

Supporting Information

Crown ether-based covalent organic frameworks for CO₂ fixation

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Section 1. Materials and Methods

All the chemicals and solvents were purchased commercially and used without further purification, unless otherwise noted. Liquid NMR spectra were recorded on a Bruker AVANCE III HD 400 MHz. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets. The solid ^{13}C NMR spectra were measured on JEOL JNM ECZ600R 600MHz. Powder X ray diffraction (PXRD) data were collected on Rigaku Smartlab using Cu $K\alpha$ radiation at 60 kV, 220 mA power. The Brunauer-Emmett-Teller (BET) surface areas were calculated by nitrogen adsorption and desorption at 77 K using ASAP2460 and the samples were activated under vacuum before analysis. Fourier transform infrared (FT-IR) spectra were obtained on Hitachi F-2500 spectrophotometer. A Scanning Electron Microscope (SEM) images were obtained with Hitachi S-4800. The conversion was analyzed by GC.

Section 2. Experimental Procedures

2.1 Synthetic Procedures

Synthesis of B_{18}C_6 :

4,4',4'',4'''-(6,7,9,10,17,18,20,21-octahydrodibenzo [b,k] [1,4,7,10,13,16] hexaoxacyclooctadecine-2,3,13,14-tetrayl) tetrabenzaldehyde (B_{18}C_6) was synthesized by using the Suzuki-Miyaura coupling reaction^[1]. Bis(3,4-dibromobenzene)-18-crown-6 (0.2 mmol), $\text{Pd}(\text{PPh}_3)_4$ (0.01 mmol) and Cs_2CO_3 (1.0 mmol) were dispersed in THF (5.0 mL), and stirred for 10 min. 4-Methoxycarbonylphenyl boronic acid (1.6 mmol) dissolved in methanol (3.0 mL), was added to the solution, and heated at 90°C for 48 h. After being cooled to room temperature, the reaction solution was washed by saturated brine and extracted through methylene

chloride. The organic phase was dried over anhydrous Na_2SO_4 and then concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (DCM: MeOH=15:1). The yield of B_{18}C_6 was about 91%. ^1H NMR (400 MHz, DMSO- d_6) δ 9.95 (s, 4H), 7.77 (d, $J = 8.2$ Hz, 8H), 7.34 (d, $J = 8.1$ Hz, 8H), 7.08 (s, 4H), 4.24 (s, 8H), 3.89 (s, 8H).

Synthesis of ETТА-B₁₈C₆-COF:

A pyrex tube (10 mL) is charged with ETТА (39.3 mg), B_{18}C_6 (77.6 mg), 1.8 mL *o*-DCB, 3.6 mL n-butanol, 0.9 mL of 6 M aqueous acetic acid. The mixture was sonicated for 30 minutes. The tube was then flash frozen at 77K and degassed by three freeze-pump-thaw cycles. The tube was sealed off and then heated at 120°C for 3 days. The resulting yellow solid was isolated by centrifugation and washed with N,N-dimethylacetamide(3×10mL), acetone(3×10mL). The powder was dried at 100 °C under vacuum overnight to afford ETТА-B₁₈C₆-COF as yellow powder in about 91% yield.

2.2 Chemical Stability Tests

Each COF sample (20mg) was immersed in 2 mL medium (DCM, THF, MeOH, 3.0 M NaOH and 1.0 M HCl) for 7 days. All the samples were isolated by centrifugation and washed with H₂O (3×10mL), then activated at 100 °C under vacuum for 12 h.

2.3 Catalytic procedures

The cycloaddition reactions were carried out in a Schlenk tube (10 mL) with a magnetic stirrer. In a typical procedure, the epoxide (1 mmol), COF (0.01 mmol) and TBAB (0.05 mmol) were added into a reaction tube. After sealing and purging with CO₂ using a balloon, the reaction tube was placed in a preheated oil bath and stirred for 24 h. After the cycloaddition reaction, the catalyst was separated from the system by filtration, and reaction mixture was analyzed by GC to

calculate the conversion of substrate.

