Electronic Supplementary Information (ESI)

Enhanced Performance in Gas Adsorption and Li Ion Battery by Docking Li^+ in Crown Ether-Based Metal-Organic Framework

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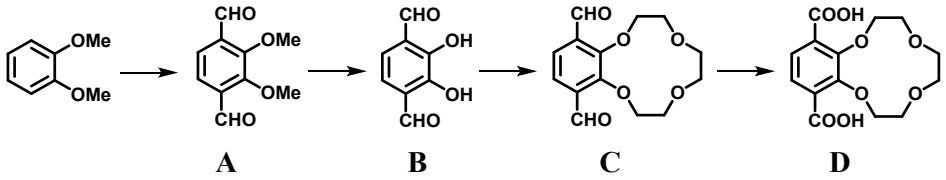
1. General information

General. All reagents and solvents were purchased from Sigma Aldrich and used as per received without further purification. ^{1}H NMR and ^{13}C NMR spectra were measured on BBFO-400 spectrometer at ambient temperature. All ^{1}H NMR spectra were reported as chemical shift δ in units of parts per million (ppm) downfield with reference to deuterated solvent (2.50 ppm for DMSO-d_6, 7.26 ppm for $CDCl_3$) or TMS (0.00 ppm). Multiplicities were presented as: s (singlet), d (doublet), t (triplet), and m (multiplet). Coupling constants J values were expressed in Hz and the number of protons was expressed as nH. ^{13}C NMR spectra were reported as chemical shift δ in units of parts per million (ppm) downfield with reference to deuterated solvent (DMSO-d_6 relative to 39.81 ppm or $CDCl_3$ relative to 77.16 ppm). High resolution mass spectrometry (HRMS) was performed on a Waters Q-tof Premier MS spectrometer. Absorption spectra were recorded on a Shimadzu UV-3600 UV-VIS-NIR spectrophotometer, while the fluorescent emission spectra were recorded on a Varian Cary Eclipse fluorescence spectrophotometer. Fourier transform infrared (FT-IR) spectra were collected with an SHIMADZU IR Prestige-21 spectrometer. Samples were packed firmly to obtain transparent films. Thermogravimetric analyses (TGA) were performed on a TGA 500 thermogravimetric analyzer by heating the samples at 20 ºC min^{-1} to 1000 ºC in a nitrogen atmosphere (60 mL min^{-1}). Powder X-ray diffraction (PXRD) studies were performed on a SHIMADZU XRD-6000 Labx diffractometer, using Cu-Ka radiation (λ = 1.5418 Å) over 2θ range of 2.5°−40°, 40 keV, and 30 mA with a scanning rate of 0.02° s^{-1} (2θ) at room temperature. Single crystal X-ray diffraction measurements were performed on a SuperNova X-ray Diffraction System from Agilent Technologies. Gas sorption analyses were conducted using Quantachrome Instruments Autosorb-iQ (Boynton Beach, Florida USA) with extra-high pure gases.

2. Experimental section



Scheme S1. Synthesis of crown ether-based organic ligand of H_2L (D).

2.1 Compound (A): This compound was synthesized in accordance to the reported method with slight modifications.[S1] A round-bottom flask was charged with 1,2-dimethoxybenzene (13.8 g, 0.1 mol), Et_2O (200 mL), and n-BuLi (250.0 mL, 0.50 mol, 2.0 M solution in hexane), and then tetramethylethylenediamine (TMEDA, 76.0 mL, 0.51 mol) was added dropwise. The mixture turned yellow, and white precipitate was formed. The mixture was refluxed for 24 h. After cooling with ice-water bath, *N,N*-dimethylformamide (DMF, 60 mL, 0.77 mol) was added dropwise. Cooling bath was removed, and after 15 min, aqueous solution of NH_4Cl (100 mL, 10% w/w) was added. The mixture was extracted with ethyl acetate (3×100 mL). The combined organic phases were washed with water (100 mL) and brine (100 mL), and then dried over anhydrous Na_2SO_4. The solution was evaporated and the obtained sample was purified by column chromatography (silica gel, hexane:ethyl acetate = 20:1) to give a pale yellow solid. The product was further purified by the crystallization from DCM/hexane as white crystals (~5 g, 30%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.45 (s, 1H), 7.64 (s, 1H), 4.06 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 190.20 (s), 157.64 (s), 135.22 (s), 123.83 (s), 63.45 (s).

HRMS: Calcd for $C_{10}H_{10}O_4$: 195.0657, Found: 195.0655.

2.2 Compound (B): This compound was synthesized in accordance to the reported method with slight modifications.[S2] A round-bottom flask was charged with compound A (2.38 g, 12.3 mmol) and CH_2Cl_2 (70 mL), and the solution was cooled with ice-water bath. Then, BBr_3 (31.0 mL, 31.0 mmol, 1 M solution in hexane) was added dropwise over 5 min. A yellow precipitate was initially formed, and the mixture became orange. After 30 min, the cooling bath was removed, and stirring was continued for 3.5 h. Then, water (100 mL) was added, and the mixture was extracted with $CHCl_3$ (3×100 mL). Combined organic phases were washed with brine (100 mL), and dried over Na_2SO_4. The solution was filtered and evaporated to obtain yellow solid. The product was crystallized from $CHCl_3$-hexane mixture to give compound B as brown crystals (1.79 g, 10.8 mmol, 88%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.89 (s, 1H), 10.03 (s, 1H), 7.28 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 196.82 (s), 151.71 (s), 124.19 (s), 123.15 (s). HRMS: Calcd for $C_8H_6O_4$: 167.0344, Found: 167.0346.

2.3 Compound (C): This compound was synthesized in accordance to the reported method with slight modifications.[S1] A round-bottom flask was charged with compound B (0.75 g, 4.50 mmol), DMF (30 mL), $ClCH_2CH_2OCH_2CH_2OCH_2CH_2Cl$ (5.6 mL, 18.0 mmol) and K_2CO_3 (2.49 g, 18.0 mmol). The mixture was stirred at 90 °C for 20 h. After cooling to room temperature, aqueous solution of HCl (50 mL, 1:9 v/v) was added, and mixture was extracted with ethyl acetate (3×50 mL). Combined organic phases were washed with brine (2×50 mL), and dried over $MgSO_4$. The solution was filtered and evaporated, and the obtained sample was purified by column chromatography (c-hexane:ethyl acetate = 1:1) to give compound C as white powder (0.11 g, 11%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.45 (s, 1H), 7.68 (s, 1H), 4.38 (s, 2H), 4.00 (s, 2H), 3.83 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 188.83 (d, J = 60.7 Hz), 155.35 (d, J = 160.1 Hz), 133.41 (d, J = 240.8 Hz), 121.79 (d, J = 359.8 Hz), 75.48 (s), 71.49 (s). HRMS: Calcd for $C_{14}H_{16}O_6$: 281.1025, Found: 281.1015.

