Electronic Supplementary Information

Construction of two heteropore covalent organic frameworks with Kagome lattices

Yuan Tian,[a,b] Shun-Qi Xu,[b] Rong-Ran Liang,[b] Cheng Qian,[a,b] Guo-Fang Jiang[a,*] and Xin Zhao[b,*]

[a] State Key Lab of Chemo/Biosensing and Chemometrics, College of Chemistry and Chemical Engineering, Hunan University, Changsha, 410082 China. Email: gfjiang@hnu.edu.cn.

[b] CAS Key Laboratory of Synthetic and Self-assembly Chemistry for Organic Functional Molecules, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Lingling Road, Shanghai 200032 China. Email: xzhao@sioc.ac.cn.

Table of Contents

Instruments and Methods……...2-3

Synthesis of the COFs…….3-4

Fig. S1-2 FT-IR Spectra of the COFs…….4-5

Fig. S3-4 Solid-state CP/MAS NMR ^{13}C Spectra the COFs…….5-6

Fig. S5 TGA traces of the COFs…….6

Fig. S6 SEM images of the COFs…….7

Fig. S7 BET plots of the COFs…….7

Fig. S8 CO_2 adsorption isotherms of the COFs…….7

Table S1 Elemental analyses of the COFs…….7

Table S2-3 Fractional atomic coordinates…….8-12

Instruments and Methods

Fourier transform infrared spectroscopy(FT-IR)

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

Solid-state ^{13}C spectroscopy

The ^{13}C CP/MAS NMR spectra of the dual-pore COFs were recorded on Agilgent DD2 600 Solid NMR System with 4 mm zirconia rotors. The spinning rate is 9 k Hz and the contact time is 3 ms.

Thermal gravimetric analysis (TGA)

Thermal gravimetric analysis was carried out on THA Q500 by heating the samples from 30 to 950 ^{o}C under nitrogen atmosphere at a heating rate of 10 ^{o}C/min.

Field-emission scanning electron microscopy (FE-SEM)

Field-emission scanning electron microscopy (FE-SEM) was performed on a JEOL model JSM-6390LV instrument.

Powder X-ray diffraction

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

Nitrogen adsorption-desorption isotherm measurement

The measurements were carried out using a Quadrasorb SI MP. Before gas adsorption measurements, the as-prepared sample (ca. 50 mg) was activated by being immersed in anhydrous dioxane for 12 h. The solvent was decanted and the sample was dried

under dynamic vacuum at 150 ^{o}C for 8 h. The resulting sample was then used for gas adsorption measurements from 0 to 1 atm at 77 K. The Brunauer-Emmett-Teller (BET) method was utilized to calculate the specific areas. By using the non-local density function theory model, the pore size distribution curves were derived from the sorption data.

Structural simulation and power X-ray diffraction analysis

The Pawley refinements were performed by the Reflux module in the Materials Studio 7.0. Before the simulations, the structures were firstly optimized in Gaussian 09 package by semiempirical calculations at PM3 level. The simulations of the two possible structures were carried out in Accelrys Materials Studio 7.0 software package. The stimulated PXRD patterns were determined by the Refled module. And the unit cell was optimized by Forcite module under molecular mechanics calculation using COMPASS II as the forcefield to give the relative total energies. P1 space group was used for the initial simulations.

Procedure for the synthesis of the COFs

COF-BTA-DAB. A mixture of 1,1'-biphenyl]-3,3',5,5'-tetracarbaldehyde (BTA)[1] (39.9 mg, 0.15 mmol) and 1,4-diaminobenzene (DAB) (32.4 mg, 0.3 mmol) in a mesitylene /dimethylacetamide/AcOH (6 M, aqueous) (5:5:1 by vol., 2.2 mL) was placed in a glass tube. The mixture was sonicated for 2 minutes and then degassed through three freeze-pump-thaw cycles. After that the tube was sealed under vacuum. The mixture was heated at 120 ^{o}C for 3 days without disturbance to yield a yellow solid. After being cooled to room temperature, the solvent was decanted and the solid was washed with anhydrous dioxane for 3 times and acetone twice and then dried under vacuum at 120 ^{o}C for 4 h to afford **COF-BTA-DAB** as a yellow powder (53.0 mg, 86.2%).

COF-BTA-BZ. A mixture of BTA (26.6 mg, 0.1 mmol) and benzidine (BZ) (36.8 mg 0.2 mmol) in mesitylene/dimethylacetamide/AcOH (6 M, aqueous) (5:5:1 by vol., 2.2 mL) in a glass tube. The mixture was sonicated for 2 minutes and then degassed through three freeze-pump-thaw cycles. After that the tube was sealed under vacuum. The mixture was heated at 120 ^{o}C for 3 days without disturbance to yield a yellow solid. After being cooled to room temperature, the solvent was decanted and the solid was washed with anhydrous dioxane for 3 times and acetone twice and then dried under vacuum at 120 ^{o}C for 4 h to afford **COF-BTA-BZ** as a yellow powder (47.0 mg, 83.6%).

