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Chemical Synthesis

Supplementary Material

Catalyst-free solid-state cross-linking of covalent organic frameworks in confined space

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Section S1. Materials and Characterizations

S1.1. Materials

All chemicals and solvents were purchased from commercial suppliers. 4,4′-diaminobiphenyl (DABP) and 4,4″-diamino-p-terphenyl (DATP) were purchased from Aladdin®. 1,2-dichlorobenzene (*o*-DCB), *N,N*-dimethylacetamide (DMAc) and diphenyl sulfone were obtained from J&K scientific LTD. Acetic acid and organic solvents including dichloromethane (DCM), *n*-hexane, acetone and tetrahydrofuran (THF) were purchased from Xilong Scientific. 1,3,5-tri(4-formylphenylethynyl)benzene (TFPEB) was synthesized. All reagents and solvents were used without further purification unless otherwise specified.

S1.2. Characterizations

Nuclear magnetic resonance (NMR) spectroscopy. ^{1}H NMR spectra were measured on a Bruker Fourier 400 MHz spectrometer. Solid-state NMR spectra were recorded at ambient pressure on a Bruker Fourier 600 MHz spectrometer using a standard CP pulse sequence probe with 3.2 mm (outside diameter) zirconia rotors.

Fourier transform infrared (FT-IR) spectroscopy. The FT-IR spectra (KBr) were obtained using a SHIMADZU IRAffinity-1 Fourier transform infrared spectrophotometer. A SHIMADZU UV-2450 spectrophotometer was used for all absorbance measurements.

Powder X-ray diffraction (PXRD) analysis. Powder X-ray diffraction (PXRD) patterns were carried out in reflection mode on a Bruker D8 advance powder diffractometer with Cu Kα (λ = 1.5418 Å) line focused radiation at 40 kV and 40 mA from 2^{θ} = 1.0 ° up to 40 ° with 0.020481 increment by Bragg-Brentano. The powdered sample was added to the glass and compacted for measurement.

Thermogravimetric analysis (TGA). Thermogravimetric analysis (TGA) was recorded on a SHIMADZU DTG-60 thermal analyzer under N_2. The operational range of the instrument was from 30 to 800 °C at a heating rate of 10 °C min^{-1} with N_2 flow rate of 30 mL min^{-1}.

Raman spectroscopy characterization. Raman spectra were recorded on a Renishaw inVia-Reflex confocal Raman microscope with an excitation wavelength of 325 nm.

X-ray photoelectron spectroscopy (XPS). XPS was obtained on an ESCALAB 250 spectrophotometer with Al-Kα radiation. The binding energy (BE) values were referred to the C single bond (C, H) contribution of the C 1s peak fixed at 284.8 eV.

Atomic force microscope (AFM). AFM images were obtained by testing with German Bruker Dimension 3100 instrument in tapping mode.

Electron paramagnetic resonance (EPR). EPR spectra are recorded on a Bruker EMXplus-10/12 spectrometer under room temperature. The microwave frequency was 9.8 GHz and the modulation amplitude microwave power was about 2 mW.

Nitrogen isotherm measurements. Nitrogen sorption experiments were performed at 77 K up to 1 bar using a nanometric sorption analyzer. The adsorption–desorption isotherms of N_2 were obtained at 77 K using a BELSORP MAX gas sorption analyzer. Before sorption analysis, the sample was evacuated at 100 ^{o}C for 12 h using a turbomolecular vacuum pump. Specific surface areas were calculated from nitrogen adsorption data by multipoint BET analysis. Quenched solid density functional theory (QS-DFT) was applied to analyze the N_2 isotherm based on the model of N_2@77 K on carbon with cylindrical pores.

Scanning electron microscopy (SEM). Scanning electron microscopy (SEM) was performed on a Zeiss Gemini SEM 300 microscope instrument. Samples were prepared by dispersing the material onto conductive adhesive tapes attached to a flat aluminum sample holder and then coated with gold.

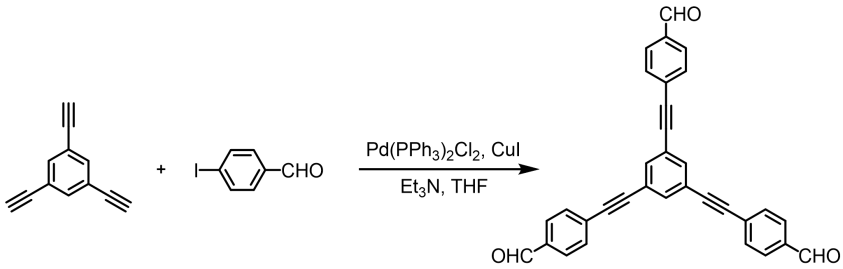
Transmission electron microscope (TEM). High resolution transmission electron microscope (HR-TEM) analysis was collected on a JEOL JEM-2100 microscope instrument at 200 kV. synthesized sample was dispersed into ethyl alcohol to obtain a highly dispersed suspension. Then, one droplet was transferred onto a carbon film supported TEM grid.

Electrical conductivity measurements. Electrochemistry experiments were conducted on a CHI660C Electrochemical Workstation (Shanghai ChenHua Electrochemical Instrument). The obtained powder was grinded before adding into a 0.5-cm die. Then the pressure of die was slowly increased to 4.0 MPa and kept for 1 hours to prepared pellets (diameter = 0.5 cm, thickness = 0.5 cm). Two pieces of gold (diameter = 0.5 cm) with wires are attached to both sides of the pellet. The current-voltage (I-V) measurement was performed in conditions by sweeping the voltage from -1.0 V to 1.0 V. The obtained conductivity was collected at 25 °C in N_2 atmosphere.

Density Functional Theory Calculations. frontier orbital calculations were performed at the Generalized gradient approximation (GGA) level in the form of Perdew-Burke-Ernzerhoff (PBE),[1] using the Dmol3 module in Materials Studio version 8.0[2]. The convergence criterion of 10^{-6} eV with max to 50 cycles was used for self-consistent field (SCF).

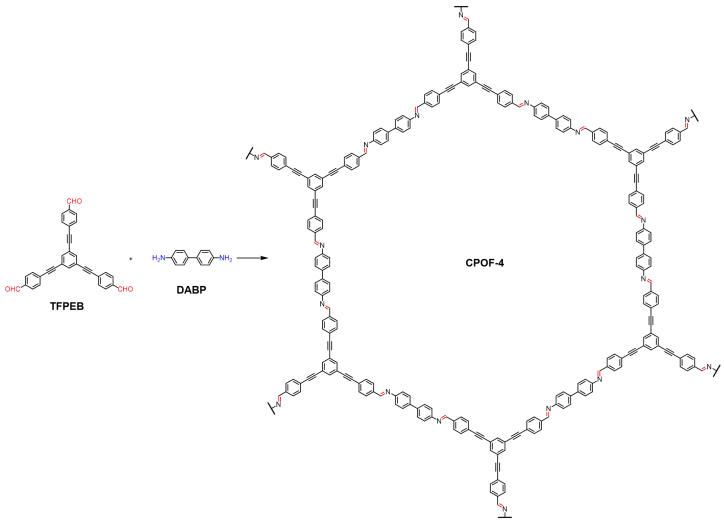
Section S2. Synthetic Procedures

Synthesis of 1,3,5-tri(4-formylphenylethynyl)benzene (TFPEB).



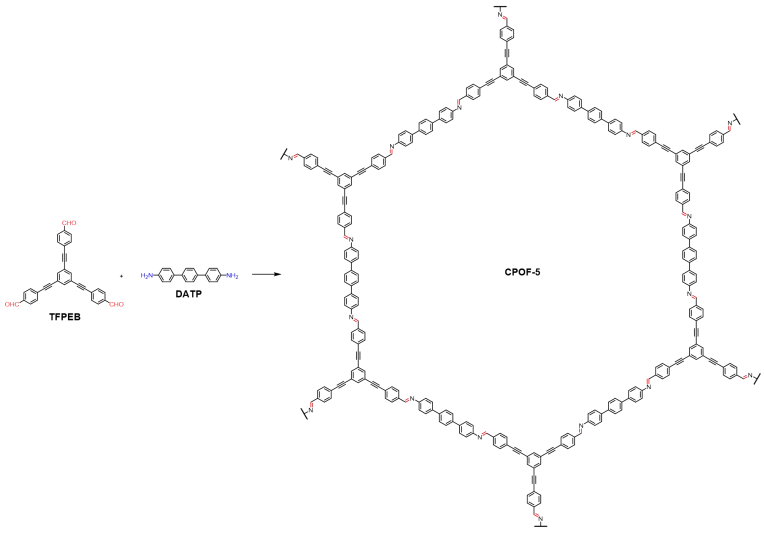
Under a nitrogen atmosphere, 1,3,5-triethynylbenzene (1.2 g, 8.0 mmol, 1.0 eq.), 4-iodobenzaldehyde (5.6 g, 24.0 mmol, 3.0 eq.), dichlorobis(triphenylphosphine)palladium(II) (0.34 g, 0.48 mmol, 0.02 eq.) were dissolved in 200 mL of anhydrous THF, Dry triethylamine (8.0 mL, 57 mmol) was added and the mixture stirred for 10 mins, then the catalyst copper(I) iodide (0.19 g, 1.0 mmol, 0.04 eq.) was added, turning the solution to dark brown. After stirring for 16 h at room temperature, the solvent was evaporated at reduced pressure and the mixture was washed with brine saturated solution of NH_4Cl and extracted with DCM. The purification was made by column chromatography on silica gel using dichloromethane as eluent to afford the desired product as a colorless solid (2.18 g, Yield: 59%); ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 10.04 (s, 3H), 7.90 (d, J = 8.3 Hz, 6H), 7.74 (s, 3H), 7.69 (d, J = 8.2 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$): δ_C 191.5, 136.0, 135.0, 132.4, 129.8, 128.9, 123.8, 91.3, 90.1.

Preparation of CPOF-4



A Pyrex tube measuring o.d. × i.d. = 10 × 8 mm^2 was charged with 1,3,5-Tri(4-formylphenylethynyl)benzene (TFPEB, 13.9 mg, 0.03 mmol), 4,4′-diaminobiphenyl (DABP, 8.3 mg, 0.045 mmol) in a mixed solution of o-dichlorobenzene (0.5 mL), dimethylacetamide (0.5 mL) and 6.0 M acetic acid (0.1 mL). The Pyrex tube was flash frozen in a liquid nitrogen bath sealed under vacuum. Upon warming to room temperature, the tube was placed in an oven at 120 °C for three days. The yellow solid was isolated by filtration and washed with THF (3 × 15 mL), acetone (3 × 15 mL) and *n*-hexane (3 × 15 mL). The powder was dried at 80 ºC under vacuum overnight to afford the CPOF-4 as a yellow crystalline solid (15.4 mg, Yield: 75%).

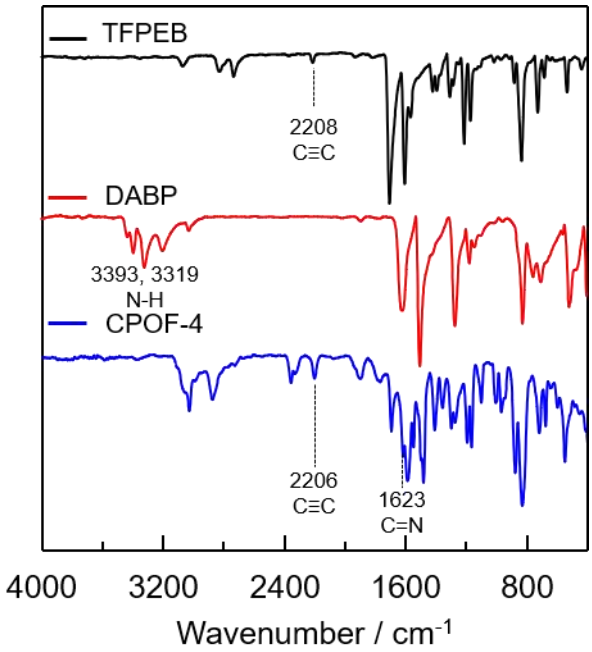
Preparation of CPOF-5



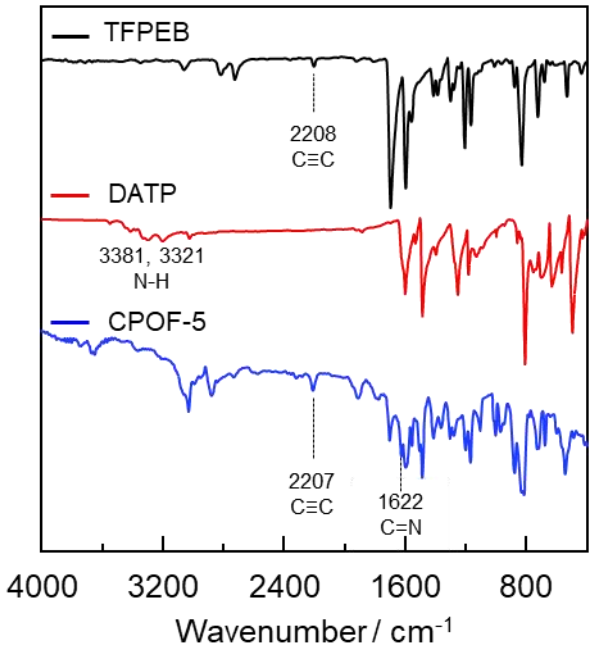
A Pyrex tube measuring o.d. × i.d. = 10 × 8 mm^2 was charged with 1,3,5-Tri(4-formylphenylethynyl)benzene (TFPEB, 13.9 mg, 0.03 mmol), 4,4″-diamino-*p*-terphenyl (DATP, 11.7 mg, 0.045 mmol) in a mixed solution of o-dichlorobenzene (0.5 mL), dimethylacetamide (0.5 mL) and 6.0 M acetic acid (0.1 mL). The Pyrex tube was flash frozen in a liquid nitrogen bath sealed under vacuum. Upon warming to room temperature, the tube was placed in an oven at 120 °C for three days. The yellow solid was isolated by filtration and washed with THF (3 × 15 mL), acetone (3 × 15 mL) and *n*-hexane (3 × 15 mL). The powder was dried at 80 ºC under vacuum overnight to afford the CPOF-5 as a yellow crystalline solid (17.1 mg, Yield: 71%).

Synthesis and activation of CL-COFs. For example, a 5 mL vial charged with CPOF-4 (100.0 mg) and diphenyl sulfone (3 g), The vial was then transferred to a tubular furnace and evacuated-filled with N_2 by five cycles. subsequently, the temperature was raised to 265 °C at the rate of 10 °C/min in N_2 flowing atmosphere with the flow rate of 20 mL/min. After heating at 265 °C for a certain period of time, the temperature was reduced to room temperature at the rate of 10 °C/min. Finally, the obtained product was washed with THF and acetone to remove the residual diphenyl sulfone, dried at 120 ºC under vacuum over-night to afford the CPOF-4-265 ºC-*X* h (*X*= 12, 48 and 84) as a brown black crystalline solid. Similarly, the thermally cross-linked products of CPOF-5 are named CPOF-5-265 ºC-*X* h (*X*= 48 and 84).

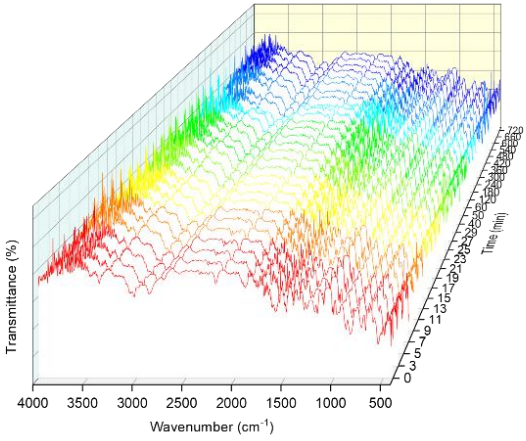
Section S3. Fourier-transform infrared spectroscopy



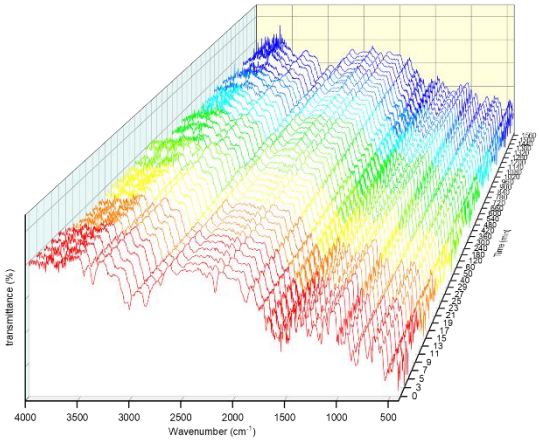
Supplementary Figure 1. FT-IR spectra of CPOF-4 (blue), DABP (red), TFPEB (black).



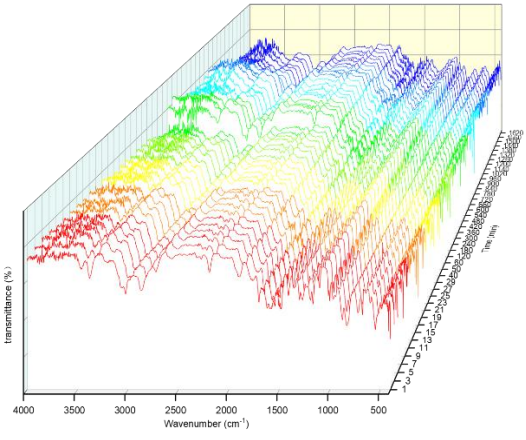
Supplementary Figure 2. FT-IR spectra of CPOF-5 (blue), DATP (red), TFPEB (black).



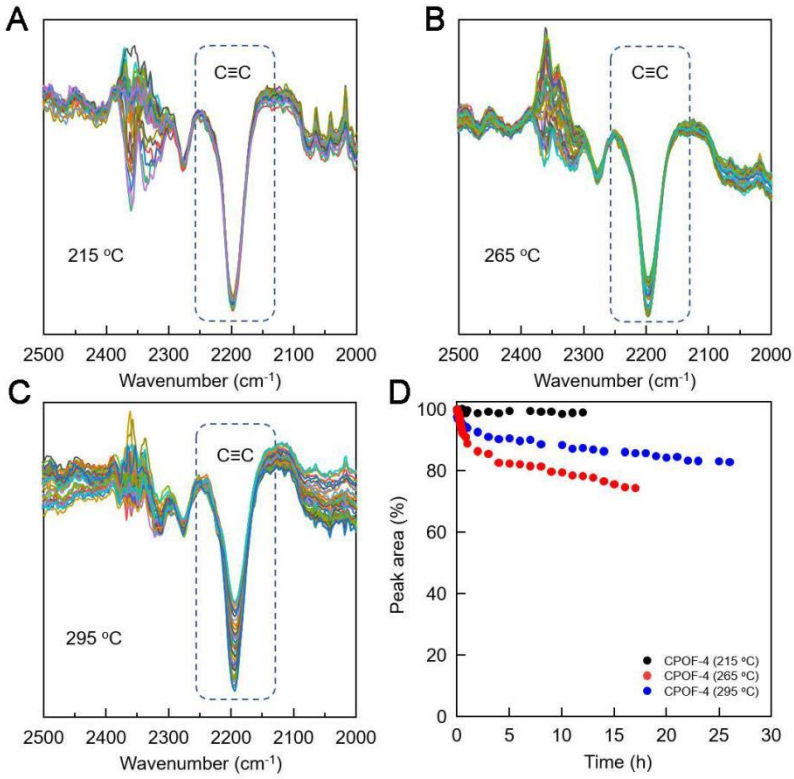
Supplementary Figure 3. In-situ variable temperature FT-IR of CPOF-4 at 215 °C.



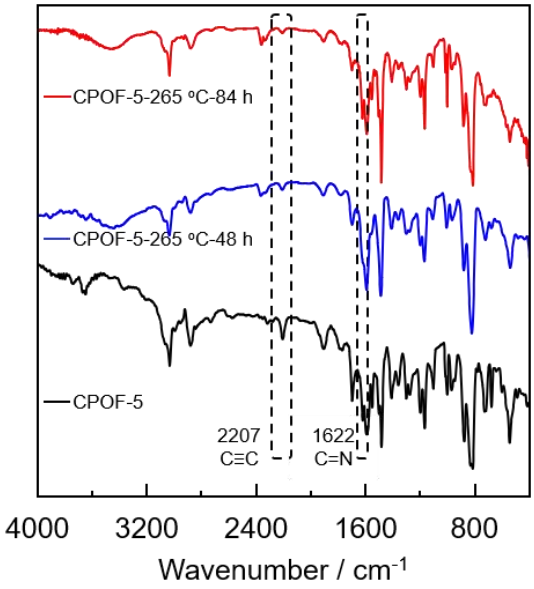
Supplementary Figure 4. In-situ variable temperature FT-IR of CPOF-4 at 265 °C.



Supplementary Figure 5. In-situ variable temperature FT-IR of CPOF-4 at 295 °C.

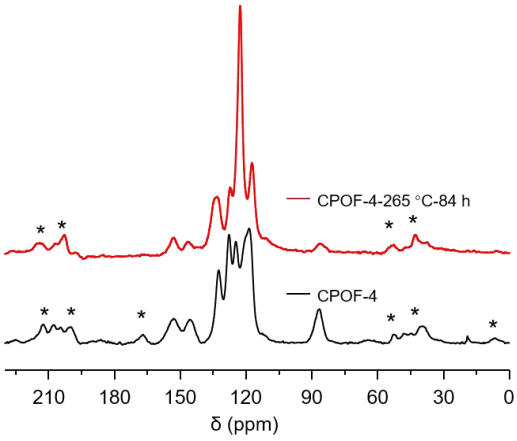


Supplementary Figure 6. (A-C) *In-situ* variable temperature FT-IR of CPOF-4 at 215 °C, 265 °C and 295 °C respectively; (D) Temperature induced variations in the peak area of C≡C stretching.

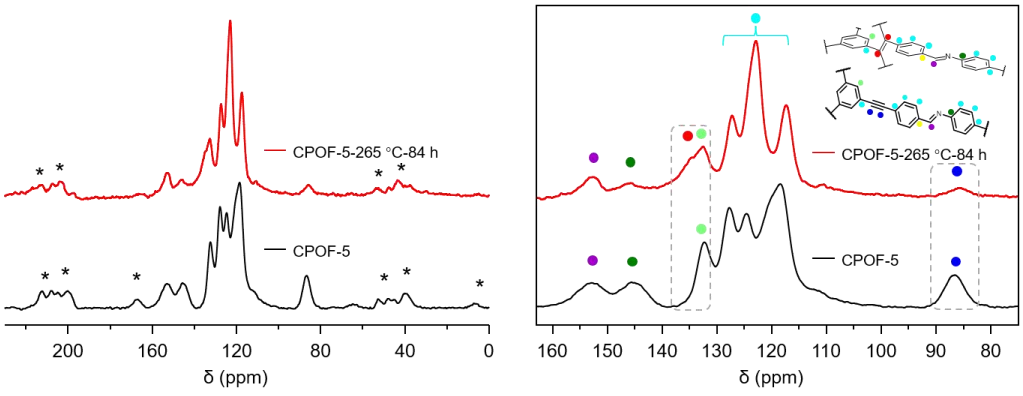


Supplementary Figure 7. FT-IR spectra analyses of CPOF-5 compared with the CPOF-5-265 °C-48 h and CPOF-5-265 °C-84 h.

