Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

# Supporting Information

# Partially H-bonded covalent organic frameworks for photocatalytic hydrogen evolution

Wenbo Dong‡, Yueyuan Xiao‡, Zhiying Qin, Bo Qiao and Longyu Li*

College of Polymer Science and Engineering, State Key Laboratory of Polymer Materials Engineering, Sichuan University, Chengdu 610065, P. R. China

# Contents

General materials and methods ........................................................................................2

Synthetic procedures....................................................................................................2

Characterization data ..................................................................................................11

Electrochemical measurements ...................................................................................16

DFT calculations.........................................................................................................19

Structural simulation...................................................................................................20

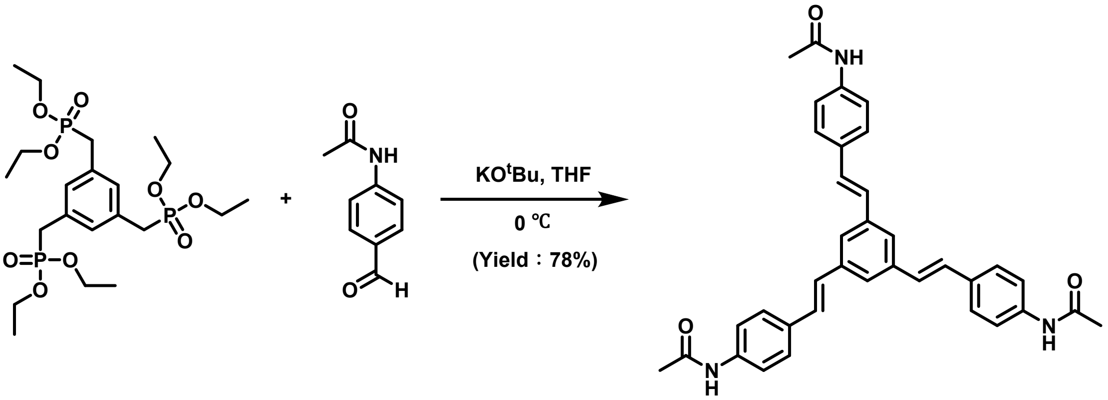
## General materials and methods

### Materials

If not stated otherwise, all reagents were purchased from commercial sources and used without any further purification. 1,3,5-tris (bromomethyl) benzene (≥ 97%), triethyl phosphite (≥ 98%), tetrahydrofuran (≥ 99.5%), potassium tert butoxide (≥ 99%), p-acetaminobenzaldehyde (≥ 98%), hydroquinone (≥ 99%), methyl iodide (≥ 98%), dimethyl sulfoxide (≥ 99%), paraformaldehyde (≥ 96%), hydrogen bromide (33 wt% in acetic acid, RG), hexamethylenetetramine (≥ 99.5%), chloroform (≥ 99%), boron tribromide (17% in methylene chloride), mesitylene (⩾ 99%), dioxane (⩾ 99.5%) o-dichlorobenzene (≥ 98%), n-butanol (≥ 99%), methanol (≥ 99.5%), ethanol (≥ 99.7%), acetone (≥ 99.5%), sodium hydroxide (≥ 99.5%), hydrochloric acid (36%-38%), dichloromethane (≥ 99.5%), acetic acid (≥ 99%), sodium sulfate anhydrous (≥ 99%), potassium chloride (≥ 99%), ascorbic acid (≥ 99%) and sodium chloride (≥ 99.5%) were purchased from Adamas-beta. Nafion D-520 dispersion was purchased from Alfa Aesar.

## Synthetic procedures

### Synthesis of 1,3,5-tris (acetylaminostyryl) benzene



Scheme S1. Synthesis of 1,3,5-tris (acetylaminostyryl) benzene.

1,3,5-tris (diethyl methylphosphonate) benzene (0.74 g, 1.4 mmol), THF (27 mL) and p-acetaminobenzaldehyde (1.14 g, 7 mmol) into a two necked flask in an ice water bath under nitrogen atmosphere, and the mixture was stirred for 20 min. After adding potassium tert butoxide (1.57 g, 14 mmol), the mixture was transferred to room temperature for overnight reaction. Then 50 mL of water was added to quench, 1 mL 10 wt% NaOH was added to adjust pH value to 13 and 10 mL of 1 M HCl was added to adjust pH value to 2. THF was remove by rotary distillation. The product was filtered naturally and washed by water and dichloromethane for 3 times, respectively. Then the solid was dried under vacuum at 40 °C to obtain a yellow solid (0.6035 g, yield 78%). $^1$H NMR (400 MHz, $(CD_3)_2SO$, ppm): $\delta$ = 2.06 (s, 9H), 7.20 (d, 3H), 7.31 (d, 3H), 7.58 (d, 6H), 7.62 (d, 6H), 7.68 (s, 3H), 10.03 (s, 3H).

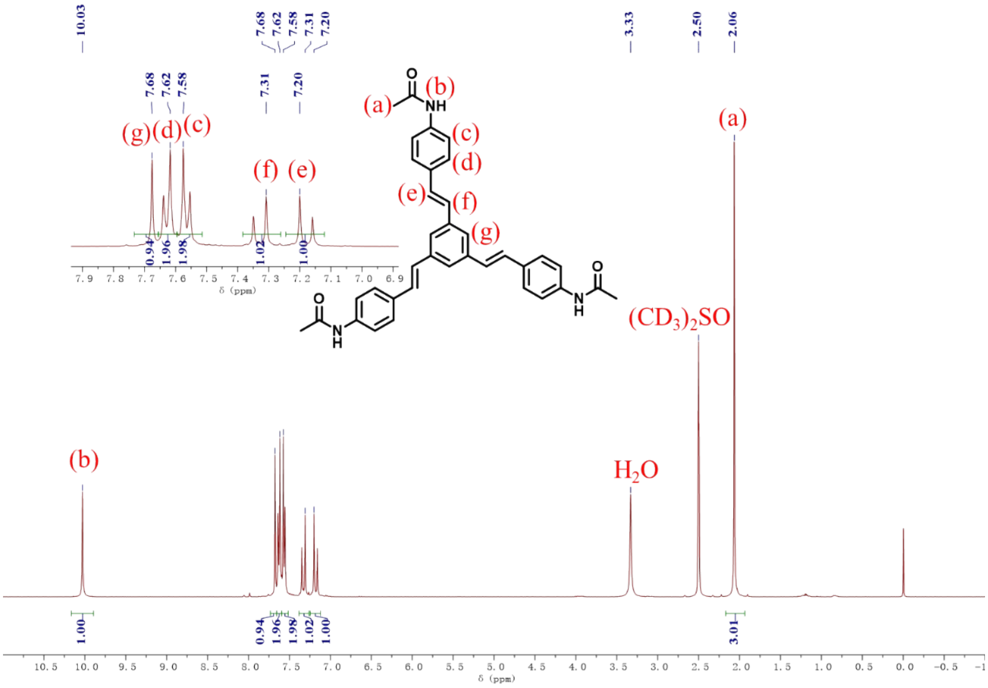
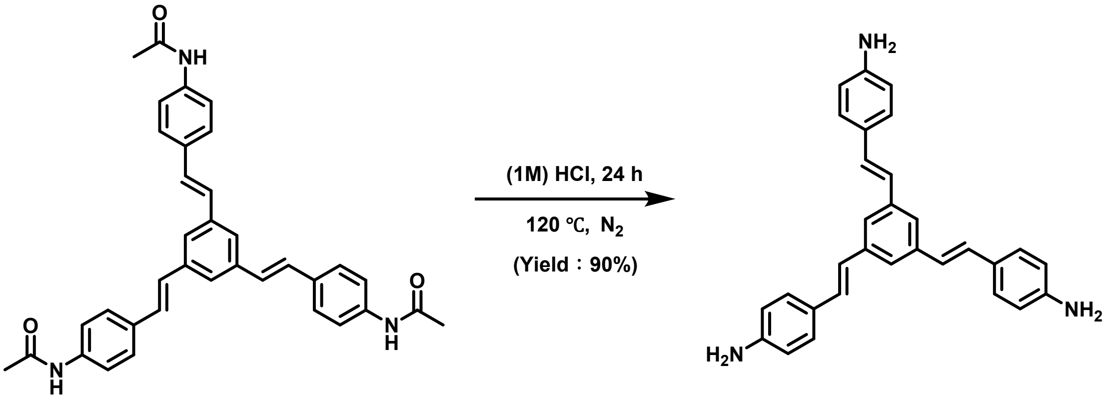


Figure S1. $^1$H-NMR spectrum of 1,3,5-tris (acetylaminostyryl) benzene.

## Synthesis of 1,3,5-tris (aminostyryl) benzene (TASB)



Scheme S2. Synthesis of 1,3,5-tris (aminostyryl) benzene (TASB).

1,3,5-tris (acetylaminostyryl) benzene (0.20 g 0.36 mmol), 1 M HCl (20 mL) and methanol (30 mL) were added to a single mouth flask under nitrogen atmosphere and refluxed at 120 °C overnight. Then 10ml of 10wt% NaOH solution was added to adjust pH value to 13. After cooling in ice water bath, the product was filtered by suction and washed with water for 3 times. Then the product was lyophilized in a lyophilizer for 24 h to obtain a yellow solid (0.1392 g, yield 90%). $^1$H NMR (400 MHz, $(CD_3)_2SO$, ppm): $\delta$ = 6.57 (d, 6H), 6.92 (d, 3H), 7.14 (d, 3H), 7.29 (d, 6H), 7.46 (s, 3H).

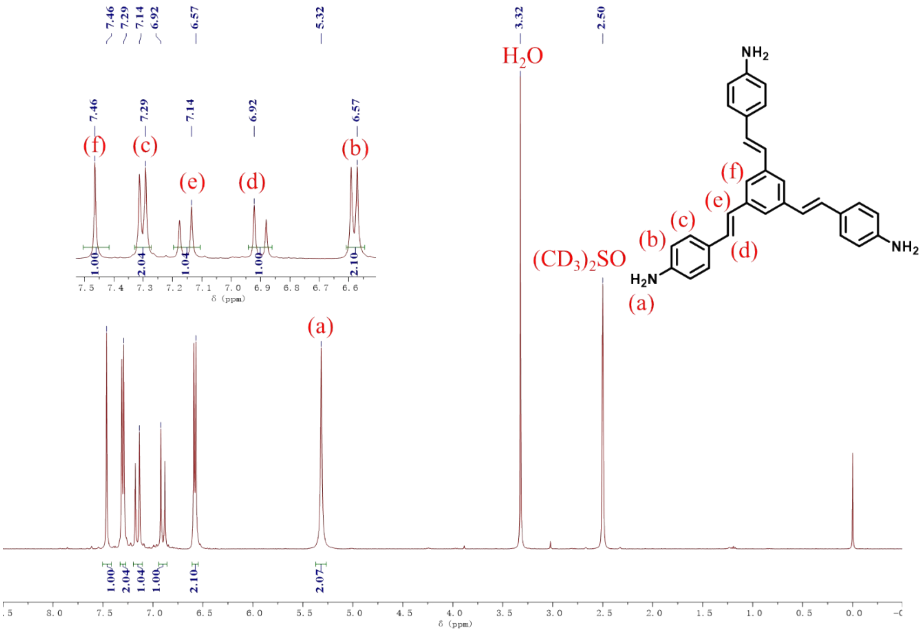


Figure S2. $^1$H-NMR spectrum of 1,3,5-tris (aminostyryl) benzene.

