Electronic Supplementary Information

Two-dimensional dual-pore covalent organic frameworks from the combination of two D_{2h} symmetrical building blocks

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Contents

Section A. 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 9k Hz and the contact time is 3ms.

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.

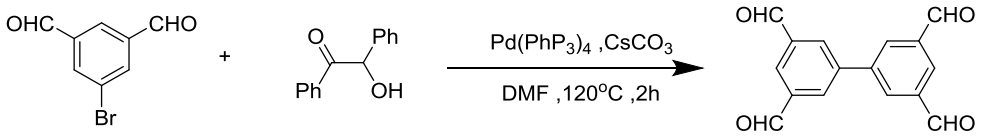
Gas adsorption-desorption isotherm measurement

The measurements were carried out using a Quadrasorb SI MP. Before gas adsorption measurements, the as-prepared sample (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 140 ^oC for 8 h. The resulting sample was then used for gas adsorption measurements from 0 to 1 atm at 77 K (for N_2 and H_2) or 273 K (for CO_2). The Brunauer-Emmett-Teller (BET) method was utilized to calculate the specific areas. By using the non-local density function theory model, the pore volume was derived from the sorption curve.

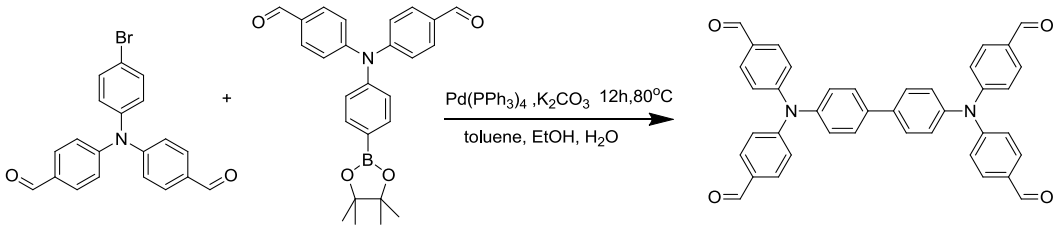
Structural simulation and power X-ray diffraction analysis

The Pawley refinements were performed by the Reflux module in the Material 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 Reflex module. P1 space group was used for the simulations.

Section B. Synthesis



[1,1'-biphenyl]-3,3',5,5'-tetracarbaldehyde (BTA). A mixture of 5-bromoisophthalaldehyde (1.278 g, 6 mmol), benzoin (763.2 mg, 3.6 mmol), $Pd(PhP_3)_4$ (346 mg, 0.3 mmol), and $CsCO_3$ (2.152 g, 6.6mmol) was dissolved in DMF (30 mL) under argon atmosphere. The mixture was heated at 120 ^oC for 2h, immediately filtered before it cooled. The filtrate was conducted centrifugal separation which gave a crude product. The crude product was then purified through centrifugal separation with CH_2Cl_2 (3×10 mL) to provide target compound as a white solid (275 mg, 35%). ^1H NMR (500 MHz, DMSO-d_6) δ 10.24 (s, 4H), 8.71 (s, 4H), 8.49 (s, 2H).^{13}C NMR (100 MHz, DMSO-d_6) δ 192.55, 139.51, 137.61, 133.18, 129.18. MS (EI)：*m/z* 266 $[M]^+$. HRMS (EI): *m/z* calcd for $C_{16}H_{10}O_4$: 266.0573, found: 266.0579 $[M]^+$.



4,4',4'',4'''-([1,1'-biphenyl]-4,4'-diylbis(azanetriyl))tetrabenzaldehyde(BDTB).
A mixture of 4,4'-((4-Bromo phenyl) azanediyl)dibenzaldehyde(758 mg, 2 mmol), 4,4'-((4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)azanediyl)dibenzaldehyd e (1.025 g, 2.4 mmol), K_2CO_3 (828 mg, 6 mmol) and $Pd(PhP_3)_4$ (116 mg, 0.1 mmol) was dissolved in a mixed solvent of toluene/ethyl alcohol/water (30/10/4 mL) under argon atmosphere. The mixture was heated at 80 ^oC for 12 h. After being cooled to room temperature, water (50 mL) was added. The mixture was extracted with CH_2Cl_2 (3 × 50 mL). The combined organic layer was washed with water and brine, and then dried over Na_2SO_4, and the solvent was evaporated. The crude product was purified

through column chromatography (DCM/PE = 3:1 and then DCM) to yield a yellow solid (653.6 mg, 54.5 %). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.90 (s, 4H), 7.87 (d, J = 8.6 Hz, 8H), 7.78 (d, J = 8.6 Hz, 4H), 7.28 (d, J = 8.6 Hz, 4H), 7.23 (d, J = 8.6 Hz, 8H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 191.69, 151.75, 144.98, 137.09, 131.82, 131.64, 128.77, 127.52, 123.26. MS (MALDI)： m/z 600.2 $[M]^+$. HRMS (MALDI): m/z calcd for $C_{40}H_{28}O_4N_2$: 600.2044, found: 600.2041 $[M]^+$.

SIOC-COF-5. BTA (26.6 mg, 0.1 mmol) and ETTA (39.2 mg, 0.1 mmol) were dissolved in a mixture of mesitylene /dimethylacetamide/ 6 M AcOH (15:5:2 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 7 days 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 **SIOC-COF-5** as a yellow powder (50.6 mg, 86.3%).

SIOC-COF-6. BDTB (36 mg, 0.06 mmol) and ETTA (23.52 mg 0.06 mmol) were dissolved in a mixture of mesitylene/dimethylacetamide/ 6 M AcOH (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 7 days 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 **SIOC-COF-6** as a yellow powder (43.6 mg, 79%).