2.4 Compound (D): This compound was synthesized in accordance to the reported method with slight modifications.[S3] Finely ground $KMnO_4$ (1.6 g, 10.4 mmol) was added in portions over 1 h to a stirred solution of compound C (0.84 g, 3.45 mmol) in acetone (10 mL), after which time no starting material was evident by TLC analysis. The mixture was concentrated to dryness under reduced pressure, and the residue was triturated with 5 N NaOH and filtered. The filtrate was acidified with concentrated HCl to give the diacid D as a white solid (0.81 g, 85%). ^{1}H NMR (400 MHz, MeOD): δ 7.55 (s, 1H), 4.26 (s, 2H), 3.89 (s, 2H), 3.79 (s, 2H). ^{13}C NMR (101 MHz, DMSO): δ 206.15 (s), 152.35 (s), 124.32 (s), 74.38 (s), 70.48 (s), 68.62 (s), 30.30 (d, J = 171.4 Hz). HRMS: Calcd for $C_{14}H_{16}O_8$: 313.0923, Found: 313.0925.

3. Preparation procedure of crown ether-based MOF

3.1 Synthesis of Zn-MOF-Crown: A solid mixture of $Zn(NO_3)_2 \cdot 6H_2O$ (1.80 g, 6.05 mmol) and 3',6'-dicarboxy-benzo-12-crown-4 (Compound D, 630 mg, 2.02 mmol) was dissolved in *N,N*-diethylformamide (DEF, 50 mL). The solution was allocated evenly into five 25-mL vials. The vials were capped tightly and placed in an oven at 85 °C for 24 hours. Colorless crystals were collected after decanting hot mother liquor. The crystals were rinsed with DMF for three times, followed by solvent exchange with CH_2Cl_2 for six times. CH_2Cl_2 was further removed with supercritical liquid CO_2 in a Tousimis Samdri PVT-30 critical point dried by the following procedures. The wet sample was placed inside the dryer and the CH_2Cl_2 was exchanged with liquid CO_2 over a period of 20 minutes, during which time the liquid CO_2 was vented under positive pressure. The venting rate of liquid CO_2 was kept below the rate of filling so as to maintain a full chamber. After 20 minutes of venting and soaking with

liquid CO_2, the temperature was raised to 40 °C. The chamber was held above the critical point with the pressure around 1300 psi for 1 hour, at which point the chamber was slowly vented over the course of 12 hours. CCDC 1431726 contains the supplementary crystallographic data for Zn-MOF-Crown.

Table S1. Crystallographic data and structural refinement summary for Zn-MOF-Crown.

Structure	Zn-MOF-Crown
Empirical formula based on atoms located by single X-ray diffraction	$C_{24}O_{25}Zn_4$
Formula weight	949.72
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system	Trigonal
Space group	$R\bar{3}m$
Unit cell dimensions	a = b = 18.2657(8) Å, c = 22.3708(15) Å
Volume	6463.8(6) $Å^3$
Z	3
Density (calculated)	0.732 Mg/m^3
Absorption coefficient	1.138 mm^{-1}
F(000)	1392
Crystal size	0.3 x 0.3 x 0.3 mm^3
Theta range for data collection	2.23 to 27.47°
Index ranges	-23 <= h <= 19 -23 <= k <= 23 -26 <= l <= 28
Reflections collected	15406
Independent reflections	1811 [R(int) = 0.1160]
Completeness	99.7%
Absorption correction	none
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1811 / 0 / 81
Goodness-of-fit on F^2	1.035
Final R indices [I>2sigma(I)]	R1 = 0.0802, wR2 = 0.1782
R indices (all data)	R1 = 0.1470, wR2 = 0.1969
Largest diff. peak and hole	0.462 and -0.428 $e.Å^{-3}$

Table S2. Atomic coordinates and equivalent isotropic displacement parameters for Zn-MOF-Crown.

Number	Label	Xfrac + ESD	Yfrac + ESD	Zfrac + ESD	Symm. op.		
1	Zn1	0.3333	0.6667	0.07962(10)	x	y	z
2	Zn2	0.44924(8)	0.72462(4)	0.13770(6)	x	y	z
3	O1	0.3333	0.6667	0.1667	x	y	z
4	O3	0.4312(3)	0.8625(6)	0.1295(5)	x	y	z
5	O2	0.4713(4)	0.8220(4)	0.0889(3)	x	y	z
6	O4	0.3910(3)	0.7820(6)	0.0492(4)	x	y	z
7	C2	0.4640(5)	0.9280(10)	0.0385(5)	x	y	z
8	C1	0.4259(2)	0.8518(5)	0.0736(4)	x	y	z
9	C3	0.5373(13)	0.9925(15)	0.0469(10)	x	y	z
10	C4	0.505(2)	0.9337(13)	-0.0010(16)	x	y	z
11	O5	0.5891(19)	0.9972(14)	0.093(2)	x	y	z
12	O6	0.5211(19)	0.888(2)	-0.0270(11)	x	y	z
13	O3	0.5687(7)	1.1375(6)	-0.1295(5)	1+x-y	2-y	-z
14	O2	0.6493(6)	1.1780(4)	-0.0889(3)	1+x-y	2-y	-z
15	O4	0.6090(7)	1.2180(6)	-0.0492(4)	1+x-y	2-y	-z
16	C2	0.5360(11)	1.0720(10)	-0.0385(5)	1+x-y	2-y	-z
17	C1	0.5741(5)	1.1482(5)	-0.0736(4)	1+x-y	2-y	-z
18	C3	0.5448(20)	1.0075(15)	-0.0469(10)	1+x-y	2-y	-z
19	C4	0.5713(24)	1.0663(13)	0.0010(16)	1+x-y	2-y	-z
20	O5	0.5919(24)	1.0028(14)	-0.093(2)	1+x-y	2-y	-z
21	O6	0.6331(28)	1.112(2)	0.0270(11)	1+x-y	2-y	-z
22	O2	0.5287(4)	1.1780(4)	-0.0889(3)	1-x	2-y	-z
23	C3	0.4627(13)	1.0075(15)	-0.0469(10)	1-x	2-y	-z
24	C4	0.495(2)	1.0663(13)	0.0010(16)	1-x	2-y	-z
25	O5	0.4109(19)	1.0028(14)	-0.093(2)	1-x	2-y	-z
26	O6	0.4789(19)	1.112(2)	0.0270(11)	1-x	2-y	-z
27	O2	0.3507(6)	0.8220(4)	0.0889(3)	-x+y	y	z
28	C3	0.4552(20)	0.9925(15)	0.0469(10)	-x+y	y	z
29	C4	0.4287(24)	0.9337(13)	-0.0010(16)	-x+y	y	z
30	O5	0.4081(24)	0.9972(14)	0.093(2)	-x+y	y	z
31	O6	0.3669(28)	0.888(2)	-0.0270(11)	-x+y	y	z
32	Zn2	0.27538(4)	0.72462(9)	0.13770(6)	1-y	1+x-y	z
33	O3	0.1375(6)	0.5687(7)	0.1295(5)	1-y	1+x-y	z
34	O2	0.1780(4)	0.6493(6)	0.0889(3)	1-y	1+x-y	z
35	O4	0.2180(6)	0.6090(7)	0.0492(4)	1-y	1+x-y	z
36	C2	0.0720(10)	0.5360(11)	0.0385(5)	1-y	1+x-y	z
37	C1	0.1482(5)	0.5741(5)	0.0736(4)	1-y	1+x-y	z
38	C3	0.0075(15)	0.5448(20)	0.0469(10)	1-y	1+x-y	z
39	C4	0.0663(13)	0.5713(24)	-0.0010(16)	1-y	1+x-y	z
40	O5	0.0028(14)	0.5919(24)	0.093(2)	1-y	1+x-y	z
41	O6	0.112(2)	0.6331(28)	-0.0270(11)	1-y	1+x-y	z