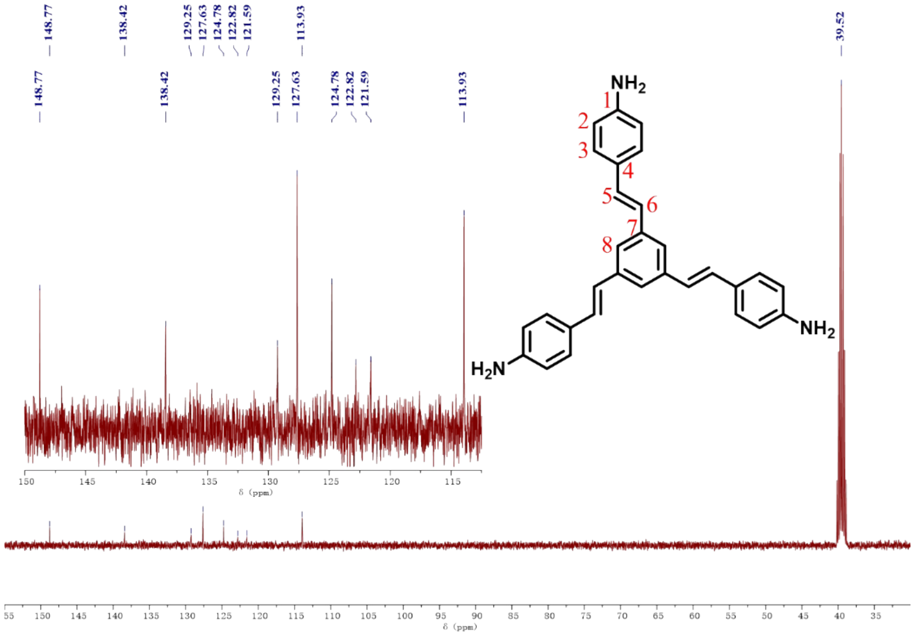
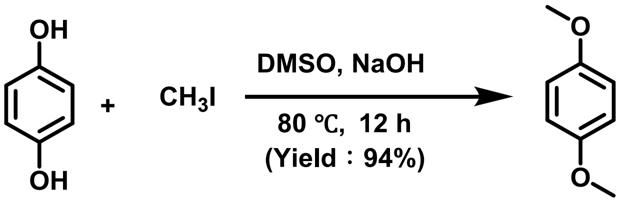


Figure S3. $^{13}$C-NMR spectrum of 1,3,5-tris (aminostyryl) benzene

## Synthesis of 1,4-dimethoxybenzene



Scheme S3. Synthesis of 1,4-dimethoxybenzene.

Hydroquinone (5.50 g, 50 mmol), sodium hydroxide (10.0 g, 250 mmol) and dimethyl sulfoxide (50 mL) were added to a double mouth flask under nitrogen atmosphere and and stirred to dissolve. Then methyl iodide (7.50mL, 120 mmol) was added in drops within 30 min. The resulting mixture was heated to 80 ºC for 12 h. After cooling to room temperature, the resulting mixture was poured into ice water. The resulting precipitate was collected by filtration, washed with water, and dried under vacuum to obtain a white powder (6.5 g, yield 94%). $^1$H NMR (400 MHz, $CDCl_3$, ppm): δ = 6.84 (s, 4H), 3.77 (s, 6H).

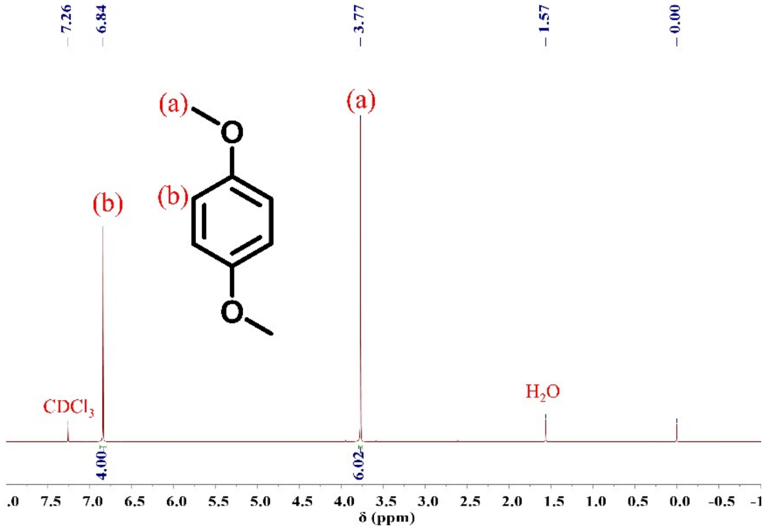
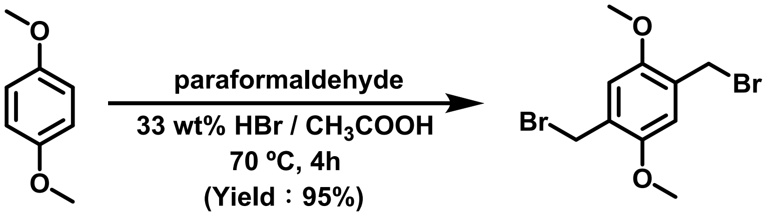


Figure S4. $^1$H-NMR spectrum of 1,4-dimethoxybenzene

## Synthesis of 1,4-bis(bromomethyl)-2,5-dimethoxybenzene



Scheme S4. Synthesis of 1,4-bis(bromomethyl)-2,5-dimethoxybenzene.

1,4-dimethoxybenzene (4.15 g, 30.0 mmol), paraformaldehyde (4.05 g, 135 mmol) and acetic acid (20 mL) were added to a double mouth flask under nitrogen atmosphere and stirred to dissolve. Then HBr (33 wt% in acetic acid, 14 mmol) was added in drops and the resulting mixture was heated to 70 ºC for 4 h. After cooling to room temperature, the resulting mixture was poured into ice water. The resulting precipitate was collected by filtration, washed with methanol, and dried under vacuum to obtain a white powder (9.13 g, yield 94%). $^1$H NMR (400 MHz, $CDCl_3$, ppm): δ = 6.87 (s, 2H), 4.54 (s, 4H), 3.87 (s, 6H).

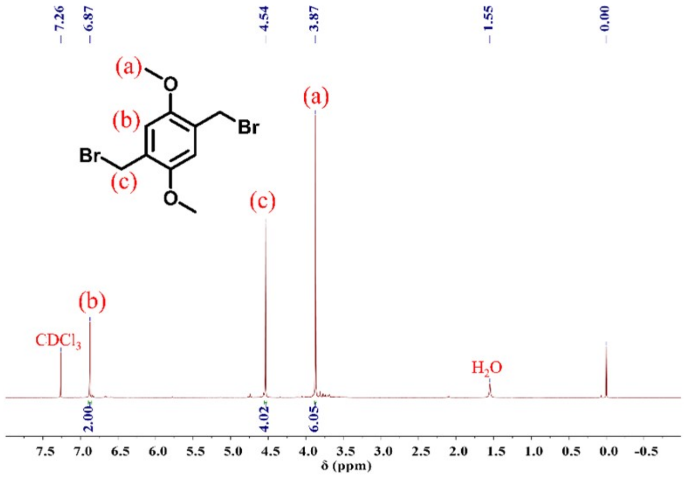
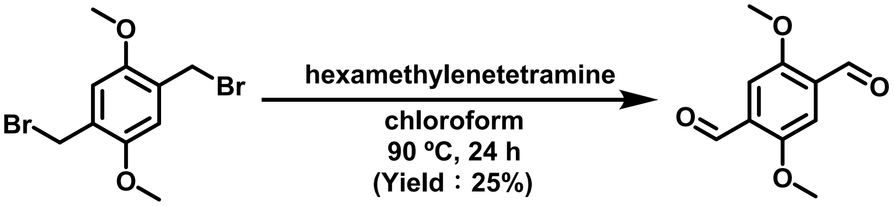


Figure S5. $^1$H-NMR spectrum of 1,4-bis(bromomethyl)-2,5-dimethoxybenzene

## Synthesis of 2,5-dimethoxyterephthalaldehyde (DMTA)



Scheme S5. Synthesis of 2,5-dimethoxyterephthalaldehyde (DMTA).

1,4-bis(bromomethyl)-2,5-dimethoxybenzene (10.0 g, 30.8 mmol), hexamethylenetetramine (12.95 g, 92.4 mmol) and chloroform (100 mL) were added to a single mouth flask under nitrogen atmosphere and refluxed at 90 ºC for 24 h. After being cooled to room temperature, the pale-yellow precipitate was collected by filtration, washed with chloroform, dried, and dissolved in water (100 mL). Then the aqueous solution was acidified with acetic acid (10 mL) and heated at 90 ºC for another 24 h. The mixture was cooled to room temperature, extracted with dichloromethane, and the organic phase was dried over anhydrous $MgSO_4$. After solvent evaporation, the residue was recrystallized from ethanol to yield a yellow needle-shaped solid (1.5 g, yield 25%). $^1H$ NMR (400 MHz, $(CD_3)_2SO$, ppm): δ = 10.40 (s, 2H), 7.44 (s, 2H), 3.94 (s, 6H).

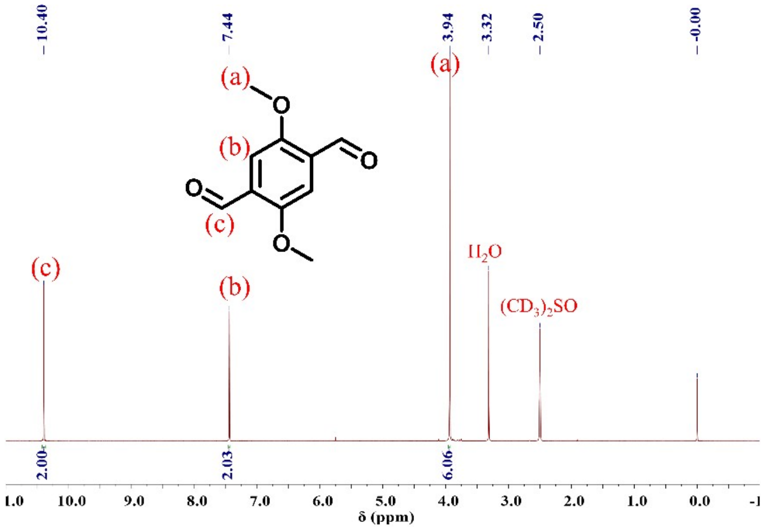
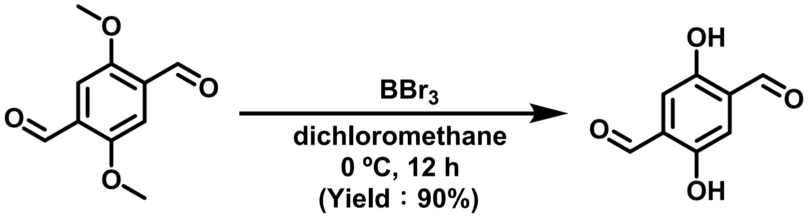


Figure S6. $^1H$-NMR spectrum of 2,5-dimethoxyterephthalaldehyde (DMTA)

## Synthesis of 2,5-dihydroxyterephthalaldehyde (DHTA)



Scheme S6. Synthesis of 2,5-dihydroxyterephthalaldehyde (DHTA).