Section S4. Solid-state ^{13}C NMR spectra



Supplementary Figure 8. ^{13}C CP-MAS NMR spectra of CPOF-4 and CPOF-4-265 °C-84 h.



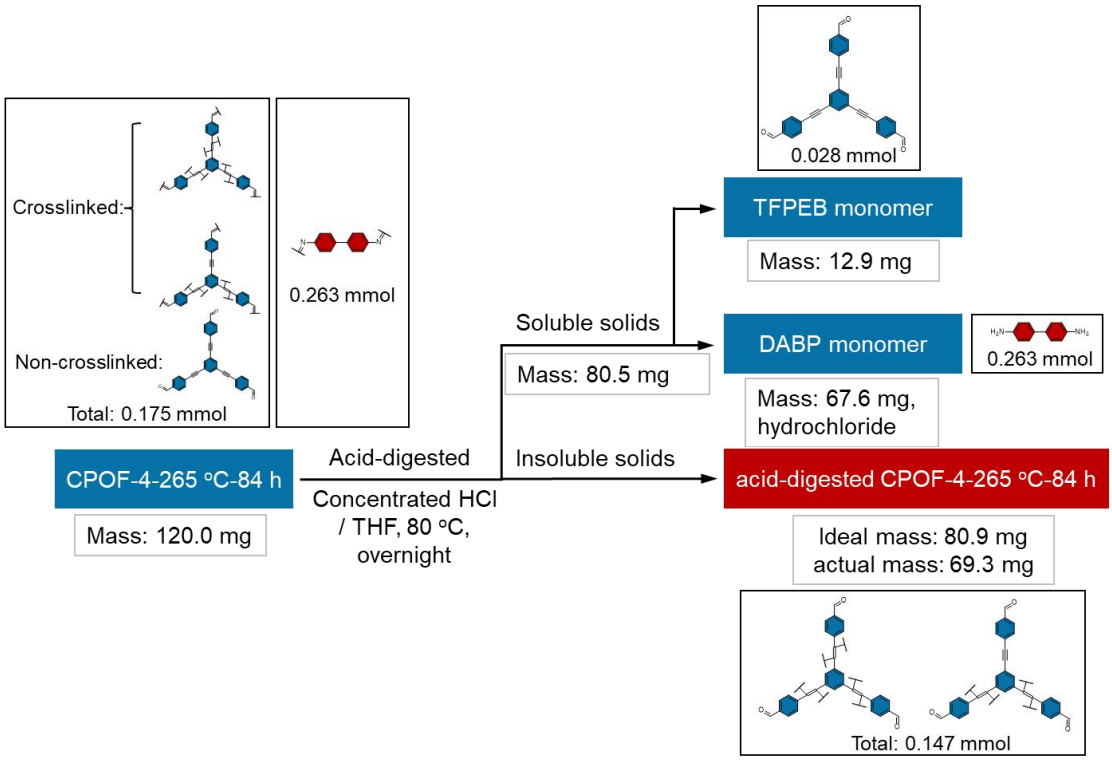
Supplementary Figure 9. ^{13}C CP-MAS NMR spectra of CPOF-5 and CPOF-5-265 °C-84 h.

Section S5. Acid-digested CPOF-4-265 ºC-84 h

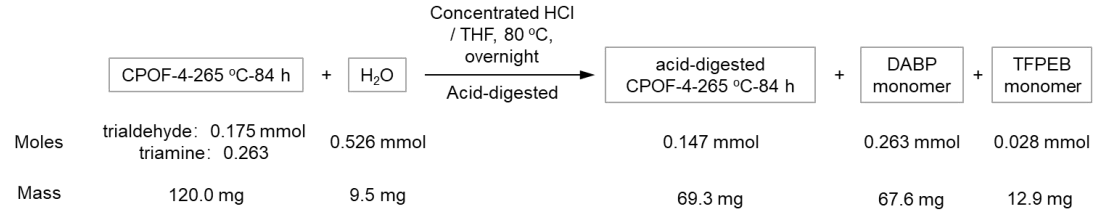
Since the conversion rate of the acetylenic groups in COFs was not particularly high, a small fraction of the original COF remained in the products, posing interference to the analysis and characterization of polyacetylene. Fortunately, the reversible imine bonds could be easily broken under acidic conditions. Thus, the acid hydrolysis experiment on CPOF-4-265 °C-84 h effectively removed the non-crosslinked residues (soluble fraction) from the reaction, while preserving the formed polyacetylene chain structures (insoluble fraction). This approach facilitated the direct characterization of polyacetylene formation.

The activated CPOF-4-265 ºC-84 h (120 mg), concentrated hydrochloric acid (5.0 mL) and THF (15.0 mL) were added into a flask. The mixture was heated at 80 ºC for overnight under nitrogen atmosphere. After cooling to room temperature, the insoluble solid was isolated by filtration and washed with deionized water, MeOH, THF and dried at 80 ºC under vacuum overnight. The collected filtrate was rotary evaporated to remove all solvents and used for subsequent characterization analysis.

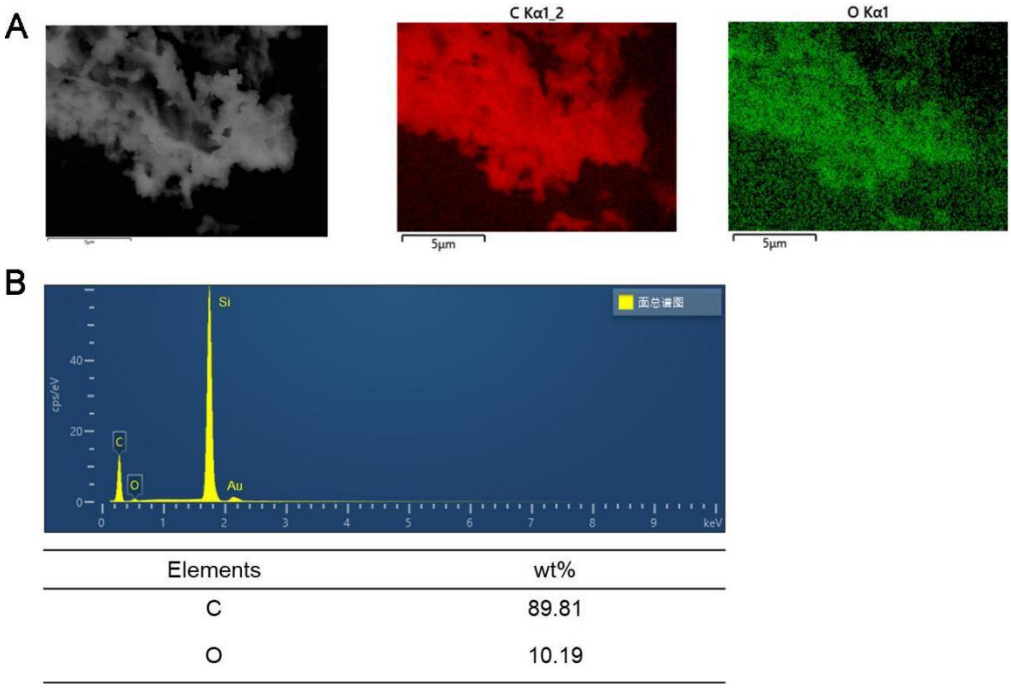
As depicted in Supplementary Figure 10, CPOF-4-265 °C-84 h comprised crosslinked and non-crosslinked segments. Following acid hydrolysis, the non-crosslinked segments were soluble in organic solvents, and characterization of the resulting soluble solid was achieved through ^{1}H-NMR spectroscopy after solvent removal. Additionally, since biphenylamine, uninvolved in the crosslinking reaction, is fully released upon hydrolysis, thus, the soluble TFPEB monomer can be quantified through ^{1}H-NMR. The measured weight of the insoluble solid obtained after acid hydrolysis was 69.3 mg, which was lower than the theoretical mass (assuming complete crosslinking of the acetylenic groups). This discrepancy can be primarily attributed to the presence of a small amount of soluble TFPEB monomer in the hydrolysis products. Additionally, precise weighing of the products obtained during the hydrolysis reaction indicated that the process adhered to the principle of mass conservation.



Supplementary Figure 10. Schematic diagram of hydrolysate analysis process.

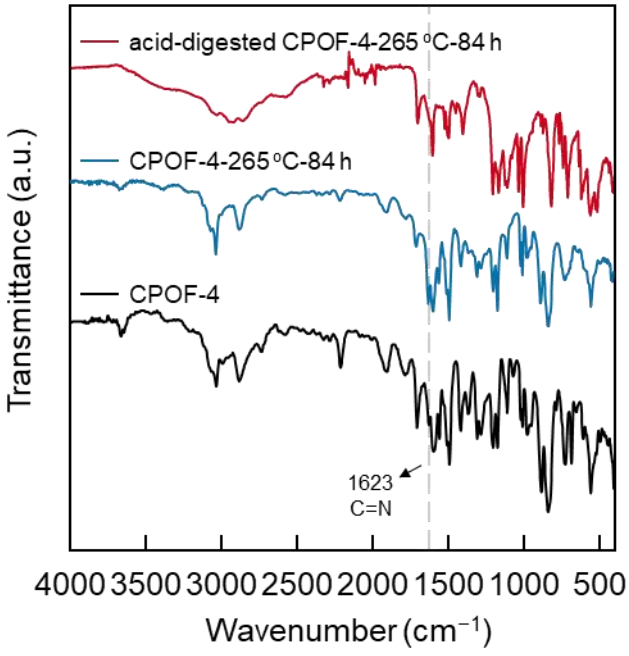


Supplementary Figure 11. The hydrolysis reaction equation of CPOF-4-265 °C-84 h.

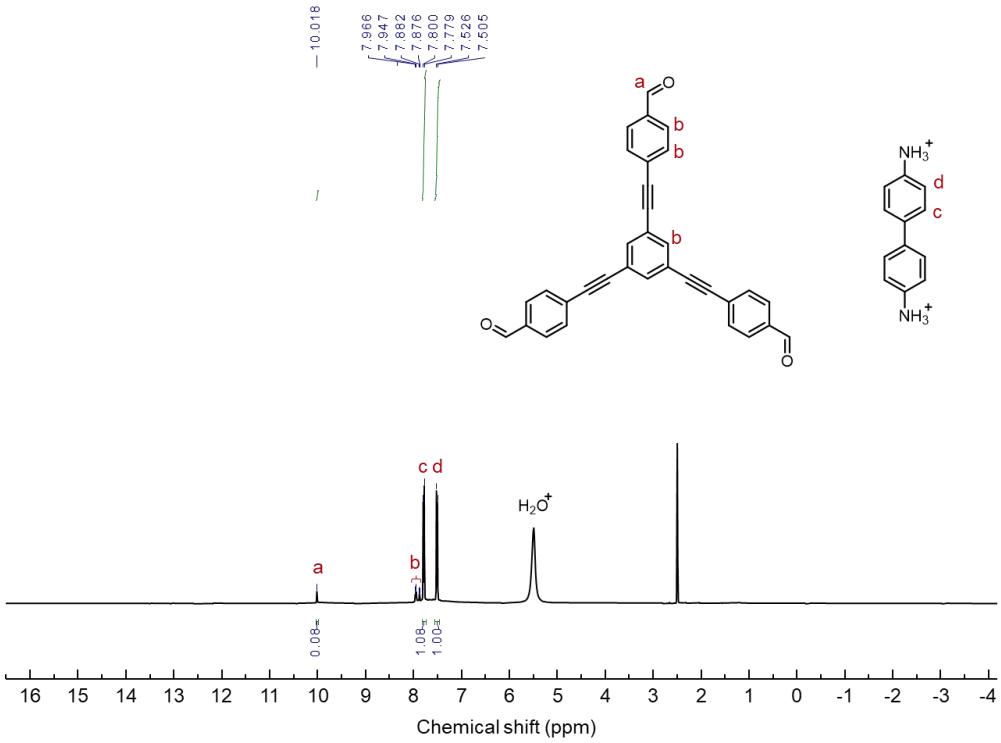


Elements	wt%
C	89.81
O	10.19

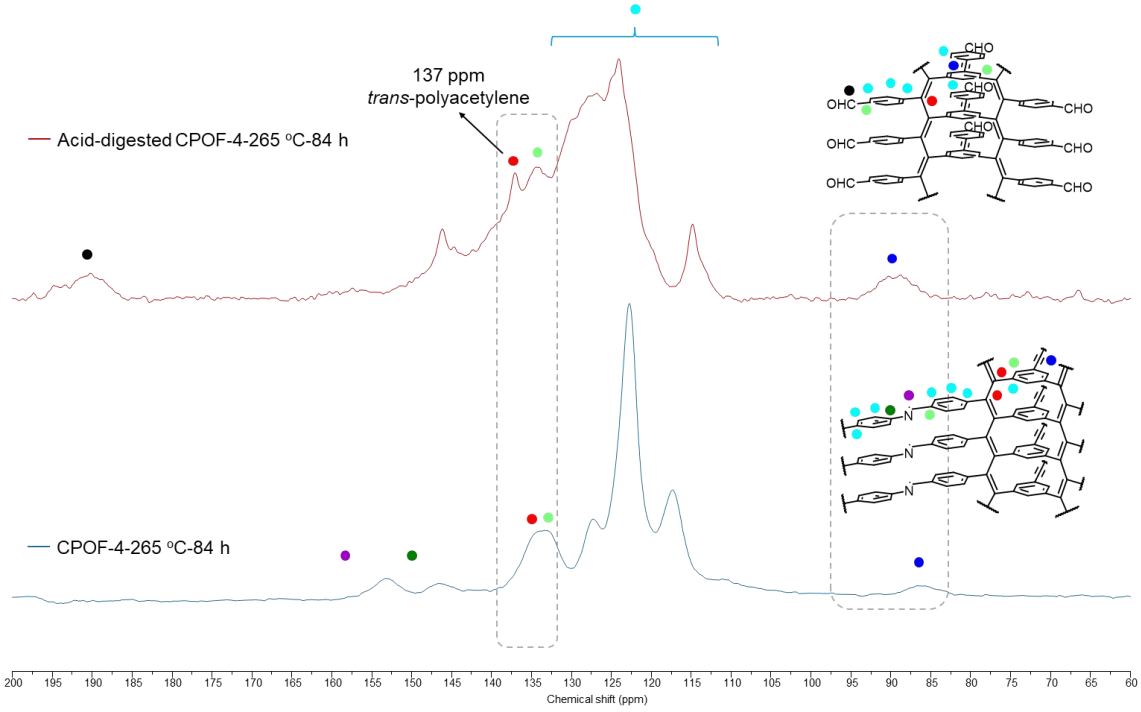
Supplementary Figure 12. (A) SEM mapping images of elements C and O in acid-digested CPOF-4-265 ºC-84 h; (B) EDS elementals content analysis from SEM-related EDS in acid-digested CPOF-4-265 ºC-84 h.



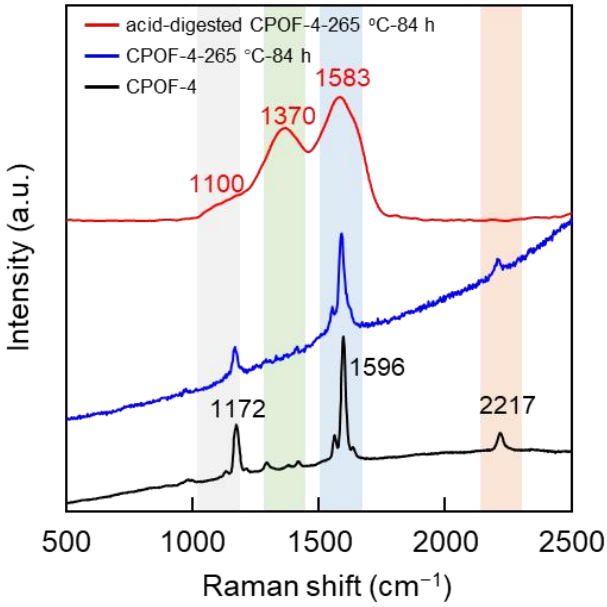
Supplementary Figure 13. FT-IR spectra of CPOF-4 (black), CPOF-4-265 ºC-84 h (dark blue), and acid-digested CPOF-4-265 ºC-84 h (red), the characteristic peak of imine bond disappeared after hydrolysis.



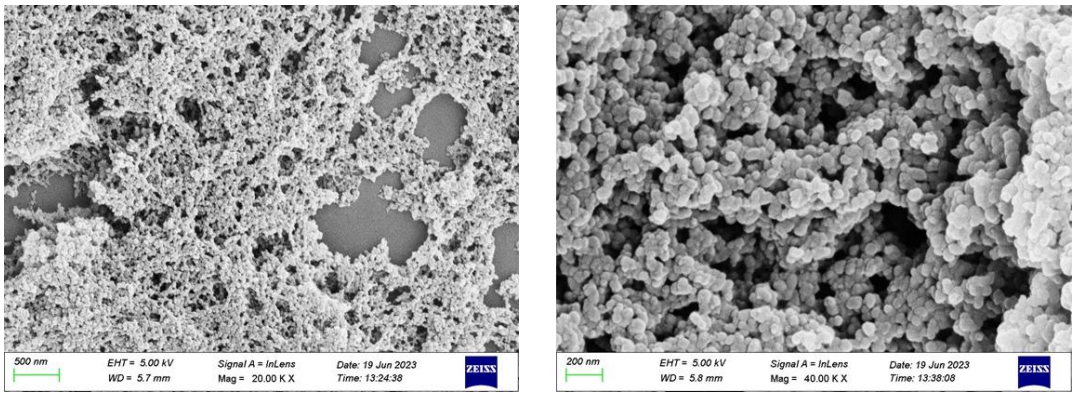
Supplementary Figure 14. The ^{1}H NMR spectra of soluble solids.



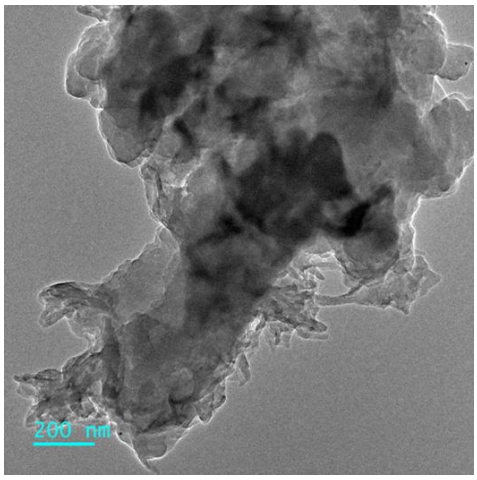
Supplementary Figure 15. ^{13}C CP-MAS NMR spectra of CPOF-4-265 °C-84 h and acid-digested CPOF-4-265 °C-84 h



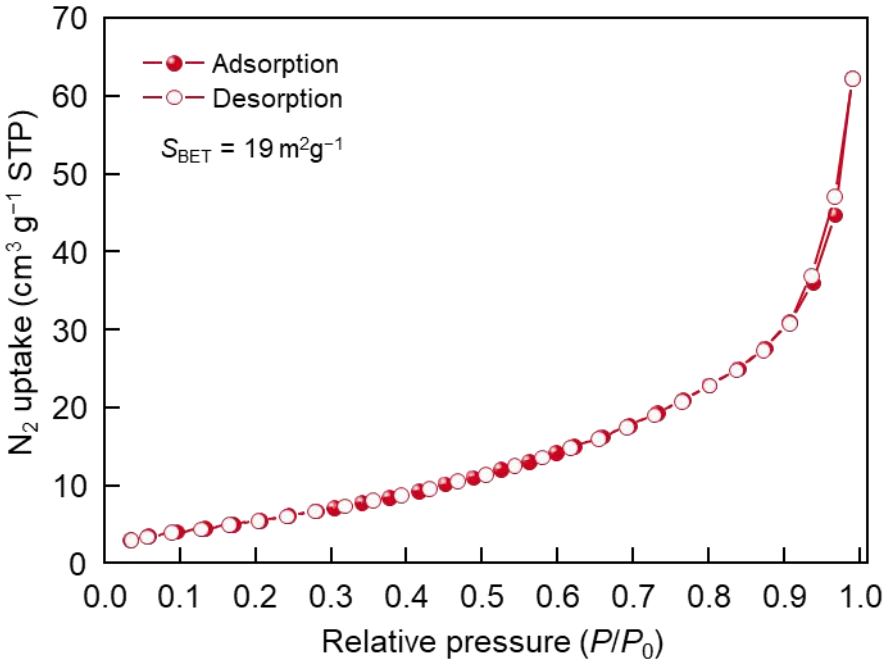
Supplementary Figure 16. Raman spectra of CPOF-4 (black), CPOF-4-265 °C-84 h (blue) and acid-digested CPOF-4-265 °C-84 h (red).



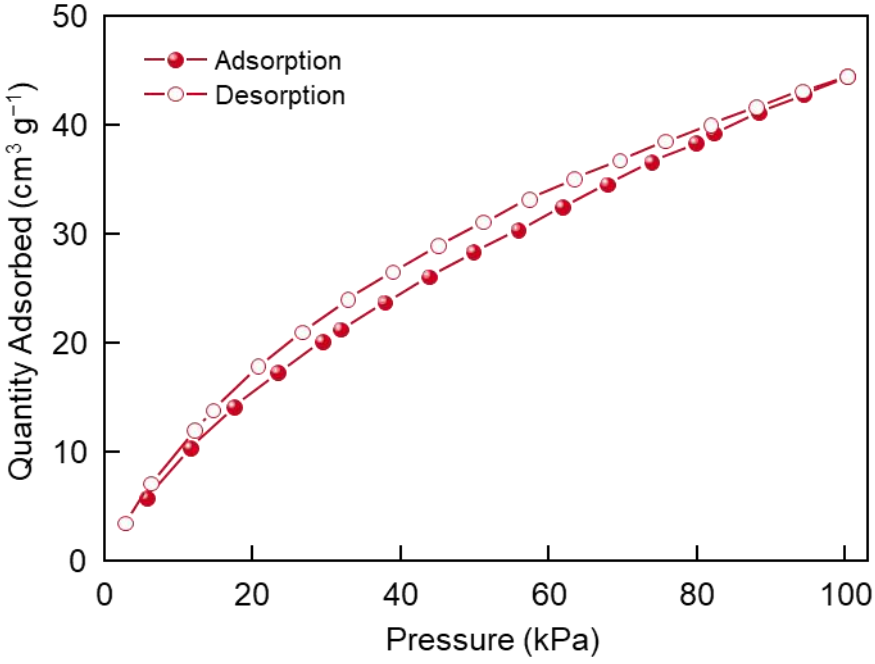
Supplementary Figure 17. SEM images of acid-digested CPOF-4-265 °C-84 h.



