Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Electronic Supplementary Information

Readily Usable Bulk Phenoxazine-Based Covalent Organic Framework Cathode Materials with Superior Kinetics and High Redox Potentials

Zhiying Meng,[a] Ying Zhang,[b] Mengqing Dong,[a] Yue Zhang,[a] Fengmin Cui,[a] Teck-Peng Loh,[ac] Yinghua Jin,[d] Wei Zhang,[d] Haishen Yang*[b] and Ya Du*[a]

a. Institute of Advanced Synthesis, School of Chemistry and Molecular Engineering, Nanjing Tech University, Nanjing 211816, China. E-mail: teckpeng@njtech.edu.cn; ias_ydu@njtech.edu.cn

b. Shanghai Key Laboratory of Materials Protection and Advanced Materials in Electric Power, Shanghai University of Electric Power, Shanghai 200090, China. E-mail: yanghsh@shiep.edu.cn

c. Division of Chemistry and Biological Chemistry, School of Physical and Mathematical Sciences, Nanyang Technological University, Singapore 637616, Singapore

d. Department of Chemistry, University of Colorado, Boulder, CO 80309, USA

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Section A COF-based electrode in relevant literature reports

Table S1. COF-based electrode electrochemical performance

Active Material	**Initial Discharge Capacity (mAh/g)**	**Potential vs. Li/Li$^+$**	**Ref.**
DAAQ-ECOF	145 (20 mA/g)	2.48 V	[1]
DABQ-TFP-COF	210 (20 mA/g)	~ 2.7 V	[1]
TEMPO-ECOF	~110 (20 mA/g)	3.6 V	[1]
Tb-DANT-COF	93.4 (1.5 C)	~ 2.5 V	[2]
Cz-COF1/Cz-COF2	310~400 (200 mA/g)	0.1- 0.5 V	[3]
DTP-ANDI-COF@CNT	68 (200 mA/g)	2.48 V	[4]
N2-COF/N3-COF	735/731 (1 A/g)	1.35 V/1.45 V	[5]
DAPO-TFB-COF/ DAPO-TpOMe-COF	64/80 (100 mA/g)	3.6 V/3.8V	This work

Section B Materials and methods

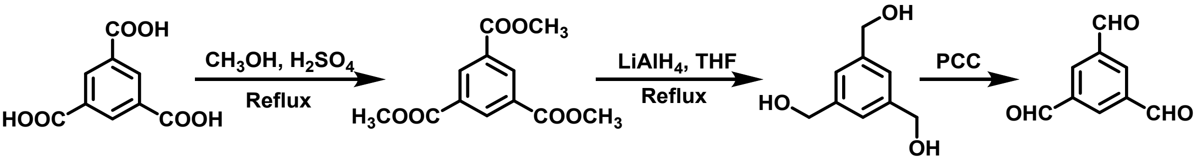
Chemicals were obtained from Energy Chemical or Aladdin, and used without further purification unless otherwise noted. The solvents were dried and distilled according to conventional procedures.

^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ or DMSO-d_6 on Bruker Avance or Jeol 400 MHz spectrometers. Melting points were recorded in degrees Celsius using a INESA SGW-X4B melting point apparatus. HRMS-ESI were recorded on XEVO G2-XS QTOF (Waters Corporation). Fourier transform infrared (FT-IR) spectra were obtained with KBr plates by using a IS10 FT-IR Spectrometer (ThermoFisher Corporation). Solid-state ^{13}C CP/MAS NMR spectra were recorded on a Bruker AvanceIII-400 MHz spectrometer. Powder X-ray diffraction (PXRD) patterns were carried out with PANalytical X'Pert Powder system and Rigaku SmartLab 3kW. Conductivity were recorded by a high resistance instrument with four-terminal method ST2722-SD and ST2643. Nitrogen gas adsorption experiments were performed on a Quantachrome Autosorb-iQ3 automatic volumetric instrument. The sizes and morphologies of the products were observed by a Quanta 250 FEG Scanning Transmission Electron Microscopy operated at 15 kV. The samples were sputtered with Au (nano-sized film) prior to imaging. Transmission electron microscope (TEM) samples were examined by using a JEM-ARM200F and JEOL 1400Plus operating at 200 kV. Thermogravimetric analyses (TGA) were carried out on a STA449 analyzer (Netzsch Corporation) under N_2 atmosphere at a heating rate of 10 ºC/min within a temperature range of 30-800 °C. Elemental analysis (EA) were recorded on vario EL cube (Elementar Corporation).

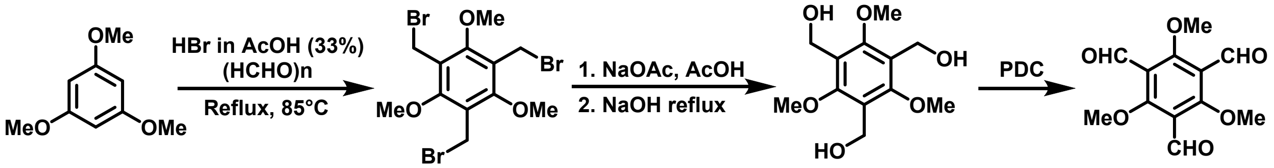
Section C Synthetic procedure

1,3,5-Triformylbenzene (TFB)[6] and 2,4,6-trimethoxy-1,3,5-triformylbenzene (TpOMe)[7] were synthesized according to the reported procedures. Their ^{1}H NMR spectra match well with those reported previously.

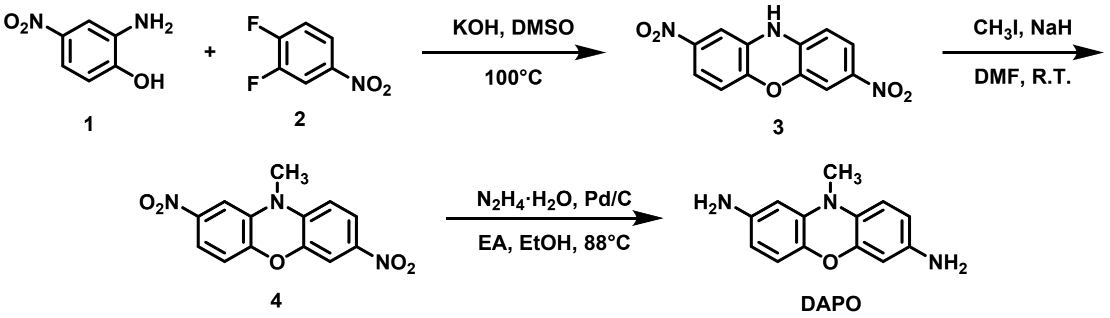
Synthesis of 1,3,5-triformylbenzene (TFB)[6]



Synthesis of 2,4,6-trimethoxy-1,3,5-triformylbenzene (TpOMe)[7]



Synthesis of 2,7-diamine-10-methyl-phenoxazine (DAPO)



Synthesis of 2,7-dinitro-10H-phenoxazine (3)[8]*:* A mixture of 2-amino-4-nitrophenol **1** (1.54 g, 10 mmol), KOH (1.18 g, 21 mmol) and DMSO (50 mL) was charged in a 250 mL three-necked flask under nitrogen atmosphere, then 3,4-difluoronitrobenzene **2** (1.1 mL, 1.59 g, 10 mmol) was added dropwise to the reaction mixture, and was stirred at 100 °C for 1 day. After the completion of the reaction, water (100 mL) was added to the reaction mixture with stirring. The red precipitate was filtered and collected. The crude product was refluxed in chloroform, then filtered to collect the dark red solid (2.31 g, 85%). M.p. >300 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ *ppm* 9.74 (s, 1H), 7.74 (dd, J = 8.8, 2.5 Hz, 1H), 7.58 (dd, J = 8.8, 2.7 Hz, 1H), 7.42 (d, J = 2.5 Hz, 1H), 7.25 (d, J = 2.7 Hz, 1H), 6.85 (d, J = 8.8 Hz, 1H), 6.56 (d, J = 8.8 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ *ppm* 147.88, 143.82, 141.53, 140.25, 137.98, 130.95, 122.55, 118.75, 115.69, 112.71, 110.65, 108.38. HRMS (ESI) *m*/*z*: $[M + H]^+$ calcd for $C_{12}H_8N_3O_5$, 274.0464; found, 274.0474.

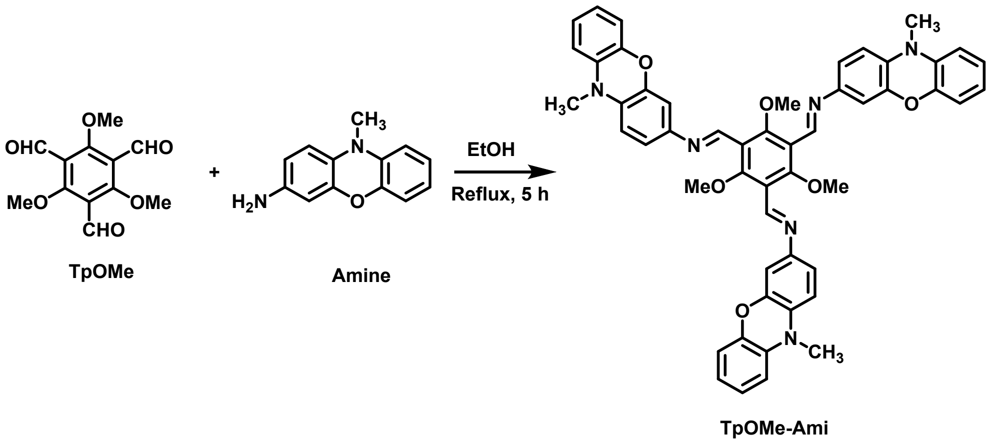
Synthesis of 10-methyl-2,7-dinitro-phenoxazine (4)[9]*:* A solution of 2,7-dinitro-10*H*- phenoxazine **3** (2.73 g, 10 mmol) in DMF (60 mL) with CH_3I (1.22 mL, 2.8 g, 20 mmol) and NaH (0.36 g, 15 mmol) was stirred at room temperature for 20 h. The water was added to the reaction mixture with stirring, then the orange color solids precipitated and which was filtered and washed by water. The solids were dried under reduced pressure to give the pure product as orange color solid (2.71 g, 94%). M.p. 268.3-268.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ *ppm* 7.86 (dd, *J* = 8.8, 2.5 Hz, 1H), 7.74 (dd, *J* = 8.9, 2.5 Hz, 1H), 7.56 (d, *J* = 2.5 Hz, 1H), 7.44 (d, *J* = 2.5 Hz, 1H), 6.78 (d, *J* = 8.7 Hz, 1H), 6.59 (d, *J* = 9.0 Hz, 1H), 3.20 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ *ppm* 148.86, 144.15, 142.71, 140.66, 139.07, 132.91, 121.57, 118.82, 115.11, 111.85, 109.73, 107.51, 31.52. HRMS (ESI) *m/z*: $[M + H]^+$ calcd for $C_{13}H_{10}N_3O_5$, 288.0620; found, 288.0627.

