Electronic Supplementary Material (ESI) for Molecular Systems Design & Engineering.

Supporting Information for:

A dehydrobenzoannulene-based two-dimensional covalent organic framework as an anode material for lithium-ion batteries

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A. Materials

Unless stated otherwise, all reagents were purchased from commercial sources and used without further purification. Tetrahydrofuran and methanol were purified by distillation over sodium and CaH_2, respectively. Dimethylformamide was purified by passage over activated alumina.

1 M $LiPF_6$ in EC/DMC (1/1, w/w) electrolyte was purchased from Sigma-Aldrich. Glass fiber separator (GF/A) was purchased from Whatman. Li chip (99.9%), Celgard (PP-PE-PP, 25 μm thickness) and Cu foil (99.99%) were purchased from the MTI corporation. All materials for electrochemical studies were stored and handled in an argon-filled glovebox (< 0.5 ppm H_2O and < 1.5 ppm O_2).

B. Instrumentation and Methods

Infrared spectra were recorded on a Thermo Scientific Nicolet iS5 with an iD7 diamond ATR attachment and are uncorrected unless otherwise stated.

^{1}H NMR spectra were recorded in deuterated solvents on a Bruker Advance DPX 400 (400 MHz). Chemical shits are reported in parts per million (ppm, δ) using the solvent as the internal standard.

Solid-state ^{13}C NMR spectra for COF samples were recorded using a Bruker AVIII 600 MHz spectrometer with wide-bore magnet (600.3 MHz) using a 3.2 mm magic angle spinning (MAS) HXY solid-state NMR probe and running 20 k scans. Cross-polarization with MAS (CP-MAS) was used to acquire ^{13}C data at 150.9 MHz. The ^{13}C cross polarization time was 2 ms at 50 kHz with a 3 s relaxation delay for ^{13}C. ^{1}H decoupling was applied during data acquisition. The decoupling power corresponded to 100 kHz. The HXY sample spinning rate was 15 kHz. A 20 Hz line broadening was applied. Spectra for DBA[12]-CHO were acquired as above with the following changes: Relaxation delay of 10 s; line broadening of 40 Hz, 2048 scans.

Surface area measurements were conducted on a Micromeritics ASAP 2020 Surface Area and Porosity Analyzer using ca. 15 mg samples. Nitrogen isotherms were generated by incremental exposure to ultra high purity nitrogen up to ca. 1 atm in a liquid nitrogen (77 K) bath. Surface parameters were determined using BET adsorption models in the instrument software. Pore size distributions were determined using the non-local density functional theory (NLDFT) model (cylindrical pore, N_2 – Cylindrical Pores – Oxide Surface) in the instrument software (Micromeritics ASAP 2020 V4.02).

Scanning electron microscopy (SEM) was performed on a FEI Helios Nanolab 600 Dual Beam Focused Ion Beam/Scanning Electron Microscope. Materials were deposited onto a film of carbon tape on an aluminum sample stub and loose sample was removed with compressed air. Samples were imaged in the SEM at 5 keV, without tilting.

The DBA-COF 3 electrode was fabricated by mixing COF powder, Super P carbon powder (MTI Corporation) and poly(vinylidenefluoride) (PVDF, Sigma-Aldrich) in N-methylpyrrolidone (Sigma-

Aldrich) solvent. The slurry was then pasted onto the Cu foil (99.99%, 15.5 mm diameter, MTI) and dried at 70 °C for 12 h under vacuum. The loading amount is about 0.34 mg/cm^2 to 0.86 mg/cm^2 on each Cu substrate.

The electrochemical process of Li intercalation into DBA-COF 3 electrode was tested using CR2032-type coin cells, each of which consisted of a Cu foil (15.5 cm in diameter) as the working electrode, a trilayer celgard (polypropylene-polyethylene-polypropylene, 25 μm thickness) and GFA separators with a Li chip (99.9%, MTI) as the counter electrode. 80 μL electrolyte is used in each cell. Galvanostatic cycling was performed in a Li-DBA-COF 3 half-cell between 0.05 V and 2.0 V (vs Li/Li$^+$) at the rate of 50 mA/g$_{(DBA\text{-}COF\ 3)}$. The cycling was carried out using an MTI battery analyzer (BST8-WA).

Rate performance cycling was acquired by a Neware battery analyzer (BTS3000). After the first high capacity cycle, 5 cycles were performed at each rate from 50 to 1000 mA g^{-1} from 0.05 to 3 V vs Li$^+$/Li.

Cyclic voltammograms for small molecules were acquired using a Gamry Reference 600 Potentiostat/Galvanostat. Measurements were performed with a Ag/AgNO$_3$ reference electrode, platinum counter electrode, and glass carbon working electrode. Each solution consisted of 0.3 mM substrate and 0.1 M TBAPF$_6$ in dry, degassed DMF. A sweep rate of 100 mV/s was used. Saturated LiPF$_6$ solution was used for LiPF$_6$ doped cycles.

Cyclic voltammograms for LIB coin cells were acquired using a Gamry Reference 600 Potentiostat/Galvanostat. Measurements were performed with a Li-metal reference/counter electrode and a 60:30:10 COF:Super P:PVDF electrode on a copper foil as the working electrode. 1 M LiPF$_6$ in EC:DMC (1:1 by volume) was used as supporting electrolyte. A sweep rate of 10 mV s^{-1} was used.

The sweep rate dependence experiments to determine faradaic/capacitative redox were run on a Bio-Logic SP-150 potentiostat. The coin cell was swept from 0.05 to 2 V vs Li$^+$/Li under varying sweep rates.

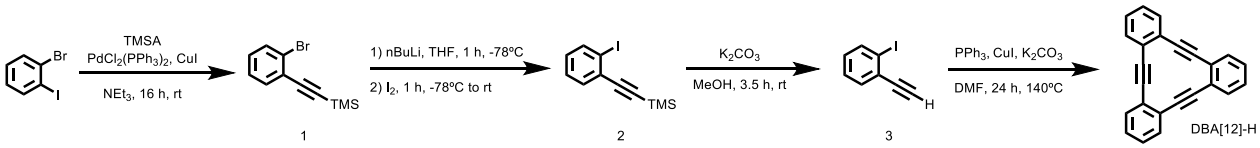
Electrochemical Impedance Spectroscopy was acquired with a Gamry Reference 600 Potentiostat/Galvanostat. Impedance measurements were run from 1 MHz to 0.1 Hz with 10 points per decade and an applied AC voltage of 10 mV.

XPS was acquired on a Kratos Axis Ultra X-ray Photoelectron Spectrometer. The pristine electrode was measured as prepared. The lithiated electrode was cycled at 50 mA g^{-1} for one full cycle from 0.05 to 3 V vs Li+/Li, then discharged one additional time. The delithiated electrode was cycled for one full cycle and discharged, and then charged one additional time. Electrodes were transferred into the XPS instrument using an air-free sample holder. C 1s spectra were acquired over 8 sweeps.

Elemental analysis was performed by Galbraith Laboratories.

C. Synthetic Methods

Synthetic Procedure for DBA[12]-H



Scheme 1. Synthesis of DBA[12]-H.

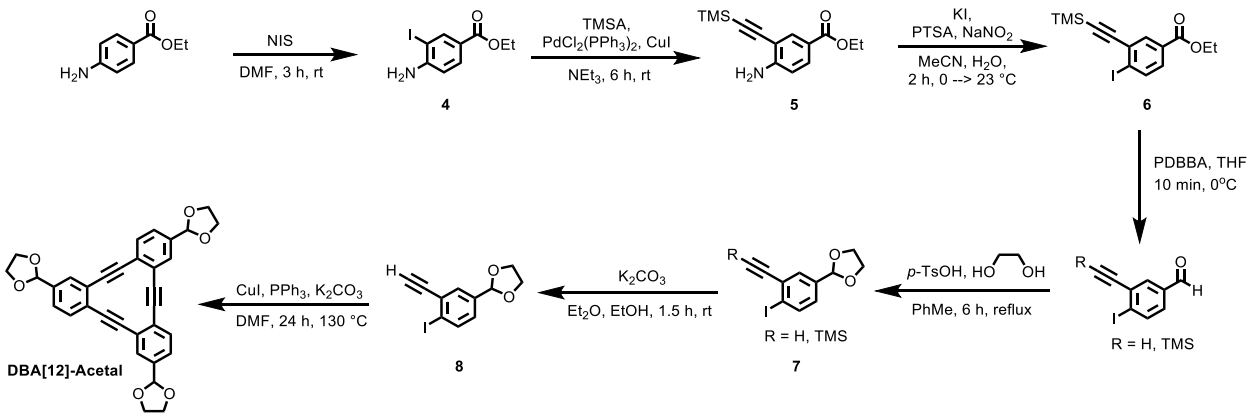
Compound 1: $PdCl_2(PPh_3)_2$ (273 mg, 0.389 mmol, 0.02 equiv.), and CuI (148 mg, 0.779 mmol, 0.04 equiv.) were combined in a dry flask in the glovebox. To this was added a degassed solution of 2-bromoiodobenzene (2.5 mL, 19.47 mmol, 1.0 equiv.) in NEt_3 (30 mL, 0.6 M) in a dry flask. Trimethylsilylacetylene (3.3 mL, 23.36 mmol, 1.2 equiv.) was then added to the reaction mixture, and the solution was stirred under an inert atmosphere overnight. The reaction was quenched with saturated NH_4Cl (~50 mL) and filtered through celite, washing with Et_2O. The product was then extracted with Et_2O (3 x 30 mL), washed with brine, dried with Na_2SO_4, and concentrated *in vacuo*. The crude material was purified by silica gel chromatography (hexanes) to yield **1** as a yellow oil (4.787 g, 18.91 mmol, 97% yield). ^{1}H-NMR ($CDCl_3$ 400 MHz) δ 7.57 (1 H, dd), 7.49 (1 H, dd), 7.24 (1 H, dt), 7.15 (1 H, dt), 0.28 (9 H, s). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 133.75, 132.51, 129.69, 127.02, 125.92, 125.41, 103.17, 99.79, -0.01.[1]