Section C. FT-IR Spectra

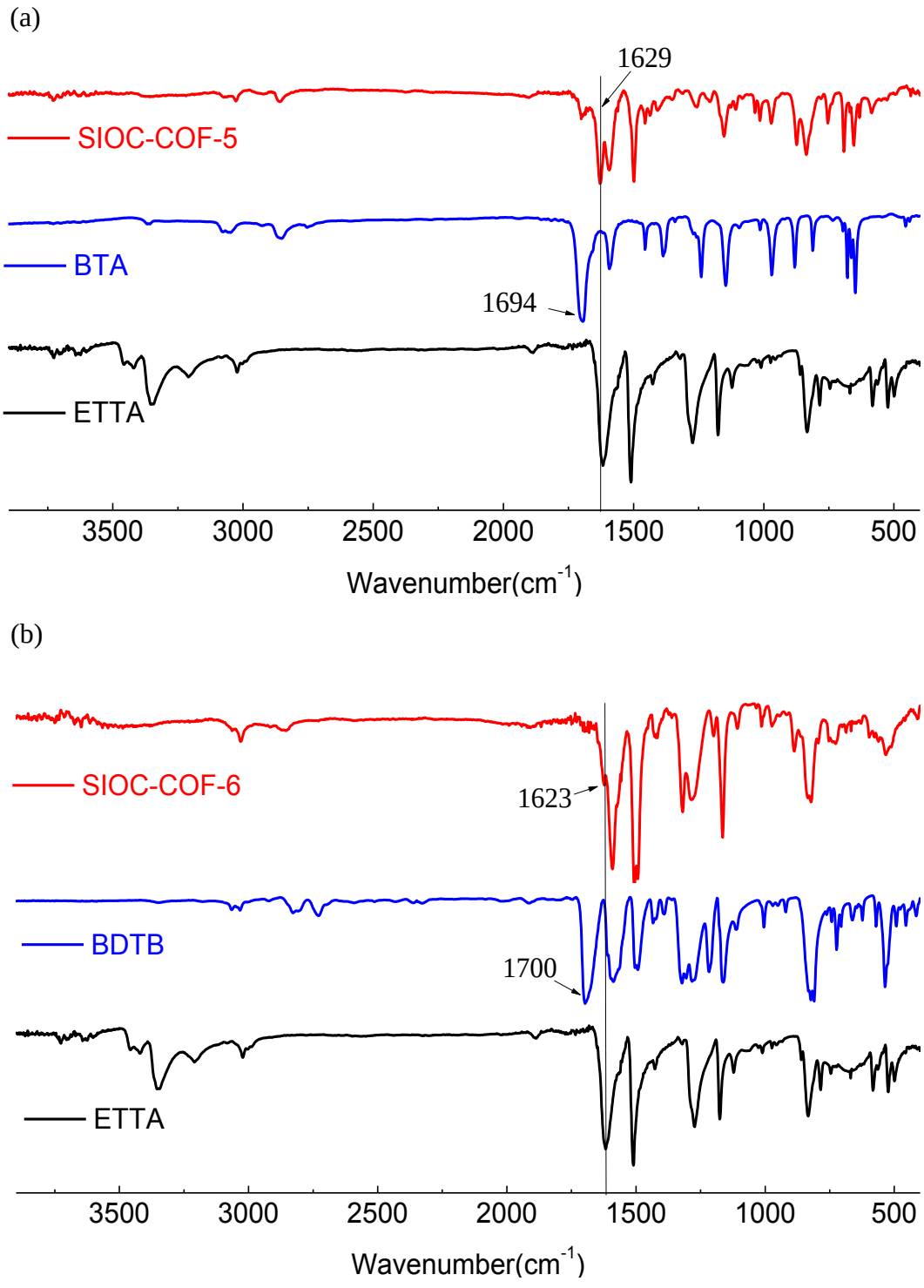


Figure S1. FT-IR spectra of (a) **SIOC-COF-5** and (b) **SIOC-COF-6**.

