Angewandte Chemie
Eine Zeitschrift der Gesellschaft Deutscher Chemiker

Supporting Information

High-Voltage Single-Ion Covalent Organic Framework Electrolytes Enabled by Nitrile Migration Ladders for Lithium Metal Batteries

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Table of Contents

1. Experimental Procedures

1.1 Materials

Acetone (99.9%), trimethylsilyl cyanide (96%), acetic acid glacial (99.8%), tetrahydrofuran (99%), 1-butanol (99%), sulfuric Acid (96%), toluene (99.8%) were purchased from Adamas. 1,2-dichlorobenzene (99.5%), 2,3,5,6-tetrafluoroterephthalaldehyde (98%), 4, 4', 4'', 4'''-(ethene-1, 1, 2, 2-tetrayl)tetraaniline (98%), hexane (97%), *n*-butyllithium (1.6 mol/L in hexane, Safe Seal), propylene carbonate (99.9%), methanol (99.9%), boron trifluoride ethyl ether (98%) and dichloromethane (99.9%) were purchased from Energy Chemical. Poly(vinylidene fluoride) were obtained from Solef. Super C65 were acquired from TIMICAL. Lithium metal was purchased from China Energy Lithium with a thickness of 400 μm. Lithium bis(trifluoromethanesulfonyl) imide (LiTFSI) was purchased from canrd and dried under 120 °C for 72 h under vacuum before storing in a glovebox with argon atmosphere. Toluene was freshly distilled from CaH_2 before using. LIR2032 coin cells were purchased from MTI. All other reagents were purchased from commercial sources and used without further purification, unless otherwise stated.

1.2 Materials Characterization

Nuclear Magnetic Resonance. Solid state ^{7}Li NMR and ^{13}C CP/MAS NMR spectra of covalent organic frameworks were recorded on a 400 WB AVANCE III 400 MHz at a spin rate of 10,000 Hz.

Infrared Spectroscopy. Infrared spectra were recorded on a Nicoletis10 FT-IR spectrometer. FT-IR spectra were recorded using the conventional KBr plate method, 32 scans were collected at a resolution of 4 cm^{-1}.

Inductively Coupled Plasma Emission Spectrometer. Inductively coupled plasma emission spectrometer (Plasma Quant PQ9,000) was used to analyze the Li^+ ion content in COF. The COF is dissolved used concentrated sulfuric acid and then the solution is diluted.

Sonication. Sonication was performed with a Chunrain CR-060S ultrasonic cleaner with a power output of 360 W and a frequency of 40 kHz.

Powdered X-ray Diffraction. Powdered X-ray diffraction (PXRD) patterns were obtained at room temperature on a RIGAKU TTRIII-18 KW. The as-obtained powder sample of COF was mounted in flat plates with a disc opening diameter of 1 cm. The line focused Cu X-ray tube was operated at 40 kV and 40 mA. The patterns were recorded in the 2θ range of 1-35° for an overall exposure time of 8 min.

Gas Adsorption. Gas adsorption isotherms were conducted on a Quadrasorb-evo Automatic Specific Surface and Pore Size Distribution (DFT model) Analyzer. 100 mg sample was prepared for testing. The samples were heated to 40 °C at a rate of 1°C/min and evacuated at 40 °C for 30 min, then heated to 120 °C at a rate of 1 °C/min heat, and evacuated at 120 °C until the outgas rate was ≤ 0.3 μmHg/min (holding the samples at 120 °C for 8 h was sufficient), at which point the tube was weighed again to determine the mass of the activated sample. The tube was then transferred to the analysis port of the instrument. UHP-grade (99.999% purity) N_2 was used for all adsorption measurements. N_2 isotherms were generated by incremental exposure to nitrogen up to 760 mmHg (1 atm) in a liquid nitrogen (77 K) bath. Brunauer-Emmett-Teller (BET) surface areas were calculated from the linear region of the N_2 isotherm at 77 K within the pressure range P/P_O of 0.05- 0.10. All BET linear fits had a minimum R^2 value of 0.9999. Before measurement, the samples were degassed and activated under vacuum at 100 °C for 24 h.

Thermogravimetric Analysis. Thermogravimetric analysis (TGA) was performed using a TGA 8,000 under N_2 by heating the sample to 800 °C at a rate of 10 °C min^{-1}.

Transmission Electron Microscopy. Transmission electron microscopy (TEM) was performed using a JEM-2100 transmission electron microscope, which was operated at 200 kV. Sample was dispersed evenly in absolute ethanol, then sonicated for 5 min and

load the sample to be tested into the sample rod for testing.

Field Emission Scanning Electron Microscopy. Field emission scanning electron microscopy (FE-SEM) was conducted using a Nova NanoSEM 450 scanning electron microscope. Samples were treated via Au sputtering for 250 s prior to observation.

Atomic Force Microscope. Atomic force microscope (AFM, NTEGRA spectra II03040111) was conducted using an atomic force microscope. The horizontal resolution was 0.2 nm, the vertical resolution was 0.01 nm, and the RMS was 0.05 nm.

X-ray photoelectron spectroscopy. X-ray photoelectron spectroscopy (XPS) and ex-situ XPS analysis were performed using an energy spectrometer (K-Alpha+).

Element Analyzer. The element content in COF was analyzed by Element analyzer (Flashsmart CHNS/OMVC).

Magnetron Sputter Deposition. Gold plating by magnetron sputter deposition (lesker PVD 75). The blocking electrode was 3 mm in diameter with gold sputtered by magnetron sputter deposition. The thickness of deposited gold is 50 nm.

1.3 Density Functional Theory Calculations and Molecular dynamics

Molecular Modeling. Structural modeling of COF was generated using the Materials Studio suite of programs. Molecular geometry optimization was performed with Materials Studio Forcite module. The initial lattice was created by starting with the space group P6. For COF structural evaluation, the lattice model was optimized using Forcite molecular dynamics module. The structure of CN-iCOF was constructed based on that of CN-COF. The hydrogen atoms of Im-COF were substituted into Li atoms and geometry optimization. Then the calculated PXRD pattern was generated with the Reflex Plus module. The lattice parameters were optimized by Pawley refinement until the R_p and R_{wp} value converged.

Density Functional Theory Calculations. Gauss View 6.0 was used for molecular modeling during DFT calculation. The Minimization geometries of grand state were calculated using Becke's three-parameter exchange functional[1] combined with the M062X correlation functional. Dispersion interaction was taken into account by DFT-D3[2] correction, and the 6-311G (d,p) basis set.[3] These analyses were performed using Gaussian16 program.[4] The orbitals were visualized using VMD and Multiwfn.[5]

$$E_{\text{binding energy}} = E_{\text{M-N-Li}} - E_{\text{M}} - 2E_{\text{Li}^+} \qquad \textbf{Equation S1}$$

Where $E_{\text{M-N-Li}}$ is the total energy of the structural unit in CN-iCOF, $E_{\text{M-N}}$ is the energy of the structural unit without Li ion, and E_{Li^+} is the energy of a single lithium ion, respectively.

Spin polarization is calculated based on density functional theory (DFT) DMol^3 package.[6] Generalized gradient approximation with Perdew-Burke-Ernzerhof functional (GGA-PBE) was used for the exchange-correlation energy.[7] Spin-polarized calculations were employed with the double numerical polarization basis set. To accommodate the van der Waals interactions, the semi-empirical Tkatchenko-Scheffler (TS) scheme was included for dispersion correction.[8] The SCF convergence for each electronic energy was set as 1.0×10^{-5} Ha, and the geometry optimization convergence criteria were set up as follows: 1.0×10^{-5} Ha for energy, 0.001 Ha Å^{-1} for force, and 0.005 Å for displacement, respectively. Li-ion migration pathways were examined by linear and quadratic synchronous transit (LST/QST) methods in combination with the conjugated gradient (CG) refinement.[9]

MD Simulations. MD simulations were performed using the Forcite module of the BIOVIA package. The object system was modeled by 10 layers of COF molecules stacked in a AA fashion, which contains a total of 360 Li^+ ions. The simulation system is periodic and fixes the geometry of the COF layer while allowing all lithium ion to move. The COMPASS force field was adopted to represent bonded and non-bonded interactions.[10] After optimization process, NVT and NPT procedures were applied to fully equilibrate the structure. Finally, NVT was used again at 298 K for 5 ns with a time step of 1 fs. Nose-Hoover thermostat was selected to provide a constant

temperature environment. Van der Waals and electrostatic potentials were also taken into account. The velocity Verlet algorithm with a time step of 1 fs was used to integrate the motion equations under an NVT ensemble with the Nose-Hoover thermostat.[11] The equilibrated trajectories were used for subsequent analysis. Configurations were visualized using Visual Molecular Dynamics software. Pair correlation functions between groups and Li^+ simulated and g_{A-B} used to calculate the coordination number using the following equation:[12]

$$NB = 4\pi \frac{NB}{V} \int r^2 g_{A-B}(r) dr \qquad \textbf{Equation S2}$$

NB is the number of *B* located around *A* within an adjacent solvent shell. *A* and *B* represent different atoms. *V* is the cell volume. Calculated MSD of lithium ions:[13]

$$D = \lim_{t\to\infty} \frac{1}{6t} < |r(t) - r(0)|^2 > \qquad \textbf{Equation S3}$$

Where *t* (time interval) is the time and the slope of *MSD* represents the diffusion coefficient.

1.4 Electrochemical measurements

The EIS measurement was carried out on Solartron EnergyLab XM with the frequency range 1 MHz to 0.1 Hz. Electrochemical stability window was determined with linear sweep voltammetry (LSV) utilizing stainless-steel/CN-iCOF/Li coin cells. The ionic conductivity (σ) was obtained from AC impedance spectroscopy using a stainless-steel/CN-iCOF/stainless-steel cell over a frequency range of 0.01 Hz to 1 MHz and at an amplitude of 10 mV. To ensure the accurate measurement of the dry solid-state electrolyte membrane, a drying procedure of CN-iCOF/ Im-COF (with additional LiTFSI) was carried out to remove trace amount of residue solvent. A layer of gold with a thickness of 50 nm has been plated for ease of conductivity measurement. The ionic conductivity (σ) was calculated by the following equation:

$$\sigma = \frac{L}{RA} \qquad \textbf{Equation S4}$$

where *L* is the pellet thickness, *R* is the resistance, and *A* is the area in contact with the electrodes. The activation energy (E_a) was determined from the slope of the Arrhenius plot.

The lithium transference number (t_{Li+}) has been performed using the Bruce-Vincent-Evans method, in which a DC signal is applied to a symmetric Li/ CN-iCOF/ Li cell. The current flowing through the cell and the impedance of the cell before and after the polarization are measured. According to this method, the t_{Li+} can be calculated according to the following equation:

$$t_{Li}^{+} = \frac{I_S[\Delta V - I_0 R_0]}{I_0[\Delta V - I_S R_S]} \qquad \textbf{Equation S5}$$

Where ΔV is the applied signal amplitude (10 mV), R_0 and R_s are the overall cell resistance values at the lithium electrode in the pristine state (before polarization) and in the steady state (after polarization), which are determined through AC Impedance. I_0 and I_s are the current values measured immediately after polarization and in the steady state condition.

The temperature dependence of ionic conductivity can be described by the Arrhenius equation as follows, where A refers to the pre-exponential factor, *T* is the temperature, E_a is the activation energy for conductivity, and *k* is Boltzmann constant.

$$\sigma = Ae^{\frac{-E_a}{kT}} \qquad \textbf{Equation S6}$$

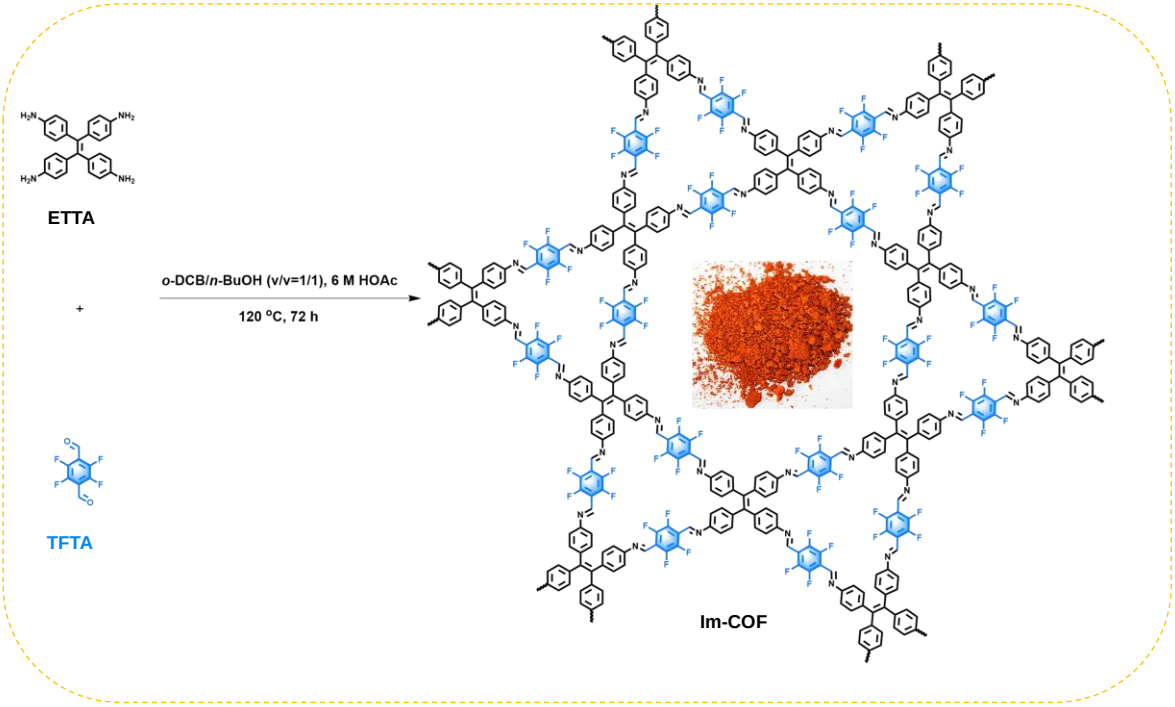
Poly(vinylidene fluoride) binder (PVDF, 5 wt %) was dissolved in *N*-methyl pyrrolidone (NMP) and stirred magnetic force at room temperature for 2 h. Cathode active materials (NCM811/$LiCoO_2$, 90 wt %) and conductive additive (Super C65, 5 wt %) were added to the binder solution, and well dispersed slurry was obtained by magnetic stirring at room temperature for 2 h. The slurry was coated on the aluminum foil substrate and dried in a vacuum oven at 100 °C for 12 h. The aluminum foil coated with active material was cut into a disc with a diameter of 15 mm and used as a working electrode. The mass loading of the active material was approximately 5.0 ~ 6.0 mg/cm^2. The electrode was dried in a vacuum oven at 100 °C for 2 h, then transferred to a glove box (Mikrouna).

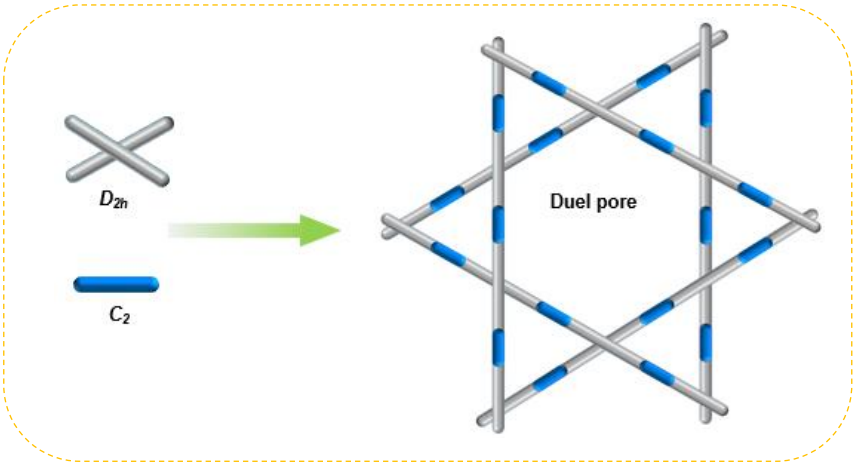
Battery assembly and electrode drying were all done in the argon glove box (Mikrouna H_2O < 0.01 ppm, O_2 < 0.01 ppm). LFP/NCM811/LCO cathode was used in conjunction with a CN-iCOF-based electrolyte and a lithium metal anode. In full battery testing, a limited amount of PC (~10 µL, 20 wt %) was added at the interface to improve interfacial contact. Linear sweep voltammetry (LSV) and electrochemical impedance spectroscopy (EIS) measurements were performed on electrochemical workstation (Solartron EnergyLab XM). The coin cells LIR2032 were assembled and rested before electrochemical measurements. The galvanostatic charge/discharge tests was performed using a NEWARE battery test system. Galvanostatic polarization test was conducted in the symmetric Li||Li setup to evaluate Li stripping/plating performance. Lithium stripping and plating test was monitored by NEWARE battery test system using symmetric Li||Li cells with the current densities of 0.1-0.2 mA cm^{-2}.