Compound 2: **1** (4.87 g, 19.22 mmol) was dissolved in dry THF (100 mL, 0.2 M) and cooled to -78 ˚C. Freshly titrated 2.5 M *n*-BuLi (13.84 mL, 1.8 equiv.) was added dropwise to the cold solution. Upon complete addition, the reaction was let stir at -78 ˚C for 1 hour. I_2 (9.27 g, 36.53 mmol, 1.9 equiv.) was then added, and the solution was slowly allowed to reach room temperature over the course of 1 hour. Upon completion, the reaction was quenched with water, extracted with Et_2O (3 x 50 mL), washed with $Na_2S_2O_3$, dried with Na_2SO_4, and concentrated *in vacuo*. The crude material was then passed through a pad of silica, washing with hexanes, to yield **2** as a dark colored oil (4.815 g, 16.04 mmol, 83% yield). ^{1}H-NMR ($CDCl_3$ 400 MHz) δ 7.84 (1 H, dd), 7.47 (1 H, dd), 7.28 (1 H, dt), 6.99 (1 H, dt). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 138.8, 132.9, 129.8, 129.7, 128.3, 127.8, 106.7, 101.4, -0.05.[1]

Compound 3: A solution of **2** (5.18 g, 17.24 mmol, 1.0 equiv.) and K_2CO_3 (2.86 g, 20.67 mmol, 1.2 equiv.) in MeOH (35 mL, 0.5 M) was stirred at room temperature until all starting material had been converted, as tracked by TLC (hexanes). The MeOH was removed *in vacuo*, the resulting oil was diluted with Et_2O (~50 mL) and filtered through celite to yield **3** as a light-yellow oil (3.35 g, 14.71 mmol, 85% yield). ^{1}H-NMR ($CDCl_3$ 400 MHz) δ 7.86 (1 H, dd), 7.51 (1 H, dd), 7.31 (1 H, dt), 7.04 (1 H, dt). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 138.9, 133.6, 130.1, 128.9, 127.2, 100.6, 85.3, 81.1.[2]

DBA[12]-H: **3** (3.1975 g, 14.02 mmol) was dissolved in dry DMF (47 mL, 0.3 M) and the solution was degassed by bubbling through N_2. The degassed solution was then transferred to a separate flask containing CuI (801 mg, 4.21 mmol, 0.3 equiv.), K_2CO_3 (5.81 g, 42.06 mmol, 3.0 equiv.), and PPh_3 (1.10 g, 4.21 mmol, 0.3 equiv.) under an inert atmosphere. The reaction mixture was then placed in a pre-heated oil bath at 130 ˚C where it was stirred under an inert atmosphere for 24 hours. Upon cooling to room temperature, the DMF was removed *in vacuo* and the crude extracted with toluene (3 x 50 mL), washed with saturated NH_4Cl, dried with Na_2SO_4, and concentrated *in vacuo*. The crude product was purified via silica gel chromatography (20% DCM/hexanes) followed by washing the solids with hot hexanes, to give DBA[12]-H as a yellow solid (0.91 g, 3.02 mmol, 65% yield). ^{1}H-NMR ($CDCl_3$ 400 MHz) δ 7.33-7.36 (6 H, m), 7.17-7.19 (6 H, m). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 132.16, 128.67, 126.85.[3]

Synthetic Procedure for DBA[12]-acetal



Scheme 2. Synthesis of DBA[12]-acetal.

Compound 4: To a stirring solution of benzocaine (6.61 g, 40.0 mmol, 1 equiv.) in DMF (40 mL, 1 M) was added N-iodosuccinimide (9.00 g, 40.0 mmol, 1 equiv.). The reaction was allowed to stir 3 hours at room temperature before crashing out with the addition of ~450 mL of water. Vacuum filtration afforded pure **4** as a pale yellow solid (10.0 g, 34.0 mmol, 85.9% yield). ^{1}H-NMR ($CDCl_3$ 400 MHz) δ 8.30 (1 H, d), 7.78 (1 H, dd), 6.67 (1 H, d), 4.58 (2 H, br s), 4.29 (2 H, q), 1.34 (3 H, t). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 165.4, 150.8, 140.9, 131.1, 121.4, 113.1, 82.1, 60.7, 14.4.

Compound 5: Triethylamine (50 mL, 0.34 M) was degassed in a dry round bottom flask by bubbling N_2, and then was added to **4** (5.00 g, 17.2 mmol, 1 equiv.), $PdCl_2(PPh_3)_2$ (119 mg, 0.17 mmol, 1 mol%), and CuI (99 mg, 0.52 mmol, 3 mol%) under an atmosphere of N_2 in a separate

dry flask. To the reaction mixture was added trimethylsilylacetylene (3.67 mL, 25.8 mmol, 1.5 equiv.) and the reaction mixture was allowed to stir for 6 hours at room temperature. The reaction mixture was concentrated in vacuo and the crude product was vacuum filtered through celite with Et_2O (~100 mL), then extracted from a saturated ammonium chloride solution with Et_2O (3 x 20 mL). The organic layers were combined and washed with brine, then dried over Na_2SO_4. The mixture was filtered and concentrated *in vacuo* to a dark residue. The crude product was purified by silica gel plug eluting 20% EtOAc/hex to afford **5** (5.10 g, 14.9 mmol, 94.4% yield) as a pale brown oil which solidified upon standing. ^{1}H-NMR ($CDCl_3$ 400 MHz) δ 8.00 (1 H, d), 7.80 (1 H, dd), 6.66 (1 H, d), 4.62 (2 H, br s), 4.31 (2 H, q), 1.36 (3 H, t), 0.27 (9 H, s). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 166.1, 151.7, 134.4, 131.6, 119.5, 113.1, 106.9, 100.6, 100.4, 60.5, 14.4, 0.02.

Compound 6: A solution of 5 (3.50 g, 13.0 mmol, 1 equiv.) in MeCN (107 mL, 0.12 M) was cooled to 0 ^{o}C. To this was added *p*-toluenesulfonic acid (10.4 g, 58.5 mmol, 4.5 equiv.) in four portions, and the mixture was allowed to stir vigorously for 15 minutes before dropwise addition of a solution of KI (8.33 g, 48.8 mmol, 3.75 equiv.) and $NaNO_2$ (2.77 g, 39 mmol, 3 equiv.) in deionized water (22 mL, 0.60 M) over 30 minutes. The reaction was allowed to stir at 0 ^{o}C for 1 hour before adding ~400 mL of deionized water to precipitate crude product. The mixture was stirred for an additional hour, then vacuum filtered to collect dark red solids before purifying by silica gel plug (20% ether/hex) to collect **6** (4.24 g, 11.3 mmol, 85% yield) as a clear, yellow oil which solidified upon standing. ^{1}H-NMR ($CDCl_3$ 400 MHz) δ 8.07 (1 H, d), 7.92 (1 H, d), 7.61 (1 H, dd), 4.36 (2 H, q), 1.39 (3 H, t), 0.29 (9 H, s). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 165.6, 139.1, 133.4, 130.5, 130.3, 130.0, 107.3, 105.8, 100.1, 61.5, 14.4, -0.1. HRMS (ESI) m/z calculated for $C_{14}H_{17}IO_2Si$ $(M + Na)^+$: 394.9935, found: 394.9935. FT-IR (solid, ATR) 2982, 2952, 2893, 2170, 1716, 1584, 1561, 1458, 1467, 1384, 1363, 1294, 1258, 1245, 1208, 1120, 1104, 1016, 939, 849, 833, 765, 751, 705, 692, 646, 579, 446, 431 cm^{-1}.

Compound 8: A solution of dry THF (15 mL, 0.71 M) and **6** (4 g, 10.7 mmol, 1 equiv.) was cooled to 0 $^{\circ}$C and PDBBA[4] (35 mL, 17.5 mmol, 1.64 equiv.) was added dropwise at 0 $^{\circ}$C while stirring vigorously. After 15 minutes, the solution was diluted with cold Et_2O, quenched dropwise with water, and a cold solution of Rochelle's salt (10 wt%) in water was added. The solution was allowed to stir overnight, then extracted with Et_2O (3 x 20 mL). The organic layers were combined and washed with brine, then dried over Na_2SO_4. The solids were filtered and concentrated *in vacuo*. Crude **7** could be purified with silica gel column chromatography (20% Et_2O/hex) to retrieve the aldehyde intermediate with either the TMS-protected or deprotected alkyne. However, due to degradation, this crude mixture was carried forward assuming quantitative yield of the aldehyde intermediate with TMS protected alkyne.

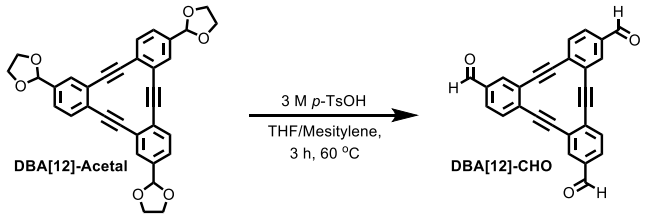
The crude solid (3.51 g, 10.7 mmol, 1 equiv.) was dissolved in toluene (40 mL 0.27 M). To this was added *p*-toluenesulfonic acid (10 mg, 0.06 mmol, 0.5 mol%) and ethylene glycol (2 mL, 35.9 mmol, 3.36 equiv.), and the reaction was stirred under reflux in a dean-stark apparatus. After 6 hours, the toluene was removed *in vacuo* and the oil was diluted with Et_2O, then washed with saturated aqueous bicarb solution. Et_2O (3 x 20 mL) was used to extract from the bicarb solution, then the organic layers were combined and washed with brine and dried over Na_2SO_4.