2,5-dimethoxyterephthalaldehyde (1.0 g, 5.15 mmol) and dichloromethane (150 mL) were added to a single mouth flask under nitrogen atmosphere and stirred to dissolve. Then boron tribromide (17% in methylene chloride, 15 mL) was added dropwise at 0 ºC under $N_2$ atmosphere. After being stirred for 12 h, water (30 mL) was added dropwise to quench the reaction. The residue was extracted with dichloromethane, washed with brine, dried over $MgSO_4$, and evaporated under reduced pressure, giving the crude compound. Then the crude compound was recrystallized from ethanol to yield a yellow solid (0.77 g, yield 90%). $^1$H NMR (400 MHz, $(CD_3)_2SO$, ppm): δ = 10.31 (d, 4H, *J*=8.8 Hz), 7.22 (s, 2H).

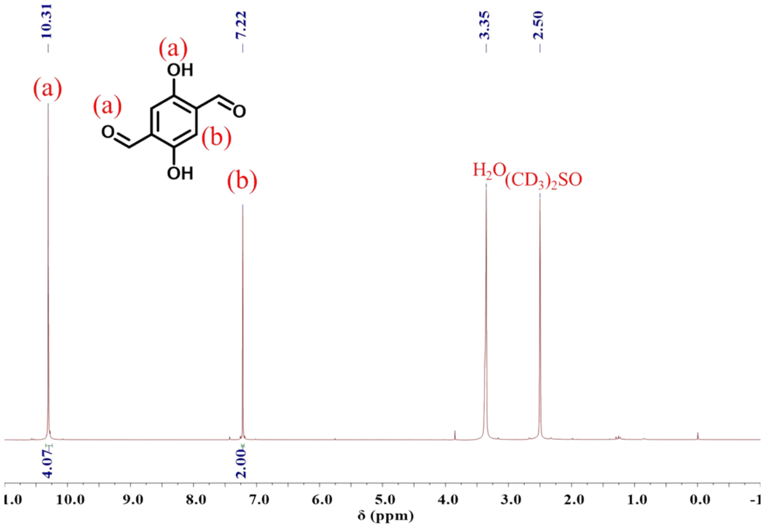
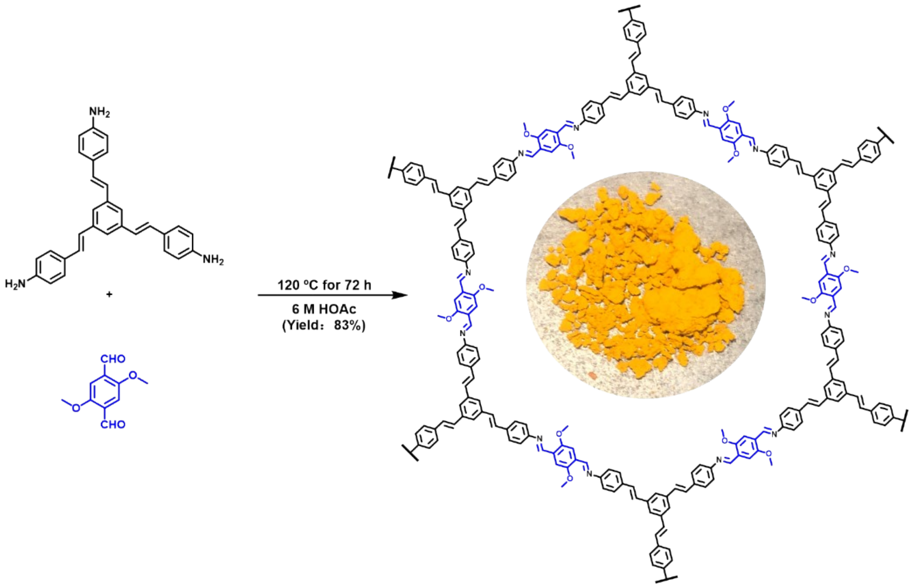


Figure S7. $^1$H-NMR spectrum of 2,5-dihydroxyterephthalaldehyde (DHTA)

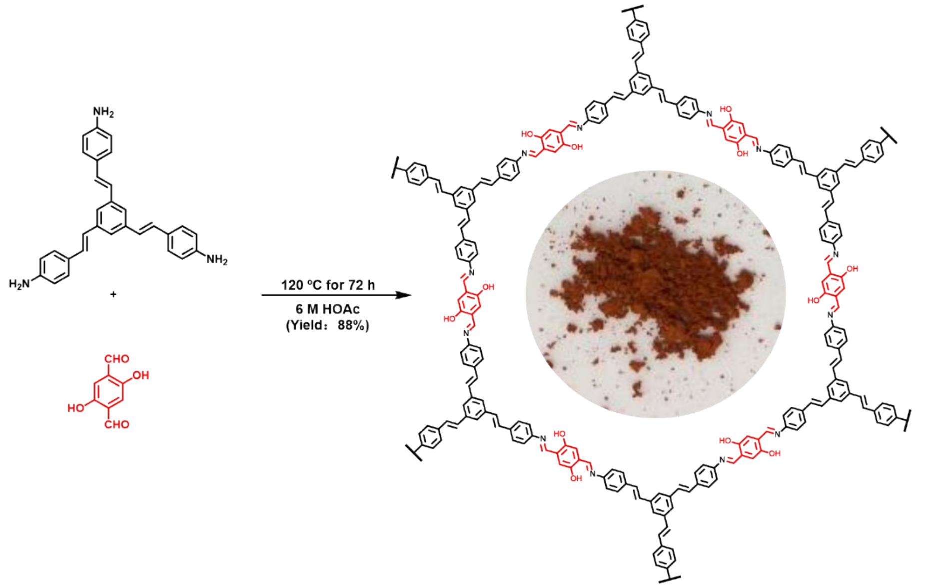
## Synthesis of COF-960-0



Scheme S7. Synthesis of COF-960-0

1,3,5-tris (acetylaminostyryl) benzene (21.5 mg, 0.05mmol) and 2,5-dimethoxyterephthalaldehyde (14.6 mg, 0.075 mmol) were added into a glass tube, then the mixture weas dissolved in n-butanol (0.5ml) and o-dichlorobenzene (0.5ml). To the mixture was added 6M HOAc aqueous solution (0.1 mL). Then the tube was flash frozen in a liquid nitrogen bath and flame sealed degassed through three freeze-pump-thaw cycles and sealed under vacuum. Upon warming to room temperature, the ampoule was placed in an oven at 120 ºC and left undisturbed for 3 days. The resulting precipitate was filtered, exhaustively washed by THF. The resulting solid was dried, and then subjected to Soxhlet extractions with THF and acetone for 1 day respectively, to remove the trapped guest molecules. The solid was washed by methanol for 12 h and then dried by supercritical $CO_2$. The powder was collected and dried under vacuum condition at 120 °C for 12 h to yield COF-960-0 as a yellow powder (27.7 mg, yield 83%).

## Synthesis of COF-960-6



Scheme S8. Synthesis of COF-960-6

1,3,5-tris (acetylaminostyryl) benzene (21.5 mg, 0.05mmol) and 2,5-dihydroxyterephthalaldehyde (12.5 mg, 0.075 mmol) were added into a glass tube, then the mixture weas dissolved in n-butanol (0.5ml) and o-dichlorobenzene (0.5ml). To the mixture was added 6M HOAc aqueous solution (0.1 mL). Then the tube was flash frozen in a liquid nitrogen bath and flame sealed degassed through three freeze-pump-thaw cycles and sealed under vacuum. Upon warming to room temperature, the ampoule was placed in an oven at 120 ºC and left undisturbed for 3 days. The resulting precipitate was filtered, exhaustively washed by THF. The resulting solid was dried, and then subjected to Soxhlet extractions with THF and acetone for 1 day respectively, to remove the trapped guest molecules. The solid was washed by methanol for 12 h and then dried by supercritical $CO_2$. The powder was collected and dried under vacuum condition at 120 °C for 12 h to yield COF-960-0 as a yellow powder (27.5 mg, yield 88%).

## Synthesis of COF-960-1 ~ -5

Other COFs, from COF-960-1 to COF-960-5, were also prepared through the similar procedure only by varying the precursor amount of 2,5-dimethoxyterephthalaldehyde (DMTA) and 2,5-dihydroxyterephthalaldehyde (DHTA). COF-960-1: 12.17 mg, 0.0625 mmol DMTA and 2.08 mg, 0.0125 mmol DHTA; COF-960-2: 9.73 mg, 0.05 mmol DMTA and 4.16 mg, 0.025 mmol DHTA; COF-960-3: 7.3 mg, 0.0375 mmol DMTA and 6.24 mg, 0.0375 mmol DHTA; COF-960-4: 4.86 mg, 0.025 mmol DMTA and 8.32 mg, 0.05 mmol DHTA; COF-960-5: 2.43 mg, 0.0125 mmol DMTA and 10.4 mg, 0.0625 mmol DHTA.

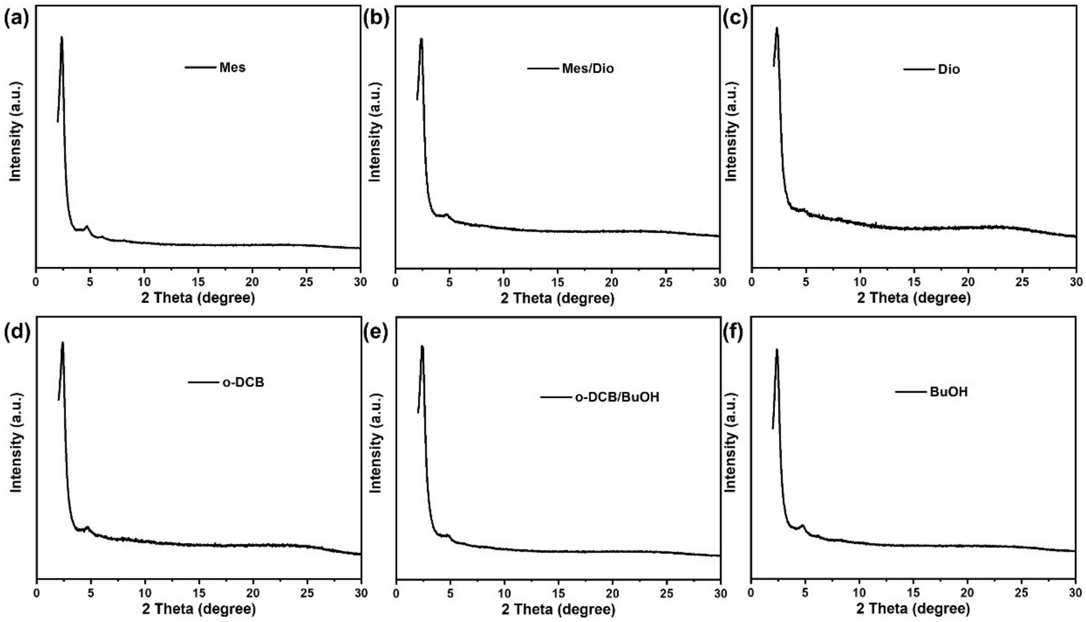


Figure S8. PXRD patterns of COF-960-0 under different solvent conditions: (a) mesitylene (Mes); (b) mesitylene (Mes)/ dioxane (Dio) (v/v=1:1); (c) dioxane (Dio); (d) o-dichlorobenzene (o-DCB); (e) dichlorobenzene (o-DCB)/ n-butanol (BuOH) (v/v=1:1), and (f) n-butanol (BuOH).