Section 3. Solution ^1H NMR Spectra

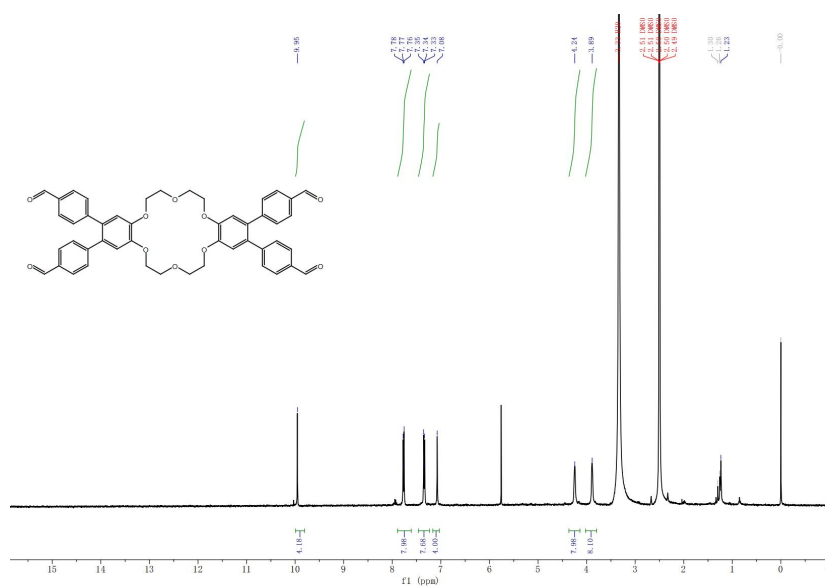


Figure S1. ^1H NMR spectra of monomer B₁₈C₆ in DMSO.

Section 4. Chemical Stability Tests

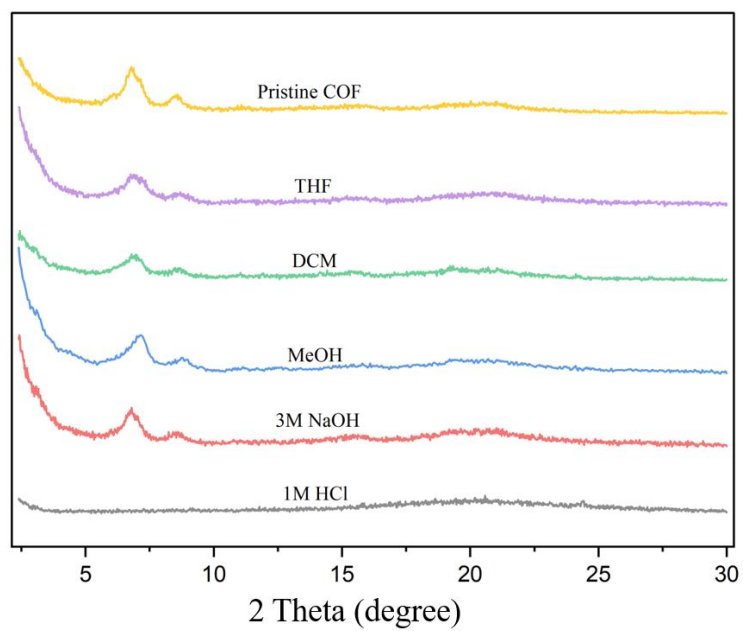


Figure S2. PXRD profiles of ETTA-B₁₈C₆-COF (yellow) after treatment for 7 days in THF (purple), DCM (green), MeOH (blue), 3M NaOH (red) and 1M HCl (gray)