1.5 Synthetic Procedures

Synthesis of Imine-linked Im-COF.

4, 4', 4'', 4'''-(ethene-1, 1, 2, 2-tetrayl)tetraaniline (**ETTA**, 59 mg, 0.15 mmol) and 2,3,5,6-tetrafluoroterephthalaldehyde (**TFTA**, 62 mg, 0.3 mmol) were dissolved in a mixture of *o*-dichlorobenzene/*n*-butanol (v/v=1:1, 6 mL) and acetic acid (6 M (aq.), 0.6 mL) into a dried Schlenk tube of 25 mL, and ultrasonicated for 10 min. After being degassed in a liquid nitrogen bath for 20 min, the tube was purged with argon and then sealed. The tube was kept at 120 °C without disturbance for 4 days to yield a reddish-brown solid at the bottom of the tube. After the reaction was completed and cooled to room temperature, the reddish-brown solid was filtered and washed precipitate with tetrahydrofuran and acetone for three times. The product was soaked in anhydrous tetrahydrofuran for 24 h, centrifuged and dried in 120 °C vacuum overnight. Reddish brown Im-COF was obtained with separation yield of ~ 92%, which was insoluble in common organic solvents such as acetone, ethanol, and *N, N*-dimethylformamide. Anal. Calcd. For $(C_{39}H_{22}F_6N_3)_n$: C, 72.4; H, 3.4; F, 17.6; N, 6.5. Found: C, 70.7; H, 3.5; N, 6.9.

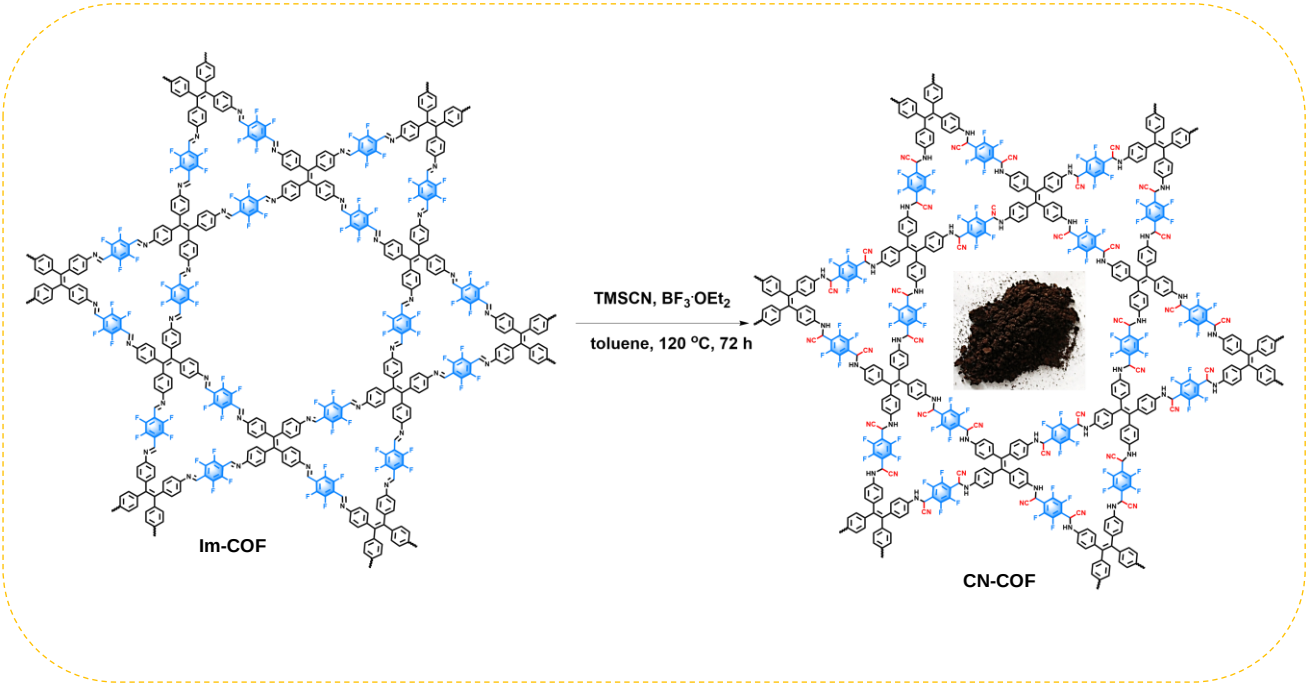


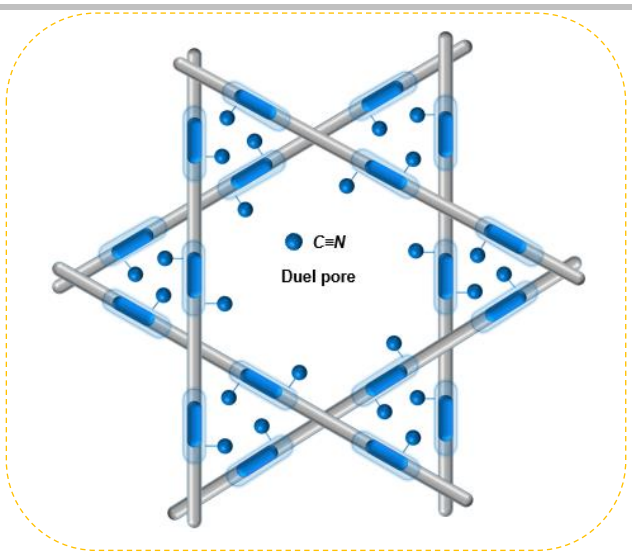


Scheme S1. Synthesis of Im-COF and dual pore topology diagrams.

Synthesis of CN-COF.[14]

A mixture of Im-COF (60 mg), BF_3•OEt_2 (60 μL), TMSCN (90 μL) in toluene (6 mL) was sealed in a Pyrex tube (35 mL) and heated under N_2 at 120 °C for 4 days. After it was allowed to cool to room temperature, and completely washed with THF and DCM, centrifuged and dried in 120 °C vacuum overnight. Dark-brown CN-COF was obtained with separation yield of ~ 90%, which was insoluble in common organic solvents such as acetone, ethanol, and *N, N*-dimethylformamide. Anal. Calcd. For $(C_{42}H_{25}F_9N_9)_n$: C, 69.3; H, 3.5; F, 15.6; N, 11.6. Found: C, 68.7; H, 3.4; N, 11.3.

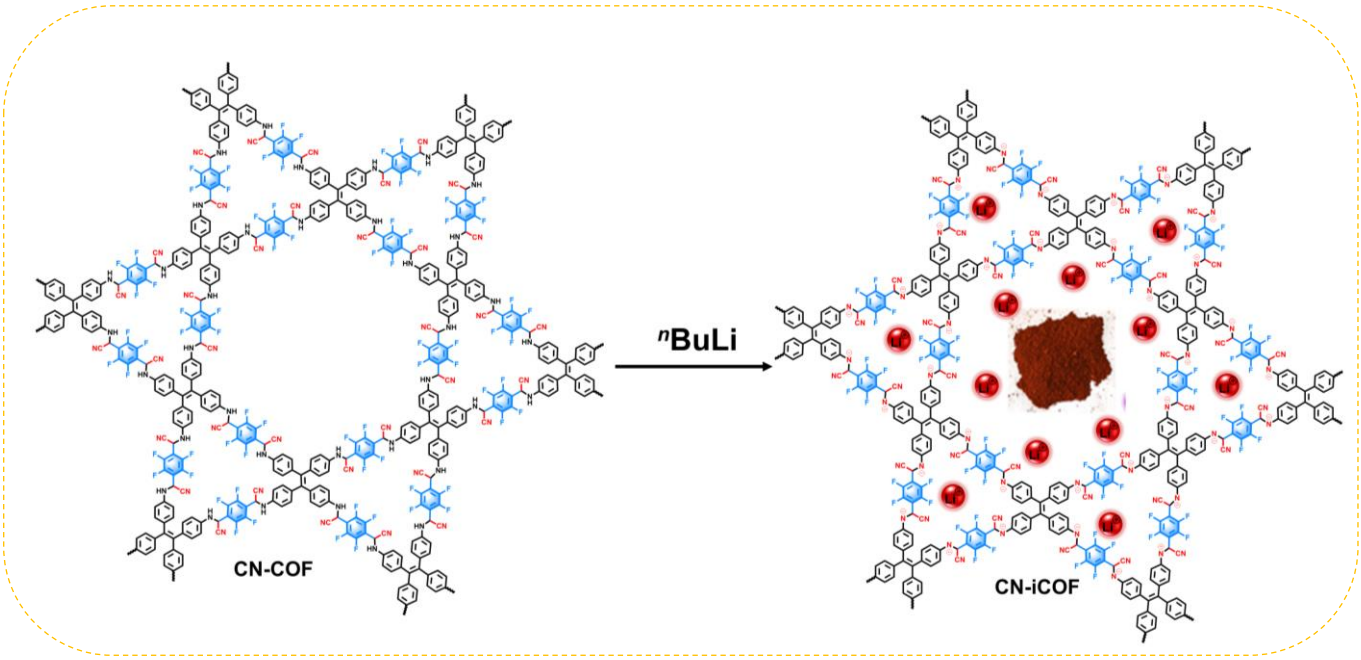


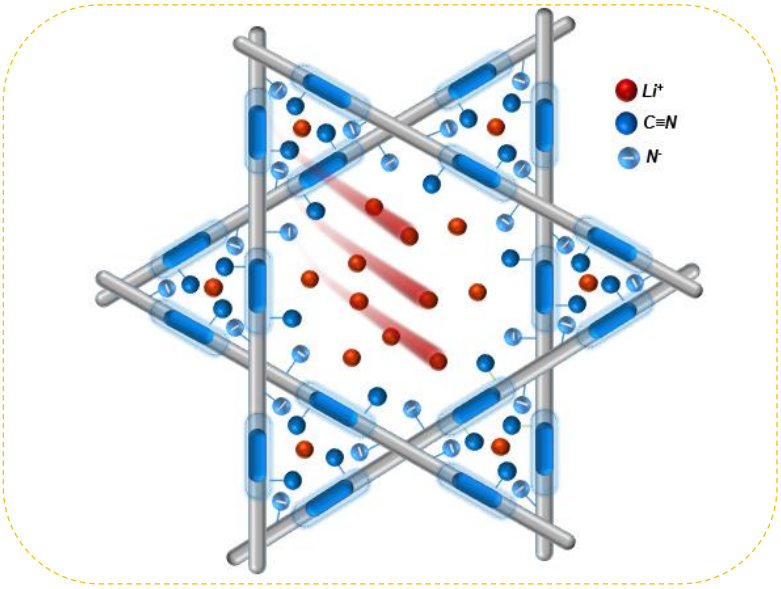


Scheme S2. Synthesis of CN-COF and dual pore topology diagrams.

Synthesis of CN-iCOF.[15]

To a well-dispersed suspension of CN-COF (20 mg) in hexane (1 mL) was added *n*-BuLi solution in hexane (1.6 M, 0.1 mL) dropwise in an ice bath over 10 min. The mixture was then stirred at room temperature for 16 h. The solid was isolated by centrifugation. Dry hexane (10 mL) was added, and the suspension was mixed well before centrifuging for 5 min. The hexane layer was decanted, and the solid was subjected to another round of washing. The washing cycle was repeated 5 times. After drying under vacuum, the product was collected as a brownish red solid (18.2 mg, 91%). Anal. Calcd for $(C_{14}H_8F_2N_2Li)_n$: C, 69.6; H, 3.1; Li, 2.8; N, 11.6. Found: C, 65.4; H, 3.0; Li, 2.9; N, 11.2.





Scheme S3. Synthesis of CN-iCOF and dual pore topology diagrams.

Table S1. Comparison of synthesis of Im-COF under different conditions.

Aldehyde monomer	Amine monomer	Solvent (1 mL, v/v)	Catalyst (HOAc, 6 M)	Yield
TFTA	ETTA	Dioxane: Mesitylene (1:1)	10%	73%
TFTA	ETTA	Dioxane: Mesitylene (2:1)	10%	69%
TFTA	ETTA	EtOH: Mesitylene (1:1)	10%	70%
TFTA	ETTA	Dioxane	10%	\
TFTA	ETTA	*o*-DCB : *n*-BuOH (1:1)	10%	92%
TFTA	ETTA	*o*-DCB : *n*-BuOH (2:1)	10%	80%

Preparation of COF solid-state electrolytes (SSEs)

50 mg of CN-iCOF was dried at 100 °C overnight in a vacuum drying oven, then placed into a membrane press tool and compressed under a pressure of 25 MPa using a uniaxial hydraulic press (Tianjin Tianguang Optical Instrument Co., Ltd. China) to form an electrolyte membrane with a diameter of 15 mm. The pressed membrane was further dried in a vacuum drying oven for 8 hours, and then transferred to a glovebox for later use.

50 mg of Im-COF was dried at 100 °C overnight in a vacuum drying oven. The powder of Im-COF (100 mg) was immersed into THF solution of 1 M LiTFSI under Ar for 24 h. Powders were collected by vacuum filtration and rinse with anhydrous THF in argon glove box. The Li-impregnated COF powder was dried in a glovebox with heating function at 80 °C for 8 h under vacuum. Then it was placed

into a membrane press tool and compressed under a pressure of 25 MPa using a uniaxial hydraulic press (Tianjin Tianguang Optical Instrument Co., Ltd. China) to form an electrolyte membrane with a diameter of 15 mm.

2. NMR Spectra

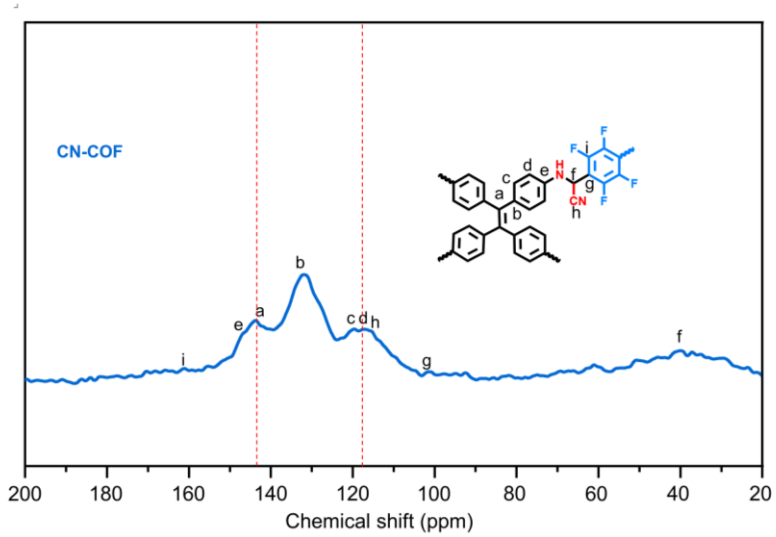


Figure S1. ^{13}C CP/MAS NMR spectrum of CN-COF.

3. FT-IR Spectra

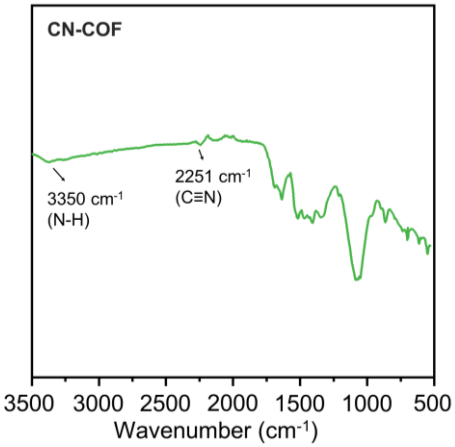


Figure S2. FT-IR spectra of CN-COF.