42	O3	-0.1375(6)	0.4312(3)	-0.1295(5)	-1+y	x	-z
43	O2	-0.1780(4)	0.4713(4)	-0.0889(3)	-1+y	x	-z
44	O4	-0.2180(6)	0.3910(3)	-0.0492(4)	-1+y	x	-z
45	C2	-0.0720(10)	0.4640(5)	-0.0385(5)	-1+y	x	-z
46	C1	-0.1482(5)	0.4259(2)	-0.0736(4)	-1+y	x	-z
47	C3	-0.0075(15)	0.5373(13)	-0.0469(10)	-1+y	x	-z
48	C4	-0.0663(13)	0.505(2)	0.0010(16)	-1+y	x	-z
49	O5	-0.0028(14)	0.5891(19)	-0.093(2)	-1+y	x	-z
50	O6	-0.112(2)	0.5211(19)	0.0270(11)	-1+y	x	-z
51	O2	-0.1780(4)	0.3507(6)	-0.0889(3)	-1+y	-x+y	-z
52	C3	-0.0075(15)	0.4552(20)	-0.0469(10)	-1+y	-x+y	-z
53	C4	-0.0663(13)	0.4287(24)	0.0010(16)	-1+y	-x+y	-z
54	O5	-0.0028(14)	0.4081(24)	-0.093(2)	-1+y	-x+y	-z
55	O6	-0.112(2)	0.3669(28)	0.0270(11)	-1+y	-x+y	-z
56	O2	0.1780(4)	0.5287(4)	0.0889(3)	1-y	1-x	z
57	C3	0.0075(15)	0.4627(13)	0.0469(10)	1-y	1-x	z
58	C4	0.0663(13)	0.495(2)	-0.0010(16)	1-y	1-x	z
59	O5	0.0028(14)	0.4109(19)	0.093(2)	1-y	1-x	z
60	O6	0.112(2)	0.4789(19)	-0.0270(11)	1-y	1-x	z
61	Zn2	0.27538(9)	0.55076(8)	0.13770(6)	-x+y	1-x	z
62	O3	0.4313(7)	0.5688(3)	0.1295(5)	-x+y	1-x	z
63	O2	0.3507(6)	0.5287(4)	0.0889(3)	-x+y	1-x	z
64	O4	0.3910(7)	0.6090(3)	0.0492(4)	-x+y	1-x	z
65	C2	0.4640(11)	0.5360(5)	0.0385(5)	-x+y	1-x	z
66	C1	0.4259(5)	0.5741(2)	0.0736(4)	-x+y	1-x	z
67	C3	0.4552(20)	0.4627(13)	0.0469(10)	-x+y	1-x	z
68	C4	0.4287(24)	0.495(2)	-0.0010(16)	-x+y	1-x	z
69	O5	0.4081(24)	0.4109(19)	0.093(2)	-x+y	1-x	z
70	O6	0.3669(28)	0.4789(19)	-0.0270(11)	-x+y	1-x	z
71	O3	0.5688(3)	0.4313(7)	-0.1295(5)	1-x	-x+y	-z
72	O2	0.5287(4)	0.3507(6)	-0.0889(3)	1-x	-x+y	-z
73	O4	0.6090(3)	0.3910(7)	-0.0492(4)	1-x	-x+y	-z
74	C2	0.5360(5)	0.4640(11)	-0.0385(5)	1-x	-x+y	-z
75	C1	0.5741(2)	0.4259(5)	-0.0736(4)	1-x	-x+y	-z
76	C3	0.4627(13)	0.4552(20)	-0.0469(10)	1-x	-x+y	-z
77	C4	0.495(2)	0.4287(24)	0.0010(16)	1-x	-x+y	-z
78	O5	0.4109(19)	0.4081(24)	-0.093(2)	1-x	-x+y	-z
79	O6	0.4789(19)	0.3669(28)	0.0270(11)	1-x	-x+y	-z
80	O2	0.6493(6)	0.4713(4)	-0.0889(3)	1+x-y	x	-z
81	C3	0.5448(20)	0.5373(13)	-0.0469(10)	1+x-y	x	-z
82	C4	0.5713(24)	0.505(2)	0.0010(16)	1+x-y	x	-z
83	O5	0.5919(24)	0.5891(19)	-0.093(2)	1+x-y	x	-z
84	O6	0.6331(28)	0.5211(19)	0.0270(11)	1+x-y	x	-z

85	O2	0.4713(4)	0.6493(6)	0.0889(3)	x	1+x-y	z
86	C3	0.5373(13)	0.5448(20)	0.0469(10)	x	1+x-y	z
87	C4	0.505(2)	0.5713(24)	-0.0010(16)	x	1+x-y	z
88	O5	0.5891(19)	0.5919(24)	0.093(2)	x	1+x-y	z
89	O6	0.5211(19)	0.6331(28)	-0.0270(11)	x	1+x-y	z
90	Zn1	0.3334	0.6666	0.25371(10)	-1/3+y	1/3+x	1/3-z
91	Zn2	0.39129(4)	0.78257(8)	0.19563(6)	-1/3+y	1/3+x	1/3-z
92	Zn2	0.39129(9)	0.60871(4)	0.19563(6)	2/3+x-y	1.33333-y	1/3-z
93	Zn2	0.21743(8)	0.60871(9)	0.19563(6)	2/3-x	1/3-x+y	1/3-z
94	Zn1	-0.3333	0.3333	-0.07962(10)	-1+y	x	-z
95	Zn1	0.6667	0.3333	-0.07962(10)	y	x	-z
96	Zn1	0.6667	1.3333	-0.07962(10)	y	1+x	-z
97	Zn2	-0.27538(4)	0.44924(8)	-0.13770(6)	-1+y	x	-z
98	Zn2	0.72462(4)	0.44924(8)	-0.13770(6)	y	x	-z
99	Zn2	-0.27538(9)	0.27538(4)	-0.13770(6)	x-y	1-y	-z
100	Zn2	0.72462(9)	1.27538(4)	-0.13770(6)	1+x-y	2-y	-z
101	Zn2	0.55076(8)	0.27538(9)	-0.13770(6)	1-x	-x+y	-z
102	Zn2	0.55076(8)	1.27538(9)	-0.13770(6)	1-x	1-x+y	-z
103	Zn2	-0.21743(8)	0.39129(4)	-0.19563(6)	-2/3+x	-1/3+y	-z
104	Zn2	0.60871(4)	0.39129(9)	-0.19563(6)	1.33333-y	2/3+x-y	-z
105	Zn2	0.60871(9)	1.21743(8)	-0.19563(6)	1/3-x+y	1.66667-x	-z
106	O3	0.5292(6)	0.7645(3)	0.2038(5)	-1/3+y	1/3+x	1/3-z
107	O3	0.2354(7)	0.4708(6)	0.2038(5)	2/3+x-y	1.33333-y	1/3-z
108	O3	0.2355(3)	0.7646(7)	0.2038(5)	2/3-x	1/3-x+y	1/3-z
109	O2	0.4887(4)	0.8046(4)	0.2444(3)	-1/3+y	1/3+x	1/3-z
110	O2	0.3160(6)	0.5113(4)	0.2444(3)	2/3+x-y	1.33333-y	1/3-z
111	O2	0.1954(4)	0.6840(6)	0.2444(3)	2/3-x	1/3-x+y	1/3-z
112	O2	0.1954(4)	0.5113(4)	0.2444(3)	2/3-x	1.33333-y	1/3-z
113	O2	0.4887(4)	0.6840(6)	0.2444(3)	-1/3+y	1/3-x+y	1/3-z
114	O2	0.3160(6)	0.8046(4)	0.2444(3)	2/3+x-y	1/3+x	1/3-z
115	O4	0.4487(6)	0.7243(3)	0.2841(4)	-1/3+y	1/3+x	1/3-z
116	O4	0.2757(7)	0.5513(6)	0.2841(4)	2/3+x-y	1.33333-y	1/3-z
117	O4	0.2757(3)	0.7243(7)	0.2841(4)	2/3-x	1/3-x+y	1/3-z

