

Supporting Information for

Fluorine-functionalized 2D Covalent Organic Frameworks with kgd Topology for Efficient C₂H₂/CO₂ Separation

Jinxin Chen,^{a†} Chuanhai Jiang,^{b†} Zhihao Xing,^a Jiahao Li,^a Fangna Dai,^b and Yongwu Peng^{*a}

^aCollege of Materials Science and Engineering, Zhejiang University of Technology, Hangzhou, 310014, China

^bSchool of Materials Science and Engineering, China University of Petroleum (East China), Qingdao 266580, China

E-mail: ywpeng@zjut.edu.cn

[†]J.X Chen and C. H. Jiang contributed equally to this work.

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1. Materials and methods

All the chemicals are commercially available, and used without further purification. All solvents were dried and distilled according to conventional methods.

Power X-ray diffraction (PXRD): PXRD patterns were collected on an X-ray diffraction (XRD) system (DX-27mini, China) using Cu K α radiation.

Fourier transform infrared (FT-IR): IR spectrum was measured on an IR spectrometer (Nicolet 6700) between the ranges of 4000 to 400 cm⁻¹.

Solution nuclear magnetic resonance (NMR): Liquid state ¹H nuclear magnetic resonance spectroscopy was collected on a Varian Mercury Plus 400 NMR Spectrometer. Liquid State ¹³C nuclear magnetic resonance spectroscopy was collected on a Bruker AscendTM 400 MHz NMR Spectrometer.

High resolution mass spectrometry (HRMS): The electrospray ionization mass spectrometry (ESI-MS) spectra were recorded using an Sciex X500R QTOF MS spectrometer.

Solid-state nuclear magnetic resonance (ssNMR): Solid-state nuclear magnetic resonance (NMR) data were performed on a Bruker AVANCE III 600 spectrometer with cross-polarization magic-angle-spinning (CP/MAS) at a resonance frequency of 150.9 MHz. ¹³C CP/MAS NMR spectra were recorded using a 4 mm MAS probe and a spinning rate of 12kHz. A contact time of 4 ms and a recycle delay of 2 s were used for the ¹³C CP/MAS NMR measurement. The chemical shifts of ¹³C were externally referenced to tetramethylsilane (TMS).

Scanning electron microscope (SEM): SEM images were collected using a GeminiSEM 500 system.

Transmission electron microscope (TEM): TEM images were obtained with a Tecnai G2 F30 S-Twin. Low-dose HRTEM imaging was conducted on an objective lens aberration-corrected electron microscope under 300 kV, which is equipped with a direct electron detection camera. The low-dose HRTEM image acquisition was conducted under a dose rate less than 1e $\text{\AA}^{-2} \text{s}^{-1}$ and a dose fractionation mode with ultrafast exposure. The image stack was aligned, projected and corrected before used for interpreting the chemical information.

Thermogravimetric analysis (TGA): TGA was performed using a TA Q5000 under flowing N₂ with 15 K min⁻¹ ramp rate. Samples were heated in a Platinum pan (800 °C, 15 °C min⁻¹) under a N₂ flux (25 mL min⁻¹).

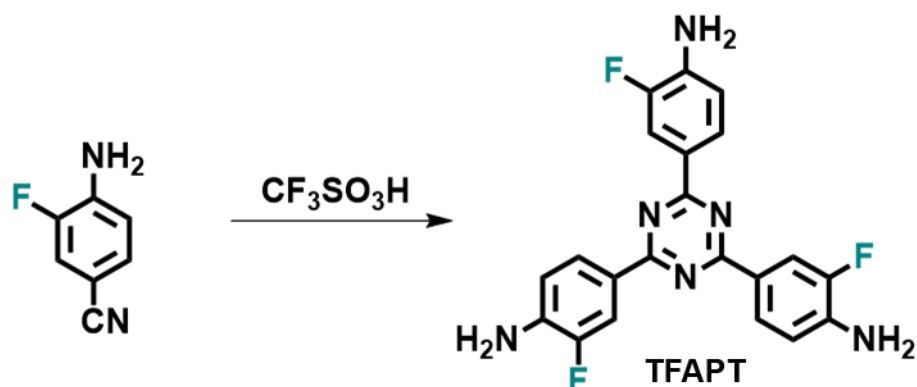
Sorption isotherm for N₂: Micrometrics ASAP2020 system were used to measure the specific surface area and pore structure using nitrogen as the adsorbate at 77 K, after outgassing the samples overnight at 120 °C.

Gas sorption: The samples were activated under vacuum for 12 hours at 120 °C. Gas adsorption experiments at 298 K were performed by using JW-BK200 surface area analyzer. A circulation constant temperature water bath was used to stabilize the temperature at 273/298 K during the test.