Synthesis of 2,7-diamine-10-methyl-phenoxazine (DAPO): The reaction is carried out in an autoclave. 10-methyl-2,7-dinitro-phenoxazine **4** (861 mg, 3 mmol) was dissolved in 10 mL EA and 30 mL EtOH, then Pd/C (70.9 mg, 0.3 mmol) and $N_2H_4 \cdot H_2O$ (5.15 mL, 5.3 g, 90 mmol) was added. The reaction was heated at 88 °C for 48 hours. After the complete reaction, the mixture was filtered on celite and washed with ethyl acetate. The filtered solution was concentrated under reduced pressure. The crude product was subjected to silica gel column chromatography with ethyl acetate/petroleum ether (1:2) as the eluent under nitrogen atmosphere to give the pure product (423.2 mg, 62%). M.p. 155.6-155.9 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ *ppm* 6.40 (dd, *J* = 8.4, 4.4 Hz, 1H), 6.39 (d, *J* = 4.3 Hz, 1H), 6.08 (dd, *J* = 8.3, 2.4 Hz, 1H), 6.03 (d, *J* = 2.4 Hz, 1H), 5.94 (d, *J* = 2.4 Hz, 1H), 5.83 (dd, *J* = 8.2, 2.3 Hz, 1H), 4.64 (d, *J* = 10.6 Hz, 2H), 2.89 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ *ppm* 145.88, 145.10, 143.21, 135.81, 135.28, 124.56, 114.95, 112.36, 107.88, 103.95, 102.24, 98.31, 30.70. HRMS (ESI) *m/z*: $[M + H]^+$ calcd for $C_{13}H_{14}N_3O$, 228.1137; found, 228.1135.

Synthesis of DAPO-TFB-COF: 1,3,5-Triformylbenzene (TFB) (48.6 mg), and 2,7-diamine-10-methyl-phenoxazine (DAPO) (102.1 mg) were dispersed in 2.0 mL mixed solution of acetonitrile and mesitylene (1:1, volume ratio). A volume of 0.6 mL of 3.0 mol/L aqueous acetic acid was then added into the suspension. The tube was degassed by three freeze-pump-thaw cycles. The reaction mixture was heated at 120°C for 3 days to obtain orange powders. The resulting powders were washed with DMF and THF, then dried at 85 °C for 12 h to afford DAPO-TFB-COF powders (132.3 mg, 98%).

Synthesis of DAPO-TpOMe–COF: 2,4,6-Trimethoxy-1,3,5-triformylbenzene (TpOMe) (37.8 mg), and 2,7-diamine-10-methyl-phenoxazine (DAPO) (51.1 mg) were dispersed in 3.0 mL mixed solution of *o*-dichlorobenzene and *n*-butanol (1:1, volume ratio). A volume of 0.6 mL of 3.0 mol/L aqueous acetic acid was then added into the suspension. The following synthesis and post-processing methods are consistent with DAPO-TFB-COF (79.8 mg, 99%).

Synthesis of TpOMe-Ami (reference compound):



Synthesis of TpOMe-Ami (reference compound): This reference compound was synthesized by the reaction between 2,4,6-trimethoxy-1,3,5-triformylbenzene (TpOMe) (25.2 mg, 0.1 mmol) and 10-methyl-phenoxazine-3-amine (Ami) (63.7 mg, 0.3 mmol), in 5 mL ethanol, under refluxing condition for 5 hours. Later, the solution was cooled to room temperature. The insoluble precipitate was collected by filtration and washed with ethanol. The solids were dried under reduced pressure to give the product as yellow solid. (80.5 mg, 96%) ^{1}H NMR (400 MHz, DMSO-d_6) δ *ppm* 8.69 (s, 3H), 6.93–6.87 (m, 6H), 6.81–6.70 (m, 15H), 3.88 (s, 9H), 3.08 (s, 9H). ^{13}C NMR (100 MHz, DMSO-d_6) δ *ppm* 161.77, 151.94, 145.29, 145.07, 144.22, 134.19, 133.28, 124.31, 121.07, 120.92, 117.51, 114.98, 112.28, 112.19, 107.33, 63.42, 30.94.

Section D Electrochemical measurements

All the electrochemical tests were performed in 2016 coin-type cells. The working electrodes were prepared by mixing 60 wt% as-prepared COFs (0.6 mg ~ 1.0 mg), 30 wt% acetylene black, 10 wt% PVDF binder in N-methyl pyrrolidone (NMP) coated on Al foil, and then dried at 80 °C for 12 h. The dried electrode was cut into a round shape with a diameter of 12 mm as cathode, lithium foil as the anode, Celgard 2400 as the separator, and 1 M $LiPF_6$ dissolved in ethylene carbonate (EC) and dimethyl carbonate (DMC) (EC/DMC = 1:1 v/v) as the electrolyte and assembled in an argon-filled glove box. The charge-discharge measurements were carried out on a NEWARE using the potential window of 1.5-4.2 V vs. Li/Li$^+$. Electrochemical Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) measurements were both conducted on a Corrtest CS350 in COM54 electrochemical workstation using the coin cells. The range voltage of CV test was 1.5-4.2V at 1 mV/s scan rates. For EIS tests, the voltage amplitude was 10 mV and the range of frequency was 100000 Hz–0.01 Hz. All the electrochemical tests were performed at room temperature.

Section E Supporting figures

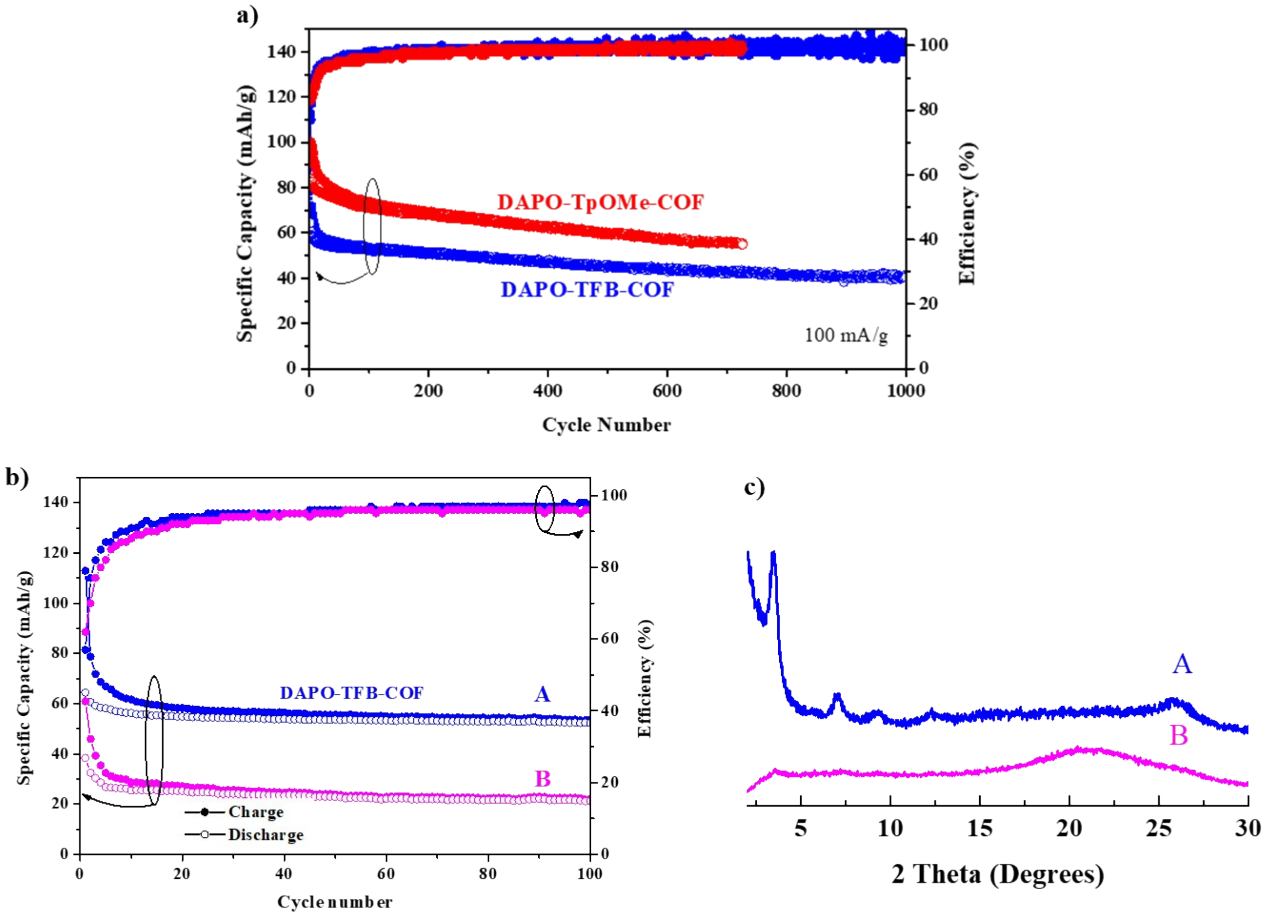


Figure S1. a) Cycle performance of DAPO-TFB-COF and DAPO-TpOMe-COF. b) Cycle stability of DAPO-TFB-COF samples from two different batches of A and B; c) The crystallinity of two different batches of DAPO-TFB-COF samples A and B.

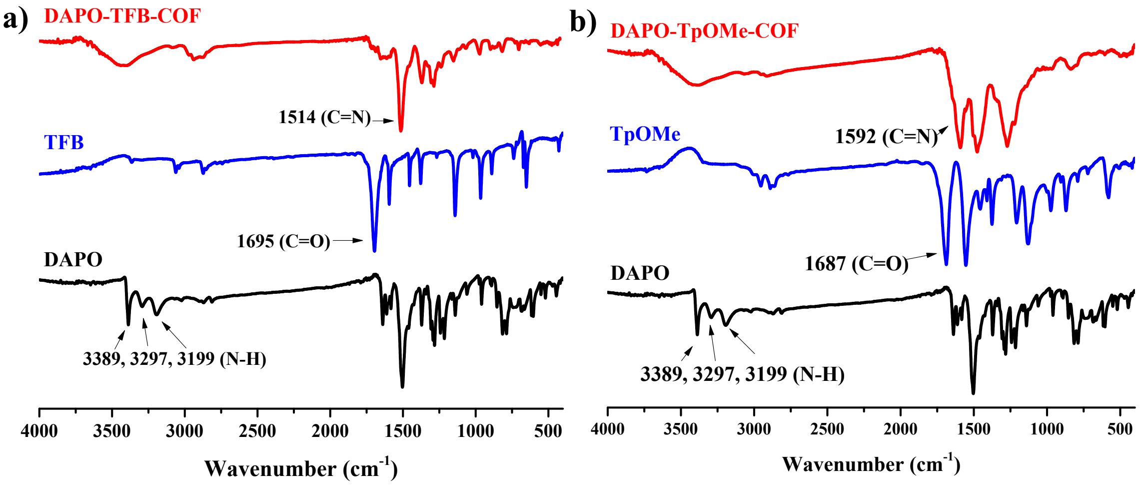


Figure S2. a) FT-IR spectra of DAPO-TFB-COF compared with the starting materials; b) FT-IR spectra of DAPO-TpOMe-COF compared with the starting materials

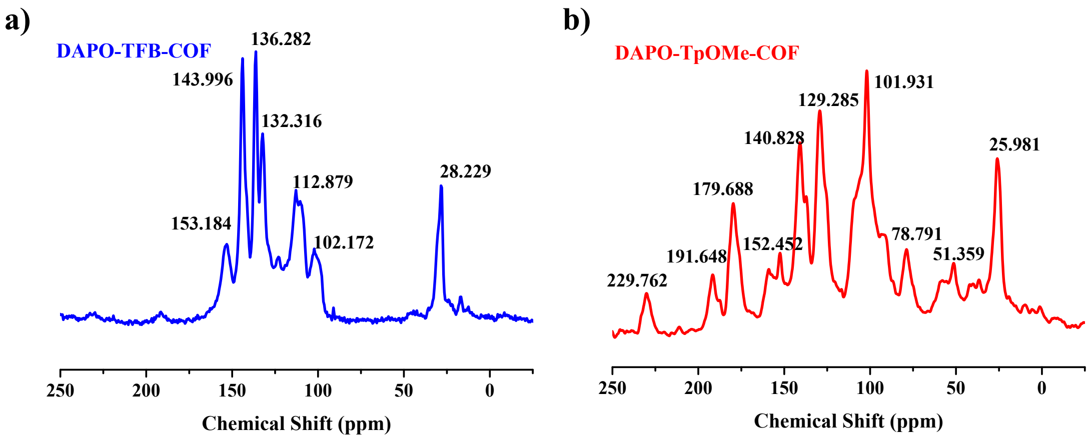


Figure S3. a) Solid-state ^{13}C NMR spectra of DAPO-TFB-COF; b) Solid-state ^{13}C NMR spectra of DAPO-TpOMe-COF.