Section D. Solid-state ^{13}C CP/MAS NMR Spectra

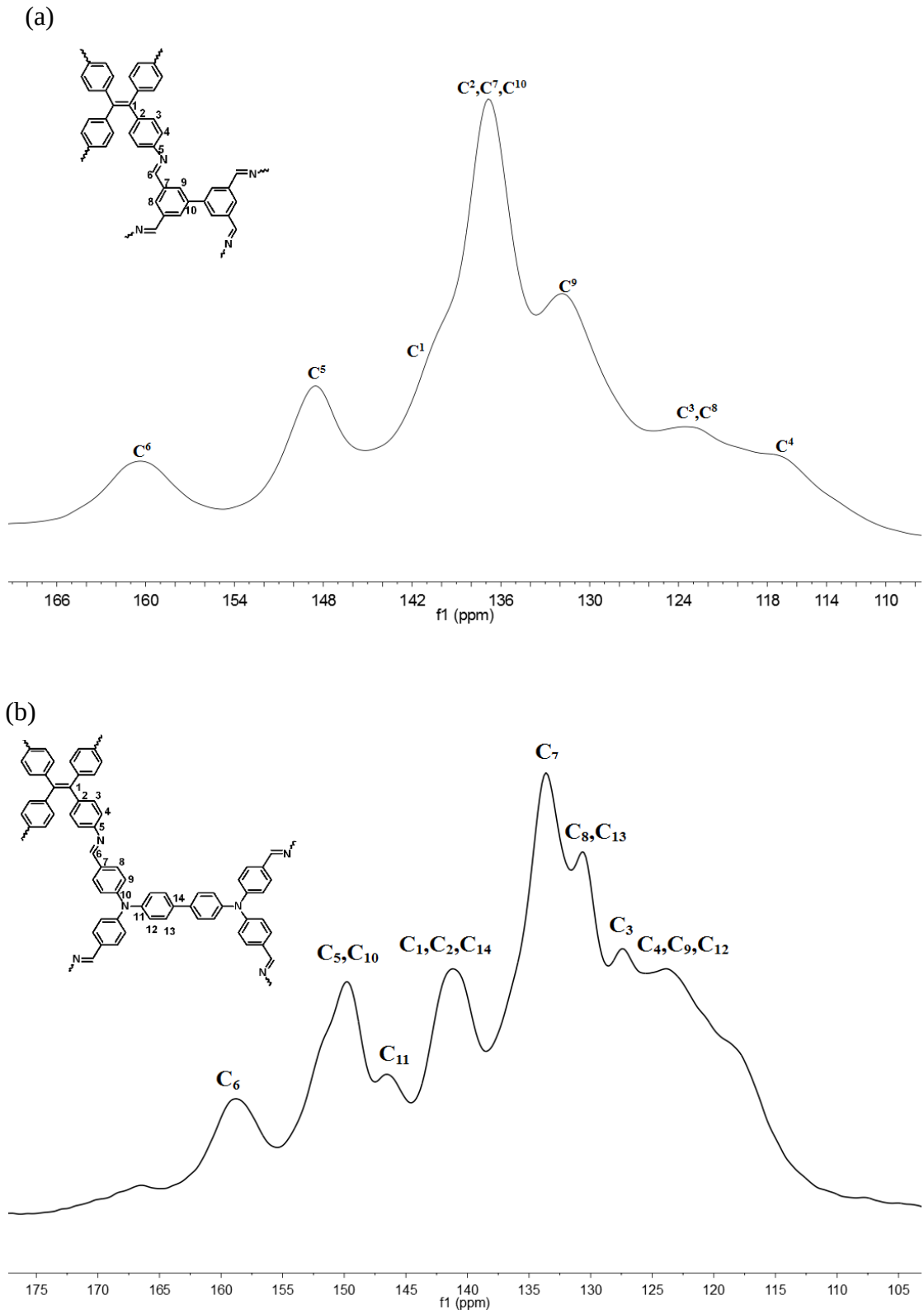
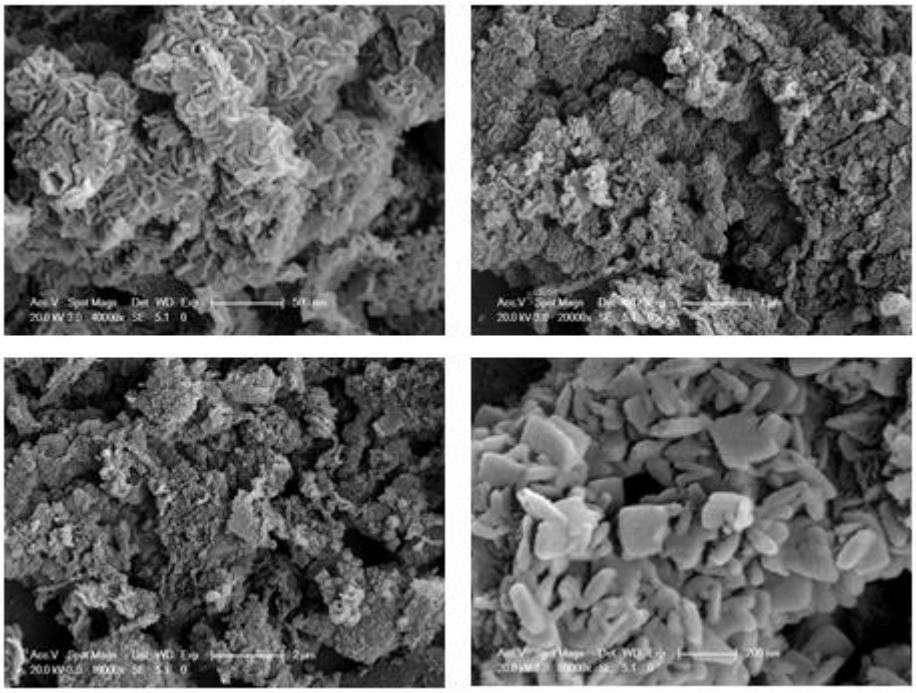


Figure S2. Solid-state ^{13}C CP/MAS NMR Spectra of (a) **SIOC-COF-5** and (b) **SIOC-COF-6**.

Section E. Field-emission Scanning Electron Microscopy

(a)



(b)