Section 5. BET Tests

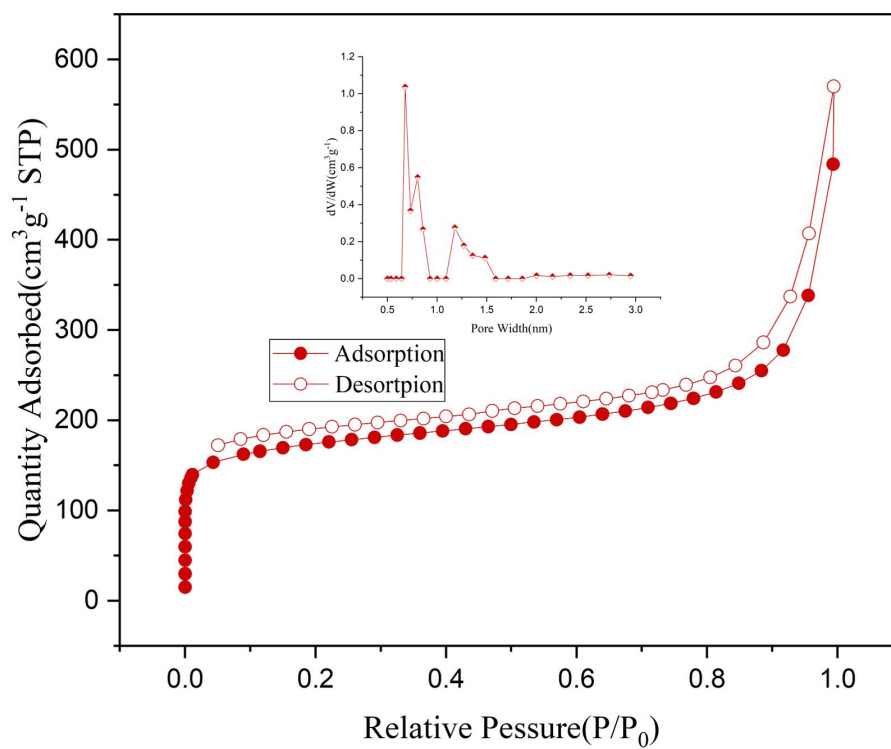


Figure S3. Nitrogen adsorption and desorption isotherms at 77 K and pore size distribution profiles for ET TA-B₁₈C₆COF

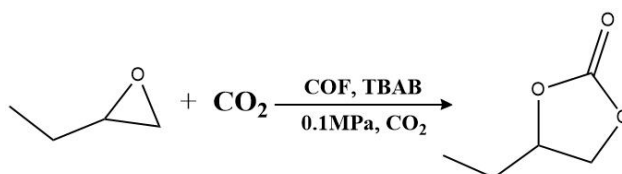
Section 6. EDS Tests



Figure S4. EDS mapping images of ET TA-B₁₈C₆COF

Section 7. Catalytic Results

Table S1. Catalytic cycloaddition of CO₂ with 1,2-epoxybutane using ETТА-B₁₈C₆-COF^a.



Entry	Co-catalyst	Catalyst	Time [h]	Temperature [°C]	Conversion ^b [%]	Selectivity ^b [%]
1	TBAB	-	24	40	38	>99
2	-	ETТА-B ₁₈ C ₆ -COF	24	40	-	-
3	TBAB	B ₁₈ C ₆	24	40	77	>99
4	TBAB	ETТА	24	40	66	>99
5	TBAB	ETТА-B ₁₈ C ₆ -COF	24	40	90	>99
6	TBAB	ETТА-B ₁₈ C ₆ -COF	6	40	9	>99
7	TBAB	ETТА-B ₁₈ C ₆ -COF	12	40	29	>99
8	TBAB	ETТА-B ₁₈ C ₆ -COF	18	40	61	>99
9	TBAB	ETТА-B ₁₈ C ₆ -COF	30	40	92	>99
10	TBAB	ETТА-B ₁₈ C ₆ -COF	24	30	64	>99
11	TBAB	ETТА-B ₁₈ C ₆ -COF	24	50	91	>99

^aReaction conditions: 1,2-epoxybutane (1 mmol), TBAB (0.05 mmol), ETТА-B₁₈C₆-COF (0.01 mmol), CO₂ (0.1 MPa), solvent free; ^bDetermined by GC.