4. X-ray Photoelectron Spectroscopy

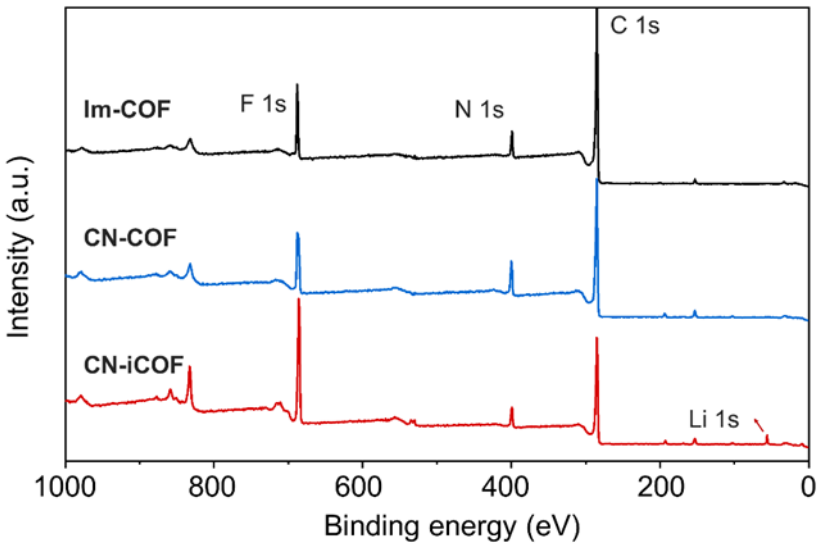


Figure S3. Full XPS spectra of Im-COF, CN-COF and CN-ICOF.

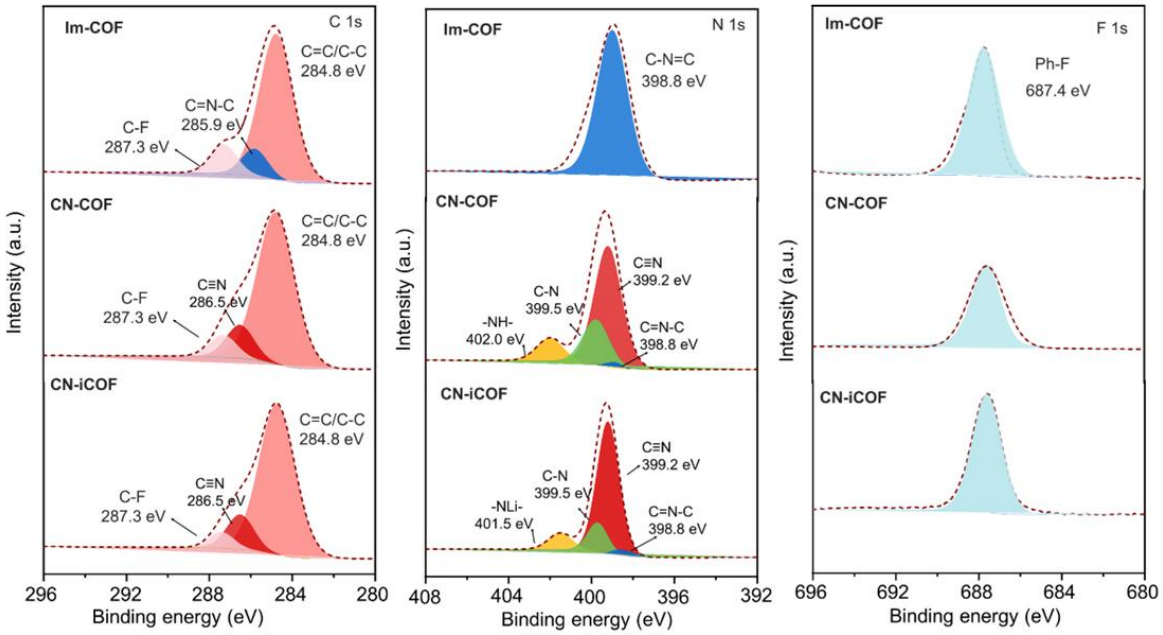


Figure S4. High-resolution XPS spectra of C 1s, N 1s and F 1s for Im-COF, CN-COF and CN-iCOF.

5. Inductively Coupled Plasma Emission Spectrometer

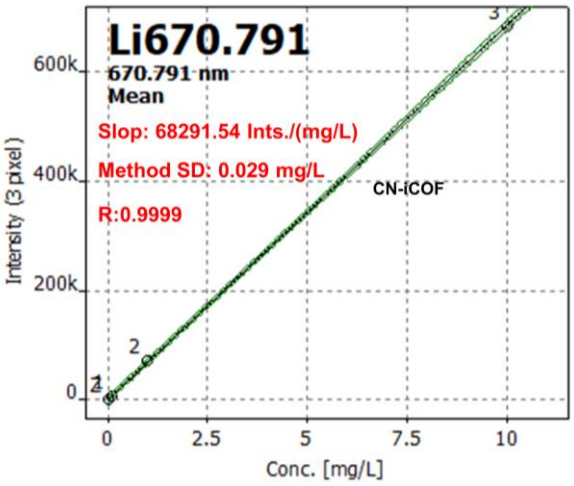


Figure S5. Inductively coupled plasma emission spectrometer for CN-iCOF.

6. Structural Modeling and X-ray Diffraction Analyses

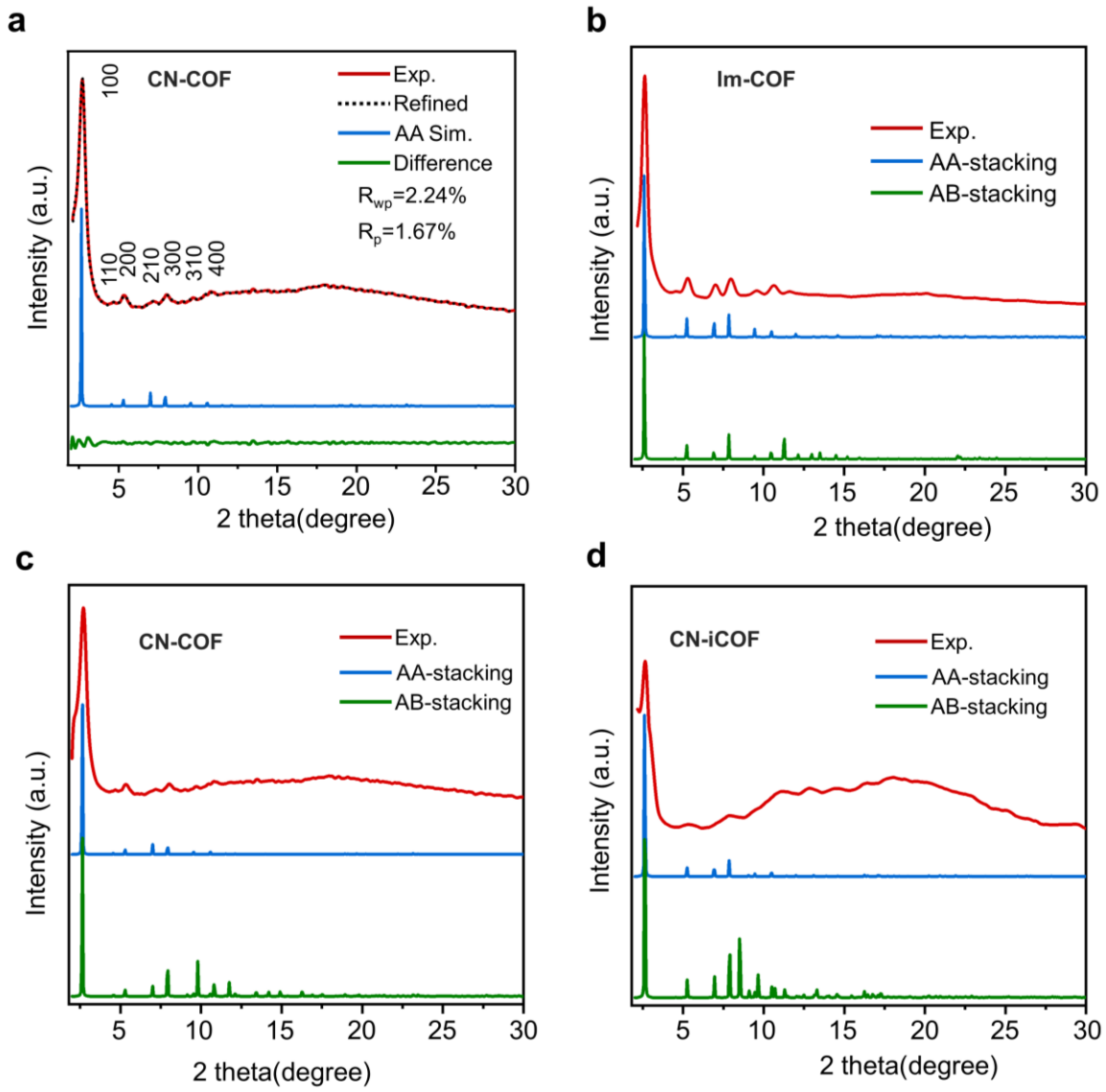


Figure S6. a) PXRD analysis of CN-COF. Observed PXRD patterns (red), refined modeling profile (black), simulated PXRD patterns (blue) and difference between the observed PXRD and refined modeling patterns (green). b-d) PXRD pattern of as-synthesized COF (red), compared with the simulated PXRD pattern of eclipsed AA-modeling (blue) and AB-modeling (green).

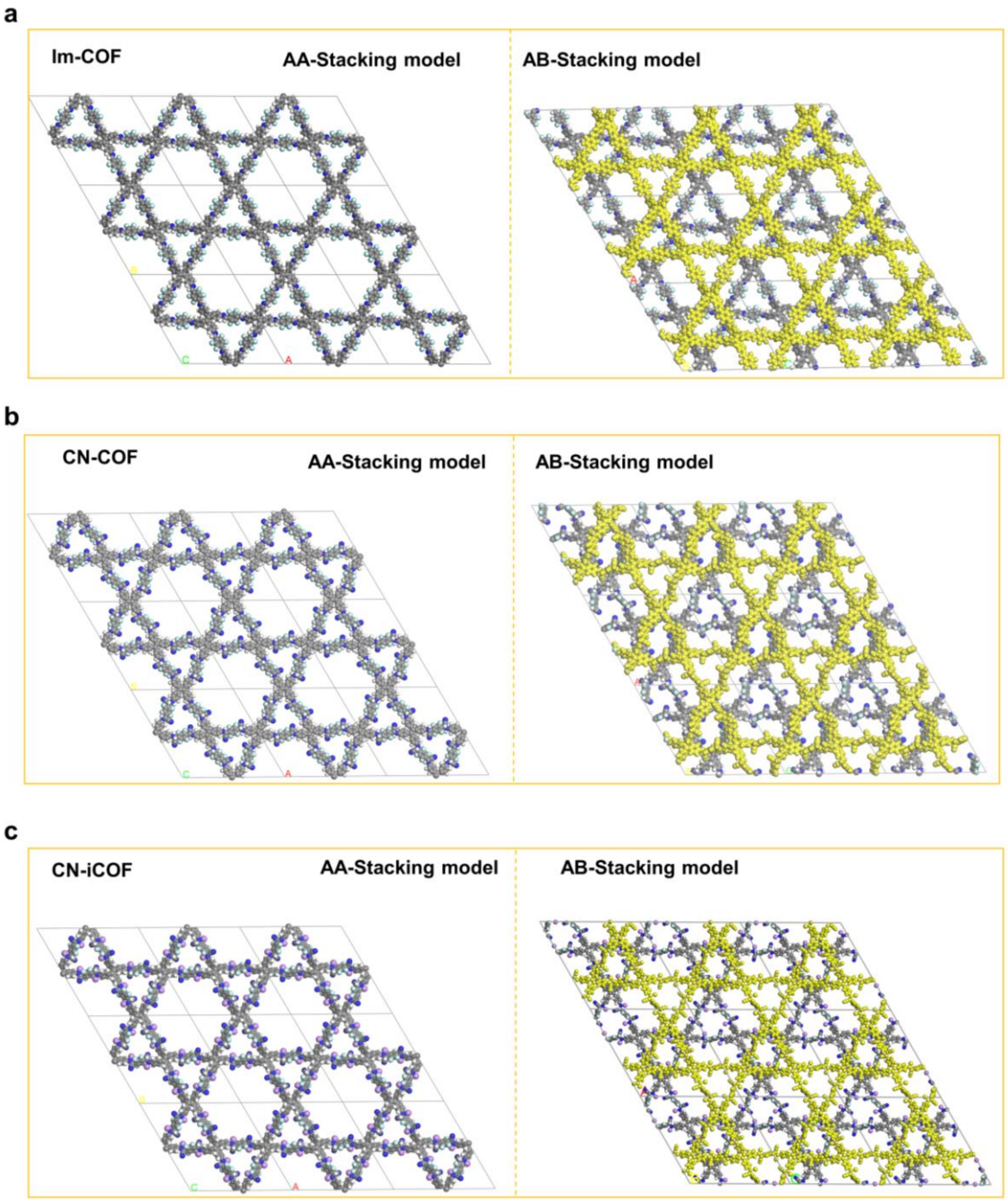


Figure S7. a-c) Different stacking patterns of Im-COF, CN-COF and CN-iCOF (AA-Stacking model and AB-Stacking model).

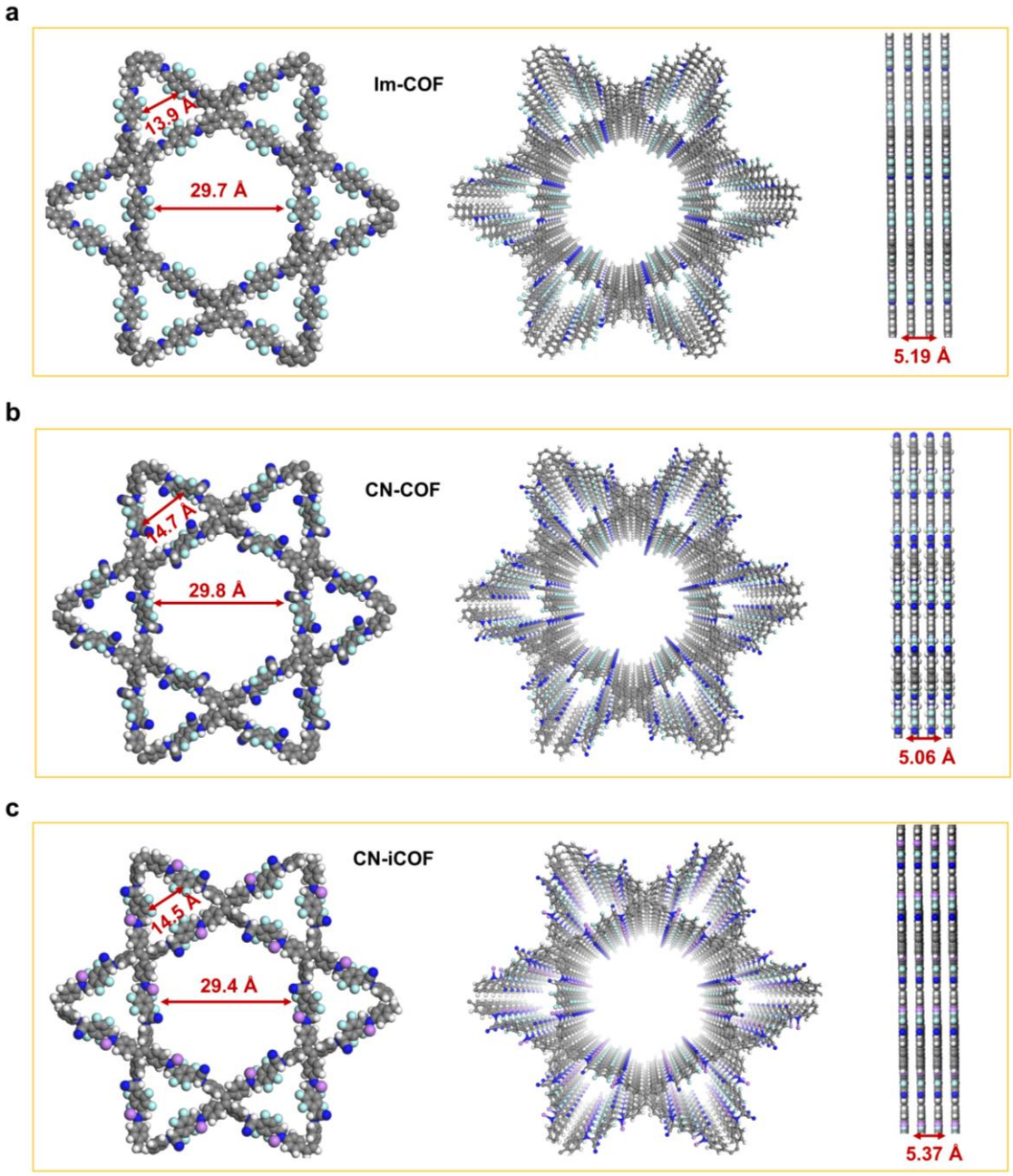


Figure S8. a-c) 3D view of Im-COF, CN-COF and CN-iCOF. Aperture and layer spacing simulation.