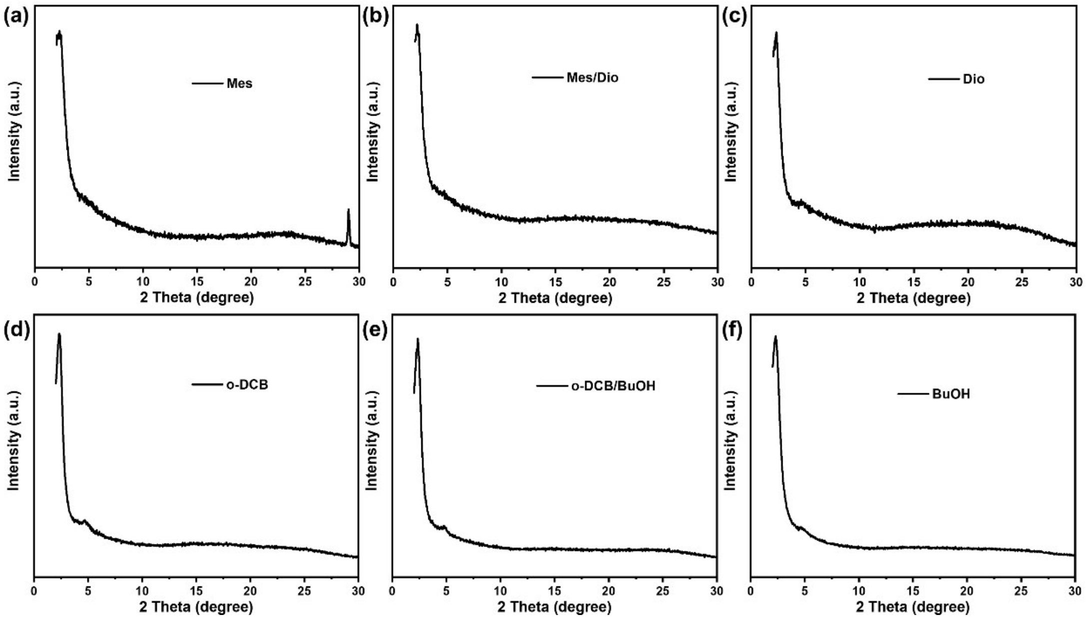


Figure S9. PXRD patterns of COF-960-6 under different solvent conditions: (a) mesitylene (Mes); (b) mesitylene (Mes)/ dioxane (Dio) (v/v=1:1); (c) dioxane (Dio); (d) o-dichlorobenzene (o-DCB); (e) dichlorobenzene (o-DCB)/ n-butanol (BuOH) (v/v=1:1), and (f) n-butanol (BuOH).

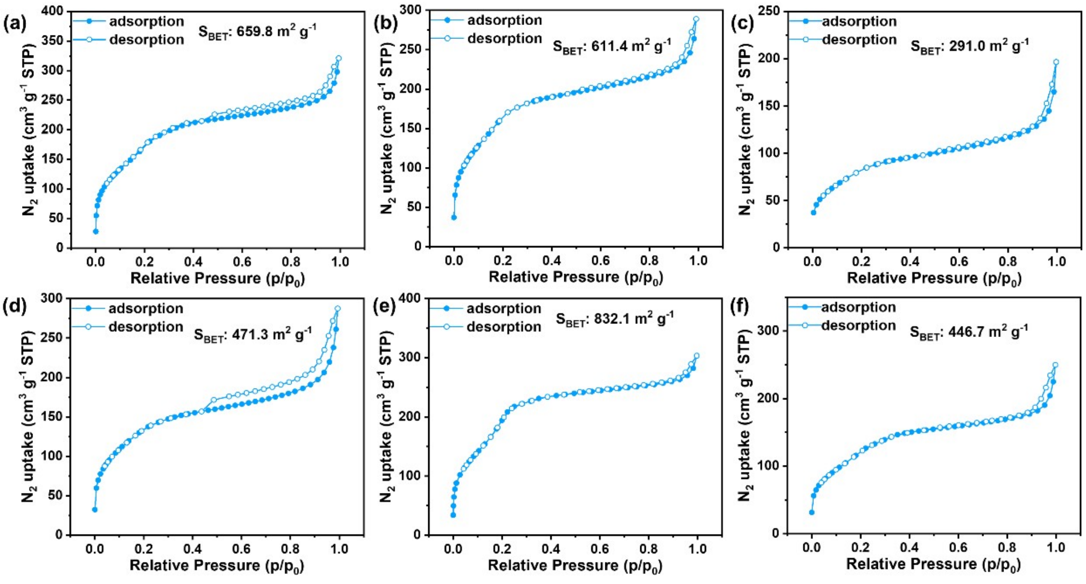


Figure S10. Nitrogen adsorption and desorption isotherms of COF-960-0 under different solvent conditions: (a) mesitylene (Mes); (b) mesitylene (Mes)/ dioxane (Dio) (v/v=1:1); (c) dioxane (Dio); (d) o-dichlorobenzene (o-DCB); (e) dichlorobenzene (o-DCB)/ n-butanol (BuOH) (v/v=1:1), and (f) n-butanol (BuOH).

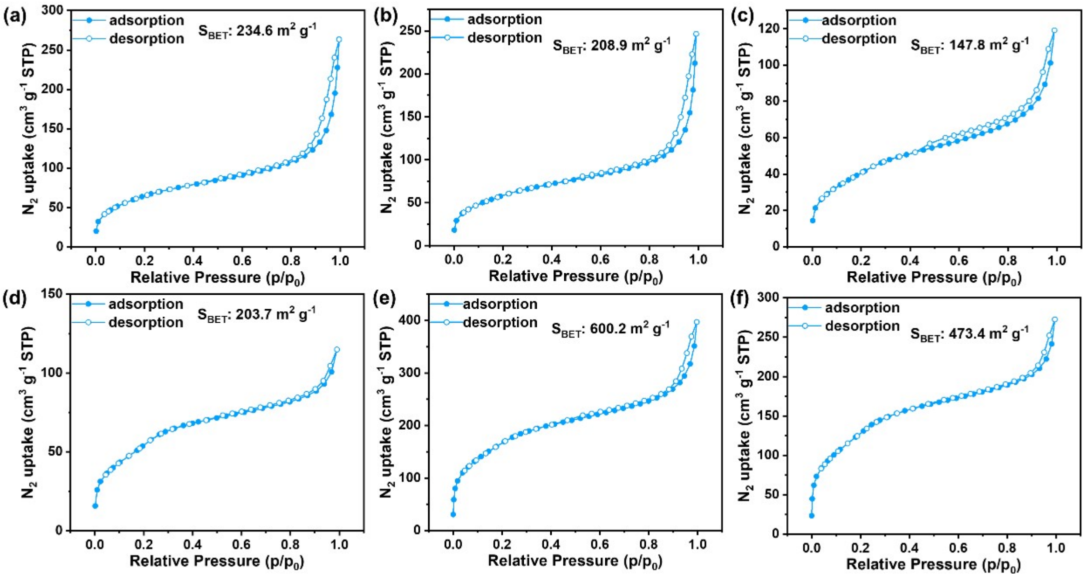


Figure S11. Nitrogen adsorption and desorption isotherms of COF-960-6 in different solvent conditions: (a) mesitylene (Mes); (b) mesitylene (Mes)/ dioxane (Dio) (v/v=1:1); (c) dioxane (Dio); (d) o-dichlorobenzene (o-DCB); (e) dichlorobenzene (o-DCB)/ n-butanol (BuOH) (v/v=1:1), and (f) n-butanol (BuOH).

## Characterization data

Table S1. General parameters of COFs derived from PXRD patterns

| COF | FWHM of (100) facet |
|---|---|
| COF-960-0 | 0.564 |
| COF-960-1 | 0.437 |
| COF-960-2 | 0.423 |
| COF-960-3 | 0.459 |
| COF-960-4 | 0.518 |
| COF-960-5 | 0.511 |
| COF-960-6 | 0.556 |