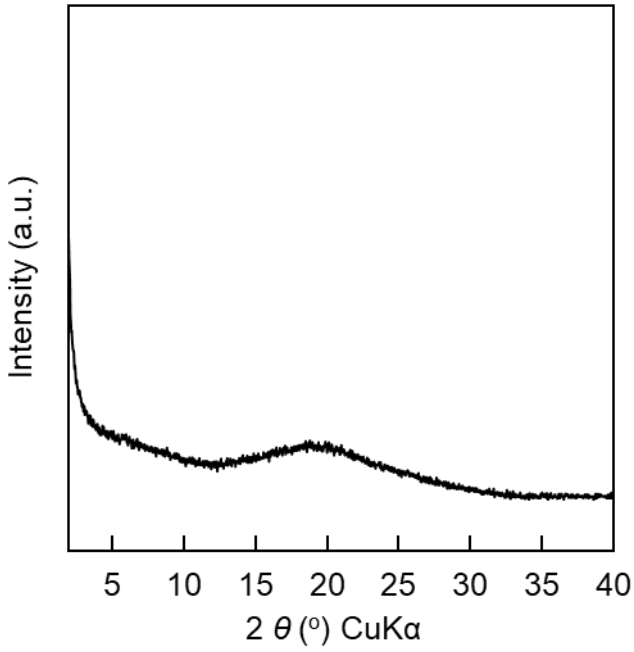
Supplementary Figure 18. TEM image of acid-digested CPOF-4-265 °C-84 h.



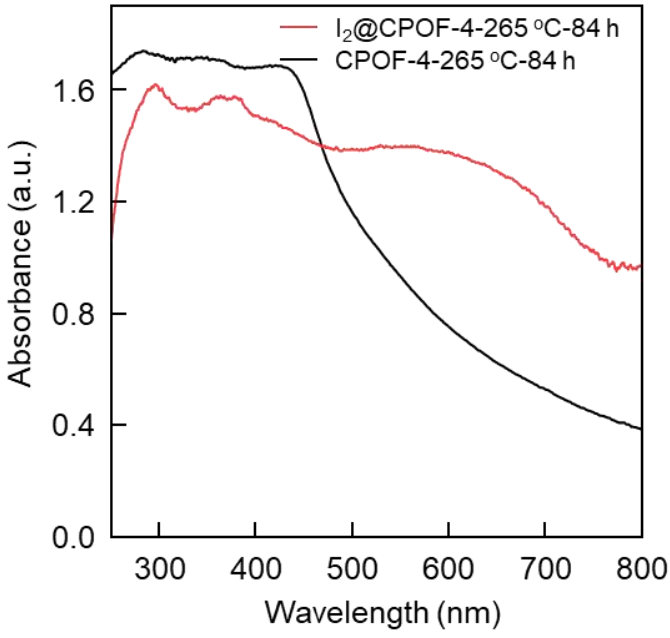
Supplementary Figure 19. N_2 sorption isotherms of acid-digested CPOF-4-265 ºC-84 h at 77 K . Solid symbols, adsorption; open symbols, desorption.



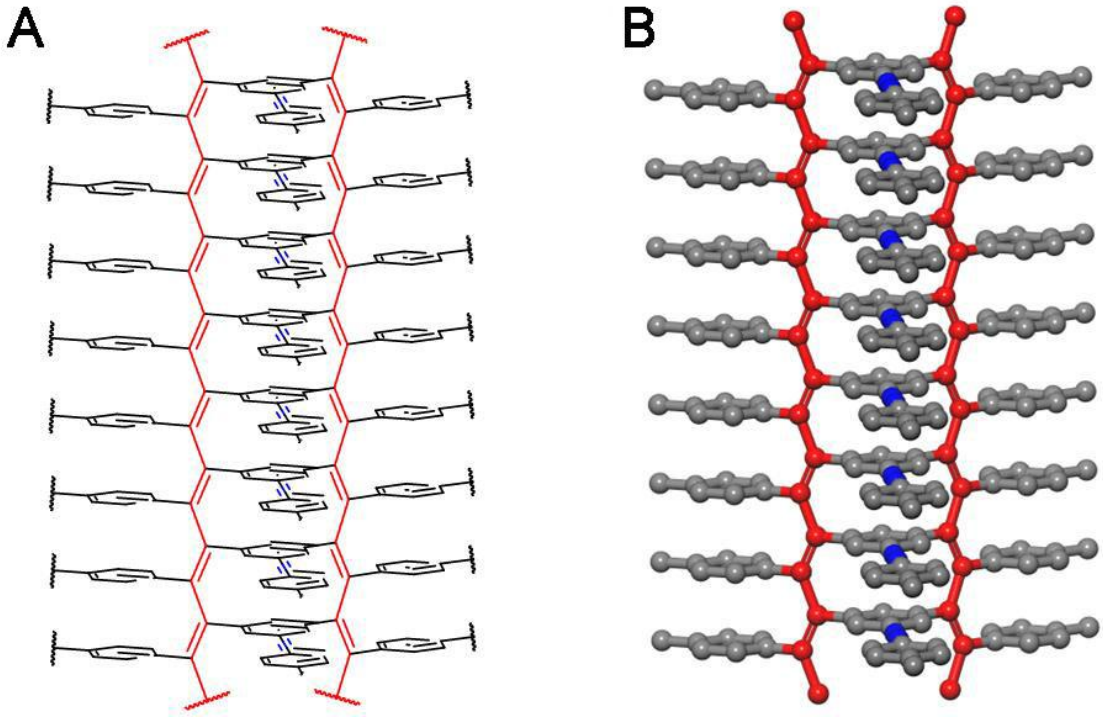
Supplementary Figure 20. CO_2 sorption isotherms of acid-digested CPOF-4-265 ºC-84 h at 273 K. Solid symbols, adsorption; open symbols, desorption.



Supplementary Figure 21. PXRD pattern of acid-digested CPOF-4-265 °C-84 h.

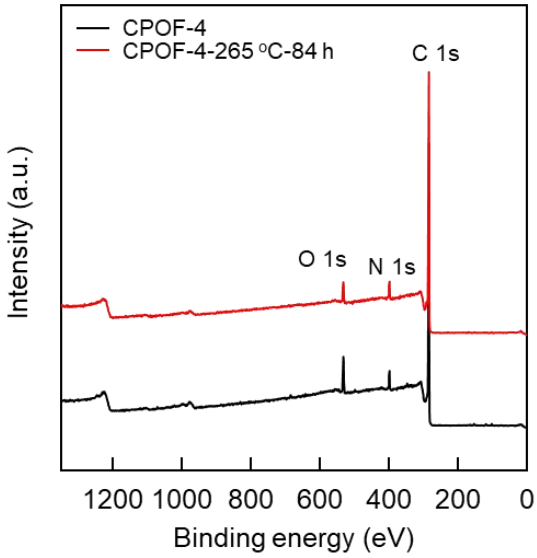


Supplementary Figure 22. Changes of UV-vis absorption spectra upon gas-phase iodine doping for the CPOF-4-265 °C-84 h. After doping with iodine, the absorption band at 250-420 nm, assigned to a π-π* transition in conjugated structure, slightly decreased in intensity. At the same time, due to the polaron electron transition another new absorption appeared at ~600 nm.

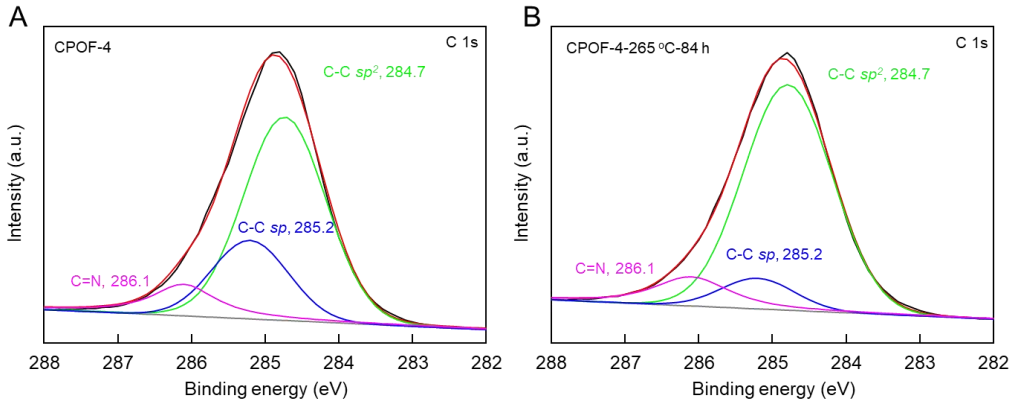


Supplementary Figure 23. (A) Proposed polyacetylene structure in CPOF-4-265 ^{o}C-84 h. Based on solid-state NMR and XPS data, we can know that about two-thirds of the acetylene groups are cross-linked (red), and one-third of the acetylene groups are not cross-linked (blue); (B) Ball-and-stick model of polyacetylene structure in CPOF-4-265 ^{o}C-84 h.

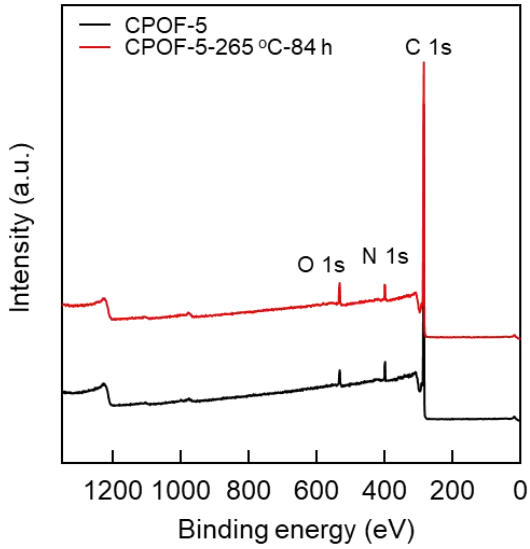
Section S6. X-ray photoelectron spectroscopy



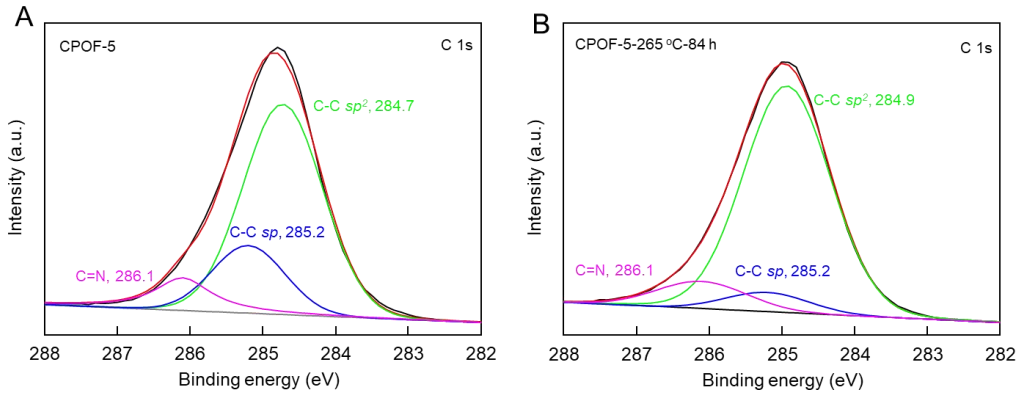
Supplementary Figure 24. XPS spectra of CPOF-4 (black), CPOF-4-265 °C-84 h (red).



Supplementary Figure 25. High-resolution C 1s XPS peak of CPOF-4 (A), CPOF-4-265 °C-84 h (B).



Supplementary Figure 26. XPS spectra of CPOF-5 (black), CPOF-5-265 °C-84 h (red).

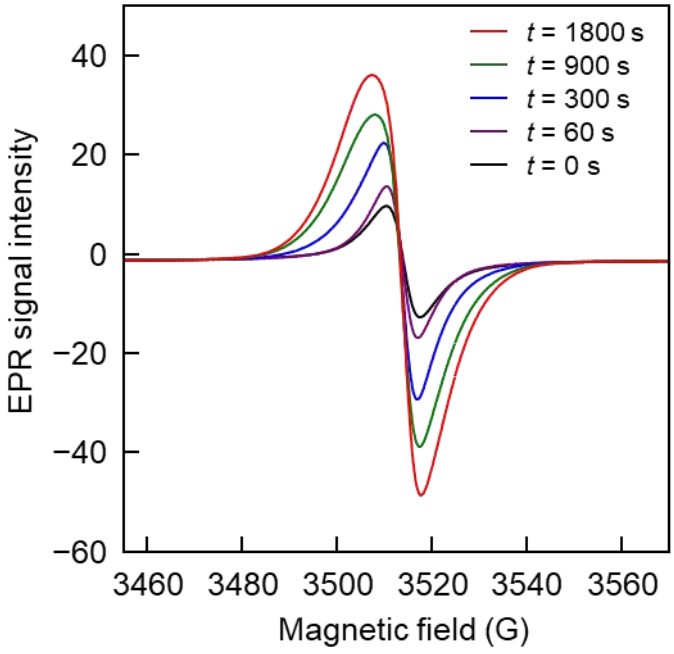


Supplementary Figure 27. High-resolution C 1s XPS peak of CPOF-5 (A), CPOF-5-265 °C-84 h (B).

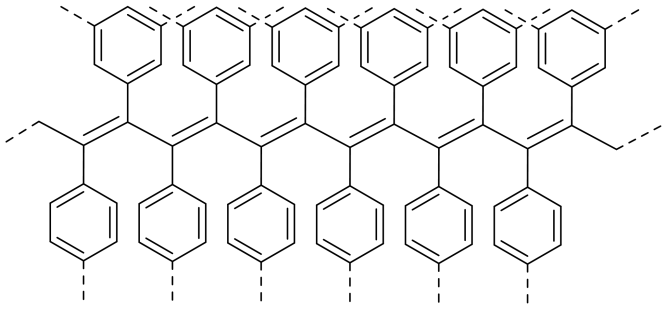
Supplementary Table 1. The atomic percentage of different C species in the sample.

Samples	Name	Peak maximum	Peak area	Atomic %
CPOF-4	C=C sp^2	284.73	148945.2	65.23
	C≡C *sp*	285.2	52991.19	23.21
	C=N	286.1	26389.14	11.56
CPOF-4-265 °C-84 h	C=C sp^2	284.79	171800.4	79.50
	C≡C *sp*	285.2	18989.14	8.79
	C=N	286.1	25309.97	11.71
CPOF-5	C=C sp^2	284.73	174267.1	69.15
	C≡C *sp*	285.2	49809.73	19.77
	C=N	286.1	27926.8	11.08
CPOF-5-265 °C-84 h	C=C sp^2	284.93	195285.2	83.34
	C≡C *sp*	285.2	15607.03	6.67
	C=N	286.1	23427.21	9.99

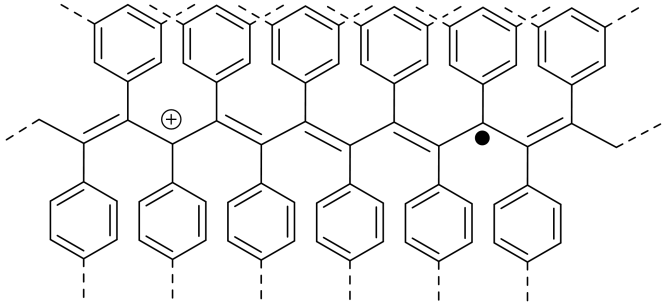
Section S7. Electron paramagnetic resonance



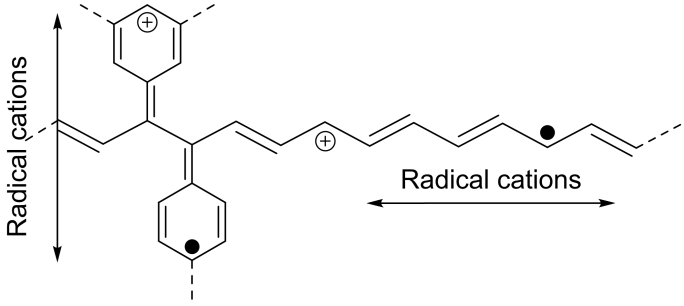
Supplementary Figure 28. EPR signal for CPOF-4-265 °C-84 h sample as a function of time after I_2 exposure at room temperature.



Supplementary Figure 29. Proposed chemical structure of disubstituted polyacetylene in CPOF-4-265 ºC-84 h.

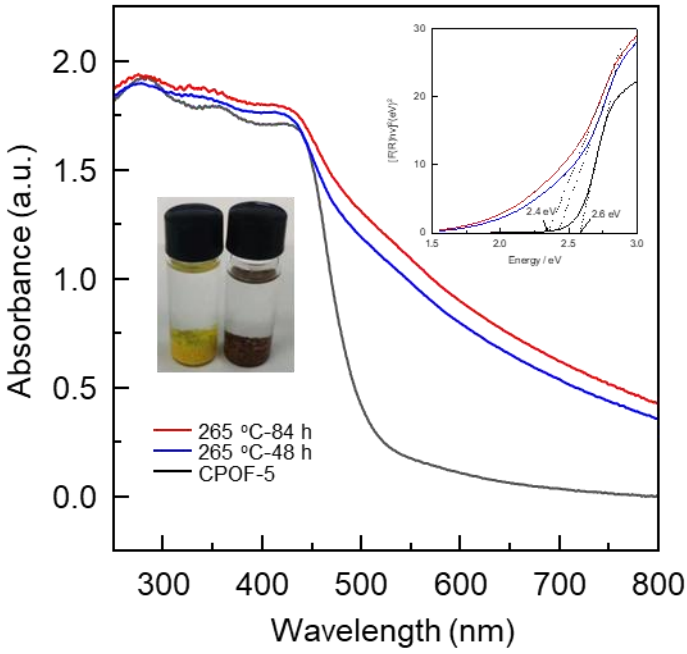


Supplementary Figure 30. Generation of charge carriers along the main chain after doping with iodine.



Supplementary Figure 31. Radical cations in the CPOF-4-265 ºC-84 h.

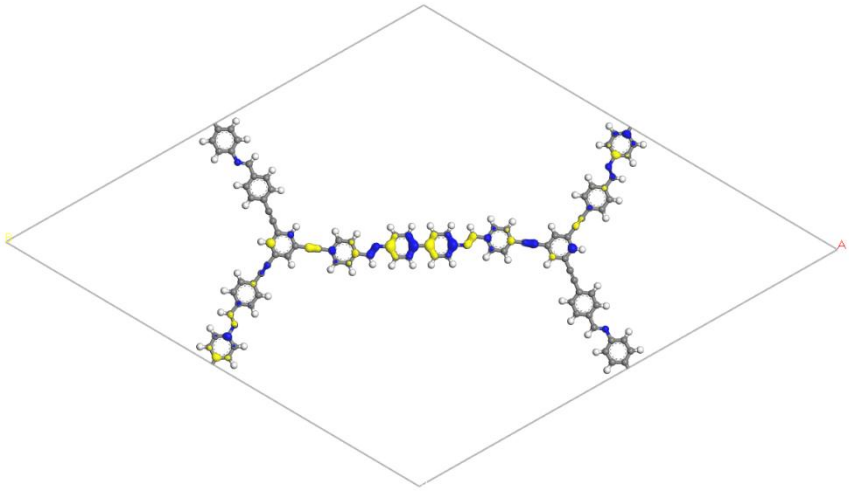
Section S8. UV-visible spectra



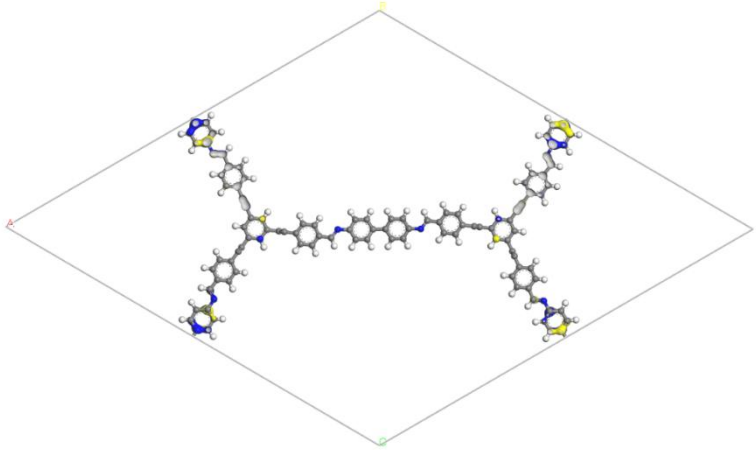
Supplementary Figure 32. UV-vis Diffuse Reflection Spectroscopy (DRS) of CPOF-5, CPOF-5-265 °C-48 h and CPOF-5-265 °C-84 h. Inset: plot of Kubelka−Munk function to determine the band gap of CPOF-5, CPOF-5-265 °C-48 h and CPOF-5-265 °C-84 h.

Section S9. Density Functional Theory Calculations

It is worth noting that even after a long time of reaction, the final conversion rate of CPOF-4 is only about 60~70%. We speculate that about two-thirds of the acetylene groups in CPOF-4 have reacted. Considering these factors, we directly connected acetylenic groups between adjacent layers on the basis of the original CPOF-4 structure, while retaining one-third of the acetylenic groups, and further optimized the structure to obtain the CPOF-4-265 ºC-48 h model with a conversion rate of two-thirds. Then, the frontier orbitals of CPOF-4 and CPOF-4-265 ºC-48 h were calculated by density functional theory calculations (DFT).

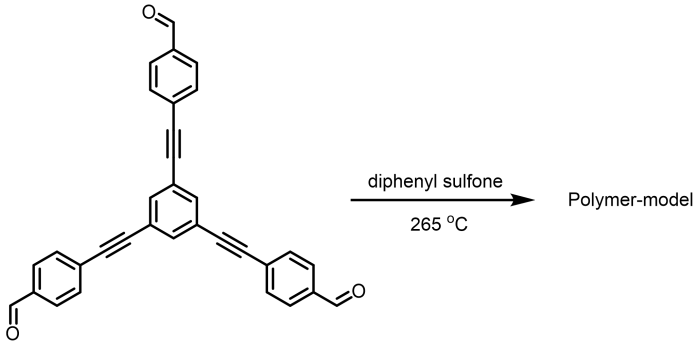


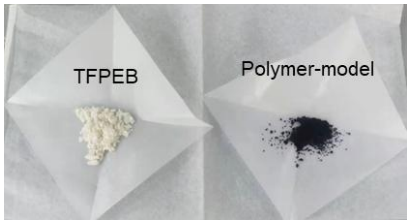
Supplementary Figure 33. The isosurface of the electron wavefunction of the HOMO of CPOF-4.



