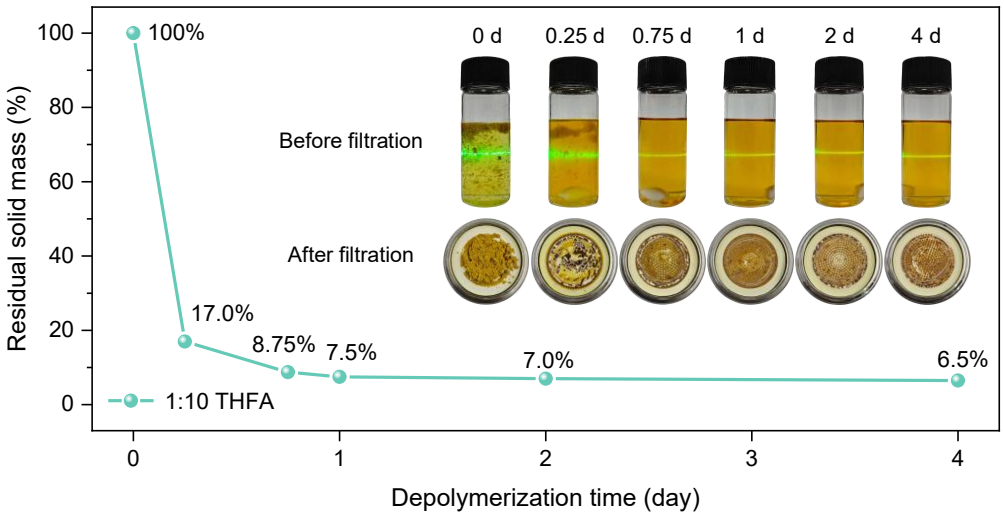


Fig. S33 Depolymerization of $[HC{\equiv}C]_{0.17}$-TAPB-DMTA COF and time-dependent residual solid mass under 1:10 THFA condition. Insert: photographs of 1:10 THFA depolymerization mixtures and residual solids collected using 0.1 μm filter.

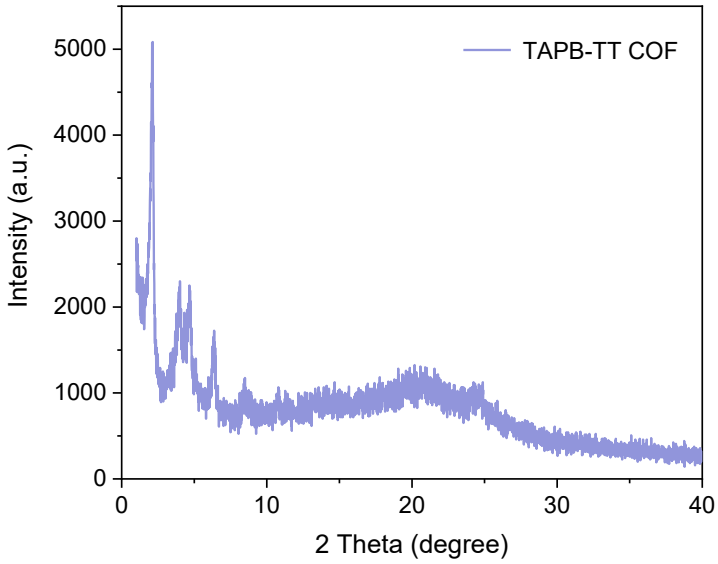


Fig. S34 PXRD pattern of TAPB-TT COF.

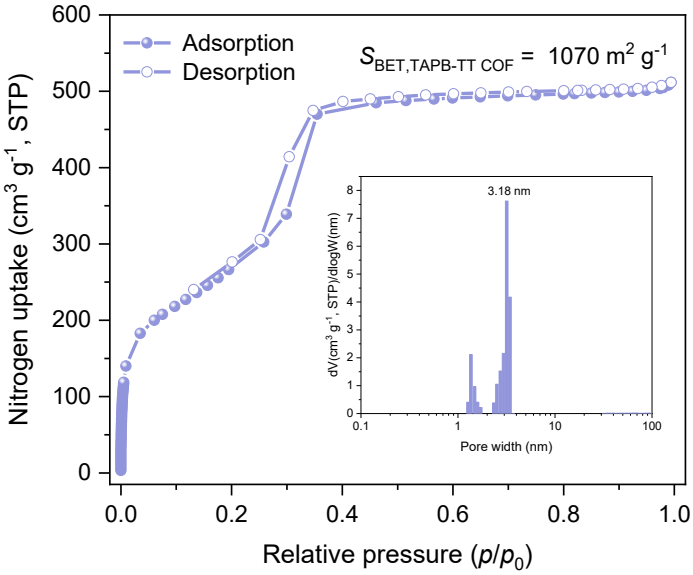


Fig. S35 Nitrogen adsorption/desorption isotherm and pore width of TAPB-TT COF.

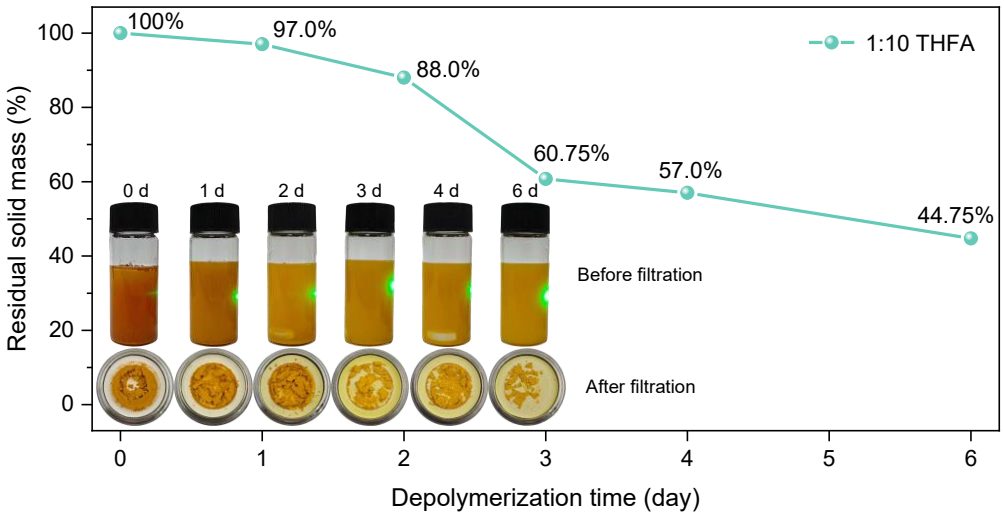


Fig. S36 Depolymerization of TAPB-TT COF and time-dependent residual solid mass under 1:10 THFA condition. Insert: photographs of 1:10 THFA depolymerization mixtures and residual solids collected using 0.1 μm filter.

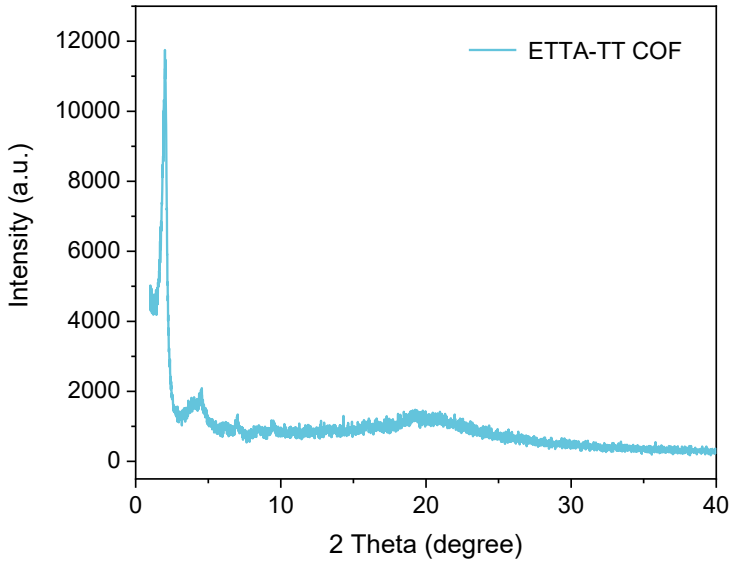


Fig. S37 PXRD pattern of ETTA-TT COF.

