Supplementary Information (SI) for Materials Chemistry Frontiers.

SUPPORTING INFORMATION

One-Pot Postsynthetic Linkage Modification of Imine Covalent Organic Frameworks via Iminium Activation

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SUPPORTING INFORMATION

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1. Instrumentation

Powder X-ray diffraction (PXRD) patterns were collected on a SmartLab 9KW desktop X-Ray diffractometer operated at 30 kV and 15 mA (step = 0.01^o, scan rate = 2 ^{o}/min).

FT-IR spectra were recorded on a PerkinElmer Frontier FT-IR spectrometer.

Liquid NMR experiment were carried out on an Vaian DLG400 (400 Hz).

Solid State NMR experiments were carried out on an Bruker AVANCE Ⅲ HD 600 MHz with a 3.2 mm HCN Balun probe with samples spinning at 10 kHz.

X-ray photoelectron spectroscopy (XPS) studies were performed with a ESCALAB Xi+ XPS instrument.

Scanning Electron Microscopy (SEM) images were recorded with an SU88220 scanning electron microscope.

Field Emission Transmission Electron Microscope (TEM) images were recorded with an JEM-F200 transmission electron microscope.

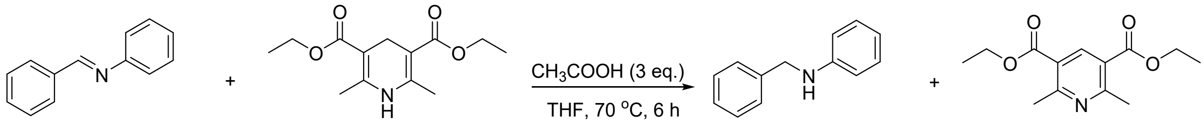
N_2 sorption isotherms were obtained on a Autosorb-IQ-MP/XR Automated Gas Sorption Analyzer at 77 K. All the samples were vacuum activated at 120 ^{o}C overnight on the instrument before analysis.

2. Chemicals

1,4-dioxane, *o*-dichlorobenzene (DCB), n-Butanol, mesitylene, and N,N-dimethylformamide (DMF) were purchased from Energy Chemical. 4-aminophenylboronic acid pinacol ester, (4-formylphenyl)boronic acid, tetrakis(triphenylphosphine)palladium, and 1,4-dihydro-2,6-dimethyl-3,5-pyridinedicarboxylate (HEH) (97%) were obtained from Adamas. All the chemicals were used as received.

3. Synthesis and characterization of COFs

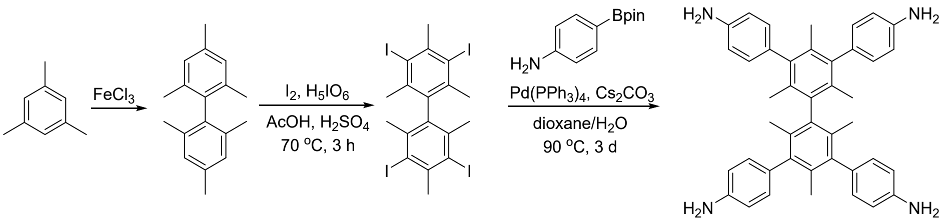
3.1 Acetic acid catalyzed reduction of *N*-benzylidenaniline to *N*-benzylaniline with Hantzsch ester



N-benzylideneaniline (18.1 mg, 0.1 mmol), HEH (26.6 mg, 0.1 mmol), and acetic acid (17.2 µL, 0.3 mmol) were mixed in 1 mL THF in a one-dram vial. The vial was heated at 70 °C on an aluminum block for 6 hours. After then, the solvent was removed, and the residual organic compounds were dissolved in $CDCl_3$ and analyzed by ^1H NMR spectroscopy and GC/MS. Spectroscopic data of *N*-benzylaniline: ^1H NMR (400 MHz, $CDCl_3$): δ = 7.42-7.30 (m, 5H), 7.19 (t, J = 7.79 Hz, 2H), 6.73 (t, J = 7.25 Hz, 1H), 6.68 (d, J = 7.35 Hz, 2H), 4.36 (s, 2H), 4.08 (br, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.17, 139.46, 129.29, 128.66, 127.54, 127.26, 117.61, 112.89, 48.37.

3.2 Synthesis of COF linkers

3.2.1 Synthesis of 3,3‘,5,5‘-tetra(p-aminophenyl)-bimesitylene (BMTA)[1]



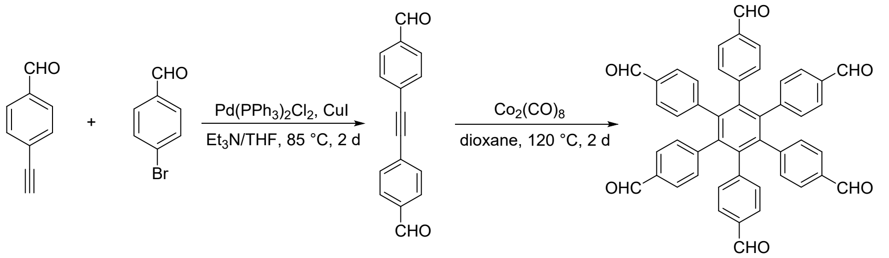
Bimesityl. $FeCl_3$ (80.00 g) was added in small portions into 180 mL mesitylene under Ar flow **(*Caution: gas generation!*)**. After stirring at room temperature for 4 h, the mixture was poured onto ice and filtered. The organic phase was separated and dried over anhydrous sodium sulfate. Mesitylene was removed by vacuum distillation. The remaining solid was recrystallized from acetone to give a white solid. Yield: 20.00 g, 19%. ^1H NMR (400 MHz, $CDCl_3$): δ = 6.93 (s, 2H); 2.29 (s, 3H); 1.87 (s, 6H).

3,3',5,5'-tetraiodo-bimesityl. Bimesityl (2.00 g, 18.39 mmol), iodine (4.26 g, 16.77 mmol), H_5IO_6 (1.91 g, 8.4 mmol), concentrated sulfuric acid (6 mL), and acetic acid (120 mL) were heated at 70 °C in an argon for 3 h. After cooled to room temperature, the reaction mixture was poured into ice water containing sodium thiosulfate. The aqueous solution was extracted with dichloromethane and the combined organic phase was evaporated to give a white solid. Yield: 3.30 g, 24% ^1H NMR (400 MHz, $CDCl_3$): δ = 3.04 (s, 6H); 2.08 (s, 12H).