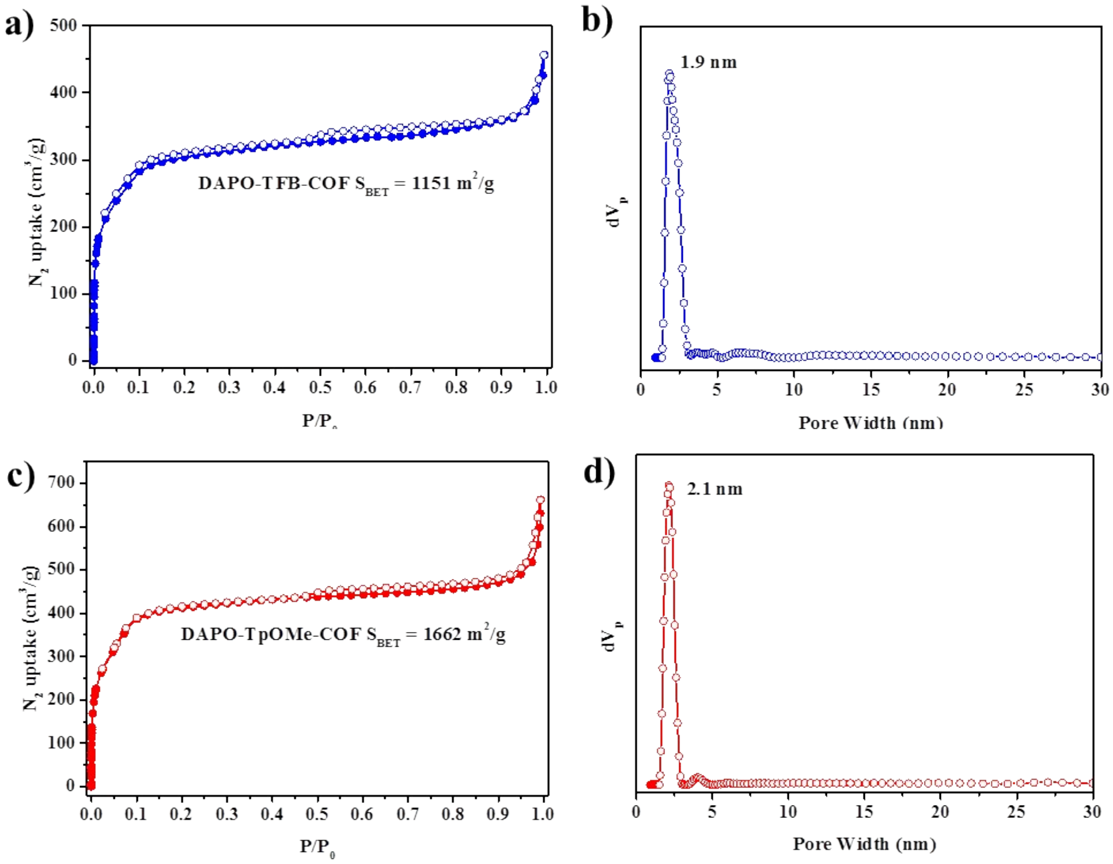


Figure S4. a) Nitrogen adsorption–desorption isotherms and b) QSDFT pore size distributions of DAPO-TFB-COF; c) Nitrogen adsorption–desorption isotherms and d) QSDFT pore size distributions of DAPO-TpOMe-COF.

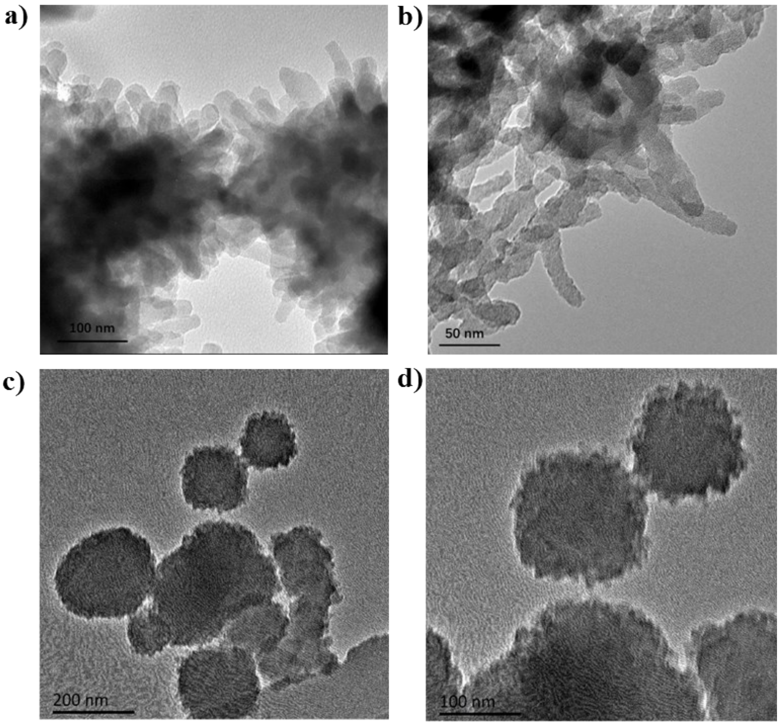


Figure S5. a, b) TEM images of DAPO-TFB-COF; c, d) TEM images of DAPO-TpOMe- COF.

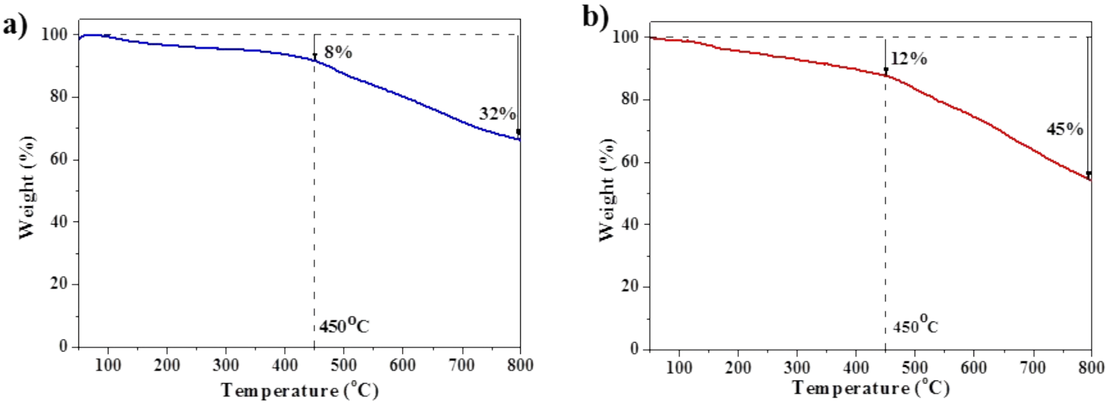


Figure S6. Thermogravimetric analysis of DAPO-TFB-COF (a) and DAPO-TpOMe-COF (b) under a nitrogen atmosphere with a heating rate of 10 °C/min.

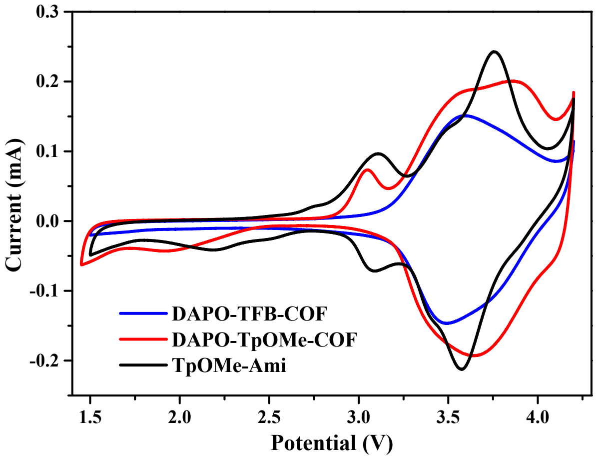


Figure S7. CV curve of DAPO-COFs and reference compound (with a scan rate of 1 mV/s)

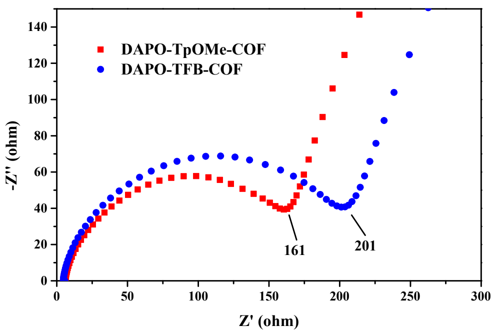


Figure S8. EIS in the form of a Nyquist plot.

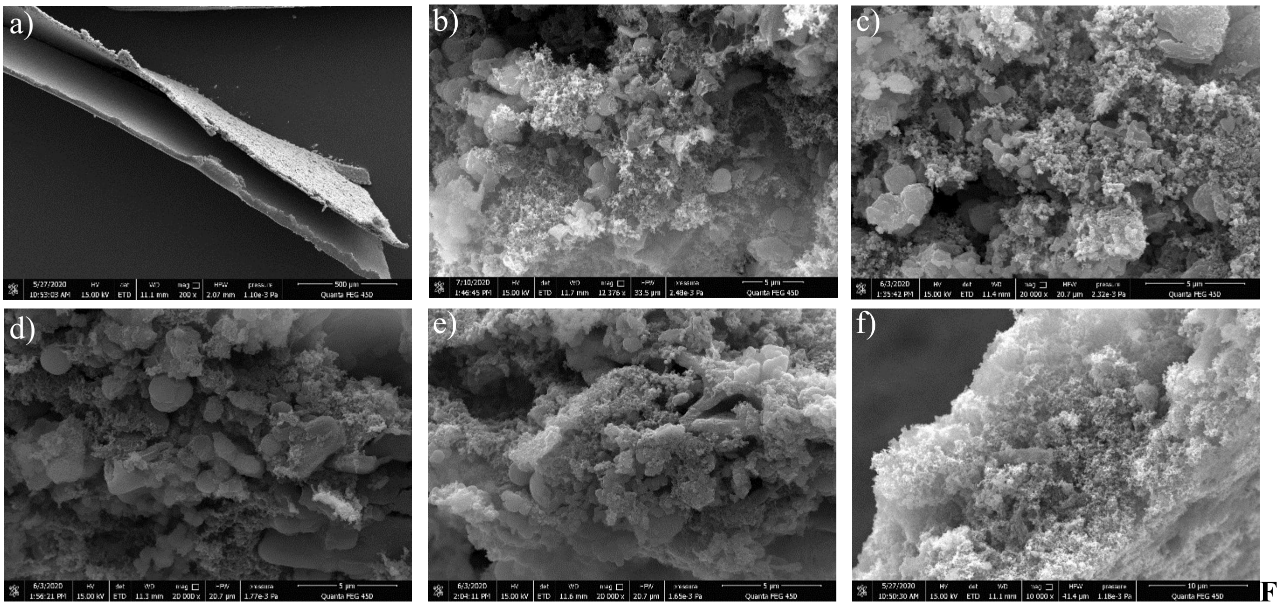


Figure S9. SEM images of section of cathodes with different magnifications before cycling（a-b） and after 5, 10, 50, 1000 cycling (c-f) of DAPO-TFB-COF, respectively