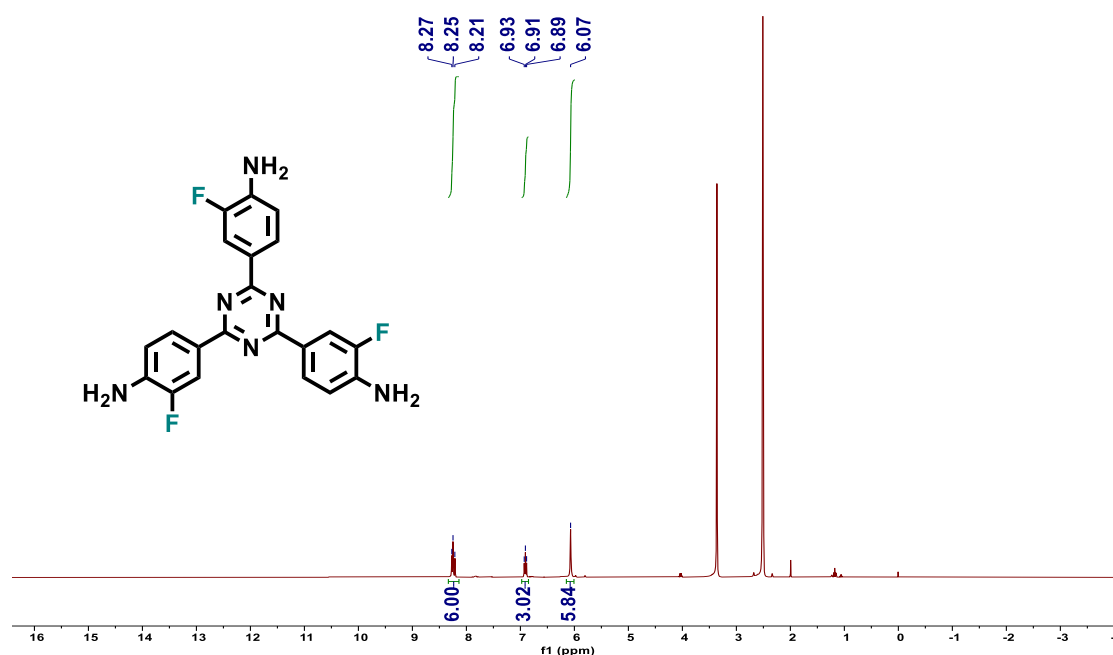
Crystal structure modeling: Structural modeling of COFs was generated using the Materials Studio^{S1} program employing the *Building (Crystal)* module, the lattice model was geometrically optimized using force-field based method (*Forcite* molecular dynamics module) and SCC-DFTB (*DFTB +* module). The Pawley fitting (*Reflex* module) was performed to optimize the lattice parameters iteratively until the Rwp value converges and the overlay of the observed with refined profiles shows good agreement. Powder indexing and Rietveld refinement were performed using EXPO2014^{S2} various topology structures were illustrated by VESTA software^{S3}.

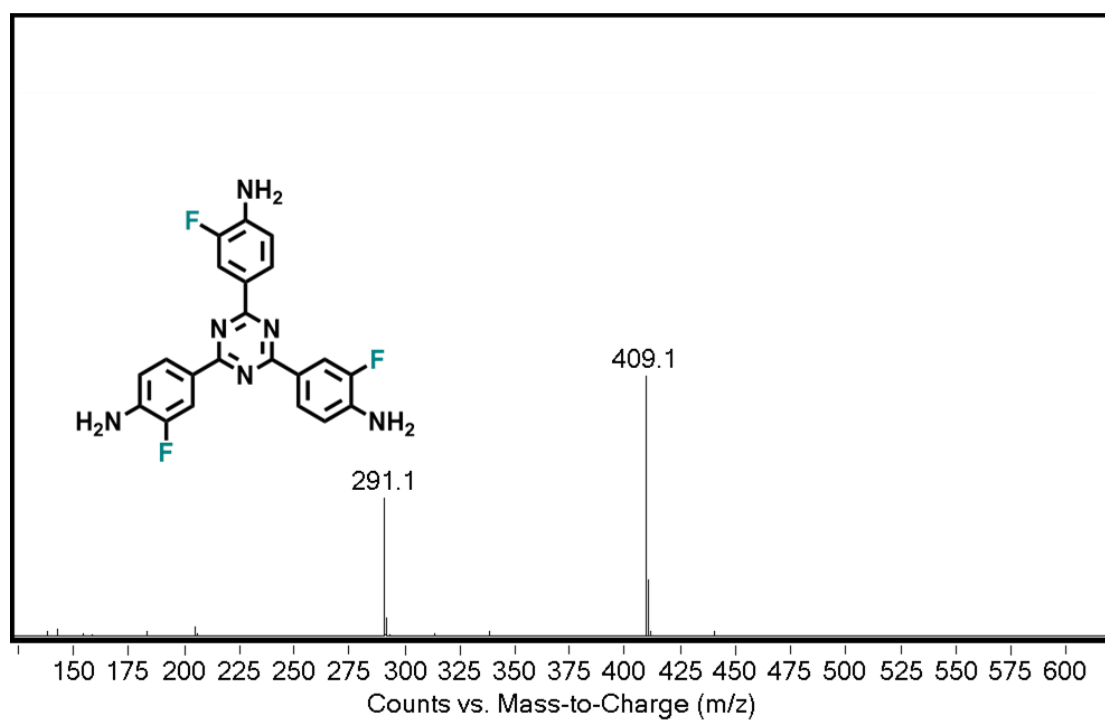
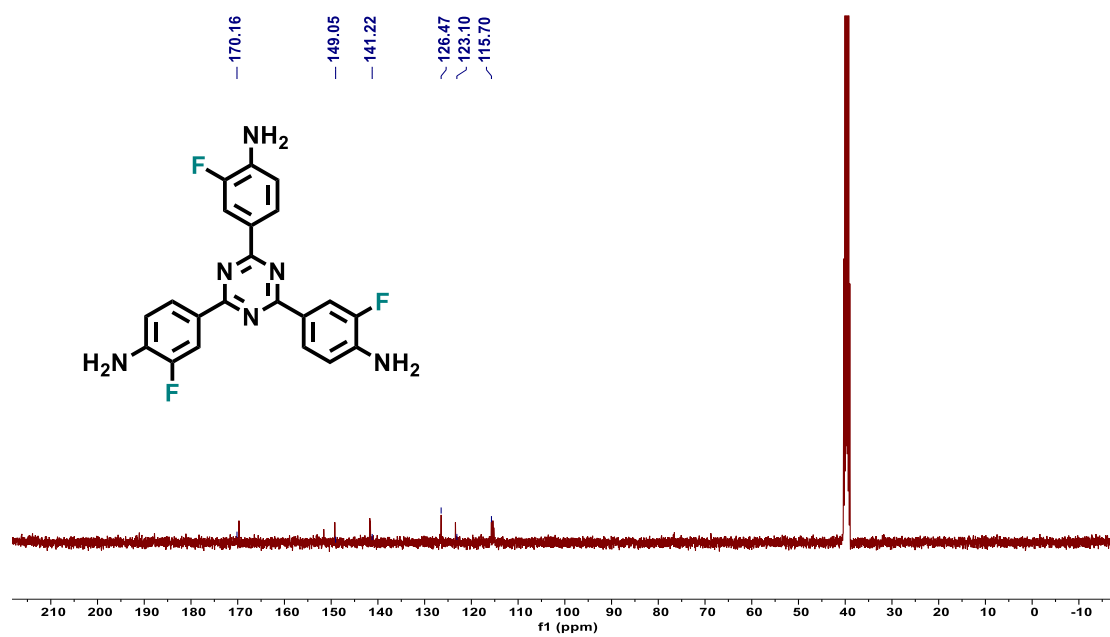
2. Synthesis and general procedures