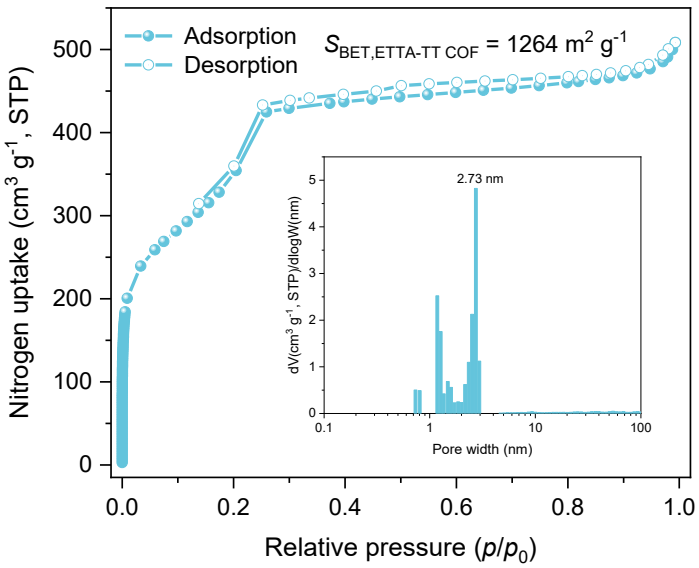


Fig. S38 Nitrogen adsorption/desorption isotherm and pore width of ETTA-TT COF.

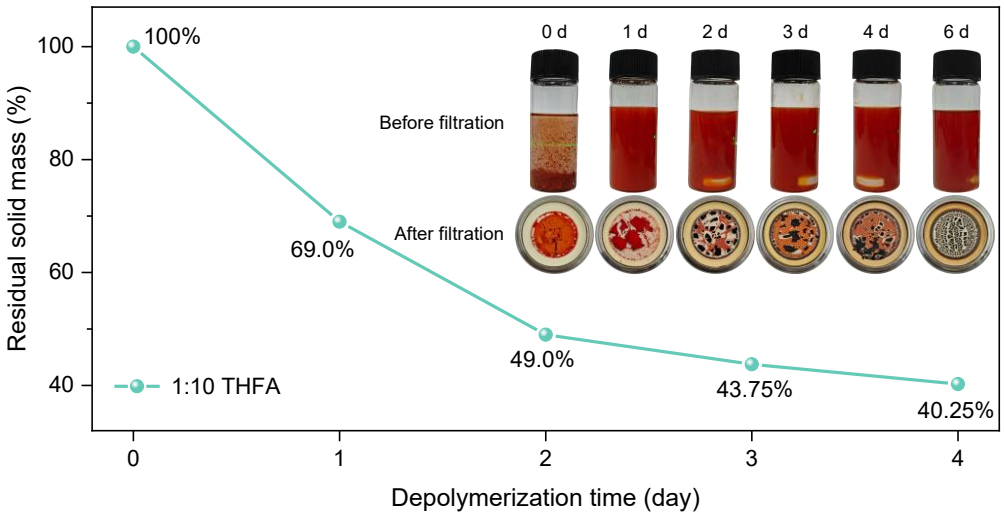


Fig. S39 Depolymerization of ETTA-TT COF and time-dependent residual solid mass under 1:10 THFA condition. Insert: photographs of 1:10 THFA depolymerization mixtures and residual solids collected using 0.1 μm filter.

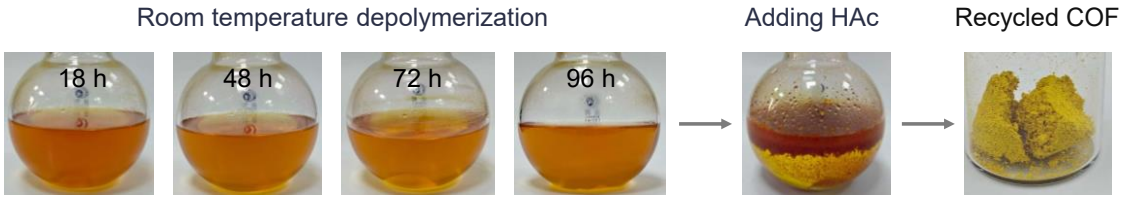


Fig. S40 Photographs of 1:10 THFA depolymerization mixture and recycled $[HC{\equiv}C]_{0.17}$-TAPB-DMTA COF using the room-temperature recycling method (1:10 THFA-RTR). Specifically, $[HC{\equiv}C]_{0.17}$-TAPB-DMTA COF (200 mg, containing 1 mmol of imine bonds) was suspended in dichloromethane (100 mL) in a 150 mL round-bottom flask equipped with a stir bar. Then THFA (1032 μL, 10 mmol) was added. The mixture was stirred at room temperature for 4 days. After complete depolymerization, aqueous acetic acid (18 mL, 6 mol L^{-1}) was directly added to depolymerization mixtures without any purification. The mixture was stirred at room temperature and ambient pressure for 24 h, generating a solid. After washing with ethanol (4 ×10 mL) and *n*-hexane (4 ×10 mL), and drying at 60 °C under vacuum, the crystalline $[HC{\equiv}C]_{0.17}$-TAPB-DMTA COF was regenerated.

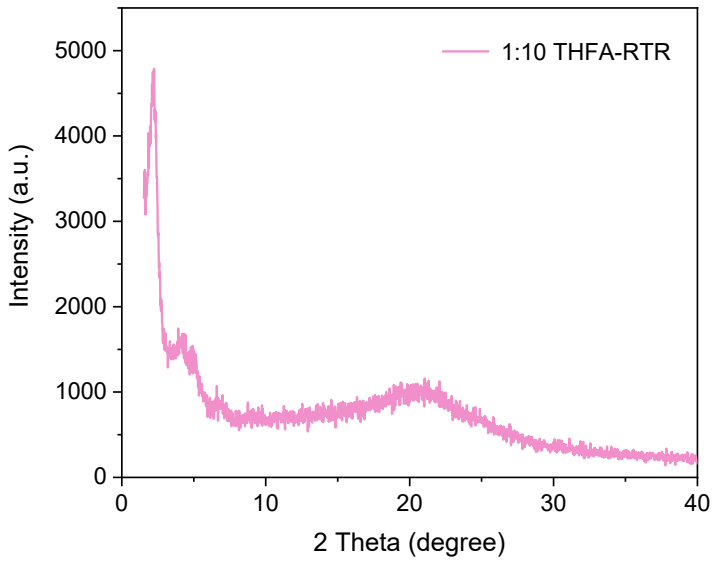


Fig. S41 PXRD pattern of the $[HC{\equiv}C]_{0.17}$-TAPB-DMTA COF recycled from 1:10 THFA depolymerization mixture and using the room-temperature recycling method (1:10 THFA-RTR).

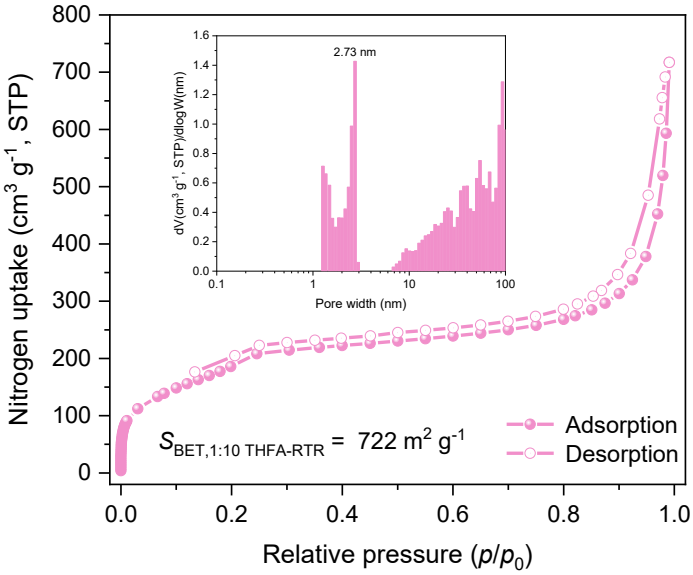


Fig. S42 Nitrogen adsorption/desorption isotherm and pore width of the $[HC{\equiv}C]_{0.17}$-TAPB-DMTA COF recycled from 1:10 THFA depolymerization mixture and using the room-temperature recycling method (1:10 THFA-RTR).