3,3′,5,5′-tetra(p-aminophenyl)-bimesitylene. 3,3',5,5'-tetraiodo-bimesityl (1.40 g, 1.9 mmol), 4-aminophenylboronic acid pinacol ester (3.30 g, 15.2 mmol), $Pd(PPh_3)_4$ (0.20 g, 0.2 mmol), and Cs_2CO_3 (4.90 g, 15.0 mmol) were loaded into a 250 mL flask under Ar. Degassed dioxane/H_2O (80 mL/8 mL) were added and the mixture were heated at 90 °C for 3 days. After cooled to room temperature, the reaction mixture was diluted with water and extracted with dichloromethane. The combined organic solvent was removed under vacuum. Purification was performed on column chromatography (ethyl acetate/n-hexane =1/1) to give a light-yellow solid

Yield: 0.23 g, 20%. ^{1}H NMR (400 MHz. $CDCl_3$): δ = 6.96 (d, J=8.0 Hz, 8H), 6.73 (d,J=8.0 Hz, 8H), 4.13 (s, 8H), 1.75 (s, 6H), 1.67 (s, 12H).

3.2.2 Synthesis of hexaformylphenylbenzene (HFPB)[2]

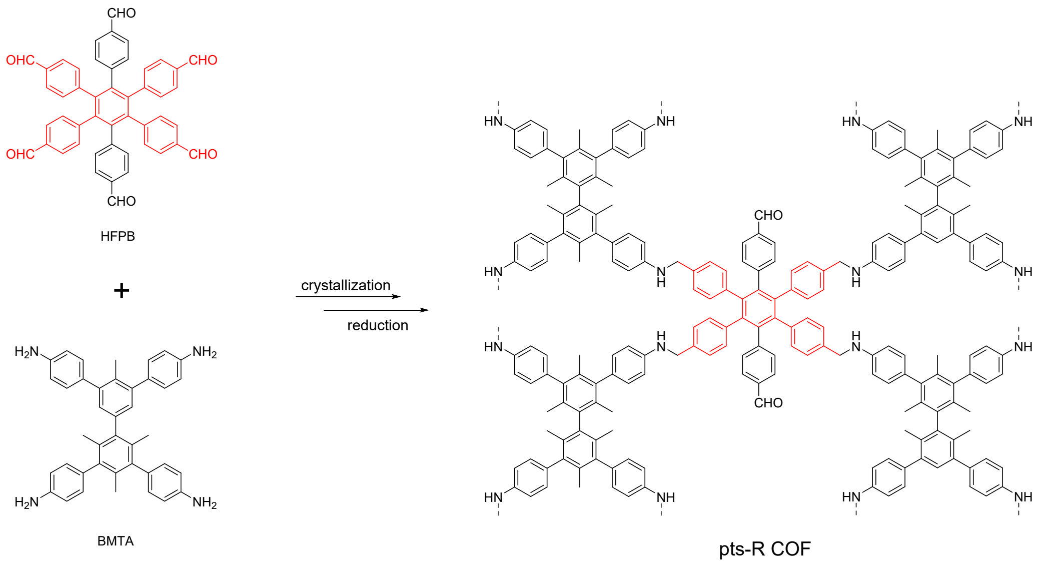


4,4'-(ethyne-1,2-diyl)dibenzaldehyde. A 250 mL two-neck flask was charged with p-acetylene benzaldehyde (2.00 g, 15.37 mmol), p-bromobenzaldehyde (2.84 g, 15.37 mmol), $Pd(PPh_3)_2Cl_2$ (539.4 mg, 0.77 mmol), and CuI (293.3 mg, 1.54 mmol) under Ar. Degassed THF (100 mL) and NEt_3 (3.12 g, 30.74 mmol) were then added via syringe. The mixture was heated at 85 ^{o}C for 2 days. After cooling to room temperature, the solvent was removed under vacuum. The resulting solid was washed with methanol, ether and a small amount of dichloromethane to give yellow solid. Yield: 1.52 g, 43%. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 10.04 (s, 2H), 7.90 (d, J = 8.3 Hz, 4H), 7.71 (d, J = 8.3 Hz, 4H).

Hexaformylphenylbenzene. 4,4'-(ethyne-1,2-diyl)dibenzaldehyde (1.52 g, 6.5 mmol) and dicobalt octacarbonyl (100 mg, 0.29 mmol) were refluxed in 80 mL dry dioxane under Ar for 2 days. After cooling to room temperature, diluted hydrochloric acid was added. The solvent was removed under reduced pressure, and the resulting residue was washed with methanol to give a white solid. Yield: 0.35 g, 42%. ^{1}H NMR (400 MHz, DMSO-d_6) δ = 9.73 (s, 6H), 7.46 (d, J = 8.1 Hz, 12H), 7.21 (d, J = 8.1 Hz, 12H).

3.3 Synthesis of reduced COFs with HEH

pts-R COF.[3]

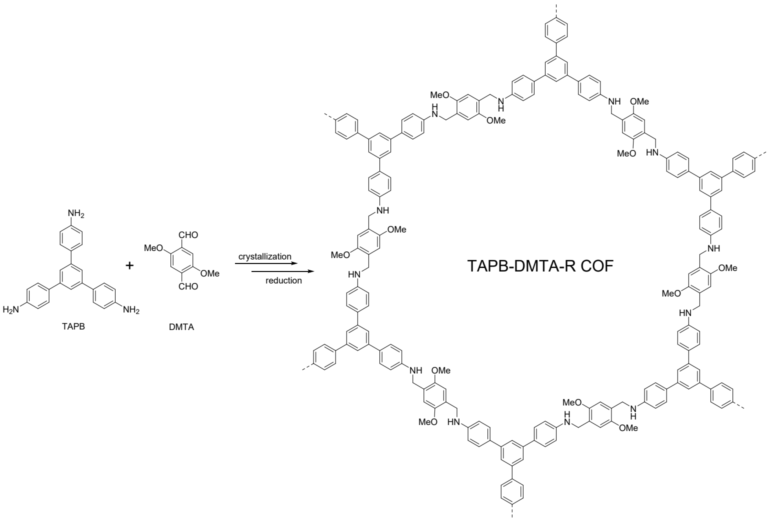


Hantzsch ester as the reducing agent. BMTA (18.1 mg, 0.03 mmol), HFB (21.1 mg, 0.3 mmol), *o*-dichlorobenzene (0.8 mL), butyl alcohol (0.8 mL) were added into a 10 mL Schlenk tube. After sonication for 5 min, 0.3 mL of 6 M AcOH was added. The tube was sealed and degassed by three freeze-pump-thaw cycles. The mixture was then heated at 120 °C for 72 h. After the reaction was cooled down, Hantzsch ester (60.79 mg, 0.24 mmol, 2.0 equiv. to imine) was added to the mixture and well mixed with the COF suspension. The mixture was heated at 120 ^oC for 24 h. The powder was filtered and washed thoroughly with THF, acetone, and n-Hexane and then dried at 60 °C in a vacuum overnight. Yield: 25.2 mg.

HCOOH as the reducing agent. To a suspension of pts COF (30.0 mg) in *o*-dichlorobenzene (0.8 mL), butyl alcohol (0.8 mL) was added formic acid (36.7 μL). The suspension was heated at 120 for 24 h. The powder was filtered and washed thoroughly with THF, acetone, and n-Hexane and then dried at 60 °C in a vacuum overnight. Yield: 18.0 mg.