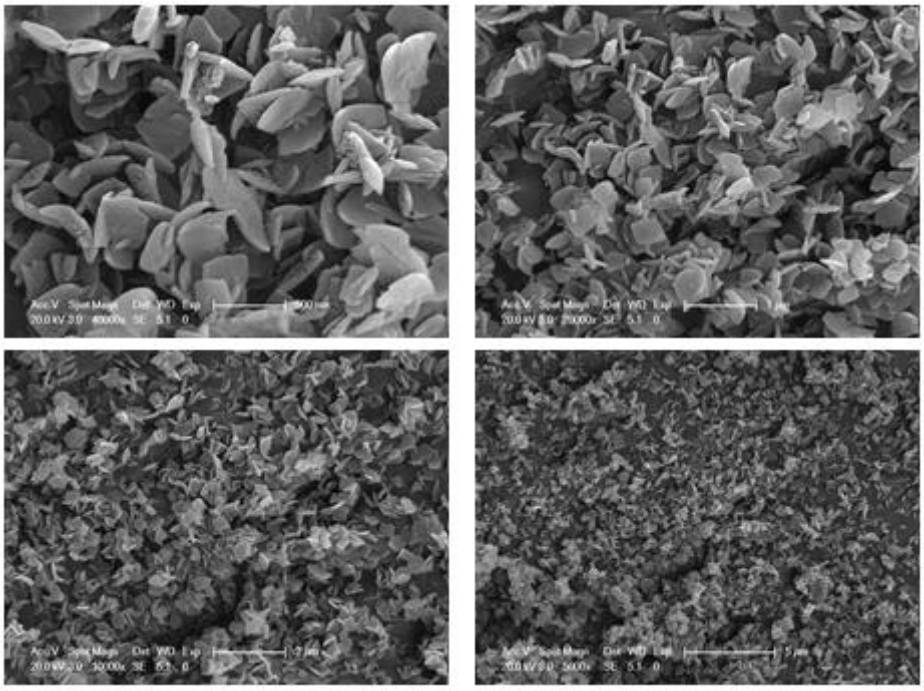


Figure S3. Field-emission SEM image of (a) **SIOC-COF-5** and (b) **SIOC-COF-6**.

Section F. Simulations of Staggered SIOC-COF-5 Structure

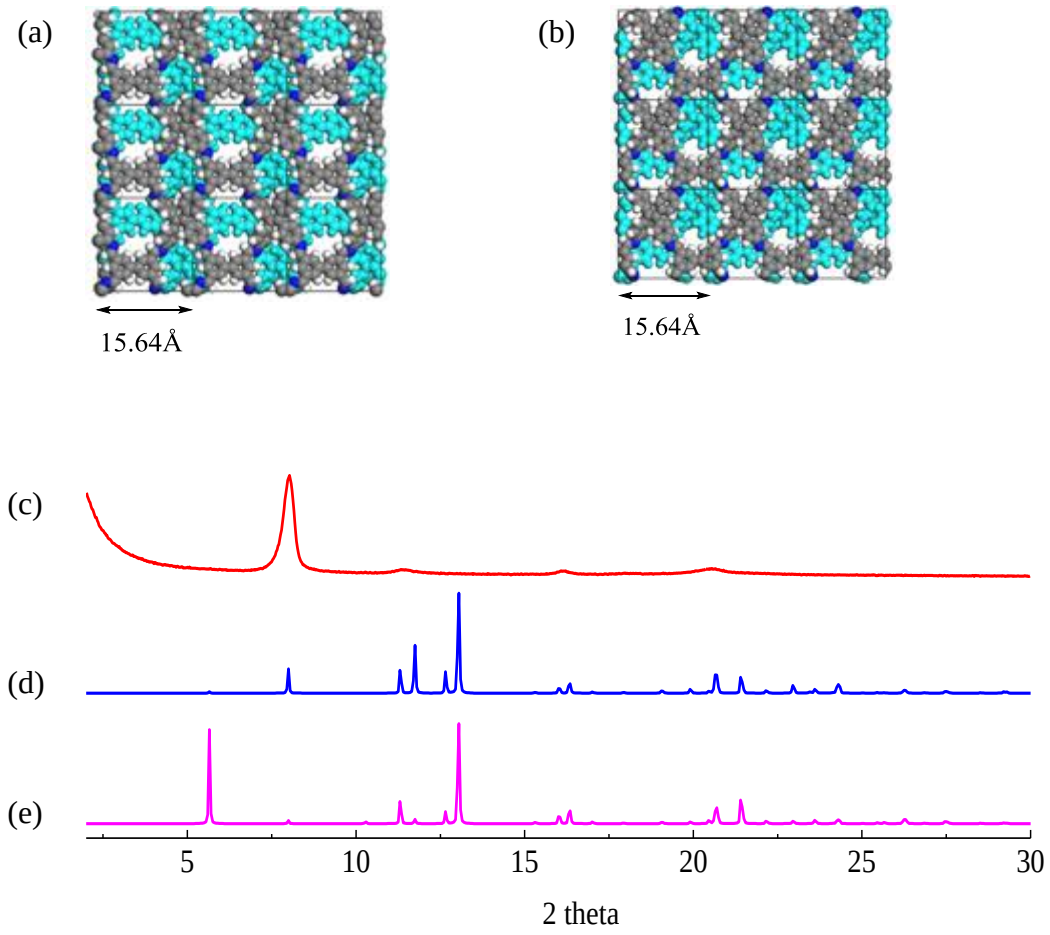


Figure S4 The simulated structures of **SIOC-COF-5** with (a) AB-1 stacking and (b) AB-2 stacking. And (c) experimental PXRD pattern and simulated PXRD patterns for (d) AB-1 stacking and (e) AB-2 stacking models of **SIOC-COF-5**.