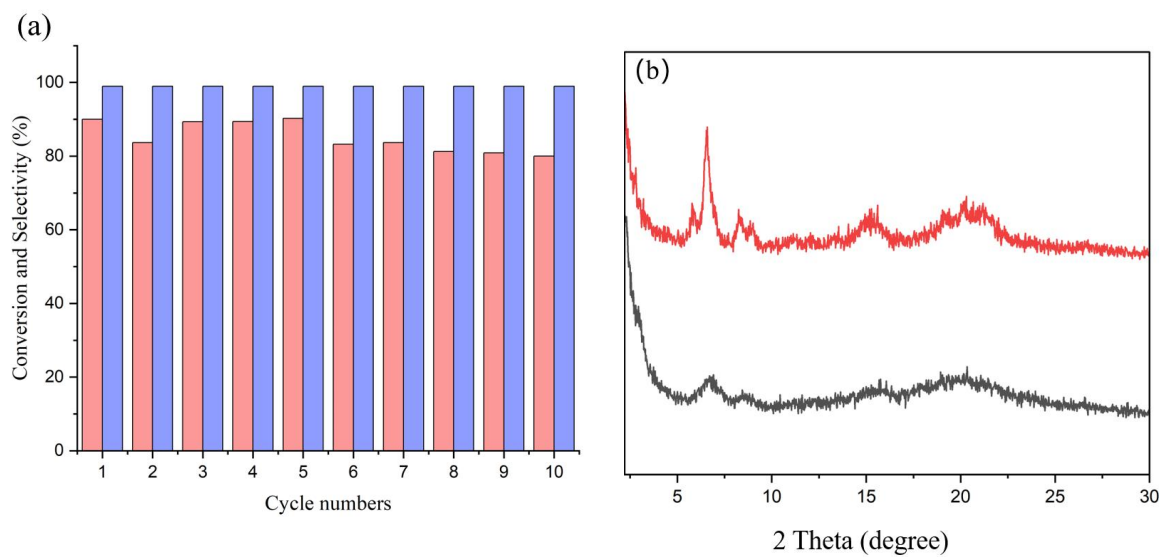


Figure S5. (a) Recycling catalytic test of ETTA-B₁₈C₆-COF for the CO₂ cycloaddition with 1,2-epoxybutane (1 mmol), solvent free, CO₂ (0.1 MPa), 40°C and 24 h. (b)PXRD curves of ETTA-B₁₈C₆-COF before (red) and after (black) ten runs.

Table S2. Summary of reported catalytic systems for coupling of CO₂ and epichlorohydrin under mild/ambient conditions.

Material	Condition	TOF(h ⁻¹)	Ref
Al-iPOP (0.1)/–	25°C, 0.1 Mpa, 8 h	124	ChemSusChem. 2017, 10, 2534–2541.
2,3-DhaTph (0.2)/TBAI (0.5)	110°C, 1 Mpa, 12 h	39.2	Catal. Sci. Technol. 2016, 6, 6152–6158.
PPS⊂COF-TpBpy-Cu (1.8)	40°C, 0.1Mpa, 24 h	23.9	J. Am. Chem. Soc. 2016, 138, 15790–15796.
ETTA-B₁₈C₆-COF (0.01) /TBAB (0.05)	40°C, 0.1Mpa, 24 h	3.9	This work
COFJLU7(0.5)/TBAB (5.0)	40°C, 0.1Mpa, 48 h	3.8	J. Mater. Chem. A. 2018, 6, 374–382.
Co-CMP (0.5) /TBAB (7.2)	25°C, 0.1Mpa, 48 h	3.4	Nat. Commun. 2013, 4, 1960–1965.
Pyridyl salicylimine (0.1)	100°C, 1 Mpa, 24 h	2.0	ACS Appl. Mater. Interfaces 2018, 10, 9478–9484.
Cr-MIL-101(1.2)/TBAB (3.4)	25°C, 0.8 Mpa, 48 h	1.6	<i>Catal.</i> 2013, 298, 179–185.
Cr(salophen) complex (2.5)/TBAB (2.5)	25°C, 0.1 Mpa, 24 h	1.6	ACS Catal. 2016, 6, 5012–5025.
USTC-253-TFA (1.0) /TBAB (6.5)	25 °C, 0.1 Mpa, 72 h	1.1	ChemSusChem. 2015, 8, 878–885.
Hf-NU-1000 (4.0) /TBAB (10)	25 °C, 0.1 Mpa, 56 h	0.1	J. Am. Chem. Soc. 2014, 136, 15861–15864.

Section 8. Structural Simulation

Table S3a. Atomic space position of the AA-stacking mode of ET TA-B₁₈C₆-COF.