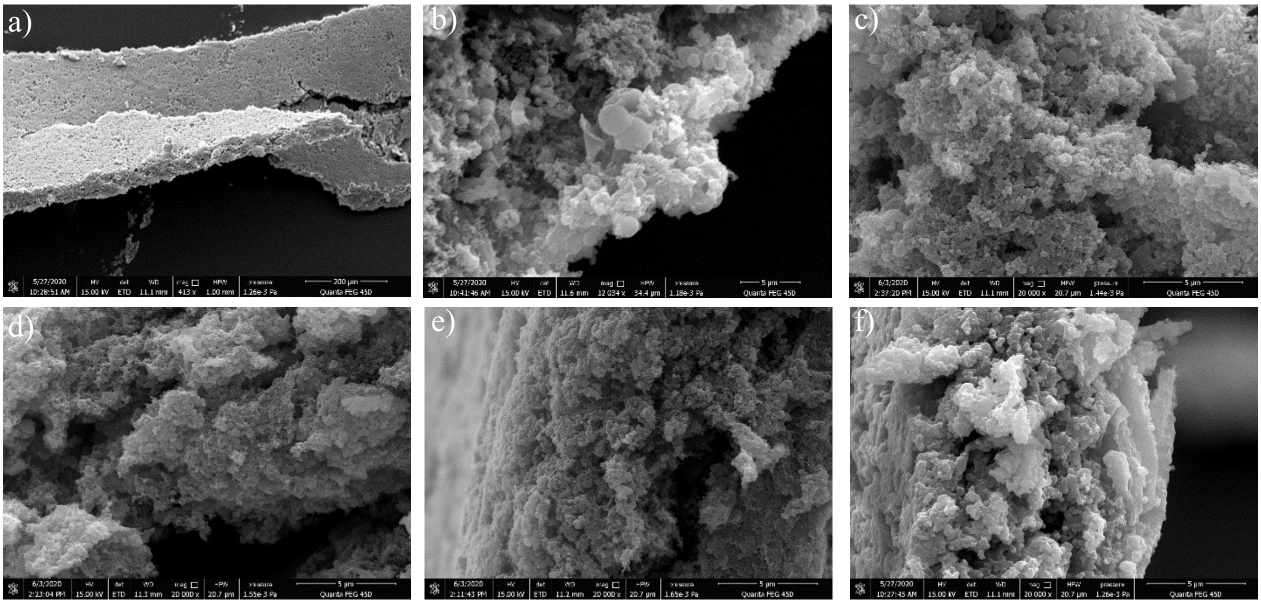


Figure S10. SEM images of section of cathodes with different magnifications before cycling（a-b） and after 5, 10, 50, 1000 cycling (c-f) of DAPO-TpOMe-COF, respectively.

Section F Supporting tables

Table S2. Fractional atomic coordinates for the unit cell of DAPO-TFB-COF with AA stacking.

P6/*m*							
a = b = 29.83 Å, c = 3.92 Å; α = β = 90 °, γ = 120 °							
Atom	***x***	***y***	***z***	**Atom**	***x***	***y***	***z***
H1	0.25542	0.77087	0.00000	C16	1.36075	-4.54033	0.00000
H2	0.45562	0.28758	0.00000	C17	1.41651	-4.40126	0.00000
H3	0.60510	0.13783	0.00000	C18	1.36075	-4.37339	0.00000
H4	0.60500	0.28759	0.00000	C19	1.44400	-4.37343	0.00000
H5	0.52175	0.37077	0.00000	C20	1.41651	-4.31812	0.00000
H6	0.45562	0.20416	0.00000	C21	1.36075	-4.29025	0.00000
H7	0.68835	0.13812	0.00000	C22	1.33287	-4.31788	0.00000
H8	0.48815	0.43817	0.00000	C23	1.49977	-4.48477	0.00000
H9	0.28872	0.53767	0.00000	C24	1.19424	-5.04008	0.00000
H10	0.33864	0.43764	0.00000	C25	1.16636	-5.06805	0.00000
H11	0.48815	0.60464	0.00000	C26	1.19424	-5.12355	0.00000
H12	0.43872	0.70381	0.00000	C27	1.24961	-5.15123	0.00000
H13	0.28872	0.70428	0.00000	C28	1.27749	-5.12359	0.00000
H14	0.51448	0.51720	-0.25954	C29	1.24961	-5.06775	0.00000
H15	0.51448	0.47307	0.06954	C30	1.27749	-5.04012	0.00000
H16	0.51448	0.53335	0.19000	C31	1.11059	-5.04017	0.00000
H17	0.35494	-0.02879	0.00000	C32	1.27749	-4.95698	0.00000
H18	0.25542	0.17062	0.00000	C33	1.33287	-4.98466	0.00000
H19	0.20547	0.12102	0.00000	C34	1.36075	-4.95669	0.00000
H20	0.52184	-0.02873	0.00000	C35	1.33287	-4.90119	0.00000
H21	0.57179	0.02087	0.00000	C36	1.27749	-4.87351	0.00000
H22	0.42193	0.17087	0.00000	C37	1.24961	-4.90114	0.00000
H23	1.02180	0.03764	0.00000	C38	1.44400	-4.95673	0.00000
H24	0.85516	0.20413	0.00000	C39	1.41651	-4.90142	0.00000
H25	0.75534	0.25397	0.00000	C40	1.49977	-4.98461	0.00000
H26	0.75521	0.10478	0.00000	C41	1.52765	-4.95697	0.00000
H27	0.95380	0.13165	-0.26824	C42	1.49977	-4.90113	0.00000
H28	0.98177	0.10360	0.14767	C43	1.44400	-4.87326	0.00000
H29	0.91954	0.16599	0.12058	C44	1.44400	-5.04021	0.00000
H30	0.17213	1.00405	0.00000	C45	2.02757	-5.04023	0.00000
H31	0.17226	0.85429	0.00000	C46	1.99969	-4.98439	0.00000
H32	0.32164	0.85425	0.00000	C47	1.94431	-4.95671	0.00000
H33	0.32164	0.93772	0.00000	C48	1.91643	-4.98468	0.00000
H34	0.08852	1.00395	0.00000	C49	1.94431	-5.04019	0.00000
H35	0.44893	0.94510	-0.26814	C50	1.99969	-5.06786	0.00000
H36	0.42117	0.94533	0.14915	C51	1.86106	-4.87353	0.00000
H37	0.48372	0.94482	0.11899	C52	1.83318	-4.90117	0.00000
H38	0.92234	0.93766	0.00000	C53	1.83318	-4.81803	0.00000

H39	1.02176	0.88801	0.00000	C54	1.77742	-4.79016	0.00000
C1	1.27749	-4.20707	0.00000	C55	1.74992	-4.81798	0.00000
C2	1.49977	-4.73452	0.00000	C56	1.77742	-4.87329	0.00000
C3	1.52765	-4.79036	0.00000	C57	1.94431	-4.87358	0.00000
C4	1.58302	-4.81804	0.00000	N1	1.69416	-4.79011	0.00000
C5	1.61090	-4.79007	0.00000	N2	1.44400	-4.62351	0.00000
C6	1.58302	-4.73457	0.00000	N3	1.44400	-4.45690	0.00000
C7	1.52765	-4.70689	0.00000	N4	1.33287	-4.23474	0.00000
C8	1.49977	-4.65138	0.00000	N5	1.24961	-4.98462	0.00000
C9	1.49977	-4.81799	0.00000	N6	1.41651	-4.98456	0.00000
C10	1.66628	-4.81775	0.00000	N7	1.52765	-4.87350	0.00000
C11	1.41651	-4.56820	0.00000	N8	2.08333	-5.06810	0.00000
C12	1.44400	-4.54004	0.00000	N9	1.91643	-4.90121	0.00000
C13	1.41651	-4.48473	0.00000	O1	1.33287	-4.40135	0.00000
C14	1.36075	-4.45686	0.00000	O2	1.36075	-4.87355	0.00000
C15	1.33287	-4.48449	0.00000	O3	1.86106	-4.95700	0.00000

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

P6/m							
a = b = 29.88 Å, c = 3.92 Å; α = β = 90 °, γ = 120 °							
Atom	***x***	***y***	***z***	**Atom**	***x***	***y***	***z***
H1	0.04341	-0.11061	0.00000	C15	1.73095	-5.90404	0.00000
H2	0.47411	0.25747	0.00000	C16	1.87035	-6.09910	0.00000
H3	0.40799	0.09052	0.00000	C17	1.89823	-6.07113	0.00000
H4	0.64150	0.02410	0.00000	C18	1.89823	-6.15460	0.00000
H5	0.70884	-0.00954	0.00000	C19	1.95400	-6.18247	0.00000
H6	0.80869	0.09025	0.00000	C20	1.98188	-6.15484	0.00000
H7	0.70887	0.14009	0.00000	C21	1.95400	-6.09900	0.00000
H8	0.87626	-0.17676	0.00000	C22	1.45214	-6.01544	0.00000
H9	0.97607	-0.22660	0.00000	C23	1.36849	-5.68098	0.00000
H10	0.97611	-0.07697	0.00000	C24	1.39637	-5.65301	0.00000
H11	0.44052	0.32497	0.00000	C25	1.36849	-5.59717	0.00000
H12	0.24071	0.42476	0.00000	C26	1.31273	-5.56930	0.00000
H13	0.29062	0.32487	0.00000	C27	1.28485	-5.59727	0.00000
H14	0.44052	0.49225	0.00000	C28	1.31273	-5.65311	0.00000
H15	0.39047	0.59194	0.00000	C29	1.36849	-5.51370	0.00000
H16	0.24071	0.59217	0.00000	C30	1.31273	-5.48583	0.00000
H17	0.37430	0.05656	0.00000	C31	1.39637	-5.48573	0.00000
H18	0.47421	-0.14304	0.00000	C32	1.36849	-5.43022	0.00000
H19	0.52416	-0.09344	0.00000	C33	1.31273	-5.40235	0.00000
H20	0.20702	0.05670	0.00000	C34	1.28485	-5.42999	0.00000
H21	0.15706	0.00662	0.00000	C35	1.39637	-5.98757	0.00000
H22	0.30692	-0.14324	0.00000	C36	1.36849	-6.01554	0.00000
H23	0.46685	0.40456	-0.25954	C37	1.39637	-6.07104	0.00000