The solution was filtered and concentrated *in vacuo* to a crude oil which was purified by silica gel column chromatography (20% Et_2O/hex) to collect fractions containing the acetal protected intermediate with TMS-protected and free alkyne. These fractions were concentrated *in vacuo* to afford a yellow oil. For the next step, the oil was assumed to be entirely TMS-protected alkyne intermediate.

The yellow oil (1.31 g, 3.23 mmol, 1 equiv.) was dissolved in Et_2O (20 mL, 0.18 M) before adding MeOH (40 mL, 0.09 M) and K_2CO_3 (0.73 g, 5.29 mmol, 1.64 equiv.) while stirring. The reaction was allowed to stir for 3 hours, then was filtered to remove solids, concentrated *in vacuo*, and washed with water. Diethyl ether (3 x 20 mL) was used to extract from the water, then the organic layers were combined and washed with brine and dried over Na_2SO_4. The solution was filtered and concentrated *in vacuo* to afford **8** as a pale oil in quantitative yield which solidified upon storage in the refrigerator. ^{1}H-NMR ($CDCl_3$ 400 MHz) δ 7.83 (1 H, d), 7.59 (1 H, d), 7.11 (1 H, dd), 5.71 (1 H, s), 3.94-4.08 (4 H, m), 3.42 (1 H, s). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 138.8, 138.4, 131.4, 128.7, 128.1, 102.4, 101.1, 84.9, 81.4, 81.4, 65.3. HRMS (ESI) m/z calculated for $C_{11}H_9IO_2$ $(M + Na)^+$: 322.9539, found: 392.9540. FT-IR (oil, ATR) 3284, 2951, 2883, 1592, 1458, 1412, 1353, 1227, 1164, 1127, 1082, 1010, 969, 941, 892, 823, 771, 721, 627, 558, 542, 492, 469 cm^{-1}.

DBA[12]-acetal: **8** (1.62 g, 5.57 mmol) was dissolved in dry DMF (75 mL, 0.07 M) and loaded into a flame-dried round-bottom flask before degassing by bubbling N_2 for 1 hour. Meanwhile, under argon atmosphere, a separate flame-dried round-bottom flask with stir bar was charged with K_2CO_3 (2.31 g, 16.7 mmol), CuI (318 mg, 1.67 mmol), and PPh_3 (219 mg, 0.836 mmol). The flask was covered with a septum and liquids were added via cannula transfer. The reaction was stirred in an oil bath preheated to 130 ^oC for 24 hours. After, the reaction was allowed to cool to room temperature before removing the solvent *in vacuo*. The residue was dissolved in DCM and vacuum filtered through celite before extracting with DCM (3 x 15 mL). The organic layers were combined and washed with brine, then dried over Na_2SO_4. The Na_2SO_4 salts were removed by filtration and the solvent was removed *in vacuo* to leave a dark crude residue. Column chromatography (3% ether/DCM) followed by recrystallization from toluene yielded **DBA[12]-acetal** (463 mg, 0.896 mmol, 50% yield) as fluffy yellow crystals. ^{1}H-NMR ($CDCl_3$ 400 MHz) δ 7.46 (1 H d), 7.34 (1 H, d), 7.28 (1 H dd) 5.75 (1 H, s), 4.00-4.14 (4 H, m). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 138.8, 132.1, 130.1, 127.4, 126.8, 126.8, 102.8, 93.2, 92.8, 65.4. HRMS (ESI) m/z calculated for $C_{33}H_{24}O_6$ (M + Na)+ : 539.1465, found: 539.1460. FT-IR (powder, ATR) 2954, 2887, 1979, 1601, 1550, 1494, 1434, 1403, 1367, 1333, 1278, 1197, 1150, 1094, 1074, 1025, 939, 906, 885, 836, 793, 721, 695, 622, 556, 479 cm^{-1}.

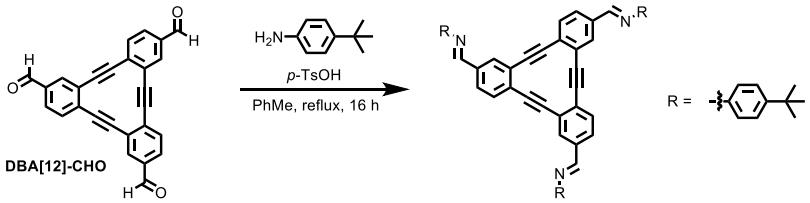
Synthetic Procedure for DBA[12]-CHO



Scheme 3. Deprotection from DBA[12]-acetal to DBA[12]-CHO.

DBA[12]-CHO: To **DBA[12]-acetal** (214 mg, 0.414 mmol) was added THF (5 mL, 0.08 M), mesitylene (10 mL, 0.04 M), and an aqueous solution of 3 M tosylic acid (5 mL, 0.08 M). The solution was stirred at 60 ^{o}C for 3 hours before vacuum filtering off the yellow solids. The solids were washed thoroughly with water followed by a saturated bicarbonate solution, then water again. Minimal amounts of cold acetone were used to air-dry the product on the filter before collecting **DBA[12]-CHO** (151 mg, 0.393 mmol, 95% yield) as bright yellow solids. ^{1}H-NMR ($CDCl_3$ 400 MHz) δ 9.97 (1 H s), 7.90 (1 H d), 7.76 (1 H dd), 7.55 (1 H, dd). CPMAS ^{13}C-NMR (600 MHz, 15 kHz) δ 161.4, 136.4, 132.6, 131.5, 129.4, 127.4, 126.0, 95.1, 93.3, 91.6. HRMS (LDI) m/z calculated for $C_{27}H_{12}O_3$ $(M + Na)^+$: 384.0781, found: 384.0779. FT-IR (powder, ATR) 3052, 2819, 2771, 2718, 2208, 1718, 1686, 1590, 1543, 1493, 1417, 1373, 1317, 1278, 1261, 1188, 1107, 1076, 1008, 963, 953, 941, 926, 902, 877, 826, 792, 713, 628, 581, 508, 480, 464 cm^{-1}.

Synthetic Procedure for DBA[12]-imine



Scheme 4. Condensation of *t*-butylaniline with DBA[12]-CHO to form imine-linked analog of DBA-COF 3, DBA[12]-Imine.

DBA[12]-imine: DBA[12]-CHO (30.0 mg, 0.08 mmol), 4-*tert*-butylaniline (0.19 mL, 1.2 mmol, 15 equiv.), and *p*-toluenesulfonic acid (1.0 mg, 0.006 mmol, 0.07 equiv.) were combined in toluene (5.0 mL, 0.016 M) and refluxed overnight with a Dean-Stark apparatus. After cooling down the toluene was removed *in vacuo*, then the residual solids were dissolved in DCM and washed with aqueous saturated bicarbonate solution. The solids were collected and dried with Na_2SO_4

before concentration *in vacuo* to a yellow oil. Hexanes were added to precipitate solids which were filtered and washed with dry MeOH to **DBA[12]-imine** as a yellow powder (14.3 mg, 0.018 mmol, 23% yield). ^{1}H-NMR ($CDCl_3$-d_6, 400 MHz) δ 8.40 (1 H, s), 7.92 (1 H, d), 7.73 (1 H, dd), 7.46 (1 H, d), 7.43 (2 H, d), 7.19 (2 H, d), 1.36 (9 H, s). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 157.6, 149.9, 148.9, 136.8, 132.6, 132.3, 129.0, 127.1, 126.3, 120.8, 94.7, 93.3, 34.7, 31.6. HRMS (LDI) m/z calculated for $C_{57}H_{51}N_3$ $(M + Na)^+$: 778.4156, found: 778.4154. FT-IR (powder, ATR) 2958, 2920, 2854, 1623, 1583, 1544, 1488, 1461, 1409, 1361, 1261, 1192, 1174, 1084, 1013, 819, 795, 609, 556, 475 cm^{-1}.

Synthetic Procedure for DBA-COF 3

DBA-COF 3: **DBA[12]-CHO** (37 mg, 0.096 mmol) and *p*-phenylenediamine (17.4 mg, 0.16 mmol, 1.67 equiv.) were combined in a 10.6 cm x 1.8 cm (L x W), 10 mL pre-scoured ampule (Sigma-Z184985) with *o*-dichlorobenzene/n-BuOH (19:1, 4.92 mL) and sonicated for 1 minute, reserving 1 mL of *o*-dichlorobenzene. The suspension was then frozen in liquid nitrogen before addition of 6 M acetic acid which was washed down the sides of the ampule with the reserved solvent. After freezing all liquids, the ampule was sealed under vacuum (~150 mTorr), which subsequently reduced the ampule to 8.5 cm (L) and placed in a gravity convection oven at 120 ^{o}C for 72 hours. Afterwards, the ampule was cooled to room temperature, opened, and vacuum filtered, washing with dry MeOH. The collected yellow, fluffy solids were stirred in dry DMF for 30 minutes (3 x 50 mL) then dry MeOH for 30 minutes (3 x 50 mL), filtering and washing with dry MeOH each time before drying under high vacuum to give a yellow solid (45.2 mg, 90% yield). COFs were further activated on the ASAP 2020 instrument at 150 ^{o}C for 12 hours to remove residual solvent before taking porosity measurements. FT-IR (powder, ATR) 2865, 1614, 1589, 1540, 1493, 1410, 1264, 1187, 1079, 949, 886, 837, 732, 691, 613, 537, 506, 476 cm^{-1}. Elemental Analysis for $(C_{36}H_{18}N_3)_n$: Calculated 11 : C (86.72), H (4.85), N (8.43); Observed: C (85.25), H (4.07), N (7.89).

Stability Studies: In a vial, ca. 10 mg of activated DBA-COF 3 was added, followed by solvent. The mixture was stored for 24 hours at room temperature before vacuum filtration was used to collect the solids, washing with dry MeOH. The solids were then dried *in vacuo* for two to three hours before obtaining PXRDs.

