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Electronic Supplementary Information

Regulating the topology of 2D covalent organic frameworks by the rational introduction of substituents

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Procedure for the preparation of COF-DHTA:

4,4',4'',4'''-(ethene-1,1,2,2-tetrayl)tetraaniline (**ETTA**, 30 mg, 0.0764 mmol) and 2,5-dihydroxyterephthalaldehyde (**DHTA**, 25.4 mg, 0.153 mmol) were dissolved in a mixture of 1,4-dioxane (1 mL) and acetic acid (6M (aq.), 0.1 mL) in a sealed glass ampoule. The ampoule was sealed after being degassed in a liquid nitrogen bath for 20 min, warmed to room temperature and then kept at 120 ^{o}C without disturbance for 3 days to yield a red solid at the bottom of the tube. After being cooled to room temperature, the solvent was decanted and the solid was washed with anhydrous 1,4-dioxane for 3 times and then dried under dynamic vacuum at 120 ^{o}C for 2 h to afford a red powder (29.1 mg, 58.3%), which was insoluble in common organic solvents such as acetone, ethanol, and N, N-dimethylformamide. Anal. Calcd. For $C_{42}H_{28}N_4O_4$: C, 77.29; H, 4.32; N, 8.58. Found: C, 73.84; H, 5.26; N, 7.73.

Procedure for the preparation of COF-DETA:

4,4',4'',4'''-(ethene-1,1,2,2-tetrayl)tetraaniline (**ETTA**, 30 mg, 0.0764 mmol) and 2,5-diethoxyterephthalaldehyde (**DETA**, 34.0 mg, 0.153 mmol) were dissolved in a

mixture of 1,4-dioxane (1 mL) and acetic acid (6M (aq.), 0.1 mL) in a sealed glass ampoule. The ampoule was sealed after being degassed in a liquid nitrogen bath for 20 min, warmed to room temperature and then kept at 120 ^{o}C without disturbance for 3 days to yield an orange solid at the bottom of the tube. After being cooled to room temperature, the solvent was decanted and the solid was washed with anhydrous 1,4-dioxane for 3 times and then dried under dynamic vacuum at 120 ^{o}C for 2 h to afford an orange powder (47.4 mg, 81.1%), which was insoluble in common organic solvents such as acetone, ethanol, and N, N-dimethylformamide. Anal. Calcd. For $C_{50}H_{44}N_4O_4$: C, 78.51; H, 5.80; N, 7.32. Found: C, 75.75; H, 5.90; N, 7.15.

Procedure for the preparation of COF-DBTA:

4,4',4'',4'''-(ethene-1,1,2,2-tetrayl)tetraaniline (**ETTA**, 30 mg, 0.0764 mmol) and 2,5-dibutoxyterephthalaldehyde (**DBTA**, 42.5 mg, 0.153 mmol) were dissolved in a mixture of 1,4-dioxane (1 mL) and acetic acid (6M (aq.), 0.1 mL) in a sealed glass ampoule. The ampoule was sealed after being degassed in a liquid nitrogen bath for 20 min, warmed to room temperature and then kept at 120 ^{o}C without disturbance for 3 days to yield a yellow solid at the bottom of the tube. After being cooled to room temperature, the solvent was decanted and the solid was washed with anhydrous 1,4-dioxane for 3 times and then dried under dynamic vacuum at 120 ^{o}C for 2 h to afford a yellow powder (56.4 mg, 84.2%), which was insoluble in common organic solvents such as acetone, ethanol, and N, N-dimethylformamide. Anal. Calcd. For $C_{58}H_{60}N_4O_4$: C, 79.42; H, 6.90; N, 6.39. Found: C, 77.88; H, 6.89; N, 6.32.

Instruments and Methods.

Fourier transform infrared spectroscopy (FT-IR)

Fourier transform infrared spectroscopy was carried out with a Nicolet 380 FT-IR spectrometer. The samples for IR study were prepared as KBr pellets.

Solid-state nuclear magnetic resonance (NMR) spectroscopy

The ^{13}C CP-MAS spectra of the COFs were recorded on Agilent DD2 600 Solid NMR

System with 3.2mm zirconia rotors. The spinning rate is 15 kHz and the contact time is 3 ms.

Powder X-ray diffraction

Powder X-ray diffraction measurements were carried out with an X'Pert PROX system using monochromated Cu/Kα (λ = 0.1542 nm). The samples were spread on the square recess of XRD sample holder as a thin layer.

Structural simulations and powder X-ray diffraction analyses

The simulations of the possible structures were carried out in Accelrys Material Studio 7.0 software package. The stimulated PXRD patterns were determined by the Reflex module. The initial space groups for the simulated structures were selected as P1. Pawley refinement of the experimental PXRD of **COF-DHTA** was conducted to optimize the lattice parameters iteratively until the R_{WP} value converges, resulting in the cell parameters of a = b = 37.48 Å, c = 4.52 Å, α = β = 90°， and γ = 120° with R_P = 3.50% and R_{WP} = 4.70%.

Table S1. Fractional atomic coordinates for the unit cell of dual-pore **COF-DHTA** with AA stacking.

P1							
a = b = 37.9 Å, c = 4.5 Å, α=β= 90 ºand γ = 120 º							
H	0.002981	0.417947	0.182018	C	0.423134	0.468276	0.404761
H	0.063993	0.412198	0.142692	C	0.452866	0.488328	0.623983
H	0.129327	0.518791	0.706366	C	0.445622	0.509403	0.8513
H	0.069053	0.524265	0.751421	C	0.409774	0.510691	0.854305
H	0.04615	0.535184	0.001662	C	0.389979	0.905165	0.673646
H	0.110565	0.598424	-0.06039	C	0.428912	0.938222	0.655456
H	0.093642	0.640181	0.798011	C	0.435981	0.973533	0.503331
H	0.0289	0.577548	0.857803	C	0.402925	0.975858	0.385881