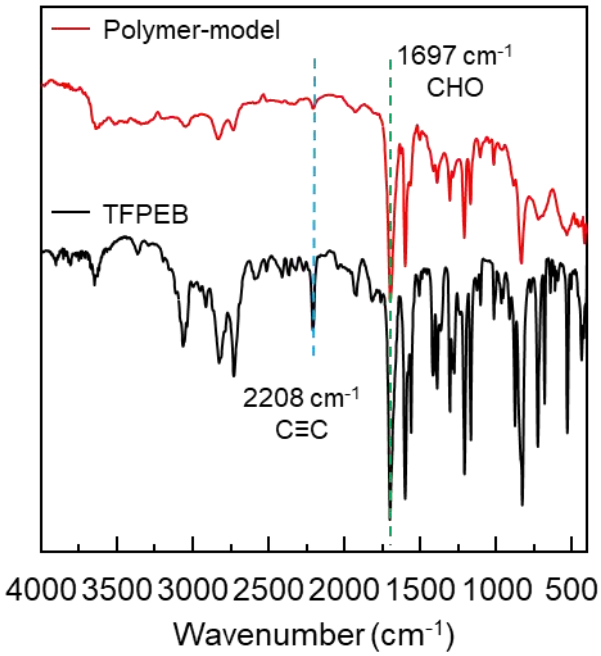
Supplementary Figure 34. The isosurface of the electron wavefunction of the HOMO of CPOF-4-265 ºC-48 h.

Section S10. Synthesis of polymer-model

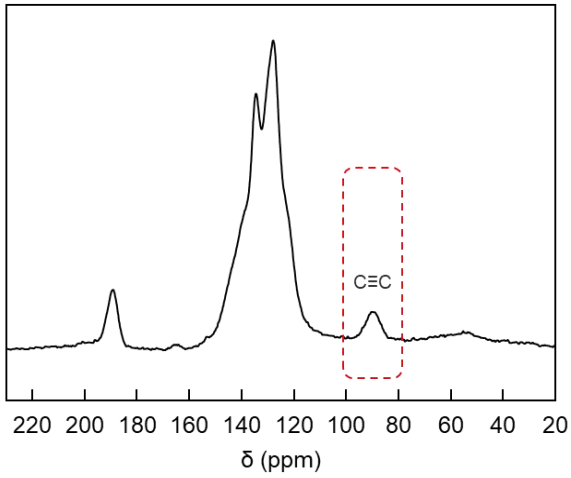




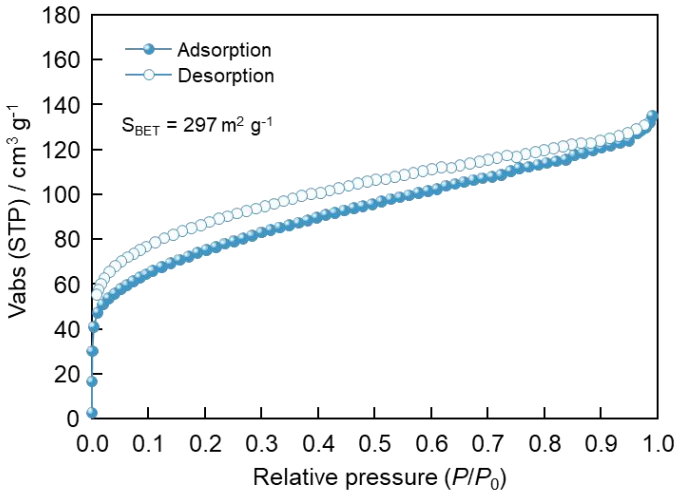
A 5 mL vial charged with TFPEB (100.0 mg) and diphenyl sulfone (3 g), The vial was then transferred to a tubular furnace and evacuated-filled with N_2 by five cycles. subsequently, the temperature was raised to 265 ºC at the rate of 10 ºC/min in N_2 flowing atmosphere with the flow rate of 20 mL/min, and kept at 265 ºC for 24 h. The temperature was reduced to room temperature at the rate of 10 ºC/min at the end of the holding time. Finally, the obtained product was washed with THF and acetone to remove the residual diphenyl sulfone, dried at 100 ºC under vacuum over-night to afford the polymer-model as a black solid.



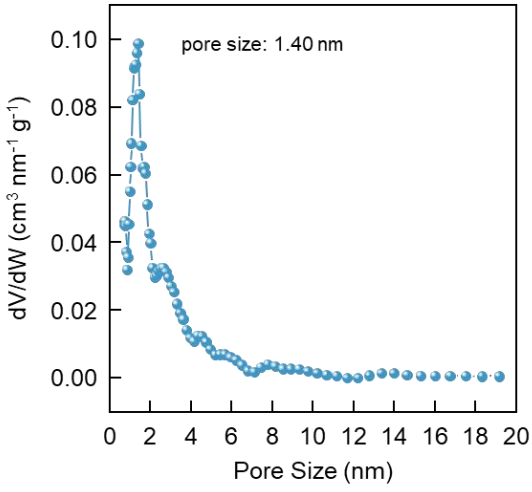
Supplementary Figure 35. FT-IR spectra of 1,3,5-tri(4-formylphenylethynyl)benzene and polymer-model.



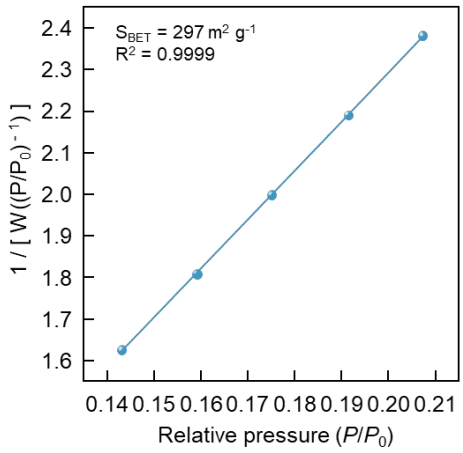
Supplementary Figure 36. ^{13}C CP-MAS NMR spectra of polymer-model.



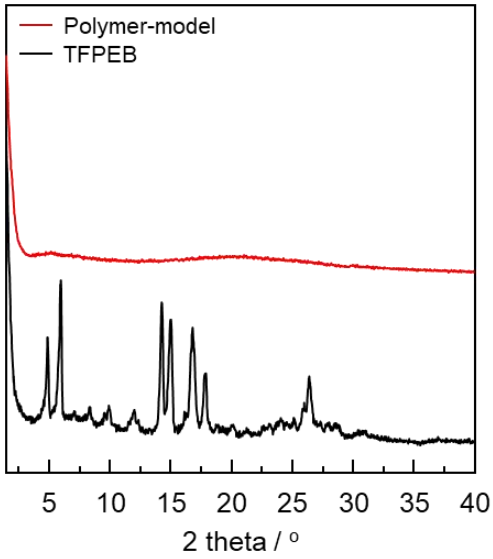
Supplementary Figure 37. N_2 sorption isotherms of polymer-model: solid symbols, adsorption; open symbols, desorption.



Supplementary Figure 38. The pore size distribution of polymer-model derived from N_2 adsorption calculated by QSDFT method.



Supplementary Figure 39. BET plots of polymer-model calculated from N_2 adsorption isotherm at 77 K.



Supplementary Figure 40. PXRD patterns for 1,3,5-tri(4-formylphenylethynyl)benzene and polymer-model.

Section S11. PXRD patterns and structures

Crystal models for 2D COFs and CL-COFs were established by Materials Studio 7.0 Software Package. Geometry optimization of the established models was performed by Materials Studio Forcite Module, which is an advanced classical molecular mechanics tool and allows for fast and reliable geometry optimization and energy calculations. Possible stacking modes were tested. Eclipsed (AA) and slipped (AB) were constructed and optimized in comparison with the experimental Powder X-ray diffraction (PXRD) data. Pawley refinement was carried out using Reflex, a software package for crystal determination from PXRD pattern. The Pawley refinement was performed to optimize the lattice parameters iteratively until the R_{wp} and R_p value converges and the overlay of the observed refined profiles shows good agreement.

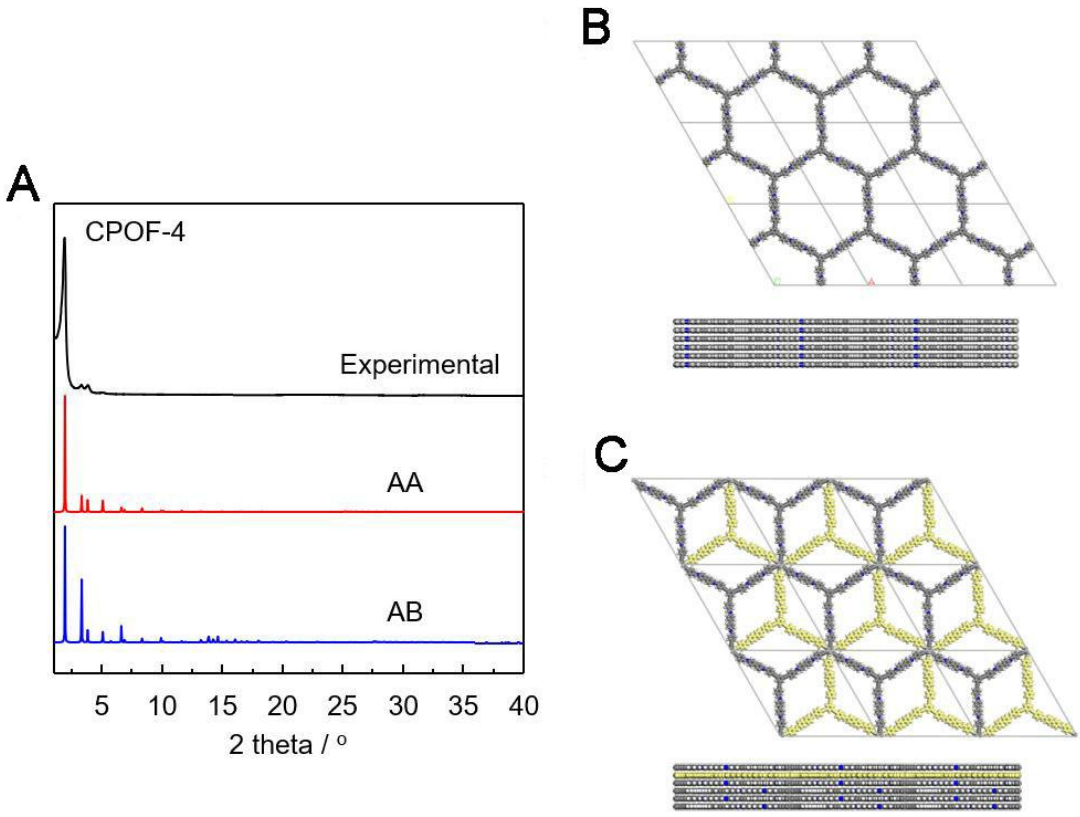
The structure models of CPOF-4-265 °C-84 h and CPOF-5-265 °C-84 h were determined by directly linking the CPOF-4 and CPOF-5 in the crystallographic *c*-direction and optimizing them in Materials Studio using the Forcite Module, respectively.

We use zero-point energy which calculated by Self-Consistent Field (SCF) to evaluate the stability of the species.

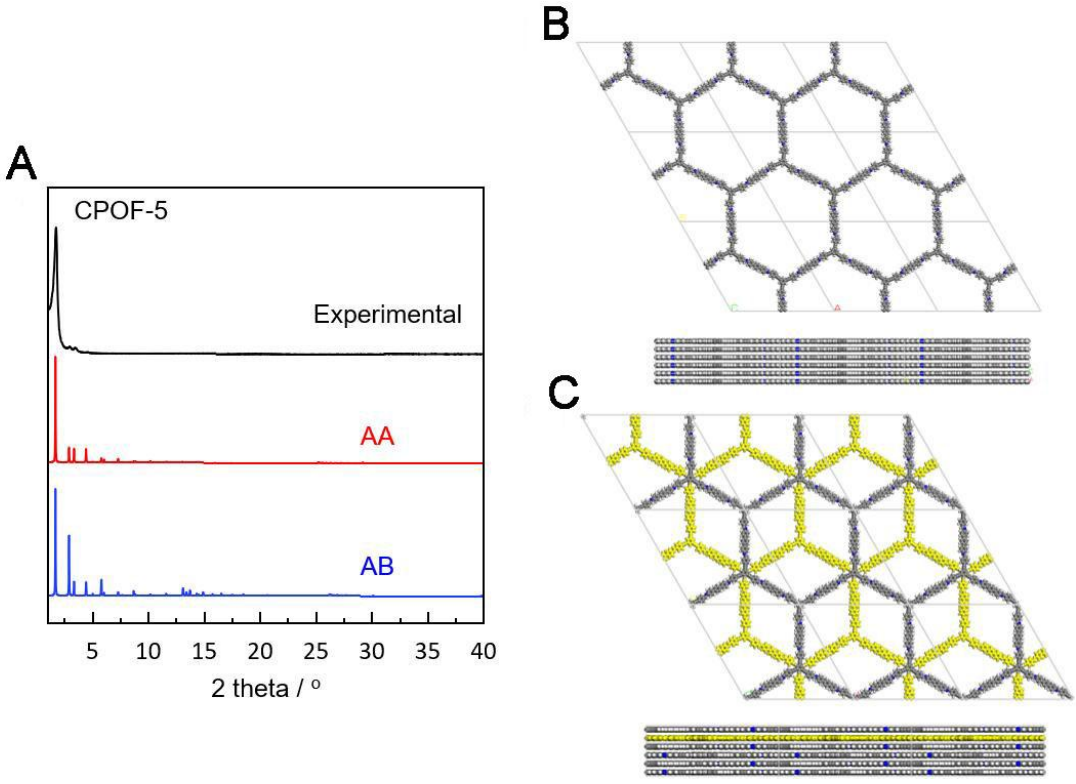
Supplementary Table 2. The Zero Point Energy for CPOF-4 and CPOF-4-265 °C-84 h, CPOF-5 and CPOF-5-265 °C-84 h, the unit is eV.

Species	Zero Point Energy (eV)	Difference (eV)
CPOF-4	-2369.8736	
CPOF-4-265 °C-84 h	-2373.1908	-3.3172
CPOF-5	-2785.8982	
CPOF-5-265 °C-84 h	-2790.0196	-4.1214

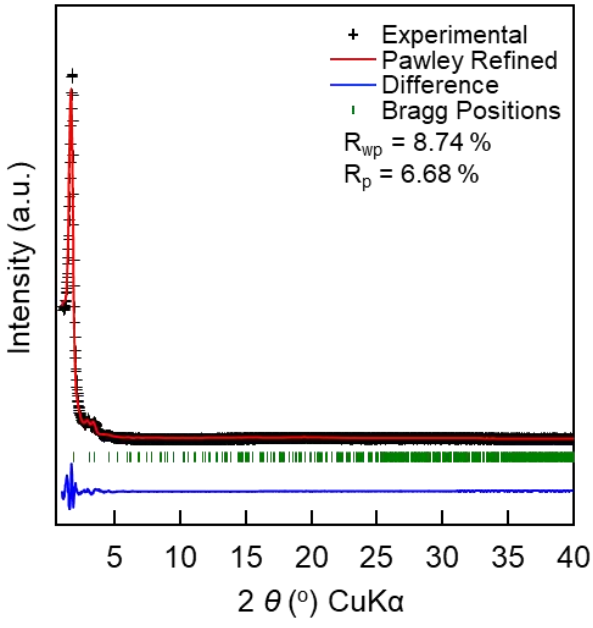
The Density Functional Theory (DFT) which base on first-principles were performed through the projector augmented wave (PAW) method by using Vienna ab initio Simulation Package (VASP) code[2,3]. The results were calculated by self-consistent field (SCF) method which base on Kohn-Sham equation. The Generalized gradient approximation (GGA) method with the Perdew-Burke-Ernzerhof (PBE) was adopted as the exchange-correlation functional. All the calculation uses gamma-centered k-points 1×1×7 based on Monkhorst–Pack kpoint grids, DFT-D3 method with Becke-Johnson damping function, 600 eV cutoff energy and the spin-polarized calculations (collinear). The convergence tolerance for the residual force and energy on each atom during structure relaxation were set to 0.05 eVÅ^{-1} and 10^{-5} eV.



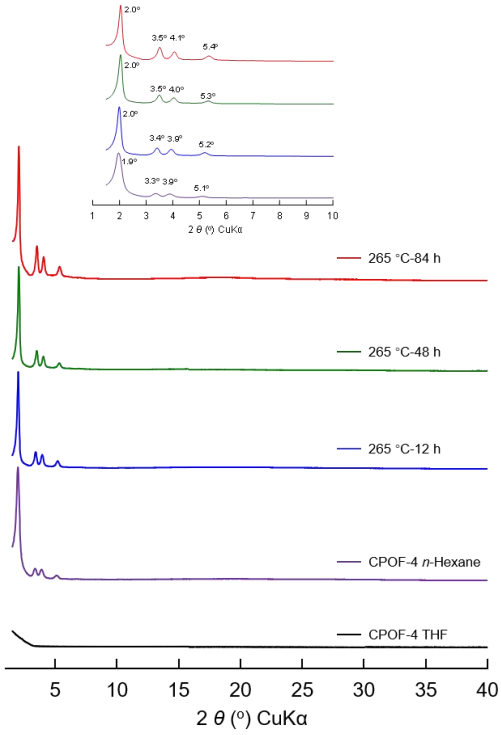
Supplementary Figure 41. (A) XRD profiles of CPOF-4: experimental (black), simulated by using AA-stacking (red) models and AB-stacking (blue) models; (B) Unit cells of AA-stacking modes; (C) Unit cells of AB-stacking modes.



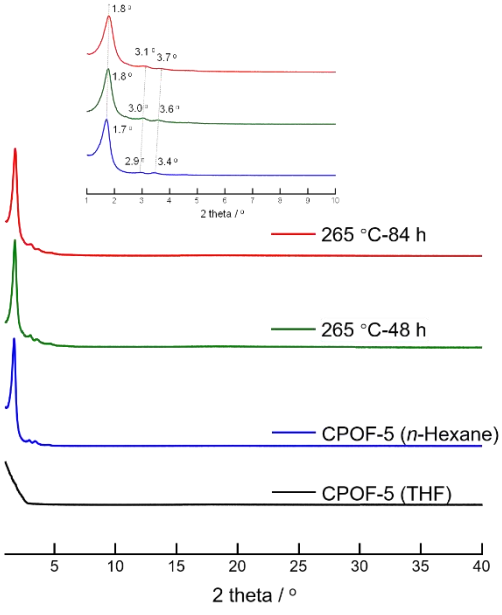
Supplementary Figure 42. (A) XRD profiles of CPOF-5: experimental (black), simulated by using AA-stacking (red) models and AB-stacking (blue) models; (B) Unit cells of AA-stacking modes; (C) Unit cells of AB-stacking modes.



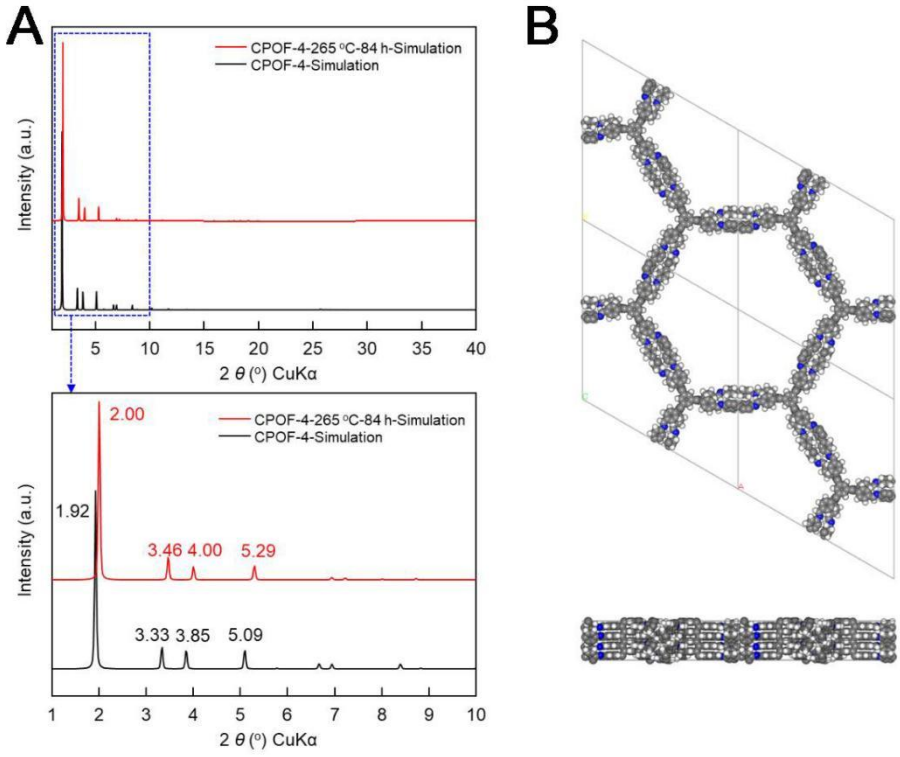
Supplementary Figure 43. PXRD profiles of CPOF-5. experimentally observed results (black), Pawley refined (red), their difference (blue) and Bragg positions (green).



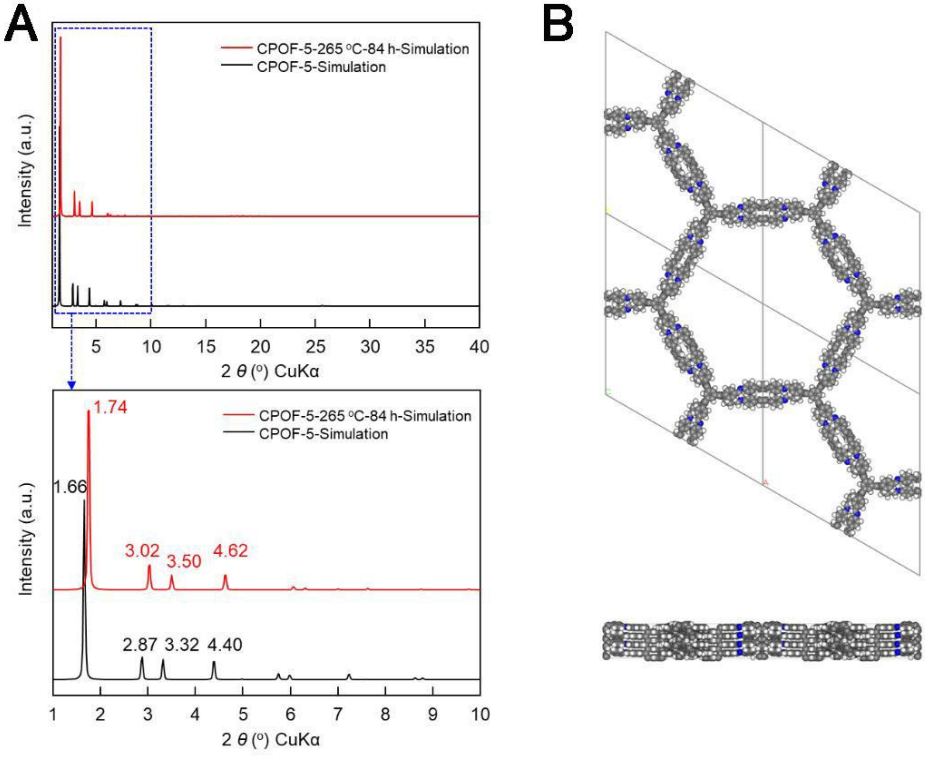
Supplementary Figure 44. PXRD spectra of CPOF-4 (THF), CPOF-4 (*n*-hexane), CPOF-4-265 °C-12 h, CPOF-4-265 °C-48 h, and CPOF-4-265 °C-84 h.