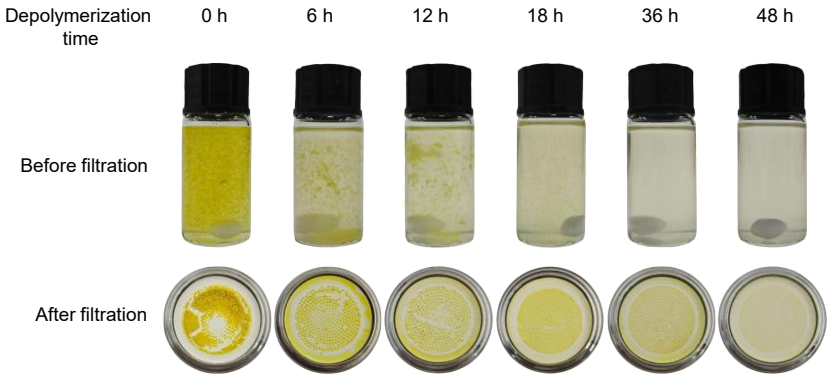


Fig. S43 Photographs of 1:3 THFA depolymerization mixtures with 4% $Sc(OTf)_3$ catalyzed and residual solids collected using 0.1 μm filter and thoroughly washed using water in order to remove uncombined $Sc(OTf)_3$.

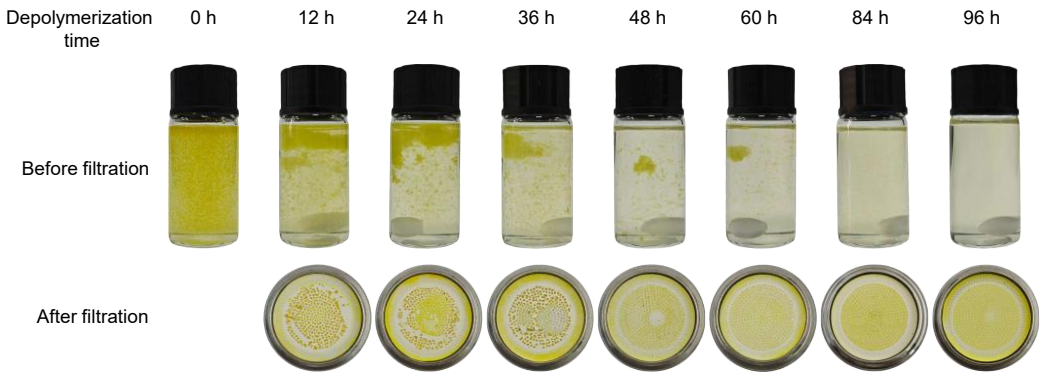


Fig. S44 Photographs of 1:3 THFA depolymerization mixtures with 0.5% $Sc(OTf)_3$ catalyzed and residual solids collected using 0.1 μm filter and thoroughly washed using water in order to remove uncombined $Sc(OTf)_3$.

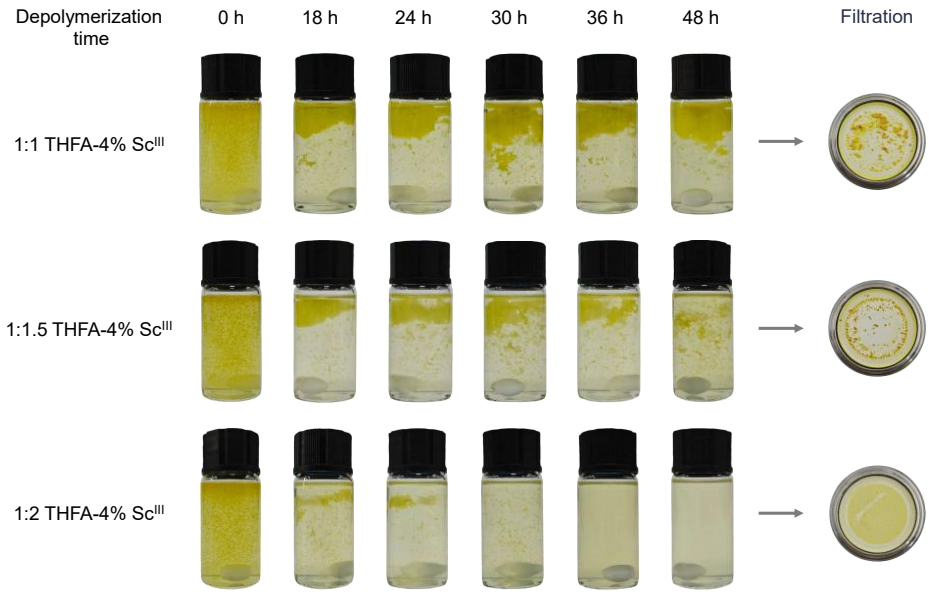


Fig. S45 Photographs of depolymerization mixtures. Molar ratios of imine bonds to THFA were 1:1, 1:1.5 and 1:2 with 4% $Sc(OTf)_3$, respectively, After depolymerization for 48 hours, the residual solids were collected using 0.1 μm filter and thoroughly washed using water in order to remove uncombined $Sc(OTf)_3$.

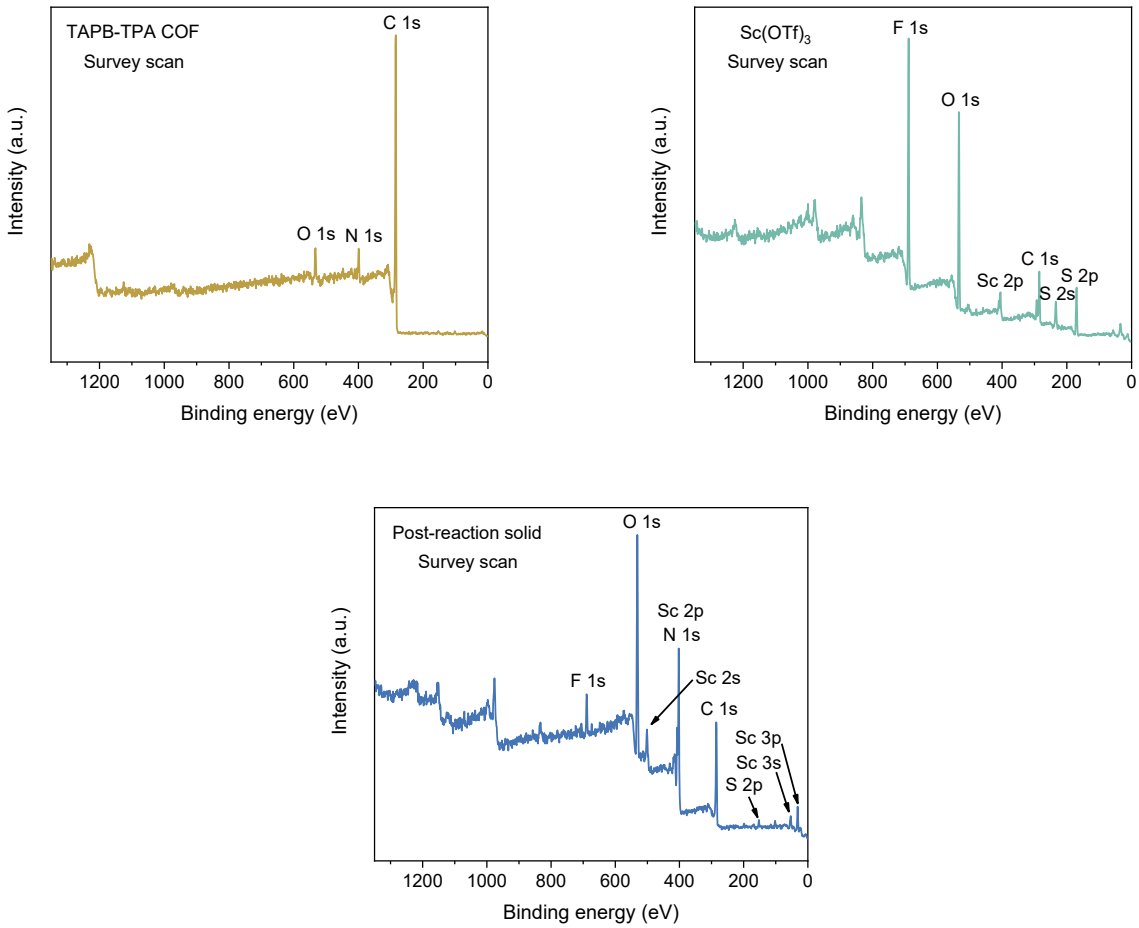


Fig. S46 XPS survey spectra of TAPB-TPA COF, $Sc(OTf)_3$ and post-reaction solid.