$NaBH_4$ as the reducing agent. pts COF (30.0 mg) was placed in a 10 mL beaker, and 5 mL methanol was added with stirring. The mixture was cooled to 0 °C, followed by the portionwise addition of $NaBH_4$ (37.83 mg, 0.768 mmol, 8 eq. to imine) within 1 h. The reaction mixture was stirred at 0 °C for 1 h and then at room temperature overnight.The powder was filtered and washed thoroughly with H_2O, acetone, and EtOH then dried at 60 °C in vacuum overnight. Yield: 19.5 mg.

TAPB-DMTA-R COF.



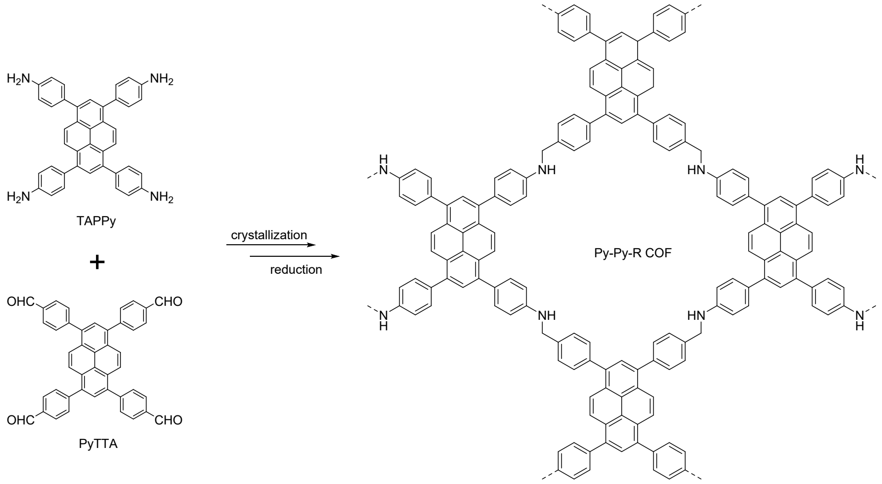
Using AcOH as a catalyst.[4] TAPB (33.5 mg, 0.0954 mmol) and DMTA (27.8 mg, 0.143 mmol) were weighed into a 4 mL vial. 1.0 mL of 4/1 p-dioxane/mesitylene was added to the vial, which was sonicated thoroughly (1-2 minutes). The vial was preheated to 70 °C using an aluminum heating block. To the preheated solution, 0.5 mL of 10.5 M acetic acid was added. The vial was capped securely, then gently swirled to mix the acid into the reaction mixture, then the reaction mixture was allowed to stand for 4 hours at 70 °C. After the specified reaction time, HEH (128 mg, 0.48 mmol, 2 equiv. to imine) was added to the mixture. Then the vial was capped and heated at 100 ^{o}C for 12 h. The precipitate was collected by filtration and washed with tetrahydrofuran (THF) and methanol. The powder was dried at 60 °C under vacuum overnight. Yield: 40 mg.

Using $Sc(OTf)_3$ as a catalyst.[5] 2,5-dimethoxyterephthalaldehyde (DMTA, 17.3 mg, 0.089 mmol) and dichloromethane (1 mL) were placed in a Biotage 20 mL high precision glass vial and sonicated for 10 s. Acetonitrile (27 mL) was added into the vial, and the resulting solution was stirred at room temperature until DMTA was dissolved. Then 1,3,5-tris(4-aminophenyl)benzene (TAPB, 20.9 mg, 0.059 mmol) was added in the vial. The vial was sealed with a cap and stirred at room temperature. $Sc(OTf)_3$ (7 mg, 0.0142 mmol), 0.08 equivalent per amine functional group in TAPB, was dissolved in 2 mL acetonitrile and injected in the reaction tube within 5 min. The reaction was stirred at room temperature for 20 hours. After the specified reaction time, HEH (90 mg, 0.354 mmol, 2 equiv. to imine) was added to the mixture. Then the vial was capped and heated at 60 ^{o}C for 12 h. The precipitate was collected by filtration and washed with tetrahydrofuran (THF) and methanol. The powder was dried at 60 °C under vacuum overnight. Yield: 30 mg.

Using $Fe(NO_3)_3·9H_2O$ as a catalyst.[6] TAPB (20.9 mg, 0.059 mmol) and DMTA (17.3 mg, 0.089 mmol) were weighed and dissolved in a mixture of 1 mL DCB and 1 mL n-Butanol in a 4 mL glass vial directly. The vial was sonicated for a while until all particles dissolved in the solvents. Then $Fe(NO_3)_3·9H_2O$ (5 mol%,3.6 mg, 0.089 mmol) was added. The vial was sonicated again for a while and placed still for 2 hours. After the specified reaction time, HEH (90 mg, 0.354 mmol, 2 equiv. to imine) was added to the mixture. Then the vial was capped and heated at 60 ^{o}C for 12 h. The precipitate was collected by filtration and washed with tetrahydrofuran (THF) and methanol. The powder was dried at 60 °C under vacuum overnight. Yield: 25 mg.

Using SbI3 as a catalyst.[7] TAPB (16.0 mg,0.045 mmol) and DMTA (13.2 mg，0.067 mmol) were dissolved in DMSO (1mL) in a 4 mL vial. The precursor solution was sonicated to guarantee a well dispersion before adding 25 μL SbI3 stock solution (46.1 mg/mL). The vial was then capped and heated at 90 °C for 24 h. After cooling down to room temperature, Hantzsch ester (51 mg, 0.20 mmol, 1.5 equiv. to imine) was added into the vial and well mixed. The vial was heated at 50 °C for 12 h. The product was filtered and washed with DMSO, THF, and methanol. The solid was dried at 60 °C under vacuum overnight. Yield: 17 mg.

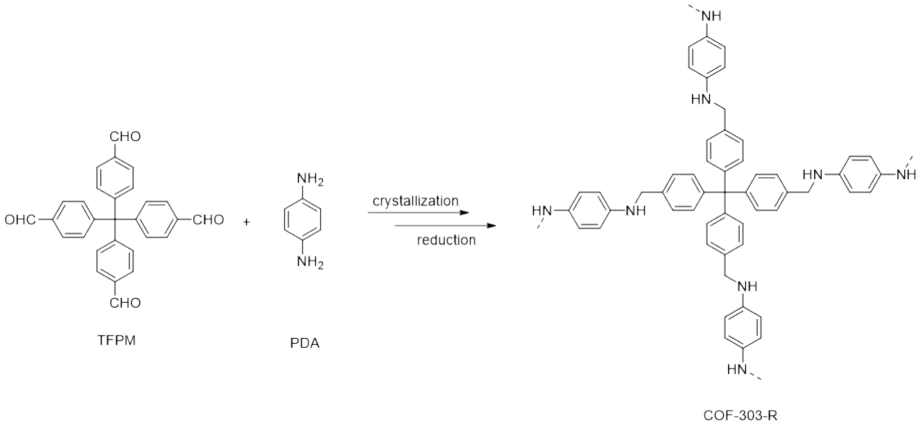
Py-Py-R COF.[8]



Py-Py-R COF. TAPPy (56.8 mg, 0.10 mmol), PyTTA (62.0 mg, 0.1 mmol), mesitylene (1.0 mL), dioxane (1.0 mL), and DMA (0.7 mL) were added into a 10 mL Schlenk tube. After sonication for 5 min, 0.1 mL of 3 M AcOH were added. The tube was sealed and degassed by three freeze-pump-thaw cycles. The mixture was then heated at 140 °C for 72 h. After the reaction was cooled down, Hantzsch ester (303.95 mg, 1.2 mmol, 3.0 equiv. to imine) was added into the mixture and well mixed with the COF suspension. The mixture was heated at 120 ^{o}C for 24 h. The powder was filtered and washed thoroughly with THF and acetone and then dried at 60 °C in a vacuum overnight. Yield: 88 mg.