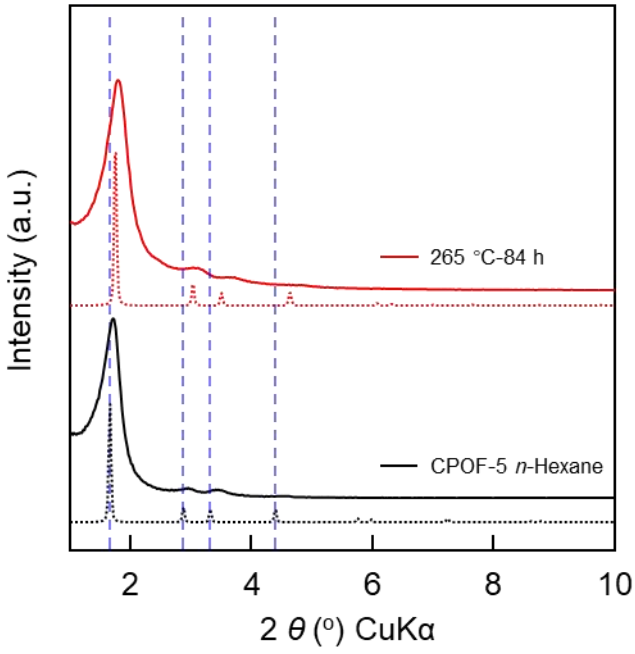
Supplementary Figure 45. PXRD spectra of CPOF-5 (THF), CPOF-5 (*n*-hexane), CPOF-5-265 °C-48 h, and CPOF-5-265 °C-84 h.



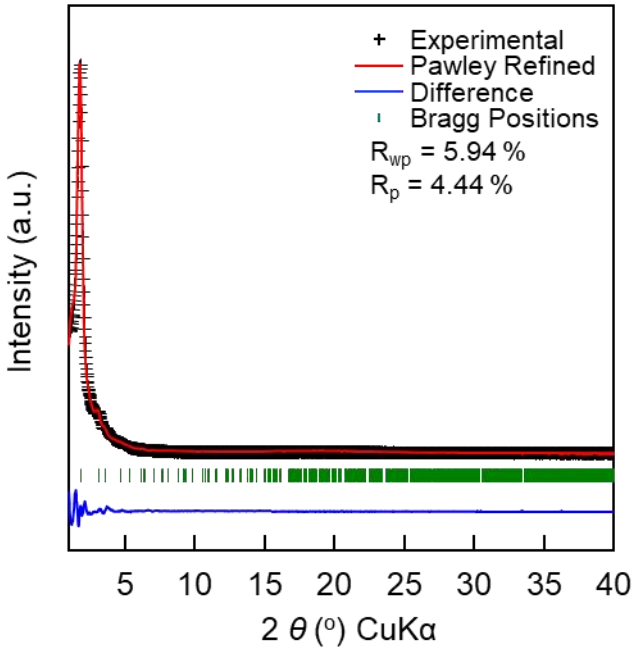
Supplementary Figure 46. (A) Simulated PXRD patterns of CPOF-4 (black) and CPOF-4-265 °C-84 h (red); (B) Schematic representation of CPOF-4-265 °C-84 h.



Supplementary Figure 47. (A) Simulated PXRD patterns of CPOF-5 (black) and CPOF-5-265 °C-84 h (red); (B) Schematic representation of CPOF-5-265 °C-84 h.

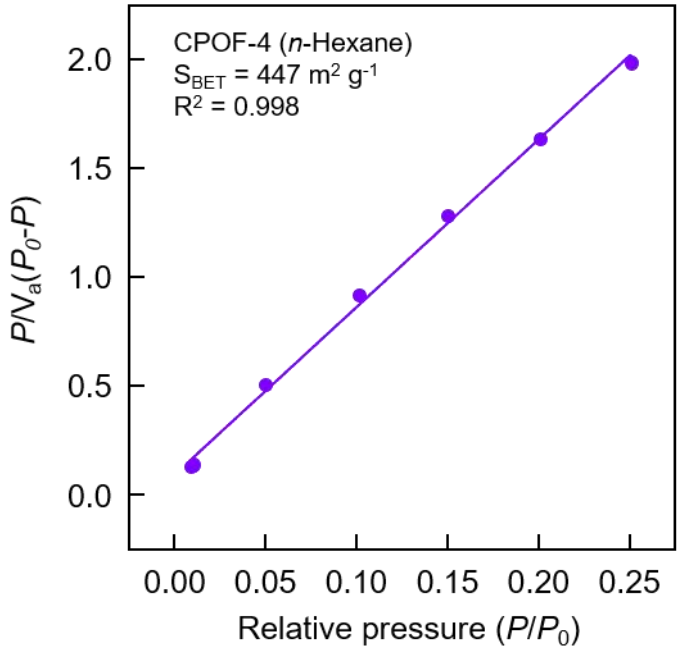


Supplementary Figure 48. PXRD patterns of CPOF-5 and CPOF-5-265 °C-84 h: experimentally observed (solid line) and simulated based on eclipsed stacking modes (dashed line).

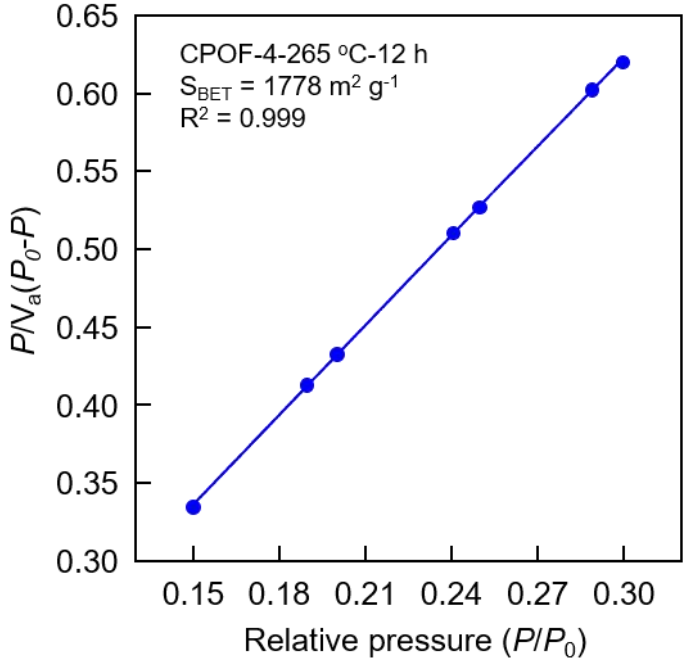


Supplementary Figure 49. PXRD patterns of CPOF-5-265 °C-84 h: comparison between the experimental (black) and Pawley refined (red) profiles, the refinement differences (blue), and the Bragg positions (green).

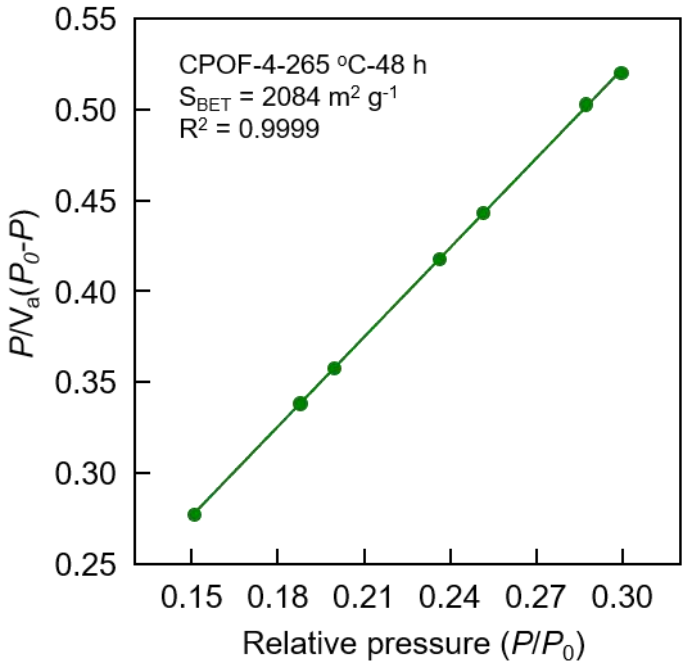
Section S12. Nitrogen adsorption



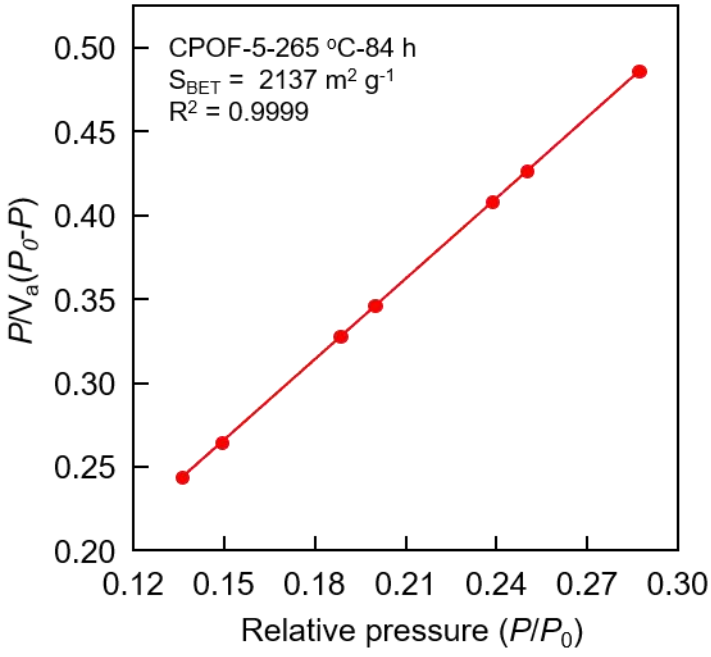
Supplementary Figure 50. BET plots of CPOF-4 (*n*-hexane) calculated from N_2 adsorption isotherm at 77 K.



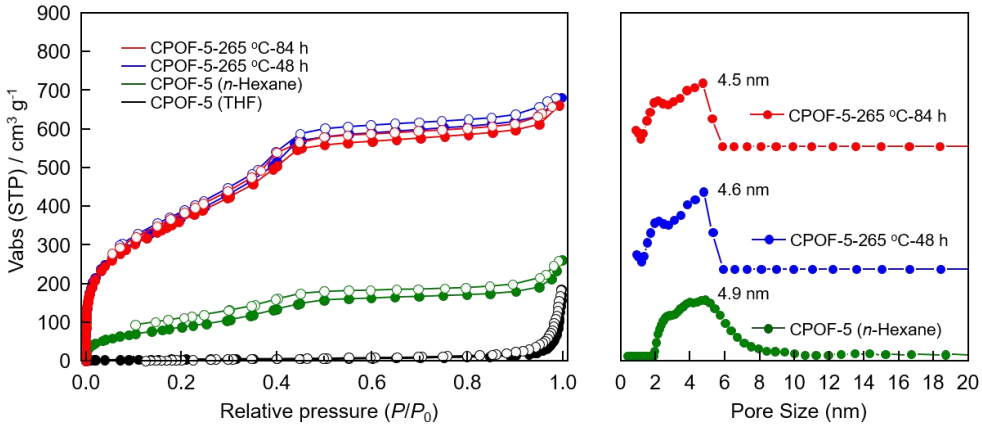
Supplementary Figure 51. BET plots of CPOF-4-265 °C-12 h calculated from N_2 adsorption isotherm at 77 K.



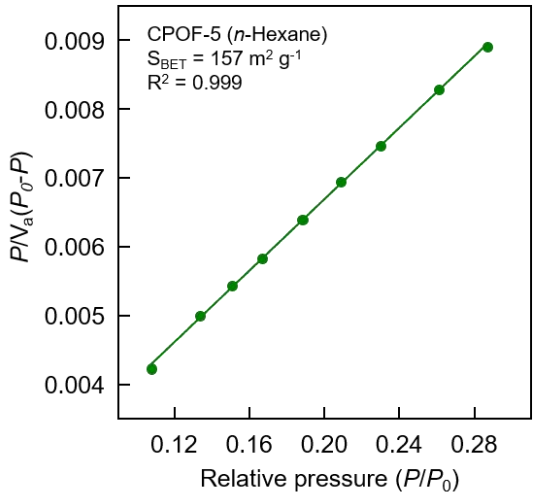
Supplementary Figure 52. BET plots of CPOF-4-265 °C-48 h calculated from N_2 adsorption isotherm at 77 K.



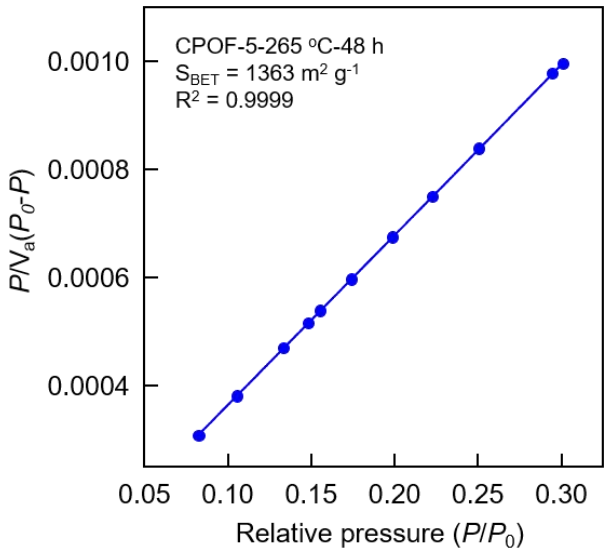
Supplementary Figure 53. BET plots of CPOF-4-265 °C-84 h calculated from N_2 adsorption isotherm at 77 K.



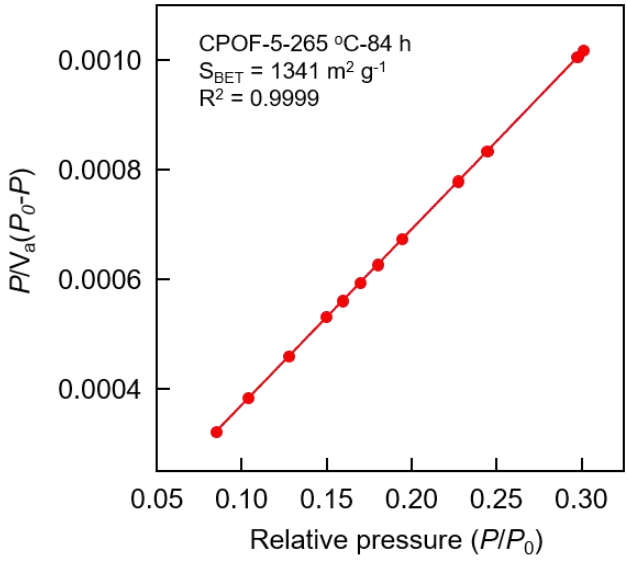
Supplementary Figure 54. N_2 sorption isotherms of CPOF-5 (THF), CPOF-5 (*n*-hexane), CPOF-5-265 °C-48 h, and CPOF-5-265 °C-84 h: solid symbols, adsorption; open symbols, desorption. The pore size distribution derived from N_2 adsorption calculated by QS-DFT method.



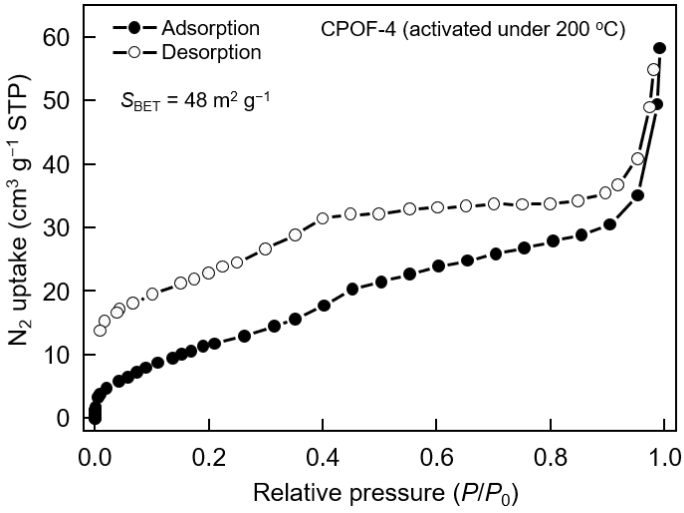
Supplementary Figure 55. BET plots of CPOF-5 (*n*-hexane) calculated from N_2 adsorption isotherm at 77 K.



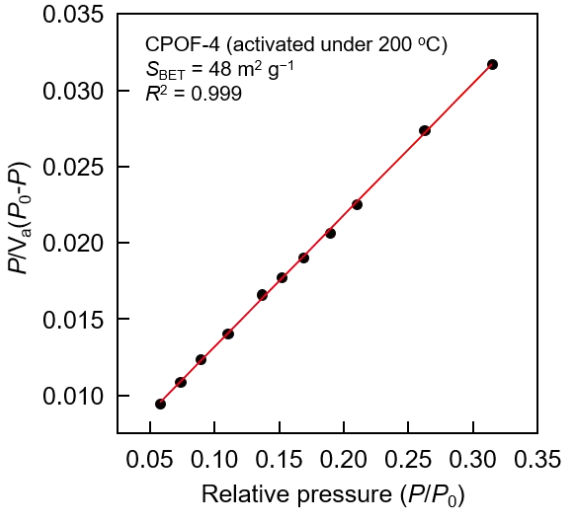
Supplementary Figure 56. BET plots of CPOF-5-265 °C-48 h calculated from N_2 adsorption isotherm at 77 K.



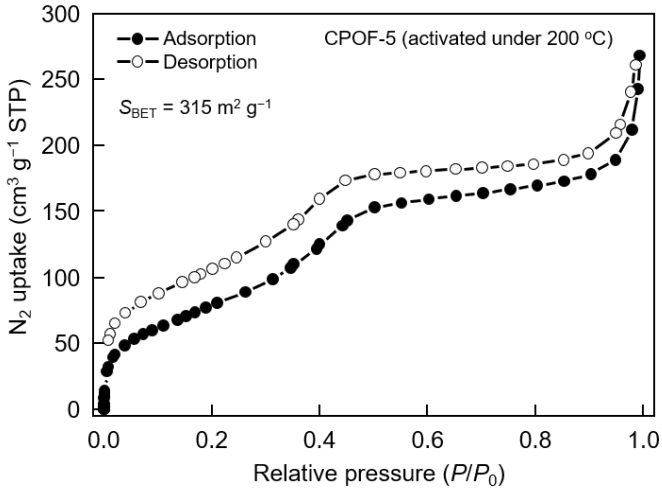
Supplementary Figure 57. BET plots of CPOF-5-265 °C-84 h calculated from N_2 adsorption isotherm at 77 K.



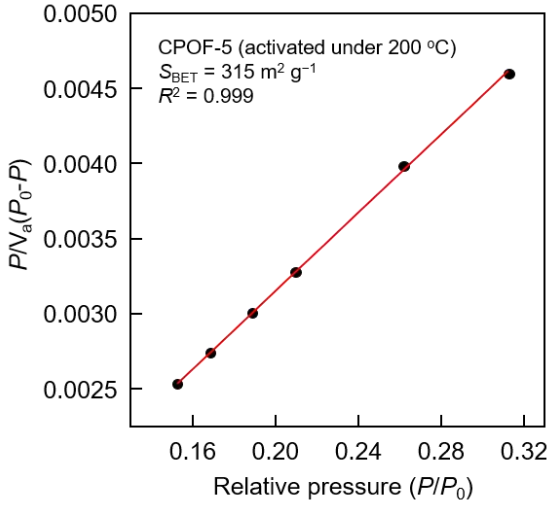
Supplementary Figure 58. N_2 sorption isotherms of CPOF-4 (activated under 200 °C): solid symbols, adsorption; open symbols, desorption.



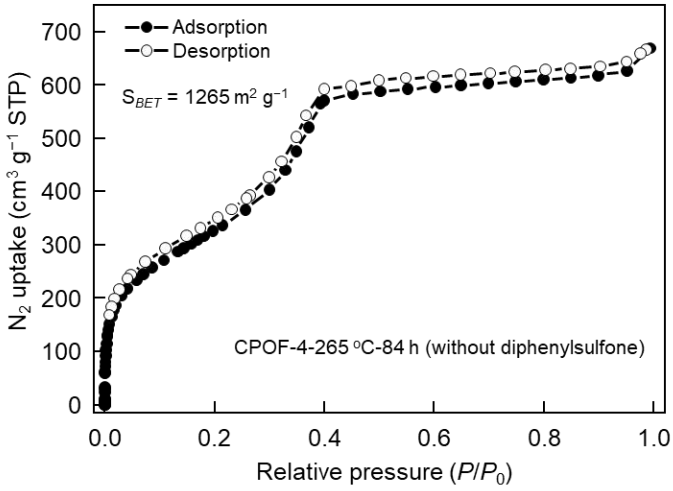
Supplementary Figure 59. BET plots of CPOF-4 (activated under 200 °C) calculated from N_2 adsorption isotherm at 77 K.



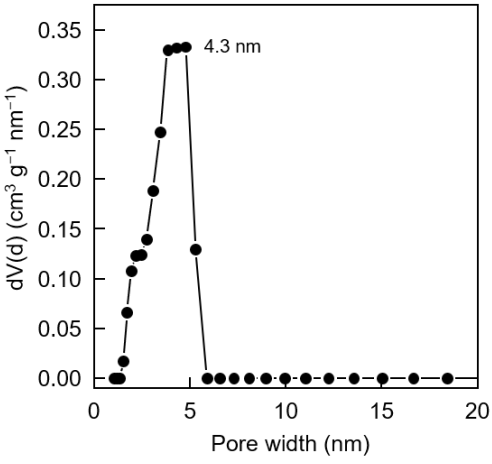
Supplementary Figure 60. N_2 sorption isotherms of CPOF-5 (activated under 200 °C): solid symbols, adsorption; open symbols, desorption.



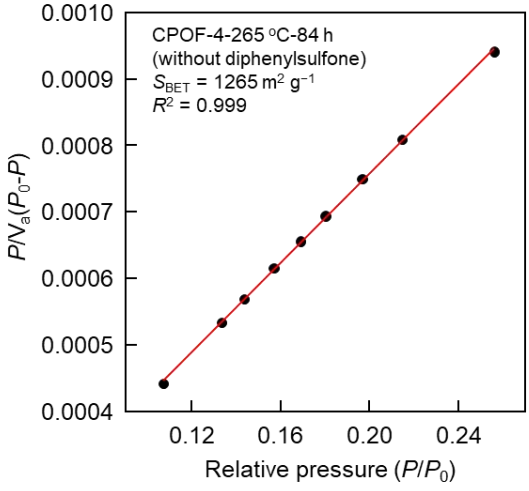
Supplementary Figure 61. BET plots of CPOF-5 (activated under 200 °C) calculated from N_2 adsorption isotherm at 77 K.