H	0.132816	0.69777	0.599162	C	0.36393	0.942824	0.408304
H	0.179859	0.521859	0.508564	C	0.492048	0.487606	0.606451
H	0.24153	0.419652	0.267793	C	0.529067	0.522746	0.612475
H	0.2433	0.540568	0.688108	C	0.488387	0.446462	0.563328
H	0.294436	0.767544	0.240641	C	0.567933	0.521004	0.625119
H	0.175333	0.76222	0.724254	C	0.532651	0.564288	0.595782
H	0.337879	0.832895	0.400061	C	0.512257	0.966737	0.392205
H	0.306234	0.439994	0.400981	C	0.48811	0.938061	0.175992
H	0.364376	0.45243	0.238661	C	0.490038	0.902805	0.140456
H	0.428205	0.452162	0.22156	C	0.515999	0.89494	0.316159
H	0.468303	0.52582	1.025516	C	0.540026	0.923931	0.532058
H	0.404551	0.527985	1.0286	C	0.53791	0.958996	0.57035
H	0.385404	0.87743	0.786297	C	0.562758	0.596793	0.761682
H	0.453925	0.936063	0.760501	C	0.565735	0.634663	0.752135
H	0.407401	1.003221	0.269018	C	0.539673	0.642135	0.574977
H	0.338441	0.944635	0.308518	C	0.510196	0.609786	0.403656
H	0.467561	0.943024	0.032308	C	0.506815	0.571714	0.412528
H	0.470829	0.880772	-0.03	C	0.45822	0.412187	0.715069
H	0.561512	0.92003	0.673923	C	0.454517	0.374349	0.672001
H	0.556539	0.980604	0.744136	C	0.480071	0.36884	0.474781
H	0.584066	0.59285	0.904385	C	0.509565	0.40319	0.319056
H	0.589602	0.659513	0.884668	C	0.513637	0.441181	0.360803
H	0.489723	0.614556	0.256745	C	0.574364	0.498569	0.846506
H	0.483549	0.547826	0.270331	C	0.609122	0.495183	0.843238
H	0.437242	0.414639	0.871214	C	0.638964	0.514267	0.622083
H	0.430367	0.348271	0.793845	C	0.632039	0.536469	0.40133
H	0.529969	0.400799	0.158013	C	0.597411	0.53983	0.402421
H	0.536601	0.466567	0.227155	C	0.518501	0.690123	0.458155
H	0.551691	0.482726	1.022009	C	0.528519	0.732189	0.432948

H	0.612999	0.476711	1.015298	C	0.566174	0.76727	0.503476
H	0.653662	0.55141	0.218284	C	0.569727	0.80511	0.473722
H	0.59298	0.556516	0.220305	C	0.538286	0.810982	0.375284
H	0.488217	0.666916	0.378285	C	0.501278	0.7762	0.297269
H	0.598985	0.831668	0.535389	C	0.497499	0.738209	0.327257
H	0.467788	0.711812	0.268375	C	0.545824	0.852385	0.363419
H	0.575058	0.876533	0.452299	C	0.495107	0.318735	0.275036
H	0.520235	0.33988	0.130336	C	0.706124	0.534115	0.468297
H	0.709025	0.559684	0.33391	C	0.488242	0.277718	0.301638
H	0.42598	0.183923	0.58257	C	0.740839	0.52797	0.463025
H	0.543116	0.294208	0.057873	C	0.454878	0.245574	0.447912
H	0.781648	0.470964	0.693463	C	0.452548	0.208048	0.464878
H	0.772677	0.581307	0.185331	C	0.481482	0.199994	0.343031
H	0.445869	0.137965	0.511015	C	0.51515	0.232532	0.197138
H	0.848749	0.4956	0.538076	C	0.516946	0.269663	0.176049
H	0.449736	0.088411	0.676453	C	0.744253	0.496487	0.601483
H	0.446319	0.023342	0.738085	C	0.780483	0.496176	0.581259
H	0.532859	0.052743	0.016204	C	0.814329	0.526005	0.431636
H	0.536746	0.118805	-0.04219	C	0.81071	0.556931	0.287294
H	0.894601	0.499355	-0.0075	C	0.774206	0.556632	0.302441
H	0.952549	0.487933	0.026059	C	0.473377	0.158686	0.383968
H	1.004267	0.577406	0.735944	C	0.850674	0.52287	0.434609
H	0.948299	0.591755	0.680208	C	0.494226	0.109303	0.312721
H	0.590249	-0.00908	0.341228	C	0.91785	0.547158	0.329583
H	0.659829	0.047336	0.400008	C	0.468444	0.081314	0.528458
H	0.614221	0.121215	0.792896	C	0.465946	0.043901	0.5626
H	0.5448	0.064815	0.751379	C	0.488982	0.033008	0.381106
H	0.933386	0.467698	0.734354	C	0.514289	0.060246	0.161778
H	0.866844	0.405114	0.722527	C	0.516743	0.097719	0.129905

H	0.91995	0.345302	0.217431	C	0.919667	0.518101	0.146666
H	0.984773	0.408193	0.21154	C	0.951879	0.510925	0.170727
H	0.868803	0.297848	0.696312	C	0.981898	0.531091	0.388594
H	0.668529	0.155776	0.322887	C	0.981066	0.561193	0.564383
H	0.822525	0.228623	0.835313	C	0.949474	0.56925	0.53291
H	0.712358	0.224386	0.227826	C	0.487065	-0.00691	0.428634
H	0.203943	0.681717	0.13121	C	0.519725	-0.0112	0.489057
H	0.215272	0.831677	0.746243	C	0.562045	0.023619	0.534894
H	0.155607	0.427645	0.183444	C	0.963983	0.442953	0.467273
H	0.316214	0.567369	0.656449	C	0.595054	0.019217	0.444726
H	0.477242	0.805898	0.170621	C	0.634441	0.051102	0.477887
H	0.621246	0.790755	0.625222	C	0.642022	0.088316	0.599537
H	0.43152	0.276833	0.563133	C	0.60896	0.092341	0.695982
H	0.569434	0.254787	0.064124	C	0.569534	0.060363	0.667942
H	0.732357	0.136374	0.804435	C	0.930259	0.441191	0.612433
H	0.802405	0.311624	0.205343	C	0.892794	0.405632	0.608883
H	0.696473	0.476352	0.818462	C	0.887943	0.370276	0.46928
H	0.866894	0.594531	0.21308	C	0.921896	0.37213	0.328123
C	-0.00568	0.511918	0.4809	C	0.95907	0.40783	0.326268
C	-0.00629	0.475852	0.482339	C	0.844504	0.300285	0.580933
C	0.031273	0.472116	0.463316	C	0.690436	0.153522	0.471517
C	0.032509	0.551834	0.433307	C	0.729885	0.1894	0.509266
C	0.030626	0.44035	0.298787	C	0.805016	0.263574	0.552842
C	0.065376	0.437203	0.275552	C	0.761856	0.191517	0.681364
C	0.101939	0.465356	0.4152	C	0.798249	0.228247	0.698873
C	0.101866	0.496339	0.587154	C	0.772488	0.261008	0.384205
C	0.067288	0.499604	0.612292	C	0.736472	0.224489	0.36473
C	0.055982	0.558496	0.176082	N	0.136857	0.461615	0.384823
C	0.092636	0.594372	0.141595	N	0.145545	0.660532	0.326048