3.2 Synthesis of Li^+@Zn-MOF-Crown: The pre-activated Zn-MOF-Crown (50.0 mg) was immersed into LiCl solution (1 mM) in DEF/H_2O (100 mL, v/v = 50:1) with stirring at room temperature for overnight. The resulting precipitate was obtained by centrifugation and washed by DEF for three times. The concentration of LiCl in remaining solution was detected by inductively coupled plasma mass spectrometry (ICP-MS) analysis. The concentration of Li^+ drops down to 0.09 mM, indicating that the lithium ion sorption capacity of Zn-MOF-Crown was ~1.2 wt %.

Table S3. ICP-MS data of Li^+ before and after doping into Zn-MOF-Crown.

Concentration of Li^+ before doping (mM)	Concentration of Li^+ after doping (mM)	Li^+ ion captured per crown ether unit
1.00	9.00×10^{-2}	0.73
10.0	7.62	1.91

4. Characterizations for physical properties

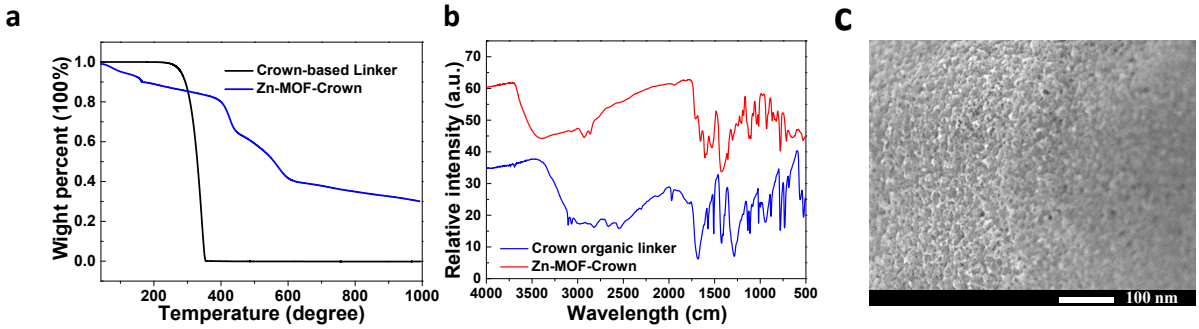


Figure S1. (a) Thermogravimetric analysis (TGA) curves and (b) FTIR spectra for crown ether-based organic linker and Zn-MOF-Crown; (c) SEM image of the Zn-MOF-Crown membrane coated for LIBs.

Table S4. Statistics for micropore and mesopore based on *t*-plot method.

Item	Micropore SA[a] ($m^2\ g^{-1}$)	External SA[a] ($m^2\ g^{-1}$)	Total Pore Volume[b] ($cc\ g^{-1}$)	Micropore Volume[a] ($cc\ g^{-1}$)
Zn-MOF-Crown	965.5	135.8	0.56	0.39
Li^+@Zn-MOF-Crown	764.6	129.0	0.49	0.31

The data were determined by N_2 adsorption/desorption isotherms at 77 K. [a] calculated by the *t*-plot method, where the contribution points are from 0.35 to 0.5 in P/P_0; [b] calculated by the point of the highest adsorption. SA = Surface Area.

5. Lithium ion battery

5.1 Battery fabrication

Standard CR2032-type coin cells were assembled in an argon-filled glovebox (Mbraun, Unilab, Germany) with Zn-MOF-Crown or Li^+@Zn-MOF-Crown based working electrode (with diameter of 12 mm). The average loading of MOF in each battery was ~1.7 mg, and the weight ratio of MOF, carbon black, and polyvinylidene fluoride binder was 80:10:10. For lithium ion battery fabrication, the metallic lithium foil was served as the counter electrode, 1 M $LiPF_6$ in ethylene carbonate (EC)−dimethyl carbonate (DME) (1:1 in volume) as the electrolyte, and a polypropylene (PP) film (Cellgard 2400) as the separator. The CV measurements were carried out using a Parstat-2273 electro-chemical potentiostat at a scanning rate of 0.2 mV/s. Galvanostatic charge−discharge cycles were tested by Neware battery tester at different current densities at room temperature.

5.2 Battery performance

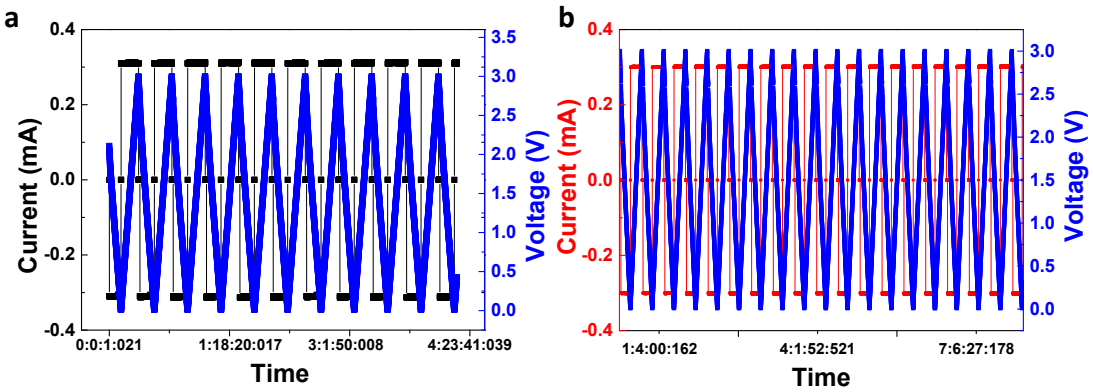


Figure S2. (a,b) Cycling performance of Li^+@Zn-MOF-Crown at 60 C for 50 cycles (1/3 C at first five cycles for activation).