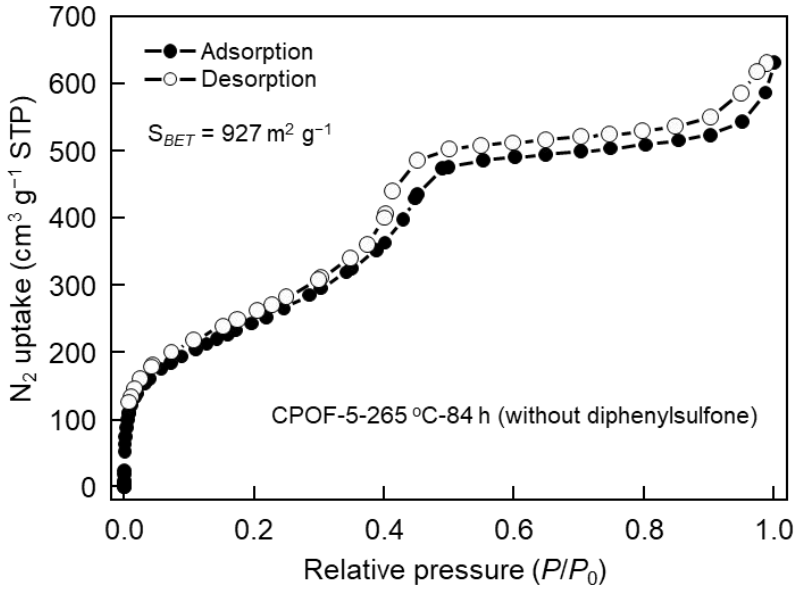
Supplementary Figure 62. N_2 sorption isotherms of CPOF-4-265 °C-84 h (without phenyl sulfone): solid symbols, adsorption; open symbols, desorption.



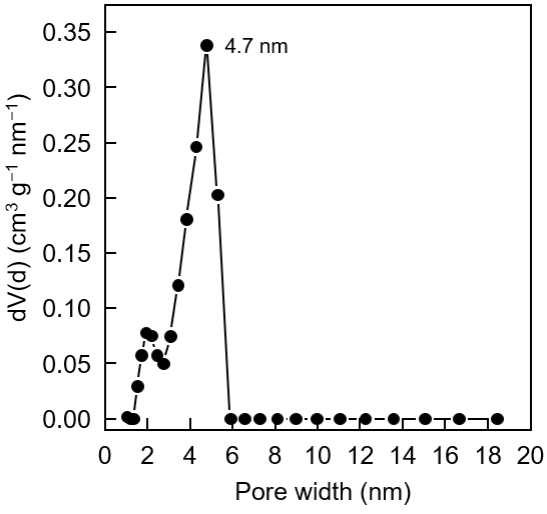
Supplementary Figure 63. The pore size distribution of CPOF-4-265 °C-84 h (without phenyl sulfone): derived from N_2 adsorption calculated by QSDFT method.



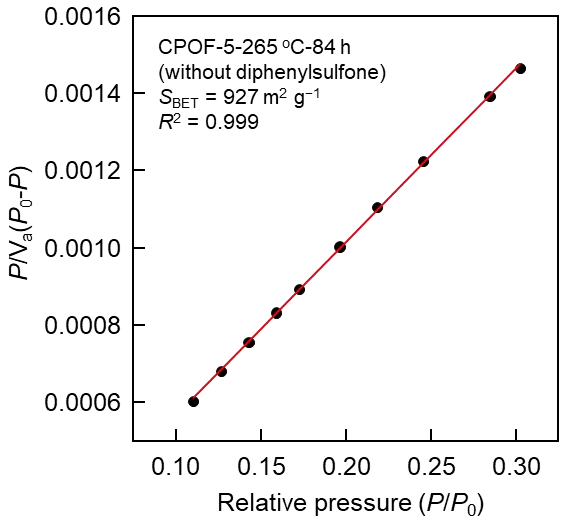
Supplementary Figure 64. BET plots of CPOF-4-265 °C-84 h (without phenyl sulfone): calculated from N_2 adsorption isotherm at 77 K.



Supplementary Figure 65. N_2 sorption isotherms of CPOF-5-265 °C-84 h (without phenyl sulfone): solid symbols, adsorption; open symbols, desorption.

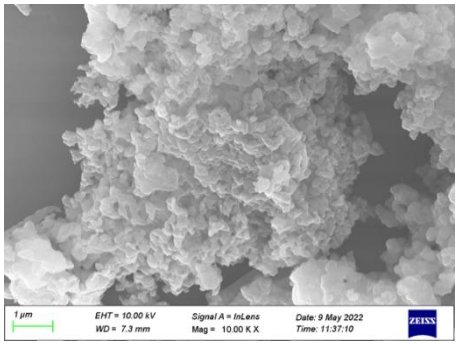


Supplementary Figure 66. The pore size distribution of CPOF-5-265 °C-84 h (without phenyl sulfone): derived from N_2 adsorption calculated by QS-DFT method.

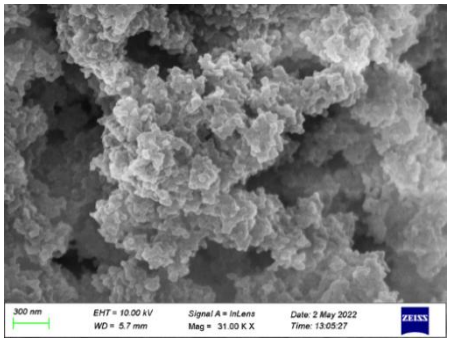


Supplementary Figure 67. BET plots of CPOF-5-265 °C-84 h (without phenyl sulfone): calculated from N_2 adsorption isotherm at 77 K.

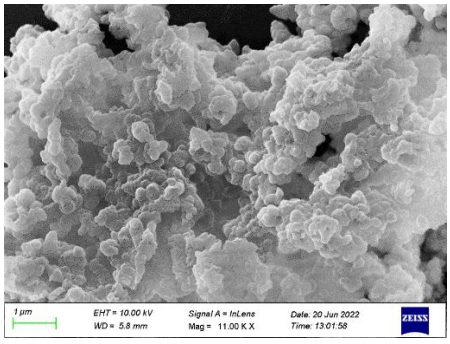
Section S13. SEM image



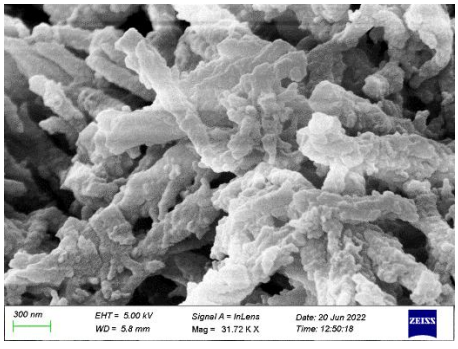
Supplementary Figure 68. SEM image of as-synthesized CPOF-4.



Supplementary Figure 69. SEM image of as-synthesized CPOF-5.

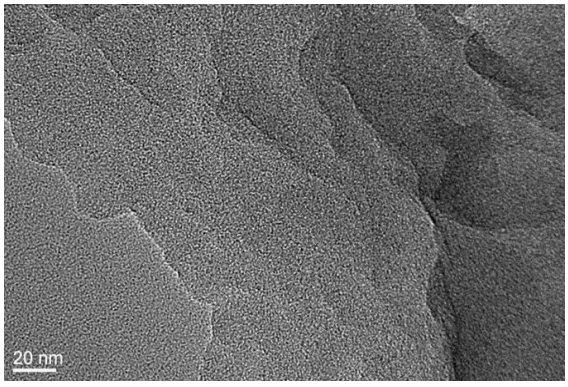


Supplementary Figure 70. SEM image of CPOF-4-265 ºC-84 h.

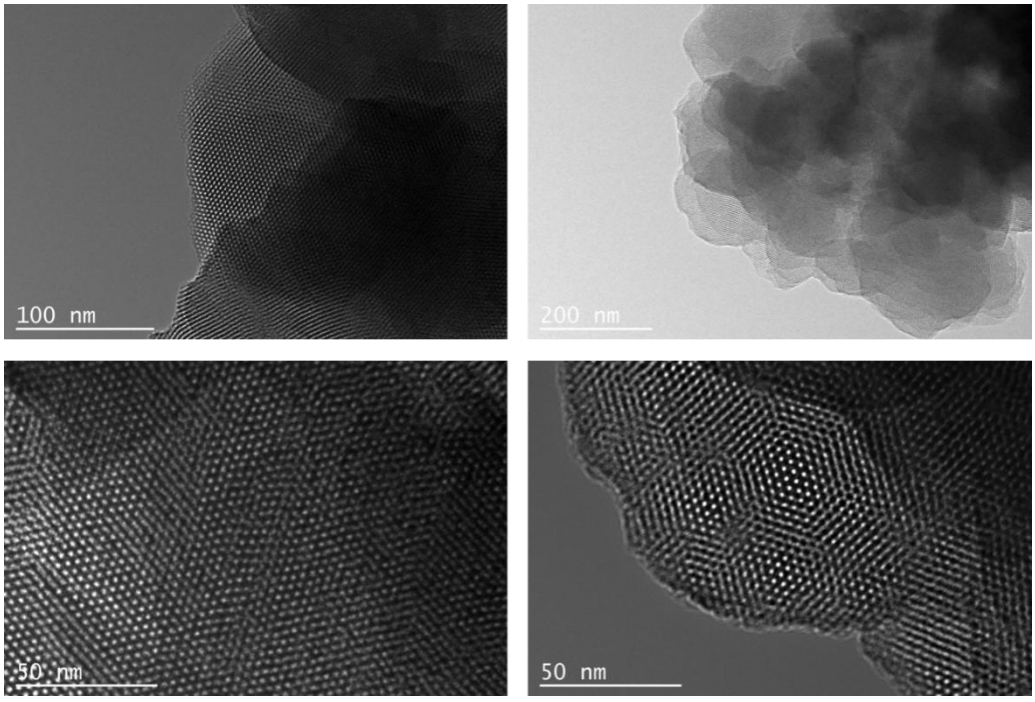


Supplementary Figure 71. SEM image of CPOF-5-265 ºC-84 h.

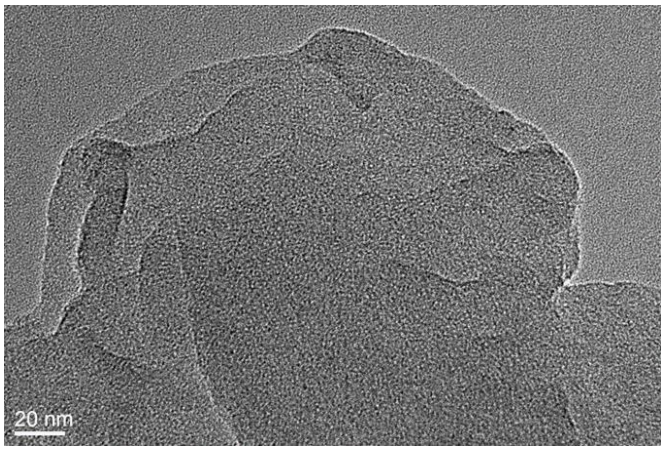
Section S14. TEM image



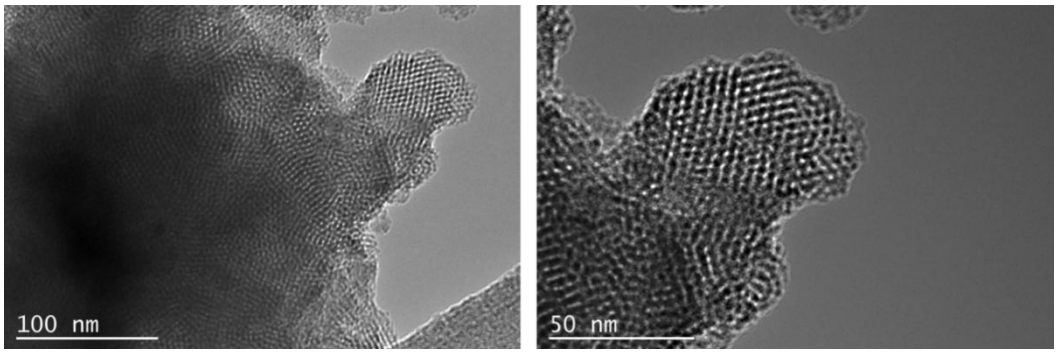
Supplementary Figure 72. TEM image of as-synthesized CPOF-4.



Supplementary Figure 73. TEM image of CPOF-4-265 ^{o}C-84 h.

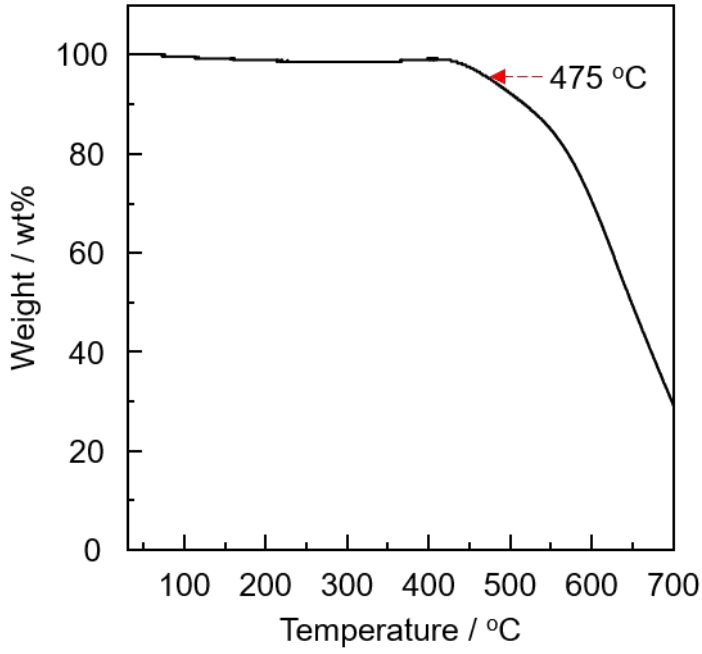


Supplementary Figure 74. TEM image of as-synthesized CPOF-5.

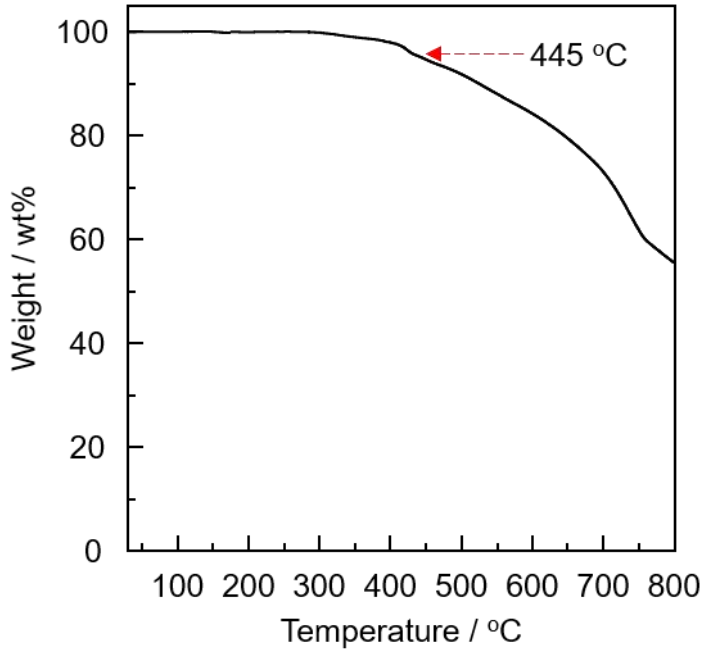


Supplementary Figure 75. TEM image of CPOF-5-265 ^{o}C-84 h.

Section S15. TGA curves

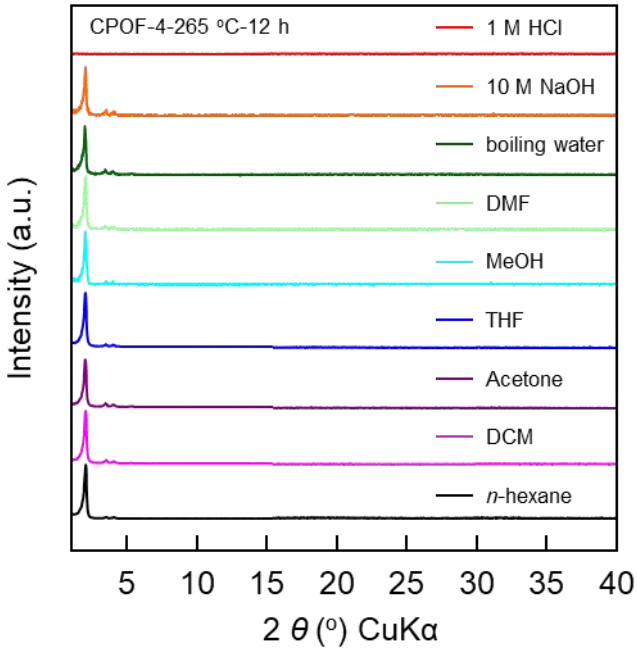


Supplementary Figure 76. TGA plot of CPOF-4 in N_2 atmosphere, weight loss 5 wt% at 475 °C.

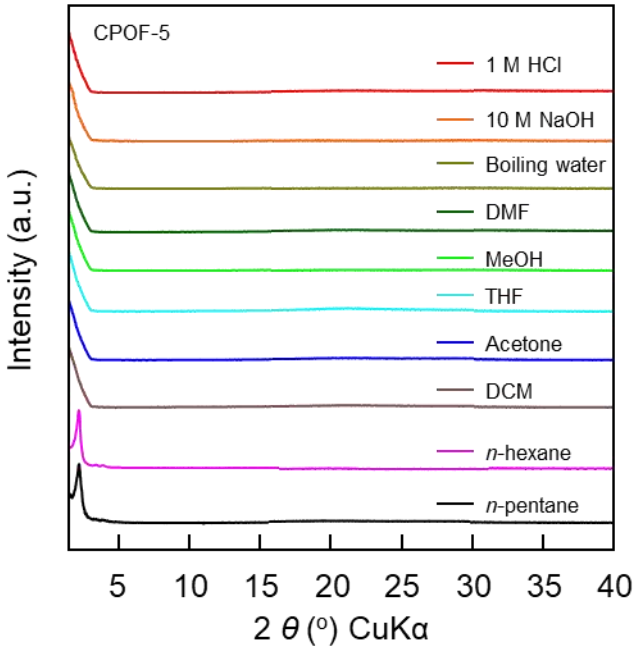


Supplementary Figure 77. TGA plot of CPOF-5 in N_2 atmosphere, weight loss 5 wt% at 445 °C.

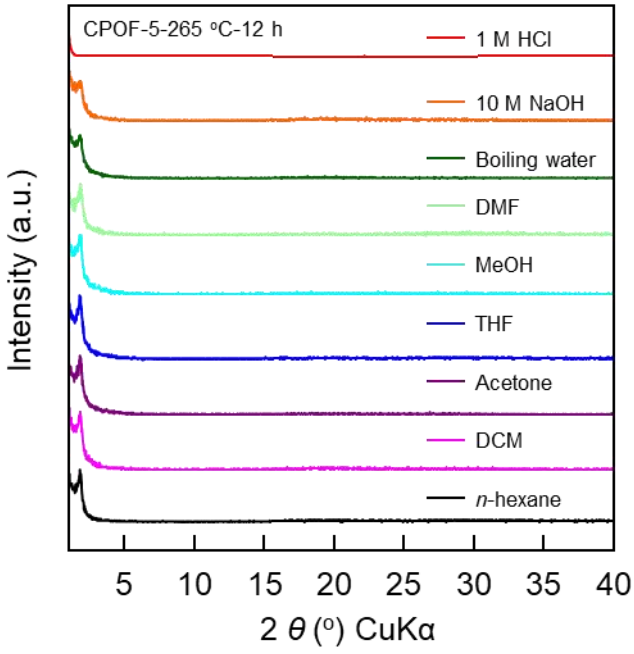
Section S16. Chemical stability tests



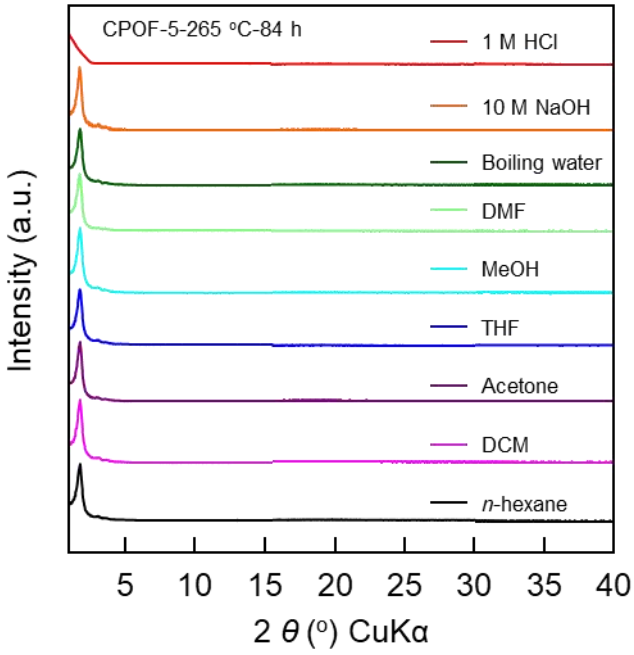
Supplementary Figure 78. PXRD patterns of CPOF-4-265 °C-12 h after treatments under different chemical environments for 24 h.



Supplementary Figure 79. PXRD patterns of CPOF-5 after treatments under different chemical environments for 24 h.



Supplementary Figure 80. PXRD patterns of CPOF-5-265 °C-12 h after treatments under different chemical environments for 24 h.



Supplementary Figure 81. PXRD patterns of CPOF-5-265 °C-84 h after treatments under different chemical environments for 24 h.

Section S17. Reaction kinetics and thermodynamic studies

In the in-situ FT-IR spectrum, the absorption peak area is calculated by integrating, then the reduction of the absorption peak area is proportional to the disappearance of the corresponding tracking group, and the conversion rate α of the group can be obtained by the following formula:

$$a = \frac{A_0 - A_t}{A_0} \times 100\% \quad \text{(Eq. S1)}$$

where A_0 is the absorption peak area of the acetylenic groups at the initial time, and A_t is the absorption peak area of the acetylenic groups at the time *t*.