C	0.107477	0.624763	0.361636	N	0.344186	0.49293	0.644821
C	0.083281	0.617701	0.617146	N	0.317834	0.872514	0.550706
C	0.046323	0.582165	0.652129	N	0.544782	0.681369	0.565959
C	0.155011	0.694023	0.465125	N	0.474054	0.329442	0.438682
C	0.173192	0.491069	0.445292	N	0.674167	0.510728	0.624119
C	0.207188	0.483852	0.454687	N	0.517104	0.858899	0.275817
C	0.196236	0.728494	0.46263	N	0.497874	0.147679	0.274594
C	0.207715	0.449847	0.33552	N	0.883741	0.551948	0.321908
C	0.242464	0.446861	0.362788	N	0.681721	0.120935	0.618281
C	0.277595	0.476282	0.503201	N	0.8501	0.334219	0.469373
C	0.277334	0.510976	0.615181	O	0.231558	0.699378	0.185747
C	0.242406	0.513465	0.591537	O	0.239928	0.831394	0.777684
C	0.231253	0.730902	0.332834	O	0.175244	0.419075	0.189349
C	0.268026	0.766979	0.348166	O	0.3109	0.542761	0.750471
C	0.27258	0.801688	0.487623	O	0.467818	0.777565	0.195171
C	0.237858	0.798942	0.625832	O	0.598784	0.764104	0.600633
C	0.201332	0.762915	0.610856	O	0.423899	0.24892	0.577666
C	0.312778	0.837299	0.477808	O	0.546264	0.228383	0.078552
C	0.310754	0.467765	0.51354	O	0.759141	0.158881	0.834733
C	0.356862	0.9067	0.546685	O	0.774084	0.292868	0.228045
C	0.379791	0.490584	0.636318	O	0.713626	0.465725	0.763116
C	0.387105	0.468968	0.413165	O	0.841302	0.58833	0.129805

Table S2. The Space Groups and Cell Parameters of the four possible structures of **COF-DHTA**.

Structure	Crystal System	Space Group	Cell Parameters
DP-AA	hexagonal	P6/m	a = b = 37.9 Å, c = 4.5 Å, α = β = 90° and γ = 120 °
DP-AB	hexagonal	P63/m	a = b = 37.9 Å, c = 9.0 Å, α = β = 90° and γ = 120 °
SP-AA	orthorhombic	CMMM	a = 29.2 Å, b = 25.4 Å, c = 4.5 Å, α = β = γ = 90 °
SP-AB	orthorhombic	FMMM	a = 29.2 Å, b = 25.4 Å, c = 9.0 Å, α = β = γ = 90 °

The Space Groups and Cell Parameters of the four possible structures of **COF-DETA** and **COF-DBTA** are same with that of **COF-DHTA**.

Nitrogen adsorption-desorption isotherm measurement

The measurements were carried out using a Quadrasorb SI MP. Before gas adsorption measurements, the as-prepared samples (ca. 50 mg) were activated by being immersed in anhydrous 1,4-dioxane for 12 h for 3 times. The solvent was decanted and the samples were dried under dynamic vacuum at 120 °C for 4 h. The resulting samples were then used for gas adsorption measurements from 0 to 1 atm at 77 K.

Thermal gravimetric analyses (TGA)

TGA were carried out on a Waters TGA Q500 by heating the samples from 30 to 950 ^{o}C under nitrogen atmosphere at a heating rate of 10 ^{o}C/min.

Scanning electron microscopy (SEM)

Scanning electron microscopy was carried out using a XL30 FEG scanning electron microscope. The samples were dispersed over a slice of conductive adhesive adhered to a flat copper platform sample holder and then coated with gold using a sputter coater (ambient temperature, 85 torr pressure in a nitrogen atmosphere, sputtered for 80 s from a solid gold target at a current of 20 mA) before being submitted to SEM characterization.

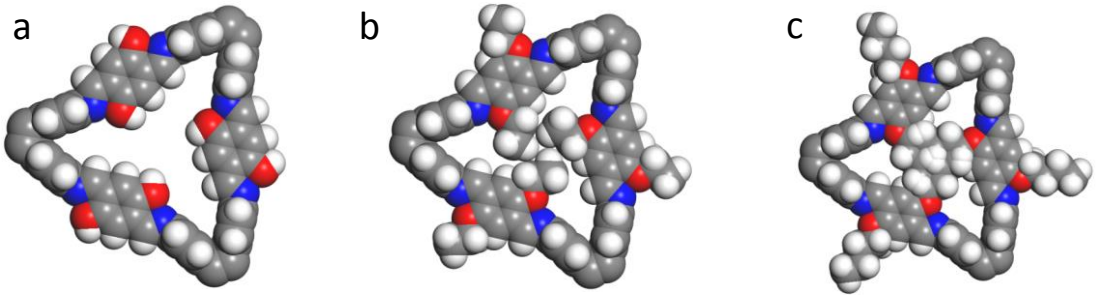

Figure S1. CPK modelings of different substituents in a triangular pore of the proposed DP-COF: (a) hydroxy, (b) ethoxy, and (c) butoxy groups.