Space group: P1			
a=28.8354Å, b=14.5041Å, c=4.4406Å			
α=91.6676°, β=94.93919°, γ=91.86846°			
C1	0.12737	-2.45474	-0.21140
O2	0.08770	-2.50204	-0.11154
C3	0.09032	-2.60006	-0.12093
C4	0.04661	-2.64122	0.01261
C5	0.16846	-2.50062	-0.29240
C6	0.20835	-2.45265	-0.38121
C7	0.25100	-2.50788	-0.42512
C8	0.24987	-2.58921	-0.59649
C9	0.28983	-2.64311	-0.62920
C10	0.33124	-2.61634	-0.48883
C11	0.33214	-2.53674	-0.31217
C12	0.29225	-2.48335	-0.27850
C13	0.37393	-2.67042	-0.51586
N14	0.37696	-2.74335	-0.68375
C15	0.41879	-2.79654	-0.70111
C16	0.42016	-2.87561	-0.88123
C17	0.46012	-2.93048	-0.88973
C18	0.49892	-2.90872	-0.71160
C19	0.49752	-2.82787	-0.53801
C20	0.45815	-2.77226	-0.53334
C21	0.54171	-2.96762	-0.70378
C22	0.58640	-2.91549	-0.67732
C23	0.53997	-3.06270	-0.70378
C24	0.62193	-2.94403	-0.48231
C25	0.66268	-2.89271	-0.45368
C26	0.66810	-2.81029	-0.61243
C27	0.63223	-2.77961	-0.80077
C28	0.59195	-2.83196	-0.83336
N29	0.70936	-2.75719	-0.56860
C30	0.58276	-3.12160	-0.71158
C31	0.49528	-3.11482	-0.67733
C32	0.45974	-3.08629	-0.48233
C33	0.41899	-3.13760	-0.45371
C34	0.41358	-3.22002	-0.61247
C35	0.44944	-3.25071	-0.80080
C36	0.48973	-3.19836	-0.83337
C37	0.58416	-3.20244	-0.53797
C38	0.62352	-3.25806	-0.53328
C39	0.66289	-3.23377	-0.70104
C40	0.66152	-3.15470	-0.88116
C41	0.62156	-3.09983	-0.88969

N42	0.70472	-3.28697	-0.68366
N43	0.37231	-3.27312	-0.56865
C44	0.36524	-3.35196	-0.69817
C45	0.70775	-3.35989	-0.51576
C46	0.71643	-2.67835	-0.69810
C47	0.75844	-2.62468	-0.63814
C48	0.75044	-3.41398	-0.48872
C49	0.32324	-3.40563	-0.63822
C50	0.79342	-2.65873	-0.45010
C51	0.83155	-2.60364	-0.37863
C52	0.83530	-2.5135	-0.49212
C53	0.80106	-2.48184	-0.69123
C54	0.76268	-2.53653	-0.76155
C55	0.74954	-3.49358	-0.31207
C56	0.78943	-3.54696	-0.27840
C57	0.83068	-3.52243	-0.42501
C58	0.83181	-3.44110	-0.59637
C59	0.79185	-3.38721	-0.62908
C60	0.28825	-3.37158	-0.45017
C61	0.25012	-3.42667	-0.37871
C62	0.24637	-3.51681	-0.49219
C63	0.28061	-3.54847	-0.69131
C64	0.31899	-3.49378	-0.76163
C65	0.87490	-2.45427	-0.39733
C66	0.87333	-3.57767	-0.38111
C67	0.20678	-3.57604	-0.39740
C68	0.91592	-2.49906	-0.31164
C69	0.95539	-2.45055	-0.21593
C70	0.95431	-3.57558	-0.21133
C71	0.91323	-3.52970	-0.29230
C72	0.16576	-3.53126	-0.31166
C73	0.12629	-3.57977	-0.21595
O74	0.99587	-2.49559	-0.11780
C75	0.99342	-2.59369	-0.10856
C76	1.03731	-2.63261	0.02961
O77	1.07508	-2.61516	-0.15799
O78	0.99398	-3.52829	-0.11146
C79	0.99136	-3.43027	-0.12075
C80	1.03507	-3.38913	0.01280
O81	1.07351	-3.41517	-0.15784
O82	0.08581	-3.53475	-0.11778
C83	0.08826	-3.43664	-0.10845
C84	0.04437	-3.39773	0.02976
H85	0.02167	-2.61522	-0.16756
H86	0.36558	-2.51514	-0.19473
H87	0.40629	-2.64891	-0.38620
H88	0.38867	-2.89565	-1.02196
H89	0.46145	-2.99363	-1.04234
H90	0.52893	-2.80687	-0.39797