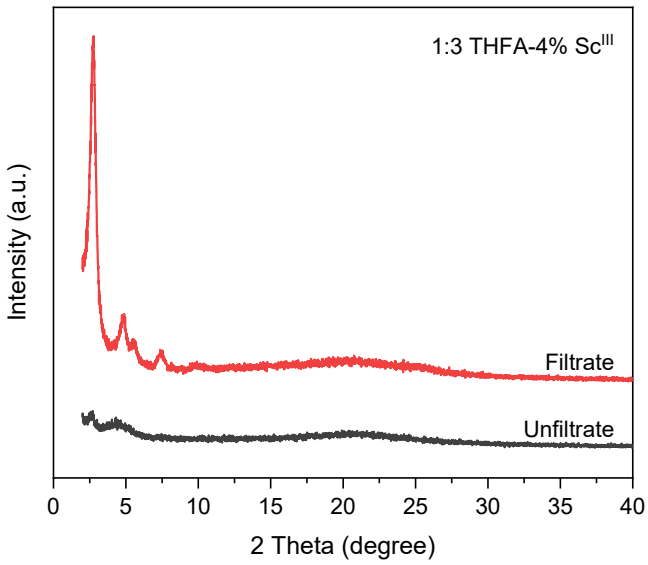


Fig. S47 PXRD patterns of TAPB-TPA COFs recycled via the RTR method from depolymerization mixtures under the condition of 1:3 THFA with 4% $Sc(OTf)_3$ catalyzed with and without a 0.1 μm filtration step prior to RTR recycling.

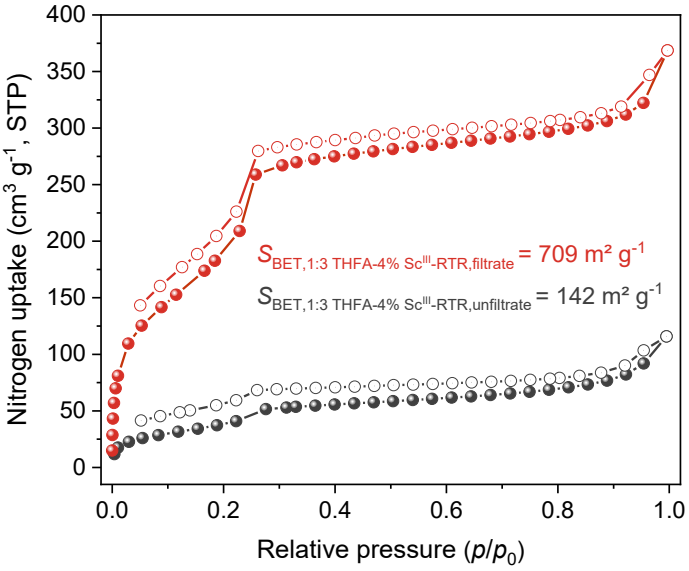


Fig. S48 Nitrogen adsorption/desorption isotherm of TAPB-TPA COFs recycled via the RTR method from depolymerization mixtures under the condition of 1:3 THFA with 4% $Sc(OTf)_3$ catalyzed with and without a 0.1 μm filtration step prior to RTR recycling.

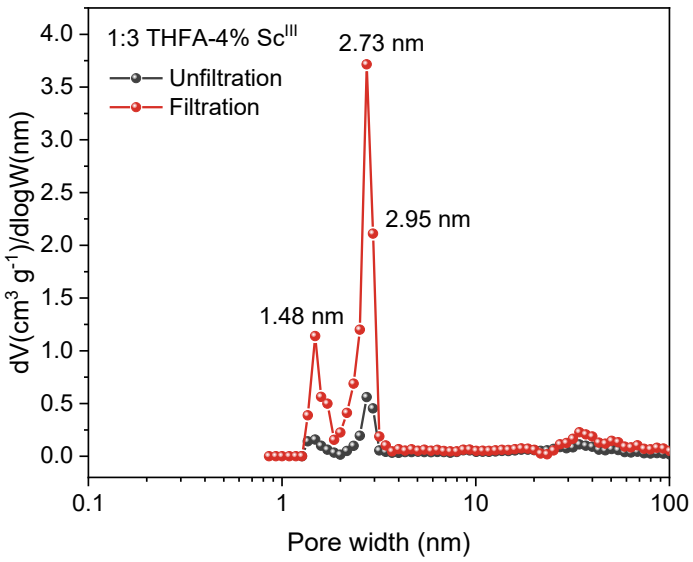


Fig. S49 Pore width of TAPB-TPA COFs recycled via the RTR method from depolymerization mixtures under the condition of 1:3 THFA with 4% $Sc(OTf)_3$ catalyzed with and without a 0.1 μm filtration step prior to RTR recycling.

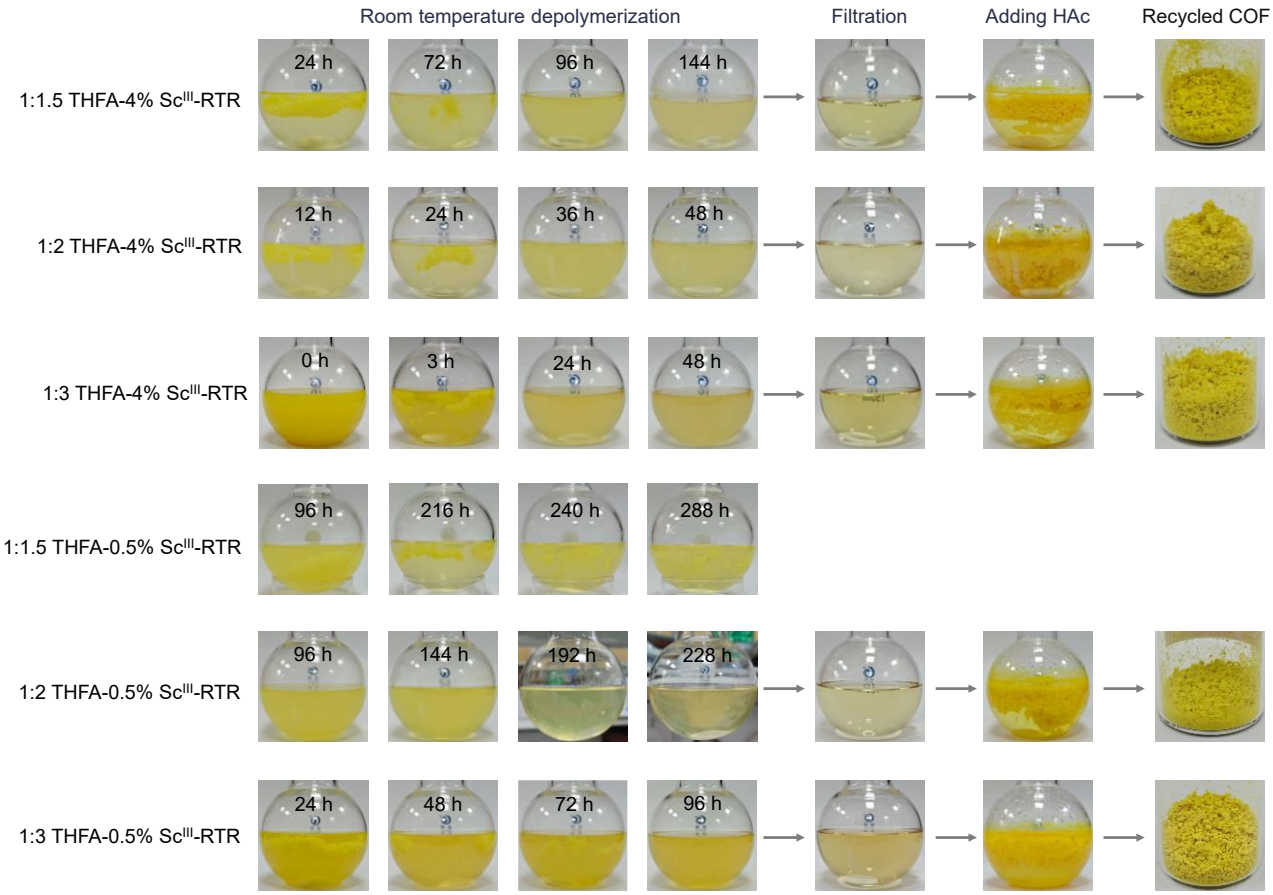


Fig. S50 Photographs of depolymerization mixtures with $Sc(OTf)_3$ catalyzed and recycled TAPB-TPA COFs. TAPB-TPA COFs were recycled through the room-temperature recycling method (Route I, RTR). Note that a filtration step was introduced before the RTR recycling. The depolymerization of TAPB-TPA COF was not completely under the condition of 1:1.5 THFA-0.5% Sc^{III} after 288 hours of reaction, as evidenced by the persistence of numerous visible particles. As complete depolymerization would require a longer time, this condition was excluded from further consideration.