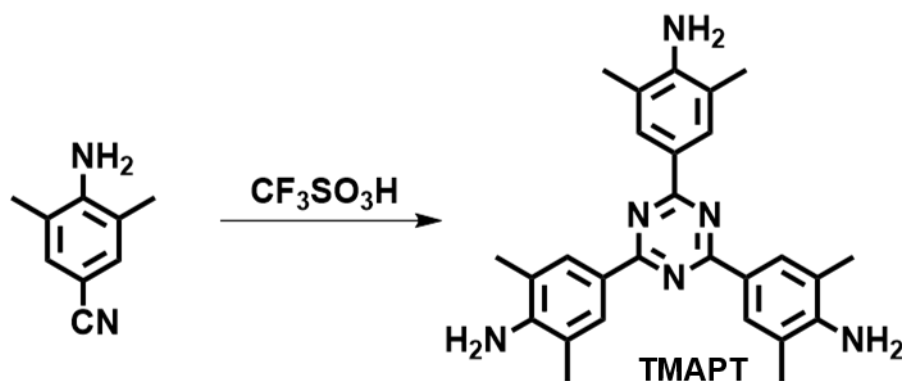
2.1 Synthesis of monomers



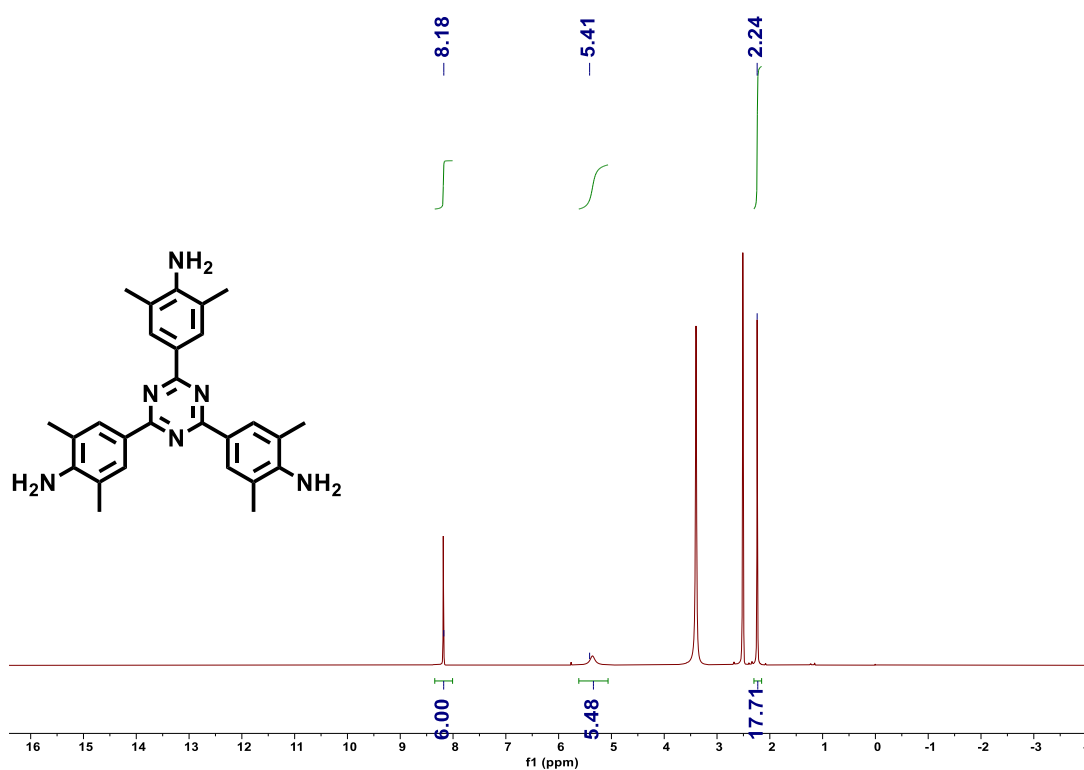
TFAPT was synthesized via superacid catalyzed trimerization of 3-fluoro-4-aminobenzonitrile. In a typical synthesis, 3-fluoro-4-aminobenzonitrile (500 mg, 3.8 mmol) was added in a round bottom flask at 0 °C. Then 2 mL trifluoromethanesulfonic acid (TFA) was added dropwise for 10 min and the resultant mixture was stirred for 24 h at room temperature in inert atmosphere. After that, 20 mL distilled water was added to the mixture and it was neutralized by adding 2 M NaOH solution until the pH reaches to 7. The resultant yellow product was filtered and washed several times with methanol and distilled water. The purified product (0.2 g) was characterized by ^1H NMR, ^{13}C NMR and MS. ^1H NMR (500 MHz, $\text{DMSO}-d_6$) δ : 8.25 (t, 6H), 7.63 (t, 3H), 6.07 (s, 6H). ^{13}C NMR (101 MHz, $\text{DMSO}-d_6$) δ : 170.16, 149.05, 141.22, 126.47, 123.10, 115.70. MS: m/z 409.1 (Calcd m/z 409.1 for $[\text{M}]^+$).