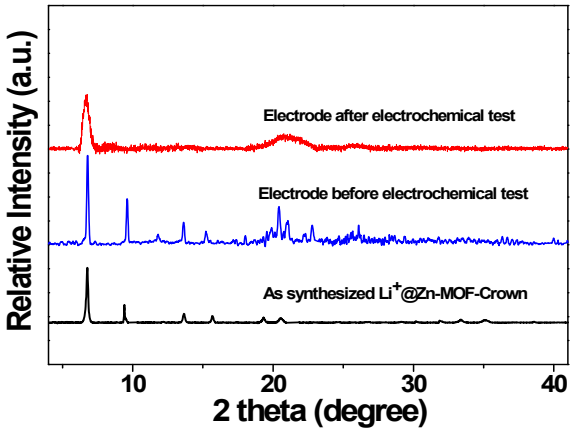


Figure S3. Powder X-ray diffraction (PXRD) patterns of Li^+@Zn-MOF-Crown (black), Li^+@Zn-MOF-Crown based electrodes before (blue) and after (red) electrochemical test. The samples after electrochemical test were dried under vacuum in the freeze dryer for 12 hours before the PXRD measurements. While some peaks from the MOF disappeared after the electrochemical test, the strongest peak was still remained, indicating that the MOF did not lose its long-range order during the charge-discharge process.

6. Comparison with literature reports

Table S5. MOFs or MOF-derived materials for LIBs.

Item	CC/DC (mAh g^{-1})	RC (mAh g^{-1})	Cycle number	Ref.
MIL-53	70/80	71	50	[S4]
MIL-177	110/425	—	2	[S5]
$Zn_3(HCOO)_6$	693/1344	560	30	[S6]
$Co_3(HCOO)_6$	870/1720	390	60	[S7]
$Zn_{1.5}$ $Co_{1.5}(HCOO)_6$	930/1570	450	60	[S8]
Mn-LCP	610/1870	390	5	[S9]
$Co_2(OH)_2BDC$	1005/1385	650	50	[S10]

CC: Charge capacity, DC: discharge capacity, RC: reversible capacity.

References

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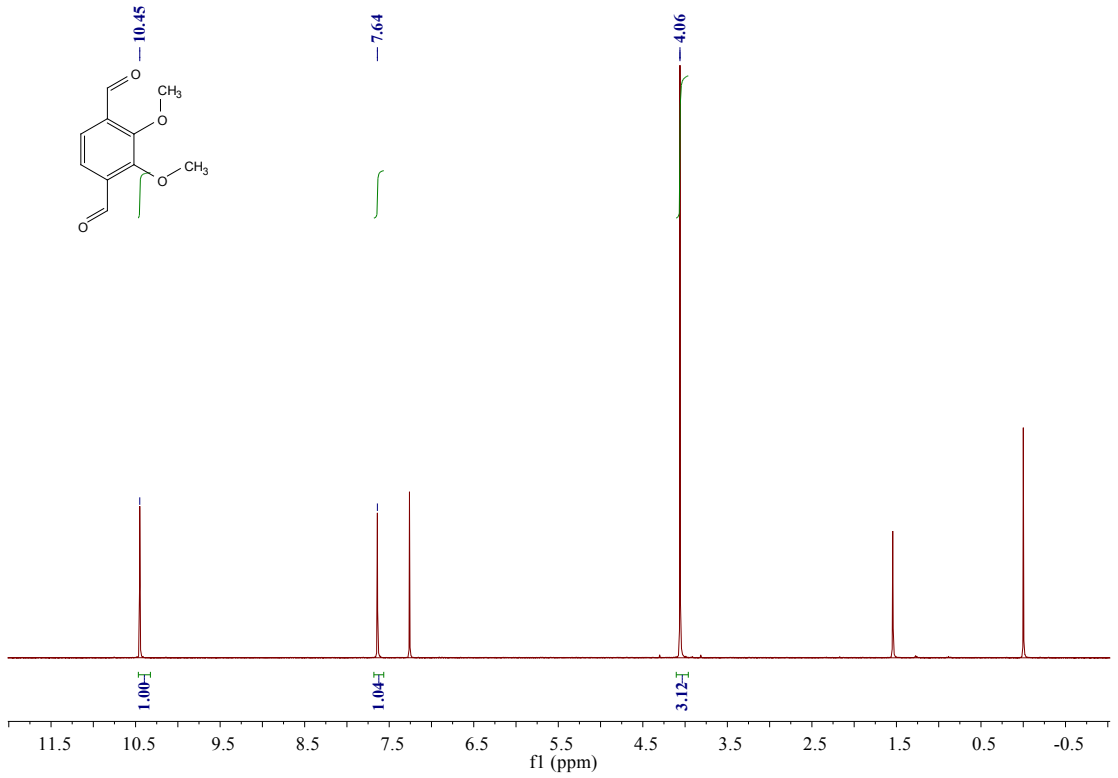
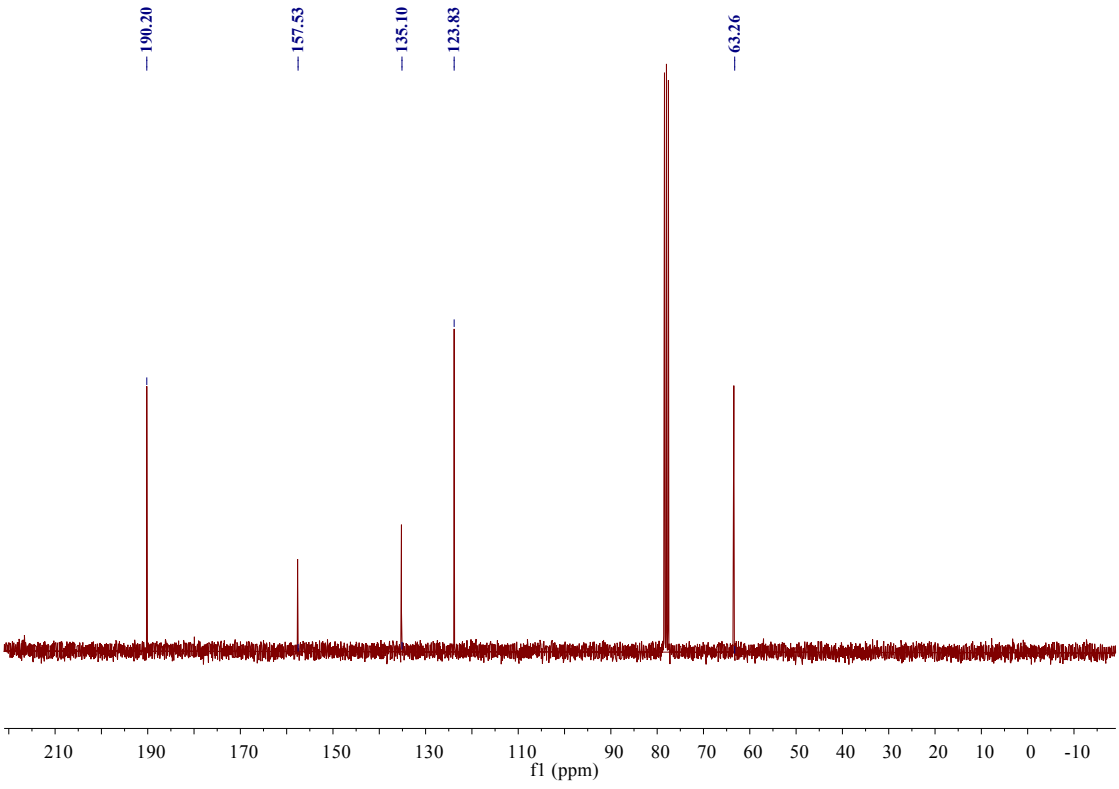
Appendix