D. FT-IR Spectroscopy

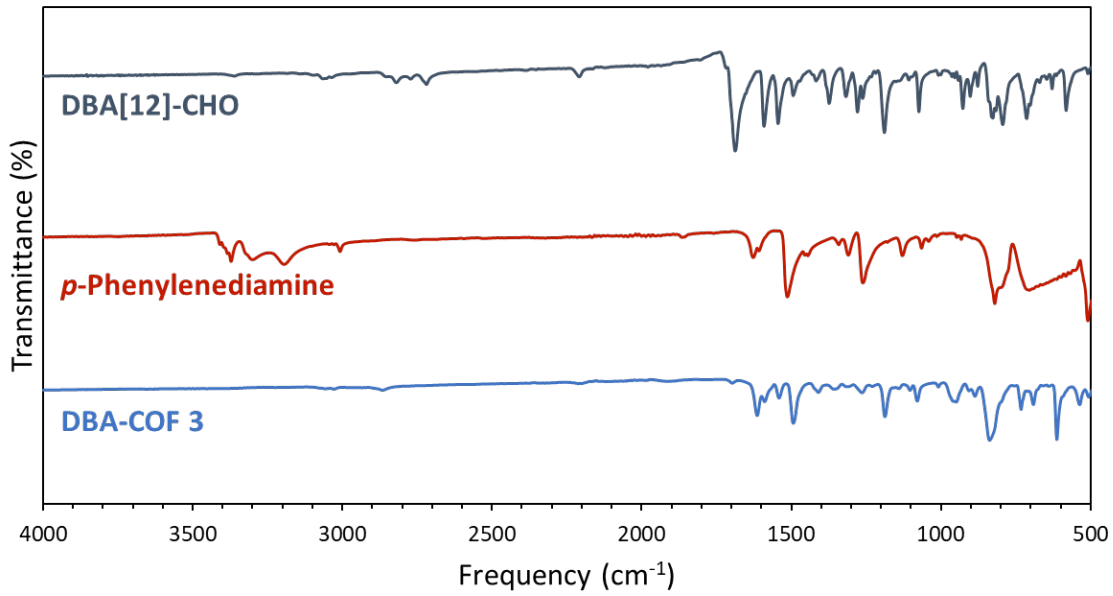


Figure S1. Comparison of DBA[12]-CHO monomer, *p*-phenylenediamine monomer, and DBA-COF 3.

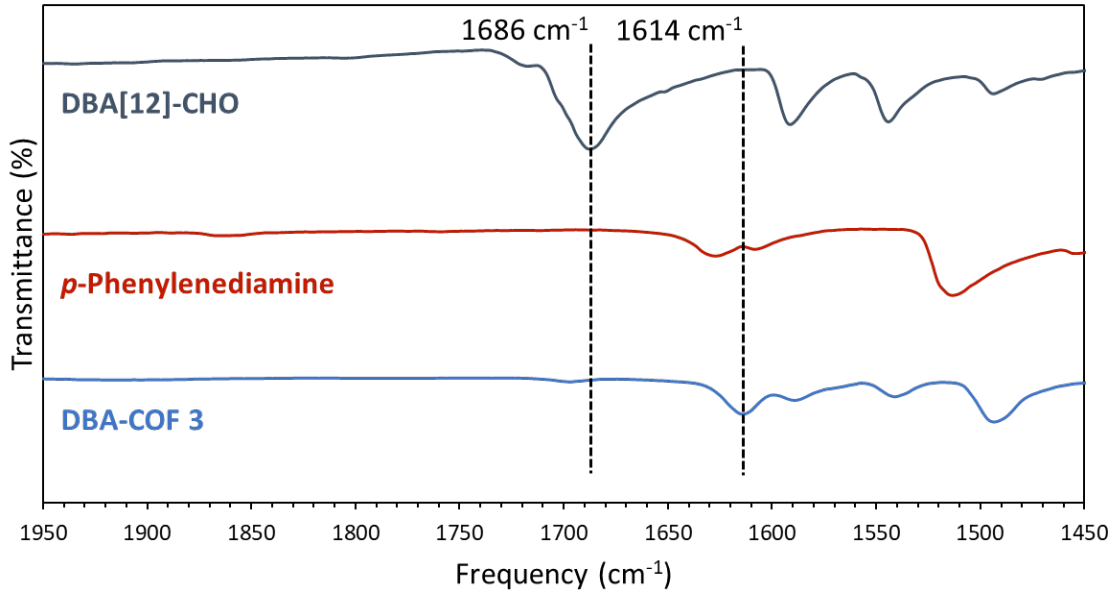
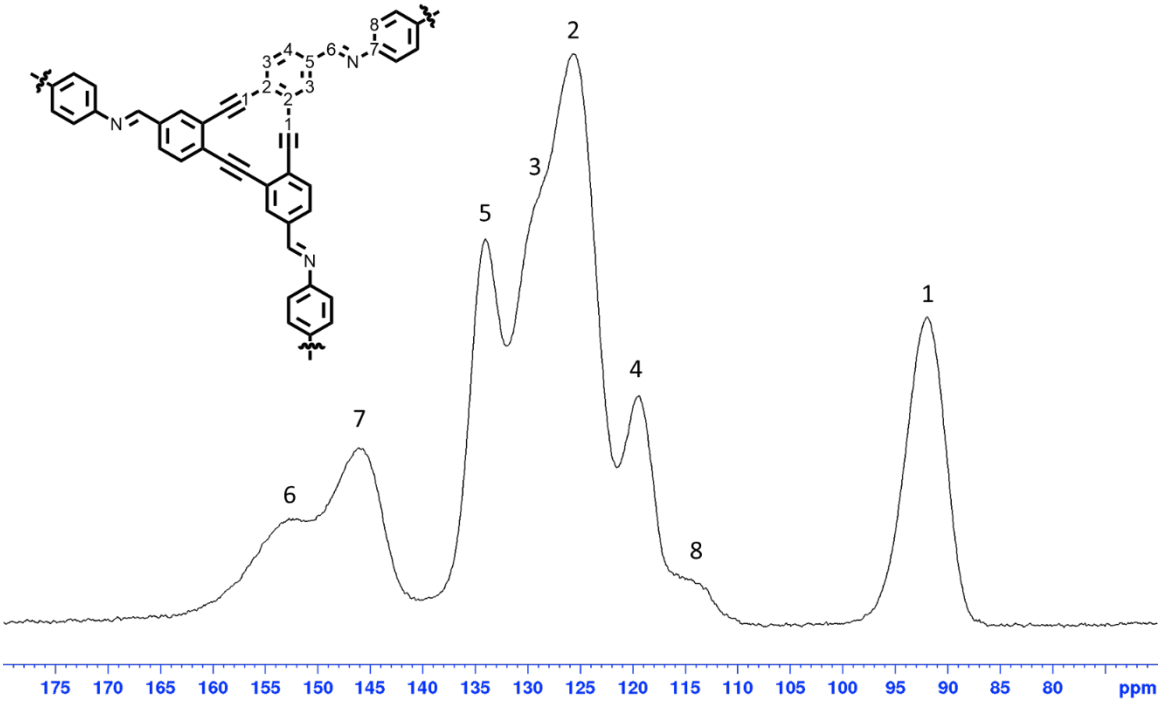


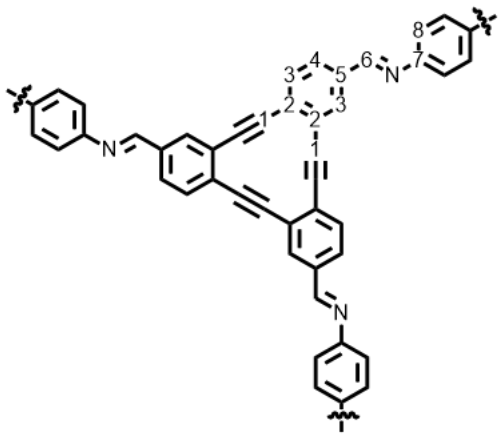
Figure S2. A comparison of the C=O stretching region for DBA[12]-CHO, *p*-phenylenediamine, and DBA-COF 3. Dotted lines mark the disappearance of the C=O stretching peak, and the appearance of a new peak at 1614 cm^{-1} attributed to formation of the C=N functional group.

Table S1. Tabulated FT-IR values and corresponding functional groups.

Frequency	Functional Group
1686	C=O of aldehyde
1614	C=N of imine

E. Solid State NMR Spectroscopy





Carbon #	Chemical Shift (ppm)
1	92.0
2	125.8
3	129.5
4	119.4
5	134.1
6	152.8
7	146.1
8	114.5

Figure S3. ^{13}C CP-MAS NMR spectrum and peak assignments of DBA-COF 3.

F. Experimental and Simulated PXRD Profiles

The simulated PXRD profiles were performed using Materials Studio 2018 using the unit cell precursor shown in Figure S4. Before the simulations were performed the precursor was optimized using the geometry optimization task and Universal Forcefield parameters from the Forcite module. DBA-COF 3 was then modeled using a primitive hexagonal unit cell with a *P*6 space group in which the stacking layers were offset by 12 Å. The a = b parameters were estimated by measuring the distance between the imine-linked phenyl ring of the COF. The c parameter was arbitrarily set at 3.4 Å. Simulation of the possible structure was performed using the Reflux Plus module to produce the expected PXRD profile. The experimental PXRDs were then subjected to a Pawley refinement using Pseudo-Voigt peak shape function and Berar-Baldinozzi asymmetry correction function to produce the refined PXRD profile.

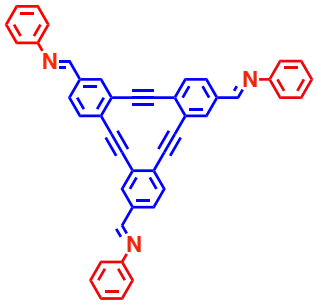


Figure S4. Precursor used to construct the hexagonal unit cell for DBA-COF 3.