Table S2. Fractional atomic coordinates for the unit cell of Im-COF with AA-stacking.

Im-COF: Space group symmetry P6				
a = b = 38.974 Å; c = 5.196 Å α = β = 90°, γ = 120°				
Atom		x	y	z
H	1	-0.524994	-0.458392	-0.262349
H	2	-0.438475	-0.417450	0.342850
H	3	-0.434097	-0.352566	0.329403
H	4	-0.520225	-0.393207	-0.280148
H	5	-0.446272	-0.302067	0.330071
H	6	-0.464462	-0.150372	-0.288382
H	7	-0.433231	-0.079524	-0.264121
H	8	-0.440349	-0.020037	-0.287361
H	9	-0.514506	-0.058988	0.380498
H	10	-0.507646	-0.118505	0.407445
H	11	0.458392	-0.066602	-0.262349
H	12	0.417450	-0.021025	0.342850
H	13	0.352566	-0.081531	0.329403
H	14	0.393207	-0.127018	-0.280148
H	15	0.302067	-0.144205	0.330071
H	16	0.150372	-0.314090	-0.288382
H	17	0.079524	-0.353706	-0.264121
H	18	0.020037	-0.420313	-0.287361
H	19	0.058988	-0.455518	0.380498
H	20	0.118505	-0.389141	0.407445
H	21	0.066602	0.524994	-0.262349
H	22	0.021025	0.438475	0.342850
H	23	0.081531	0.434097	0.329403
H	24	0.127018	0.520225	-0.280148
H	25	0.144205	0.446272	0.330071
H	26	0.314090	0.464462	-0.288382
H	27	0.353706	0.433231	-0.264121
H	28	0.420313	0.440349	-0.287361
H	29	0.455518	0.514506	0.380498
H	30	0.389141	0.507646	0.407445
H	31	0.524994	0.458392	-0.262349
H	32	0.438475	0.417450	0.342850
H	33	0.434097	0.352566	0.329403
H	34	0.520225	0.393207	-0.280148
H	35	0.446272	0.302067	0.330071
H	36	0.464462	0.150372	-0.288382
H	37	0.433231	0.079524	-0.264121

H	38	0.440349	0.020037	-0.287361
H	39	0.514506	0.058988	0.380498
H	40	0.507646	0.118505	0.407445
H	41	-0.458392	0.066602	-0.262349
H	42	-0.417450	0.021025	0.342850
H	43	-0.352566	0.081531	0.329403
H	44	-0.393207	0.127018	-0.280148
H	45	-0.302067	0.144205	0.330071
H	46	-0.150372	0.314090	-0.288382
H	47	-0.079524	0.353706	-0.264121
H	48	-0.020037	0.420313	-0.287361
H	49	-0.058988	0.455518	0.380498
H	50	-0.118505	0.389141	0.407445
H	51	-0.066602	-0.524994	-0.262349
H	52	-0.021025	-0.438475	0.342850
H	53	-0.081531	-0.434097	0.329403
H	54	-0.127018	-0.520225	-0.280148
H	55	-0.144205	-0.446272	0.330071
H	56	-0.314090	-0.464462	-0.288382
H	57	-0.353706	-0.433231	-0.264121
H	58	-0.420313	-0.440349	-0.287361
H	59	-0.455518	-0.514506	0.380498
H	60	-0.389141	-0.507646	0.407445
C	1	-0.505099	-0.435692	-0.134289
C	2	-0.482224	-0.443259	0.039541
C	3	-0.456829	-0.412709	0.207958
C	4	-0.454470	-0.375612	0.201144
C	5	-0.477397	-0.368493	0.023374
C	6	-0.502597	-0.398745	-0.142865
C	7	-0.459103	-0.300610	0.148094
C	8	-0.459281	-0.263824	0.080130
C	9	-0.439250	-0.230530	0.239740
C	10	-0.439918	-0.195350	0.185546
C	11	-0.460249	-0.193326	-0.031507
C	12	-0.479551	-0.226133	-0.194083
C	13	-0.479281	-0.261429	-0.139417
C	14	-0.462441	-0.157542	-0.088809
C	15	-0.470814	-0.103613	0.070951
C	16	-0.451738	-0.075595	-0.125482
C	17	-0.455537	-0.041686	-0.137440
C	18	-0.478740	-0.035710	0.044518
C	19	-0.497079	-0.063565	0.240475
C	20	-0.493078	-0.097126	0.254656
C	21	0.517255	0.518053	0.037852

C	22	0.435692	-0.069407	-0.134289
C	23	0.443259	-0.038965	0.039541
C	24	0.412709	-0.044119	0.207958
C	25	0.375612	-0.078857	0.201144
C	26	0.368493	-0.108905	0.023374
C	27	0.398745	-0.103852	-0.142865
C	28	0.300610	-0.158493	0.148094
C	29	0.263824	-0.195457	0.080130
C	30	0.230530	-0.208720	0.239740
C	31	0.195350	-0.244568	0.185546
C	32	0.193326	-0.266924	-0.031507
C	33	0.226133	-0.253417	-0.194083
C	34	0.261429	-0.217852	-0.139417
C	35	0.157542	-0.304899	-0.088809
C	36	0.103613	-0.367201	0.070951
C	37	0.075595	-0.376143	-0.125482
C	38	0.041686	-0.413852	-0.137440
C	39	0.035710	-0.443029	0.044518
C	40	0.063565	-0.433514	0.240475
C	41	0.097126	-0.395952	0.254656
C	42	-0.518053	-0.000797	0.037852
C	43	0.069407	0.505099	-0.134289
C	44	0.038965	0.482224	0.039541
C	45	0.044119	0.456829	0.207958
C	46	0.078857	0.454470	0.201144
C	47	0.108905	0.477397	0.023374
C	48	0.103852	0.502597	-0.142865
C	49	0.158493	0.459103	0.148094
C	50	0.195457	0.459281	0.080130
C	51	0.208720	0.439250	0.239740
C	52	0.244568	0.439918	0.185546
C	53	0.266924	0.460249	-0.031507
C	54	0.253417	0.479551	-0.194083
C	55	0.217852	0.479281	-0.139417
C	56	0.304899	0.462441	-0.088809
C	57	0.367201	0.470814	0.070951
C	58	0.376143	0.451738	-0.125482
C	59	0.413852	0.455537	-0.137440
C	60	0.443029	0.478740	0.044518
C	61	0.433514	0.497079	0.240475
C	62	0.395952	0.493078	0.254656
C	63	0.000797	-0.517255	0.037852
C	64	0.505099	0.435692	-0.134289
C	65	0.482224	0.443259	0.039541

C	66	0.456829	0.412709	0.207958
C	67	0.454470	0.375612	0.201144
C	68	0.477397	0.368493	0.023374
C	69	0.502597	0.398745	-0.142865
C	70	0.459103	0.300610	0.148094
C	71	0.459281	0.263824	0.080130
C	72	0.439250	0.230530	0.239740
C	73	0.439918	0.195350	0.185546
C	74	0.460249	0.193326	-0.031507
C	75	0.479551	0.226133	-0.194083
C	76	0.479281	0.261429	-0.139417
C	77	0.462441	0.157542	-0.088809
C	78	0.470814	0.103613	0.070951
C	79	0.451738	0.075595	-0.125482
C	80	0.455537	0.041686	-0.137440
C	81	0.478740	0.035710	0.044518
C	82	0.497079	0.063565	0.240475
C	83	0.493078	0.097126	0.254656
C	84	-0.517255	-0.518053	0.037852
C	85	-0.435692	0.069407	-0.134289
C	86	-0.443259	0.038965	0.039541
C	87	-0.412709	0.044119	0.207958
C	88	-0.375612	0.078857	0.201144
C	89	-0.368493	0.108905	0.023374
C	90	-0.398745	0.103852	-0.142865
C	91	-0.300610	0.158493	0.148094
C	92	-0.263824	0.195457	0.080130
C	93	-0.230530	0.208720	0.239740
C	94	-0.195350	0.244568	0.185546
C	95	-0.193326	0.266924	-0.031507
C	96	-0.226133	0.253417	-0.194083
C	97	-0.261429	0.217852	-0.139417
C	98	-0.157542	0.304899	-0.088809
C	99	-0.103613	0.367201	0.070951
C	100	-0.075595	0.376143	-0.125482
C	101	-0.041686	0.413852	-0.137440
C	102	-0.035710	0.443029	0.044518
C	103	-0.063565	0.433514	0.240475
C	104	-0.097126	0.395952	0.254656
C	105	0.518053	0.000797	0.037852
C	106	-0.069407	-0.505099	-0.134289
C	107	-0.038965	-0.482224	0.039541
C	108	-0.044119	-0.456829	0.207958
C	109	-0.078857	-0.454470	0.201144

C	110	-0.108905	-0.477397	0.023374
C	111	-0.103852	-0.502597	-0.142865
C	112	-0.158493	-0.459103	0.148094
C	113	-0.195457	-0.459281	0.080130
C	114	-0.208720	-0.439250	0.239740
C	115	-0.244568	-0.439918	0.185546
C	116	-0.266924	-0.460249	-0.031507
C	117	-0.253417	-0.479551	-0.194083
C	118	-0.217852	-0.479281	-0.139417
C	119	-0.304899	-0.462441	-0.088809
C	120	-0.367201	-0.470814	0.070951
C	121	-0.376143	-0.451738	-0.125482
C	122	-0.413852	-0.455537	-0.137440
C	123	-0.443029	-0.478740	0.044518
C	124	-0.433514	-0.497079	0.240475
C	125	-0.395952	-0.493078	0.254656
C	126	-0.000797	0.517255	0.037852
N	1	-0.474937	-0.330808	-0.006345
N	2	-0.466678	-0.137887	0.098171
N	3	0.330808	-0.144129	-0.006345
N	4	0.137887	-0.328791	0.098171
N	5	0.144129	0.474937	-0.006345
N	6	0.328791	0.466678	0.098171
N	7	0.474937	0.330808	-0.006345
N	8	0.466678	0.137887	0.098171
N	9	-0.330808	0.144129	-0.006345
N	10	-0.137887	0.328791	0.098171
N	11	-0.144129	-0.474937	-0.006345
N	12	-0.328791	-0.466678	0.098171
F	1	-0.499572	-0.223692	-0.402504
F	2	-0.498627	-0.293149	-0.300395
F	3	-0.420456	-0.162980	0.341620
F	4	-0.419058	-0.232699	0.448226
F	5	0.223692	-0.275881	-0.402504
F	6	0.293149	-0.205478	-0.300395
F	7	0.162980	-0.257476	0.341620
F	8	0.232699	-0.186358	0.448226
F	9	0.275881	0.499572	-0.402504
F	10	0.205478	0.498627	-0.300395
F	11	0.257476	0.420456	0.341620
F	12	0.186358	0.419058	0.448226
F	13	0.499572	0.223692	-0.402504
F	14	0.498627	0.293149	-0.300395
F	15	0.420456	0.162980	0.341620

F	16	0.419058	0.232699	0.448226
F	17	-0.223692	0.275881	-0.402504
F	18	-0.293149	0.205478	-0.300395
F	19	-0.162980	0.257476	0.341620
F	20	-0.232699	0.186358	0.448226
F	21	-0.275881	-0.499572	-0.402504
F	22	-0.205478	-0.498627	-0.300395
F	23	-0.257476	-0.420456	0.341620
F	24	-0.186358	-0.419058	0.448226

Table S3. Fractional atomic coordinates for the unit cell of CN-COF with AA-stacking.

CN-COF: Space group symmetry P6				
a = b = 39.212 Å; c = 5.064 Å α = β = 90°, γ = 120°				
H	1	0.293823	0.860338	0.699540
H	2	0.339161	0.829737	0.518102
H	3	0.391193	0.873789	0.839373
H	4	0.455165	0.936159	0.859142
H	5	0.422682	0.979439	0.186203
H	6	0.360500	0.916780	0.153598
H	7	0.180278	0.668689	0.263005
H	8	0.132832	0.695560	0.552932
H	9	0.074811	0.648517	0.805348
H	10	0.015964	0.582568	0.821922
H	11	0.066313	0.543271	0.227248
H	12	0.123961	0.608986	0.201724
H	13	-0.860338	-0.566514	0.699540
H	14	-0.829737	-0.490576	0.518102
H	15	-0.873789	-0.482596	0.839373
H	16	-0.936159	-0.480994	0.859142
H	17	-0.979439	-0.556757	0.186203
H	18	-0.916780	-0.556280	0.153598
H	19	-0.668689	-0.488411	0.263005
H	20	-0.695560	-0.562728	0.552932
H	21	-0.648517	-0.573706	0.805348
H	22	-0.582568	-0.566604	0.821922
H	23	-0.543271	-0.476958	0.227248
H	24	-0.608986	-0.485025	0.201724
H	25	0.566514	-0.293823	0.699540
H	26	0.490576	-0.339161	0.518102
H	27	0.482596	-0.391193	0.839373
H	28	0.480994	-0.455165	0.859142

H	29	0.556757	-0.422682	0.186203
H	30	0.556280	-0.360500	0.153598
H	31	0.488411	-0.180278	0.263005
H	32	0.562728	-0.132832	0.552932
H	33	0.573706	-0.074811	0.805348
H	34	0.566604	-0.015964	0.821922
H	35	0.476958	-0.066313	0.227248
H	36	0.485025	-0.123961	0.201724
H	37	-0.293823	-0.860338	0.699540
H	38	-0.339161	-0.829737	0.518102
H	39	-0.391193	-0.873789	0.839373
H	40	-0.455165	-0.936159	0.859142
H	41	-0.422682	-0.979439	0.186203
H	42	-0.360500	-0.916780	0.153598
H	43	-0.180278	-0.668689	0.263005
H	44	-0.132832	-0.695560	0.552932
H	45	-0.074811	-0.648517	0.805348
H	46	-0.015964	-0.582568	0.821922
H	47	-0.066313	-0.543271	0.227248
H	48	-0.123961	-0.608986	0.201724
H	49	0.860338	0.566514	0.699540
H	50	0.829737	0.490576	0.518102
H	51	0.873789	0.482596	0.839373
H	52	0.936159	0.480994	0.859142
H	53	0.979439	0.556757	0.186203
H	54	0.916780	0.556280	0.153598
H	55	0.668689	0.488411	0.263005
H	56	0.695560	0.562728	0.552932
H	57	0.648517	0.573706	0.805348
H	58	0.582568	0.566604	0.821922
H	59	0.543271	0.476958	0.227248
H	60	0.608986	0.485025	0.201724
H	61	-0.566514	0.293823	0.699540
H	62	-0.490576	0.339161	0.518102
H	63	-0.482596	0.391193	0.839373
H	64	-0.480994	0.455165	0.859142
H	65	-0.556757	0.422682	0.186203
H	66	-0.556280	0.360500	0.153598
H	67	-0.488411	0.180278	0.263005
H	68	-0.562728	0.132832	0.552932
H	69	-0.573706	0.074811	0.805348
H	70	-0.566604	0.015964	0.821922
H	71	-0.476958	0.066313	0.227248
H	72	-0.485025	0.123961	0.201724

C	1	-0.792632	-0.252122	0.676690
C	2	-0.791783	-0.276108	0.472607
C	3	-0.762217	-0.259254	0.279019
C	4	-0.734393	-0.218643	0.284140
C	5	-0.735134	-0.194872	0.488836
C	6	-0.764694	-0.211464	0.681422
C	7	-0.704241	-0.151586	0.504870
C	8	-0.629140	-0.108291	0.502346
C	9	-0.601864	-0.102745	0.698874
C	10	-0.565882	-0.067508	0.711833
C	11	-0.556375	-0.037512	0.527203
C	12	-0.584100	-0.043122	0.331930
C	13	-0.619942	-0.078467	0.316937
C	14	-0.517651	-0.000125	0.532957
C	15	-0.822010	-0.319910	0.459146
C	16	-0.896383	-0.366599	0.504118
C	17	-0.927249	-0.374585	0.677524
C	18	-0.960419	-0.412270	0.689187
C	19	-0.963281	-0.442874	0.528643
C	20	-0.932307	-0.434275	0.353338
C	21	-0.899126	-0.396691	0.341292
C	22	-0.712751	-0.129764	0.303863
C	23	-0.812391	-0.341269	0.658002
C	24	0.252122	-0.540509	0.676690
C	25	0.276108	-0.515675	0.472607
C	26	0.259254	-0.502963	0.279019
C	27	0.218643	-0.515750	0.284140
C	28	0.194872	-0.540262	0.488836
C	29	0.211464	-0.553230	0.681422
C	30	0.151586	-0.552654	0.504870
C	31	0.108291	-0.520849	0.502346
C	32	0.102745	-0.499119	0.698874
C	33	0.067508	-0.498374	0.711833
C	34	0.037512	-0.518863	0.527203
C	35	0.043122	-0.540978	0.331930
C	36	0.078467	-0.541476	0.316937
C	37	0.000125	-0.517526	0.532957
C	38	0.319910	-0.502100	0.459146
C	39	0.366599	-0.529783	0.504118
C	40	0.374585	-0.552664	0.677524
C	41	0.412270	-0.548149	0.689187
C	42	0.442874	-0.520407	0.528643
C	43	0.434275	-0.498032	0.353338
C	44	0.396691	-0.502436	0.341292