Section G. Simulations of Staggered SIOC-COF-6 Structure

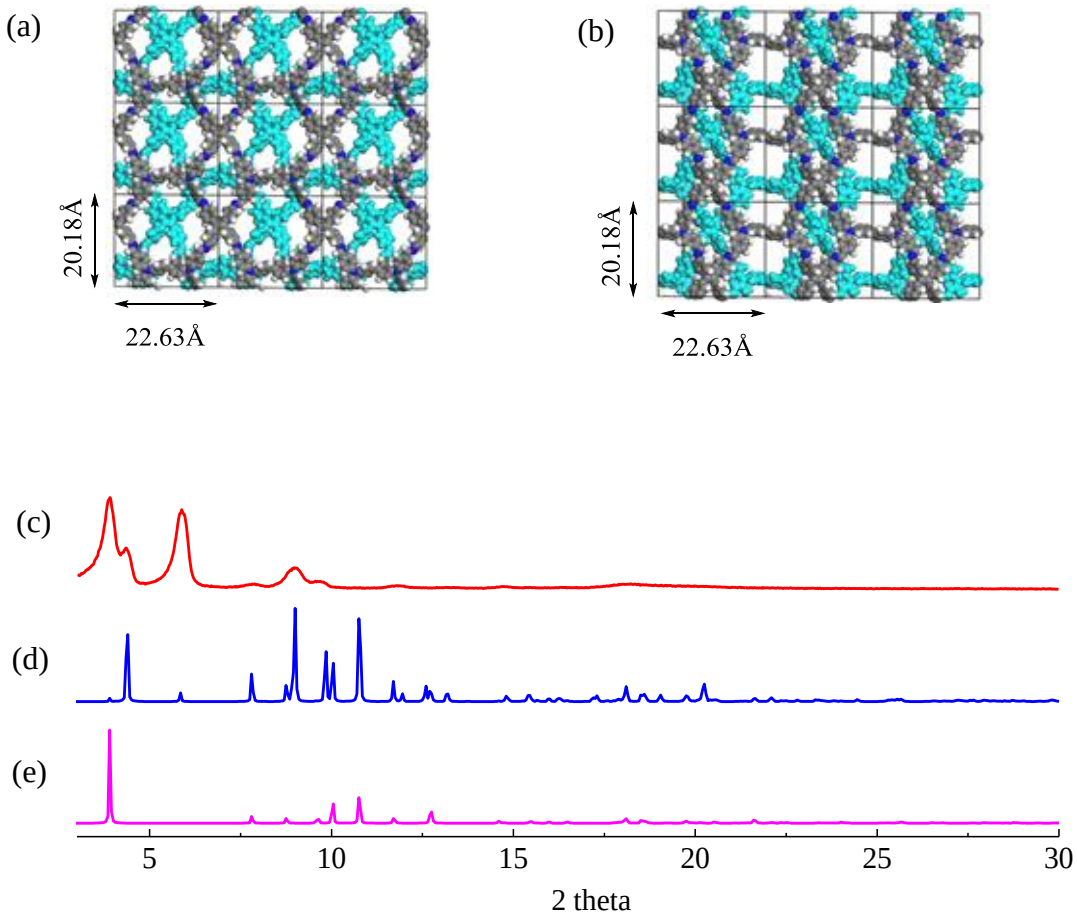


Figure S5 The simulated structures of **SIOC-COF-6** with (a) AB-1 stacking and (b) AB-2 stacking. And (c) experimental PXRD pattern and simulated PXRD patterns for (d) AB-1 stacking and (e) AB-2 stacking models of **SIOC-COF-6**.

Section H. BET Surface Area Plots

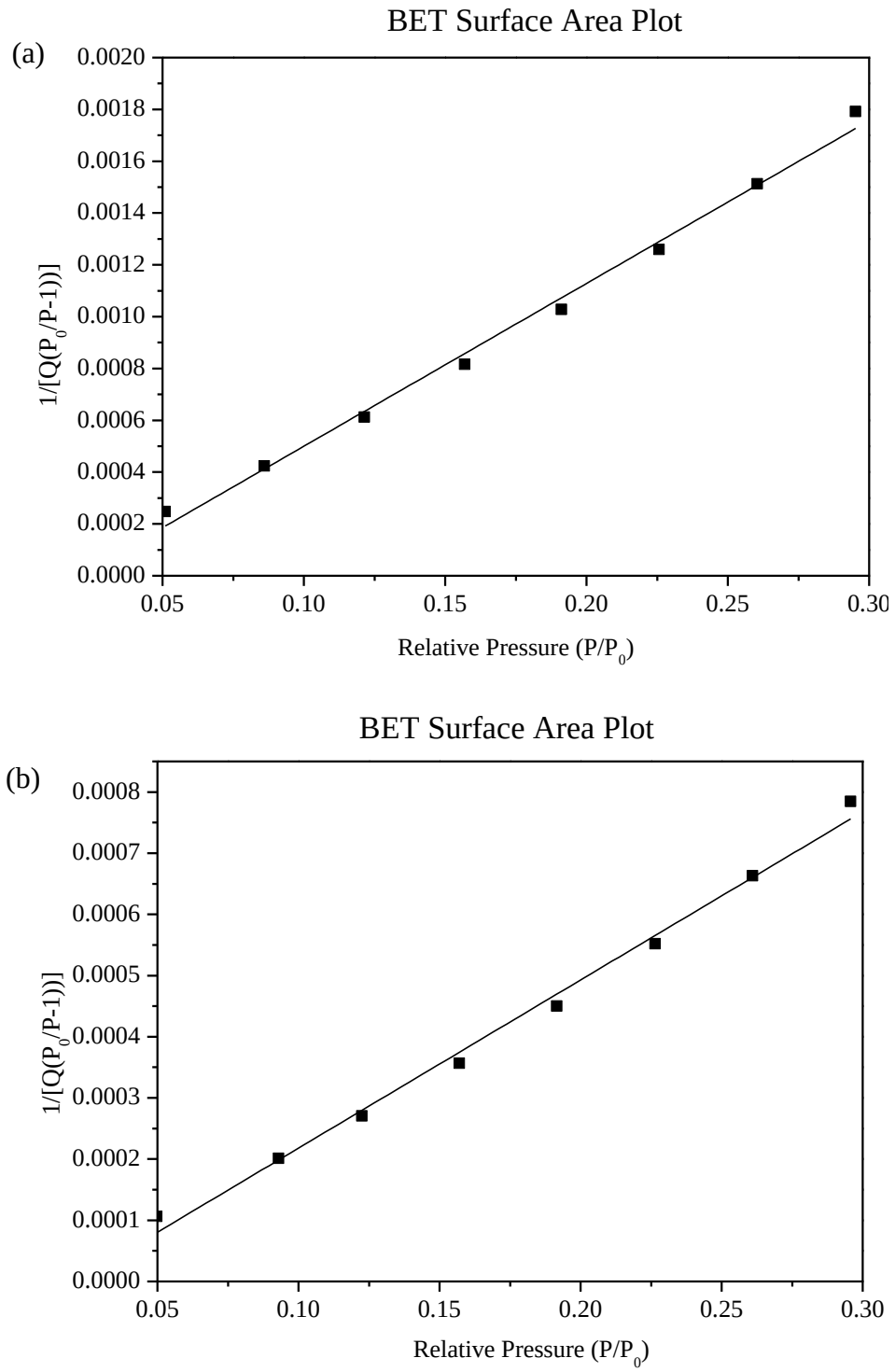


Figure S6. BET surface area plots for (a) **SIOC-COF-5** and (b) **SIOC-COF-6** calculated from their N_2 absorption isotherms.