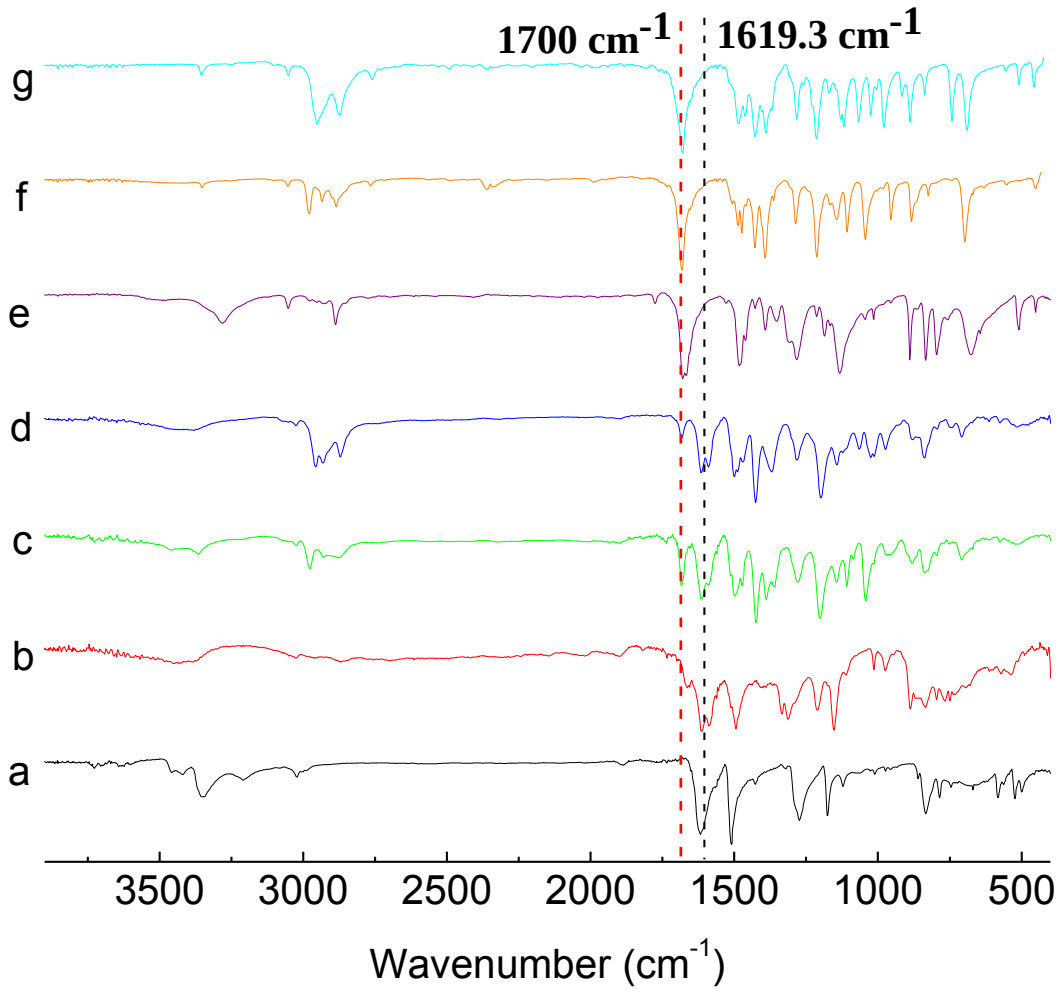

Figure S2. FT-IR spectra of (a) **ETTA**, (b) **COF-DHTA**, (c) **COF-DETA**, (d) **COF-DBTA**, (e) **DHTA**, (f) **DETA**, and (g) **DBTA.** The peaks around 1700 cm^{-1} in the spectra of the COFs can be attributed to vibrations of the residual aldehyde groups at the edges of the COFs.

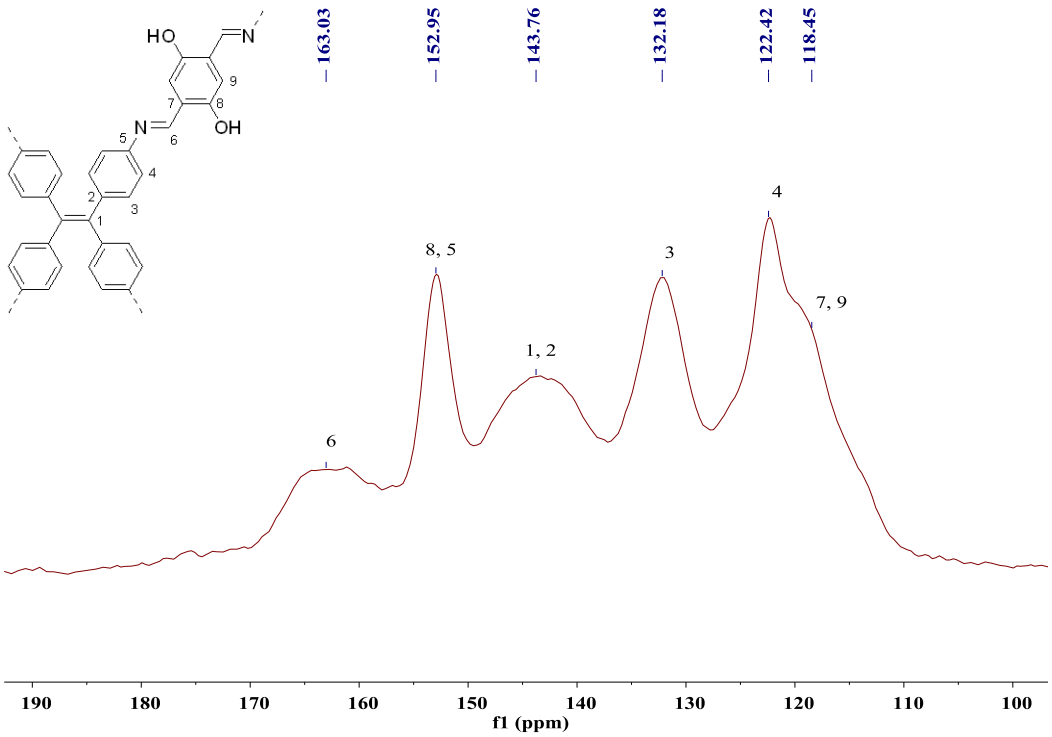

Figure S3. Solid-state ^{13}C CP-MAS NMR spectrum of **COF-DHTA**.