H_3PO_4@Py-Py-R COF. Phosphoric acid (100 mg) was dissolved in anhydrous tetrahydrofuran (THF, 4 mL) to form a homogeneous solution. This solution was introduced into samples of Py-Py COF (40 mg), which had been pre-dried under vacuum at 120 °C overnight. The resulting mixture was stirred at room temperature for 3 h. The THF was then slowly removed by evaporation under vacuum at 70 °C over a period of 6 hours. Subsequently, the vials were placed in an oven at 70 °C for 12 h. This afforded H_3PO_4@Py-Py-R COF quantitatively.

COF-303-R.



Synthesis of reduced COF-303-R: TFPM (21.6 mg, 0.05 mmol), phenylenediamine (10.8 mg, 0.10 mmol), and 1,4-dioxane (1 mL) were loaded into a 10 mL Schlenk tube. The mixture was sonicated before 0.2 mL of 6 M

AcOH was added. The tube was sealed and degassed by three freeze-pump-thaw cycles. The mixture was then heated at 120 ^{o}C for 72 h. After the reaction was cooled down, Hantzsch ester (50.7 mg, 0.20 mmol, 1 equiv. to imine) was added to the mixture and well mixed with the COF suspension. The mixture was heated at 120 ^{o}C for 6 h. The powder was filtered and washed thoroughly with methanol, THF, and chloroform and then dried at 60 ^{o}C in a vacuum overnight. Yield: 25.0 mg.

4. Electrochemical impedance spectroscopy

Approximately 40 mg of the sample was weighed, ground into fine powder, and loaded into a custom-made mold. The powder was pressed into a pellet using a tablet press under a pressure of 6–8 MPa for 10 min. The thickness (l, unit: cm) and diameter (d, unit: cm) of the pellet were accurately measured and recorded with a vernier caliper. Conductive silver paste was applied to both bottom surfaces of the pellet, and copper wires with a diameter of 0.2 mm (the enamel coating at both ends of the wires was scraped off with a blade in advance) were led out from both sides. During the application of the silver paste, it was ensured that the conductive silver paste did not seep into the side surfaces of the pellet. Subsequently, the prepared pellet was fixed between two dry glass slides, placed in a desiccator for 24 h of drying, and then transferred to a constant temperature and humidity chamber for temperature and humidity control, with a stabilization time of 1 h for the variable-temperature tests. Finally, the copper wires led out from both ends of the pellet were connected to the two electrodes of an electrochemical workstation for testing.

5. Supporting figures

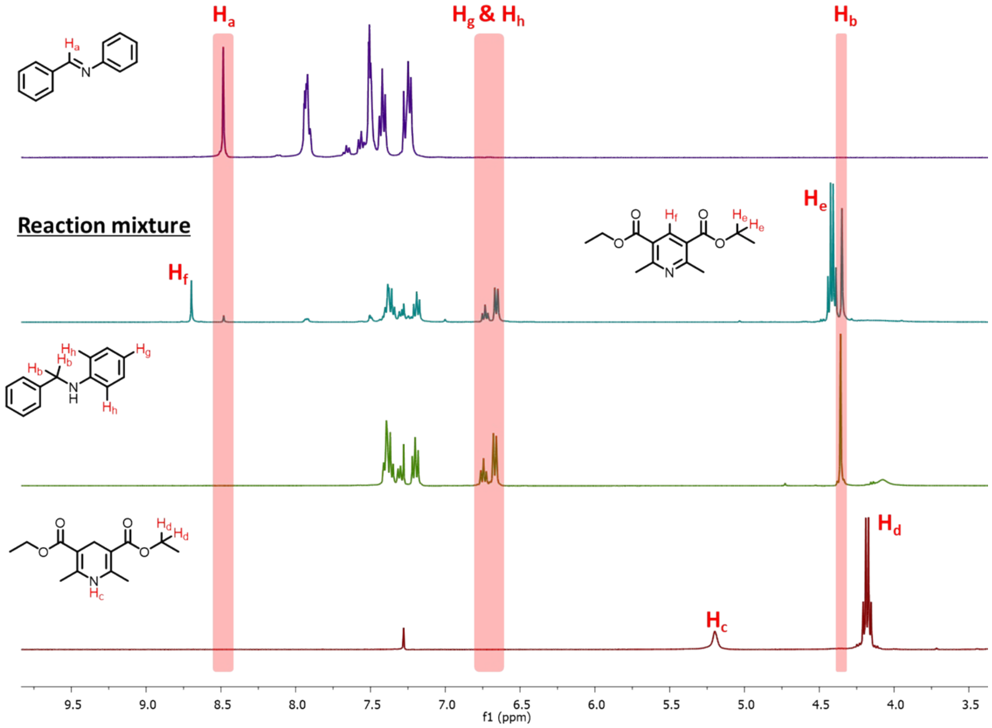


Figure S1. ^{1}H NMR spectra of *N*-benzylideneaniline (purple line), the model reduction reaction mixture (cyano line), *N*-Benzylaniline (green line), and Hantzsch ester (maroon line) in $CDCl_3$.