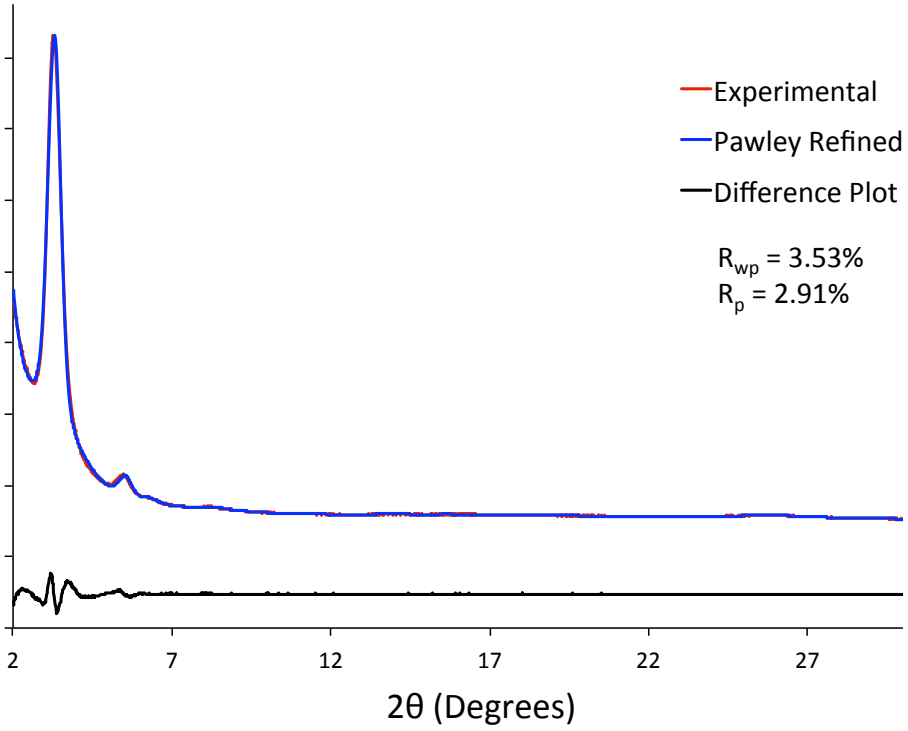


Figure S5. Experimental (red), Pawley refined (blue), and difference plot (black) PXRD patterns of DBA-COF 3.

Table S2. Fractional atomic coordinates for the hexagonal unit cell of DBA-COF 3 calculated using the Materials Studio 2018.

DBA-COF 3			
Hexagonal, *P*6 space group a=b= 32.265, c = 3.4			
Atom	**x**	**y**	**z**
C1	0.470403	0.783023	0.742286
C2	0.427596	0.749739	0.733810
C3	0.418651	0.705884	0.728544
C4	0.410230	0.668900	0.723993
C5	0.399053	0.624361	0.718385
C6	0.432025	0.614360	0.721537
C7	0.422429	0.571536	0.716287
C8	0.457799	0.562225	0.719803
N9	0.450618	0.523072	0.715201
C10	0.484259	0.512658	0.718397
C11	0.527843	0.544743	0.726856
C12	0.559930	0.533540	0.729784
C13	0.548985	0.490301	0.724327
N14	0.582626	0.479887	0.727524
C15	0.575446	0.440734	0.722922

G. BET Surface Area Analysis

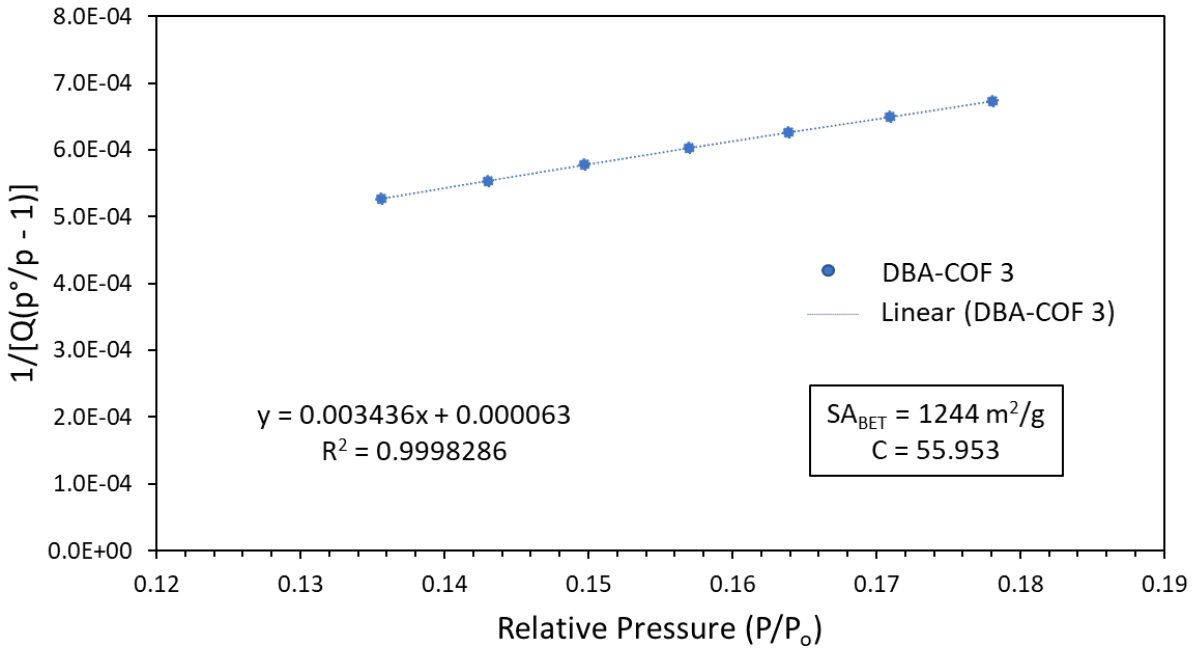


Figure S6. Linear surface area plot for DBA-COF 3.

H. TGA Profile

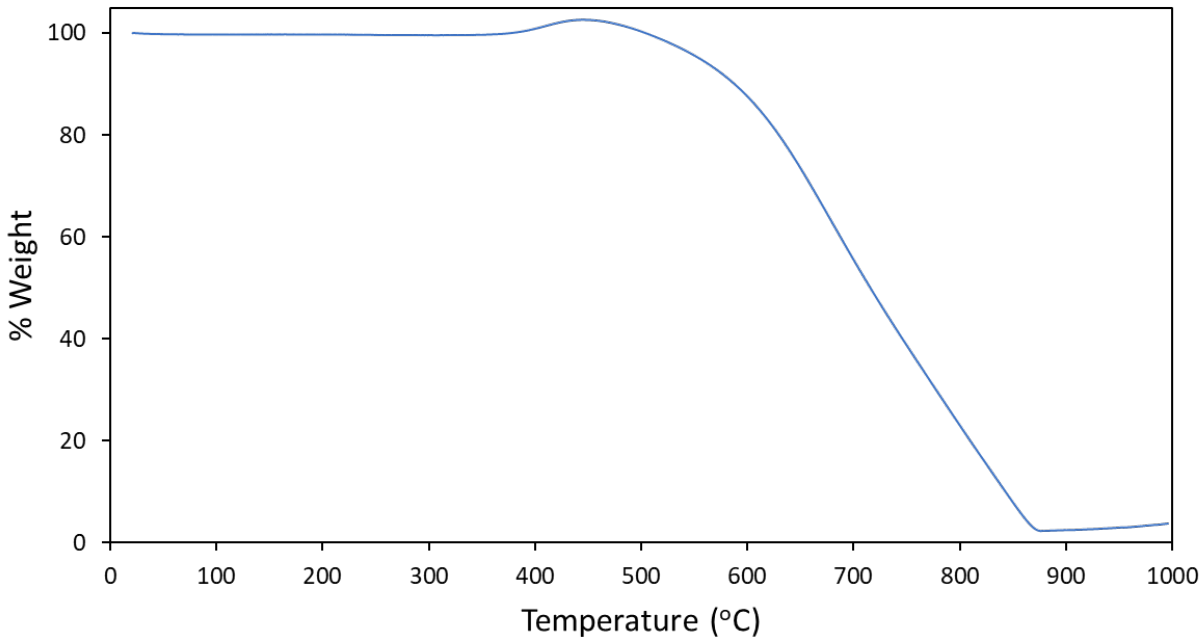


Figure S7. TGA profile for DBA-COF 3. The material maintains 95% of its mass up until 555 °C.