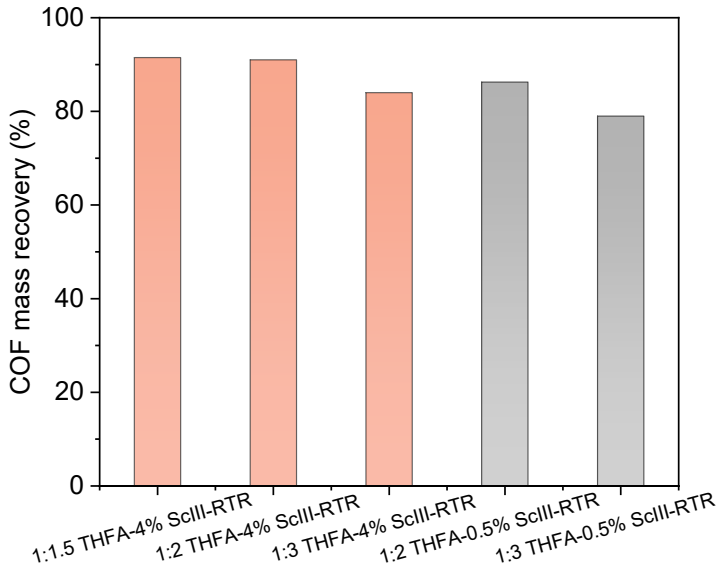


Fig. S51 COF mass recovery of recycled TAPB-TPA COFs.

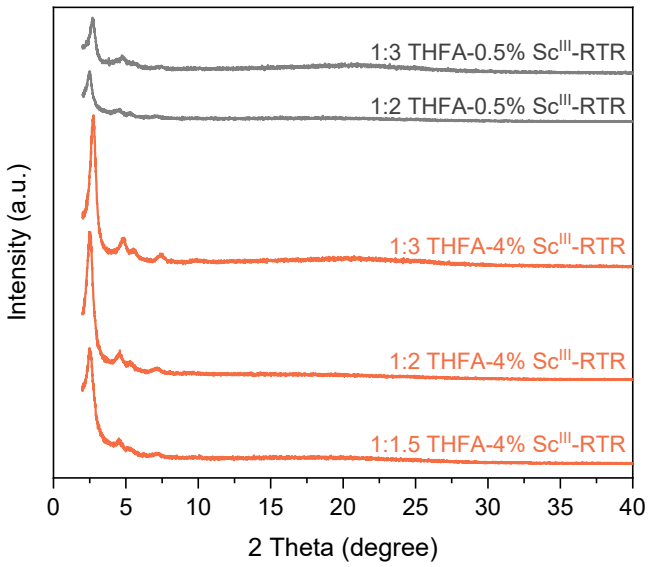


Fig. S52 PXRD patterns of recycled TAPB-TPA COFs.

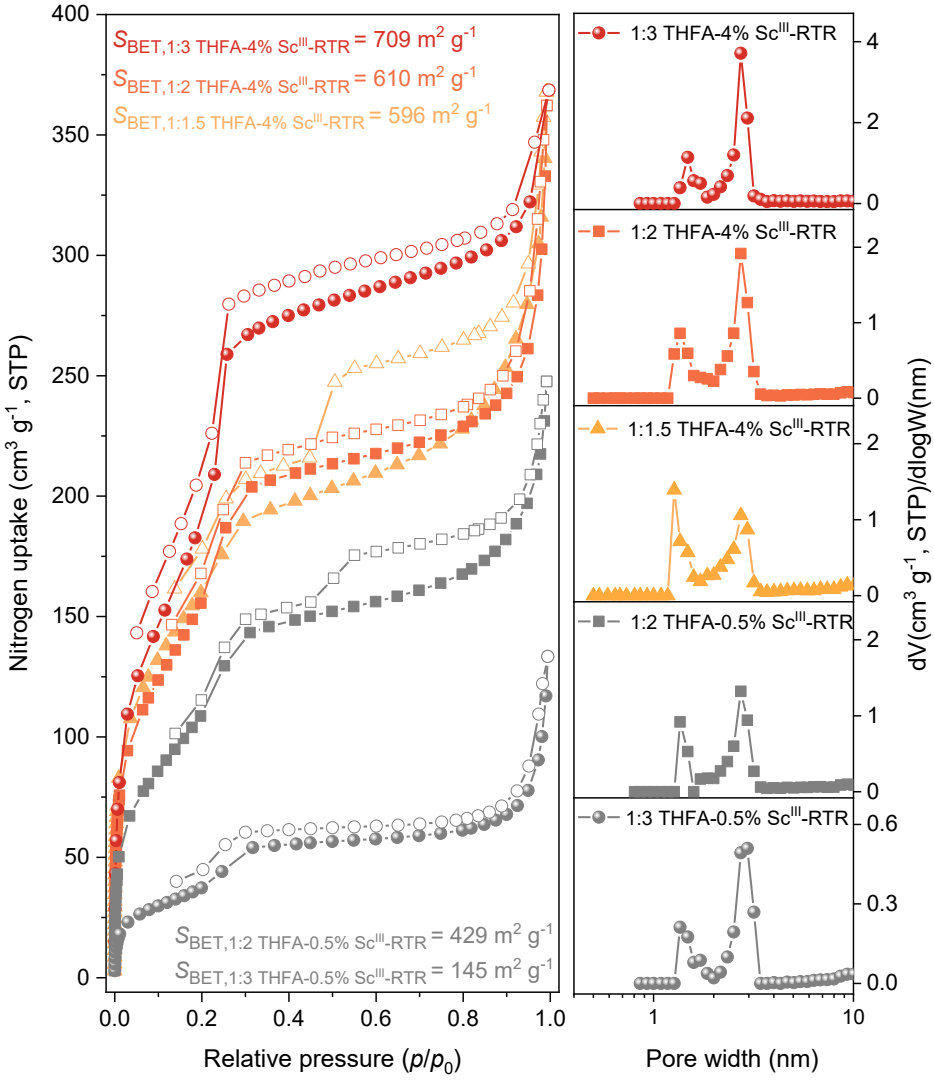


Fig. S53 Nitrogen adsorption/desorption isotherms and pore width distributions of recycled TAPB-TPA COFs.

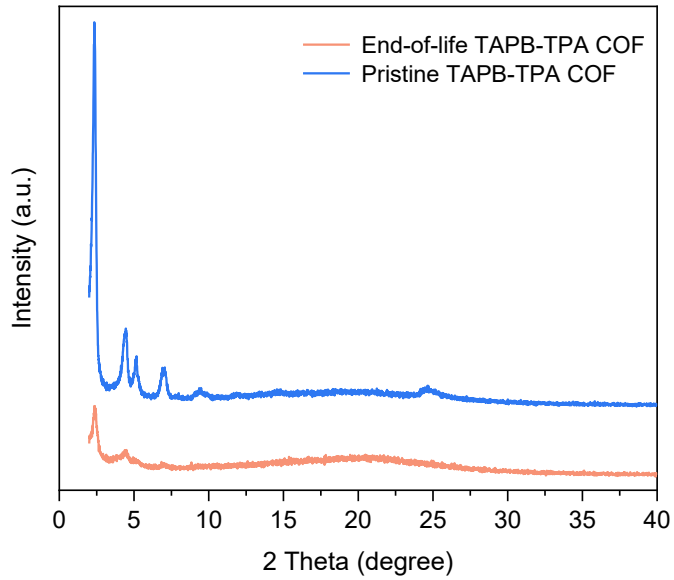


Fig. S54 Comparison of PXRD patterns of the end-of-life and the pristine TAPB-TPA COF.

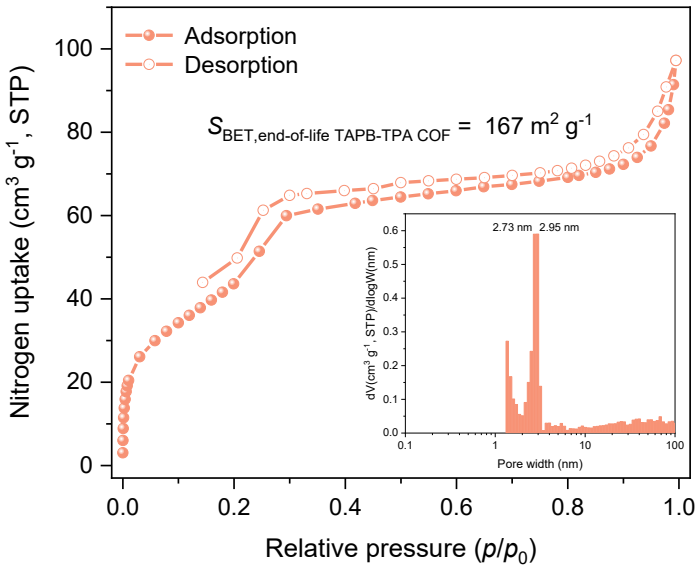


Fig. S55 Nitrogen adsorption/desorption isotherms and pore width distributions of end-of-life TAPB-TPA COF.