H24	0.46685	0.36044	0.06954	C38	1.45214	-6.09892	0.00000
H25	0.46685	0.42072	0.19000	C39	1.48002	-6.07128	0.00000
H26	0.90772	0.01757	-0.26824	C40	1.28485	-6.01530	0.00000
H27	0.93569	-0.01048	0.14767	C41	1.31273	-6.07114	0.00000
H28	0.87346	0.05191	0.12058	C42	1.22909	-5.98743	0.00000
H29	0.40153	-0.16956	-0.26821	C43	1.20121	-6.01540	0.00000
H30	0.37364	-0.16953	0.14821	C44	1.22909	-6.07124	0.00000
H31	0.43599	-0.16960	0.12000	C45	1.28485	-6.09911	0.00000
H32	0.24526	0.67500	-0.10732	C46	1.45214	-5.59741	0.00000
H33	0.30298	0.67494	0.10732	C47	1.89823	-5.98765	0.00000
H34	0.27323	-0.17682	0.00000	C48	1.39637	-6.15485	0.00000
H35	0.20698	-0.34402	0.00000	C49	2.06552	-6.15474	0.00000
H36	0.30634	-0.33782	0.16993	C50	1.22909	-6.15471	0.00000
H37	0.49835	0.25015	0.14821	C51	1.20121	-6.18268	0.00000
H38	0.52625	0.25012	-0.26821	C52	1.14545	-6.15481	0.00000
H39	0.56070	0.25008	0.12000	C53	1.11756	-6.18244	0.00000
H40	0.63414	-0.01328	-0.25954	C54	1.14545	-6.23828	0.00000
H41	0.63414	-0.05740	0.06954	C55	1.20121	-6.26616	0.00000
H42	0.63414	0.00288	0.19000	C56	1.22909	-6.23819	0.00000
H43	0.32222	-0.23320	-0.26824	C57	1.22909	-6.32199	0.00000
H44	0.35019	-0.26125	0.14767	C58	1.53578	-5.76459	0.00000
H45	0.28796	-0.19885	0.12058	C59	1.61942	-6.01525	0.00000
H46	0.15060	-0.33680	-0.26821	C60	1.31273	-6.23842	0.00000
H47	0.12271	-0.33677	0.14821	C61	1.14545	-6.32209	0.00000
H48	0.18506	-0.33684	0.12000	C62	1.06180	-6.07110	0.00000
H49	0.04709	-0.09855	0.06954	C63	1.36849	-5.84826	0.00000
H50	0.04709	-0.05442	-0.25954	N1	1.64730	-5.90380	0.00000
H51	0.04709	-0.03827	0.19000	N2	1.87035	-6.01529	0.00000
H52	0.39123	0.11434	0.14821	N3	1.48002	-5.98747	0.00000
H53	0.36334	0.14219	-0.26821	N4	1.39637	-5.73682	0.00000
H54	0.32888	0.17659	0.12000	N5	1.39637	-5.56954	0.00000
C1	1.45214	-5.84816	0.00000	N6	1.36849	-6.09901	0.00000
C2	1.48002	-5.90400	0.00000	N7	1.28485	-5.34651	0.00000
C3	1.53578	-5.93187	0.00000	N8	2.03764	-6.18271	0.00000
C4	1.56366	-5.90390	0.00000	N9	1.20121	-6.09887	0.00000
C5	1.53578	-5.84806	0.00000	N10	1.28485	-6.34987	0.00000
C6	1.48002	-5.82019	0.00000	O1	1.56366	-5.82043	0.00000
C7	1.45214	-5.76469	0.00000	O2	1.39637	-5.82029	0.00000
C8	1.45214	-5.93163	0.00000	O3	1.56366	-5.98738	0.00000
C9	1.61942	-5.93177	0.00000	O4	1.81459	-6.07122	0.00000
C10	1.70307	-5.93167	0.00000	O5	1.28485	-5.51379	0.00000
C11	1.73095	-5.98751	0.00000	O6	1.31273	-5.98767	0.00000
C12	1.78671	-6.01539	0.00000	O7	1.28485	-6.26606	0.00000
C13	1.81459	-5.98742	0.00000	O8	1.11756	-6.26625	0.00000

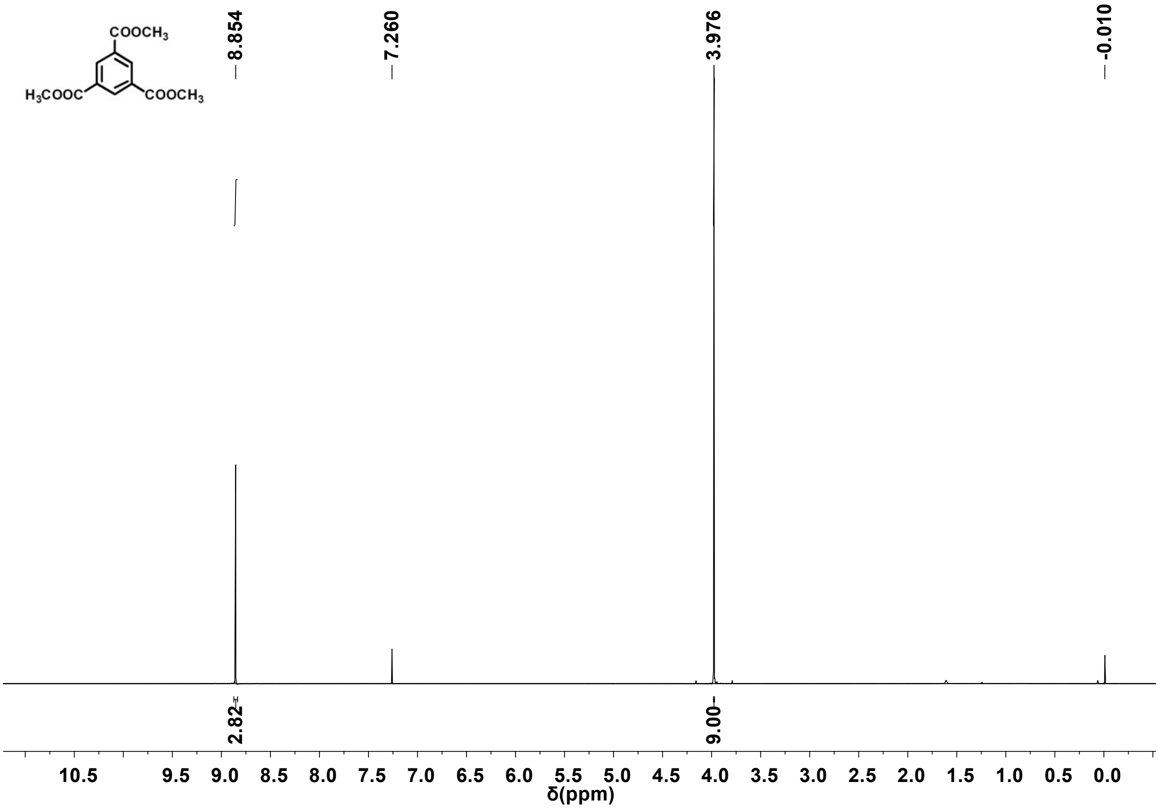
C14	1.78671	-5.93191	0.00000	O9	1.11756	-6.09897	0.00000

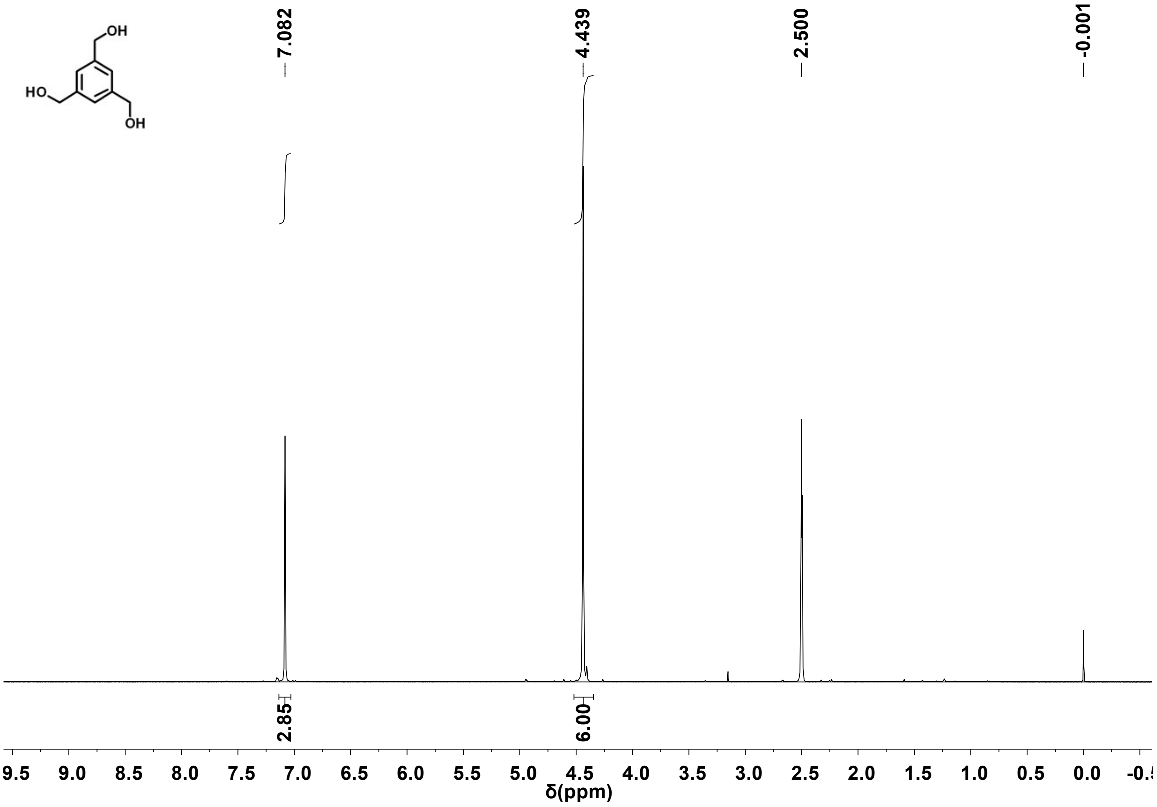
Table S4. Elemental analysis of the DAPO-COFs

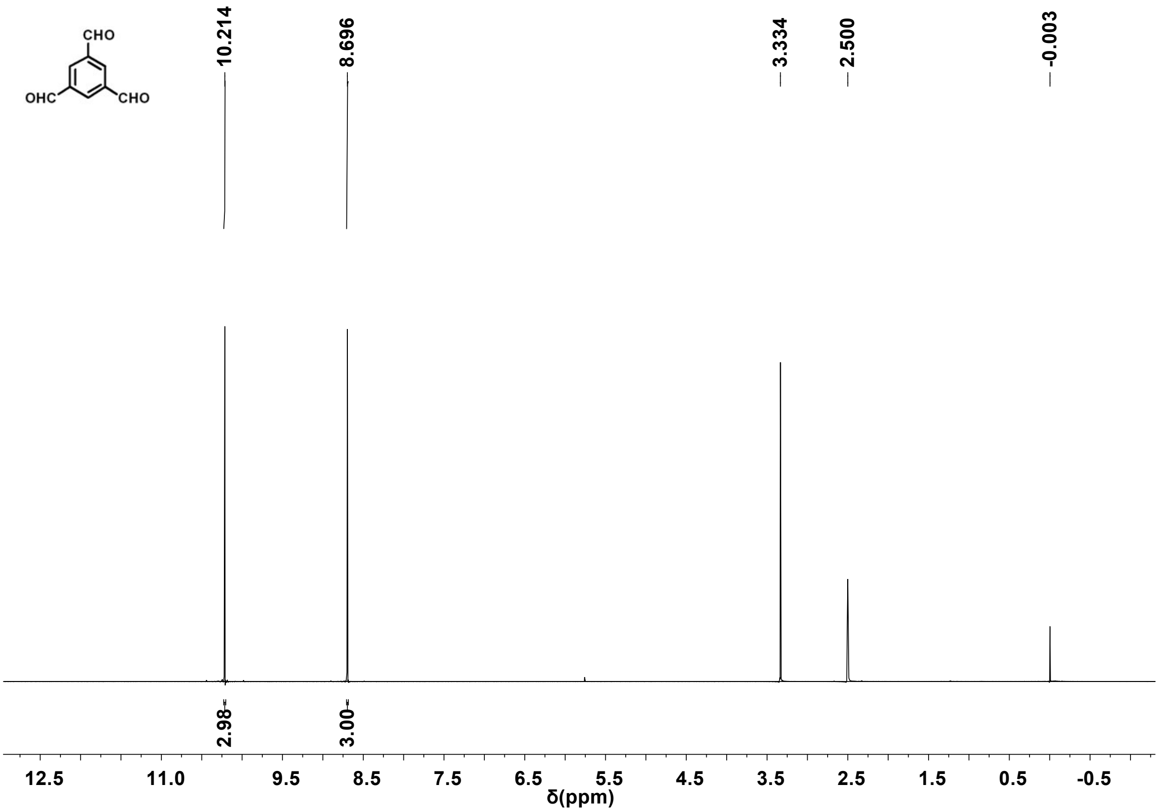
Sample	Expected C%	Expected H%	Expected N%	Found C%	Found H%	Found N%
DAPO-TFB-COF	76.25	4.35	14.05	69.54	4.86	12.81
DAPO-TpOMe-COF	70.19	4.74	11.7	63.91	5.38	11.17