Quantitative analysis of infrared spectroscopy is based on the Lambert-Beer law, and the absorbance *A* is proportional to the measured component concentration *c* and the optical path length *b* of the incident light passing through the sample, that is:

$$A = abc \quad \text{(Eq. S2)}$$

where *a* is the molar absorption coefficient. At constant optical path length, the measured *A* is only related to the type *a* and concentration *c* of the component. Thus, Eq. S2 can be transformed re-written as follow:

$$A = Kc \quad (K = ab, \text{ is a constant}) \quad \text{(Eq. S3)}$$

From the rate equation of the chemical reaction, the consumption rate of acetylenic groups in 2D COFs can be expressed by:

$$r = -\frac{dc}{dt} = kc^n \quad \text{(Eq. S4)}$$

where *n* is the reaction order; *k* is the reaction rate constant. Thus, Eq. S4 can be transformed re-written as Eq. S5.

$$r = -\frac{1}{K}\frac{dA}{dt} = k\frac{1}{K^n}A^n - \frac{dA}{dt} = kK^{1-n}A^n \quad \text{(Eq. S5)}$$

where *A* is the characteristic peak absorbance of acetylenic groups. When the reaction rate is independent of the concentration of the substance, the reaction follows a zero-order reaction model. Thus, Eq. S5 can be transformed re-written as follow:

$$r = kK \quad \text{(Eq. S6)}$$

The integral of the above equation can be transformed into:

$$A = kKt \quad \text{(Eq. S7)}$$

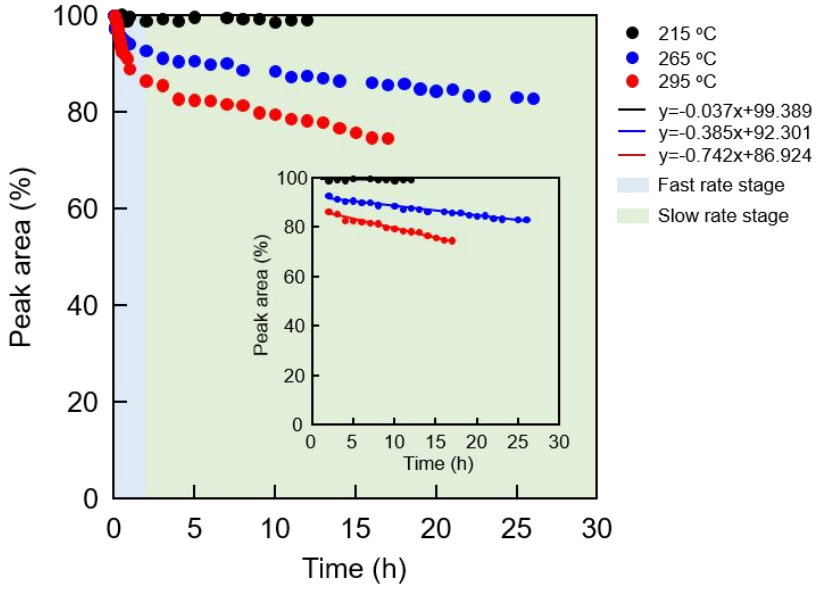
Since the absorbance of the acetylene group is directly proportional to its concentration Thus, Eq. S7 can be transformed re-written as Eq. S8.

$$c = kt \qquad \text{(Eq. S8)}$$

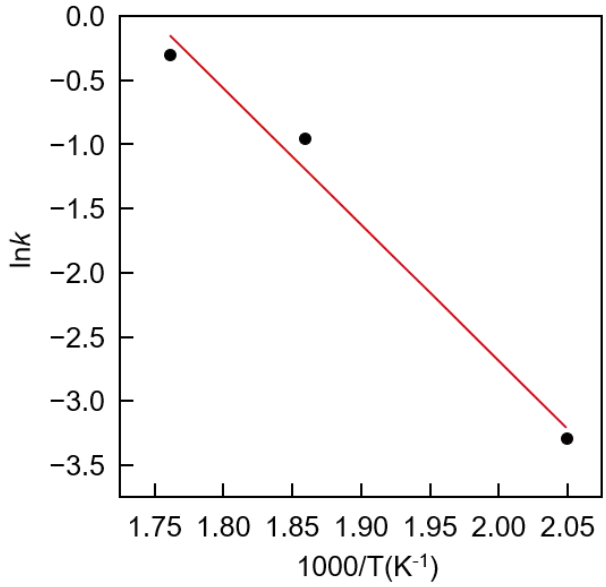
The rate constant k values at each reaction temperature obtained from the slope of each straight line are listed in Supplementary Table 3.

Supplementary Table 3. Constants of rate at various temperatures

Temperature (°C)	k (A h^{-1})
215	0.037
265	0.385
295	0.742



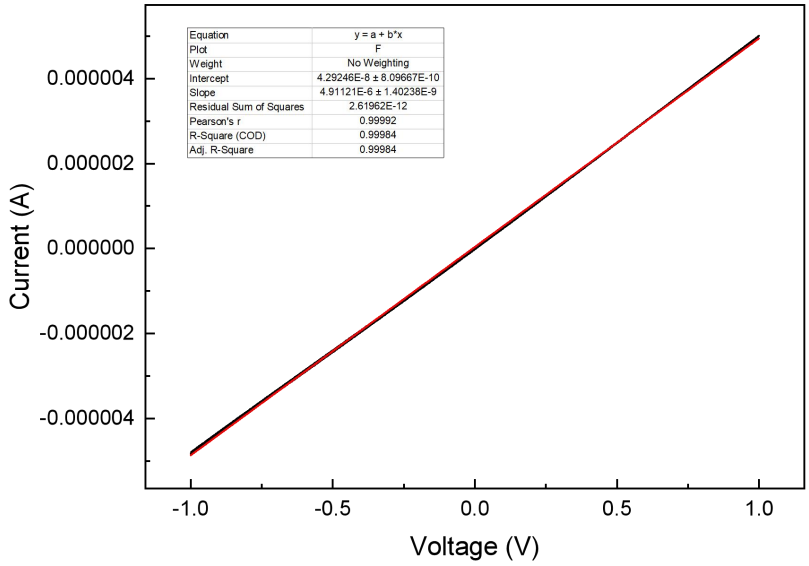
Supplementary Figure 82. In-situ variable temperature FT-IR of CPOF-4 at 215 °C, 265 °C and 295 °C respectively.



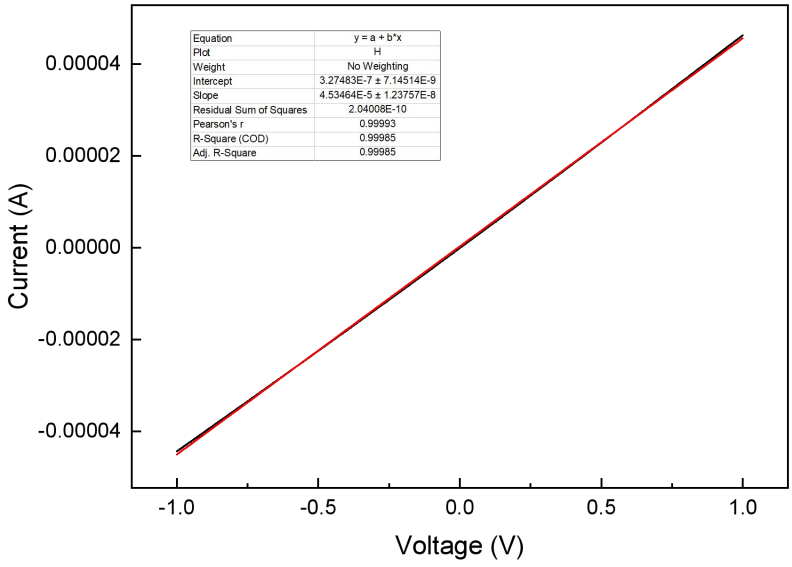
Supplementary Figure 83. Relationship between constants of rate and temperature.

Section S18. Electrical conductivity measurements

Iodine doping: A 20 mL brown vial was charged with 5 g iodine. A small vial (5 mL) charged with the powder of CPOF-4 or CPOF-4-265 °C-84 h was left into the brown vial, which was further capped tightly and kept in the dark at 75 °C for 24 h. After the doping samples were cooled to room temperature, a certain number of doping samples were separated for further experiments[4-7].



Supplementary Figure 84. I-V curves of I_2@CPOF-4.



Supplementary Figure 85. I-V curves of I_2@CPOF-4-265 °C-84 h.

Section S19. Unit cell parameters and fractional atomic coordinates

Supplementary Table 4. Unit cell parameters and fractional atomic coordinates for CPOF-4 calculated based on the slipped AA stacking mode.

Space group		*P*6/*m*	
Unit cell		$a = b = 53.8678$ Å, $c = 3.4685$ Å, $\alpha = \beta = 90^{o}$, $\gamma = 120^{o}$	
Pawley refinement		$R_p = 3.12\%$, $R_{wp} = 4.74\%$	
Atoms	x	y	z
C	0.32133	0.68449	0.00000
C	0.35116	0.69650	0.00000
C	0.27288	0.64235	0.00000
C	0.24722	0.63202	0.00000
H	0.31204	0.69830	0.00000
C	0.58990	0.39114	0.00000
C	0.57790	0.40891	0.00000
C	0.59565	0.43891	0.00000
C	0.62552	0.45072	0.00000
C	0.63748	0.43291	0.00000
C	0.61970	0.40310	0.00000
C	0.58352	0.45815	0.00000
N	0.55594	0.44776	0.00000
C	0.54092	0.46357	0.00000
C	0.55482	0.49363	0.00000
C	0.53898	0.50772	0.00000
C	0.50861	0.49236	0.00000
C	0.49511	0.46207	0.00000
C	0.51105	0.44810	0.00000
H	0.57596	0.36809	0.00000
H	0.55479	0.39917	0.00000
H	0.63961	0.47374	0.00000
H	0.66058	0.44238	0.00000
H	0.59821	0.48099	0.00000

H	0.57789	0.50664	0.00000
H	0.55129	0.53075	0.00000
H	0.47220	0.44839	0.00000
H	0.49996	0.42489	0.00000

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Supplementary Table 5. Unit cell parameters and fractional atomic coordinates for CPOF-5 calculated based on the slipped AA stacking mode.

Space group		*P*6/*m*	
Unit cell		$a = b = 61.4909$ Å, $c = 3.4829$ Å, $\alpha = \beta = 90^{o}$, $\gamma = 120^{o}$	
Pawley refinement		$R_p = 6.68\%$, $R_{wp} = 8.74\%$	
Atoms	x	y	z
C	0.35432	0.63474	0.00000
C	0.34369	0.65092	0.00000
C	0.36323	0.62119	0.00000
C	0.39995	0.61534	0.00000
C	0.41031	0.59962	0.00000
C	0.39464	0.57337	0.00000
C	0.36848	0.56317	0.00000
C	0.35816	0.57892	0.00000
C	0.37387	0.60501	0.00000
N	0.42935	0.56546	0.00000
C	0.40518	0.55643	0.00000
C	0.46856	0.56502	0.00000
C	0.48253	0.55275	0.00000
C	0.47065	0.52620	0.00000
C	0.44404	0.51280	0.00000
C	0.43020	0.52522	0.00000
C	0.44243	0.55154	0.00000
C	0.47393	0.48631	0.00000
C	0.51221	0.52606	0.00000
C	0.48571	0.51276	0.00000
C	0.35943	0.67702	0.00000
H	0.41222	0.63552	0.00000
H	0.43052	0.60786	0.00000
H	0.35606	0.54302	0.00000
H	0.33795	0.57081	0.00000

H	0.39224	0.53646	0.00000
H	0.47815	0.58533	0.00000
H	0.50259	0.56468	0.00000
H	0.43324	0.49263	0.00000
H	0.41001	0.51394	0.00000
H	0.45386	0.47443	0.00000
H	0.52298	0.54623	0.00000
H	0.37963	0.68503	0.00000

627 **Supplementary Table 6.** Unit cell parameters and fractional atomic coordinates for
628 CPOF-4-265 °C-84 h.

Space group		*P*1	
Unit cell		a = 50.9905 Å, b = 50.9040 Å, c = 5.2398 Å, α = 90.0°, β = 90.4°, γ = 119.9°	
Pawley refinement		R_p = 3.65%, R_{wp} = 5.47%	
Atoms	x	y	z
C	0.31433	0.68140	0.48147
C	0.34622	0.69679	0.48263
C	0.26406	0.63379	0.48422
C	0.24924	0.63171	0.25208
C	0.57449	0.36052	0.15211
C	0.55133	0.36821	0.14680
C	0.55880	0.39881	0.14137
C	0.58926	0.42112	0.14673
C	0.61232	0.41372	0.15094
C	0.60529	0.38337	0.15206
C	0.53676	0.40961	0.11671
C	0.48845	0.40622	0.15006
C	0.49202	0.42636	0.95212
C	0.47567	0.44171	0.95082
C	0.45519	0.43732	0.14721
C	0.45021	0.41566	0.33659
C	0.46662	0.40016	0.33653
C	0.31295	0.63281	0.48113
C	0.29756	0.64936	0.48054
C	0.36053	0.63010	0.48803
C	0.36327	0.61788	0.25629
C	0.64383	0.21293	0.21486
C	0.63536	0.18184	0.21196
C	0.60458	0.15937	0.20715

C	0.58289	0.16841	0.21147
C	0.59107	0.19911	0.21382
C	0.62159	0.22177	0.21431
C	0.59294	0.12637	0.18129
C	0.59506	0.08064	0.20403
C	0.57494	0.06508	0.00197
C	0.55880	0.03341	0.99473
C	0.56233	0.01633	0.18931
C	0.58391	0.03197	0.38327
C	0.60023	0.06387	0.38906
C	0.36141	0.67995	0.48346
C	0.34490	0.64802	0.48220
C	0.36417	0.73037	0.48878
C	0.37651	0.74527	0.25781
C	0.78953	0.43198	0.22461
C	0.81985	0.45614	0.23057
C	0.84392	0.45006	0.23996
C	0.83719	0.41995	0.23796
C	0.80723	0.39608	0.23190
C	0.78303	0.40159	0.22751
C	0.87634	0.47343	0.26229
C	0.91949	0.52301	0.21585
C	0.93746	0.52096	0.41110
C	0.96900	0.53889	0.40559
C	0.98334	0.55957	0.20766
C	0.96543	0.56273	0.01846
C	0.93367	0.54479	0.02475
C	0.68399	0.31693	0.43874
C	0.65204	0.30261	0.43644
C	0.73555	0.36426	0.44599
C	0.75136	0.37559	0.21597
C	0.39430	0.59235	0.26423

C	0.39698	0.56624	0.26143
C	0.37155	0.53720	0.25625
C	0.34274	0.53461	0.25909
C	0.33985	0.56083	0.26179
C	0.36574	0.58999	0.26354
C	0.37610	0.51052	0.24275
C	0.41434	0.49421	0.18364
C	0.39759	0.46367	0.25729
C	0.41066	0.44497	0.24514
C	0.44060	0.45653	0.15929
C	0.45706	0.48719	0.08729
C	0.44401	0.50563	0.09934
C	0.68682	0.36597	0.43725
C	0.70170	0.34875	0.43862
C	0.63972	0.37016	0.42918
C	0.63020	0.37610	0.16063
C	0.40315	0.80189	0.26592
C	0.42965	0.83029	0.26536
C	0.45834	0.83303	0.26542
C	0.46017	0.80633	0.26981
C	0.43356	0.77761	0.26958
C	0.40477	0.77522	0.26710
C	0.48549	0.86387	0.25747
C	0.50328	0.91888	0.20596
C	0.53360	0.93161	0.28554
C	0.55298	0.96326	0.27971
C	0.54235	0.98261	0.19449
C	0.51190	0.96947	0.11640
C	0.49278	0.93808	0.12205
C	0.63748	0.31990	0.43480
C	0.65478	0.35167	0.43531
C	0.63417	0.26949	0.44092

C	0.62963	0.25422	0.20827
C	0.19268	0.60528	0.25537
C	0.16527	0.60541	0.25343
C	0.16466	0.63252	0.26134
C	0.19238	0.65995	0.27313
C	0.22005	0.65985	0.26975
C	0.22033	0.63232	0.26002
C	0.13488	0.63119	0.25930
C	0.08015	0.59919	0.16694
C	0.06752	0.60924	0.35439
C	0.03593	0.59709	0.36448
C	0.01680	0.57509	0.18574
C	0.02970	0.56550	0.99839
C	0.06100	0.57739	0.98992
C	0.31556	0.68271	0.98153
C	0.34744	0.69680	0.98257
C	0.26417	0.63578	0.98432
C	0.24867	0.62444	0.75192
C	0.60561	0.40763	0.65011
C	0.60287	0.43371	0.64786
C	0.62826	0.46278	0.65208
C	0.65710	0.46542	0.65813
C	0.66005	0.43923	0.65832
C	0.63421	0.41006	0.65374
C	0.62369	0.48947	0.65339
C	0.58525	0.50599	0.62493
C	0.60233	0.53607	0.71185
C	0.58919	0.55470	0.72268
C	0.55881	0.54353	0.64740
C	0.54203	0.51333	0.56123
C	0.55519	0.49497	0.55003
C	0.31179	0.63303	0.98103

C	0.29763	0.65086	0.98043
C	0.35876	0.62847	0.98792
C	0.36978	0.62394	0.75679
C	0.59708	0.19822	0.71353
C	0.57060	0.16980	0.71093
C	0.54190	0.16703	0.71164
C	0.54004	0.19371	0.71580
C	0.56663	0.22245	0.71632
C	0.59543	0.22487	0.71540
C	0.51475	0.13616	0.70854
C	0.49686	0.08096	0.67228
C	0.46680	0.06861	0.75406
C	0.44747	0.03695	0.75813
C	0.45790	0.01720	0.68105
C	0.48809	0.02997	0.60032
C	0.50715	0.06137	0.59587
C	0.36133	0.67881	0.98342
C	0.34360	0.64688	0.98202
C	0.36584	0.73028	0.98895
C	0.37054	0.74584	0.75740
C	0.80737	0.39461	0.73253
C	0.83476	0.39446	0.73688
C	0.83536	0.36736	0.72749
C	0.80765	0.33995	0.71147
C	0.77999	0.34008	0.71118
C	0.77970	0.36760	0.72351
C	0.86513	0.36866	0.73054
C	0.91982	0.40063	0.82478
C	0.93253	0.39070	0.63693
C	0.96413	0.40291	0.62718
C	0.98321	0.42484	0.80664
C	0.97023	0.43429	0.99447

C	0.93892	0.42234	0.00259
C	0.68625	0.31920	0.93886
C	0.65440	0.30400	0.93671
C	0.73635	0.36640	0.94586
C	0.75084	0.36830	0.71456
C	0.42546	0.63937	0.76458
C	0.44856	0.63159	0.75965
C	0.44099	0.60095	0.75513
C	0.41053	0.57872	0.76218
C	0.38752	0.58620	0.76424
C	0.39464	0.61658	0.76512
C	0.46284	0.59003	0.72279
C	0.51134	0.59395	0.71046
C	0.50625	0.57464	0.50155
C	0.52240	0.55924	0.47707
C	0.54413	0.56268	0.66120
C	0.55040	0.58339	0.86294
C	0.53425	0.59904	0.88569
C	0.68854	0.36844	0.93740
C	0.70323	0.35128	0.93884
C	0.64104	0.37144	0.92927
C	0.63674	0.38219	0.66100
C	0.35649	0.78724	0.76173
C	0.36504	0.81834	0.75739
C	0.39584	0.84076	0.75559
C	0.41747	0.83164	0.76448
C	0.40922	0.80092	0.76678
C	0.37867	0.77832	0.76485
C	0.40755	0.87371	0.72585
C	0.40519	0.91929	0.72315
C	0.42485	0.93368	0.51832
C	0.44099	0.96528	0.50048

C	0.43797	0.98346	0.68724
C	0.41691	0.96894	0.88442
C	0.40053	0.93710	0.90059
C	0.63986	0.32152	0.93496
C	0.65679	0.35364	0.93552
C	0.63600	0.27005	0.94102
C	0.62366	0.25485	0.70896
C	0.21046	0.56806	0.76074
C	0.18012	0.54392	0.75872
C	0.15606	0.55003	0.75168
C	0.16282	0.58015	0.75254
C	0.19280	0.60401	0.75589
C	0.21698	0.59846	0.75831
C	0.12360	0.52667	0.73166
C	0.08052	0.47705	0.77669
C	0.06253	0.47913	0.58173
C	0.03099	0.46117	0.58726
C	0.01667	0.44044	0.78496
C	0.03460	0.43729	0.97403
C	0.06636	0.45525	0.96769
H	0.30262	0.69425	0.48248
H	0.56853	0.33692	0.15509
H	0.52780	0.35053	0.14265
H	0.59572	0.44494	0.14570
H	0.63572	0.43175	0.15409
H	0.54601	0.43322	0.06382
H	0.50783	0.43047	0.79985
H	0.47928	0.45728	0.79645
H	0.43471	0.41175	0.49125
H	0.46356	0.38456	0.48903
H	0.30016	0.60825	0.48188
H	0.66756	0.23006	0.21467

H	0.65256	0.17529	0.20755
H	0.55896	0.15159	0.20958
H	0.57350	0.20517	0.21407
H	0.56919	0.11259	0.12948
H	0.57149	0.07759	0.85124
H	0.54331	0.02224	0.83716
H	0.58715	0.01961	0.53685
H	0.61579	0.07563	0.54480
H	0.38592	0.69164	0.48613
H	0.77117	0.43689	0.21828
H	0.82459	0.47937	0.23157
H	0.85521	0.41447	0.24165
H	0.80290	0.37293	0.22937
H	0.89168	0.46540	0.31759
H	0.92708	0.50494	0.56506
H	0.98226	0.53561	0.54975
H	0.97609	0.57843	0.86259
H	0.92010	0.54662	0.87373
H	0.69496	0.30336	0.44140
H	0.41458	0.61443	0.26453
H	0.41955	0.56919	0.26018
H	0.32262	0.51244	0.25535
H	0.31755	0.55851	0.26038
H	0.35701	0.48785	0.26161
H	0.37480	0.45441	0.32720
H	0.39731	0.42146	0.30111
H	0.48032	0.49719	0.02571
H	0.45711	0.52918	0.04407
H	0.70016	0.39050	0.43775
H	0.38137	0.80077	0.26323
H	0.42730	0.85031	0.26274
H	0.48204	0.80770	0.27011

H	0.43530	0.75726	0.26971
H	0.50786	0.86670	0.28009
H	0.54216	0.91734	0.35529
H	0.57630	0.97259	0.34017
H	0.50260	0.98349	0.05503
H	0.46941	0.92845	0.06215
H	0.61299	0.30875	0.43325
H	0.19227	0.58377	0.25175
H	0.14435	0.58386	0.24853
H	0.19259	0.68131	0.28072
H	0.24122	0.68113	0.27476
H	0.13296	0.65015	0.32986
H	0.08182	0.62515	0.49951
H	0.02633	0.60417	0.51515
H	0.01546	0.54763	0.86696
H	0.07050	0.56896	0.84961
H	0.30477	0.69645	0.98262
H	0.58536	0.38553	0.64920
H	0.58028	0.43072	0.64443
H	0.67720	0.48761	0.66247
H	0.68236	0.44159	0.66340
H	0.64282	0.51203	0.67932
H	0.62546	0.54501	0.77492
H	0.60281	0.57785	0.78869
H	0.51845	0.50359	0.50703
H	0.54184	0.47176	0.48463
H	0.29811	0.60852	0.98179
H	0.61888	0.19938	0.71236
H	0.57298	0.14980	0.70854
H	0.51815	0.19232	0.71660
H	0.56486	0.24278	0.71690
H	0.49244	0.13341	0.73137

H	0.45841	0.08320	0.81815
H	0.42435	0.02792	0.82014
H	0.49726	0.01568	0.54498
H	0.53034	0.07072	0.53429
H	0.38580	0.68960	0.98612
H	0.80780	0.41614	0.73539
H	0.85568	0.41600	0.74384
H	0.80743	0.31860	0.70168
H	0.75883	0.31883	0.69984
H	0.86710	0.34977	0.65880
H	0.91829	0.37486	0.49123
H	0.97379	0.39594	0.47619
H	0.98442	0.45209	0.12656
H	0.92936	0.43068	0.14325
H	0.69780	0.30619	0.94151
H	0.43148	0.66299	0.76371
H	0.47208	0.64921	0.75270
H	0.40398	0.55488	0.76006
H	0.36410	0.56822	0.76361
H	0.45326	0.56616	0.67596
H	0.48939	0.57128	0.35896
H	0.51769	0.54440	0.31421
H	0.56678	0.58646	0.00943
H	0.53841	0.61396	0.04681
H	0.70166	0.39298	0.93781
H	0.33275	0.77015	0.75892
H	0.34788	0.82494	0.74910
H	0.44141	0.84841	0.76465
H	0.42675	0.79480	0.76866
H	0.43140	0.88743	0.68002
H	0.42790	0.92027	0.37377
H	0.45608	0.97552	0.34078

H	0.41411	0.98215	0.03259
H	0.38535	0.92623	0.05851
H	0.61536	0.31017	0.93337
H	0.22880	0.56313	0.76223
H	0.17536	0.52068	0.75745
H	0.14482	0.58565	0.74965
H	0.19716	0.62717	0.75594
H	0.10821	0.53470	0.67869
H	0.07290	0.49518	0.42801
H	0.01772	0.46446	0.44328
H	0.02395	0.42157	0.12976
H	0.07995	0.45342	0.11853
N	0.50818	0.39356	0.17286
N	0.60853	0.11307	0.23204
N	0.88740	0.50174	0.19902
N	0.40330	0.51519	0.20206
N	0.48163	0.88703	0.21817
N	0.11136	0.60688	0.17075
N	0.59633	0.48496	0.62267
N	0.51852	0.11286	0.67600
N	0.88862	0.39291	0.82056
N	0.49198	0.60666	0.75425
N	0.39171	0.88704	0.76117
N	0.11261	0.49831	0.79301

Supplementary Table 7. Unit cell parameters and fractional atomic coordinates for CPOF-5-265 °C-84 h.