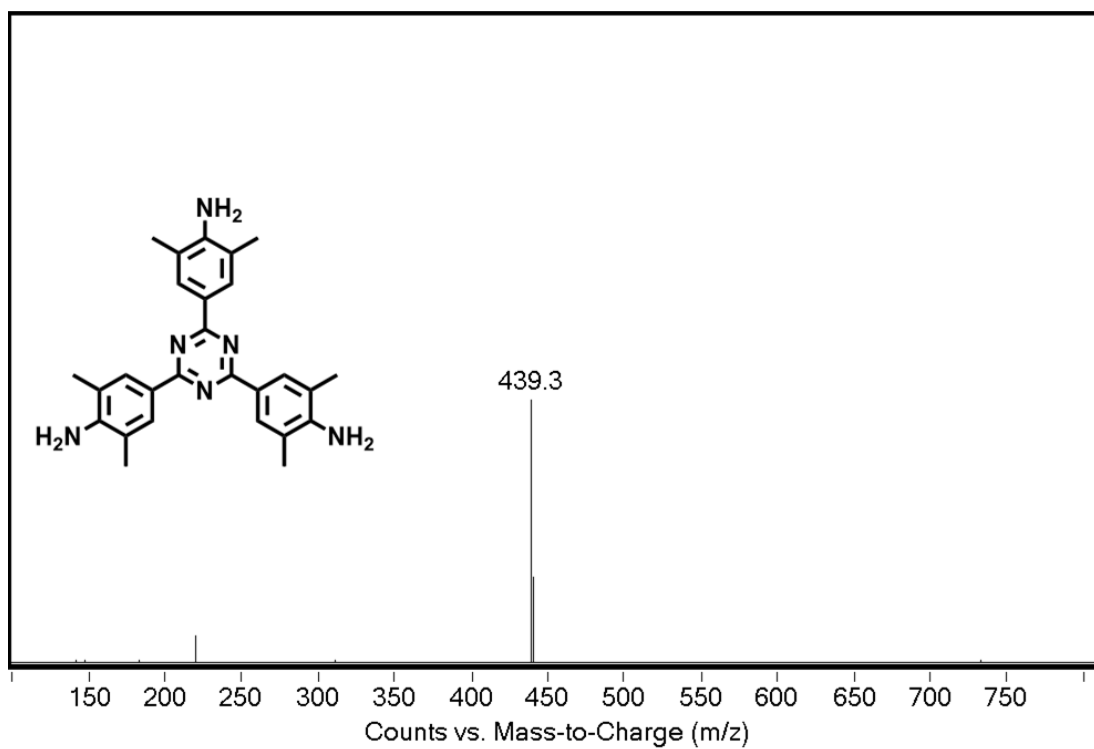
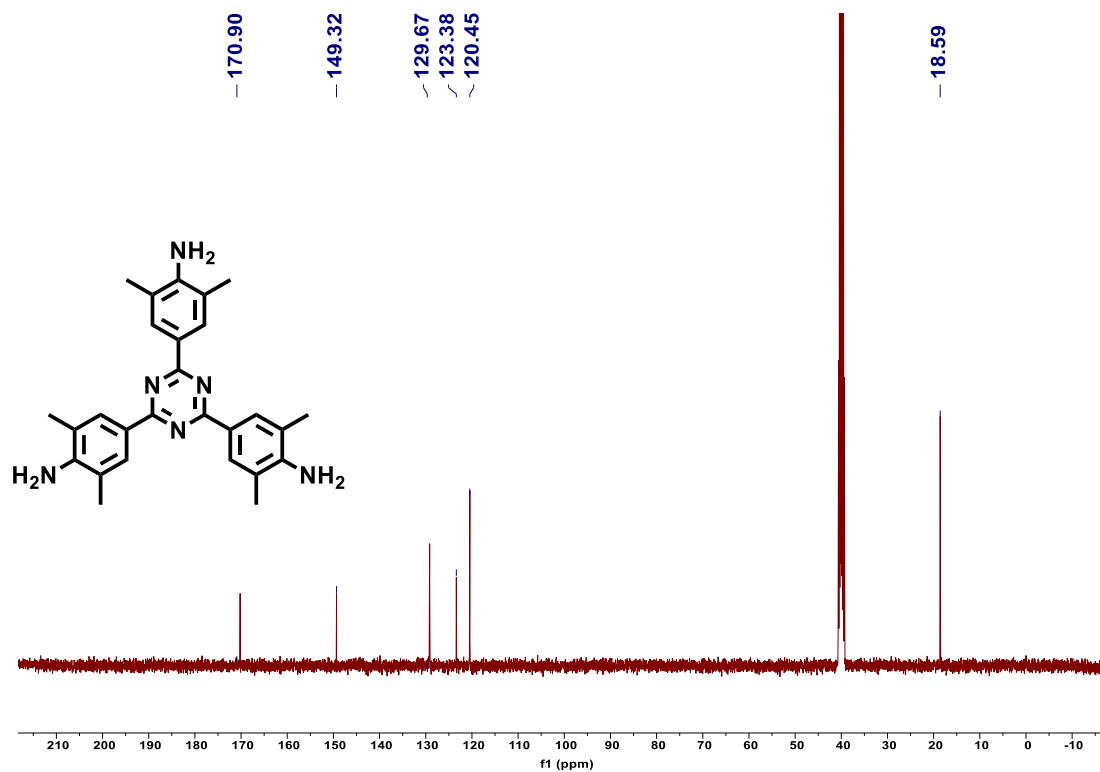