I. SEM Micrographs

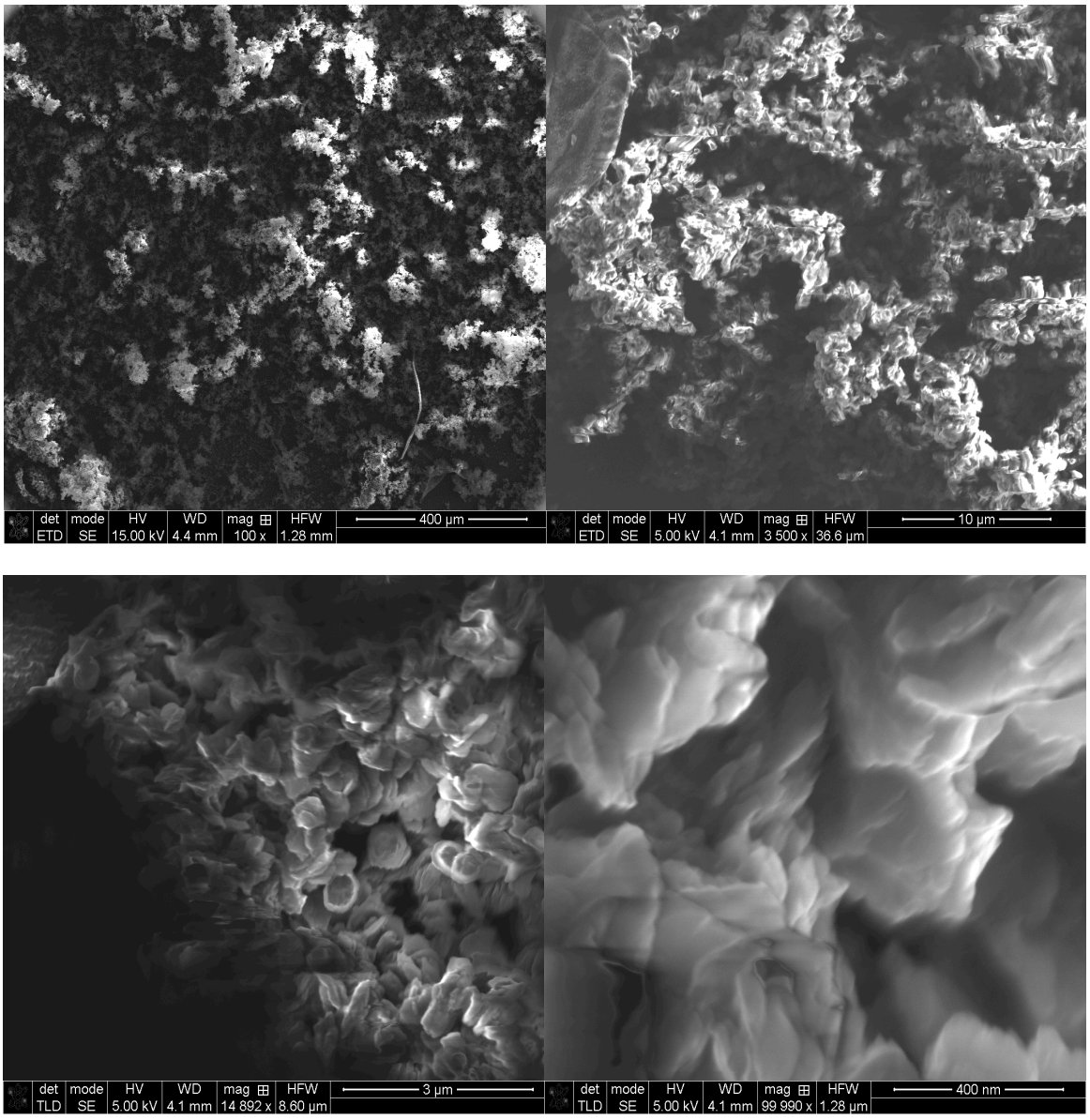


Figure S8. Scanning electron microscopy (SEM) images of DBA-COF 3 at different magnifications.

J. COF Stability Studies

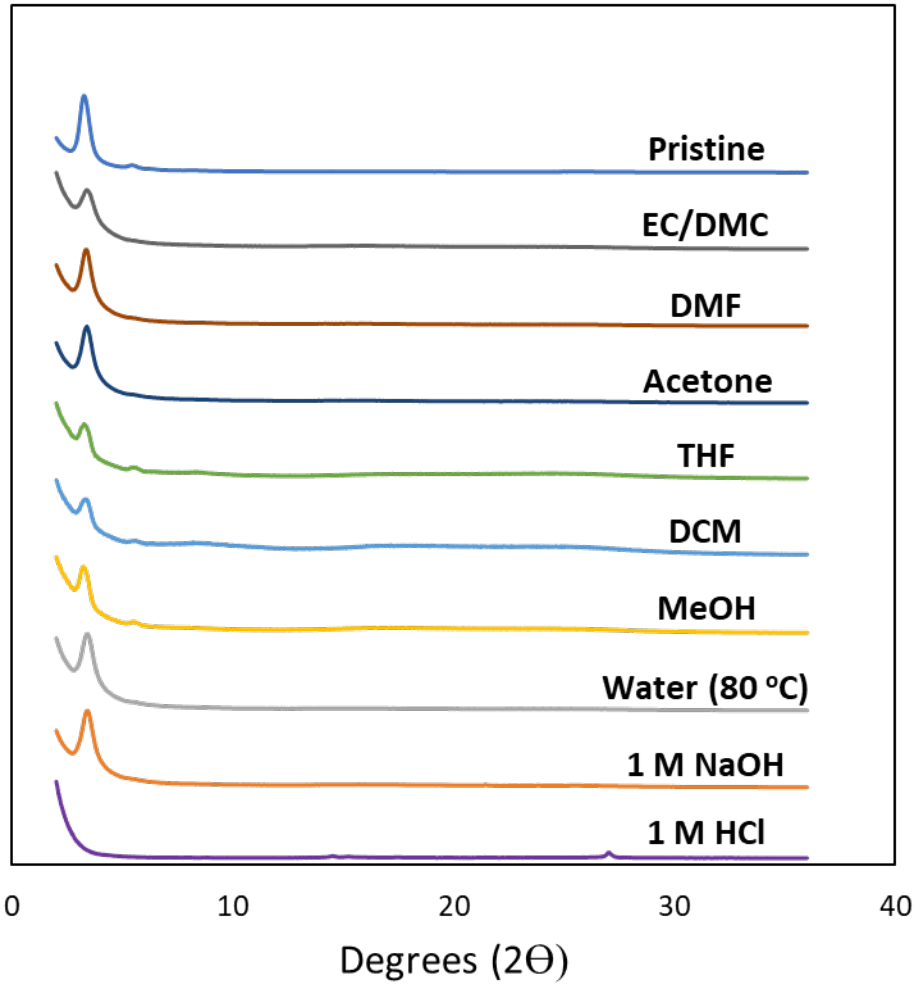


Figure S9. Overlaid PXRDs of DBA-COF 3 samples after soaking for 24 hrs.

K. Cyclic Voltammetry

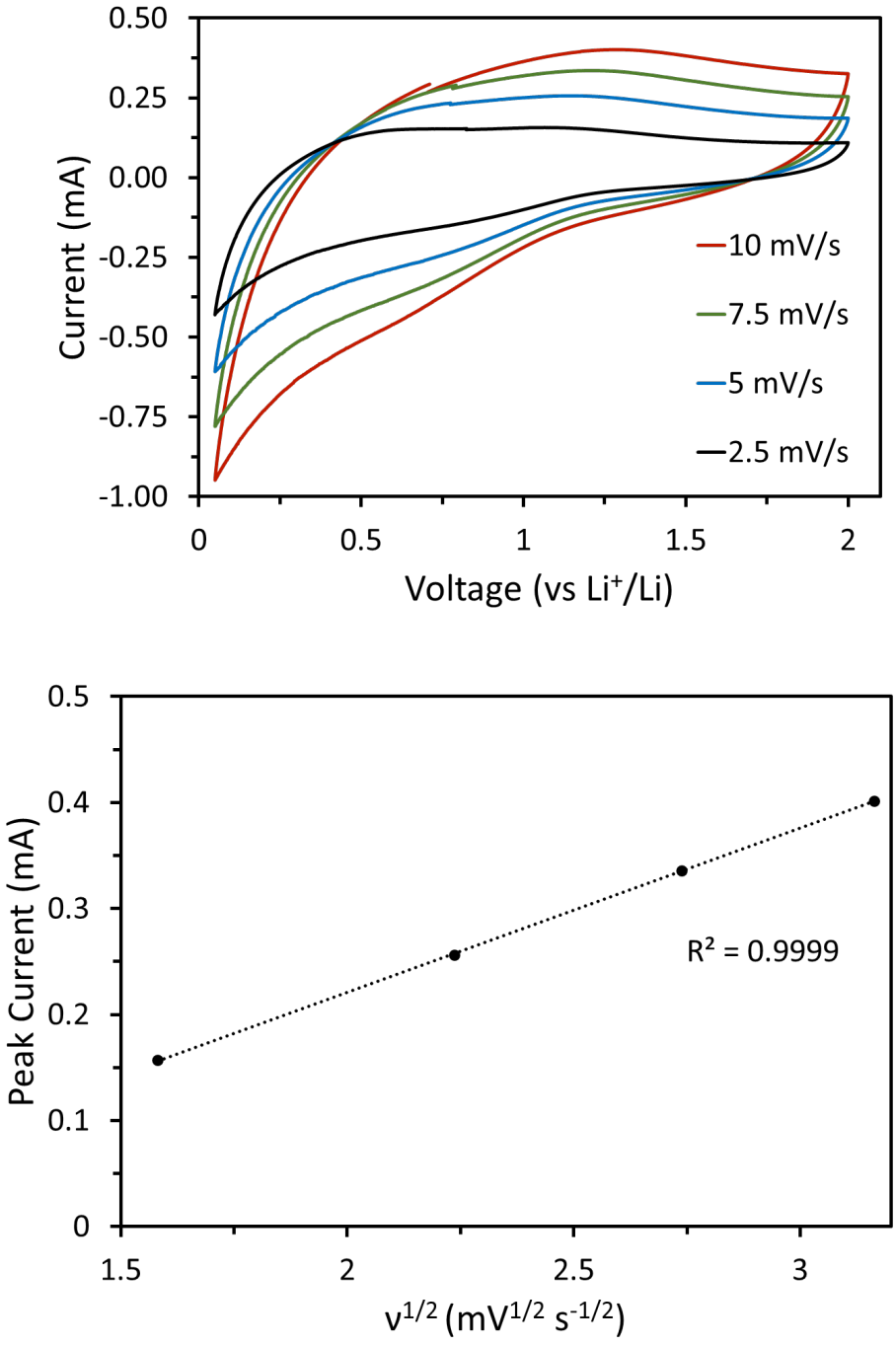


Figure S10. Cyclic voltammograms for the assembled LIB taken at increasing sweep rates (top), and a plot of peak current vs the square root of the sweep rate (bottom).