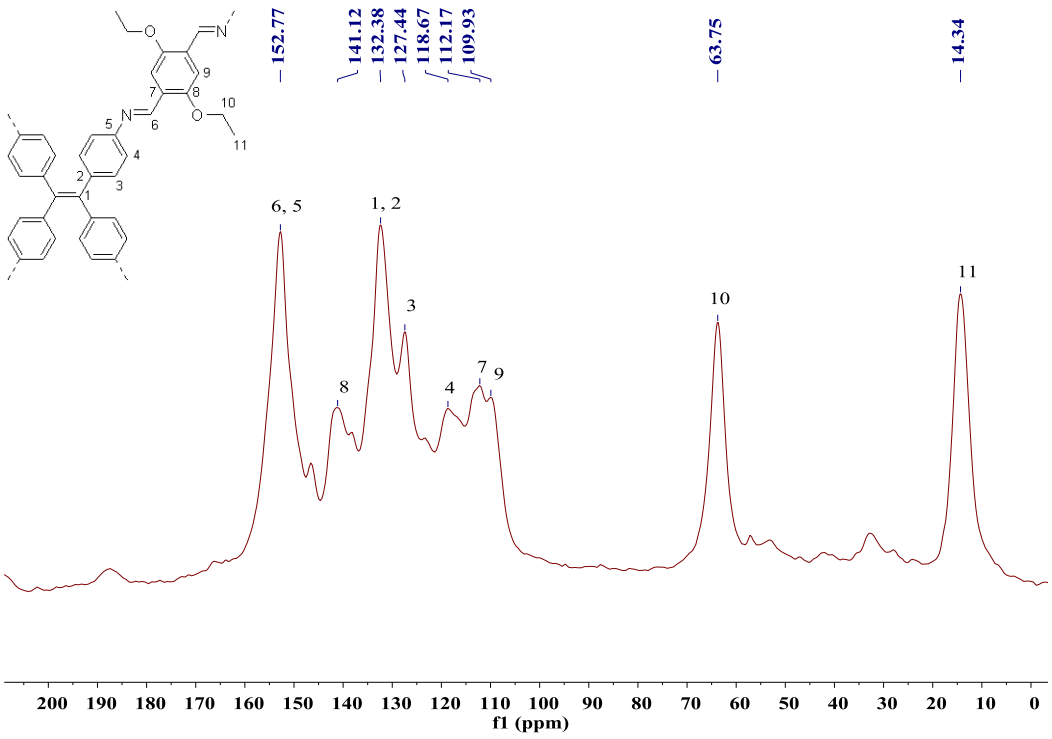

Figure S4. Solid-state ^{13}C CP-MAS NMR spectrum of **COF-DETA**.

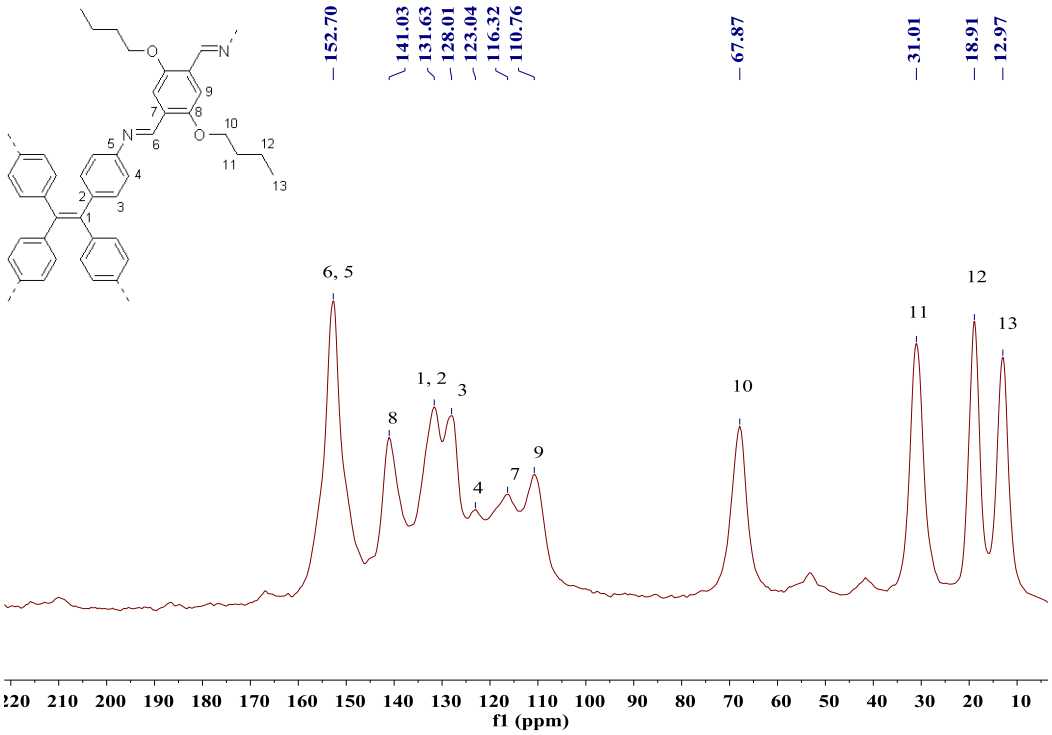

Figure S5. Solid-state ^{13}C CP-MAS NMR spectrum of **COF-DBTA**.