C	45	0.129764	-0.582987	0.303863
C	46	0.341269	-0.471122	0.658002
C	47	0.540509	0.792632	0.676690
C	48	0.515675	0.791783	0.472607
C	49	0.502963	0.762217	0.279019
C	50	0.515750	0.734393	0.284140
C	51	0.540262	0.735134	0.488836
C	52	0.553230	0.764694	0.681422
C	53	0.552654	0.704241	0.504870
C	54	0.520849	0.629140	0.502346
C	55	0.499119	0.601864	0.698874
C	56	0.498374	0.565882	0.711833
C	57	0.518863	0.556375	0.527203
C	58	0.540978	0.584100	0.331930
C	59	0.541476	0.619942	0.316937
C	60	0.517526	0.517651	0.532957
C	61	0.502100	0.822010	0.459146
C	62	0.529783	0.896383	0.504118
C	63	0.552664	0.927249	0.677524
C	64	0.548149	0.960419	0.689187
C	65	0.520407	0.963281	0.528643
C	66	0.498032	0.932307	0.353338
C	67	0.502436	0.899126	0.341292
C	68	0.582987	0.712751	0.303863
C	69	0.471122	0.812391	0.658002
C	70	0.792632	0.252122	0.676690
C	71	0.791783	0.276108	0.472607
C	72	0.762217	0.259254	0.279019
C	73	0.734393	0.218643	0.284140
C	74	0.735134	0.194872	0.488836
C	75	0.764694	0.211464	0.681422
C	76	0.704241	0.151586	0.504870
C	77	0.629140	0.108291	0.502346
C	78	0.601864	0.102745	0.698874
C	79	0.565882	0.067508	0.711833
C	80	0.556375	0.037512	0.527203
C	81	0.584100	0.043122	0.331930
C	82	0.619942	0.078467	0.316937
C	83	0.517651	0.000125	0.532957
C	84	0.822010	0.319910	0.459146
C	85	0.896383	0.366599	0.504118
C	86	0.927249	0.374585	0.677524
C	87	0.960419	0.412270	0.689187
C	88	0.963281	0.442874	0.528643

C	89	0.932307	0.434275	0.353338
C	90	0.899126	0.396691	0.341292
C	91	0.712751	0.129764	0.303863
C	92	0.812391	0.341269	0.658002
C	93	-0.252122	0.540509	0.676690
C	94	-0.276108	0.515675	0.472607
C	95	-0.259254	0.502963	0.279019
C	96	-0.218643	0.515750	0.284140
C	97	-0.194872	0.540262	0.488836
C	98	-0.211464	0.553230	0.681422
C	99	-0.151586	0.552654	0.504870
C	100	-0.108291	0.520849	0.502346
C	101	-0.102745	0.499119	0.698874
C	102	-0.067508	0.498374	0.711833
C	103	-0.037512	0.518863	0.527203
C	104	-0.043122	0.540978	0.331930
C	105	-0.078467	0.541476	0.316937
C	106	-0.000125	0.517526	0.532957
C	107	-0.319910	0.502100	0.459146
C	108	-0.366599	0.529783	0.504118
C	109	-0.374585	0.552664	0.677524
C	110	-0.412270	0.548149	0.689187
C	111	-0.442874	0.520407	0.528643
C	112	-0.434275	0.498032	0.353338
C	113	-0.396691	0.502436	0.341292
C	114	-0.129764	0.582987	0.303863
C	115	-0.341269	0.471122	0.658002
C	116	-0.540509	-0.792632	0.676690
C	117	-0.515675	-0.791783	0.472607
C	118	-0.502963	-0.762217	0.279019
C	119	-0.515750	-0.734393	0.284140
C	120	-0.540262	-0.735134	0.488836
C	121	-0.553230	-0.764694	0.681422
C	122	-0.552654	-0.704241	0.504870
C	123	-0.520849	-0.629140	0.502346
C	124	-0.499119	-0.601864	0.698874
C	125	-0.498374	-0.565882	0.711833
C	126	-0.518863	-0.556375	0.527203
C	127	-0.540978	-0.584100	0.331930
C	128	-0.541476	-0.619942	0.316937
C	129	-0.517526	-0.517651	0.532957
C	130	-0.502100	-0.822010	0.459146
C	131	-0.529783	-0.896383	0.504118
C	132	-0.552664	-0.927249	0.677524

C	133	-0.548149	-0.960419	0.689187
C	134	-0.520407	-0.963281	0.528643
C	135	-0.498032	-0.932307	0.353338
C	136	-0.502436	-0.899126	0.341292
C	137	-0.582987	-0.712751	0.303863
C	138	-0.471122	-0.812391	0.658002
N	1	-0.664193	-0.145838	0.478760
N	2	-0.862726	-0.327683	0.494904
N	3	-0.719169	-0.111916	0.149390
N	4	-0.805255	-0.358686	0.811430
N	5	0.145838	-0.518355	0.478760
N	6	0.327683	-0.535044	0.494904
N	7	0.111916	-0.607253	0.149390
N	8	0.358686	-0.446569	0.811430
N	9	0.518355	0.664193	0.478760
N	10	0.535044	0.862726	0.494904
N	11	0.607253	0.719169	0.149390
N	12	0.446569	0.805255	0.811430
N	13	0.664193	0.145838	0.478760
N	14	0.862726	0.327683	0.494904
N	15	0.719169	0.111916	0.149390
N	16	0.805255	0.358686	0.811430
N	17	-0.145838	0.518355	0.478760
N	18	-0.327683	0.535044	0.494904
N	19	-0.111916	0.607253	0.149390
N	20	-0.358686	0.446569	0.811430
N	21	-0.518355	-0.664193	0.478760
N	22	-0.535044	-0.862726	0.494904
N	23	-0.607253	-0.719169	0.149390
N	24	-0.446569	-0.805255	0.811430
F	1	-0.766672	-0.187166	0.868311
F	2	-0.821127	-0.268447	0.868584
F	3	-0.706900	-0.201862	0.087356
F	4	-0.760306	-0.283041	0.088351
F	5	0.187166	-0.579506	0.868311
F	6	0.268447	-0.552680	0.868584
F	7	0.201862	-0.505037	0.087356
F	8	0.283041	-0.477265	0.088351
F	9	0.579506	0.766672	0.868311
F	10	0.552680	0.821127	0.868584
F	11	0.505037	0.706900	0.087356
F	12	0.477265	0.760306	0.088351
F	13	0.766672	0.187166	0.868311
F	14	0.821127	0.268447	0.868584

F	15	0.706900	0.201862	0.087356
F	16	0.760306	0.283041	0.088351
F	17	-0.187166	0.579506	0.868311
F	18	-0.268447	0.552680	0.868584
F	19	-0.201862	0.505037	0.087356
F	20	-0.283041	0.477265	0.088351
F	21	-0.579506	-0.766672	0.868311
F	22	-0.552680	-0.821127	0.868584
F	23	-0.505037	-0.706900	0.087356
F	24	-0.477265	-0.760306	0.088351

Table S4. Fractional atomic coordinates for the unit cell of CN-iCOF with AA-stacking.

CN-iCOF: Space group symmetry P6				
a = b = 38.694 Å; c = 5.371 Å α = β = 90°, γ = 120°				
H	1	0.527520	0.691767	0.500000
H	2	0.484920	0.610415	0.500000
H	3	0.480608	0.542767	0.500000
H	4	0.567613	0.595088	0.500000
H	5	0.566001	0.645321	0.500000
H	6	0.491835	0.815433	0.500000
H	7	0.577359	0.922775	0.500000
H	8	0.574658	0.986937	0.500000
H	9	0.459056	0.922790	0.500000
H	10	0.463245	0.863052	0.500000
H	11	-0.691767	-0.164246	0.500000
H	12	-0.610415	-0.125495	0.500000
H	13	-0.542767	-0.062159	0.500000
H	14	-0.595088	-0.027475	0.500000
H	15	-0.645321	-0.079320	0.500000
H	16	-0.815433	-0.323598	0.500000
H	17	-0.922775	-0.345416	0.500000
H	18	-0.986937	-0.412280	0.500000
H	19	-0.922790	-0.463734	0.500000
H	20	-0.863052	-0.399807	0.500000
H	21	0.164246	-0.527520	0.500000
H	22	0.125495	-0.484920	0.500000
H	23	0.062159	-0.480608	0.500000
H	24	0.027475	-0.567613	0.500000
H	25	0.079320	-0.566001	0.500000
H	26	0.323598	-0.491835	0.500000
H	27	0.345416	-0.577359	0.500000

H	28	0.412280	-0.574658	0.500000
H	29	0.463734	-0.459056	0.500000
H	30	0.399807	-0.463245	0.500000
H	31	-0.527520	-0.691767	0.500000
H	32	-0.484920	-0.610415	0.500000
H	33	-0.480608	-0.542767	0.500000
H	34	-0.567613	-0.595088	0.500000
H	35	-0.566001	-0.645321	0.500000
H	36	-0.491835	-0.815433	0.500000
H	37	-0.577359	-0.922775	0.500000
H	38	-0.574658	-0.986937	0.500000
H	39	-0.459056	-0.922790	0.500000
H	40	-0.463245	-0.863052	0.500000
H	41	0.691767	0.164246	0.500000
H	42	0.610415	0.125495	0.500000
H	43	0.542767	0.062159	0.500000
H	44	0.595088	0.027475	0.500000
H	45	0.645321	0.079320	0.500000
H	46	0.815433	0.323598	0.500000
H	47	0.922775	0.345416	0.500000
H	48	0.986937	0.412280	0.500000
H	49	0.922790	0.463734	0.500000
H	50	0.863052	0.399807	0.500000
H	51	-0.164246	0.527520	0.500000
H	52	-0.125495	0.484920	0.500000
H	53	-0.062159	0.480608	0.500000
H	54	-0.027475	0.567613	0.500000
H	55	-0.079320	0.566001	0.500000
H	56	-0.323598	0.491835	0.500000
H	57	-0.345416	0.577359	0.500000
H	58	-0.412280	0.574658	0.500000
H	59	-0.463734	0.459056	0.500000
H	60	-0.399807	0.463245	0.500000
Li	1	-0.464393	-0.306072	-0.500000
Li	2	-0.434045	-0.146018	-0.500000
Li	3	0.306072	-0.158321	-0.500000
Li	4	0.146018	-0.288027	-0.500000
Li	5	0.158321	0.464393	-0.500000
Li	6	0.288027	0.434045	-0.500000
Li	7	0.464393	0.306072	-0.500000
Li	8	0.434045	0.146018	-0.500000
Li	9	-0.306072	0.158321	-0.500000
Li	10	-0.146018	0.288027	-0.500000
Li	11	-0.158321	-0.464393	-0.500000

Li	12	-0.288027	-0.434045	-0.500000
C	1	-0.463545	-0.215203	-0.500000
C	2	-0.498954	-0.216894	-0.500000
C	3	-0.525581	-0.248715	-0.500000
C	4	-0.516535	-0.277914	-0.500000
C	5	-0.481090	-0.276077	-0.500000
C	6	-0.454812	-0.244712	-0.500000
C	7	-0.472480	-0.308233	-0.500000
C	8	-0.474344	-0.368697	-0.500000
C	9	-0.486634	-0.391521	-0.500000
C	10	-0.489009	-0.428787	-0.500000
C	11	-0.478956	-0.443293	-0.500000
C	12	-0.466356	-0.420281	-0.500000
C	13	-0.464275	-0.383254	-0.500000
C	14	-0.481882	-0.482836	-0.500000
C	15	-0.508165	-0.184567	-0.500000
C	16	-0.479591	-0.110613	-0.500000
C	17	-0.452692	-0.078439	-0.500000
C	18	-0.454179	-0.043113	-0.500000
C	19	-0.482591	-0.039355	-0.500000
C	20	-0.509060	-0.071544	-0.500000
C	21	-0.507815	-0.106991	-0.500000
C	22	-0.434122	-0.291221	-0.500000
C	23	-0.512372	-0.182285	-0.500000
C	24	0.215203	-0.248341	-0.500000
C	25	0.216894	-0.282060	-0.500000
C	26	0.248715	-0.276866	-0.500000
C	27	0.277914	-0.238621	-0.500000
C	28	0.276077	-0.205013	-0.500000
C	29	0.244712	-0.210100	-0.500000
C	30	0.308233	-0.164246	-0.500000
C	31	0.368697	-0.105647	-0.500000
C	32	0.391521	-0.095113	-0.500000
C	33	0.428787	-0.060222	-0.500000
C	34	0.443293	-0.035663	-0.500000
C	35	0.420281	-0.046075	-0.500000
C	36	0.383254	-0.081021	-0.500000
C	37	0.482836	0.000954	-0.500000
C	38	0.184567	-0.323598	-0.500000
C	39	0.110613	-0.368978	-0.500000
C	40	0.078439	-0.374253	-0.500000
C	41	0.043113	-0.411066	-0.500000
C	42	0.039355	-0.443236	-0.500000
C	43	0.071544	-0.437516	-0.500000

C	44	0.106991	-0.400824	-0.500000
C	45	0.291221	-0.142901	-0.500000
C	46	0.182285	-0.330088	-0.500000
C	47	0.248341	0.463545	-0.500000
C	48	0.282060	0.498954	-0.500000
C	49	0.276866	0.525581	-0.500000
C	50	0.238621	0.516535	-0.500000
C	51	0.205013	0.481090	-0.500000
C	52	0.210100	0.454812	-0.500000
C	53	0.164246	0.472480	-0.500000
C	54	0.105647	0.474344	-0.500000
C	55	0.095113	0.486634	-0.500000
C	56	0.060222	0.489009	-0.500000
C	57	0.035663	0.478956	-0.500000
C	58	0.046075	0.466356	-0.500000
C	59	0.081021	0.464275	-0.500000
C	60	-0.000954	0.481882	-0.500000
C	61	0.323598	0.508165	-0.500000
C	62	0.368978	0.479591	-0.500000
C	63	0.374253	0.452692	-0.500000
C	64	0.411066	0.454179	-0.500000
C	65	0.443236	0.482591	-0.500000
C	66	0.437516	0.509060	-0.500000
C	67	0.400824	0.507815	-0.500000
C	68	0.142901	0.434122	-0.500000
C	69	0.330088	0.512372	-0.500000
C	70	0.463545	0.215203	-0.500000
C	71	0.498954	0.216894	-0.500000
C	72	0.525581	0.248715	-0.500000
C	73	0.516535	0.277914	-0.500000
C	74	0.481090	0.276077	-0.500000
C	75	0.454812	0.244712	-0.500000
C	76	0.472480	0.308233	-0.500000
C	77	0.474344	0.368697	-0.500000
C	78	0.486634	0.391521	-0.500000
C	79	0.489009	0.428787	-0.500000
C	80	0.478956	0.443293	-0.500000
C	81	0.466356	0.420281	-0.500000
C	82	0.464275	0.383254	-0.500000
C	83	0.481882	0.482836	-0.500000
C	84	0.508165	0.184567	-0.500000
C	85	0.479591	0.110613	-0.500000
C	86	0.452692	0.078439	-0.500000
C	87	0.454179	0.043113	-0.500000