Reference

1 Y. Tian, S.-Q. Xu, Q. Cheng, Z.-F. Pang, G.-F. Jiang and X. Zhao, *Chem. Commun.*, 2016, **52**, 11704-11707.

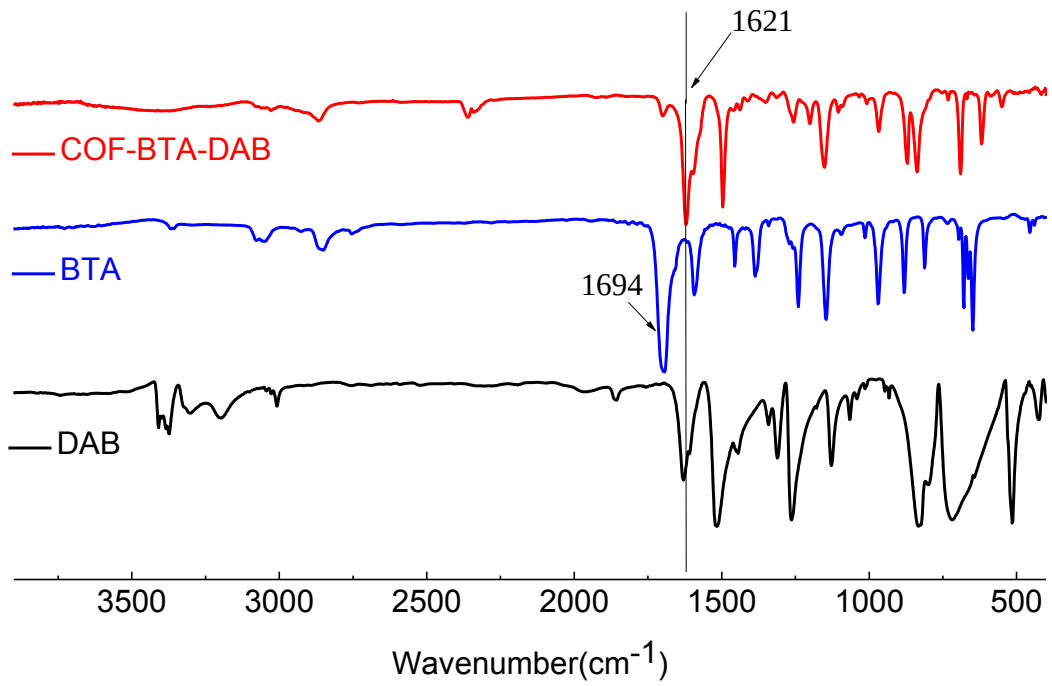

Fig. S1 FT-IR spectra of **COF-BTA-DAB**, BTA and DAB.