H91	0.45779	-2.70653	-0.39256
H92	0.61774	-3.00986	-0.34473
H93	0.69170	-2.91806	-0.30024
H94	0.63595	-2.71170	-0.92780
H95	0.56300	-2.80709	-0.98819
H96	0.46394	-3.02045	-0.34475
H97	0.38997	-3.11225	-0.30027
H98	0.44573	-3.31861	-0.92784
H99	0.51868	-3.22323	-0.98819
H100	0.55275	-3.22345	-0.39795
H101	0.62389	-3.32378	-0.39249
H102	0.69301	-3.13467	-1.02188
H103	0.62023	-3.03669	-1.04231
H104	0.39199	-3.38073	-0.86221
H105	0.67636	-3.38427	-0.38154
H106	0.68968	-2.64958	-0.86214
H107	0.73477	-2.50922	-0.91992
H108	0.71610	-3.51518	-0.19464
H109	0.29087	-3.29875	-0.35516
H110	0.34691	-3.52109	-0.92000
H111	1.04121	-2.64483	0.28194
H112	1.03938	-3.40893	0.25967

Table S3b. Atomic space position of the AB-stacking mode of ET TA-B₁₈C₆-COF.

Space group: P1			
a=29.2648Å, b=15.0158Å, c=8.8932Å			
$\alpha=87.9297^\circ$, $\beta=92.6375^\circ$, $\gamma=91.9377^\circ$			
C1	0.77044	0.56102	0.40617
O2	0.73077	0.51372	0.45610
C3	0.73340	0.41570	0.45141
C4	0.68968	0.37454	0.51817
C5	0.81153	0.51514	0.36567
C6	0.85142	0.56311	0.32127
C7	0.89407	0.50788	0.29931
C8	0.89294	0.42655	0.21363
C9	0.93290	0.37265	0.19727
C10	0.97432	0.39942	0.26746
C11	0.97521	0.47902	0.35579
C12	0.93532	0.53241	0.37262
C13	0.01700	0.34534	0.25394
N14	0.02003	0.27241	0.17000
C15	0.06187	0.21922	0.16132
C16	0.06324	0.14015	0.07126
C17	0.10320	0.08528	0.06701
C18	0.14199	0.10704	0.15607
C19	0.14059	0.18789	0.24287
C20	0.10123	0.24350	0.24520
C21	0.18478	0.04815	0.15998
C22	0.22947	0.10027	0.17321
C23	0.18304	0.95306	0.15998
C24	0.26501	0.07173	0.27072
C25	0.30576	0.12305	0.28503
C26	0.31117	0.20547	0.20566
C27	0.27531	0.23615	0.11149
C28	0.23502	0.18380	0.09519
N29	0.35244	0.25857	0.22757
C30	0.22583	0.89416	0.15608
C31	0.13835	0.90094	0.17321
C32	0.10282	0.92947	0.27071
C33	0.06206	0.87816	0.28501
C34	0.05665	0.79574	0.20564
C35	0.09252	0.76505	0.11147
C36	0.13280	0.81740	0.09519
C37	0.22723	0.81332	0.24289
C38	0.26660	0.75770	0.24523
C39	0.30596	0.78199	0.16135
C40	0.30459	0.86106	0.07129
C41	0.26463	0.91593	0.06703
N42	0.34780	0.72879	0.17004
N43	0.01538	0.74264	0.22755