C	88	0.482591	0.039355	-0.500000
C	89	0.509060	0.071544	-0.500000
C	90	0.507815	0.106991	-0.500000
C	91	0.434122	0.291221	-0.500000
C	92	0.512372	0.182285	-0.500000
C	93	-0.215203	0.248341	-0.500000
C	94	-0.216894	0.282060	-0.500000
C	95	-0.248715	0.276866	-0.500000
C	96	-0.277914	0.238621	-0.500000
C	97	-0.276077	0.205013	-0.500000
C	98	-0.244712	0.210100	-0.500000
C	99	-0.308233	0.164246	-0.500000
C	100	-0.368697	0.105647	-0.500000
C	101	-0.391521	0.095113	-0.500000
C	102	-0.428787	0.060222	-0.500000
C	103	-0.443293	0.035663	-0.500000
C	104	-0.420281	0.046075	-0.500000
C	105	-0.383254	0.081021	-0.500000
C	106	-0.482836	-0.000954	-0.500000
C	107	-0.184567	0.323598	-0.500000
C	108	-0.110613	0.368978	-0.500000
C	109	-0.078439	0.374253	-0.500000
C	110	-0.043113	0.411066	-0.500000
C	111	-0.039355	0.443236	-0.500000
C	112	-0.071544	0.437516	-0.500000
C	113	-0.106991	0.400824	-0.500000
C	114	-0.291221	0.142901	-0.500000
C	115	-0.182285	0.330088	-0.500000
C	116	-0.248341	-0.463545	-0.500000
C	117	-0.282060	-0.498954	-0.500000
C	118	-0.276866	-0.525581	-0.500000
C	119	-0.238621	-0.516535	-0.500000
C	120	-0.205013	-0.481090	-0.500000
C	121	-0.210100	-0.454812	-0.500000
C	122	-0.164246	-0.472480	-0.500000
C	123	-0.105647	-0.474344	-0.500000
C	124	-0.095113	-0.486634	-0.500000
C	125	-0.060222	-0.489009	-0.500000
C	126	-0.035663	-0.478956	-0.500000
C	127	-0.046075	-0.466356	-0.500000
C	128	-0.081021	-0.464275	-0.500000
C	129	0.000954	-0.481882	-0.500000
C	130	-0.323598	-0.508165	-0.500000
C	131	-0.368978	-0.479591	-0.500000

C	132	-0.374253	-0.452692	-0.500000
C	133	-0.411066	-0.454179	-0.500000
C	134	-0.443236	-0.482591	-0.500000
C	135	-0.437516	-0.509060	-0.500000
C	136	-0.400824	-0.507815	-0.500000
C	137	-0.142901	-0.434122	-0.500000
C	138	-0.330088	-0.512372	-0.500000
N	1	-0.472262	-0.330834	-0.500000
N	2	-0.477153	-0.146339	-0.500000
N	3	-0.403930	-0.277866	-0.500000
N	4	-0.515736	-0.180168	-0.500000
N	5	0.330834	-0.141427	-0.500000
N	6	0.146339	-0.330813	-0.500000
N	7	0.277866	-0.126065	-0.500000
N	8	0.180168	-0.335569	-0.500000
N	9	0.141427	0.472262	-0.500000
N	10	0.330813	0.477153	-0.500000
N	11	0.126065	0.403930	-0.500000
N	12	0.335569	0.515736	-0.500000
N	13	0.472262	0.330834	-0.500000
N	14	0.477153	0.146339	-0.500000
N	15	0.403930	0.277866	-0.500000
N	16	0.515736	0.180168	-0.500000
N	17	-0.330834	0.141427	-0.500000
N	18	-0.146339	0.330813	-0.500000
N	19	-0.277866	0.126065	-0.500000
N	20	-0.180168	0.335569	-0.500000
N	21	-0.141427	-0.472262	-0.500000
N	22	-0.330813	-0.477153	-0.500000
N	23	-0.126065	-0.403930	-0.500000
N	24	-0.335569	-0.515736	-0.500000
F	1	-0.420543	-0.242496	-0.500000
F	2	-0.437369	-0.184822	-0.500000
F	3	-0.542460	-0.308171	-0.500000
F	4	-0.560278	-0.251327	-0.500000
F	5	0.242496	-0.178047	-0.500000
F	6	0.184822	-0.252547	-0.500000
F	7	0.308171	-0.234290	-0.500000
F	8	0.251327	-0.308950	-0.500000
F	9	0.178047	0.420543	-0.500000
F	10	0.252547	0.437369	-0.500000
F	11	0.234290	0.542460	-0.500000
F	12	0.308950	0.560278	-0.500000
F	13	0.420543	0.242496	-0.500000

F	14	0.437369	0.184822	-0.500000
F	15	0.542460	0.308171	-0.500000
F	16	0.560278	0.251327	-0.500000
F	17	-0.242496	0.178047	-0.500000
F	18	-0.184822	0.252547	-0.500000
F	19	-0.308171	0.234290	-0.500000
F	20	-0.251327	0.308950	-0.500000
F	21	-0.178047	-0.420543	-0.500000
F	22	-0.252547	-0.437369	-0.500000
F	23	-0.234290	-0.542460	-0.500000
F	24	-0.308950	-0.560278	-0.500000

7. Surface Area and Porosity Measurements

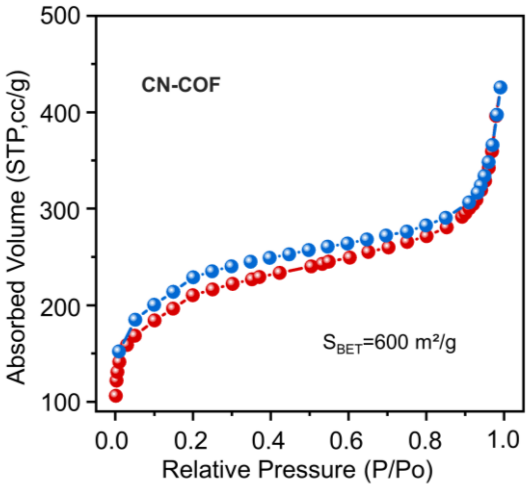


Figure S9. Nitrogen adsorption-desorption isotherms of CN-COF. Adsorption and desorption points are represented by red and blue spheres respectively.

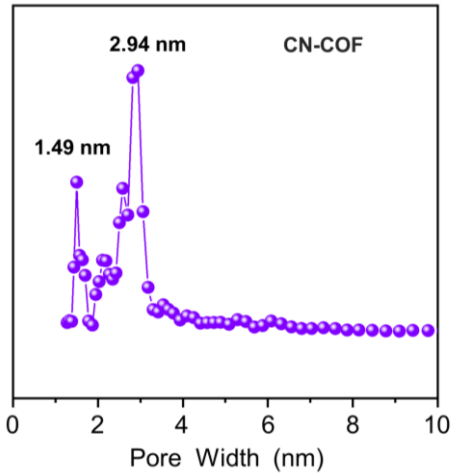


Figure S10. Pore size distribution of CN-COF.

8. FE-SEM and TEM Images of COFs

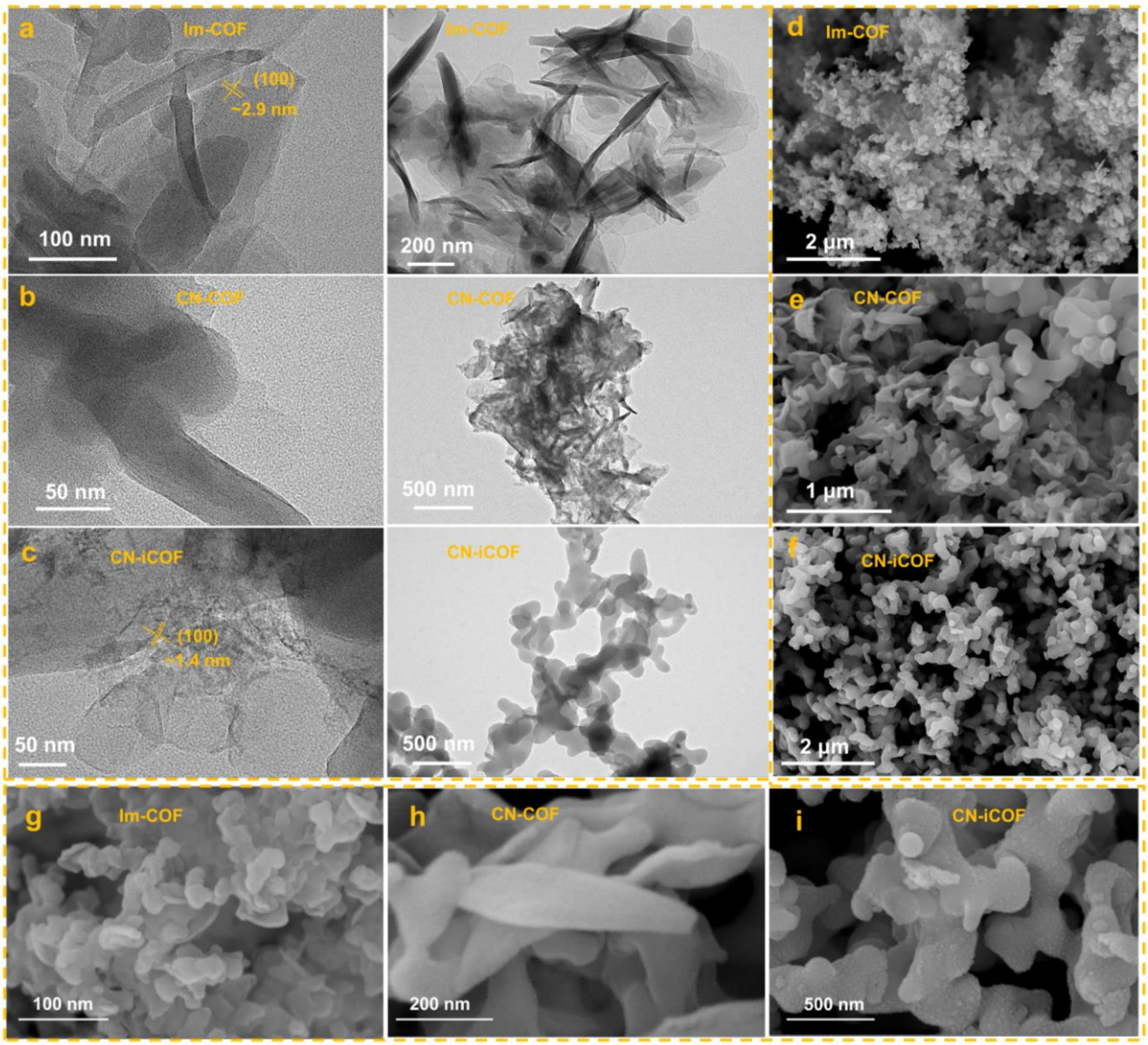


Figure S11. TEM image of Im-COF (a), CN-COF (b) and CN-iCOF (c). FE-SEM image of Im-COF (d and g), CN-COF (e and h) and CN-iCOF (f and i).

9. Thermogravimetric Analysis

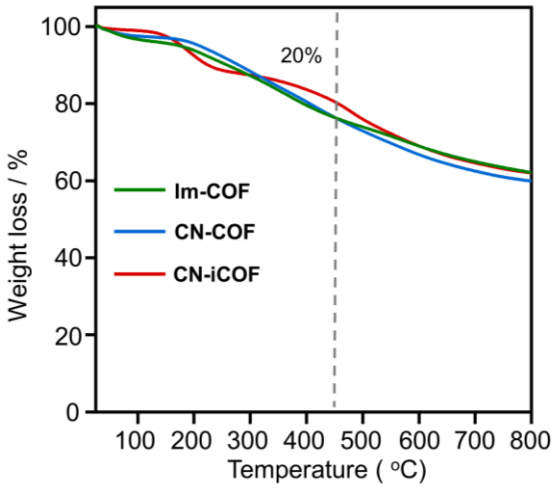


Figure S12. TGA analysis for Im-COF, CN-COF and CN-iCOF under N_2 atmosphere.

10. Theoretical Calculation of DFT and In Situ FT-IR Spectra

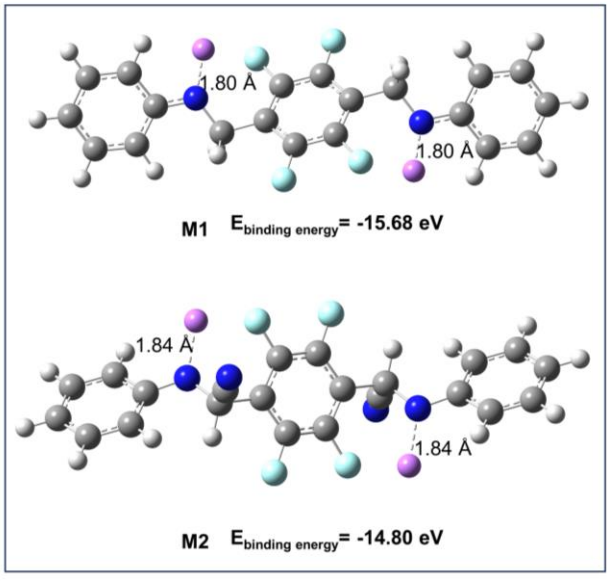


Figure S13. Structural optimization of structural units M1 and M2 and changes in binding energy and bond length.

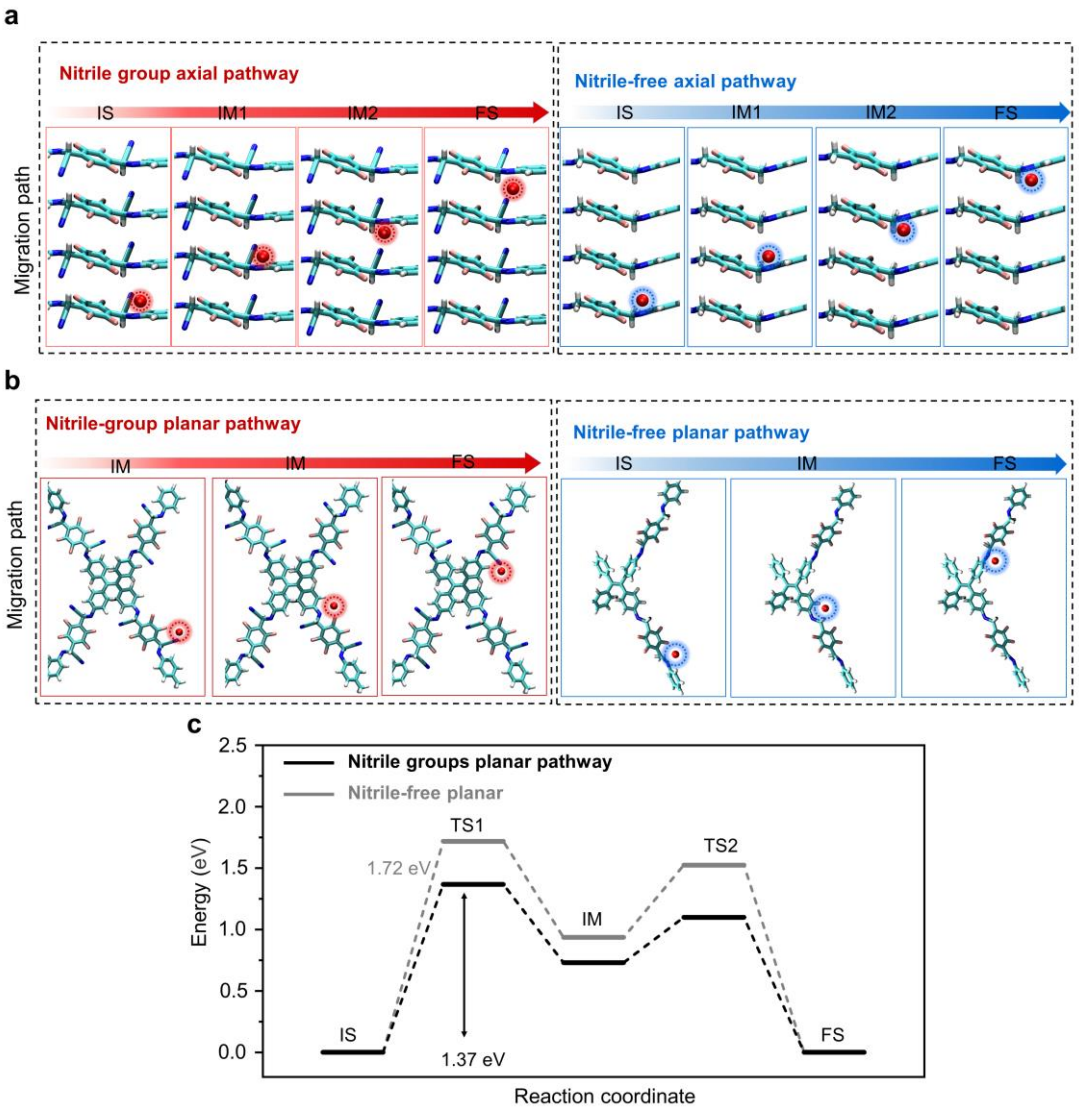


Figure S14. Theoretical elucidation of Li-ion migration behaviors inside the pore. a) The hopping distance of lithium ions in the nitrile groups and nitrile-free axial pathway. b) The hopping distance of lithium ions in the nitrile groups and cyano-free plane pathway. (c) Li-ion migration correlation energy diagram. The initial, intermediate, and final states are abbreviated as IS, IM, and FS, respectively.