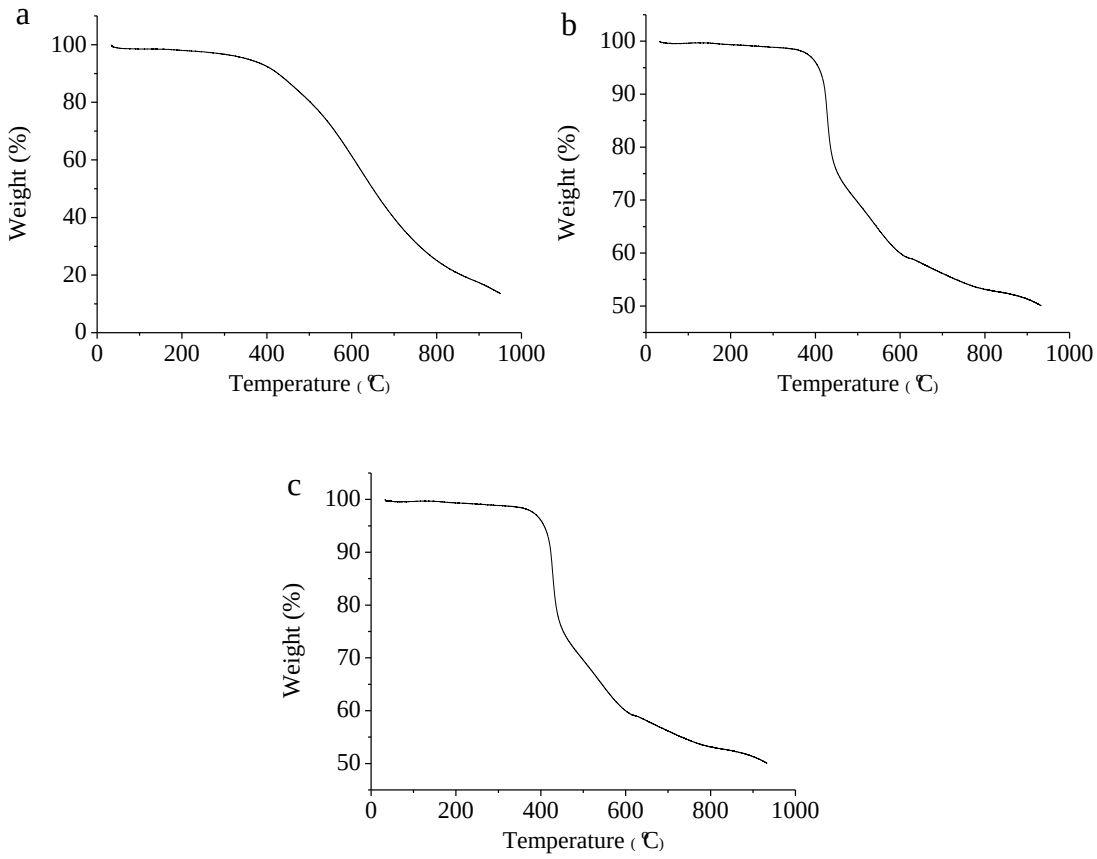

Figure S6. TGA traces of (a) **COF-DHTA**, (b) **COF-DETA**, and (c) **COF-DBTA**.

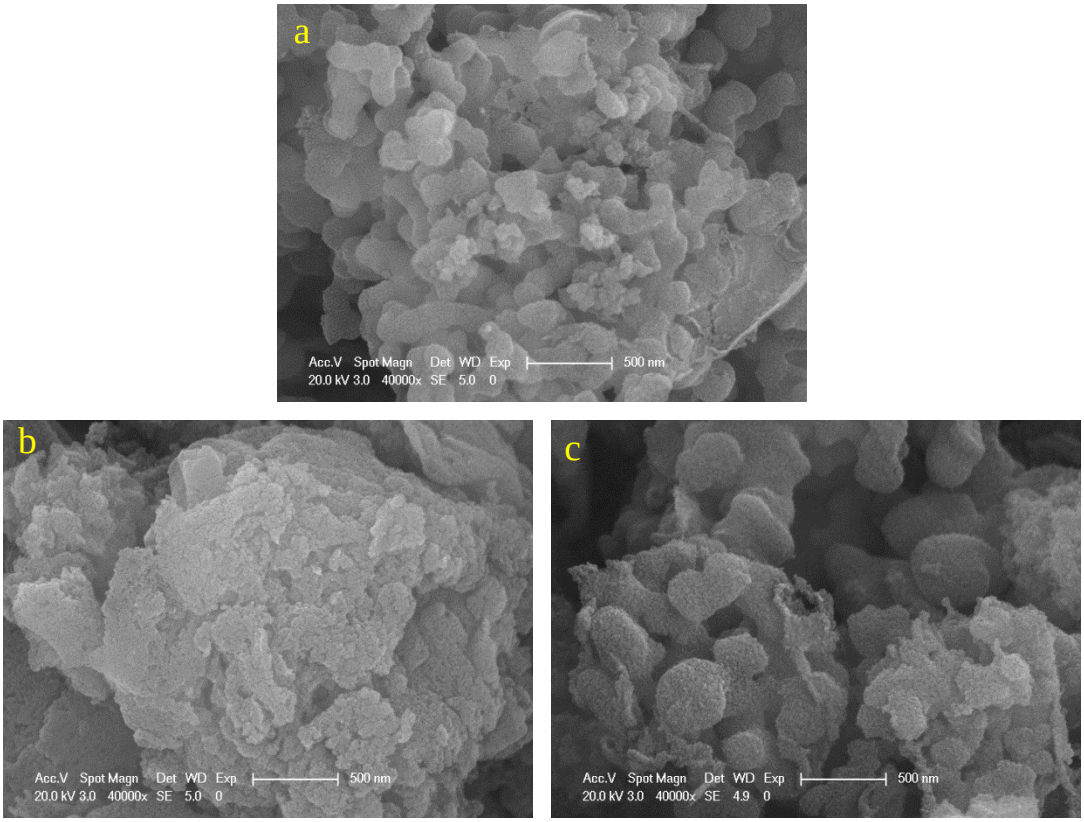

Figure S7. SEM images of (a) **COF-DHTA**, (b) **COF-DETA**, and(c) **COF-DBTA**.