C44	0.00831	0.66380	0.16279
C45	0.35082	0.65587	0.25399
C46	0.35951	0.33741	0.16282
C47	0.40151	0.39108	0.19280
C48	0.39351	0.60178	0.26751
C49	0.96631	0.61013	0.19276
C50	0.43650	0.35703	0.28682
C51	0.47462	0.41212	0.32256
C52	0.47837	0.50226	0.26581
C53	0.44414	0.53392	0.16626
C54	0.40576	0.47923	0.13110
C55	0.39261	0.52218	0.35583
C56	0.43251	0.46880	0.37267
C57	0.47375	0.49333	0.29937
C58	0.47488	0.57466	0.21369
C59	0.43492	0.62855	0.19733
C60	0.93132	0.64418	0.28679
C61	0.89320	0.58909	0.32252
C62	0.88945	0.49895	0.26578
C63	0.92368	0.46729	0.16622
C64	0.96206	0.52198	0.13106
C65	0.51797	0.56149	0.31321
C66	0.51641	0.43809	0.32132
C67	0.84985	0.43972	0.31317
C68	0.55899	0.51670	0.35605
C69	0.59846	0.56521	0.40391
C70	0.59738	0.44018	0.40621
C71	0.55630	0.48606	0.36572
C72	0.80883	0.48450	0.35604
C73	0.76936	0.43599	0.40390
O74	0.63895	0.52017	0.45297
C75	0.63649	0.42207	0.45759
C76	0.68038	0.38315	0.52668
O77	0.71815	0.40060	0.43288
O78	0.63706	0.48747	0.45614
C79	0.63443	0.58549	0.45150
C80	0.67815	0.62664	0.51827
O81	0.71659	0.60059	0.43295
O82	0.72888	0.48101	0.45298
C83	0.73133	0.57912	0.45765
C84	0.68745	0.61803	0.52675
H85	0.66474	0.40054	0.42809
H86	0.00865	0.50062	0.41450
H87	0.04936	0.36685	0.31877
H88	0.03174	0.12011	0.00089
H89	0.10452	0.02213	-0.00930
H90	0.17200	0.20889	0.31288
H91	0.10086	0.30923	0.31559
H92	0.26081	0.00590	0.33951

H93	0.33477	0.09770	0.36175
H94	0.27902	0.30406	0.04797
H95	0.20607	0.20867	0.01778
H96	0.10701	0.99531	0.33950
H97	0.03305	0.90351	0.36174
H98	0.08881	0.69715	0.04795
H99	0.16175	0.79253	0.01777
H100	0.19582	0.79231	0.31290
H101	0.26696	0.69198	0.31563
H102	0.33608	0.88109	0.00093
H103	0.26331	0.97907	-0.00928
H104	0.03506	0.63503	0.08077
H105	0.31943	0.63149	0.32110
H106	0.33276	0.36618	0.08080
H107	0.37784	0.50654	0.05191
H108	0.35918	0.50058	0.41455
H109	0.93394	0.71701	0.33429
H110	0.98998	0.49467	0.05187
H111	0.68429	0.37093	0.65284
H112	0.68245	0.60683	0.64170
C113	0.12737	0.54526	0.89430
O114	0.08770	0.49796	0.94423
C115	0.09032	0.39994	0.93954
C116	0.04661	0.35878	1.00630
C117	0.16846	0.49938	0.85380
C118	0.20835	0.54735	0.80940
C119	0.25100	0.49212	0.78744
C120	0.24987	0.41079	0.70176
C121	0.28983	0.35689	0.68540
C122	0.33124	0.38366	0.75559
C123	0.33214	0.46326	0.84391
C124	0.29225	0.51665	0.86075
C125	0.37393	0.32958	0.74207
N126	0.37696	0.25665	0.65812
C127	0.41879	0.20346	0.64944
C128	0.42016	0.12439	0.55939
C129	0.46012	0.06952	0.55513
C130	0.49892	0.09128	0.64420
C131	0.49752	0.17213	0.73100
C132	0.45815	0.22774	0.73333
C133	0.54171	0.03238	0.64811
C134	0.58640	0.08451	0.66134
C135	0.53997	0.93730	0.64811
C136	0.62193	0.05597	0.75885
C137	0.66268	0.10729	0.77316
C138	0.66810	0.18971	0.69379
C139	0.63223	0.22039	0.59962
C140	0.59195	0.16804	0.58332
N141	0.70936	0.24281	0.71570