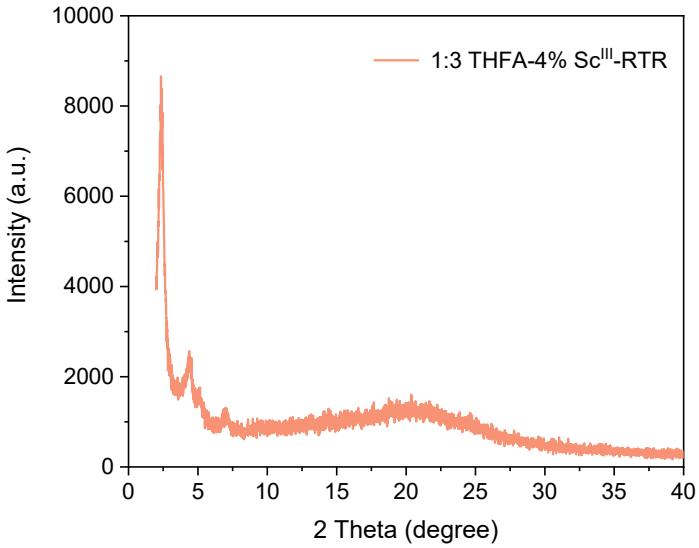


Fig. S56 PXRD pattern of TAPB-TPA COF recycled via the RTR method from the end-of-life TAPB-TPA COF depolymerization mixtures under the condition of 1:3 THFA with 4% $Sc(OTf)_3$ catalyzed.

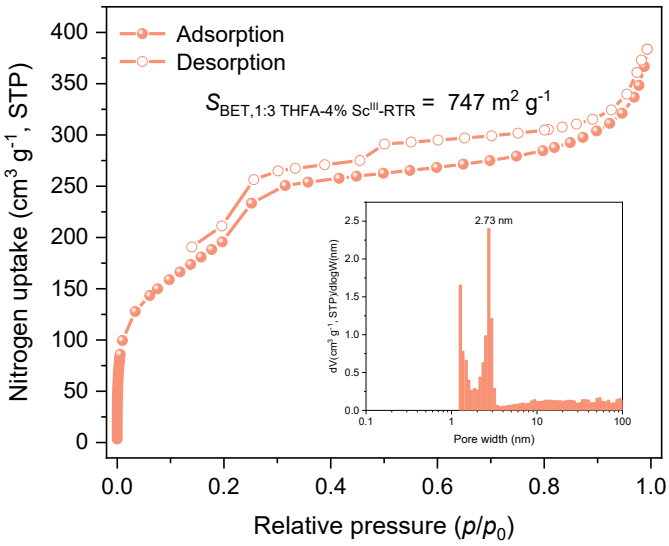


Fig. S57 Nitrogen adsorption/desorption isotherms and pore width distributions of TAPB-TPA COF recycled via the RTR method from the end-of-life TAPB-TPA COF depolymerization mixtures under the condition of 1:3 THFA with 4% $Sc(OTf)_3$ catalyzed.

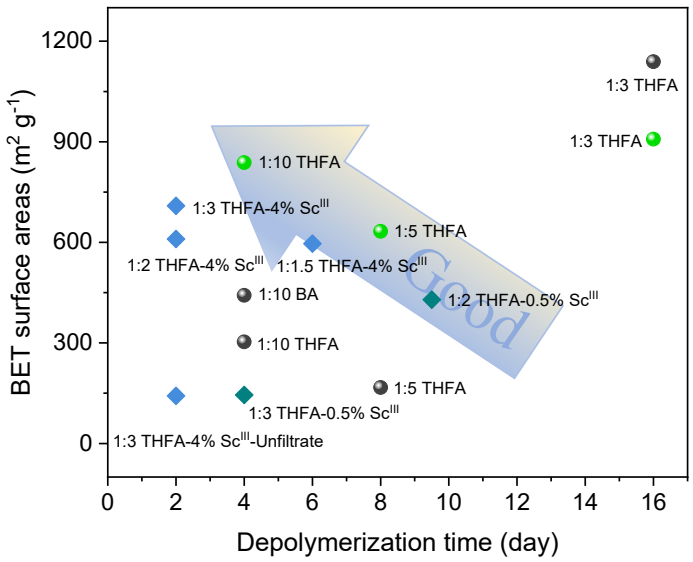


Fig. S58 BET surface areas versus depolymerization time of recycled TAPB-TPA COFs. Black symbols, using solvothermal recycling method; Other symbols, using room-temperature recycling method.

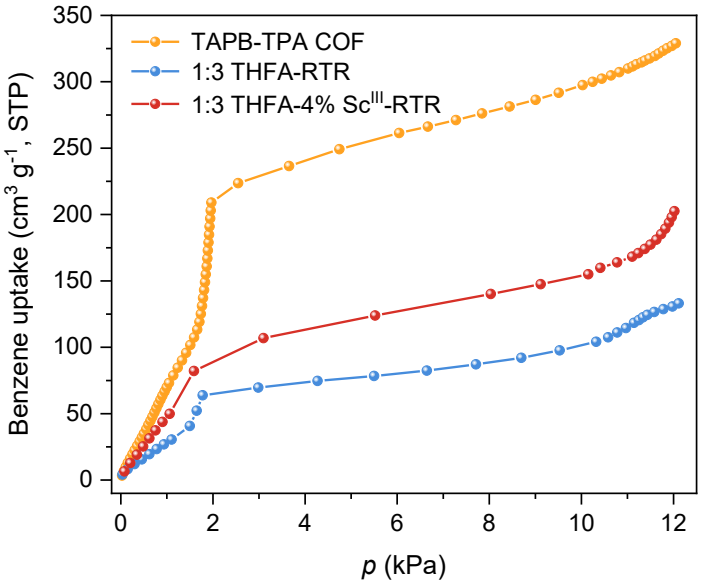


Fig. S59 Benzene vapor adsorption isotherms at 298 K of recovered and pristine TAPB-TPA COFs.

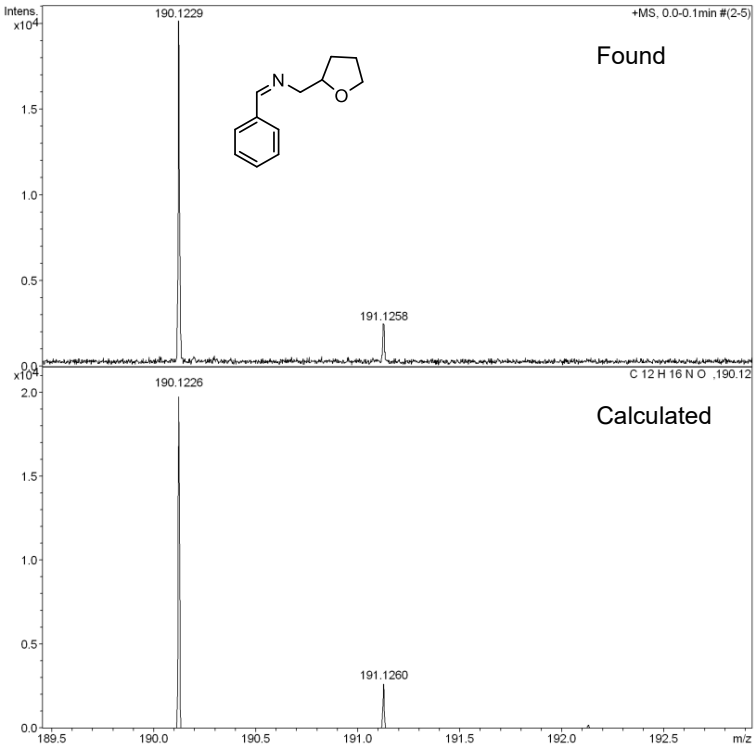


Fig. S60 MS spectrum (raw data) of model Reaction I mixture (see also Fig. 1b and 1c).