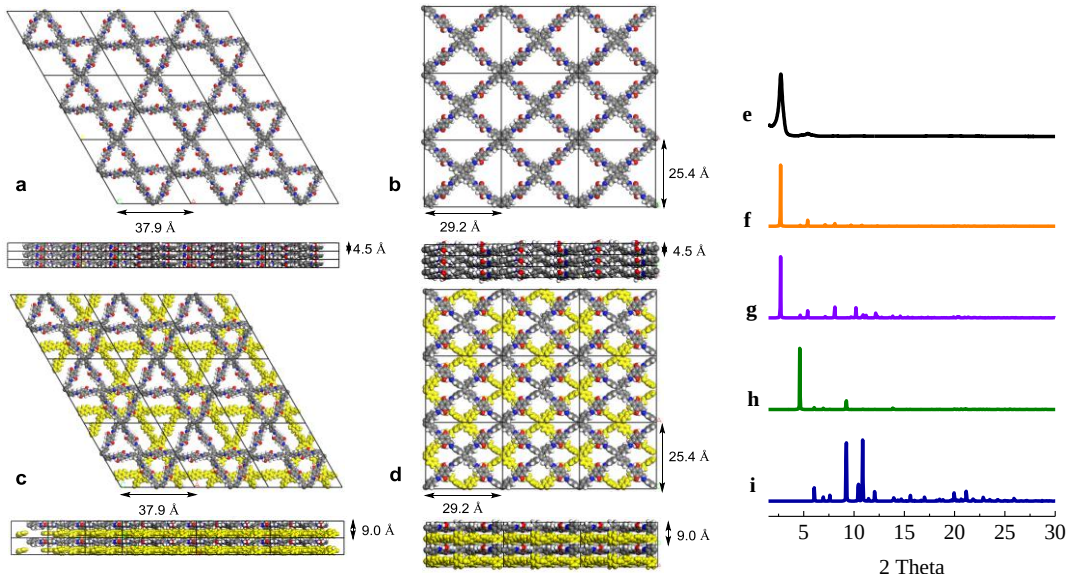

Figure S8. Left: **DHTA**-based (a) DP-AA structure, (b) SP-AA structure, (c) DP-AB structure, and (d) SP-AB structure. Right: (e) Experimental PXRD pattern of **COF-DHTA**, and simulated PXRD patterns for (f) **DHTA**-based DP-AA structure, (g) DP-AB structure, (h) SP-AA structure, and (i) SP-AB structure.

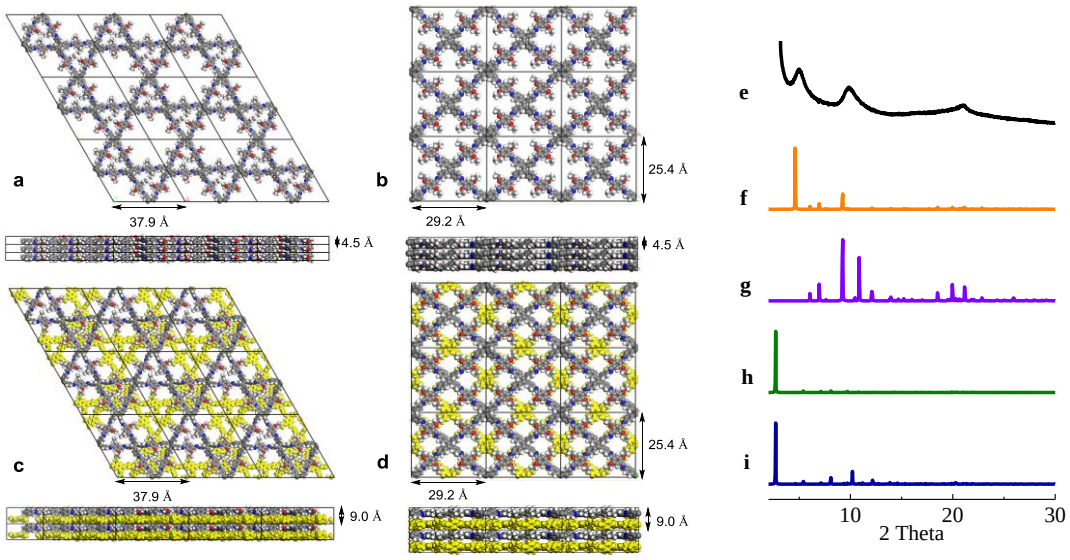

Figure S9. Left: **DETA**-based (a) DP-AA structure, (b) SP-AA structure, (c) DP-AB structure, and (d) SP-AB structure. Right: (e) Experimental PXRD pattern of **COF-DETA**, and simulated PXRD patterns for (f) **DETA**-based SP-AA structure, (g) SP-AB structure, (h) DP-AA structure, and (i) DP-AB structure.

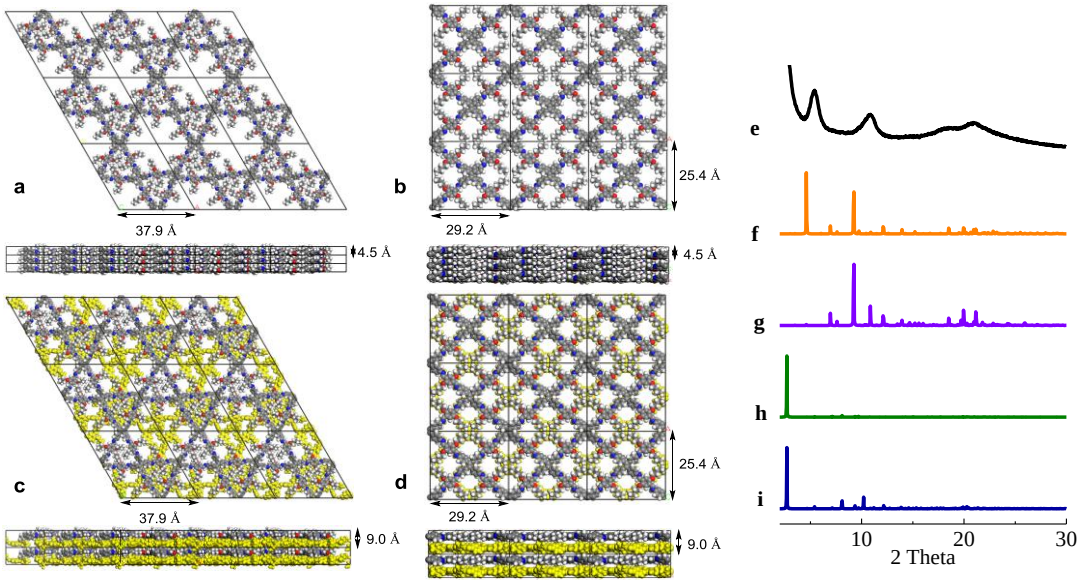

Figure S10. Left: **DBTA**-based (a) DP-AA structure, (b) SP-AA structure, (c) DP-AB structure, and (d) SP-AB structure. Right: (e) Experimental PXRD pattern of **COF-DBTA**, and simulated PXRD patterns for (f) **DBTA**-based SP-AA structure, (g) SP-AB structure, (h) DP-AA structure, and (i) DP-AB structure.