C142	0.58276	0.87840	0.64421
C143	0.49528	0.88518	0.66133
C144	0.45974	0.91371	0.75884
C145	0.41899	0.86240	0.77314
C146	0.41358	0.77998	0.69376
C147	0.44944	0.74929	0.59960
C148	0.48973	0.80164	0.58331
C149	0.58416	0.79756	0.73101
C150	0.62352	0.74194	0.73336
C151	0.66289	0.76623	0.64948
C152	0.66152	0.84530	0.55942
C153	0.62156	0.90017	0.55515
N154	0.70472	0.71303	0.65817
N155	0.37231	0.72688	0.71567
C156	0.36524	0.64804	0.65092
C157	0.70775	0.64011	0.74212
C158	0.71643	0.32165	0.65095
C159	0.75844	0.37532	0.68093
C160	0.75044	0.58602	0.75564
C161	0.32324	0.59437	0.68089
C162	0.79342	0.34127	0.77495
C163	0.83155	0.39636	0.81068
C164	0.83530	0.48650	0.75394
C165	0.80106	0.51816	0.65438
C166	0.76268	0.46347	0.61922
C167	0.74954	0.50642	0.84396
C168	0.78943	0.45304	0.86080
C169	0.83068	0.47757	0.78749
C170	0.83181	0.55890	0.70181
C171	0.79185	0.61279	0.68546
C172	0.28825	0.62842	0.77491
C173	0.25012	0.57333	0.81065
C174	0.24637	0.48319	0.75391
C175	0.28061	0.45153	0.65435
C176	0.31899	0.50622	0.61919
C177	0.87490	0.54573	0.80133
C178	0.87333	0.42233	0.80944
C179	0.20678	0.42396	0.80130
C180	0.91592	0.50094	0.84418
C181	0.95539	0.54945	0.89203
C182	0.95431	0.42442	0.89434
C183	0.91323	0.47030	0.85385
C184	0.16576	0.46874	0.84417
C185	0.12629	0.42023	0.89202
O186	0.99587	0.50441	0.94110
C187	0.99342	0.40631	0.94572
C188	0.03731	0.36739	1.01480
O189	0.07508	0.38484	0.92100
O190	0.99398	0.47171	0.94427

C191	0.99136	0.56973	0.93963
C192	0.03507	0.61087	1.00640
O193	0.07351	0.58483	0.92108
O194	0.08581	0.46525	0.94111
C195	0.08826	0.56336	0.94577
C196	0.04437	0.60227	1.01488
H197	0.02167	0.38478	0.91622
H198	0.36558	0.48486	0.90263
H199	0.40629	0.35109	0.80690
H200	0.38867	0.10435	0.48902
H201	0.46145	0.00637	0.47883
H202	0.52893	0.19313	0.80101
H203	0.45779	0.29347	0.80372
H204	0.61774	0.99014	0.82763
H205	0.69170	0.08194	0.84988
H206	0.63595	0.28830	0.53610
H207	0.56300	0.19291	0.50591
H208	0.46394	0.97955	0.82762
H209	0.38997	0.88775	0.84986
H210	0.44573	0.68139	0.53608
H211	0.51868	0.77677	0.50590
H212	0.55275	0.77655	0.80102
H213	0.62389	0.67622	0.80375
H214	0.69301	0.86533	0.48906
H215	0.62023	0.96331	0.47885
H216	0.39199	0.61927	0.56890
H217	0.67636	0.61573	0.80923
H218	0.68968	0.35042	0.56893
H219	0.73477	0.49078	0.54004
H220	0.71610	0.48482	0.90268
H221	0.29087	0.70125	0.82242
H222	0.34691	0.47891	0.54000
H223	0.04121	0.35517	1.14097
H224	0.03938	0.59107	1.12983

Section 9. Supporting References

- (1). D.W. Lim, S. A. Chyun, M. P. Suh, Hydrogen storage in a potassium-ion-bound metal–organic framework incorporating crown ether struts as specific cation binding sites. *Angew. Chem. Int. Ed.* 2014, 53, 7819-7822.