Section I. Supporting Tables

Table S1 Elemental analysis of **SIOC-COF-5** and **SIOC-COF-6**

		C (%)	H (%)	N (%)
SIOC-COF-5	Theoretical	85.98	4.47	9.55
	Found	81.01	5.27	8.42
SIOC-COF-6	Theoretical	86.06	4.82	9.12
	Found	82.98	5.27	8.00

The low content of carbon might be attributed to unreacted peripheral aldehyde groups.

Table S2 Summary of H_2 and CO_2 uptake capacities of some COFs at low pressure reported in recent literature.

	BET surface area ($m^2\ g^{-1}$)	H_2 uptake (wt%, 1.0 bar, 77 K)	CO_2 uptake (wt%, 1.0 bar, 273 K)	Ref.
CTV-COF-1	1245	1.23	\	1
ACOF-1	1176	0.99	17.7	2
COF-5	1670	0.84	5.9	3
COF-103	3530	1.29	7.6	3
IL-COF-1	2723	1.3	6.0	4
TpPa-1	535	1.1	15.3	5
TpBD	537	0.7	8.5	6
HP-COF-1	1197	\	10.6	7
DhaTph	1305	1.53	12.8	8
COF-DhaTab	1480	1.07	15.3	9
TAPB-TFP	567	1.08	18	10
N-COF	1700	\	12	11
RT-COF-1	329	\	8.6	12
$[HO_2C]_{100\%}$-H_2P-COF	364	\	18	13
$[EtNH_2]_{50}$-H_2P-COF	1044	\	15.7	14

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Table S3 Fractional atomic coordinates for the unit cell of SIOC-COF-5 with AA stacking.

SIOC-COF-5: Space group symmetry P2/M a=b=15.64 Å c= 4.3 Å α = β = γ = 90 °			
Atom	x (Å)	y (Å)	z (Å)
H	0.275292	0.978337	1.311154
H	0.352396	1.113232	1.312615
H	0.178521	1.215572	0.622215
H	0.102353	1.07849	0.619038
H	0.073644	0.766571	1.147524
H	0.150999	0.638948	1.15416
H	0.373549	0.767586	0.78976
H	0.296553	0.901757	0.780306
H	0.072805	1.110964	1.223469
H	-0.02252	1.229012	1.271822
H	-0.21488	1.093754	0.743297
H	-0.12113	0.973485	0.691654
H	-0.11132	0.896315	1.254628
H	-0.19237	0.766147	1.16957
H	-0.01355	0.688074	0.452424
H	0.063911	0.826876	0.52702
H	0.625961	0.583367	1.086881
H	0.676645	0.315736	1.256916
H	0.86575	0.475327	0.829611
H	0.525022	0.570772	1.361302
H	0.309958	0.431251	1.014921
H	0.546466	0.301246	1.182727
H	0.395352	0.642372	1.347694
H	-0.27366	0.675654	0.899707
H	-0.09571	1.335695	0.929761
H	0.435888	1.216728	1.0742
C	0.03855	0.945251	0.95161
C	0.127462	0.938068	0.967428
C	-0.01529	0.867485	0.900054
C	0.176724	0.851255	0.971887
C	0.181791	1.018238	0.962263
C	-0.01513	1.027432	0.965342
C	0.254376	1.02892	1.150965
C	0.298349	1.106103	1.15144
C	0.271697	1.176009	0.96763
C	0.201329	1.163256	0.771476

C	0.15873	1.085845	0.765785
C	0.140048	0.773319	1.072246
C	0.1841	0.696866	1.073185
C	0.269014	0.691754	0.975875
C	0.307088	0.768359	0.872828
C	0.262474	0.845433	0.869577
C	0.009926	1.10294	1.118793
C	-0.04465	1.17234	1.143826
C	-0.12726	1.170777	1.015815
C	-0.15154	1.097151	0.853179
C	-0.09694	1.027999	0.826436
C	-0.08997	0.852157	1.072141
C	-0.13626	0.778083	1.021952
C	-0.10893	0.716841	0.803342
C	-0.03616	0.734772	0.624688
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C	0.412132	0.511209	1.185637
C	0.376536	0.432477	1.09527
C	0.422084	0.355064	1.113701
C	0.507524	0.359403	1.20132
C	0.371055	0.594727	1.180981
C	-0.22739	0.624084	0.854994
C	-0.16091	1.318013	1.002348
C	0.390235	1.269785	1.045805
N	-0.14944	0.637791	0.771413
N	0.310691	0.611774	0.984068
N	0.310538	1.257237	0.979847
N	-0.18432	1.239577	1.045358

Table S4 Fractional atomic coordinates for the unit cell of SIOC-COF-6 with AA stacking.