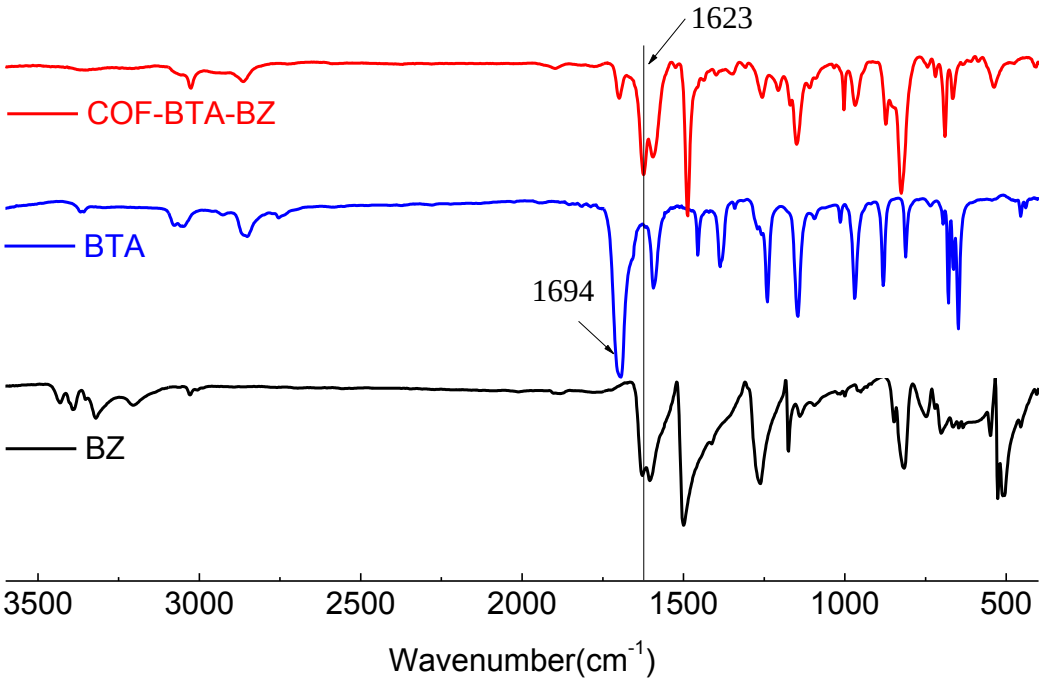

Figure S2. FT-IR spectra of **COF-BTA-BZ**, BTA and BZ.

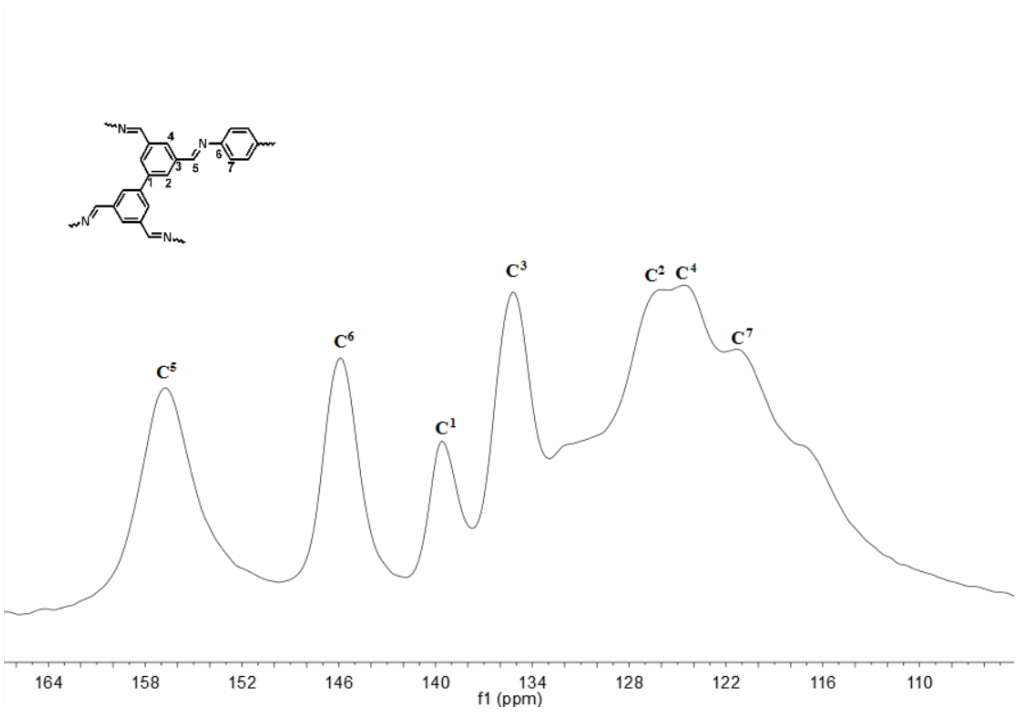

Fig. S3 Solid-state CP/MAS ^{13}C NMR Spectrum of **COF-BTA-DAB**.