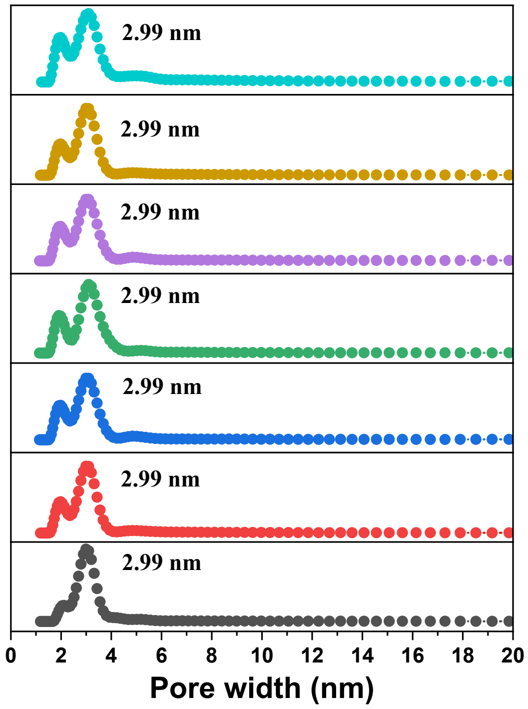


Figure S12. Pore size distributions of all COFs

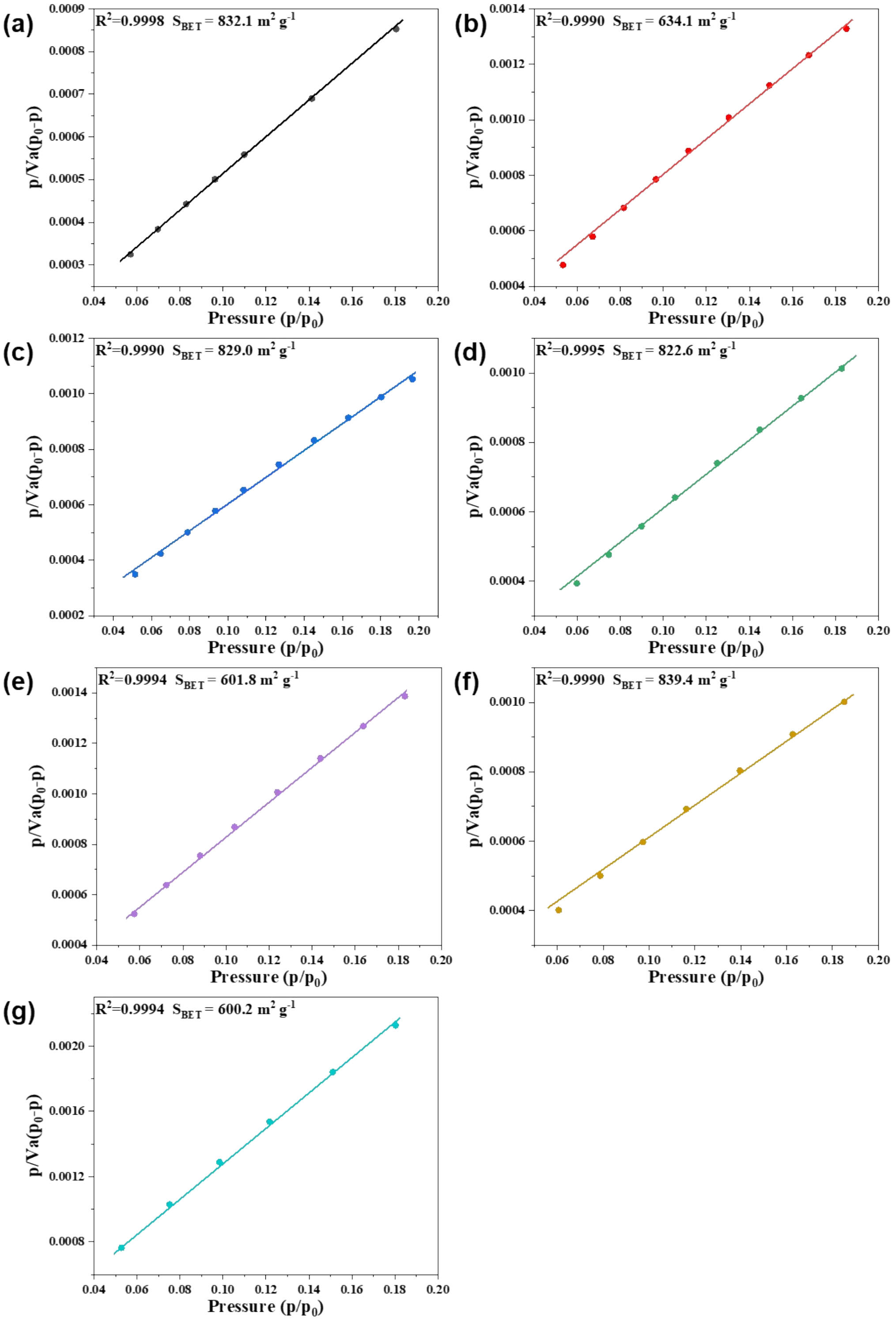


Figure S13. BET plot of (a) COF-960-0, (b) COF-960-1, (c) COF-960-2, (d) COF-960-3, (e) COF-960-4, (f) COF-960-5, and (g) COF-960-6 calculated from $N_2$ adsorption isotherm at 77K.

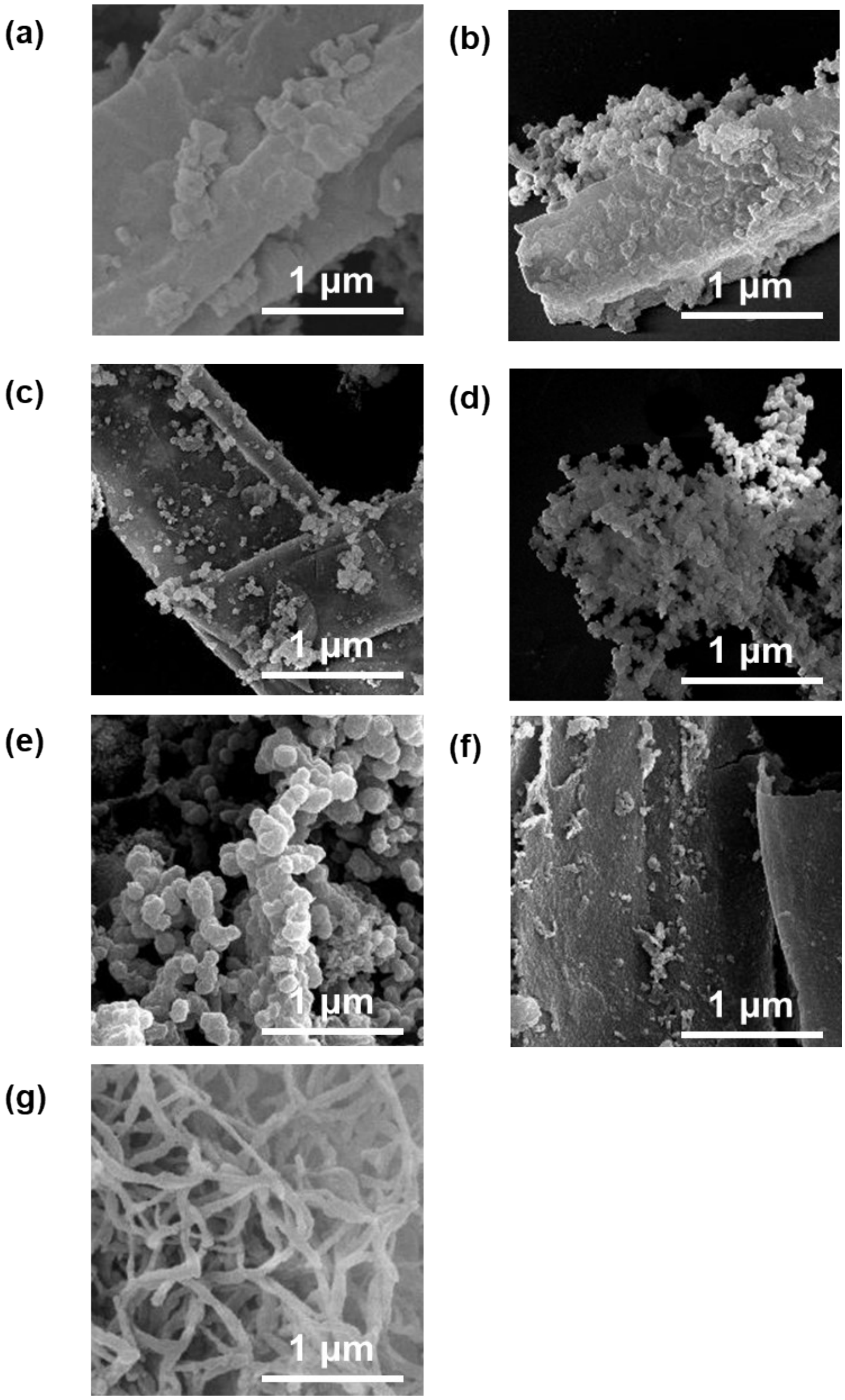


Figure S14. SEM images of (a) COF-960-0, (b) COF-960-1, (c) COF-960-2, (d) COF-960-3, (e) COF-960-4, (f) COF-960-5, and (g) COF-960-6.

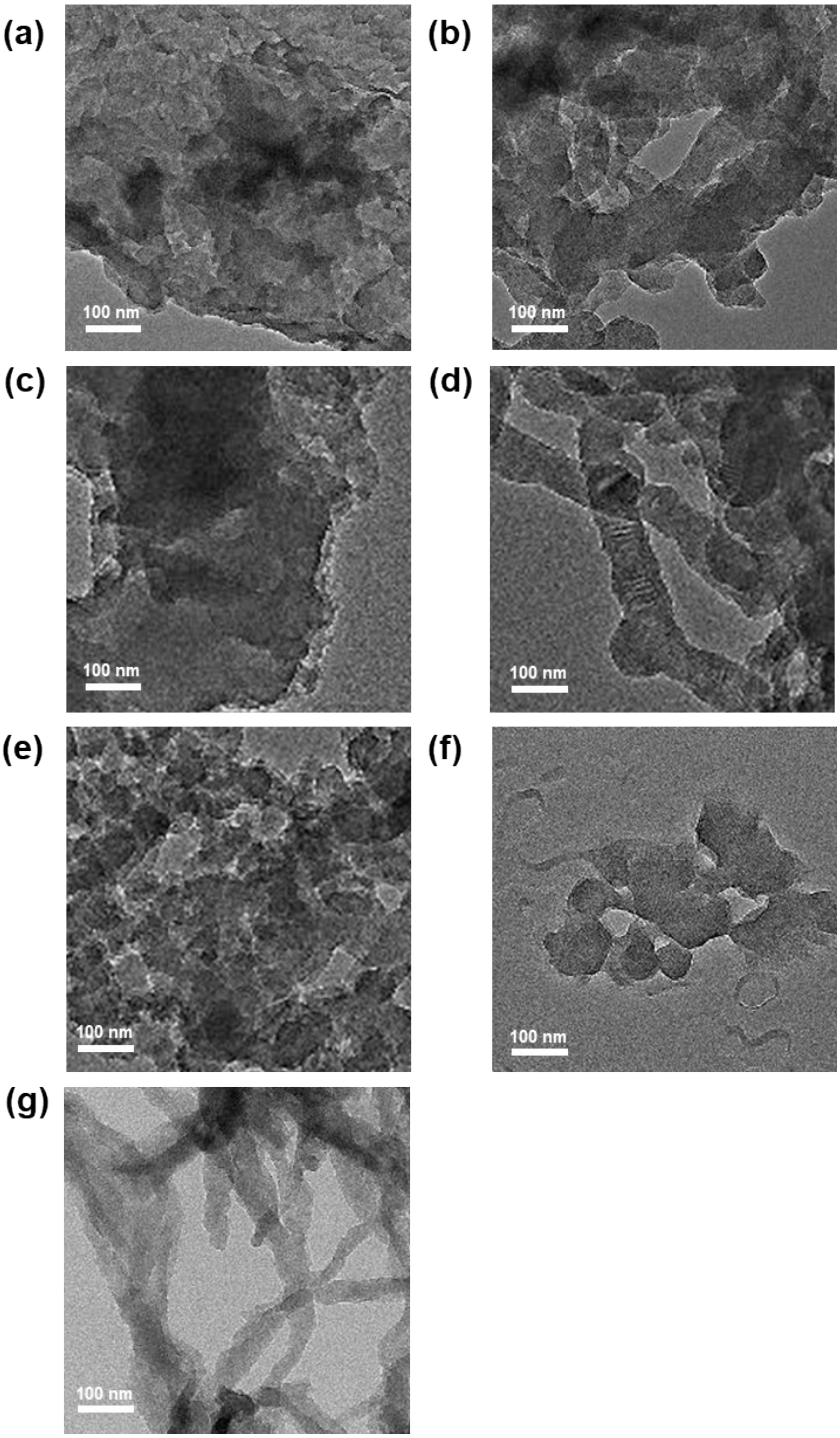


Figure S15. TEM images of (a) COF-960-0, (b) COF-960-1, (c) COF-960-2, (d) COF-960-3, (e) COF-960-4, (f) COF-960-5, and (g) COF-960-6.