1. Compound A (NMR and MS spectra)





Elemental Composition Report

Single Mass Analysis
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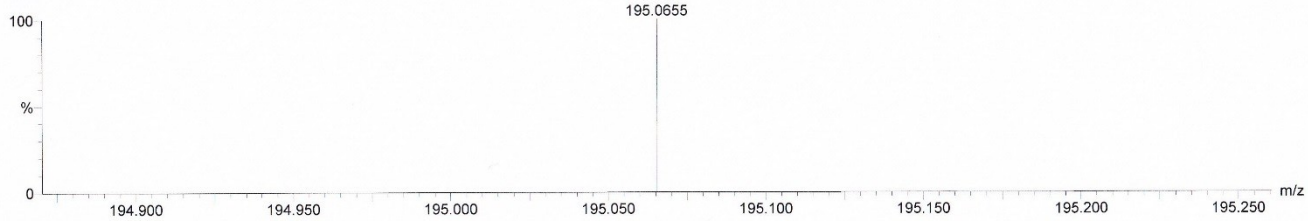
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

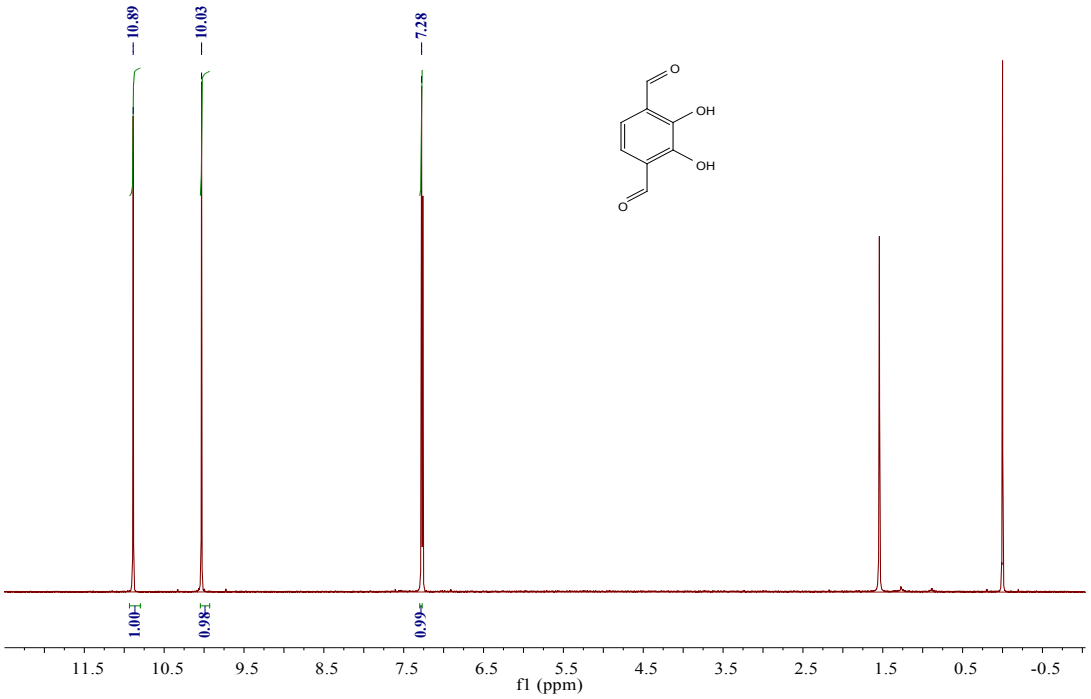
Monoisotopic Mass, Even Electron Ions
4 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-10 H: 0-11 O: 0-4
C10H10O4
LINYI-1 405 (8.856)

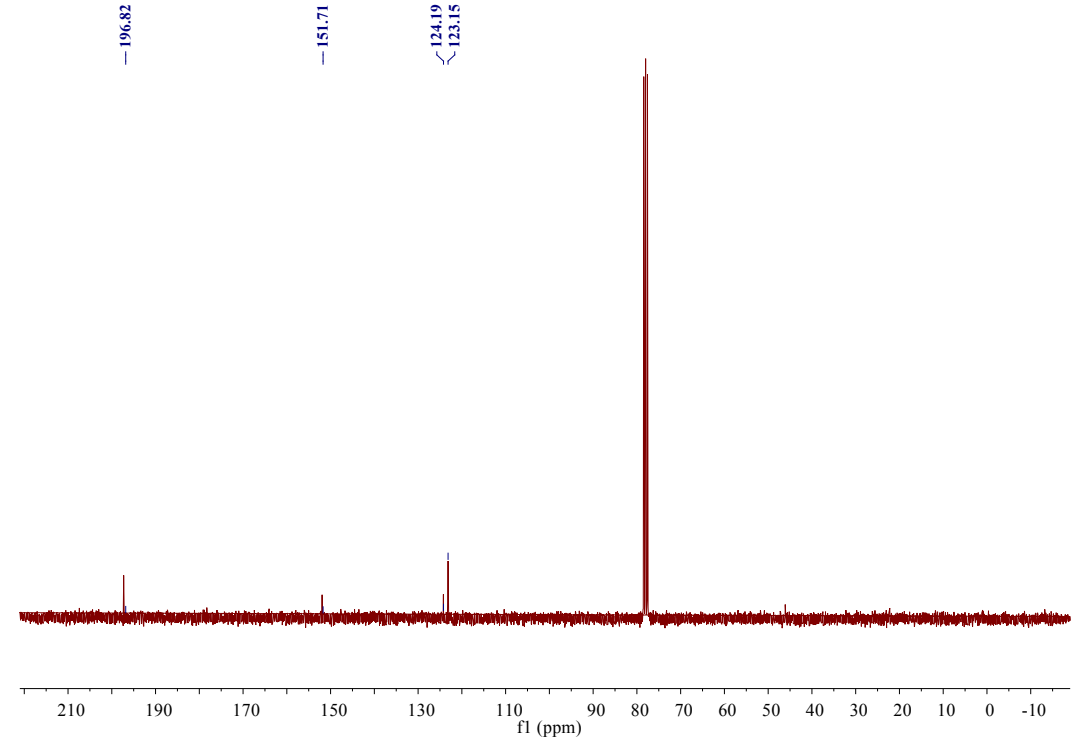
1: TOF MS ES+
1.01e+000



Minimum:				-1.5			
Maximum:		5.0	100.0	50.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
195.0655	195.0657	-0.2	-1.0	5.5	10.4	0.0	C10 H11 O4