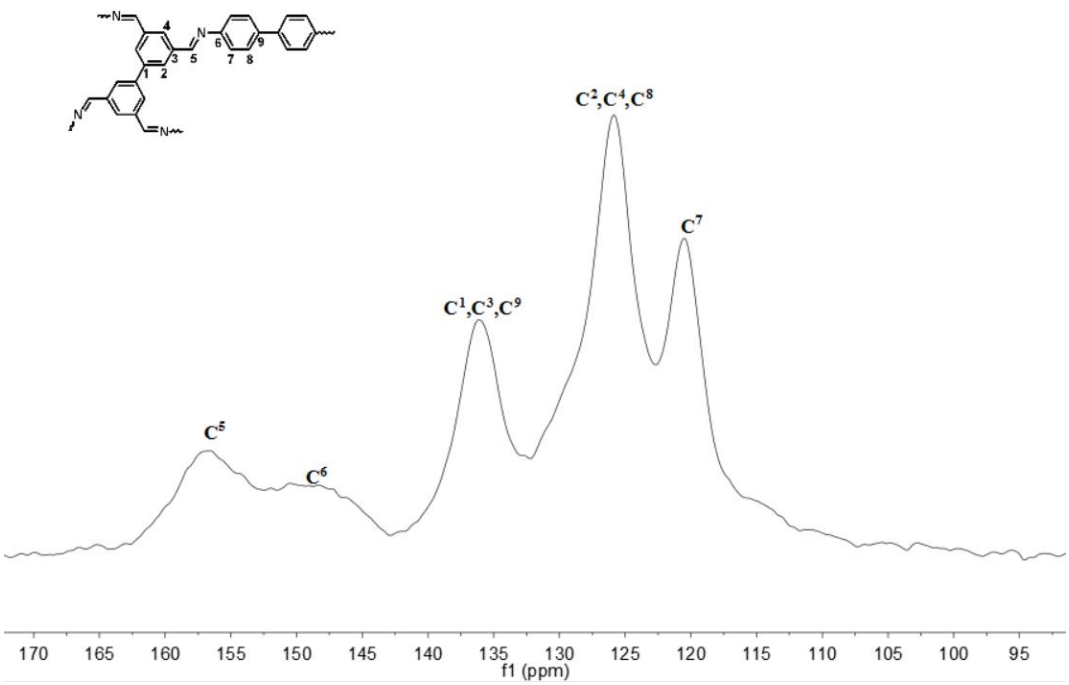

Fig. S4 Solid-state CP/MAS ^{13}C NMR spectrum of **COF-BTA-BZ**.

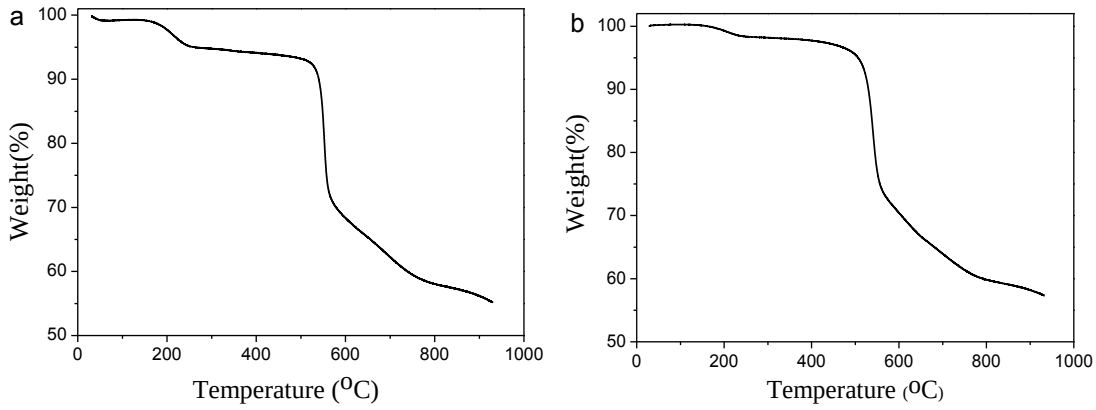

Fig. S5 TGA traces of (a) **COF-BTA-DAB** and (b) **COF-BTA-BZ**.

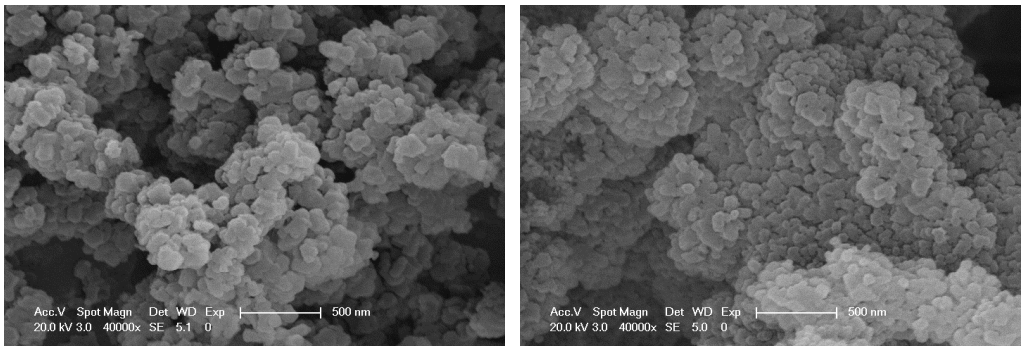

Fig. S6 SEM images of **COF-BTA-DAB** (left) and **COF-BTA-BZ** (right).