SIOC-COF-6: Space group symmetry P2/M a= 22.63 Å, b=20.18, Å c= 4.9 Å α = β = 90 °, γ = 90.5 °			
Atom	x (Å)	y (Å)	z (Å)
H	0.483582	0.602321	-0.5211
H	0.552694	0.512655	-0.59221
H	0.651588	0.574654	0.122952
H	0.580015	0.661938	0.206948
H	0.365827	0.655013	0.466202
H	0.316978	0.554899	0.621663
H	0.391821	0.446645	-0.0572
H	0.430352	0.546984	-0.24436
H	0.55996	0.723848	-0.4793
H	0.613024	0.827131	-0.53311
H	0.517425	0.909795	0.153787
H	0.465789	0.804719	0.219466
H	0.420736	0.794775	-0.34683
H	0.357444	0.889282	-0.29654
H	0.242306	0.777041	0.239165
H	0.302472	0.683067	0.19453
H	0.603071	0.942828	-0.65372
H	0.574252	0.415862	-0.28355
H	0.272827	0.456391	0.725687
H	0.338707	0.942329	0.245539
H	1.070848	0.2538	0.634645
H	0.976263	0.262365	0.417261
H	1.031917	0.119284	-0.19746
H	1.127005	0.114537	0.012994
H	0.899375	0.270984	0.225556
H	0.801724	0.270401	0.028396
H	0.852451	0.115633	-0.53574
H	0.950273	0.113515	-0.33735
H	1.115815	0.049343	0.411905
H	1.17017	-0.04663	0.25999
H	1.335059	0.056538	0.418236
H	1.281194	0.153485	0.562044
H	0.684874	0.163063	-0.7871
H	0.622079	0.063655	-0.81254
H	0.709454	-0.01536	-0.09627
H	0.77297	0.082607	-0.07518

H	0.800417	0.318296	-0.47806
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C	0.282037	0.78114	0.11074
C	0.319015	0.727325	0.089889
C	0.617997	0.961193	-0.45359
C	0.622155	0.425414	-0.29991
C	0.286318	0.420339	0.569484
C	0.291138	0.94333	0.197608
C	1.062497	0.22372	0.450634
C	1.008262	0.228572	0.323891
C	0.993192	0.190253	0.09039
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C	1.105817	0.180155	0.353443
C	0.935304	0.192397	-0.03524
C	0.890984	0.23644	0.056516
C	0.835242	0.236789	-0.05644
C	0.820039	0.193608	-0.27111
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C	0.72743	0.25158	-0.38053
C	1.194071	0.234087	0.521517
C	1.193769	0.112794	0.463601
C	1.164413	0.052589	0.406231
C	1.195643	-0.00263	0.323084
C	1.257505	-0.00197	0.308025
C	1.286543	0.054233	0.411148
C	1.255709	0.110284	0.489068
C	0.690523	0.123208	-0.63526
C	0.655225	0.066739	-0.64854
C	0.658882	0.016903	-0.45038
C	0.703446	0.023143	-0.25252
C	0.740057	0.07849	-0.24077
C	0.753087	0.314263	-0.42683
C	0.719623	0.371302	-0.4032
C	0.659353	0.368559	-0.3359
C	0.633675	0.305902	-0.30129
C	0.666629	0.248686	-0.31976
C	1.238054	0.25137	0.33146
C	1.268682	0.310677	0.353421
C	1.256159	0.356968	0.559072
C	1.212682	0.338913	0.750056
C	1.182228	0.278879	0.733686
N	0.264447	0.897796	0.056189
N	0.601363	0.935985	-0.22225
N	0.645639	0.483772	-0.27731
N	0.3236	0.433221	0.375818
N	1.162028	0.173753	0.484905
N	0.761911	0.192771	-0.38347