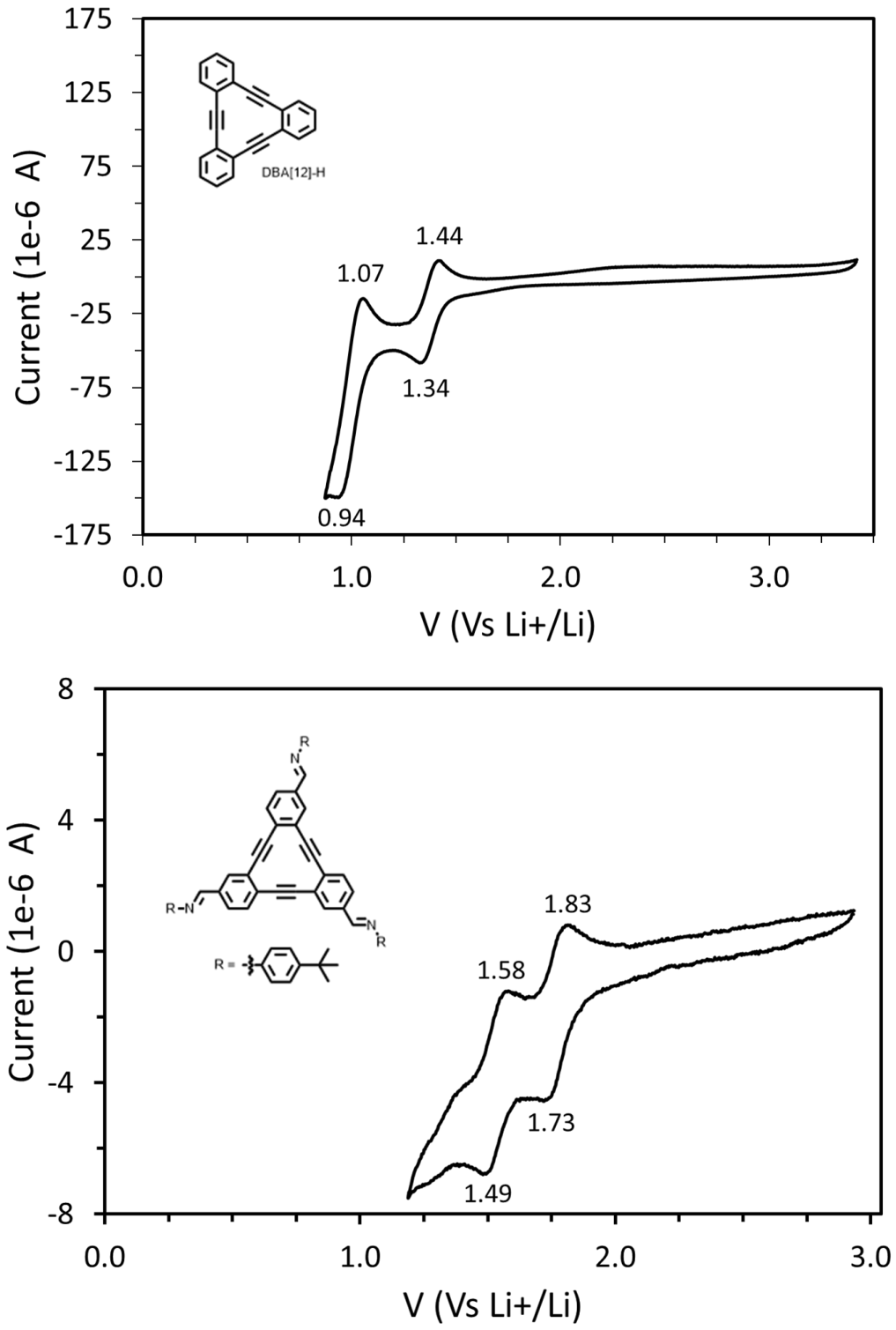


Figure S11. Cyclic Voltammogram of DBA[12]-H (top) and DBA[12]-Imine (bottom) without $LiPF_6$ present in the electrolyte.

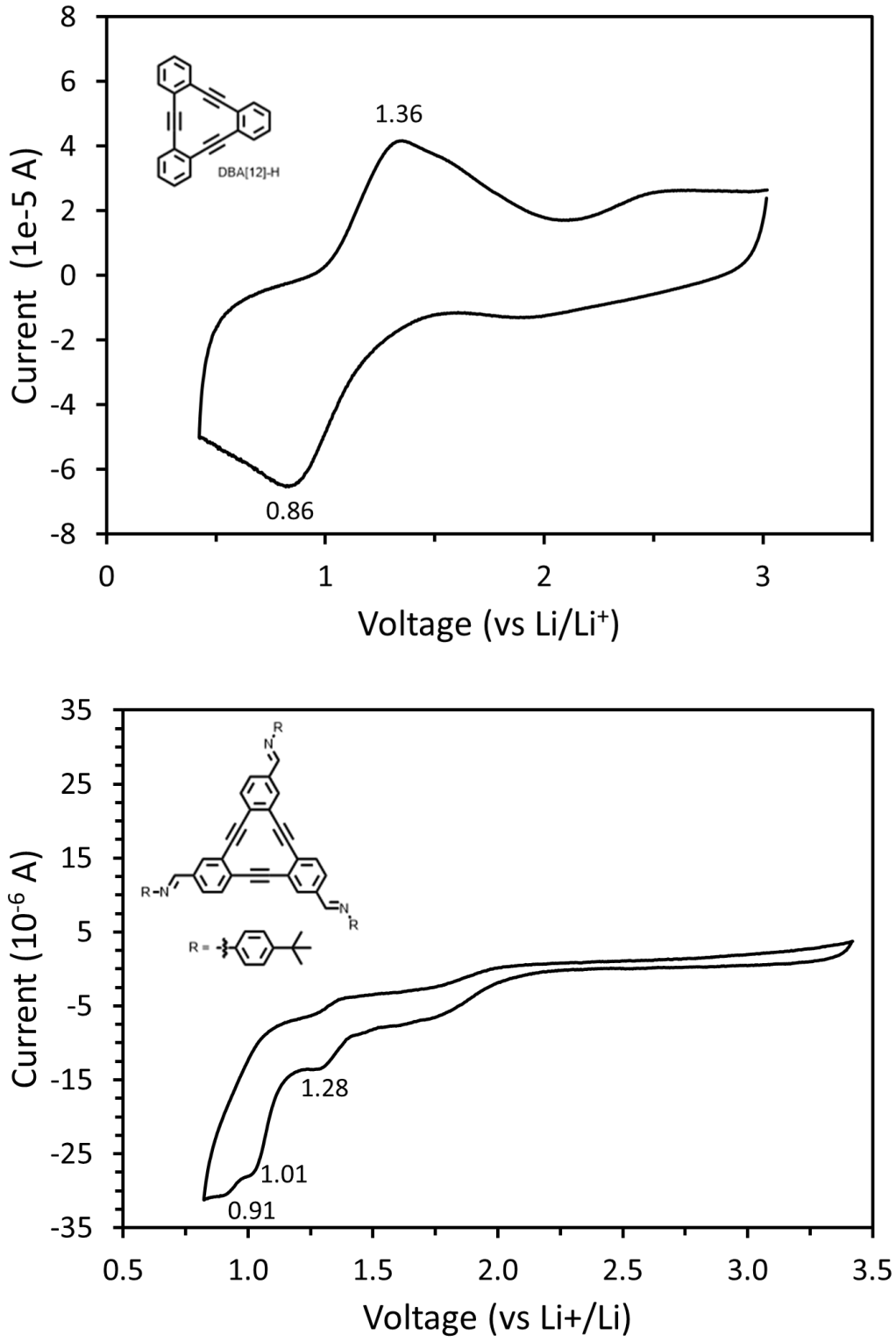


Figure S12. Cyclic Voltammogram of DBA[12]-H (top) and DBA[12]-Imine (bottom) with $LiPF_6$ present in the electrolyte.

L. Electrochemical Impedance Spectroscopy (EIS)

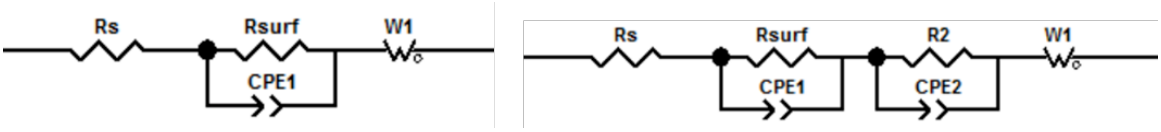


Figure S13. A schematic of the cell circuit models used to determine impedance values. The left model was used up to cycle 40. The right model was used for the remaining cycles to account for the second semicircle.

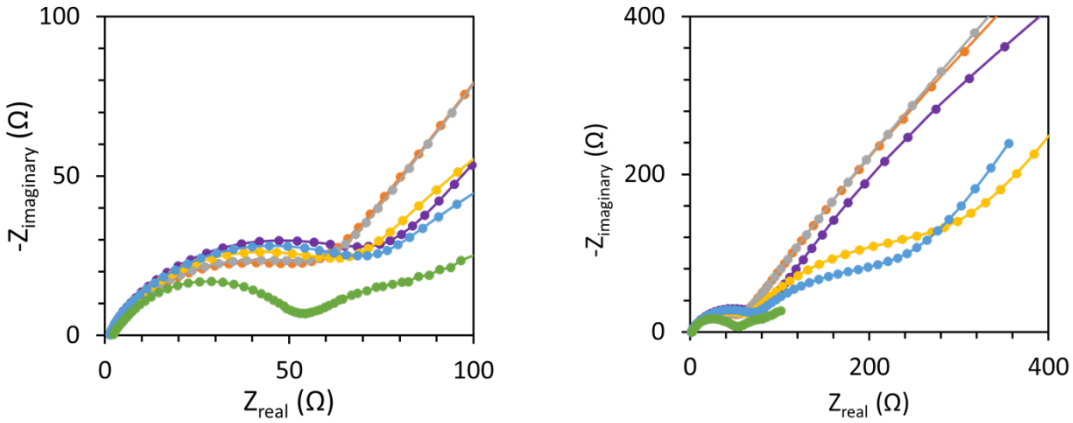


Figure S14. Impedance spectra of DBA-COF 3 LIB as assembled (green), after 10 cycles (purple), 20 cycles (orange), 30 cycles (gray), 40 cycles (gold) and 50 cycles (light blue).