2. Compound B (NMR and MS spectra)





Elemental Composition Report

Single Mass Analysis
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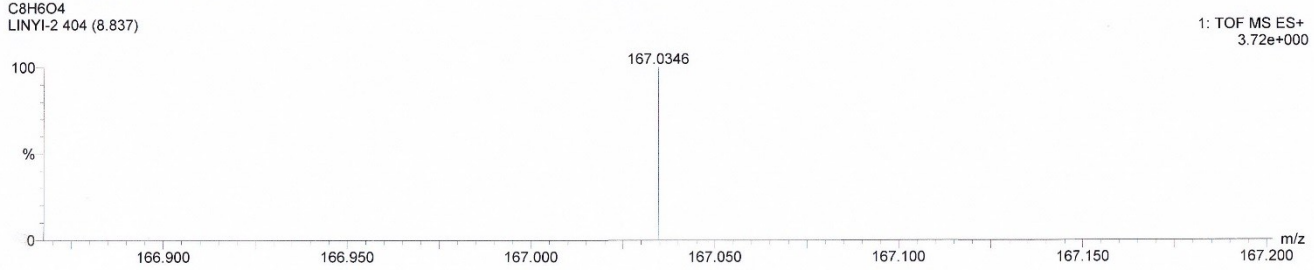
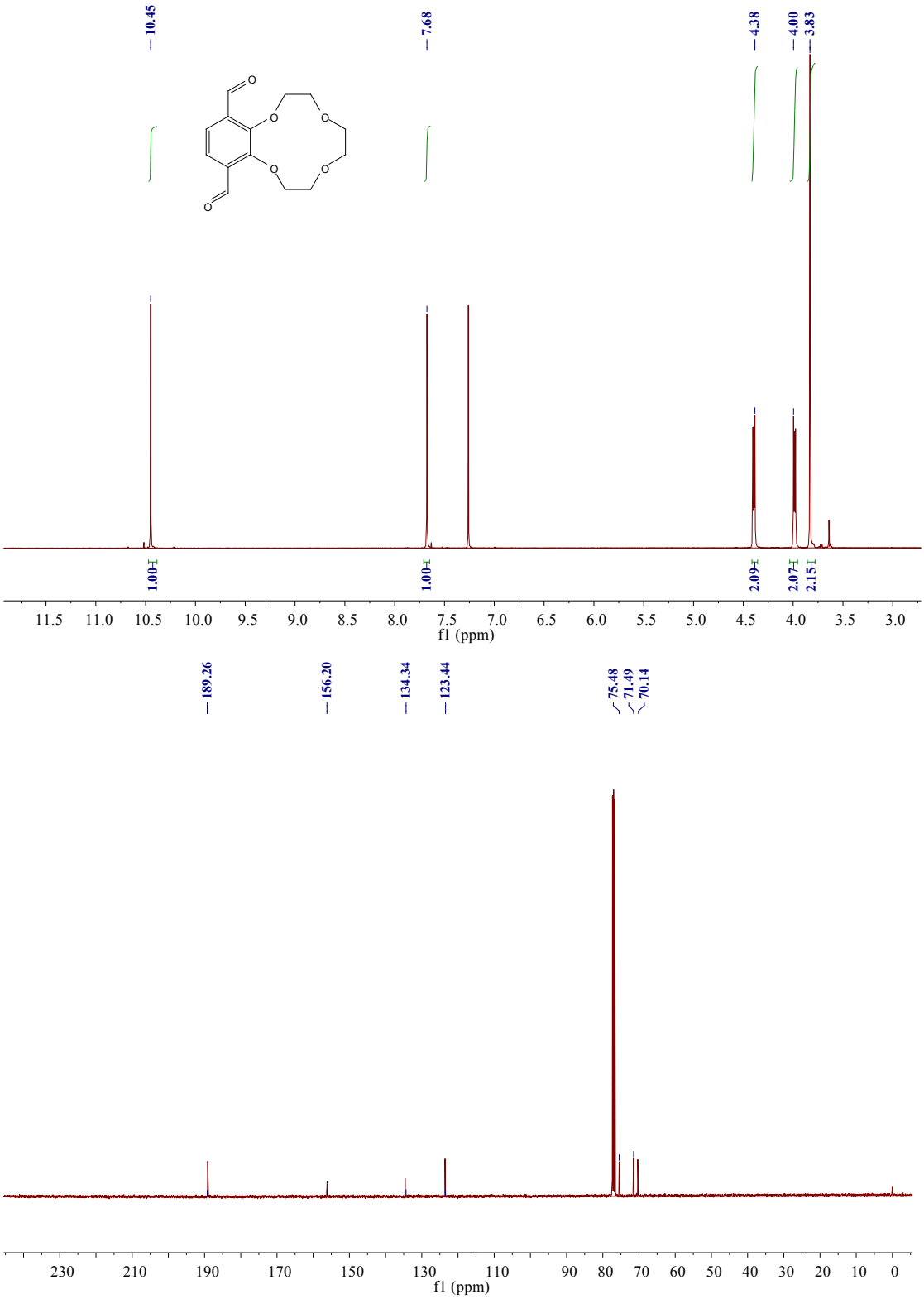
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
4 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-10 H: 0-11 O: 0-4
C8H6O4
LINYI-2 404 (8.837)



Minimum:				-1.5			
Maximum:		5.0	100.0	50.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
167.0346	167.0344	0.2	1.2	5.5	9.9	0.0	C8 H7 O4

3. Compound C (NMR and MS spectra)



Elemental Composition Report **Page 1**

Single Mass Analysis
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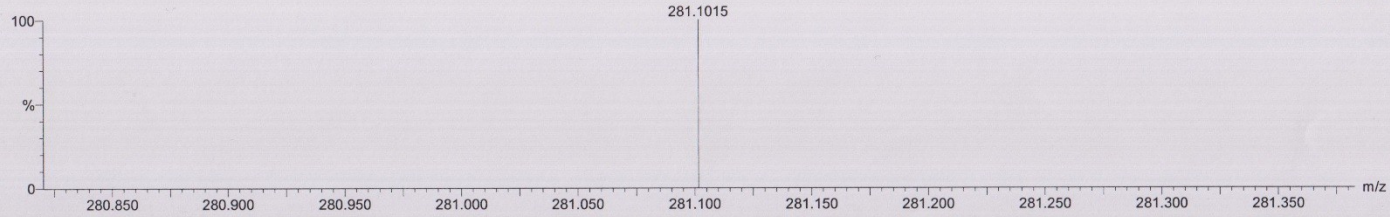
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