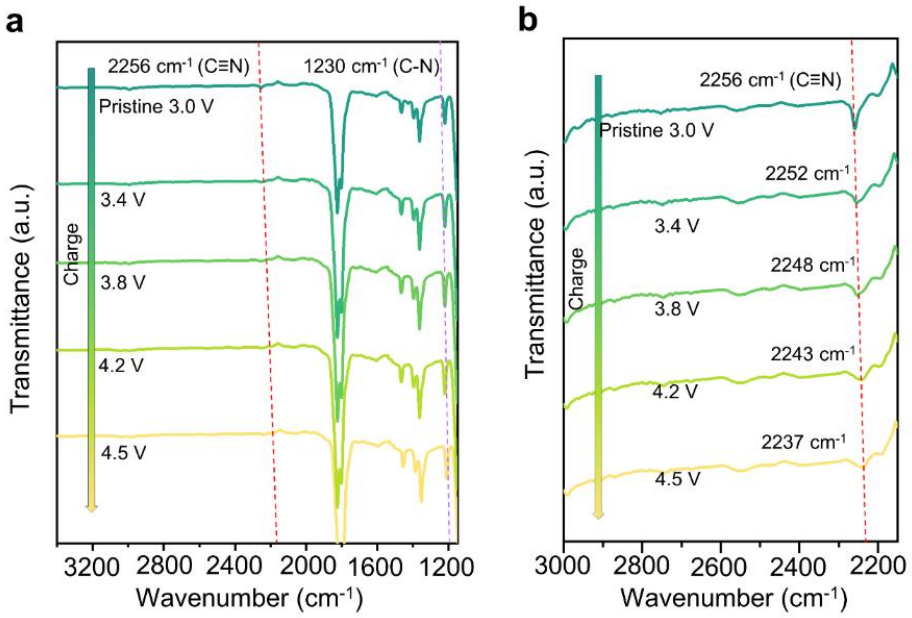


Figure S15. In situ FT-IR spectra of CN-iCOF at different charging voltages (3.0-4.5 V).

11. AFM Test Morphology and Young's Modulus

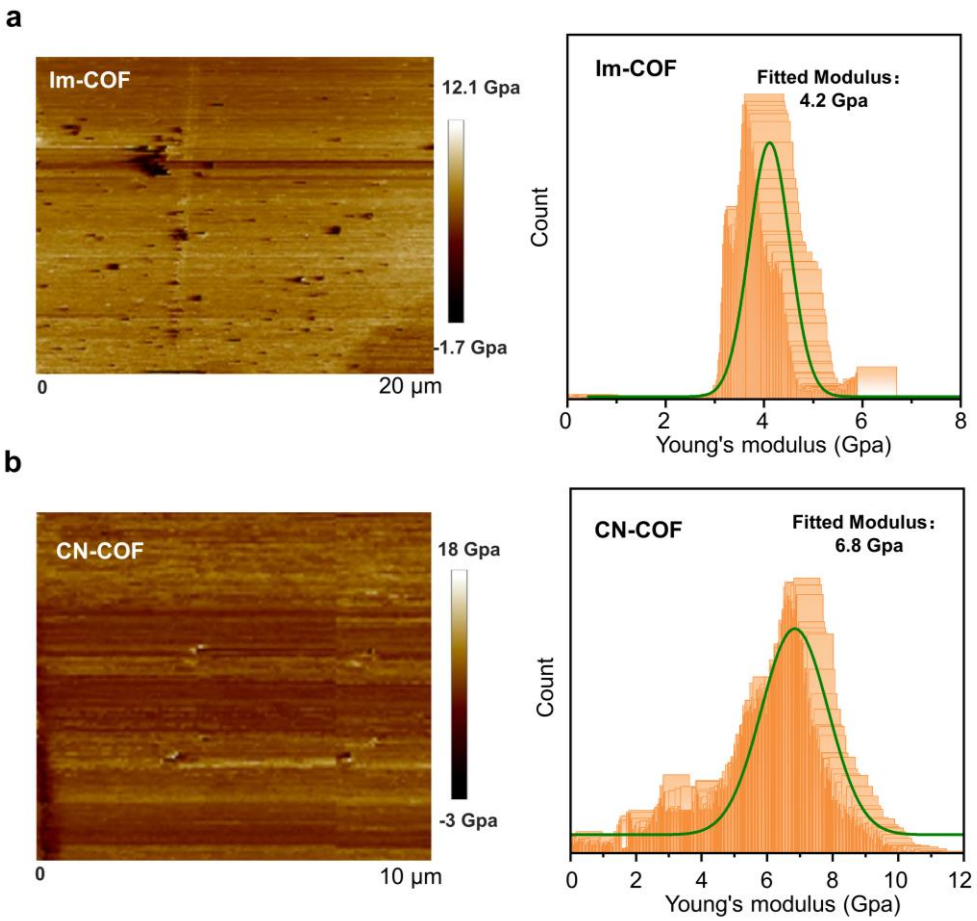


Figure S16. Force mapping and Young's modulus of the Im-COF (a) and CN-COF (b) film prepared at room temperature.

12. Molecular Dynamics Simulation

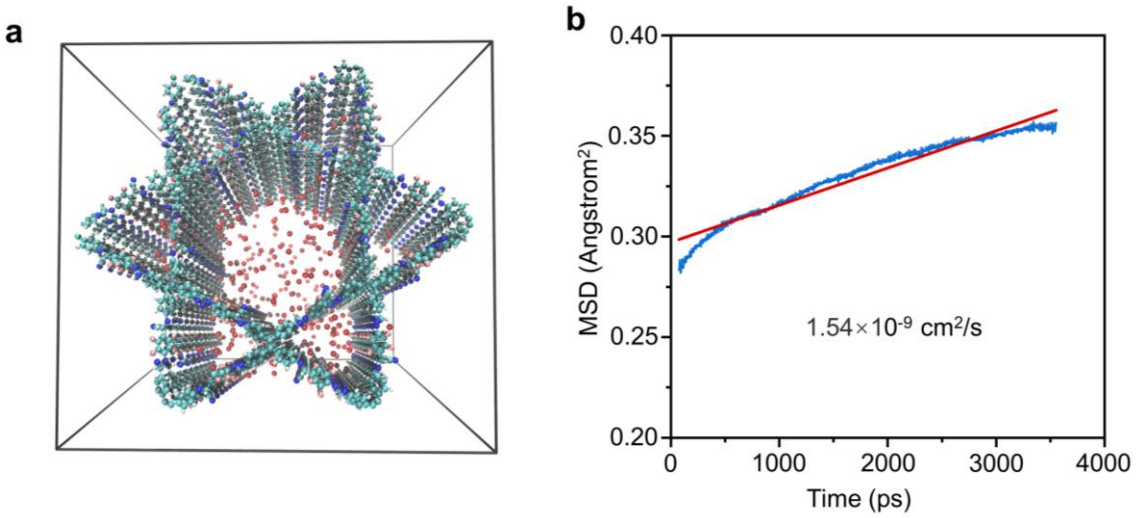


Figure S17. a) Snapshots of CN-iCOF obtained by MD simulation at 298 K. b) The diffusion coefficient of lithium ion was calculated by equation S2-S3, where D_{Li+} = 1.54×10^{-9} cm^2 s^{-1}.

13. Electrochemical Characteristics

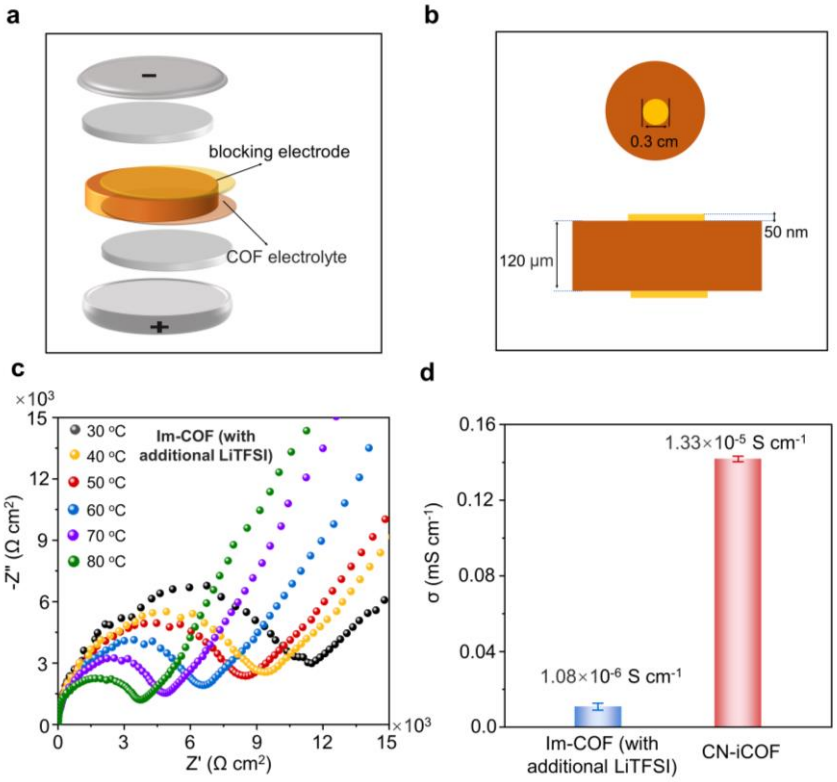


Figure S18. a) The blocking electrode sputtered with gold formed by magnetron sputter deposition. b) Top view and side view schematic images to illustrate the size of gold deposition on COF SSE. c) Measured temperature-dependent electrochemical impedance spectroscopy plots using stainless steel//stainless steel cells with deposited gold on Im-COF (with additional LiTFSI) SSE prepared at varied temperatures. d) Ionic conductivity of Im-COF (with additional LiTFSI) and CN-iCOF at 30 °C (without PC).

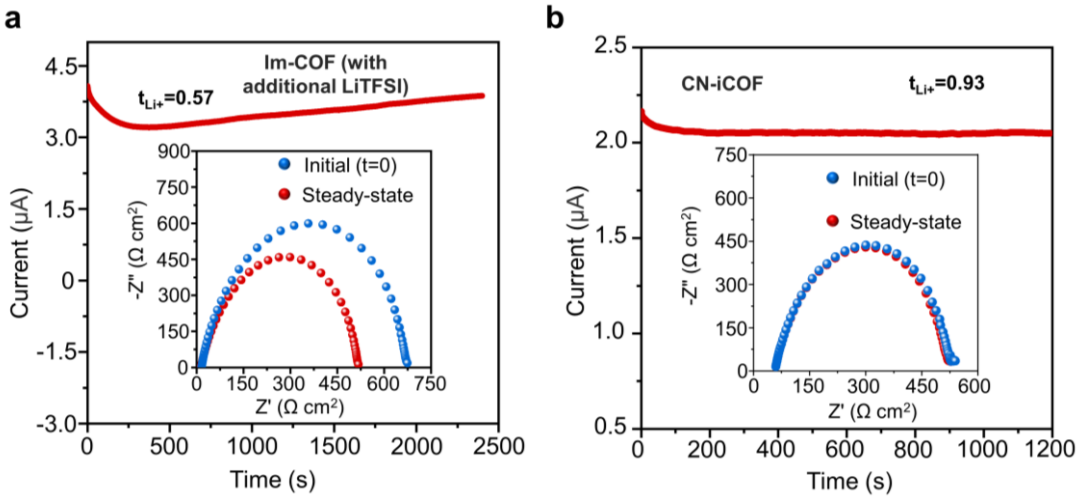


Figure S19. Measurement of lithium transport number at room temperature. a) Measurement of lithium transport number of Im-COF (with additional LiTFSI) at room temperature. b) Measurement of lithium transport number of CN-iCOF at room temperature. Inset: AC impedance spectra before and after polarization. CN-iCOF exhibited a high lithium transference number of 0.93 at room temperature. However, Im-COF (with additional LiTFSI) exhibited lithium transference number of 0.57 at room temperature.

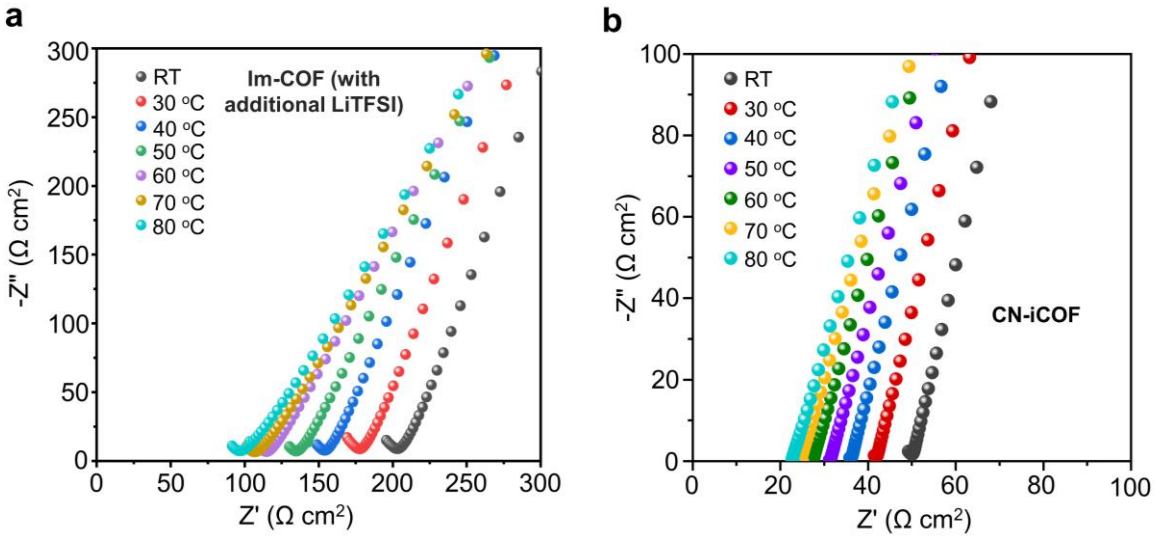


Figure S20. a) EIS profiles of Im-COF (with additional LiTFSI) measured at varied temperatures (20 wt % PC, 5.71×10^{-5} S cm^{-1}). b) EIS profiles of CN-iCOF measured at varied temperatures (20 wt % PC, 2.41×10^{-4} S cm^{-1})

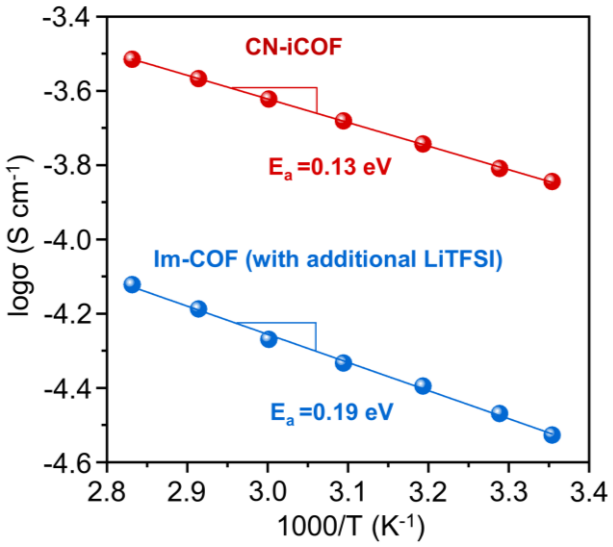


Figure S21. Temperature-dependent conductivity measurements and activation energy of CN-iCOF with 20 wt % PC and Im-COF (with additional LiTFSI and 20 wt % PC).

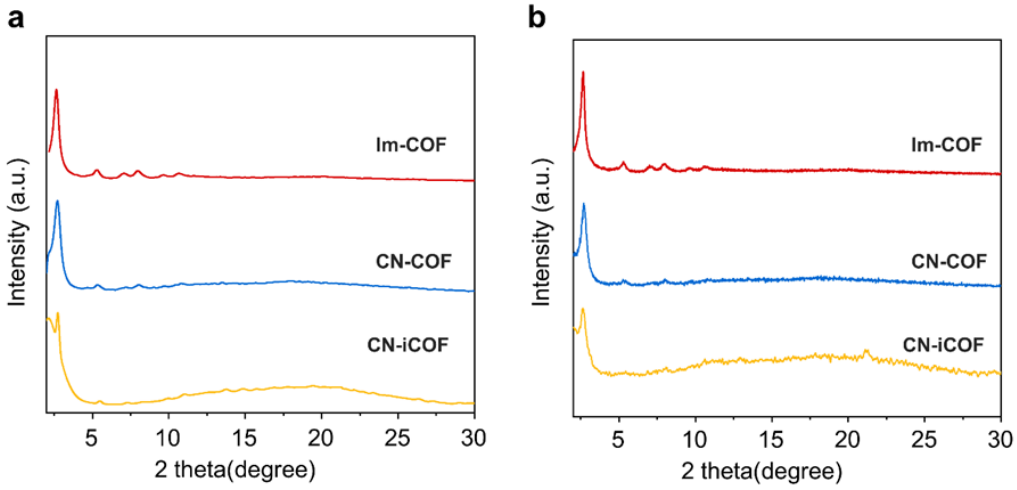


Figure S22. PXRD spectra of Im-COF/LiTFSI, CN-COF/LiTFSI, and CN-iCOF a) before cycling and b) after 200 hours cycling in Li||COFs||Li cells (0.3 mAh cm^{-2}, 0.1 mA cm^{-2}).