Space group		*P*1	
Unit cell		a = 58.3743 Å, b = 58.3390 Å, c = 5.3044 Å, α = 89.9°, β = 89.9°, γ = 120.2°	
Pawley refinement		R_p = 4.44%, R_{wp} = 5.94%	
Atoms	x	y	z
C	0.35781	0.63374	0.45974
C	0.34588	0.6507	0.45462
C	0.36076	0.6238	0.22764
C	0.38873	0.6027	0.23518
C	0.39135	0.58016	0.23794
C	0.36899	0.55453	0.24258
C	0.34366	0.55179	0.23824
C	0.34089	0.5744	0.23384
C	0.36346	0.59999	0.23412
C	0.37267	0.53127	0.26045
C	0.43144	0.52638	0.40465
C	0.44183	0.50963	0.42858
C	0.42613	0.48246	0.37595
C	0.39971	0.47245	0.29931
C	0.38923	0.48935	0.27654
C	0.4052	0.51655	0.32921
C	0.43325	0.44634	0.20663
C	0.45557	0.46873	0.58812
C	0.43795	0.46517	0.39321
C	0.36211	0.67836	0.45463
C	0.36724	0.72316	0.45872
C	0.35054	0.69437	0.45424
C	0.37236	0.73642	0.22602
C	0.3612	0.77267	0.22858

C	0.36906	0.79977	0.22667
C	0.39616	0.81908	0.2287
C	0.415	0.81097	0.23124
C	0.40733	0.78409	0.23218
C	0.38035	0.76473	0.23137
C	0.40633	0.84783	0.22335
C	0.38741	0.89789	0.19969
C	0.39824	0.92542	0.17925
C	0.42453	0.94174	0.09669
C	0.43954	0.92992	0.03204
C	0.42873	0.9026	0.05167
C	0.40273	0.88631	0.14158
C	0.45476	0.98546	0.89085
C	0.43231	0.98502	0.27348
C	0.43685	0.97105	0.0841
C	0.32275	0.6829	0.45496
C	0.27712	0.64289	0.46067
C	0.30635	0.65521	0.45515
C	0.26353	0.63468	0.2291
C	0.22685	0.58721	0.23409
C	0.19968	0.56806	0.23261
C	0.18066	0.57609	0.23427
C	0.18912	0.6032	0.2359
C	0.21606	0.62232	0.23591
C	0.23514	0.61446	0.236
C	0.15186	0.55762	0.22929
C	0.10113	0.48854	0.20414
C	0.07359	0.47198	0.18281
C	0.05763	0.48223	0.09996
C	0.06981	0.50921	0.03616
C	0.09715	0.52559	0.0567
C	0.11307	0.51559	0.14668

C	0.01426	0.4691	0.892
C	0.014	0.44675	0.2747
C	0.02831	0.46537	0.086
C	0.31803	0.63914	0.45513
C	0.6422	0.36624	0.52106
C	0.65412	0.34928	0.52618
C	0.63501	0.37234	0.25328
C	0.58755	0.36118	0.25074
C	0.56839	0.36906	0.25269
C	0.57638	0.39617	0.25032
C	0.60347	0.41503	0.24748
C	0.6226	0.40734	0.24676
C	0.61478	0.38034	0.24763
C	0.55789	0.40635	0.25561
C	0.4888	0.38741	0.28118
C	0.4722	0.39824	0.30202
C	0.48237	0.42454	0.3839
C	0.50932	0.43958	0.44734
C	0.52574	0.42877	0.42731
C	0.51582	0.40275	0.33819
C	0.46913	0.45472	0.59029
C	0.4469	0.43234	0.20841
C	0.46547	0.43685	0.39711
C	0.63788	0.32162	0.52616
C	0.63275	0.27682	0.52205
C	0.64946	0.3056	0.52655
C	0.62385	0.26398	0.25405
C	0.60273	0.21474	0.24728
C	0.5802	0.18943	0.24509
C	0.55459	0.18602	0.24081
C	0.55187	0.20862	0.24491
C	0.57448	0.23414	0.24857

C	0.60005	0.23731	0.24777
C	0.53134	0.15892	0.22332
C	0.52643	0.0952	0.07876
C	0.50967	0.06795	0.05443
C	0.4825	0.05632	0.10702
C	0.47249	0.07268	0.18411
C	0.48941	0.10017	0.20722
C	0.5166	0.11155	0.1545
C	0.44633	0.01278	0.27581
C	0.46878	0.01312	0.89361
C	0.46519	0.0271	0.08917
C	0.67724	0.31706	0.52583
C	0.72286	0.35707	0.52012
C	0.69364	0.34475	0.52565
C	0.7361	0.36109	0.25243
C	0.78535	0.389	0.24317
C	0.8105	0.39157	0.24034
C	0.81354	0.36916	0.23686
C	0.79074	0.34384	0.24257
C	0.76539	0.34112	0.24725
C	0.76259	0.36374	0.24589
C	0.84047	0.37279	0.21915
C	0.90461	0.43149	0.07312
C	0.93181	0.44185	0.04998
C	0.94312	0.42613	0.10445
C	0.92646	0.3997	0.18201
C	0.89901	0.38925	0.20406
C	0.88797	0.40526	0.14967
C	0.98626	0.43314	0.27566
C	0.98662	0.45558	0.89332
C	0.9723	0.43792	0.0882
C	0.68197	0.36083	0.52568

C	0.35691	0.63294	0.95981
C	0.3446	0.64955	0.9547
C	0.36499	0.62764	0.72762
C	0.41245	0.63881	0.7359
C	0.43162	0.63095	0.74008
C	0.42363	0.60384	0.73999
C	0.39655	0.58497	0.73755
C	0.37741	0.59265	0.73527
C	0.38523	0.61964	0.73411
C	0.44212	0.59366	0.74694
C	0.51121	0.61259	0.77224
C	0.5278	0.60176	0.79435
C	0.51761	0.5755	0.87828
C	0.49065	0.56051	0.94248
C	0.47424	0.57132	0.92122
C	0.48418	0.59729	0.83003
C	0.53078	0.54538	0.0874
C	0.55311	0.56762	0.70435
C	0.5345	0.56318	0.89291
C	0.36063	0.67746	0.95421
C	0.36605	0.72287	0.95873
C	0.34905	0.69362	0.95419
C	0.37614	0.73599	0.72677
C	0.39725	0.78522	0.73198
C	0.41979	0.81054	0.73086
C	0.4454	0.81395	0.72748
C	0.44811	0.79134	0.7313
C	0.42551	0.76582	0.73356
C	0.39994	0.76266	0.73299
C	0.46867	0.84106	0.71126
C	0.4737	0.90491	0.56882
C	0.49047	0.93219	0.54695

C	0.51758	0.94379	0.60168
C	0.52751	0.92735	0.67829
C	0.51059	0.89983	0.69909
C	0.48346	0.88849	0.64438
C	0.55359	0.98709	0.77452
C	0.53146	0.98729	0.39251
C	0.53488	0.97304	0.58666
C	0.32132	0.68162	0.95498
C	0.27663	0.64166	0.96062
C	0.30537	0.65376	0.95515
C	0.2639	0.63887	0.7284
C	0.21464	0.61095	0.73609
C	0.18949	0.60837	0.73559
C	0.18644	0.63077	0.73135
C	0.20923	0.6561	0.73359
C	0.23459	0.65882	0.73485
C	0.2374	0.63621	0.73486
C	0.15949	0.62713	0.71525
C	0.09533	0.56838	0.57358
C	0.06814	0.55804	0.55056
C	0.05685	0.57381	0.60369
C	0.07352	0.60025	0.68002
C	0.10095	0.61067	0.70185
C	0.11198	0.59463	0.64859
C	0.01366	0.56681	0.77427
C	0.01346	0.54444	0.39238
C	0.02769	0.56206	0.58717
C	0.31693	0.63772	0.9556
C	0.64308	0.36702	0.021
C	0.65539	0.35042	0.0261
C	0.63923	0.37616	0.75313
C	0.61126	0.39726	0.74713

C	0.60863	0.4198	0.74765
C	0.631	0.44543	0.75064
C	0.65633	0.44817	0.7471
C	0.6591	0.42556	0.74562
C	0.63653	0.39997	0.7467
C	0.62731	0.4687	0.76642
C	0.56852	0.47364	0.90908
C	0.55812	0.4904	0.93123
C	0.57381	0.51754	0.8765
C	0.60025	0.52753	0.79955
C	0.61074	0.51062	0.77852
C	0.59476	0.48345	0.83329
C	0.56675	0.5536	0.70404
C	0.54433	0.53136	0.08669
C	0.56199	0.53484	0.89198
C	0.63936	0.3225	0.02658
C	0.63395	0.27709	0.02206
C	0.65095	0.30635	0.0266
C	0.62765	0.26355	0.75467
C	0.63883	0.22732	0.74634
C	0.63097	0.20022	0.74206
C	0.60388	0.18091	0.74248
C	0.58502	0.18901	0.74527
C	0.59269	0.21588	0.74735
C	0.61966	0.23525	0.74847
C	0.59371	0.15217	0.73544
C	0.61261	0.10209	0.70837
C	0.60178	0.07459	0.68575
C	0.57555	0.05838	0.60203
C	0.56059	0.0703	0.53864
C	0.57139	0.09759	0.5604
C	0.59734	0.11375	0.65131

C	0.54549	0.01496	0.39232
C	0.56762	0.01485	0.77471
C	0.56323	0.02909	0.58676
C	0.67868	0.31835	0.02581
C	0.72338	0.35833	0.02017
C	0.69462	0.34622	0.02564
C	0.73647	0.36529	0.75159
C	0.77314	0.41276	0.74086
C	0.80031	0.43191	0.73618
C	0.81933	0.42388	0.73694
C	0.81088	0.39678	0.7406
C	0.78394	0.37766	0.74362
C	0.76485	0.38552	0.74384
C	0.84813	0.44235	0.72956
C	0.89883	0.51145	0.70366
C	0.92637	0.52801	0.68189
C	0.94235	0.5178	0.59838
C	0.93016	0.49085	0.53406
C	0.90283	0.47447	0.55493
C	0.88689	0.48443	0.64589
C	0.98581	0.53095	0.39081
C	0.98591	0.55322	0.77314
C	0.97168	0.53465	0.58452
C	0.68306	0.36225	0.0252
N	0.39638	0.53531	0.30135
N	0.39166	0.85814	0.17221
N	0.14126	0.53255	0.17771
N	0.53282	0.39168	0.30742
N	0.53537	0.13926	0.18239
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N	0.46467	0.86074	0.67047

N	0.13962	0.60342	0.67519
N	0.6036	0.46467	0.80723
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H	0.3261	0.53228	0.24131
H	0.32126	0.57201	0.23138
H	0.35574	0.51143	0.24812
H	0.44413	0.54734	0.4409
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H	0.41998	0.44336	0.05275
H	0.45919	0.48269	0.73753
H	0.38352	0.68732	0.45582
H	0.34029	0.75791	0.22629
H	0.35413	0.80558	0.22362
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H	0.42735	0.86055	0.25551
H	0.36723	0.88565	0.26545
H	0.38606	0.93391	0.22741
H	0.45994	0.94184	0.9711
H	0.44089	0.89433	0.9968
H	0.45825	0.97532	0.73884
H	0.41886	0.97453	0.42636
H	0.31398	0.69547	0.45642
H	0.24139	0.58088	0.23203
H	0.19361	0.54721	0.2302
H	0.17479	0.60984	0.23421
H	0.222	0.64314	0.23496

H	0.13937	0.56611	0.26156
H	0.1131	0.4804	0.26995
H	0.06481	0.45119	0.23041
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H	0.10571	0.54614	0.00233
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H	0.58125	0.34027	0.2533
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H	0.61008	0.43604	0.24858
H	0.6434	0.42238	0.24645
H	0.56635	0.42739	0.22296
H	0.48072	0.36723	0.21604
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H	0.54626	0.44094	0.48132
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H	0.53237	0.20655	0.24214
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H	0.51151	0.1559	0.23571
H	0.54739	0.10359	0.04246
H	0.51816	0.0559	0.00073
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H	0.48121	0.11218	0.2693
H	0.44332	0.02301	0.43014
H	0.48276	0.02361	0.74417
H	0.686	0.3045	0.52437

H	0.78365	0.40664	0.24298
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H	0.94409	0.46245	0.99586
H	0.93464	0.38712	0.22491
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H	0.97578	0.41984	0.42957
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H	0.41875	0.65973	0.73462
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H	0.48201	0.54013	0.00439
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H	0.54834	0.93576	0.72138

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H	0.55646	0.97665	0.92787
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H	0.17239	0.58851	0.73539
H	0.20744	0.67368	0.7302
H	0.25199	0.67846	0.73355
H	0.15675	0.6441	0.72779
H	0.10346	0.55565	0.53683
H	0.05585	0.53744	0.49743
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H	0.02373	0.54079	0.24259
H	0.30453	0.61629	0.95751
H	0.59365	0.37778	0.74868
H	0.58878	0.41689	0.74882
H	0.67388	0.46769	0.74951
H	0.67873	0.42795	0.74586
H	0.64424	0.48854	0.7527
H	0.55583	0.4527	0.94698
H	0.53751	0.48191	0.98489
H	0.6128	0.54838	0.75642
H	0.631	0.51879	0.71638
H	0.58005	0.55652	0.55027
H	0.54067	0.51746	0.23712
H	0.61794	0.3134	0.02563
H	0.65973	0.24208	0.74736
H	0.64591	0.19442	0.7394
H	0.56402	0.17447	0.74321
H	0.57765	0.22155	0.74849

H	0.57266	0.13943	0.76646
H	0.63273	0.11425	0.77491
H	0.61392	0.06603	0.73304
H	0.54024	0.05845	0.47694
H	0.55928	0.10593	0.50625
H	0.54212	0.02531	0.24131
H	0.58094	0.02513	0.9284
H	0.68782	0.30612	0.02433
H	0.7586	0.41909	0.74168
H	0.80638	0.45276	0.73292
H	0.82521	0.39014	0.73882
H	0.778	0.35684	0.74601
H	0.86063	0.43386	0.76063
H	0.88686	0.51956	0.77021
H	0.93514	0.54878	0.72981
H	0.94182	0.48219	0.47243
H	0.89427	0.45395	0.50022
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H	0.97563	0.55632	0.92636
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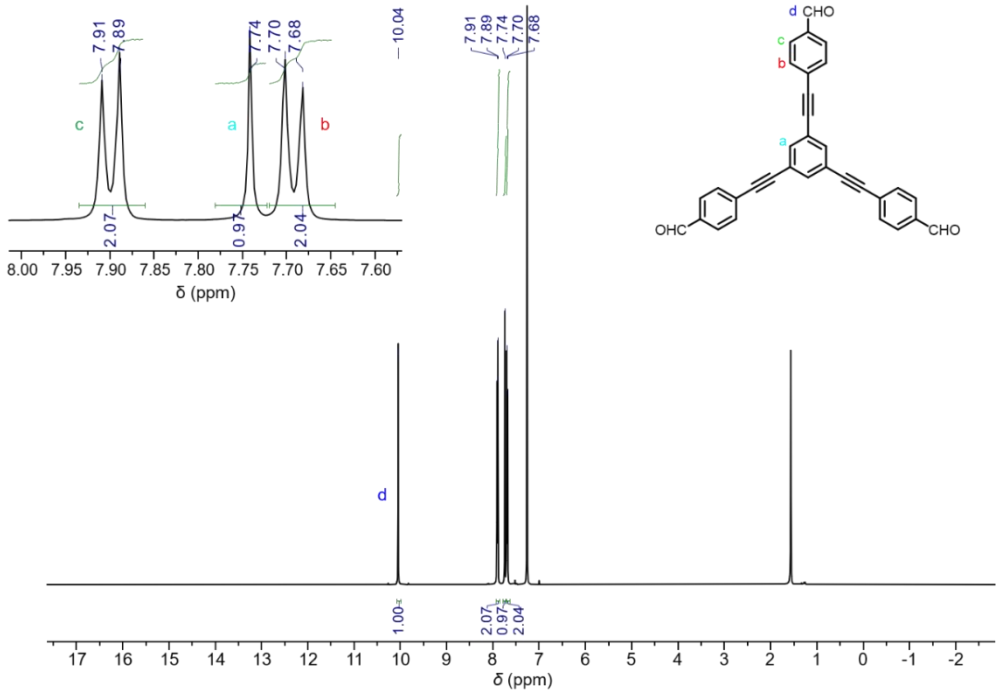
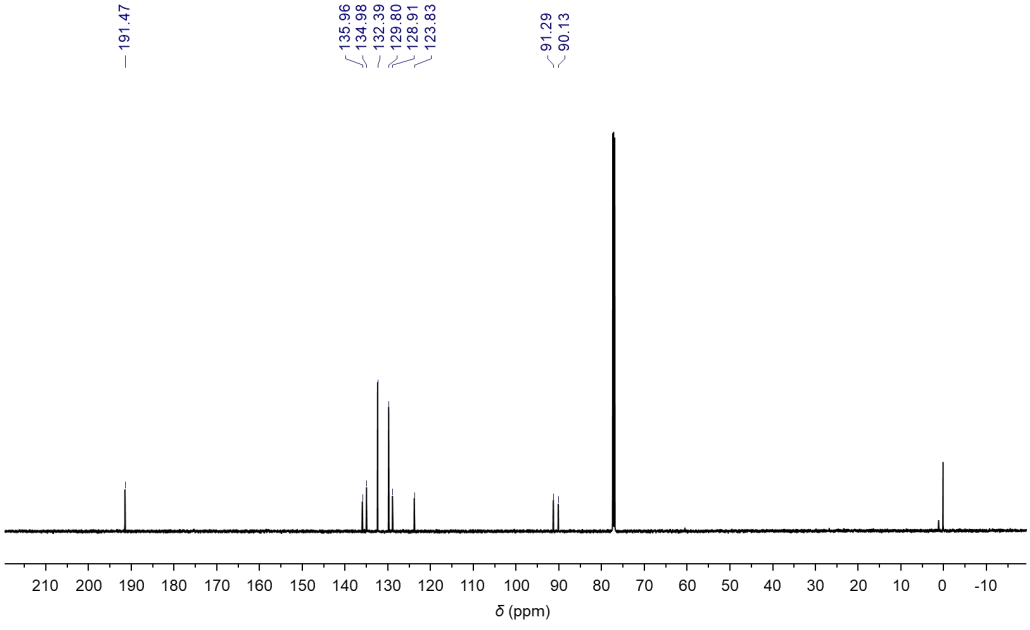


Supplementary Figure 86. The ^{1}H NMR spectra of 1,3,5-tri(4-formylphenylethynyl)benzene in $CDCl_3$.



Supplementary Figure 87. The ^{13}C NMR spectra of 1,3,5-tri(4-formylphenylethynyl)benzene in $CDCl_3$.

Section S20. References

[1] Perdew JP, Burke K, Ernzerhof M. Generalized gradient approximation made simple. *Phys Rev Lett* 1996;77:3865. [DOI: 10.1103/PhysRevLett.77.3865]

[2] Kresse G, Furthmüller J. Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set. *Comput Mater Sci* 1996;6:15. [DOI: 10.1016/0927-0256(96)00008-0]

[3] Kresse G, Furthmuller J. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Physical Review B Condensed Matter* 1996;54:11169. [DOI: 10.1103/PhysRevB.54.11169]

[4] Yin ZJ, Xu SQ, Zhan TG, Qi QY, Wu ZQ, Zhao X. Ultrahigh volatile iodine uptake by hollow microspheres formed from a heteropore covalent organic framework. *Chem Commun* 2017;53:7266. [PMID: 28265612 DOI: 10.1039/c7cc01045a]

[5] Wang P, Xu Q, Li Z, Jiang W, Jiang Q, Jiang D. Exceptional iodine capture in 2D covalent organic frameworks. *Adv Mater* 2018;e1801991. [PMID: 29806216 DOI: 10.1002/adma.201801991]

[6] Xing G, Zheng W, Gao L, et al. Nonplanar rhombus and kagome 2D covalent organic frameworks from distorted aromatics for electrical conduction. *J Am Chem Soc* 2022;144:5042. [PMID: 35189061 DOI: 10.1021/jacs.1c13534]

[7] Li H, Chang J, Li S, et al. Three-dimensional tetrathiafulvalene-based covalent organic frameworks for tunable electrical conductivity. *J Am Chem Soc* 2019;141:13324. [PMID: 31398976 DOI: 10.1021/jacs.9b06908]