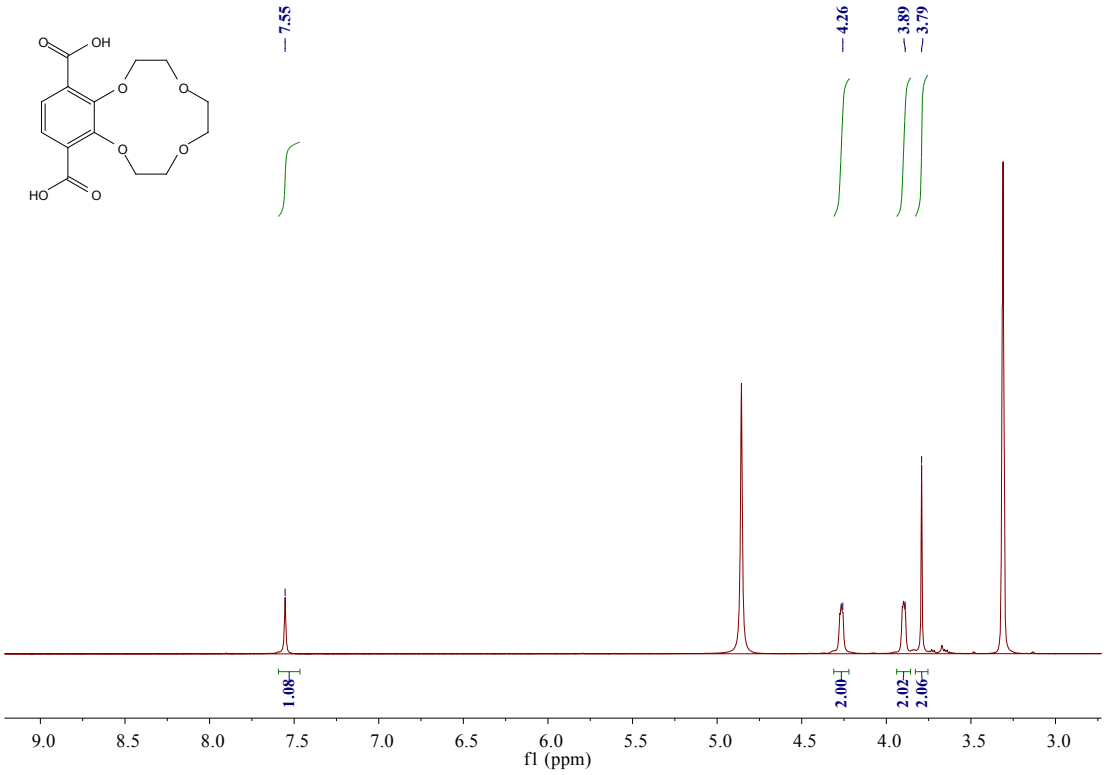
Monoisotopic Mass, Even Electron Ions
11 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-20 H: 0-20 O: 0-8
C18H17NO
BLY-1 4 (0.101) Cm (4:13)

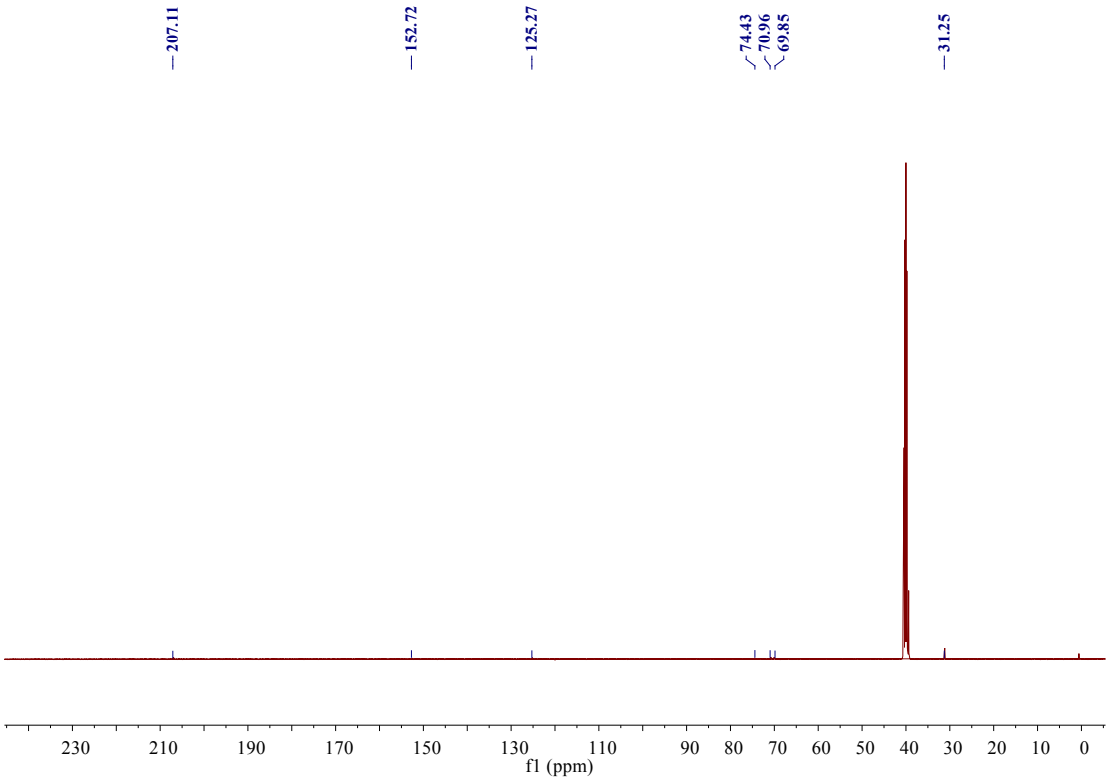
1: TOF MS ES+
1.61e+002



Minimum:				-1.5			
Maximum:		100.0	15.0	50.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
281.1015	281.1025	-1.0	-3.6	6.5	18.5	0.0	C14 H17 O6

4. Compound D (NMR and MS spectra)





Elemental Composition Report **Page 1**

Single Mass Analysis
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Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
10 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
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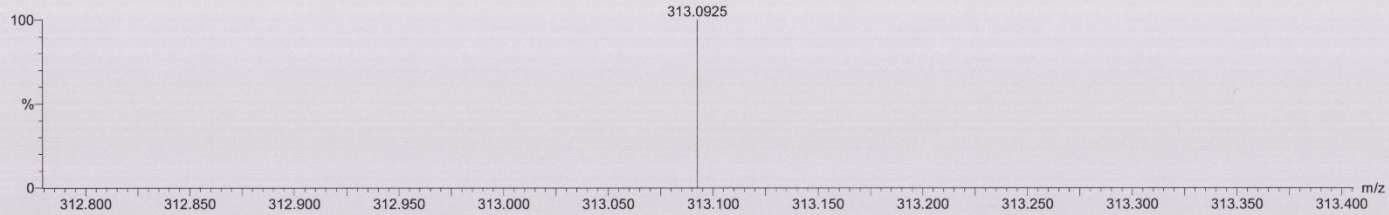
C14H16O8
BLY-2 6 (0.139)

1: TOF MS ES+
4.05e+000



Minimum:				-1.5			
Maximum:		100.0	15.0	50.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
313.0925	313.0923	0.2	0.6	6.5	11.5	0.0	C14 H17 O8