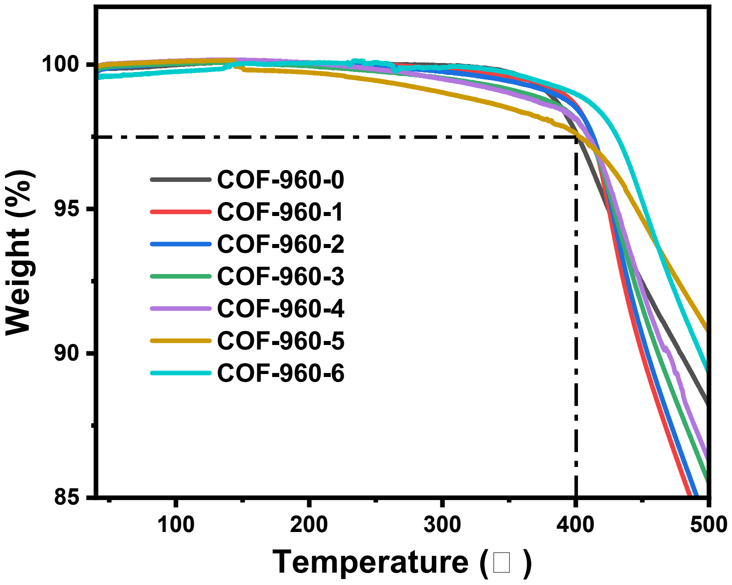


Figure S16 TGA profiles of all COFs.

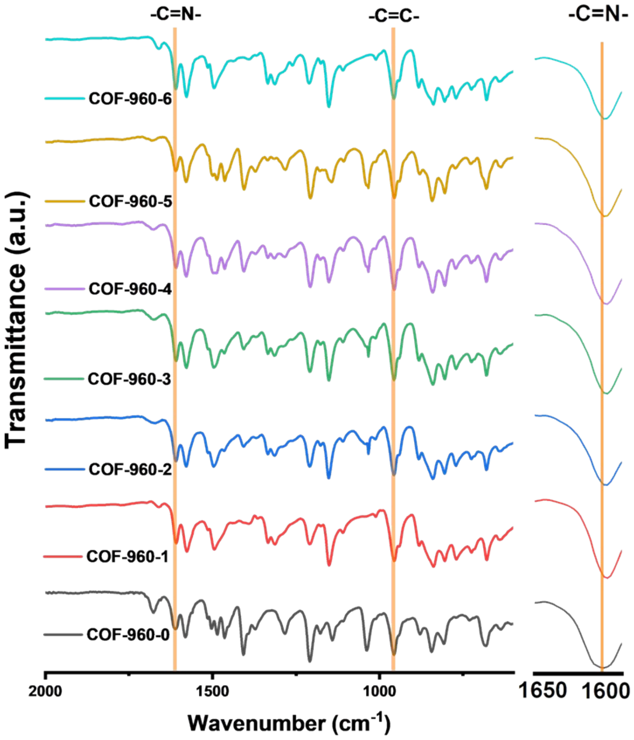


Figure S17 FTIR spectra of COF-960-0, COF-960-1, COF-960-2, COF-960-3, COF-960-4, COF-960-5, and COF-960-6.

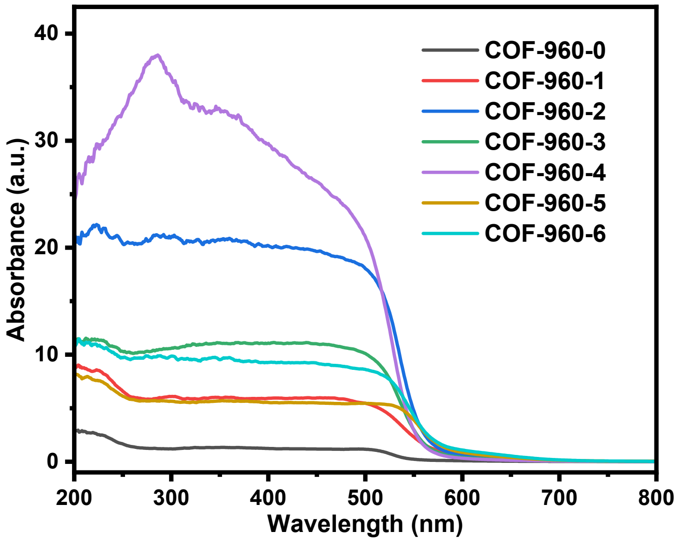


Figure S18 UV-vis spectra of COF-960-0, COF-960-1, COF-960-2, COF-960-3, COF-960-4, COF-960-5, and COF-960-6.

## Electrochemical measurements

Indium-tin oxide (ITO) glasses were firstly cleaned by sonication in ethanol and acetone for 30 min and dried under nitrogen flow. 5 mg of COF powder was mixed with 200 μL ethanol and ultra-sonicated for 30 min to get a slurry. Then 50 μL 5% Nafion was added into the slurry for another 30 min ultra-sonication. The slurry was spreading onto ITO glass. After air drying, the boundary of the electrode was covered with an effective area of 1 $cm^2$. A conventional three electrodes cell was used with a platinum sheet (1 $cm^2$) as the counter electrode and an Ag/AgCl electrode (saturated KCl aqueous solution) as reference electrode. The electrolyte was a 0.2 M $Na_2SO_4$ aqueous solution (pH 6.8) and was purged with nitrogen gas for 1 h prior to the measurements. The working electrodes were immersed in the electrolyte for 60 s before any measurements were taken. The photocurrent measurements were conducted with a CHI760e workstation, with the working electrodes irradiated from the front side. The visible light was generated by a 300W xenon lamp (CEL-HXF300, Beijing China Education Au-light Co., Ltd) with a 420 nm cut-off filter, and was chopped manually. For Mott-Schottky experiments, the perturbation signal was 5 mV with the frequency from 1000-3000 Hz. The electrochemical impedance spectra (EIS) were performed in dark at open-circuit voltage with AC amplitude of 5 mV in the frequencies range of 0.01 Hz to $10^5$ Hz.

The applied potentials vs. Ag/AgCl are converted to RHE potentials using the following equation:

$E_{RHE} = E_{Ag/AgCl} + 0.0591pH + E_{\theta Ag/AgCl}$ ($E_{\theta Ag/AgCl} = 0.199$ V)

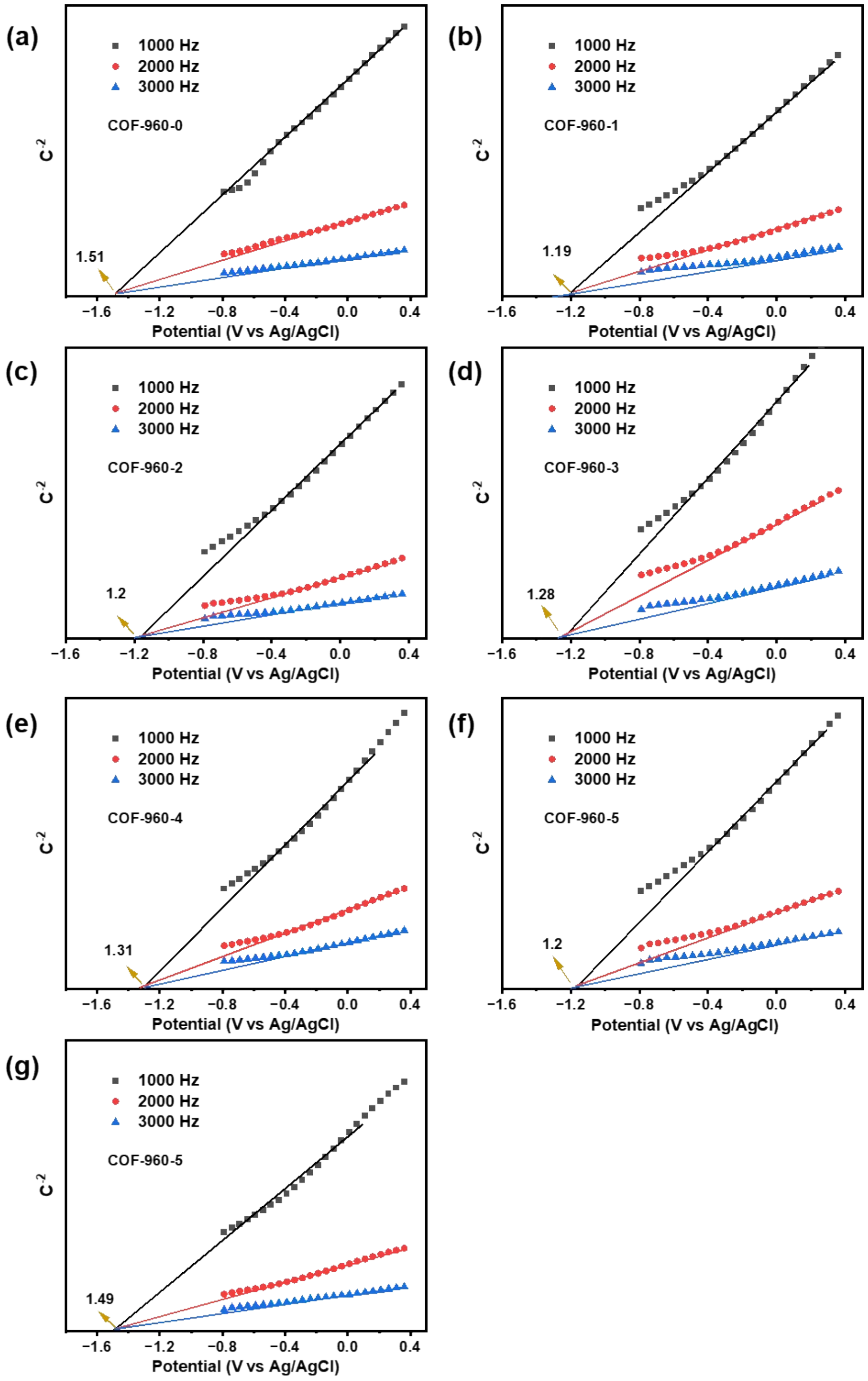


Figure S19. Mott- Schottky plots of (a) COF-960-0, (b) COF-960-1, (c) COF-960-2, (d) COF-960-3, (e) COF-960-4, (f) COF-960-5, and (g) COF-960-6.