Section G NMR spectra

^{1}H NMR



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CHO
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3.334
2.500
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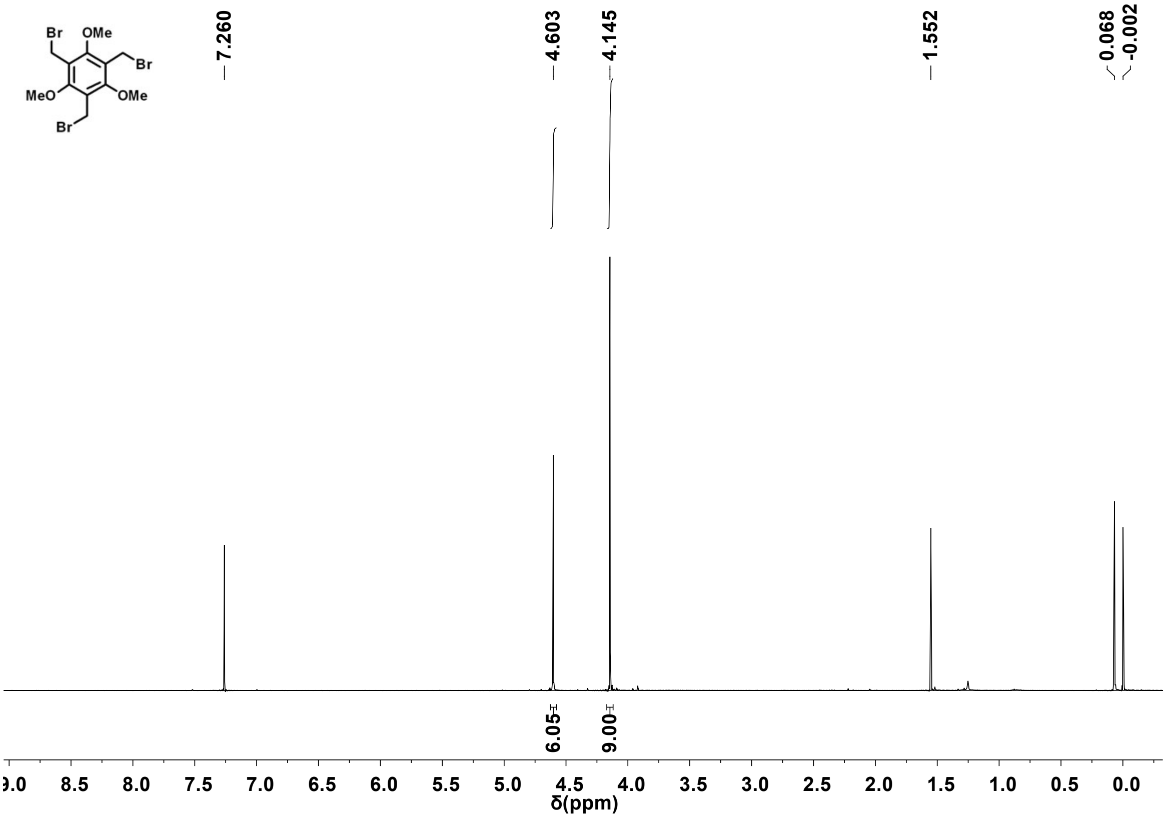
2.98
3.00
12.5
11.0
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
δ(ppm)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OMe
Br
MeO
OMe
Br
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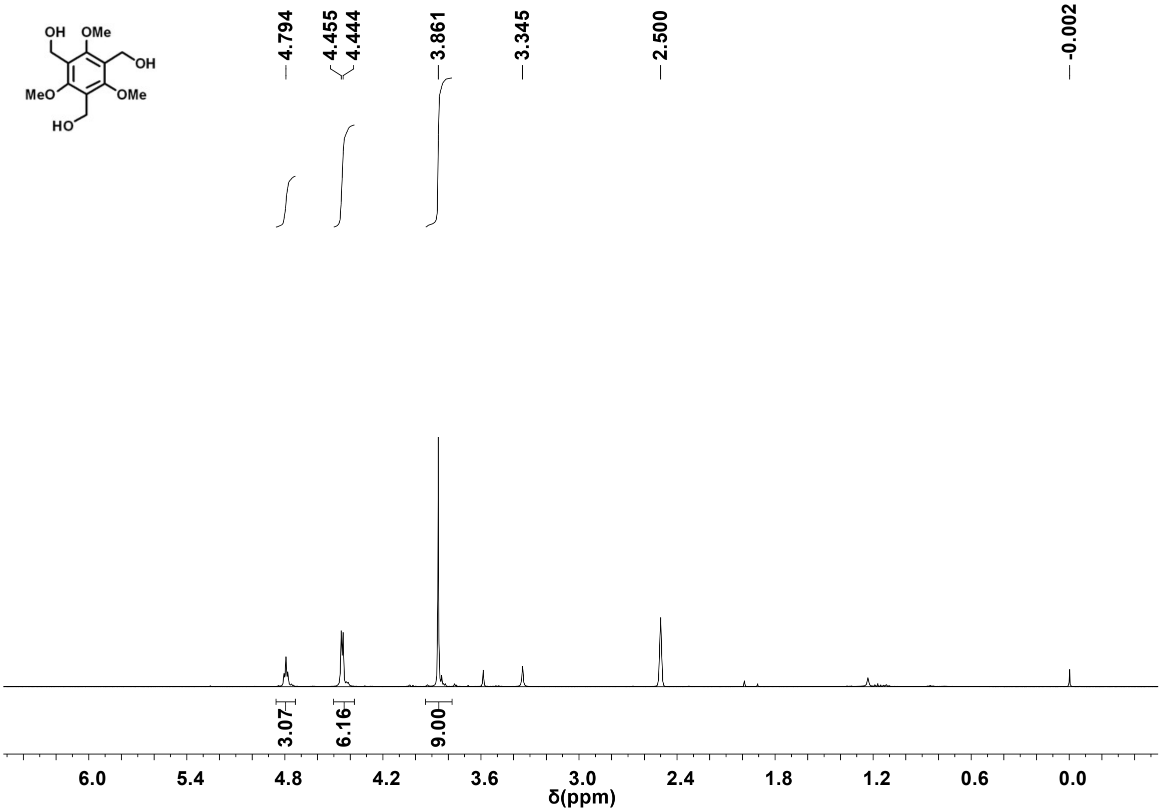
4.603
4.145
1.552
0.068
-0.002
6.05
9.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
δ(ppm)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OH
MeO
OMe
HO
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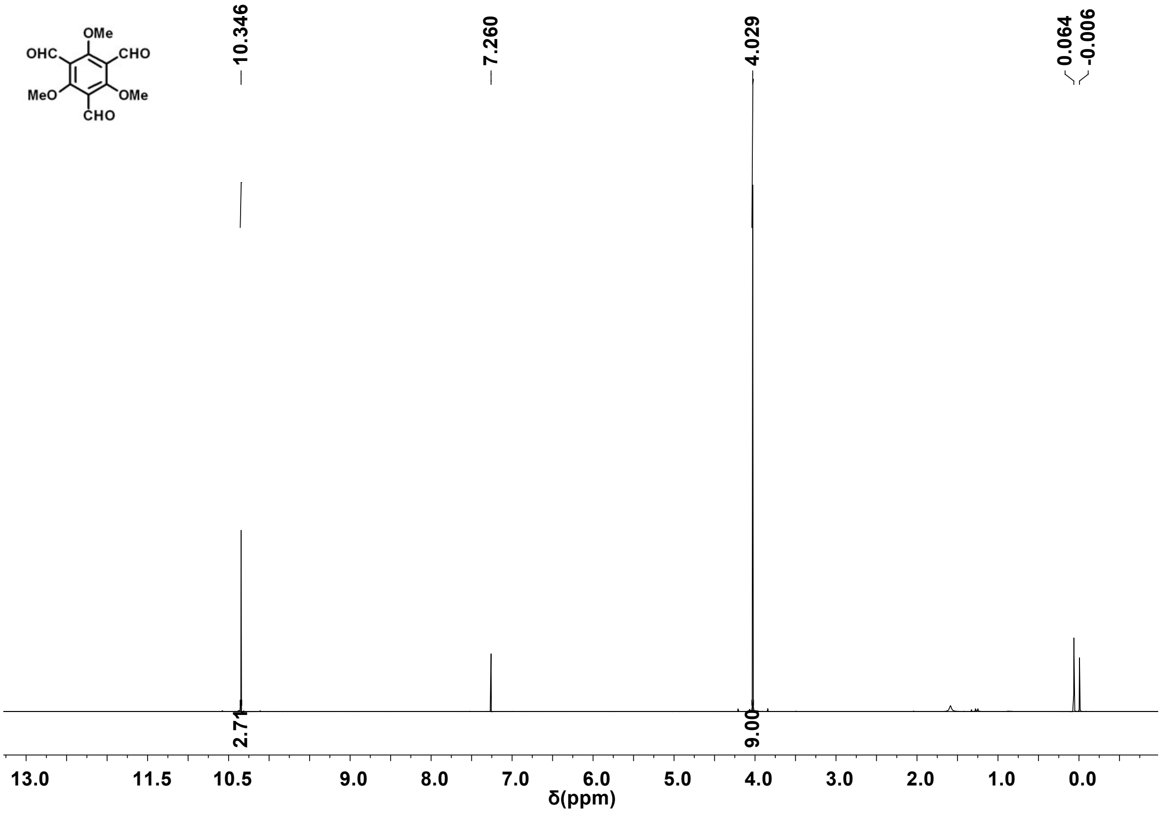
4.444
3.861
3.345
2.500
-0.002
3.07
6.16
9.00
6.0
5.4
4.8
4.2
3.6
3.0
2.4
1.8
1.2
0.6
0.0
δ(ppm)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CHO
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13.0
11.5
10.5
9.0
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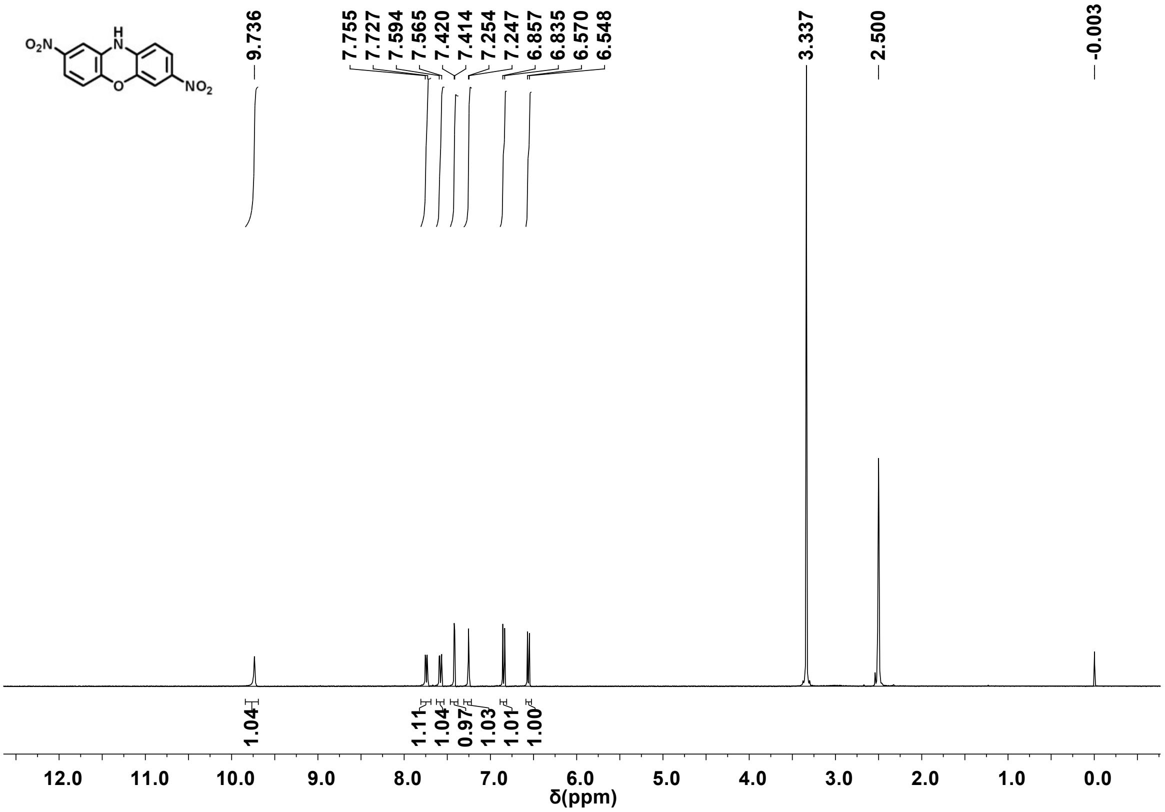
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
δ(ppm)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H
N
O
NO₂
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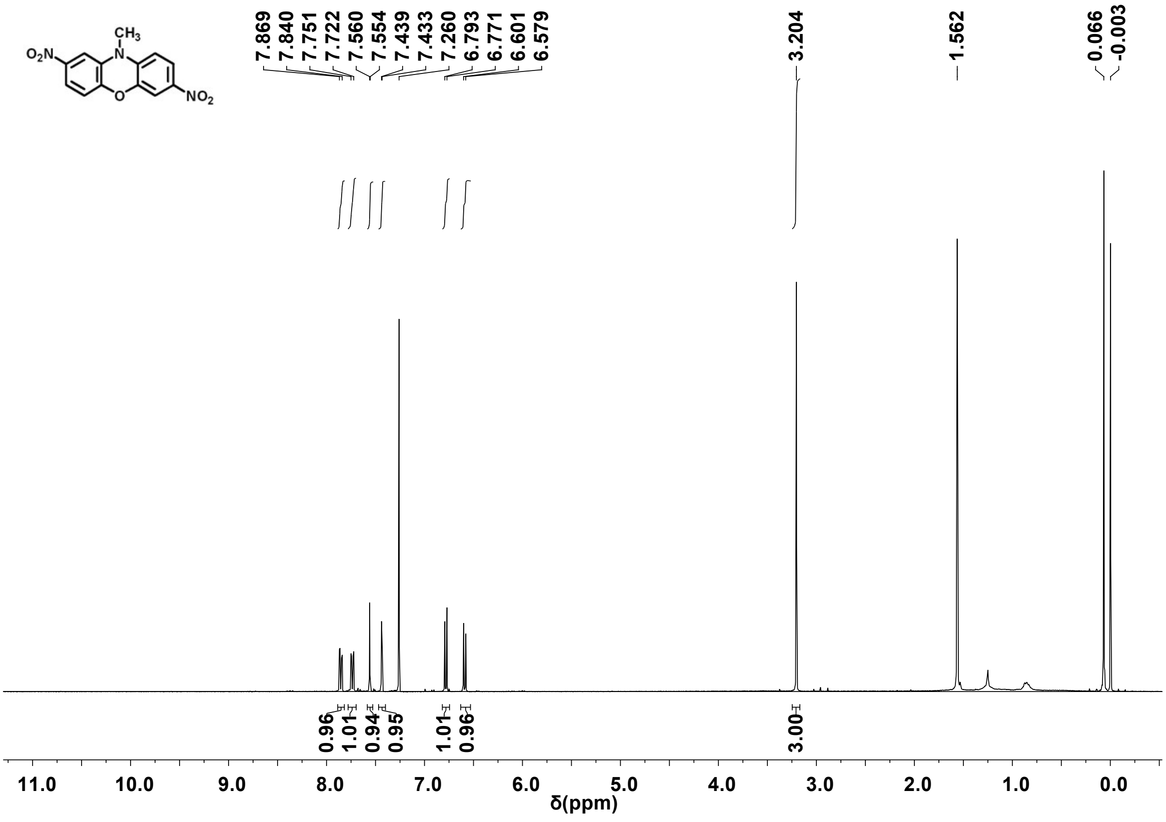
7.755
7.727
7.594
7.565
7.420
7.414
7.254
7.247
6.857
6.835
6.570
6.548
3.337
2.500
-0.003
1.04
1.11
1.04
0.97
1.03
1.01
1.00
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
δ(ppm)