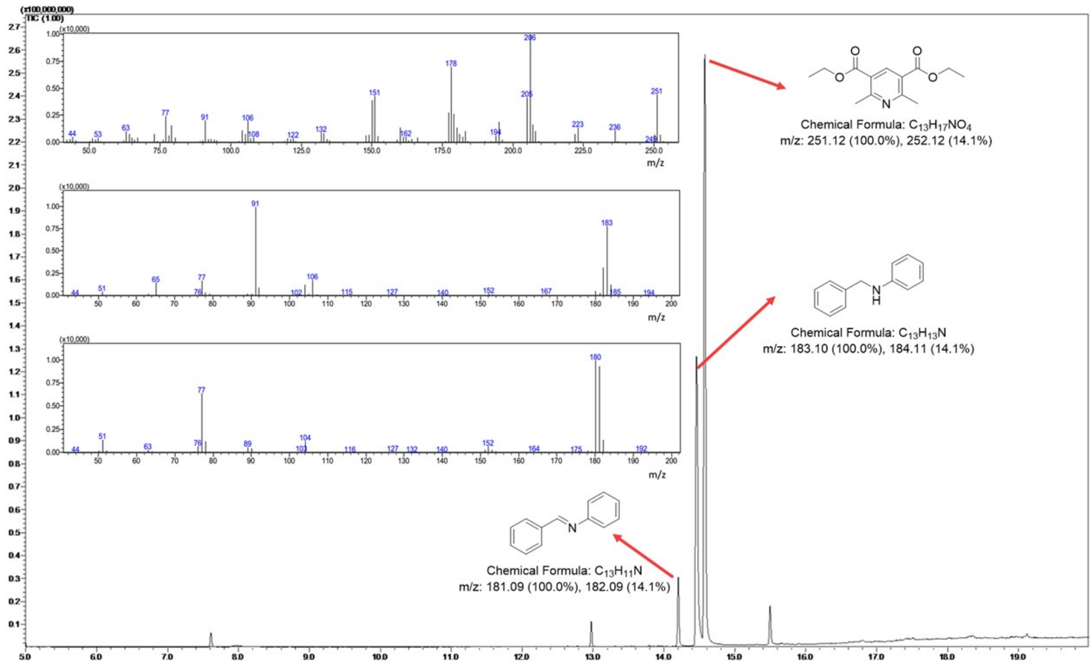


Figure S2. GC Chromatogram of the model reduction reaction mixture (inset shows the corresponding EI mass spectra).

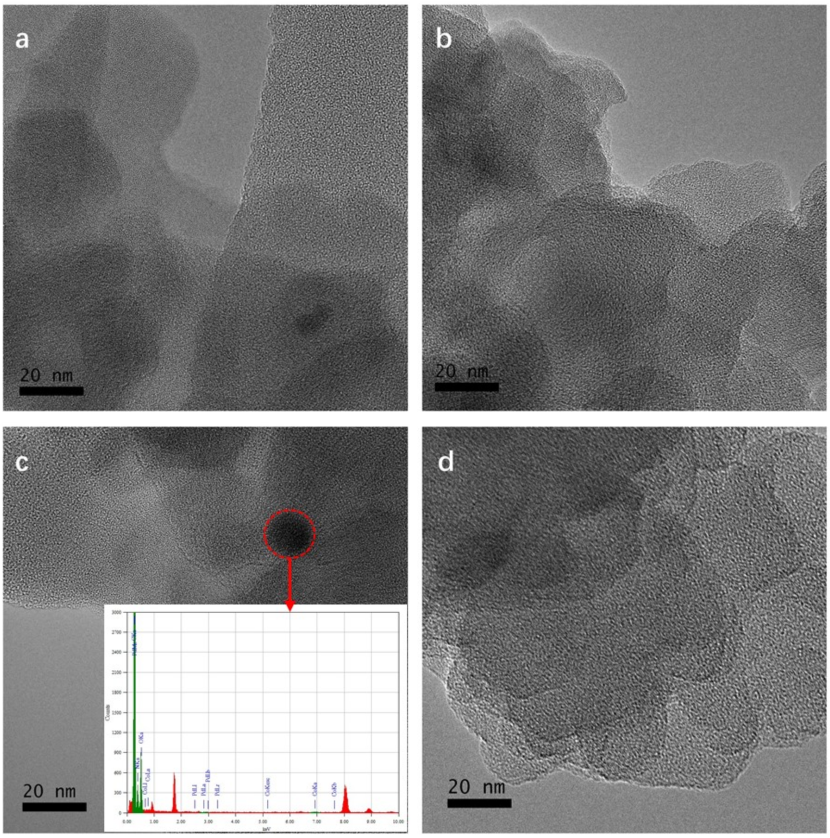


Figure S3. TEM image of **(a)** pts, **(b)** pts-R$_{\mathrm{HEH}}$, **(c)** pts-R$_{\mathrm{HCOOH}}$, **(d)** pts-R$_{\mathrm{NaBH4}}$ (the inset in c shows the EDX spectrum of Pd nanoparticle).

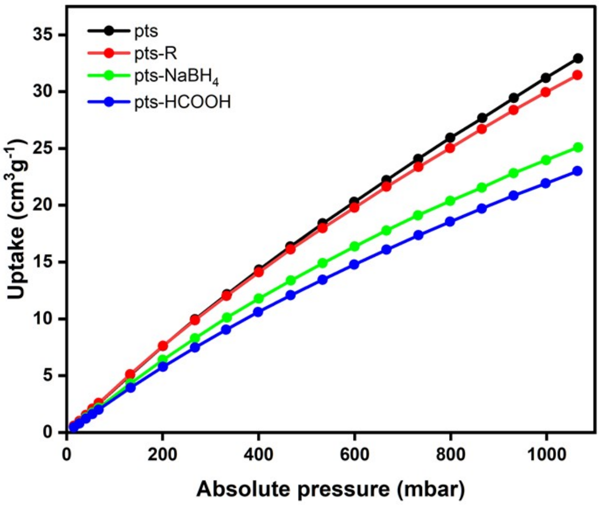


Figure S4. CO$_2$ adsorption isotherms of pts, pts-R$_{\mathrm{HEH}}$, pts-R$_{\mathrm{NaBH4}}$, and pts-R$_{\mathrm{HCOOH}}$ COF at room temperature.

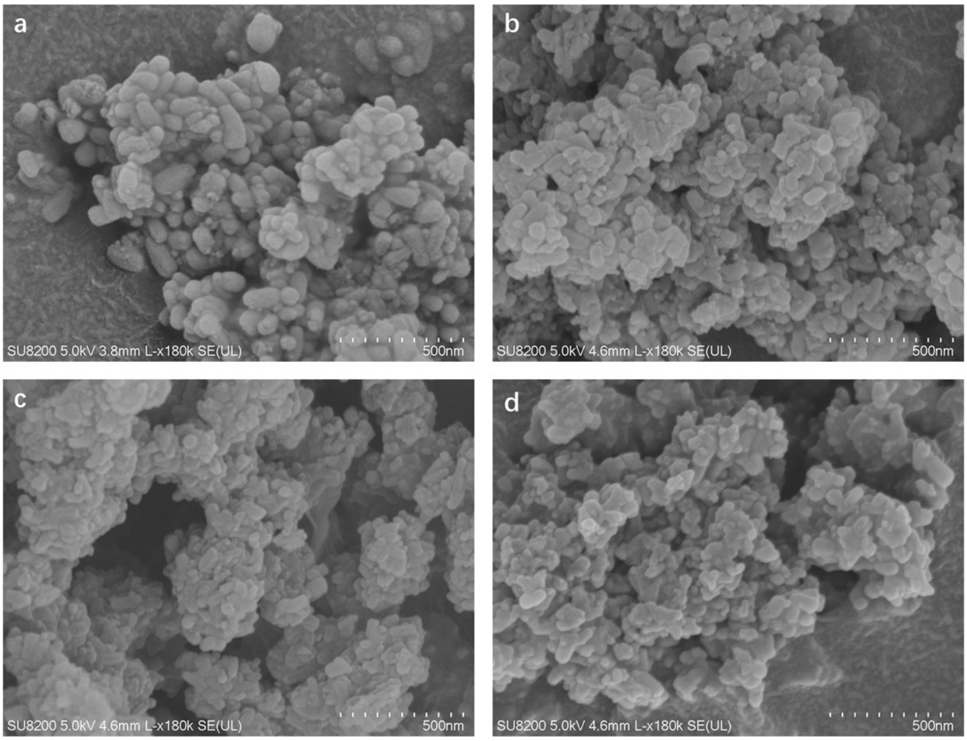


Figure S5. SEM image of **(a)** pts, **(b)** pts-R_{HEH}, **(c)** pts-R_{HCOOH}, **(d)** pts-R_{NaBH4}

Table S1. Comparison of different reduction methods for pts COF.