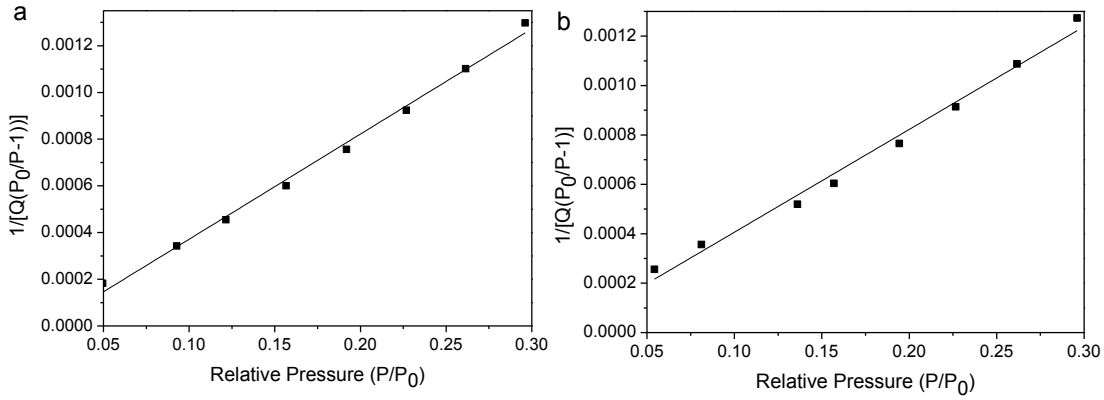

Fig. S7 BET surface area plots for (a) **COF-BTA-DAB** and (b) **COF-BTA-BZ** calculated from their N_2 absorption isotherms.

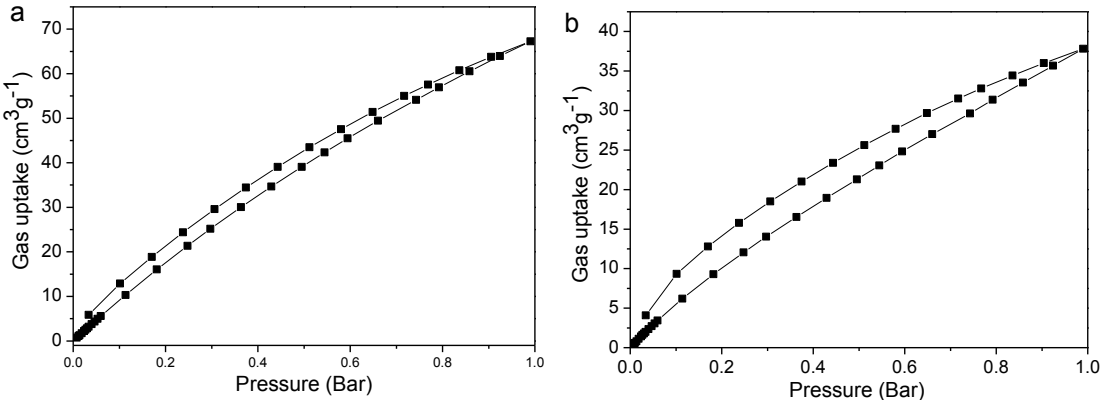

Fig. S8 CO_2 adsorption isotherms of (a) **COF-BTA-DAB** and (b) **COF-BTA-BZ** at 273 K.

Table S1 Elemental analyses of **COF-BTA-DAB** and **COF-BTA-BZ**.

		C (%)	H (%)	N (%)
COF-BTA-DAB	Theoretical	81.93	4.42	13.56
	Found	76.28	4.84	12.04
COF-BTA-BZ	Theoretical	85.38	4.66	9.96
	Found	83.13	4.91	9.36

Table S2 Fractional atomic coordinates for the unit cell of **COF-BTA-DAB** with DP-AA stacking.