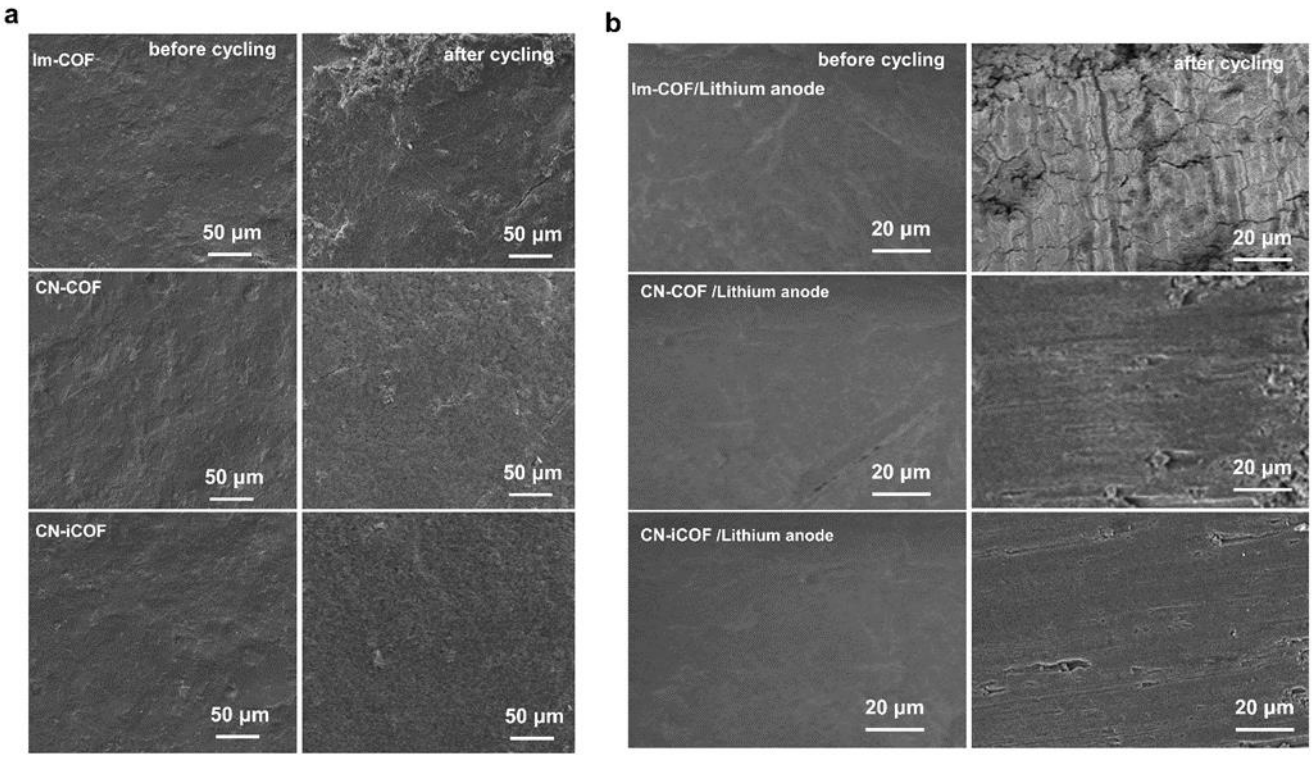


Figure S23. a) Top-surface SEM images of Im-COF/LiTFSI, CN-COF/LiTFSI, and CN-iCOF before and after cycling in Li||Li cells (0.3 mAh cm^{-2}, 0.1 mA cm^{-2}). b) Top-surface SEM images of lithium metal electrode employing Im-COF/LiTFSI, CN-COF/LiTFSI, and CN-iCOF before and after cycling in Li||Li cells (0.3 mAh cm^{-2}, 0.1 mA cm^{-2}).

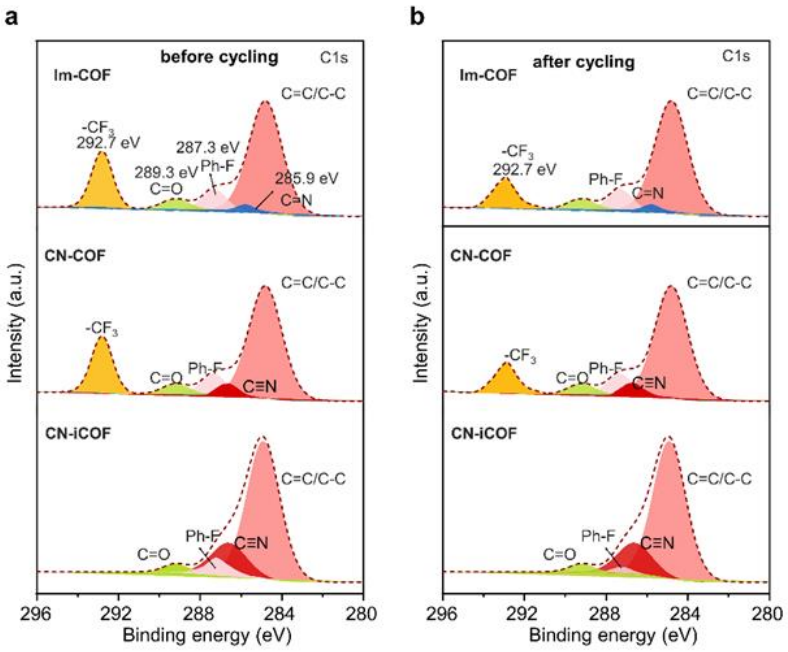


Figure S24. C 1s XPS spectrum of Im-COF/LiTFSI, CN-COF/LiTFSI and CN-iCOF before and after cycling in Li||Li cells (0.3 mAh cm^{-2}, 0.1 mA cm^{-2}).

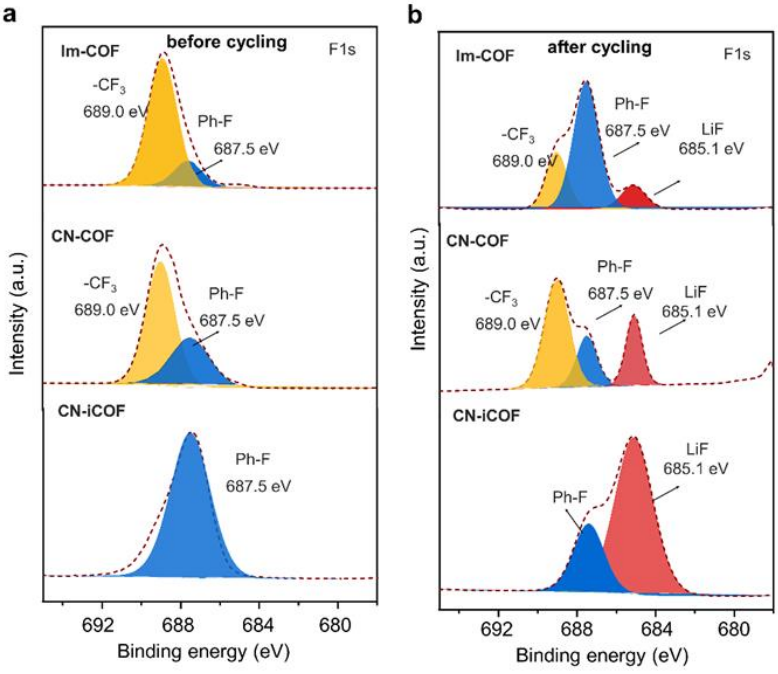


Figure S25. F 1s XPS spectrum of Im-COF/LiTFSI, CN-COF/LiTFSI, and CN-iCOF before and after cycling in Li||Li cells (0.3 mAh cm^{-2}, 0.1 mA cm^{-2}).

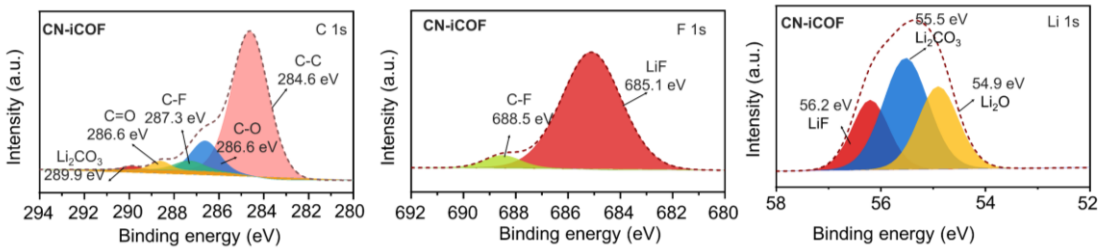


Figure S26. C 1s, F 1s and Li 1s XPS spectra of lithium metal electrode after 200 h cycling in Li||CN-iCOF||Li cells.

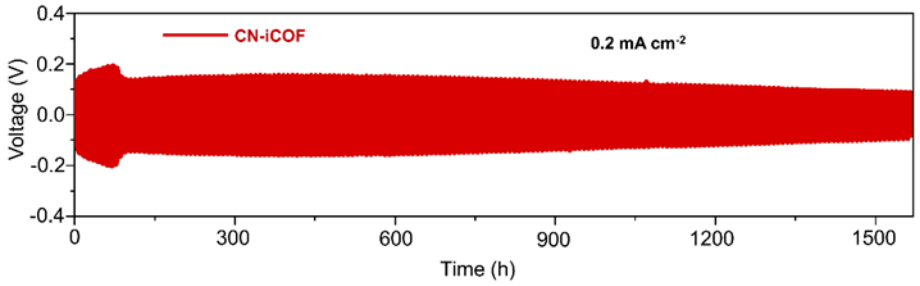


Figure S27. Voltage profile of the Li||Li symmetric cells used CN-iCOF SSE at 0.2 mA cm^{-2} at 25 °C.

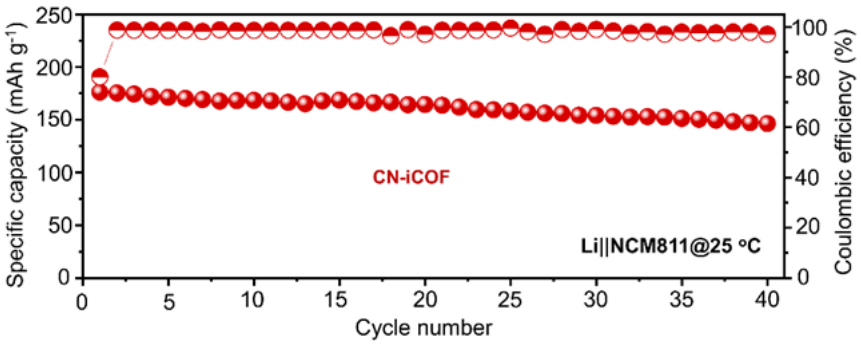


Figure S28. Long-term cycling Charging–discharging curves in Li||NCM811 cells at 25 °C and C-rate of 0.05 C.

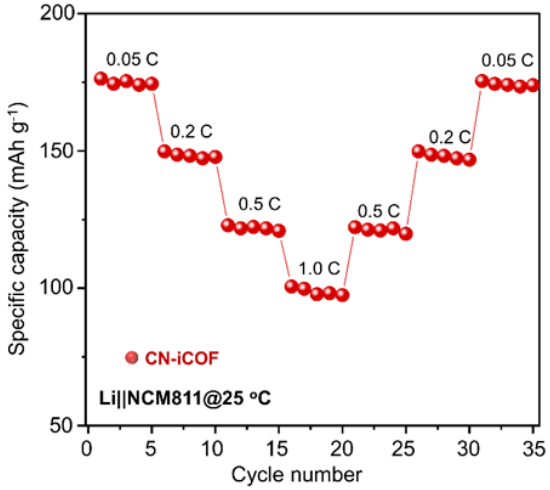


Figure S29. At different rates of 0.05 C, 0.2 C, 0.5 C, and 1.0 C, the capacities of Li||NCM811 assembled with CN-ICOF electrolyte are 176, 150, 123, and 101 mAh g^{-1}, respectively.

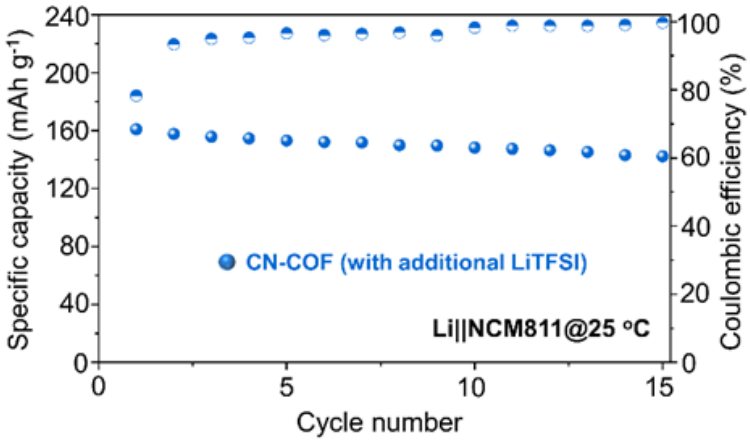


Figure S30. The cycling performance of Li||NCM811 full-cell with CN-COF electrolyte at 0.1 C.

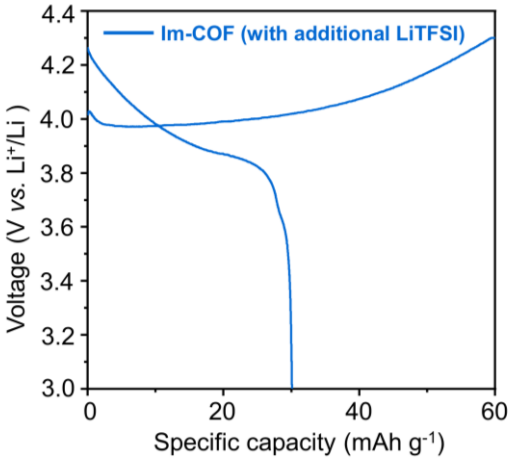


Figure S31. The charging–discharging curves of solid Li/LCO batteries with Im-COF (with additional LiTFSI).

Table S5. Performance summary of COF-based lithium-ion electrolytes.

Material	Conductivity (S cm^{-1}) (solvent-free)	E_a (eV)	EW	t_{Li+}	Ref.
CN-iCOF	1.33×10^{-5} (30 °C)	0.13	5.5 V	0.93	This work
Zwitt-COF-LiTFSI	1.65×10^{-4} (RT)	0.149	4.75	0.31	*Adv. Mater.* **2023,** *35,* 2301308.
COF+C-SPE	1.3×10^{-4} (RT)	/	5.2	0.62	*Adv. Sci.* **2022,** *9,* 2200390.
CF_3-Li-ImCOF	5.0×10^{-7} (RT)	0.10	4.3	0.81	*J. Am. Chem. Soc.* **2019,** *141,* 7518-7525.
TpPa-SO_3Li	2.7×10^{-5} (RT)	0.18	/	0.90	*J. Am. Chem. Soc.* **2019,** *141,* 5880-5885.
PEG-Li+@EB-COF-ClO_4	1.93×10^{-5} (30 °C)	0.21	/	0.60	*J. Am. Chem. Soc.* **2019,** *141,* 1923-1927.
ICOF-2/PVDF	3.05×10^{-5} (RT)	0.24	4.0	0.80	*Angew. Chem. Int. Ed.* **2016,** *55,* 1737-1741.
Ge-COF-1/$LiPF_6$	1.1×10^{-6} (30 °C)	0.26	/	0.67	*Chem.Eur. J.* **2019,** *25,* 13479-13483.
COF-PEO-9-Li	7.94×10^{-6} (100 °C)	0.47	4.2	/	*J. Am. Chem. Soc.* **2019,** *141,* 1227-1234.
Li@TPB-BMTP-COF	6.04×10^{-6} (40 °C)	0.87	/	/	*J. Am. Chem. Soc.* **2018,** *140,* 7429-7432.
Li-CON-TFSI	5.74×10^{-5} (30 °C)	0.34	3.8	0.63	*J. Am. Chem. Soc.* **2018,** *140,* 896-899.
Im-COF-TFSI	$2.92. \times 10^{-5}$ (30 °C)	0.32	4.2	/	*Mater. Chem. Front.* **2020,** *4*, 1164-1173.

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