Reductant	HEH	$NaBH_4$	HCOOH
Process	One-pot	Two-step	Two-step (metal removal required)
Loading (relative to imine)	3 equiv.	8 equiv.	10 equiv.
Yield	68%	65%	60%
Chemo-selectivity	Good	Poor	Poor
Cost (per gram COF)[a]	1.87 CNY	7.55 CNY	0.17 CNY
Atom economy	Low	Moderate	Moderate

[a] The prices of the reagents are taken from the website of Aladdin as of April 2026.

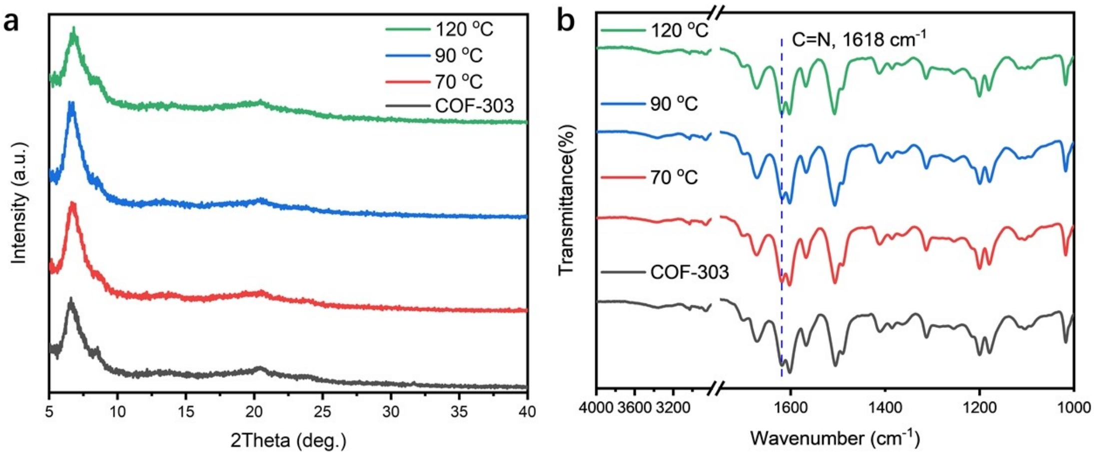


Figure S6. PXRD patterns (a) and FT-IR spectra (b) of COF-303 before and after reaction with Hantzsch ester at different temperatures.

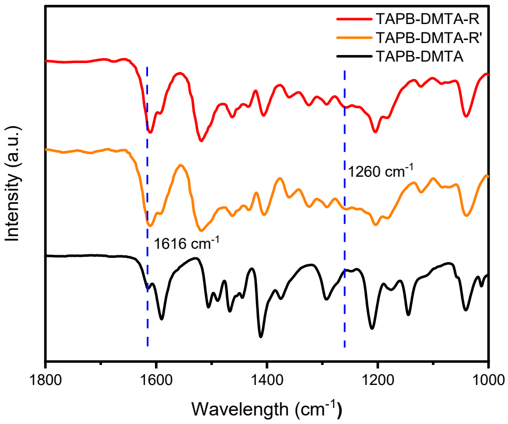


Figure S7. FT-IR spectra of TAPB-DMTA, TAPB-DMTA-R' (partial reduction), and TAPB-DMTA-R prepared using AcOH as the catalyst.

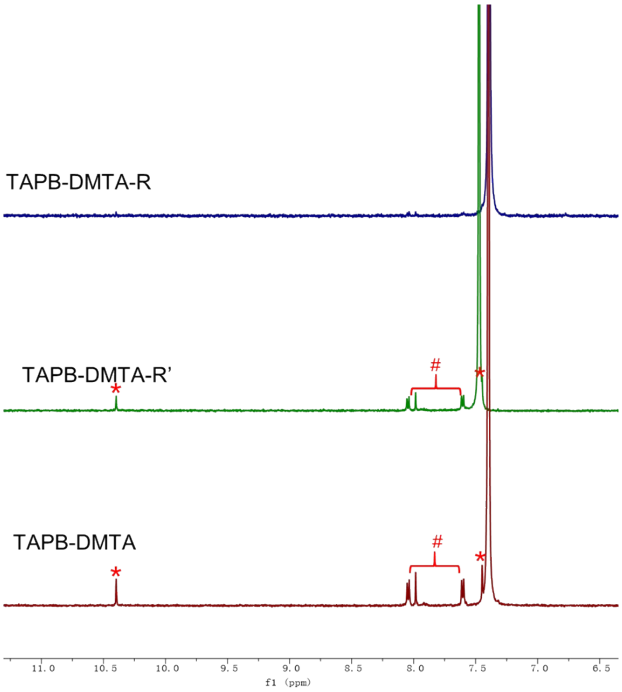


Figure S8. ^{1}H NMR spectra of acid-digested TAPB-DMTA, TAPB-DMTA-R', and TAPB-DMTA-R. * and $^{\#}$ denote the characteristic peaks of DMTA and TAPB, respectively.

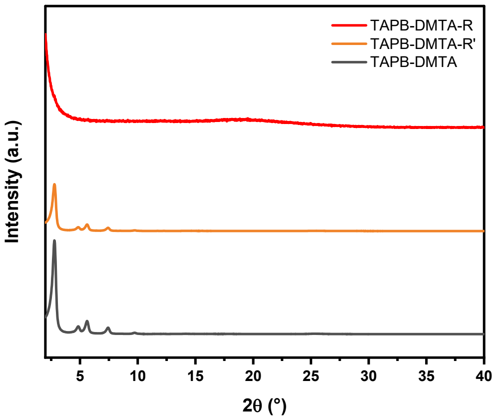


Figure S9. PXRD patterns of TAPB-DMTA, TAPB-DMTA-R' (partial reduction), and TAPB-DMTA-R prepared using AcOH as the catalyst.