COF-BTA-DAB: Space group symmetry P-6 a = b = 29.35 Å, c = 3.6 Å α = β = 90 °, γ = 120 °							
H	-0.04151	0.512671	1.256205	C	-0.04151	0.512671	1.256205
H	0.111754	0.565613	0.770059	C	0.111754	0.565613	0.770059
H	0.070961	0.677035	1.200789	C	0.070961	0.677035	1.200789
H	-0.05932	0.446029	0.958154	C	-0.05932	0.446029	0.958154
H	-0.00021	0.348606	1.37991	C	-0.00021	0.348606	1.37991
H	0.10284	0.495389	0.939042	C	0.10284	0.495389	0.939042
H	0.178802	0.656537	0.779549	C	0.178802	0.656537	0.779549
H	0.07926	0.36318	1.25967	C	0.07926	0.36318	1.25967
H	0.547225	0.601431	0.782336	C	0.547225	0.601431	0.782336
H	0.601139	0.489582	0.919905	C	0.601139	0.489582	0.919905
H	0.710774	0.654818	0.939225	C	0.710774	0.654818	0.939225
H	0.475403	0.541302	0.695166	C	0.475403	0.541302	0.695166
H	0.36789	0.38418	1.056414	C	0.36789	0.38418	1.056414
H	0.532297	0.440115	1.100912	C	0.532297	0.440115	1.100912
H	0.686386	0.718687	0.847918	C	0.686386	0.718687	0.847918
H	0.689949	0.515995	1.00627	C	0.689949	0.515995	1.00627
H	0.382157	0.512497	0.709907	C	0.382157	0.512497	0.709907
H	0.394816	0.325057	1.249115	C	0.394816	0.325057	1.249115
H	0.151043	0.352398	1.150251	C	0.151043	0.352398	1.150251
H	0.235023	0.354371	1.080598	C	0.235023	0.354371	1.080598
H	0.308897	0.51707	0.721469	C	0.308897	0.51707	0.721469
H	0.225107	0.514964	0.792603	C	0.225107	0.514964	0.792603
H	0.257848	0.724169	0.931447	C	0.257848	0.724169	0.931447
H	0.341883	0.806433	0.935039	C	0.341883	0.806433	0.935039
H	0.259461	0.894168	0.883825	C	0.259461	0.894168	0.883825
H	0.17552	0.812119	0.881166	C	0.17552	0.812119	0.881166
H	0.697061	0.796516	0.831344	C	0.697061	0.796516	0.831344
H	0.70084	0.881246	0.789404	C	0.70084	0.881246	0.789404
H	0.533799	0.801648	0.544606	C	0.533799	0.801648	0.544606
H	0.530105	0.716848	0.58825	C	0.530105	0.716848	0.58825
H	0.74663	0.50546	1.332019	C	0.74663	0.50546	1.332019
H	0.824395	0.498258	1.458561	C	0.824395	0.498258	1.458561
H	0.923566	0.665024	1.248106	C	0.923566	0.665024	1.248106
H	0.846079	0.672175	1.122195	C	0.846079	0.672175	1.122195
H	0.38755	0.253164	1.484129	C	0.38755	0.253164	1.484129
H	0.382084	0.167621	1.528187	C	0.382084	0.167621	1.528187
H	0.545912	0.238853	1.207761	C	0.545912	0.238853	1.207761

H	0.551335	0.324017	1.165069	C	0.551335	0.324017	1.165069
H	0.98685	0.652513	1.422099	C	0.98685	0.652513	1.422099
H	0.888898	0.337205	1.432777	C	0.888898	0.337205	1.432777
H	0.830082	0.307225	1.033804	C	0.830082	0.307225	1.033804
H	0.744652	0.243311	0.786162	C	0.744652	0.243311	0.786162
H	0.792494	0.125131	0.767623	C	0.792494	0.125131	0.767623
H	0.878266	0.188852	1.013081	C	0.878266	0.188852	1.013081
H	0.45329	-0.0536	0.851476	C	0.45329	-0.0536	0.851476
H	0.563939	0.106073	1.164159	C	0.563939	0.106073	1.164159
H	0.398324	0.046917	1.261746	C	0.398324	0.046917	1.261746
H	0.514226	-0.06731	0.969486	C	0.514226	-0.06731	0.969486
H	0.669318	-0.00445	0.519537	C	0.669318	-0.00445	0.519537
H	0.610528	0.099397	0.757253	C	0.610528	0.099397	0.757253
H	0.537026	0.164685	1.370345	C	0.537026	0.164685	1.370345
H	0.725146	0.084716	0.412855	C	0.725146	0.084716	0.412855
H	0.333946	0.957908	1.107009	C	0.333946	0.957908	1.107009
H	0.54364	0.873433	0.836539	C	0.54364	0.873433	0.836539
C	0.009633	0.596379	1.230358	C	0.009633	0.596379	1.230358
C	-0.00264	0.544505	1.167383	C	-0.00264	0.544505	1.167383
C	0.033505	0.5323	1.006653	C	0.033505	0.5323	1.006653
C	0.083672	0.57472	0.908192	C	0.083672	0.57472	0.908192
C	0.098045	0.626465	0.978875	C	0.098045	0.626465	0.978875
C	0.060217	0.636345	1.135315	C	0.060217	0.636345	1.135315
C	0.021795	0.478077	0.977326	C	0.021795	0.478077	0.977326
C	-0.02818	0.435493	1.013734	C	-0.02818	0.435493	1.013734
C	-0.05095	0.38613	1.168418	C	-0.05095	0.38613	1.168418
C	-0.00382	0.382446	1.232982	N	-0.00382	0.382446	1.232982
C	0.048931	0.416512	1.135634	N	0.048931	0.416512	1.135634
C	0.062194	0.465315	0.998414	N	0.062194	0.465315	0.998414
C	0.149903	0.667757	0.880253	N	0.149903	0.667757	0.880253
C	0.089143	0.401897	1.151149	N	0.089143	0.401897	1.151149
C	0.210122	0.761765	0.903886	N	0.210122	0.761765	0.903886
C	0.181783	0.433923	0.981663	N	0.181783	0.433923	0.981663
C	0.630556	0.634102	0.843693	N	0.630556	0.634102	0.843693
C	0.579096	0.592386	0.815692	N	0.579096	0.592386	0.815692
C	0.56604	0.539243	0.853007	N	0.56604	0.539243	0.853007
C	0.608572	0.530133	0.899147	N	0.608572	0.530133	0.899147
C	0.660036	0.570336	0.943382	N	0.660036	0.570336	0.943382

Table S3 Fractional atomic coordinates for the unit cell of **COF-BTA-BZ** with DP-AA stacking.