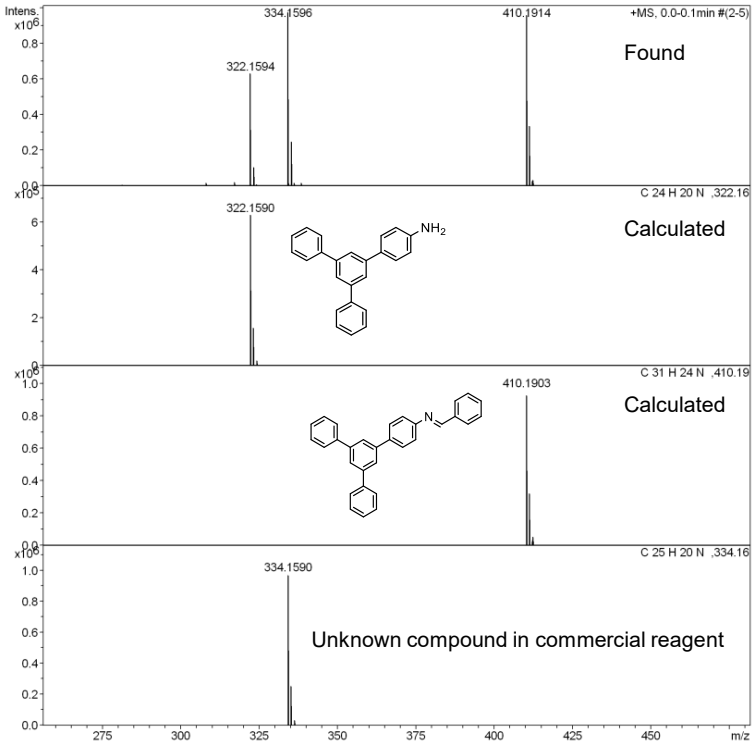


Fig. S61 MS spectrum (raw data) of model Reaction II mixture (see also Fig. 1b and 1c).

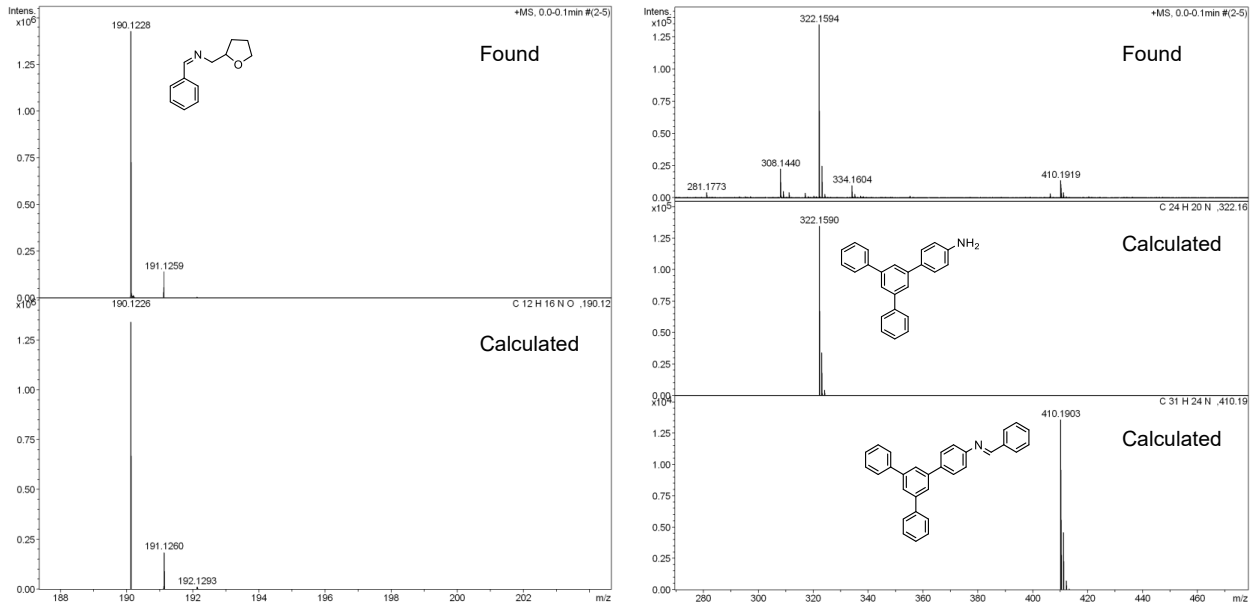


Fig. S62 MS spectrum (raw data) of model Reaction III mixture (see also Fig. 1b and 1c).

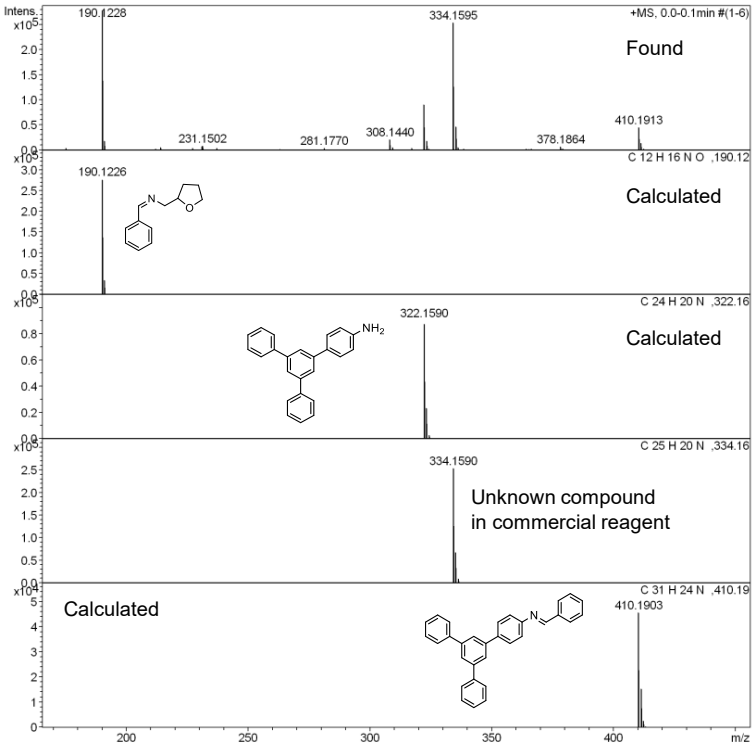


Fig. S63 MS spectrum (raw data) of model Reaction IV mixture (see also Fig. 1b and 1c).

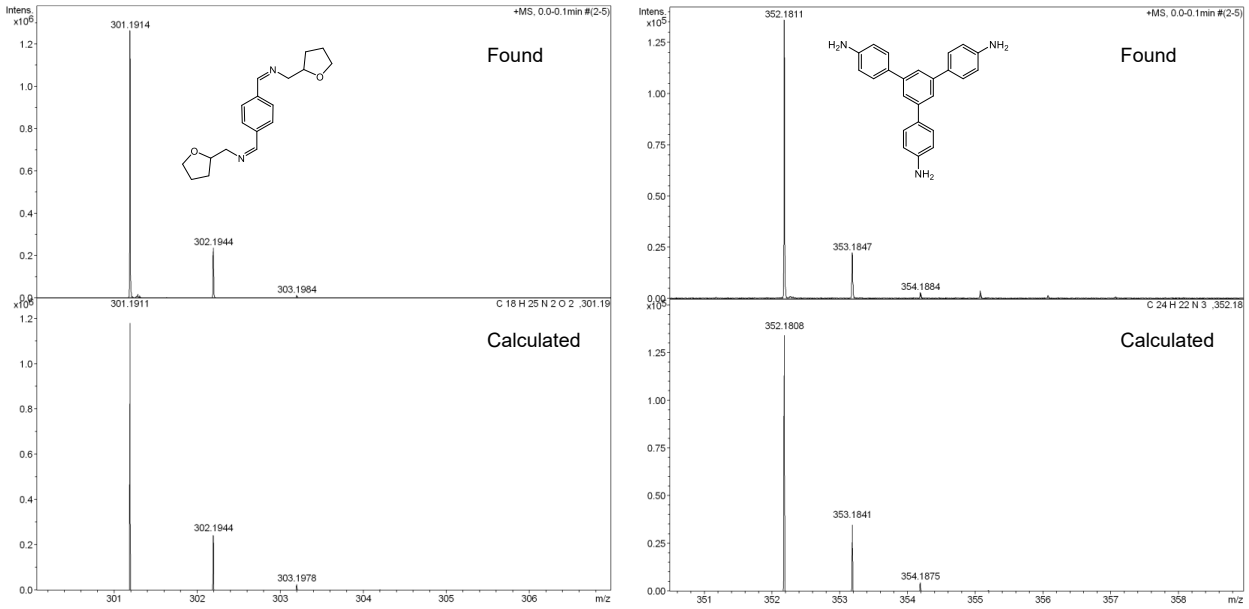


Fig. S64 MS spectrum (raw data) of 1:10 THFA depolymerization mixture (see also Fig. 2c).