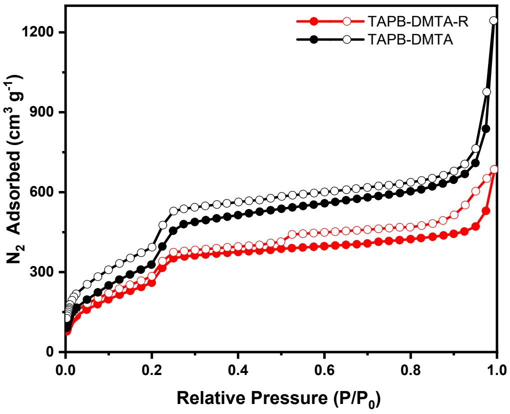


Figure S10. N_2 isotherms of TAPB-DMTA and TAPB-DMTA-R.

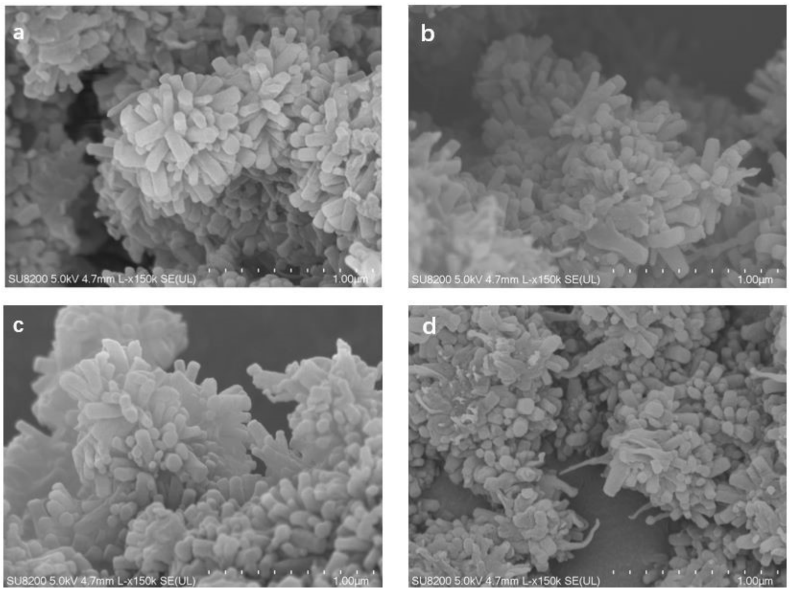


Figure S11. SEM images of TAPB-DMTA COF catalyzed by (a) AcOH, (b) $Sc(OTf)_3$, (c) $Fe(NO_3)_3 \cdot 9H_2O$, (d) SbI_3, respectively.

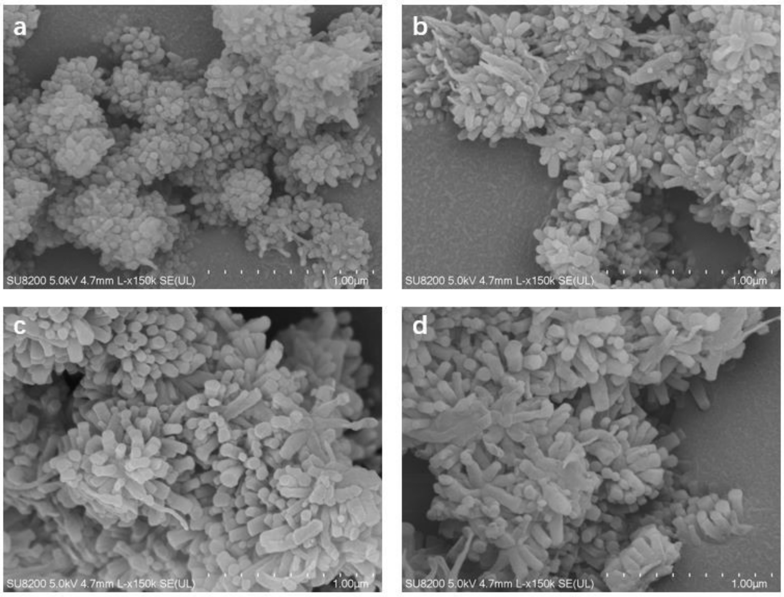


Figure S12. SEM images of TAPB-DMTA-R COF synthesized and modified by (a) AcOH, (b) $Sc(OTf)_3$, (c) $Fe(NO_3)_3 \cdot 9H_2O$, and (d) SbI_3, respectively.

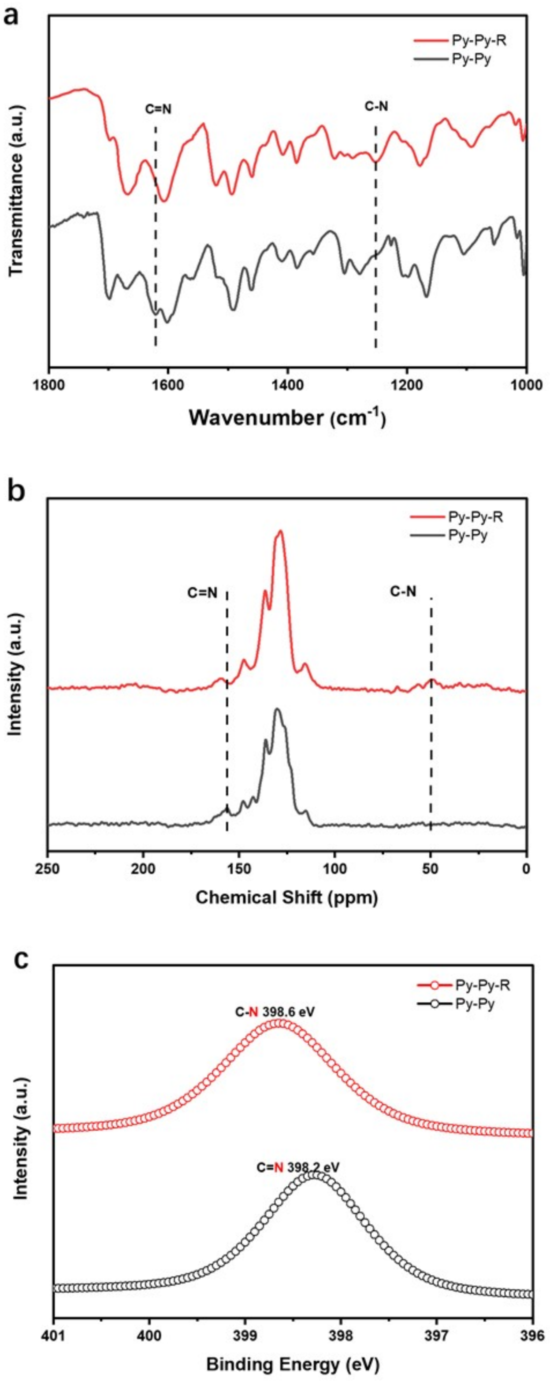


Figure S13. Comparison of a) FT-IR, b) solid state ^{13}C NMR, and c) XPS N 1s spectra of Py-Py and Py-Py-R.