O₂N
CH₃
N
O
NO₂
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7.751
7.722
7.560
7.554
7.439
7.433
7.260
6.793
6.771
6.601
6.579
3.204
1.562
0.066
-0.003
0.96
1.01
0.94
0.95
1.01
0.96
3.00
11.0
10.0
9.0
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7.0
6.0
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4.0
3.0
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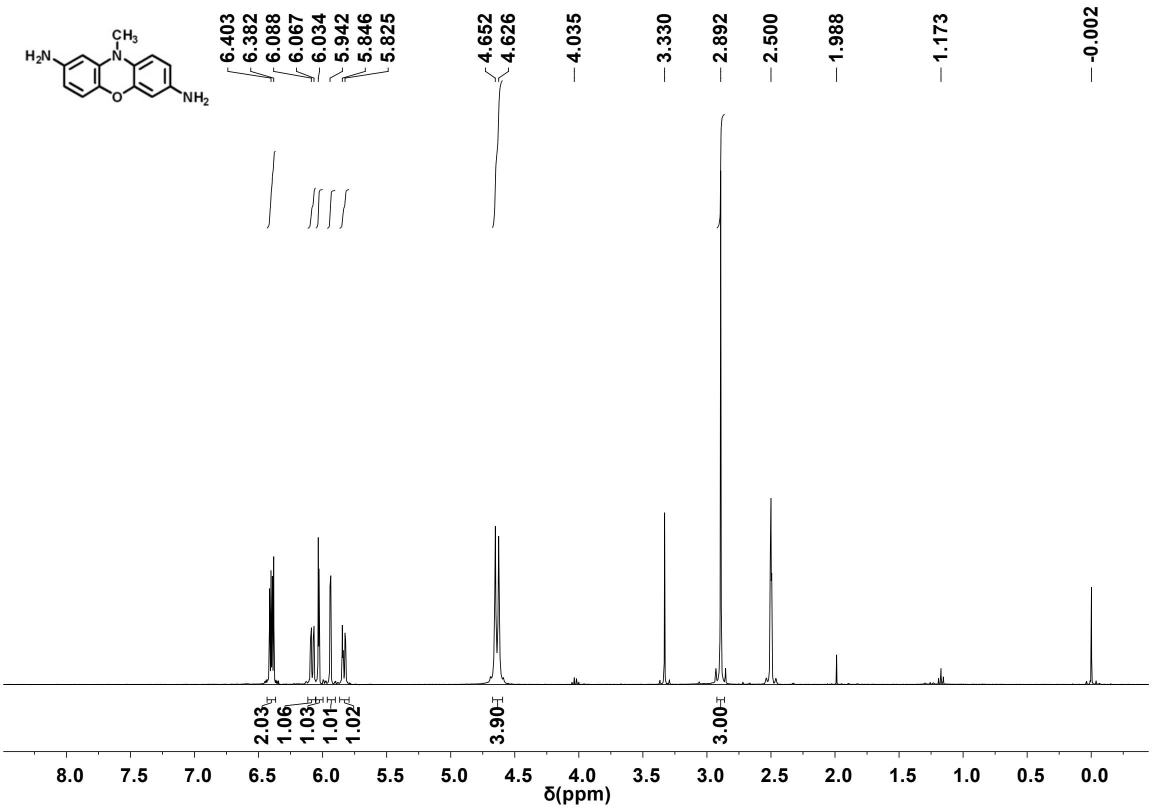
δ(ppm)



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O
NH_2
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5.942
5.846
5.825
4.652
4.626
4.035
3.330
2.892
2.500
1.988
1.173
-0.002
2.03
1.06
1.03
1.01
1.02
3.90
3.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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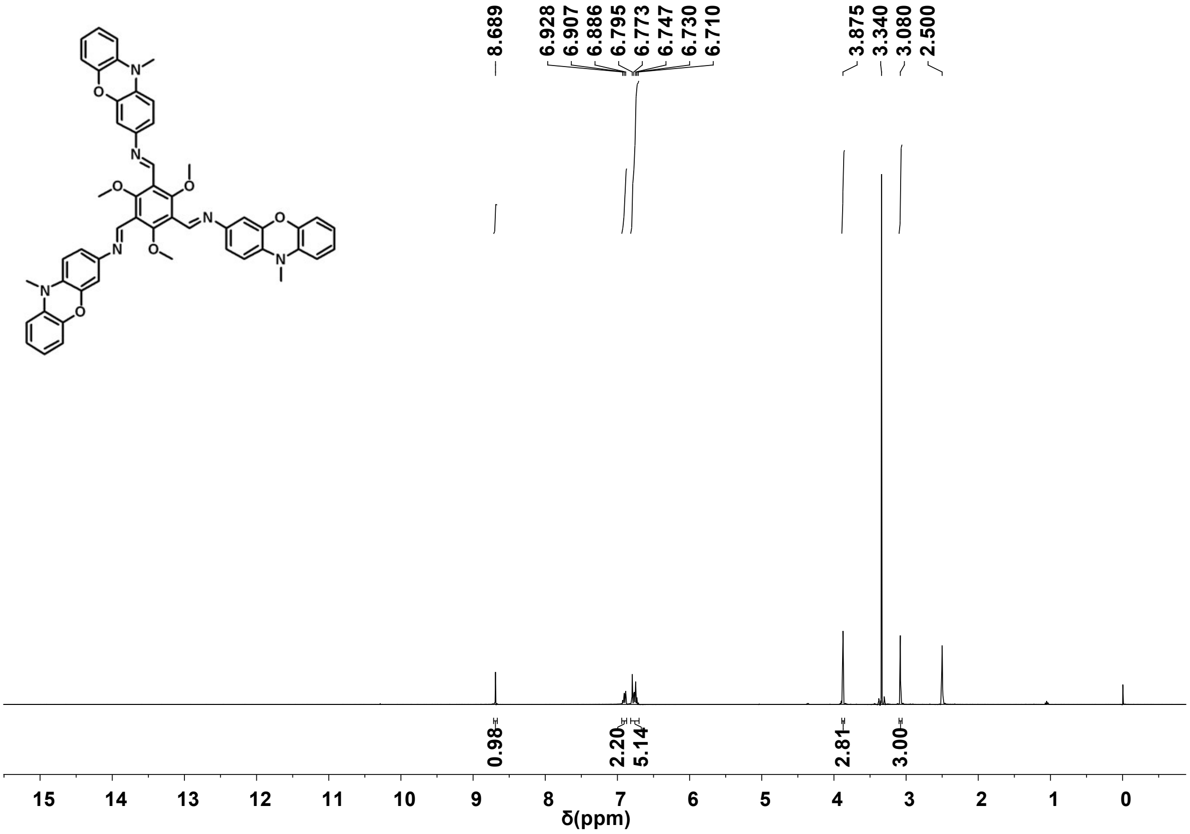
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
δ(ppm)