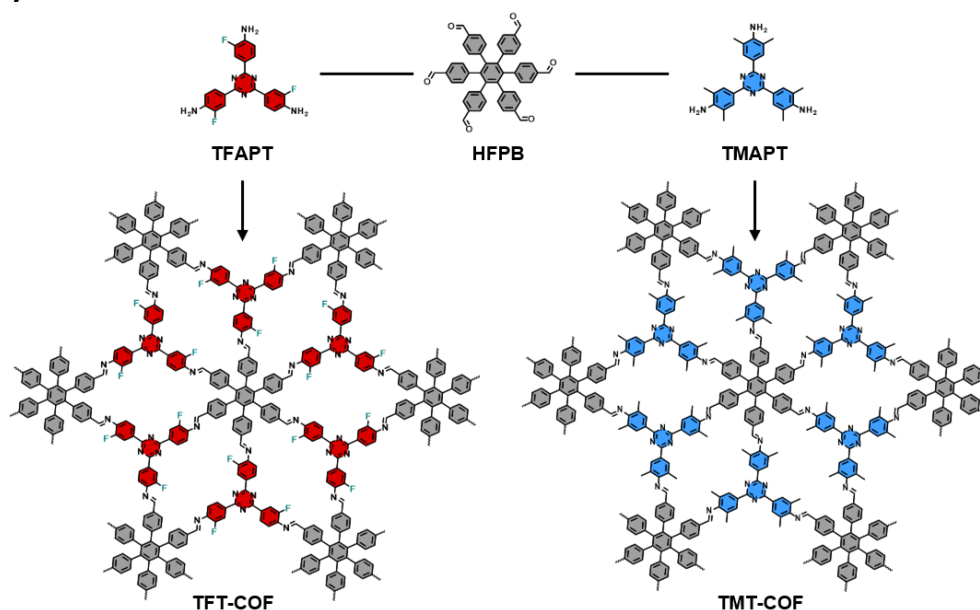


TMAPT was synthesized following the same protocol of TFAPT with minor modifications. Typically, 4-amino-3,5-dimethyl-benzonitrile (500 mg, 3.5 mmol) and 2 mL chloroform (CHCl₃) were added in a round bottom flask at 0 °C. Then 1 mL trifluoromethanesulfonic acid (TFA) was added dropwise for 20 min and the resultant mixture was stirred for 24 h at room temperature in inert atmosphere. After that, 20 mL distilled water was added to the mixture and it was neutralized by adding 2 M NaOH solution until the pH reaches to 7. The resultant yellow product was filtered and washed several times with methanol and distilled water. The purified product (0.15 g) was characterized by ¹H NMR, ¹³C NMR and MS. ¹H NMR (500 MHz, DMSO-*d*₆) δ: 8.18 (s, 6H), 5.41 (s, 6H), 2.24 (s, 18H). ¹³C NMR (101 MHz, DMSO-*d*₆) δ: 170.20, 149.32, 129.15, 123.38, 120.45, 18.15. MS: m/z 438 (Calcd m/z 439.8 for [M]⁺).





2.2 Synthesis and characterization of COFs



Tft-COF: A 10 mL Pyrex tube was charged with Hexa(4-formylphenyl)benzene (HFPB) (21 mg, 0.03 mmol), Tris(4-aminophenyl-3-fluoro)triazine (24.48 mg, 0.06 mmol) and N, N-Dimethylacetamide/*n*-butanol (v/v=1:2, 1.2 mL). After the mixture was sonicated for 5 min, a clear solution was obtained. Subsequently, 0.6 mL of Trifluoroacetic acid were added. Afterwards, the tube was flash frozen at 77 K using a liquid N₂ bath and degassed by three freeze-pump-thaw cycles, sealed under vacuum and then heated at 120 °C for 3 days. A yellow precipitate was formed, which was collected by centrifugation and washed with anhydrous ethanol, anhydrous acetone, and anhydrous tetrahydrofuran, separately. The collected sample was then solvent-exchanged with anhydrous tetrahydrofuran for 2-3 times and dried at 120 °C under vacuum for 12 h to give a yellow powder (30 mg, 66% isolated yield).

Tmt-COF: A 10 mL Pyrex tube was charged with hexa(4-formylphenyl)benzene (HFPB) (21 mg, 0.03 mmol), Tris(4-aminophenyl-3,5-Dimethyl)triazine (26.34 mg, 0.06 mmol) and N, N-Dimethylacetamide/*n*-butanol (v/v=1:2, 1.2 mL). After the mixture was sonicated for 5 min, a clear solution was obtained. Subsequently, 0.6 mL of Trifluoroacetic acid was added. Afterward, the tube was flash-frozen at 77 K using a liquid N₂ bath and degassed by three freeze-pump-thaw cycles, sealed under vacuum, and then heated at 120 °C for 3 days. A yellow precipitate was formed, which was collected by centrifugation and washed with anhydrous ethanol, anhydrous acetone, and anhydrous tetrahydrofuran, separately. The collected sample was then solvent-exchanged with anhydrous tetrahydrofuran for 2-3 times and dried at 120 °C under vacuum for 12 h to give a yellow powder (40 mg, 84% isolated yield).

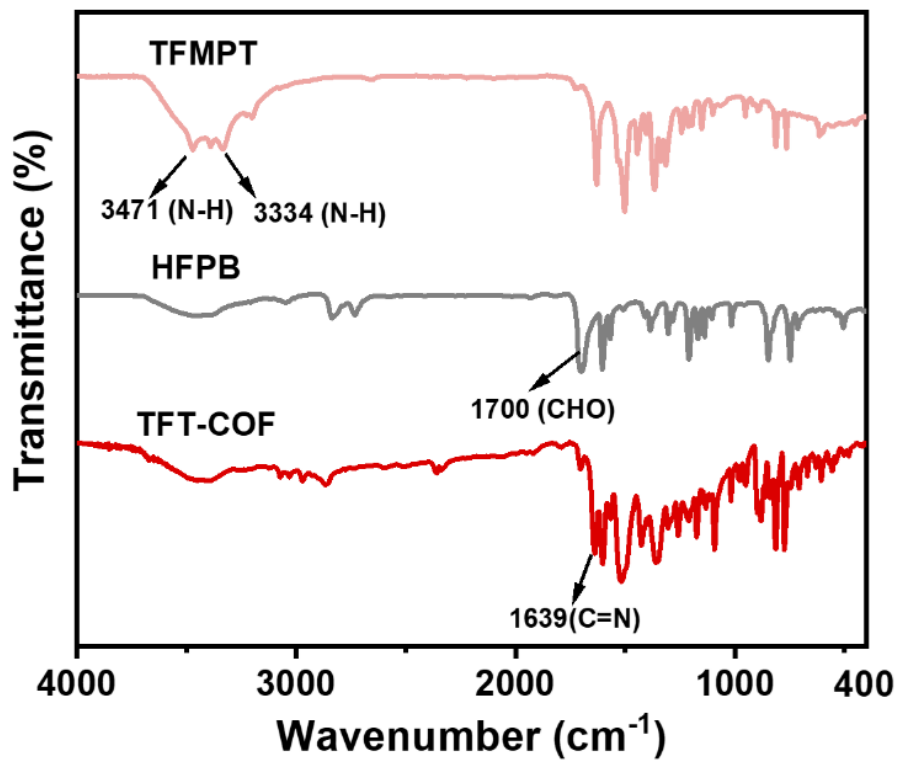


Figure S1. FT-IR spectra of TAFPT, HFPB, and TFT-COF.