Section J. ^{1}H NMR and ^{13}C NMR Spectra of the Tetraldehydes

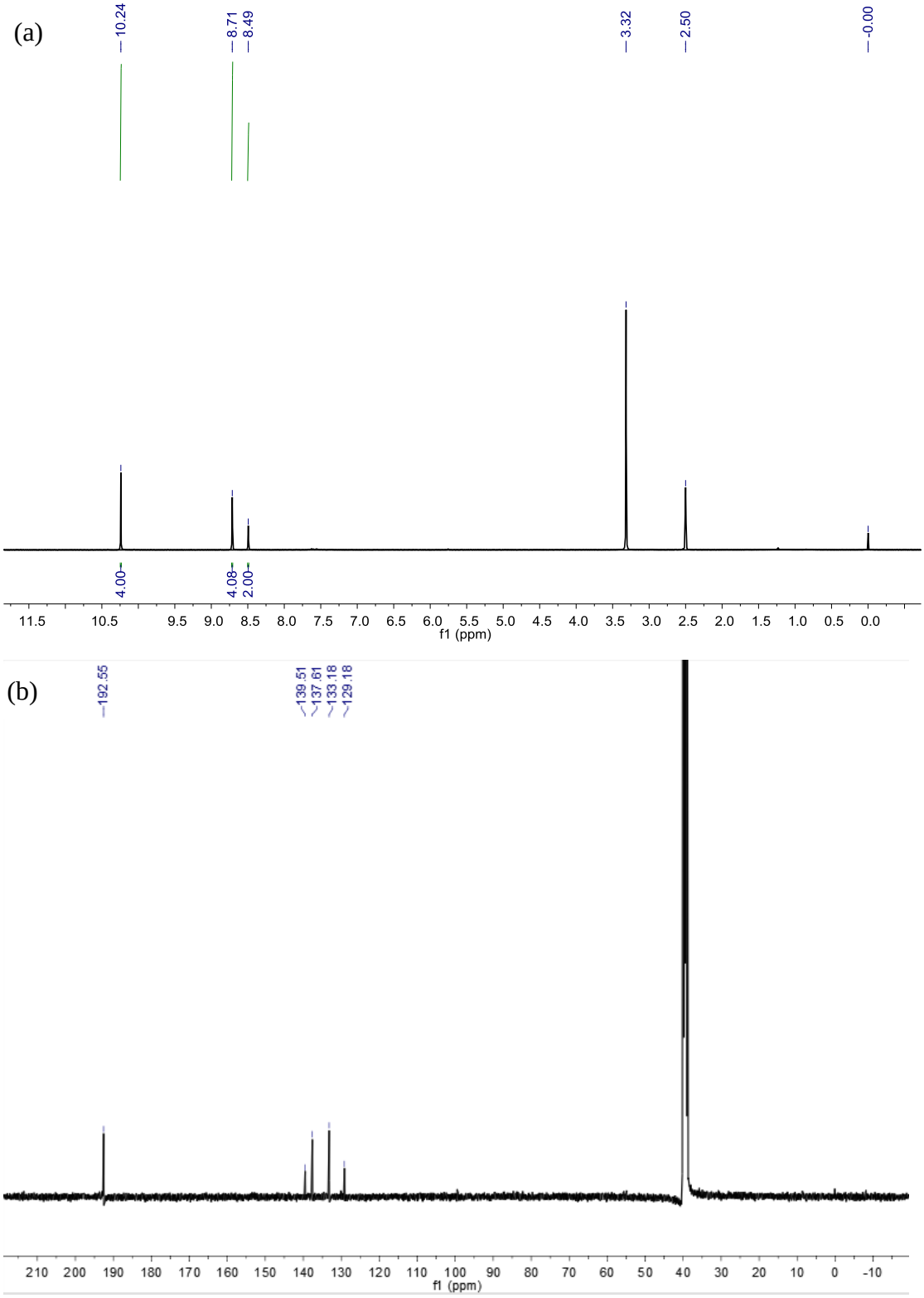

Figure S7. (a) ^{1}H NMR and (b) ^{13}C NMR spectra of BTA in DMSO-*d*6.

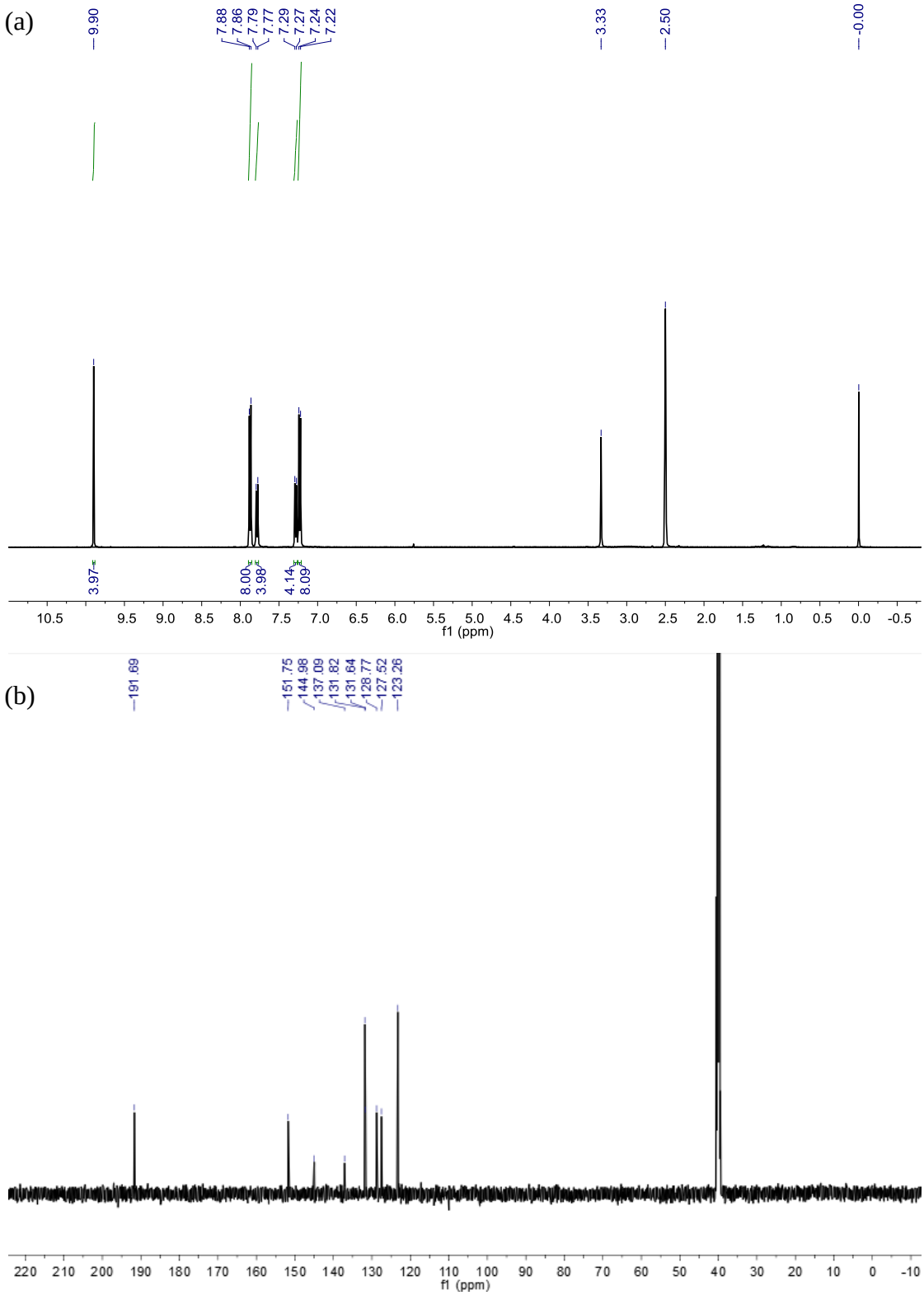

Figure S8. (a) ^{1}H NMR and (b) ^{13}C NMR spectra of BDTB in DMSO-*d*6.