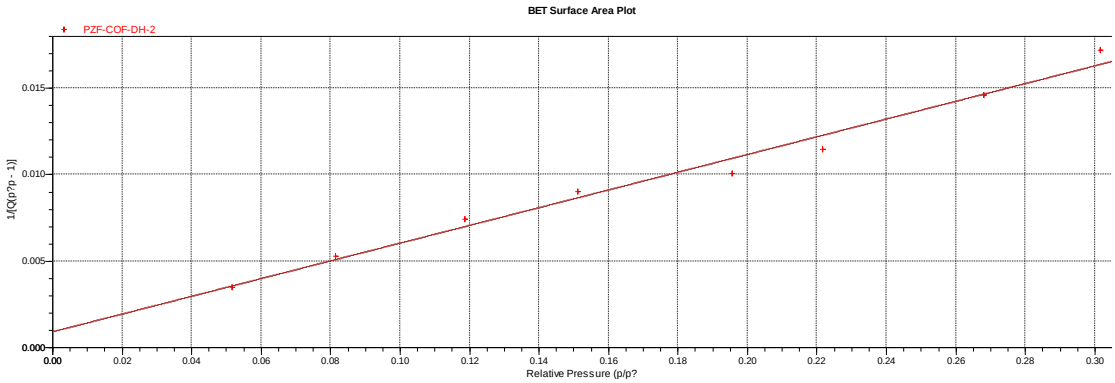

Figure S11. BET surface area plot for **COF-DHTA** calculated from the isotherm.

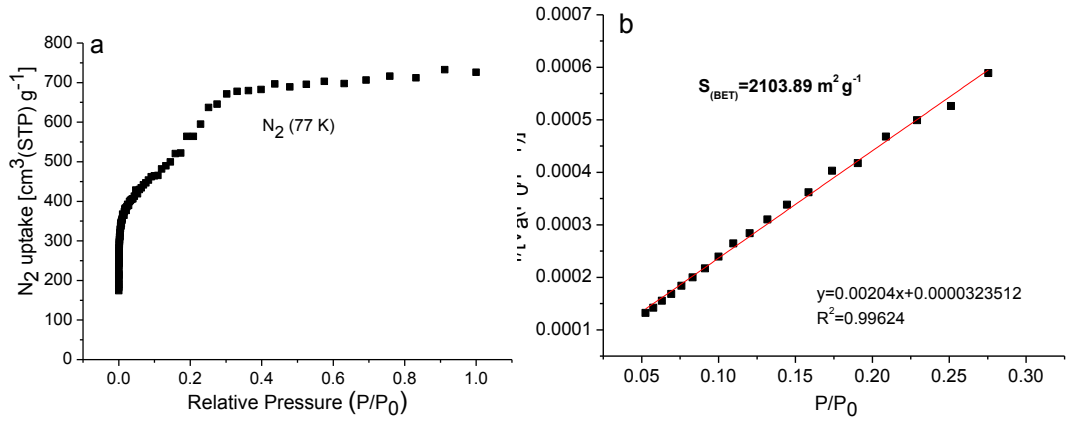

Figure S12. (a) Simulated N_2 adsorption isotherm of **COF-DHTA**, and (b) BET plot of the simulated N_2 adsorption isotherm of **COF-DHTA**, which generates a theoretical BET surface area of 2103.89 m^2g^{-1}. The simulations were performed according to the procedure reported in literature (E. L. Spitler, B. T. Koo, J. L. Novotney, J. W. Colson, F. J. Uribe-Romo, G. D. Gutierrez, P. Clancy and W. R. Dichtel, *J. Am. Chem. Soc.*, 2011, **133**, 19416-19421.)

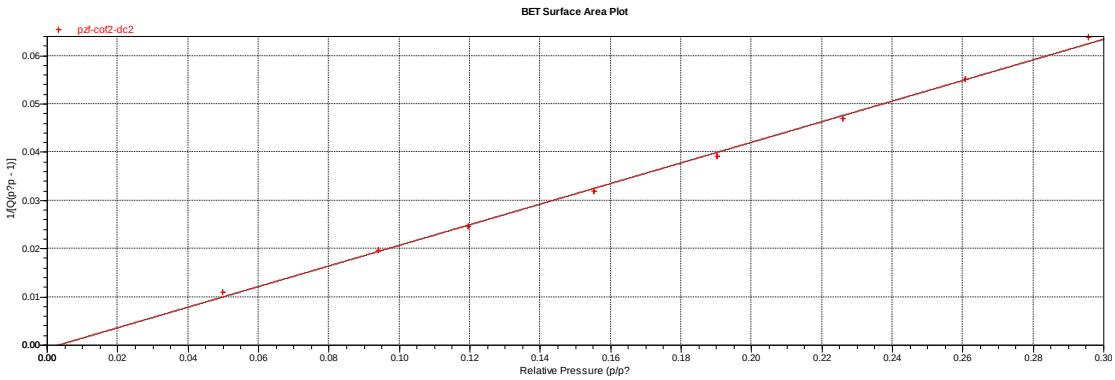

Figure S13. BET surface area plot for **COF-DETA** calculated from the isotherm.

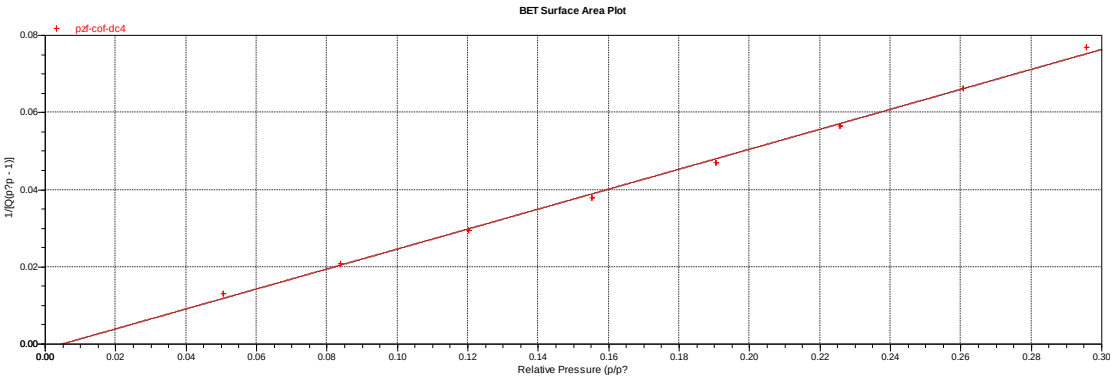

Figure S14. BET surface area plot for **COF-DBTA** calculated from the isotherm.