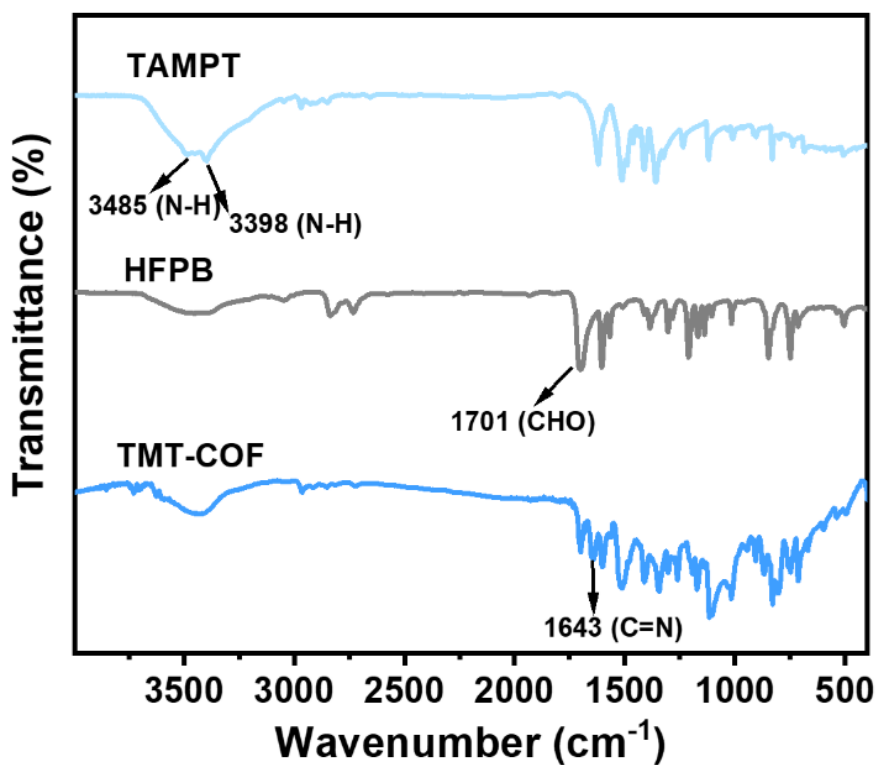


Figure S2. FT-IR spectra of TAMPT, HFPB, and TMT-COF

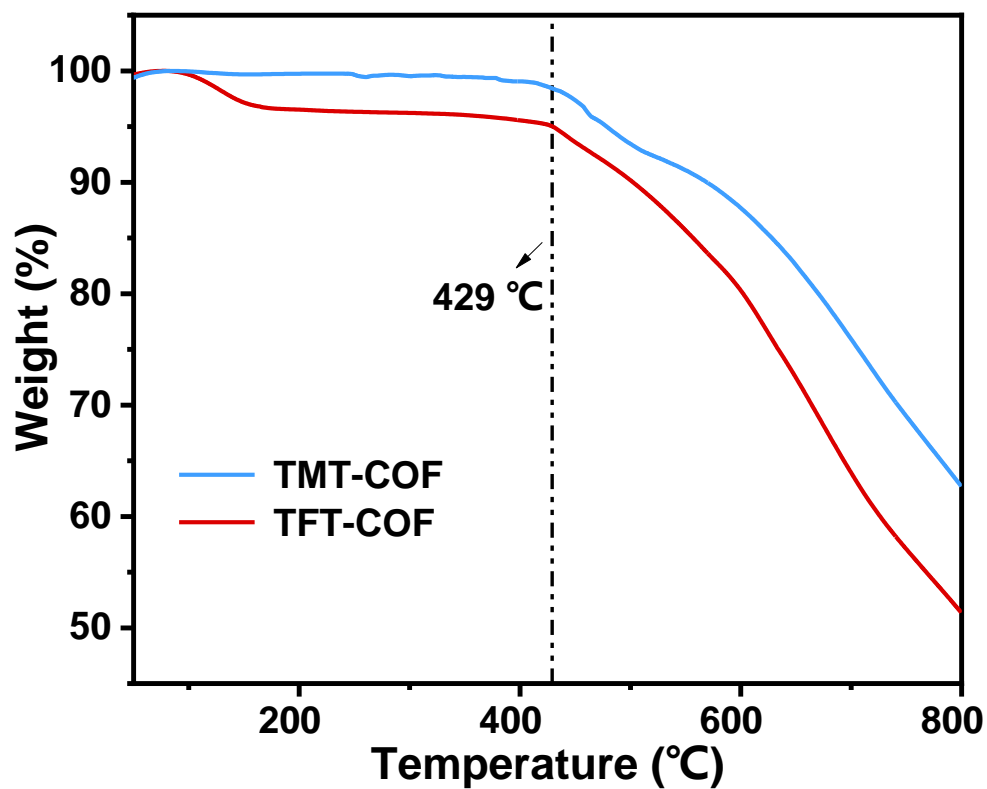


Figure S3. TGA curves of TFT-COF and TMT-COF.