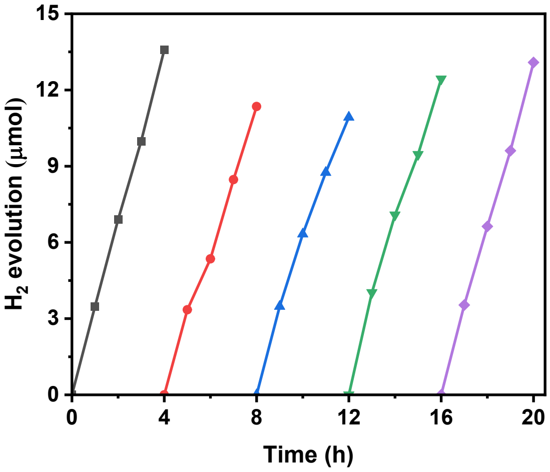


Figure S20 Five-times cycle test of COF-960-5

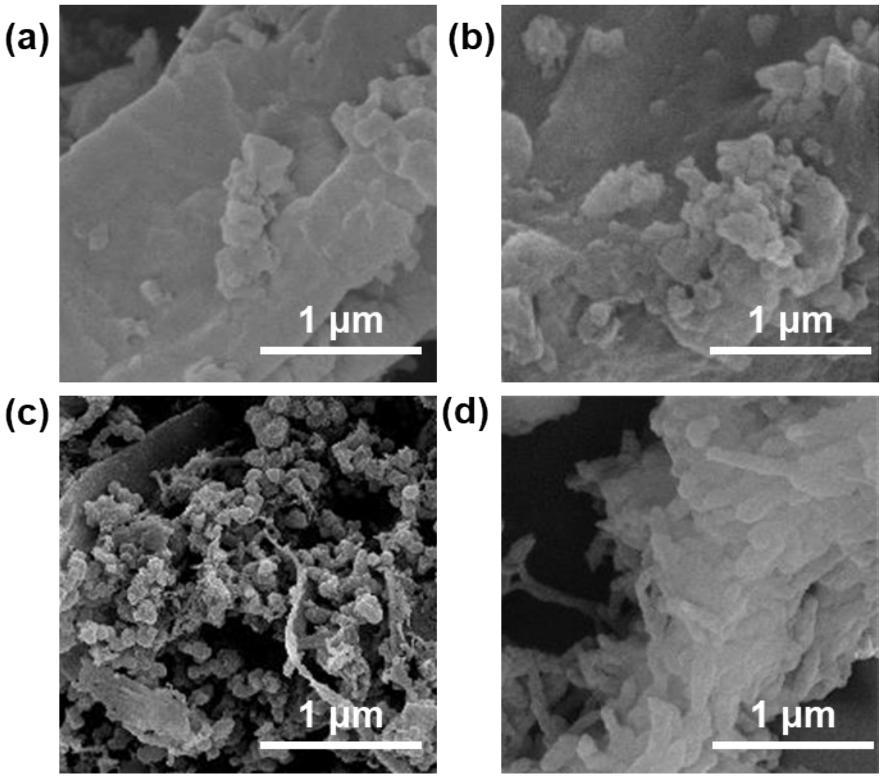


Figure S21. SEM images of (a) COF-960-0, (b) recycled COF-960-0, (c) COF-960-5, and (d) recycled COF-960-5.

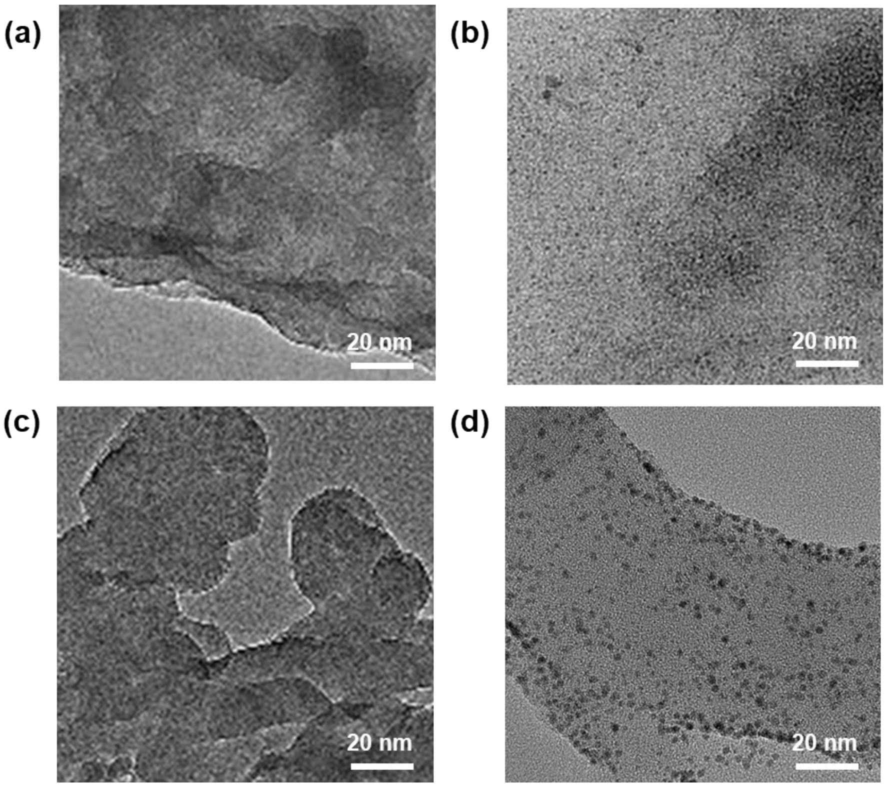


Figure S22. TEM images of (a) COF-960-0, (b) recycled COF-960-0, (c) COF-960-5, and (d) recycled COF-960-5.

## DFT calculations

DFT calculations were carried out using the B3LYP functional and the 6-311G (d, p) basis set as implemented in Gaussian09 program (Revision D. 01). Multiwfn is used for electronic orbitals analysis. Visualisation images of electronic orbitals were obtained from VMD software (version 1.9.3).

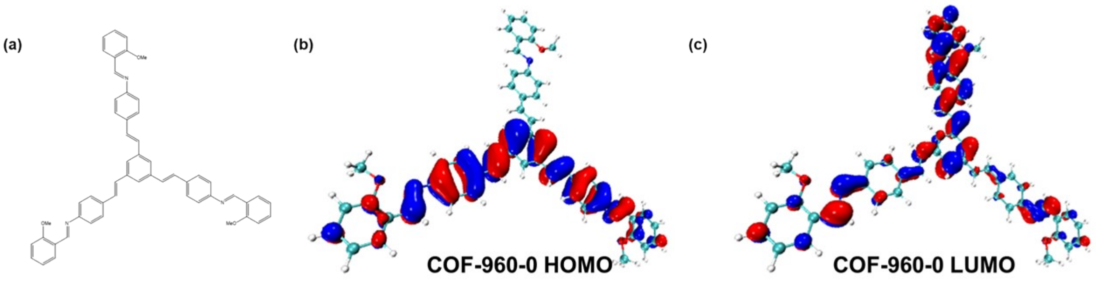


Figure S23. HOMO and LUMO of the fragment of COF-960-0.

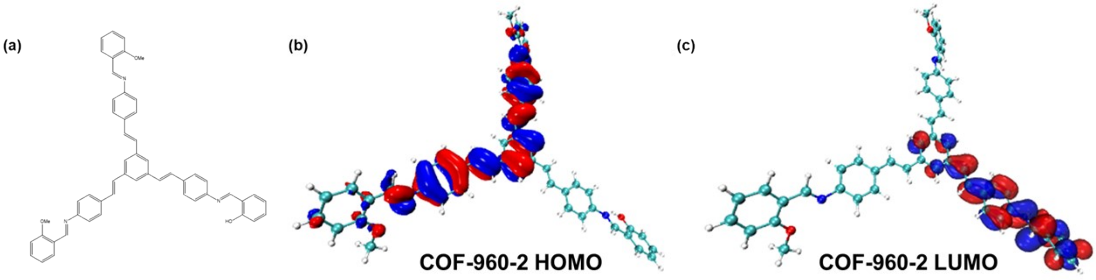


Figure S24. HOMO and LUMO of the fragment of COF-960-2.

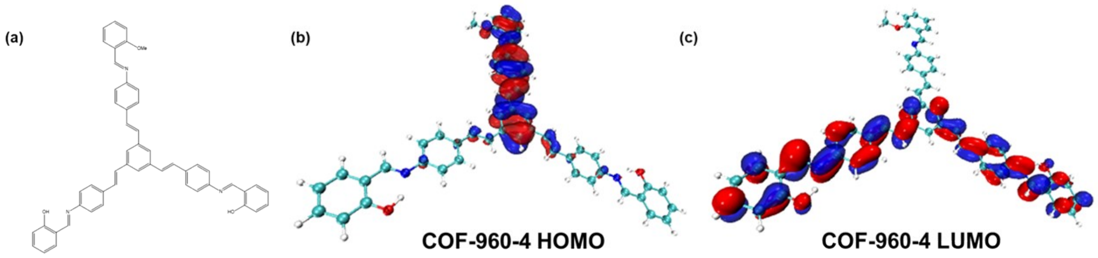


Figure S25. HOMO and LUMO of the fragment of COF-960-4.

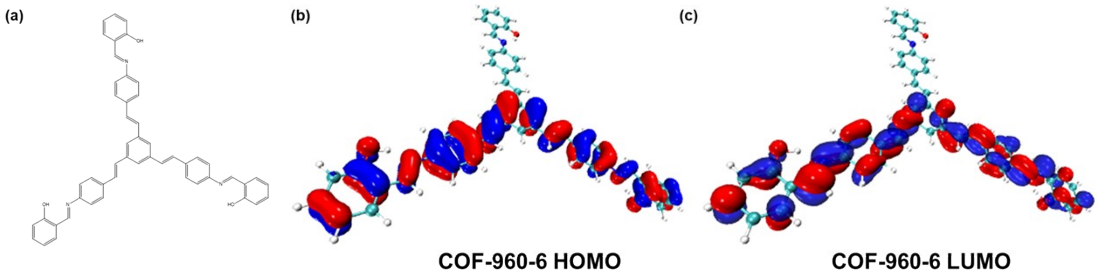


Figure S26. HOMO and LUMO of the fragment of COF-960-6.

## Structural simulation

Molecular modeling of all COFs was generated with the Materials Studio (ver. 8.0) suite of programs. Pawley refinement was carried out using Reflex, a software package for crystal determination from PXRD pattern. Unit cell dimension was set to the theoretical parameters. The Pawley refinement was performed to optimize the lattice parameters iteratively until the $R_{wp}$ value converges and the overlay observed with refined profiles shows good agreement. The lattice models (cell parameters, atomic positions, and total energy) were then fully optimized using Materials Studio Forcite molecular dynamics module method. P1 space group was chosen for the primitive models in the initial simulations.