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O
N
O
N
O
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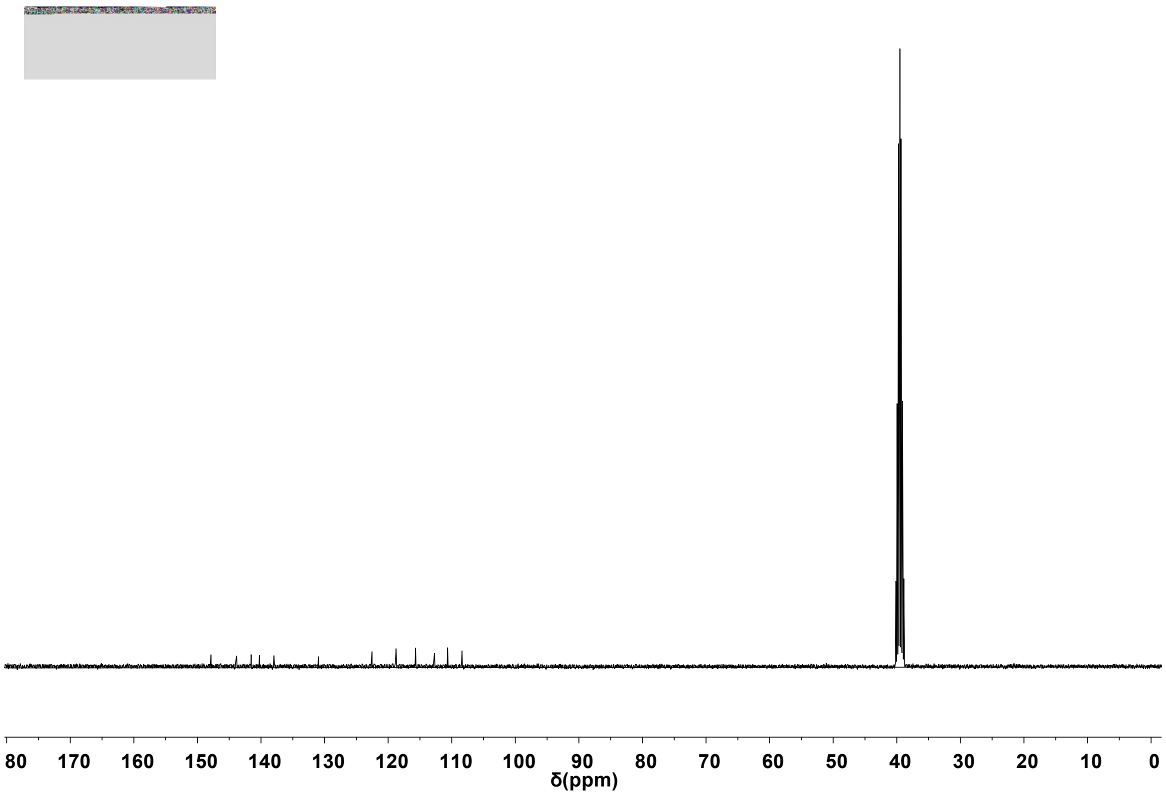
6.928
6.907
6.886
6.795
6.773
6.747
6.730
6.710
3.875
3.340
3.080
2.500
0.98
2.20
5.14
2.81
3.00
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
δ(ppm)

^{13}C NMR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160
150
140
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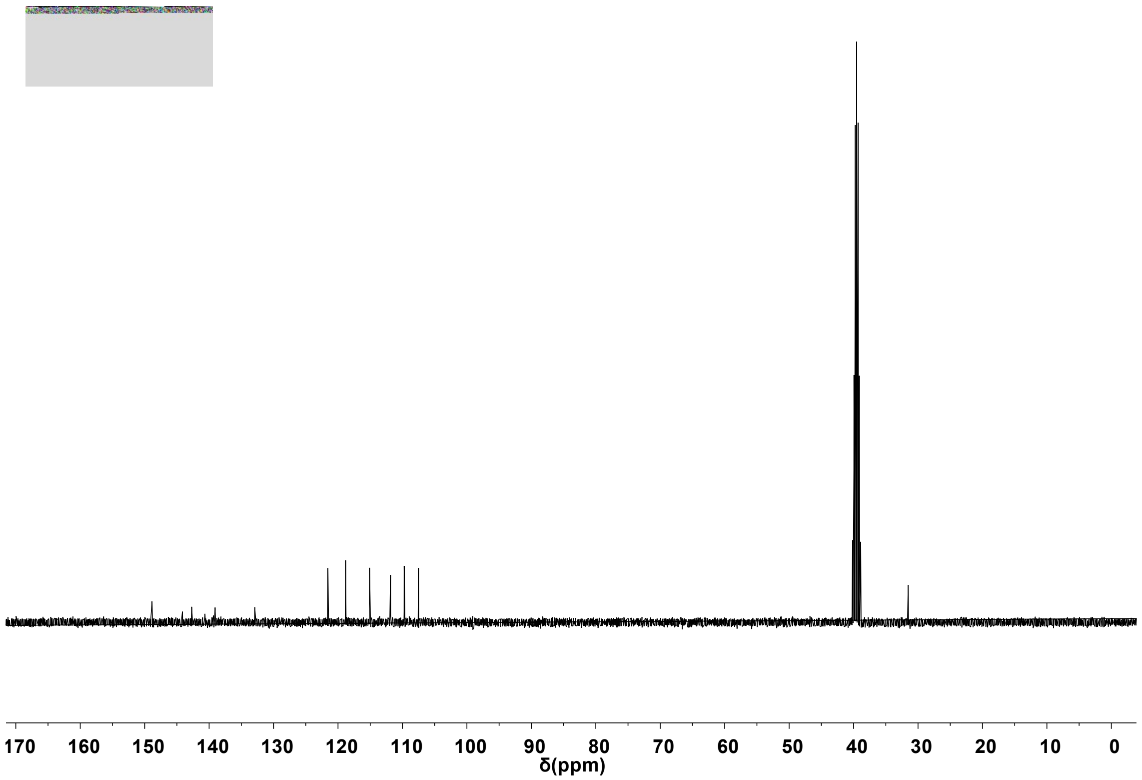
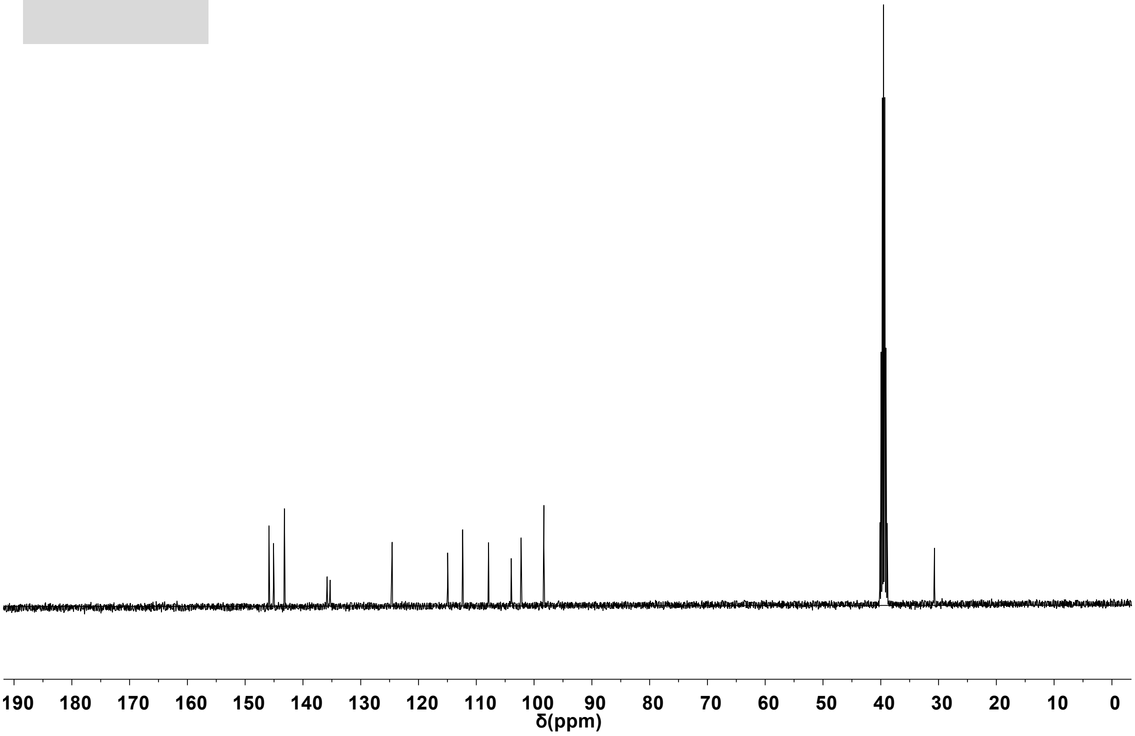
120
110
100
90
80
70
60
50
40
30
20
10
0
δ(ppm)


170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
δ(ppm)


190
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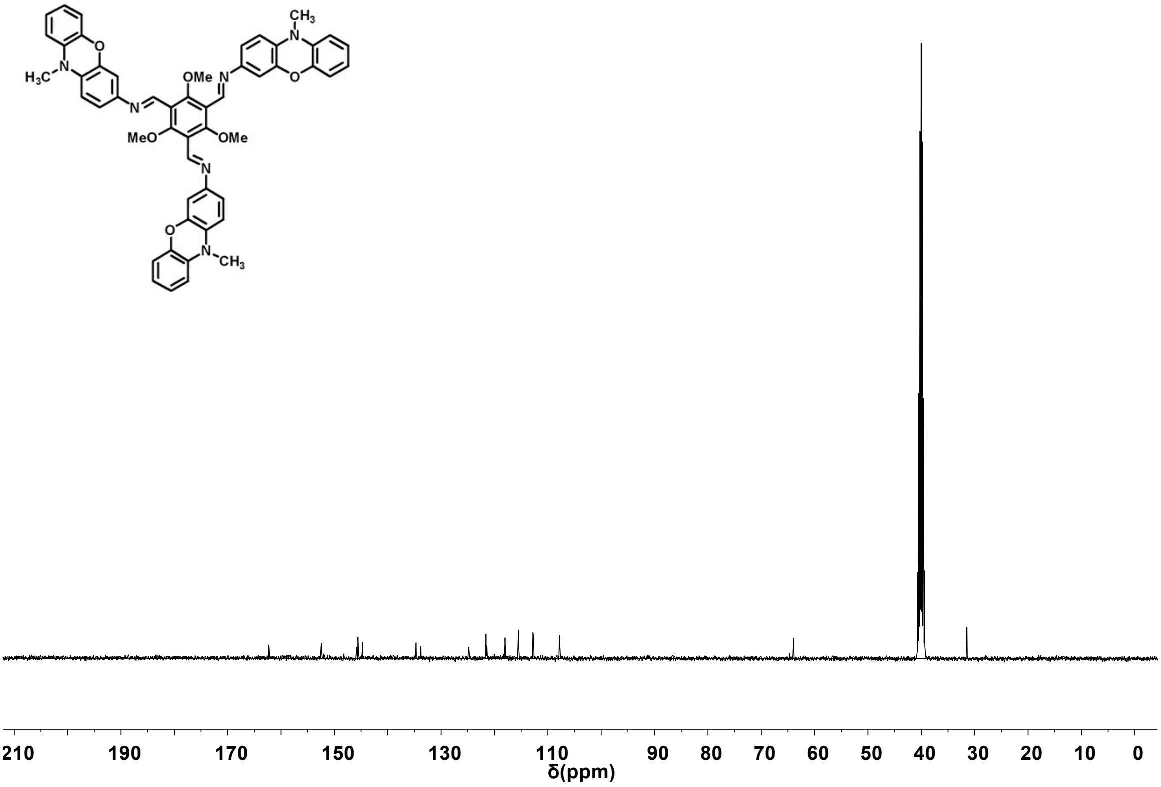
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
δ(ppm)


CH$_3$
N
O
H$_3$C
N
O
OMe
N
N
MeO
OMe
N
O
N
CH$_3$
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
δ(ppm)

Section H Supporting references

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