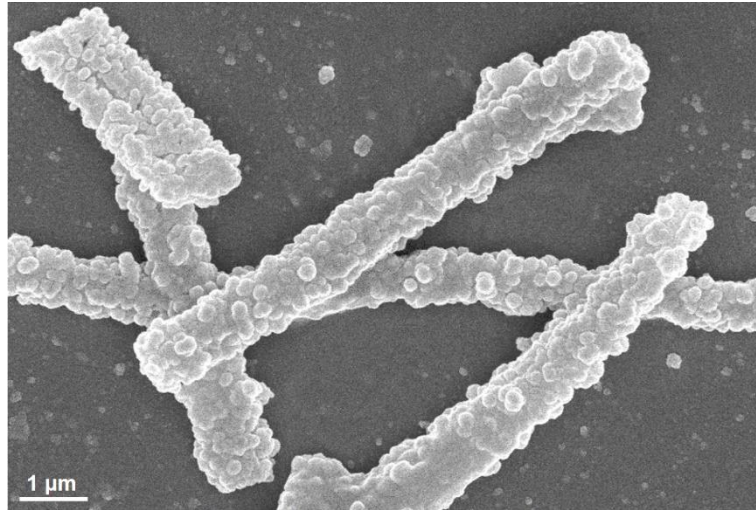


Figure S4. SEM image of TFT-COF.

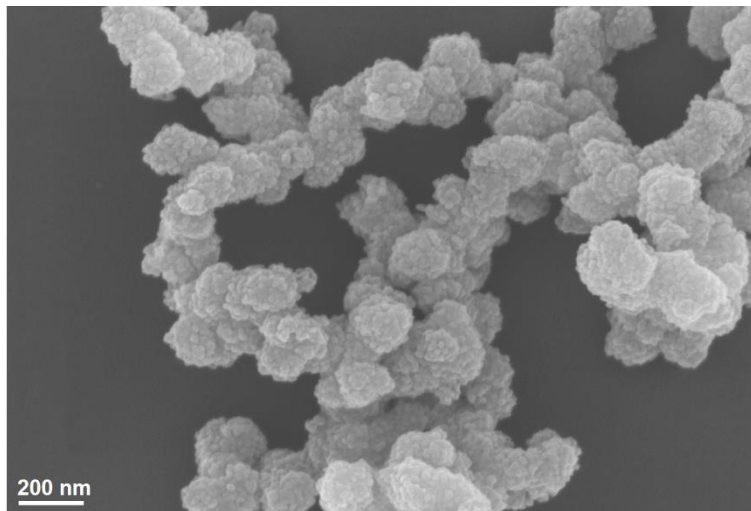


Figure S5. SEM image of TMT-COF.

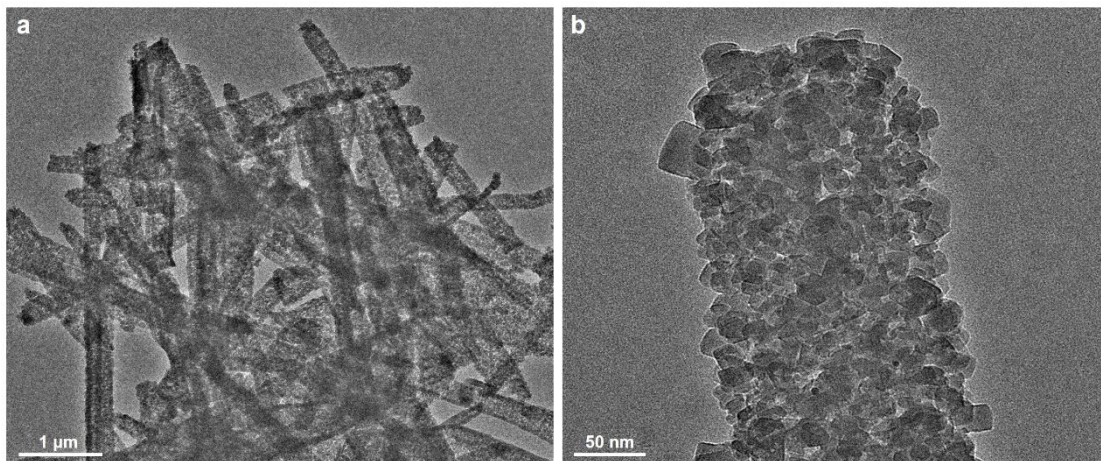


Figure S6. TEM images of TFT-COF.

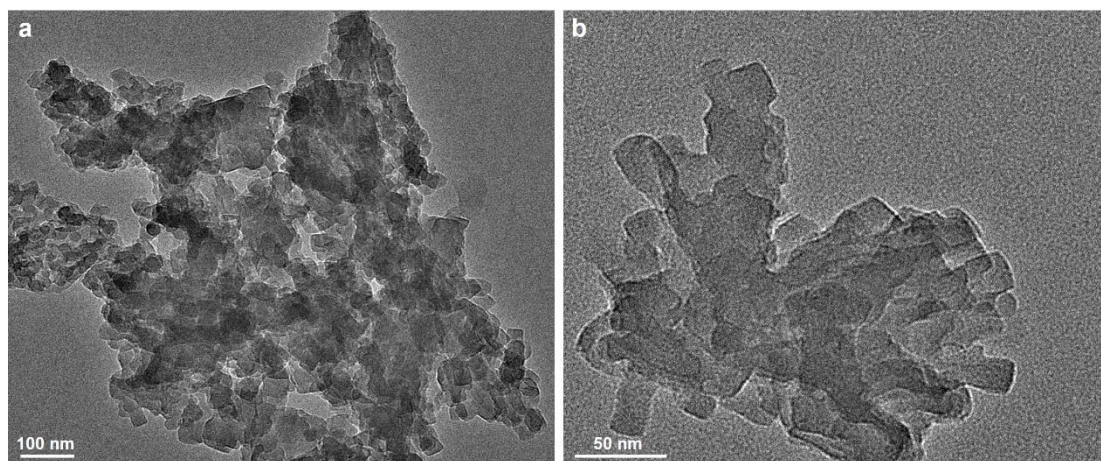


Figure S7. TEM images of TMT-COF.