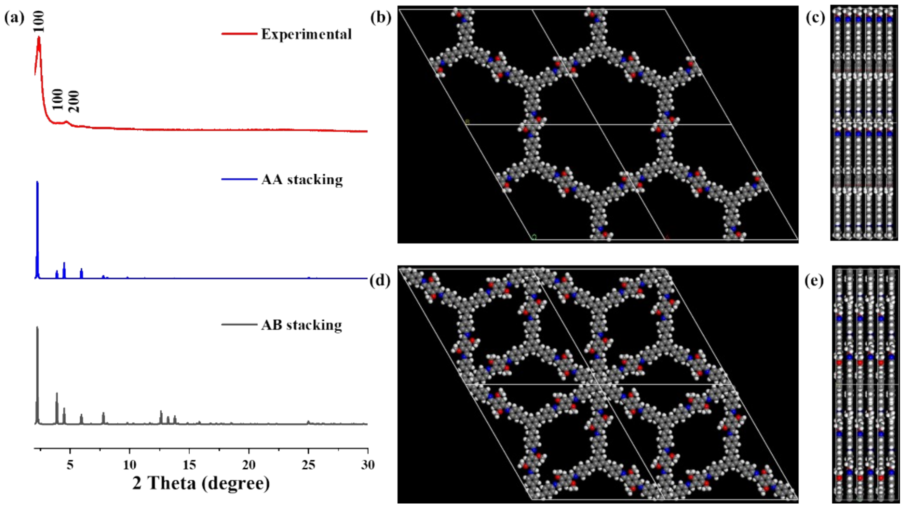


Figure S27. (a) The experimental, simulated AA stacking, simulated AB stacking of COF-960-0; (b) and (c) for top view and side view of simulated AA stacking, respectively; (d) and (e) the top view and side view of AB stacking (gray, carbon; blue, nitrogen; white, hydrogen; and red, oxygen.)

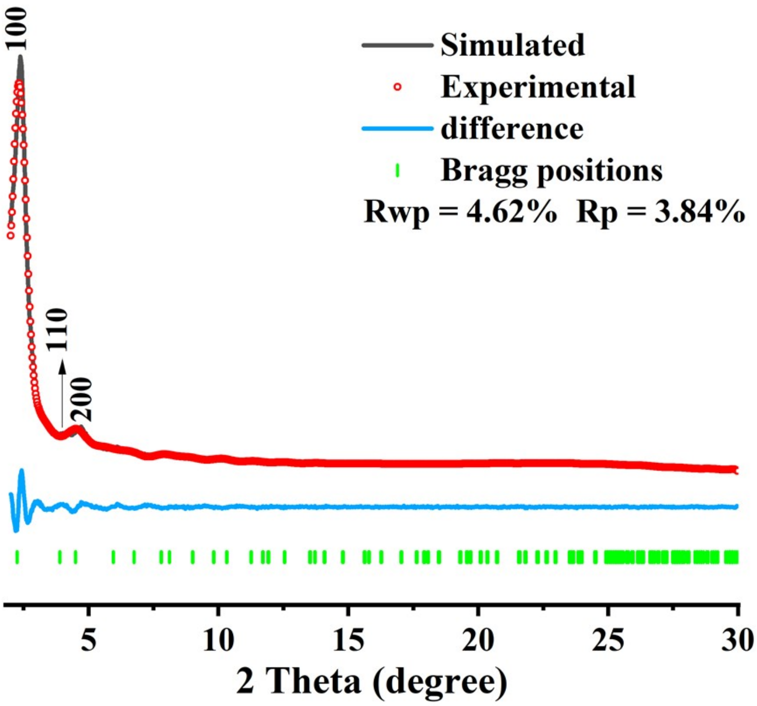


Figure S28. PXRD patterns of COF-960-0

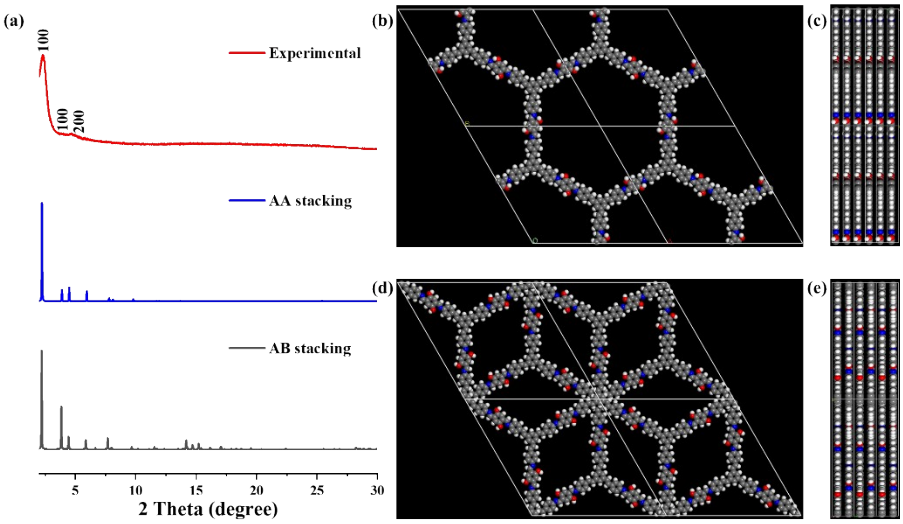


Figure S29. (a) The experimental, simulated AA stacking, simulated AB stacking of COF-960-6; (b) and (c) for top view and side view of simulated AA stacking, respectively; (d) and (e) the top view and side view of AB stacking (gray, carbon; blue, nitrogen; white, hydrogen; and red, oxygen.)

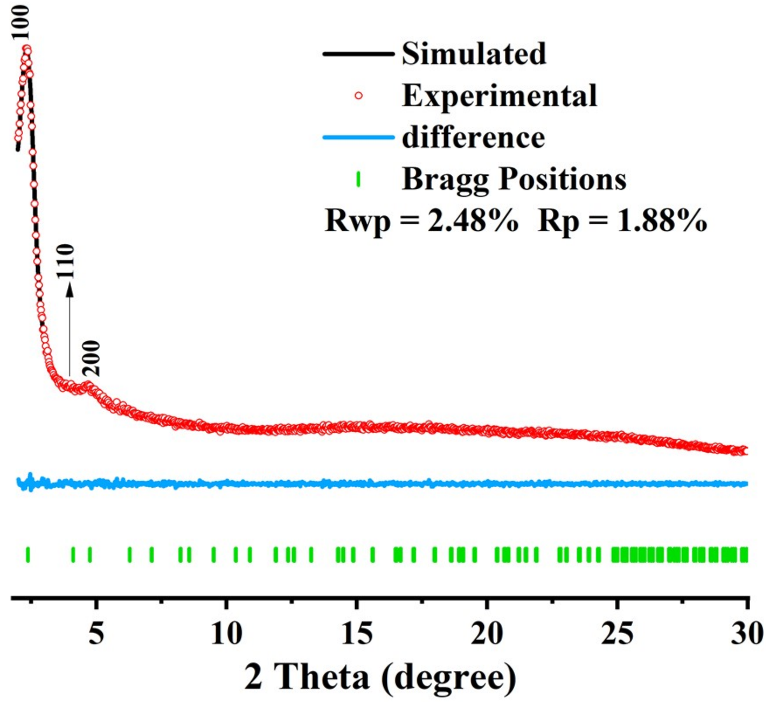


Figure S30. PXRD patterns of COF-960-6

Table S2. Unit cell parameters and fractional atomic coordinates for COF-960-0 based on the AA-stacking.

| Space group | P6 (No. 168) | | |
|---|---|---|---|
| Calculated unit cell | a = b = 45.3898 Å, c = 3.5616 Å<br>α = β = 90°, γ = 120° | | |
| Atom | x/a | y/b | z/c |
| C1 | 0.31097 | 0.67939 | 0.5 |
| C2 | 0.29809 | 0.64413 | 0.5 |
| C3 | 0.35846 | 0.73862 | 0.5 |
| C4 | 0.37035 | 0.60855 | 0.5 |
| C5 | 0.40389 | 0.79852 | 0.5 |
| C6 | 0.38206 | 0.56102 | 0.5 |
| C7 | 0.40445 | 0.54831 | 0.5 |
| C8 | 0.43977 | 0.57069 | 0.5 |
| C9 | 0.45231 | 0.60579 | 0.5 |
| C10 | 0.4299 | 0.61849 | 0.5 |
| N11 | 0.46336 | 0.55849 | 0.5 |
| C12 | 0.45411 | 0.52649 | 0.5 |
| C13 | 0.48587 | 0.96441 | 0.5 |
| C14 | 0.01395 | 0.53507 | 0.5 |
| C15 | 0.02166 | 0.48583 | 0.5 |
| O16 | 0.04328 | 0.472 | 0.5 |
| C17 | 0.0271 | 0.43589 | 0.5 |
| H18 | 0.29278 | 0.68986 | 0.5 |
| H19 | 0.3396 | 0.74827 | 0.5 |
| H20 | 0.34211 | 0.58871 | 0.5 |
| H21 | 0.35344 | 0.54265 | 0.5 |
| H22 | 0.39408 | 0.51967 | 0.5 |
| H23 | 0.48092 | 0.62418 | 0.5 |
| H24 | 0.44027 | 0.64712 | 0.5 |
| H25 | 0.42594 | 0.50646 | 0.5 |
| H26 | 0.02506 | 0.56383 | 0.5 |
| H27 | 0.0426 | 0.42757 | 0.67682 |
| H28 | 0.02528 | 0.42641 | 0.19981 |
| H29 | 0.00046 | 0.42474 | 0.62337 |

Table S3. Unit cell parameters and fractional atomic coordinates for COF-960-6 based on the AA-stacking.

| Space group | P6 / m (No. 175) | | |
|---|---|---|---|
| Calculated unit cell | a = b = 45.2930 Å, c = 3.5208 Å<br>α = β = 90°, γ = 120° | | |
| Atom | x/a | y/b | z/c |
| C1 | 0.31228 | 0.68099 | -0.5 |
| C2 | 0.29763 | 0.64537 | -0.5 |
| C3 | 0.36174 | 0.73972 | -0.5 |
| C4 | 0.36939 | 0.60704 | -0.5 |
| C5 | 0.40681 | 0.7996 | -0.5 |
| C6 | 0.37878 | 0.55799 | -0.5 |
| C7 | 0.39984 | 0.54387 | -0.5 |
| C8 | 0.43548 | 0.5649 | -0.5 |
| C9 | 0.44947 | 0.59982 | -0.5 |
| C10 | 0.42848 | 0.61403 | -0.5 |
| N11 | 0.45837 | 0.55197 | -0.5 |
| C12 | 0.451 | 0.523 | -0.5 |
| C13 | 0.48784 | 0.96458 | -0.5 |
| C14 | 0.01198 | 0.53493 | -0.5 |
| C15 | 0.02302 | 0.4877 | -0.5 |
| O16 | 0.04402 | 0.47362 | -0.5 |
| H17 | 0.0666 | 0.48964 | -0.5 |
| H18 | 0.29631 | 0.69239 | 0.5 |
| H19 | 0.34527 | 0.74849 | 0.5 |
| H20 | 0.34417 | 0.59067 | 0.5 |
| H21 | 0.3514 | 0.54138 | 0.5 |
| H22 | 0.38811 | 0.51663 | 0.5 |
| H23 | 0.47688 | 0.61603 | 0.5 |
| H24 | 0.44039 | 0.64123 | 0.5 |
| H25 | 0.42555 | 0.50569 | 0.5 |
| H26 | 0.02066 | 0.56194 | 0.5 |