COF-BTA-BZ: Space group symmetry P-6 a = b = 37.88 Å, c = 3.6 Å α = β = 90 °, γ = 120 °							
H	0.384515	0.9724	1.348593	C	0.234756	0.497838	0.744588
H	0.52895	0.892588	0.94794	C	0.200892	0.502168	0.731407
H	0.526818	0.442393	1.072938	C	0.162364	0.47008	0.834009
H	0.482419	0.521299	1.446951	C	0.158967	0.433069	0.950678
H	0.398876	0.398948	1.100886	C	0.192306	0.427973	0.963761
H	0.580959	0.485701	1.328212	C	0.946629	0.388448	1.159979
H	0.657439	0.608051	0.943334	C	0.983672	0.593972	1.079555
H	0.530749	0.564153	1.125142	C	0.91205	0.565303	0.932113
H	0.419752	0.351987	0.937281	C	0.903181	0.316998	1.036775
H	0.412094	0.500472	1.434416	C	0.866927	0.317276	0.960618
H	0.650768	0.507603	1.206659	C	0.83029	0.281625	0.934728
H	0.633776	0.653391	0.838281	C	0.827855	0.243185	0.98985
H	0.365779	0.514598	1.241256	C	0.865191	0.24335	1.05282
H	0.307052	0.521675	1.087047	C	0.901465	0.279355	1.077564
H	0.237967	0.392127	0.811823	C	0.789379	0.206179	1.015096
H	0.297348	0.385935	0.974626	C	0.754019	0.20602	1.155599
H	0.264562	0.52372	0.666638	C	0.718325	0.170027	1.210497
H	0.204198	0.531379	0.640724	C	0.715151	0.132375	1.127159
H	0.129492	0.407764	1.043914	C	0.749535	0.132071	0.984376
H	0.18866	0.399266	1.073937	C	0.785567	0.167697	0.927947
H	0.922077	0.394025	1.250237	C	0.909536	0.600956	0.964701
H	0.991886	0.626222	1.070041	C	0.873908	0.600714	0.888302
H	0.867588	0.34631	0.918079	C	0.837968	0.563951	0.781378
H	0.802484	0.283006	0.878658	C	0.8414	0.528379	0.739552
H	0.864907	0.214599	1.103322	C	0.877335	0.529313	0.816764
H	0.929526	0.278517	1.134966	C	0.799121	0.561894	0.769026
H	0.755638	0.234744	1.237056	C	0.796062	0.597182	0.693523
H	0.691787	0.170803	1.324101	C	0.76063	0.597541	0.764282
H	0.74799	0.103204	0.911116	C	0.725919	0.562936	0.902005
H	0.811731	0.166287	0.813662	C	0.727836	0.527227	0.959728
H	0.935947	0.629576	1.058419	C	0.76296	0.526199	0.890279
H	0.872535	0.628632	0.937608	C	0.610535	0.71003	0.707213
H	0.814696	0.499356	0.657473	C	0.612187	0.74662	0.646099
H	0.878866	0.501223	0.788109	C	0.578042	0.75162	0.723651
H	0.822895	0.625262	0.595191	C	0.541408	0.71617	0.841163
H	0.759608	0.625606	0.712141	C	0.540469	0.679897	0.901078