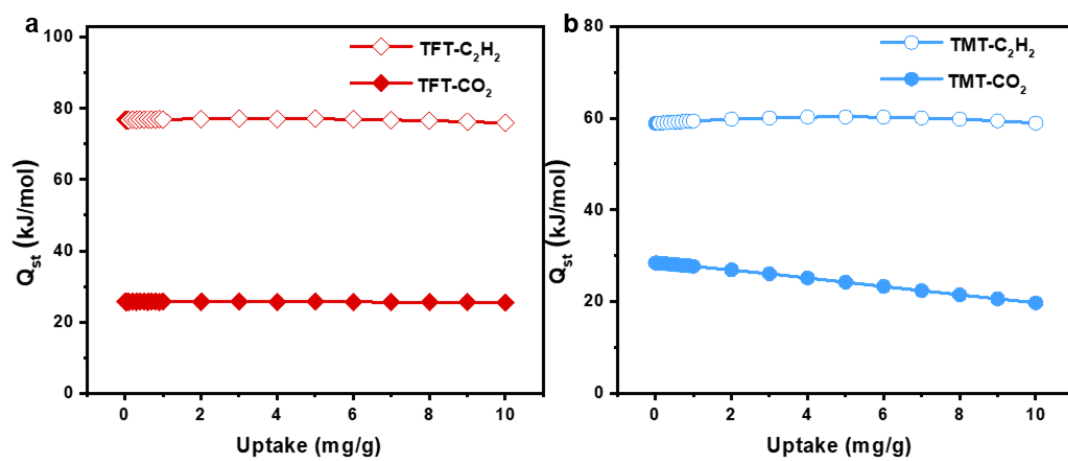


Figure S8. The coverage-dependent adsorption enthalpies (Q_{st}) of C_2H_2 and CO_2 for (a) TFT-COF, and (b) TMT-COF.

2.3 Unit cell parameters and fractional atomic coordinates

Table S1. Unit cell parameters and fractional atomic coordinates for **TFT-COF** calculated based on ABC stacking.

Space group	<i>R</i> 3		
Calculated unit cell	$a = 26.0484\text{\AA}, b = 26.0484\text{\AA},$ $c = 11.7319\text{\AA}$		
	$\alpha = 90.0000^\circ, \beta = 90.0000^\circ,$ $\gamma = 120.0000^\circ$		
Atoms	X	Y	Z
C1	0.03117	0.06274	0.00006
C2	0.0645	0.12812	0.0179
C3	0.06217	0.1672	-0.06127
C4	0.09394	0.22839	-0.0423
C5	0.12929	0.25136	0.05577
C6	0.13183	0.21222	0.1345
C7	0.09943	0.1512	0.11595
C8	0.83227	0.14822	-0.07517
N1	0.15701	0.35309	0.01705
C9	0.19313	0.41623	0.02754
C10	0.16615	0.45105	0.02187
C11	0.20038	0.51287	0.02578
C12	0.26256	0.54096	0.03223
C13	0.28943	0.5058	0.03894
C14	0.25527	0.44409	0.03597
C15	0.29938	0.60641	0.0293
N2	0.35946	0.633	0.02924
C16	0.96879	0.93724	-0.00318
C17	0.93709	0.87177	-0.02026
C18	0.89547	0.83279	0.05881
C19	0.86636	0.77154	0.04051
C20	0.87952	0.74841	-0.05632
C21	0.92154	0.78741	-0.13471
C22	0.94959	0.84848	-0.11728
C23	0.15035	0.83467	0.07593
N3	0.80315	0.64696	-0.02311
C24	0.77585	0.58372	-0.0324
C25	0.81009	0.556	-0.04267
C26	0.78295	0.49434	-0.04381

C27	0.72105	0.45899	-0.03448
C28	0.68676	0.48686	-0.027
C29	0.71408	0.54872	-0.02417
C30	0.69271	0.39357	-0.03068
N4	0.63276	0.3592	-0.03063

Table S2. Unit cell parameters and fractional atomic coordinates for **TMT-COF** calculated based on ABC stacking.

Space group		<i>R</i> 3	
Calculated unit cell		$a = 26.0091 \text{ \AA}, b = 26.0091 \text{ \AA},$ $c = 11.7562 \text{ \AA}$ $\alpha = 90.0000^\circ, \beta = 90.0000^\circ,$ $\gamma = 120.0000^\circ$	
Atoms	X	Y	Z
C1	0.03184	0.06273	-0.00071
C2	0.06544	0.12803	0.01705
C3	0.06453	0.16707	-0.06381
C4	0.09365	0.22806	-0.04253
C5	0.12428	0.25083	0.06042
C6	0.12558	0.2117	0.14083
C7	0.09659	0.15085	0.11896
C8	0.84584	0.16121	-0.08567
N9	0.15917	0.35278	0.00904
C10	0.19396	0.41584	0.02408
C11	0.16633	0.45069	0.0172
C12	0.20088	0.51266	0.02422
C13	0.26291	0.5408	0.03326
C14	0.29006	0.50598	0.04048
C15	0.25649	0.44397	0.0349
C16	0.29955	0.60633	0.03072
N17	0.35971	0.63317	0.03063
C23	0.10053	0.42367	-0.00169
C26	0.28844	0.409	0.03302
C27	0.96819	0.93726	-0.00357
C28	0.93554	0.8719	-0.02101
C29	0.8952	0.83332	0.05992
C30	0.86294	0.77224	0.03942
C31	0.8708	0.74894	-0.06285
C32	0.91143	0.78765	-0.14353
C33	0.94364	0.84855	-0.12242
C34	0.15871	0.8437	0.0844
N35	0.80368	0.6471	-0.01022
C36	0.77622	0.58401	-0.02436
C37	0.81114	0.55639	-0.03286
C38	0.78317	0.49445	-0.03986

C39	0.72113	0.4592	-0.03604
C40	0.68672	0.48695	-0.02917
C41	0.71381	0.54894	-0.02089
C42	0.69273	0.39365	-0.03424
N43	0.63271	0.35921	-0.03413
C49	0.87798	0.59183	-0.02724
C52	0.67611	0.57736	-0.00499

3. References

- (S1) Materials Studio; Accelrys: San Diego.
- (S2) <http://www.ba.ic.cnr.it/softwareic/expo/>
- (S3) <http://www.jp-minerals.org/vesta/en/>