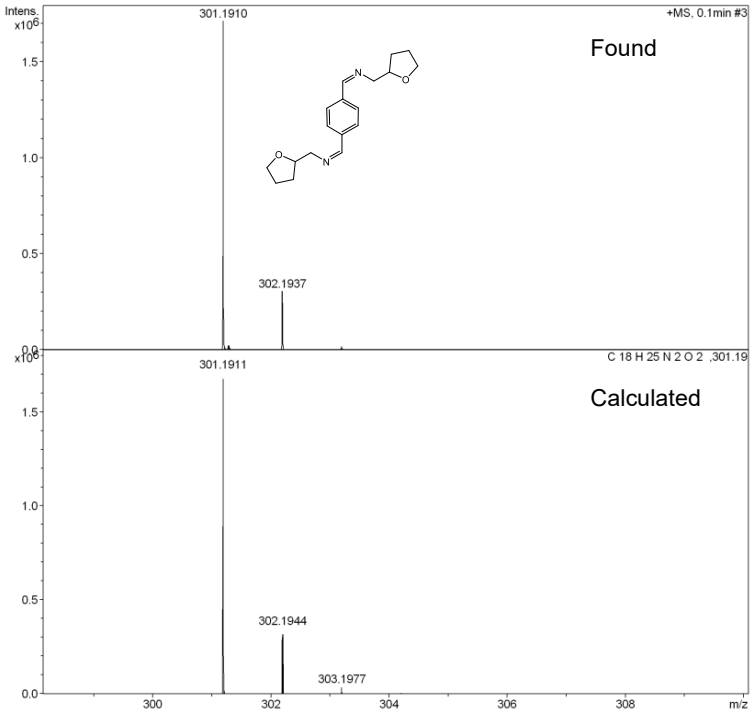


Fig. S65 MS spectrum (raw data) of compound B1 purified by flash column chromatography (see also Fig. 2d and 2e).

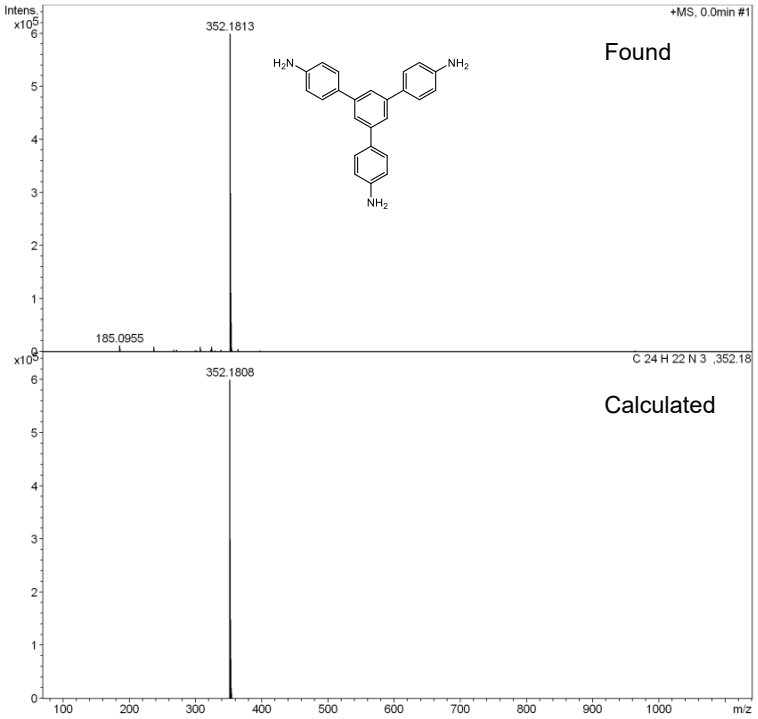


Fig. S66 MS spectrum (raw data) of compound B2 purified by flash column chromatography (see also Fig. 2d and 2e).

Section S3. Supplementary Table

Table S1. Comparison of FWHM and BET surface area of pristine and recycled TAPB-TPA COF under various recycling conditions.

Conditions	FWHM (2θ, Degree)[a]	BET surface area (m^2 g^{-1})
TAPB-TPA COF	0.32597	1778
1:3 THFA-STR	0.36253	1139
1:3 BA-STR	0.38061	735
1:10 THFA-STR	0.58784	303
1:10 BA-STR	0.4871	442

[a] The FWHM values were calculated at the dominant diffraction peak, corresponding to the (100) plane of TAPB-TPA COF.

Table S2. Summary of depolymerization process and two recycling routes.

	Depolymerization			Recycling				
	Conditions	**Time (day)**	**Residual solid mass**	**Method**	**Treatment & Reaction Time (day)**	**COF mass recovery**	**BET surface area (m^2 g^{-1})**	**Total time (day)**
Route I: Room-temperature recycling (RTR)	1:3 THFA-RTR (imine:THFA = 1:3)	16	10.0% in 4 days 3.1% in 16 days	No purification for depolymerization mixtures. Directly adding aqueous acetic acid (18 mL, 6 mol L^{-1}) and reacted at room temperature & ambient pressure for 24 h.	1.5	66%±6%	908	(5.5)[a] 17.5
	1:5 THFA-RTR (imine:THFA = 1:5)	8	7.0% in 4 days 4.0% in 8 days		1.5	74%±4%	633	9.5
	1:10 THFA-RTR (imine:THFA = 1:10)	4	2.2% in 4 days		1.5	82%±6%	838	5.5
Route II: Solvothermal recycling (STR)	1:3 THFA-STR (imine:THFA = 1:3)	16	10.0% in 4 days 3.1% in 16 days	Evaporation and drying for depolymerization mixtures. Adding glacial acetic acid, water, 1,4-dioxane, 1,3,5-trimethylbenzene, and treated in a Teflon-sealed autoclave at 70 °C for 24 h.	2.5	90%±7%	1139	(6.5)[a] 18.5
	1:5 THFA-STR (imine:THFA = 1:5)	8	7.0% in 4 days 4.0% in 8 days		2.5	75%±6%	167	10.5
	1:10 THFA-STR (imine:THFA = 1:10)	4	2.2% in 4 days		2.5	79%±8%	303	6.5
	1:3 BA-STR (imine:BA = 1:3)	16	-		2.5	88%	735	(6.5)[a] 18.5
	1:10 BA-STR (imine:BA = 1:10)	4	–		2.5	80%±7%	442	6.5

[a] Considering that 1:3 THFA condition can depolymerize 90% of TAPB-TPA COF within 4 days, either 1:3 THFA-RTR or THFA-STR as an alternative strategy is recommended for the high-quality COF recycling.

Table S3. Summary of $Sc(OTf)_3$-catalyzed depolymerization process and recycled through the RTR method.

Depolymerization			**Recycling**				
Conditions	**Time (hour)**	**Residual solid mass (200 mg COF depolymerization)**	**Method**	**Treatment & Reaction Time (day)**	**COF mass recovery**	**BET surface area (m^2 g^{-1})**	**Total time (day)**
1:3 THFA-4% Sc^{III}-RTR (imine:THFA = 1:3)	48	5.0% in 48 hours	No purification for depolymerization mixtures. Directly adding aqueous acetic acid (18 mL, 6 mol L^{-1}) and reacted at room temperature & ambient pressure for 24 h.	1.5	73%	142	3.5
1:1.5 THFA-4% Sc^{III}-RTR (imine:THFA = 1:1.5)	144	3.7% in 144 hours	Depolymerization mixtures were filtered using 0.1 μm filter paper. Adding aqueous acetic acid (18 mL, 6 mol L^{-1}) into the filtered solution and reacted at room temperature & ambient pressure for 24 h.	1.5	92%	596	7.5
1:2 THFA-4% Sc^{III}-RTR (imine:THFA = 1:2)	48	5.1% in 48 hours		1.5	91%	610	3.5
1:3 THFA-4% Sc^{III}-RTR (imine:THFA = 1:3)	48	5.0% in 48 hours		1.5	84%	709	3.5
1:2 THFA-0.5% Sc^{III}-RTR (imine:THFA = 1:2)	228	1.5% in 228 hours		1.5	86%	429	11.0
1:3 THFA-0.5% Sc^{III}-RTR (imine:THFA = 1:3)	96	1.9% in 96 hours		1.5	79%	145	5.5