H	0.701349	0.499513	1.067032	C	0.581658	0.791211	0.728737
H	0.76394	0.498497	0.961887	C	0.61912	0.826723	0.828518
H	0.638014	0.708151	0.650267	C	0.620898	0.863417	0.885101
H	0.640981	0.772719	0.549742	C	0.586434	0.867736	0.841904
H	0.514432	0.718431	0.913957	C	0.549658	0.833342	0.732563
H	0.512278	0.653737	1.006301	C	0.547174	0.796311	0.674525
H	0.646397	0.824382	0.884495	C	0.059398	0.45294	0.956794
H	0.649936	0.889795	0.972205	C	0.065804	0.490851	1.063201
H	0.522189	0.83568	0.691572	C	0.034162	0.496532	1.208293
H	0.517748	0.770027	0.59417	C	-0.0048	0.461333	1.243941
H	0.095975	0.517689	1.020099	C	-0.01262	0.423113	1.130927
H	-0.02969	0.46484	1.359046	C	0.020034	0.419791	0.990665
H	0.01465	0.389835	0.900317	C	0.040487	0.536865	1.269318
H	0.10538	0.565021	1.366784	C	0.080056	0.570667	1.316123
H	0.061856	0.647861	1.146585	C	0.088541	0.610345	1.259103
H	-0.0223	0.519748	1.16311	C	0.055776	0.616645	1.189792
H	0.082767	0.415151	0.733923	C	0.015607	0.584849	1.163035
H	0.153628	0.636158	1.365987	C	0.008529	0.545424	1.208477
H	0.475673	-0.04249	1.44932	C	0.091363	0.446496	0.813652
H	0.561755	0.081881	1.151076	C	0.130365	0.643113	1.265039
H	0.433983	0.040684	1.188788	C	0.450126	-0.00454	1.321152
H	0.511842	-0.05676	1.132229	C	0.482305	-0.01167	1.375496
H	0.63801	-0.01917	0.990585	C	0.523157	0.018255	1.304513
H	0.604302	0.067691	1.34711	C	0.530571	0.058022	1.21816
H	0.54023	0.131215	1.048006	C	0.499271	0.066758	1.174875
H	0.691167	0.049722	1.085111	C	0.459387	0.034957	1.230902
H	0.54406	0.188639	0.906566	C	0.554049	0.006926	1.255791
H	0.543044	0.249733	0.728417	C	0.544086	-0.03327	1.153452
H	0.41121	0.177555	0.577571	C	0.573516	-0.04347	1.063893
H	0.413298	0.11698	0.768488	C	0.614244	-0.01213	1.070179
H	0.537097	0.295162	0.410042	C	0.626186	0.028065	1.163601
H	0.539232	0.35933	0.544953	C	0.595885	0.036562	1.265521
H	0.416059	0.293182	0.971649	C	0.508067	0.107093	1.062918
H	0.413177	0.229244	0.848362	C	0.668742	0.059213	1.149807
H	0.32459	0.918361	1.291119	C	0.478666	0.148104	0.854662
H	0.261691	0.857127	1.123964	C	0.514783	0.185958	0.830262
H	0.330812	0.79581	0.882374	C	0.51437	0.220436	0.718467
H	0.393301	0.857632	1.060338	C	0.47693	0.219286	0.634531
H	0.216769	0.809493	0.750453	C	0.440887	0.180348	0.641235
H	0.151132	0.747616	0.845574	C	0.441955	0.146248	0.754582
H	0.212937	0.684633	1.241555	C	0.474963	0.256235	0.616449
H	0.27807	0.745369	1.157708	C	0.509816	0.294305	0.525486

C	0.408045	0.963486	1.342812	C	0.511296	0.330496	0.606988
C	0.561713	0.914997	0.963149	C	0.47801	0.331361	0.768602
C	0.363577	0.892291	1.192047	C	0.442538	0.29395	0.839517
C	0.461782	0.415327	1.087941	C	0.440458	0.257482	0.760211
C	0.50129	0.446883	1.14809	C	0.326112	0.891527	1.199248
C	0.510065	0.486108	1.270794	C	0.290647	0.857267	1.09549
C	0.476432	0.491297	1.351107	C	0.290712	0.821057	0.983974
C	0.436678	0.461124	1.280787	C	0.329115	0.822773	0.96797
C	0.430181	0.423303	1.156511	C	0.364167	0.857326	1.073258
C	0.550639	0.520605	1.244435	C	0.253297	0.783096	0.947062
C	0.5852	0.515584	1.249982	C	0.216204	0.781853	0.852168
C	0.623282	0.545974	1.134179	C	0.179272	0.747274	0.912275
C	0.627466	0.58358	1.034573	C	0.176905	0.711776	1.057733
C	0.595087	0.591268	1.036026	C	0.213366	0.711795	1.129914
C	0.557172	0.559715	1.143816	C	0.250569	0.74597	1.0708
C	0.452169	0.375507	0.951867	N	0.400472	0.926596	1.290473
C	0.404095	0.470066	1.329839	N	0.590062	0.905807	0.913515
C	0.656644	0.537762	1.114858	N	0.481566	0.368896	0.865416
C	0.602402	0.630921	0.918498	N	0.368517	0.443911	1.203911
C	0.574898	0.675882	0.840912	N	0.690925	0.56538	0.97563
C	0.335508	0.449432	1.124694	N	0.572686	0.638575	0.922191
C	0.337655	0.487516	1.148704	N	0.940755	0.352919	1.066828
C	0.304868	0.491796	1.054941	N	0.947397	0.56396	1.015892
C	0.267417	0.457491	0.935155	N	0.128717	0.475904	0.835779
C	0.265948	0.419199	0.908149	N	0.138547	0.677822	1.124697
C	0.299157	0.415699	1.001398	N	0.4779	0.11259	0.977525
C	0.231879	0.46074	0.869989	N	0.6778	0.096812	1.184554