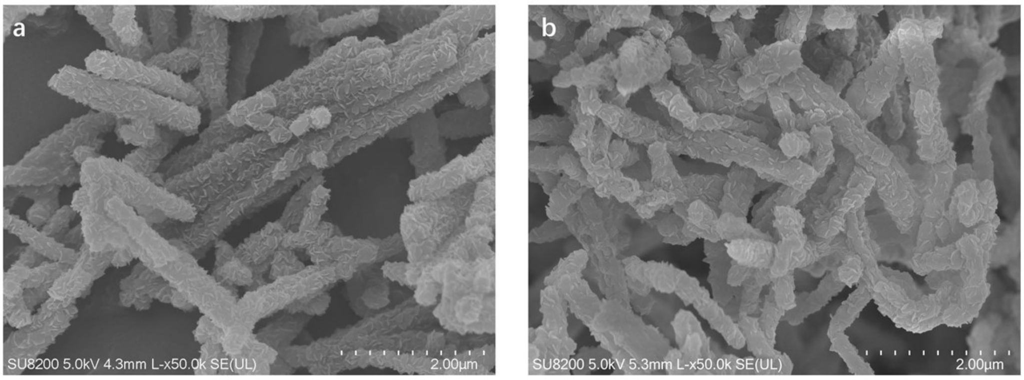


Figure S14. SEM image of (a) Py-Py and (b) Py-Py-R

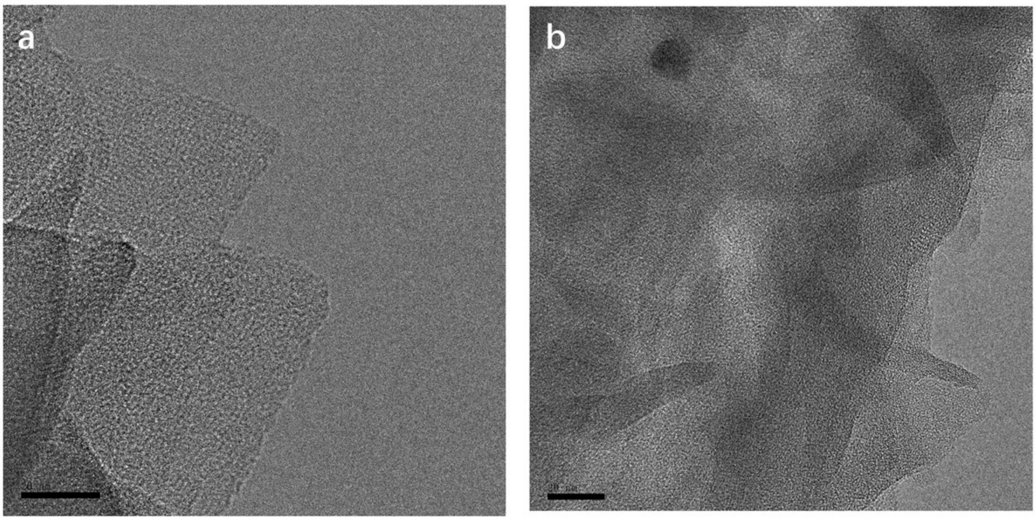


Figure S15. TEM image of (a) Py-Py and (b) Py-Py-R.

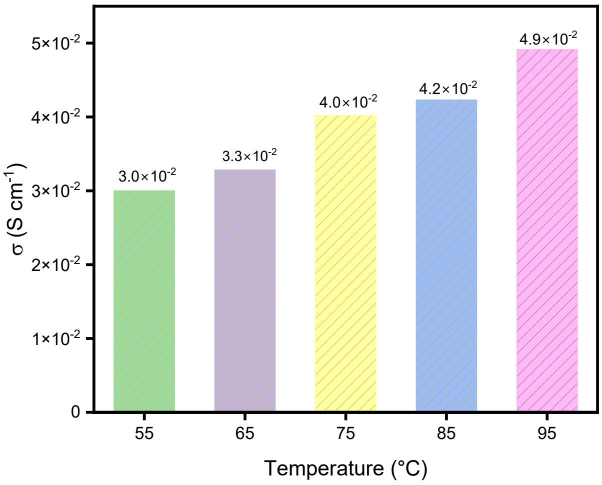


Figure S16. Proton conductivity of H_3PO_4@Py-Py-R at different temperatures (85 RH%)

Table S2. Comparison of proton conductivities of reported H_3PO_4-loaded COF materials.

Material	H_3PO_4 (wt%)	RH (%)	T (°C)	σ (S cm^{-1})	E_a (eV)	References
Py-Py-R	100.0	80	95	4.90×10^{-2}	0.16	This work
Tp-Azo	5.7	98	25	9.90×10^{-4}	0.11	*J. Am. Chem. Soc*. **2014**, 136, 6570.
TpBpy-MC	12.4	-	120	2.50×10^{-3}	0.11	*J. Mater. Chem. A* **2016**, 4, 2682.
TpBpy-ST	17.7	-	120	1.98×10^{-3}	0.12	
Aza-COF-1	3.8	97	50	1.23×10^{-3}	0.29	*Chem. Mater*. **2019**, 31, 819.
Aza-COF-2	4.8	97	50	4.80×10^{-3}	0.45	
EB-COF	56.5	-	180	2.77×10^{-2}	0.35	*J. Mater. Chem. A*, **2020**, 8, 13702
COF-F6-H	62.0	-	140	4.20×10^{-2}	0.09	*J. Am. Chem. Soc.* **2020**,142,14357.
NKCOF-1	8.8	98	80	1.13×10^{-1}	0.14	*Angew. Chem. Int. Ed.* **2020**, 59, 3678.
NKCOF-2	2.0	98	80	4.28×10^{-2}	0.24	
NKCOF-3	4.9	98	80	1.12×10^{-2}	0.40	
NKCOF-4	4.2	98	80	7.71×10^{-2}	0.08	
TPB-DMeTP	266.6	-	160	1.91×10^{-1}	0.34	*Nat. Commun*. **2020**, 11, 1981
TPB-DABI	66.1	-	160	1.52×10^{-1}	0.17	*Angew. Chem. Int. Ed.* **2021**, 60, 12918.
NKCOF-10	31.0	90	25	6.97×10^{-2}	0.06	*Nat. Commun*. **2021**, 12, 1982.
NKCOF-54	131.1	-	160	2.33×10^{-2}	0.29	*Angew. Chem. Int. Ed.* **2023**, 62, e202217240
TPB−DMeTP	292.8	-	160	3.06×10^{-1}	0.27	*J. Am. Chem. Soc.* **2024**,146,18151.
TPB−TMBPDA	239.7	-	160	4.29×10^{-2}	0.20	
TTA−TFPB	170.2	-	160	1.12×10^{-2}	0.46	
TTA−TFB	111.6	-	160	1.97×10^{-3}	0.57	
ACOF-1	75.0	-	160	6.82×10^{-5}	0.75	
USTB-5o	231.0	-	140	6.30×10^{-2}	0.20	*Nat. Chem*. **2024**, 16, 114.

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