Table S3. Calculated impedance values for specific charge/discharge cycles with their corresponding coulombic efficiency values.

# of Cycles	Impedance (Ω)	Coulombic Efficiency (%)
1	46.21	44.9
10	59.73	89.6
20	45.72	93.7
30	47.83	95.1
40	61.85, 231.0	95.7
50	66.67, 192.8	97.9

M. X-ray Photoelectron Spectroscopy (XPS)

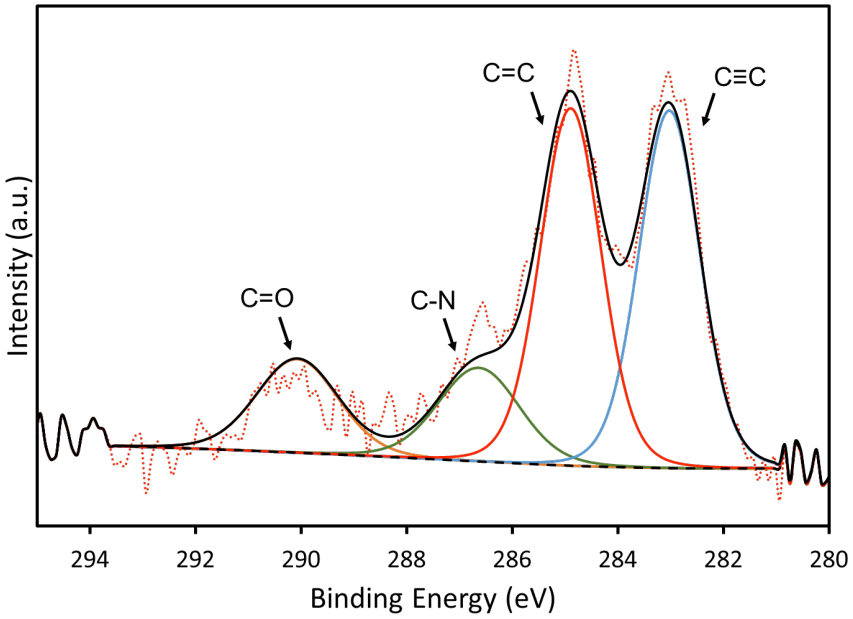


Figure S15. XPS for the C 1s region of a pristine coin cell. The C 1s spectrum could be deconvoluted to 4 peaks centered around 290.0, 286.6, 284.8, and 282.9 eV, corresponding to C=O, C-N, C=C, and C≡C functional groups, respectively.

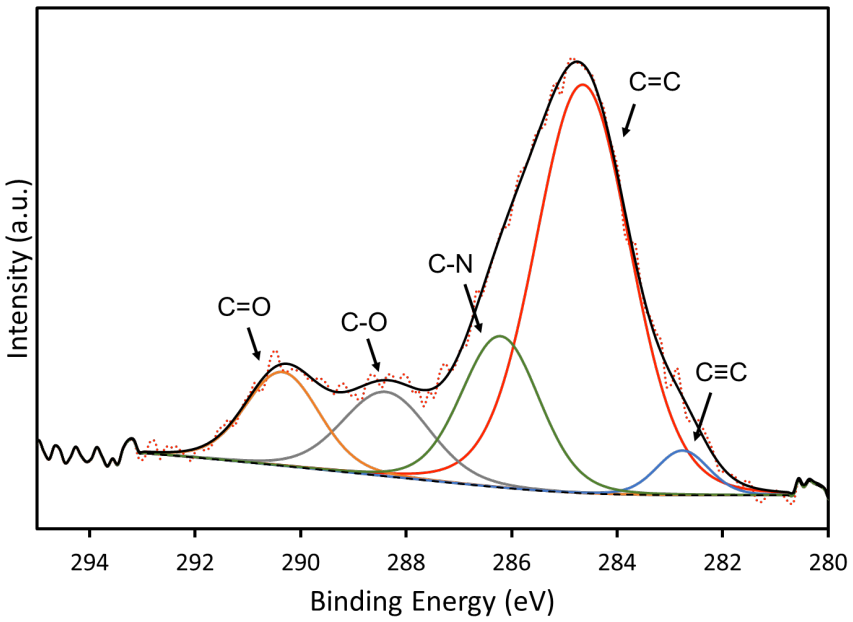


Figure S16. XPS for the C 1s region of a lithiated coin cell. The C 1s spectrum could be deconvoluted to reveal 5 peaks centered around 290.5, 288.4, 286.2, 284.4, and 282.8 eV, corresponding to the C=O, C-O, C-N, C=C, and C≡C, respectively.

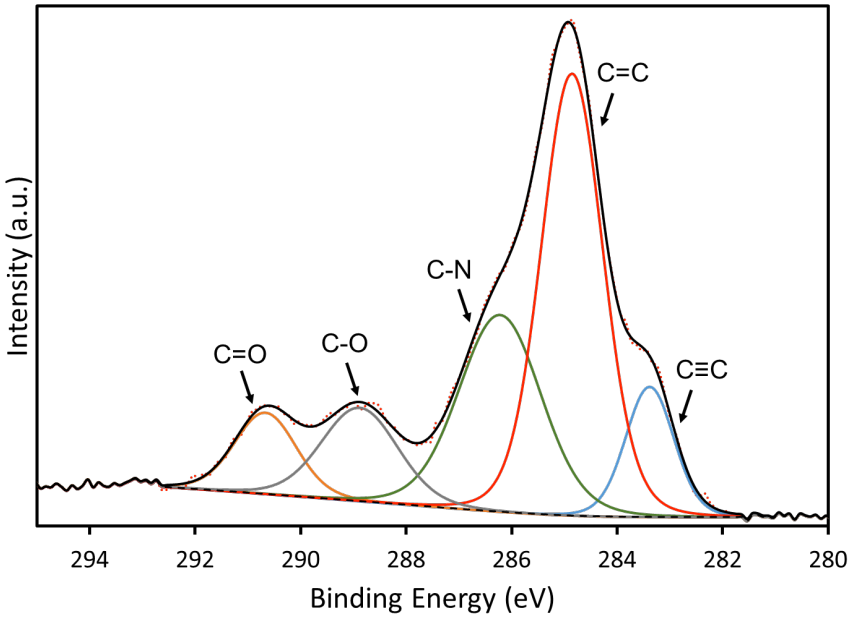
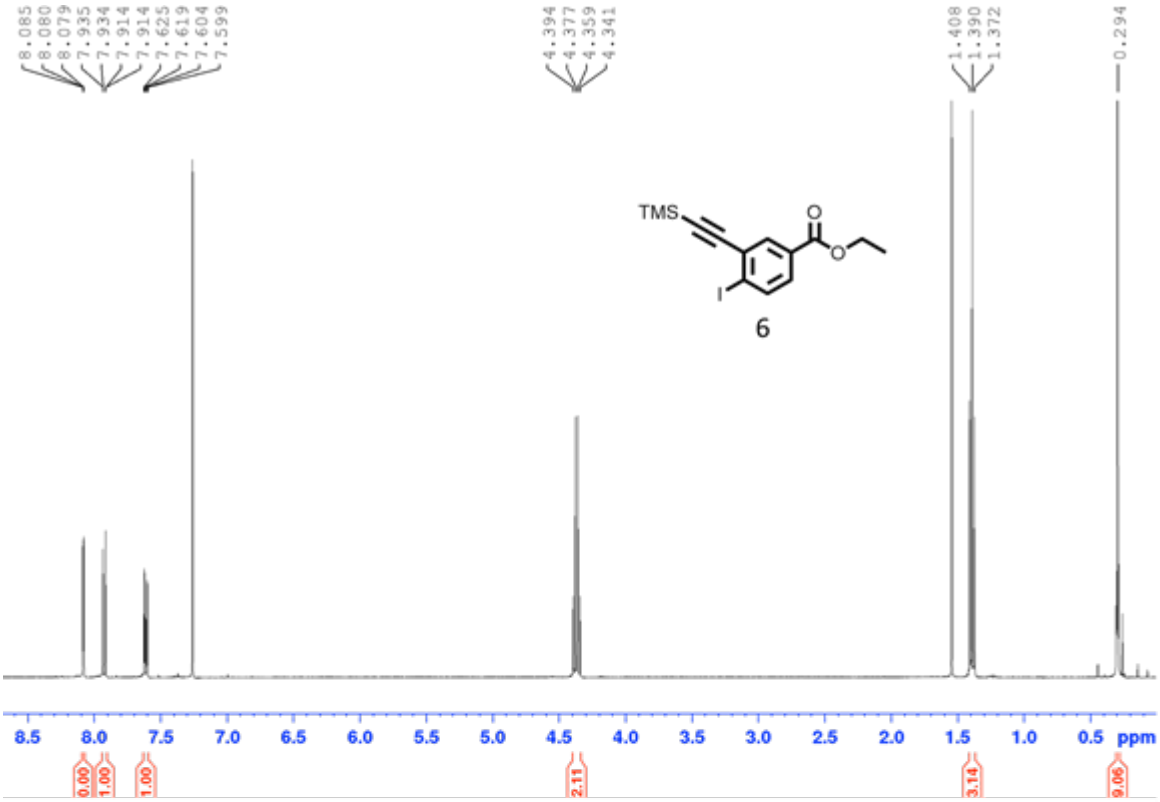
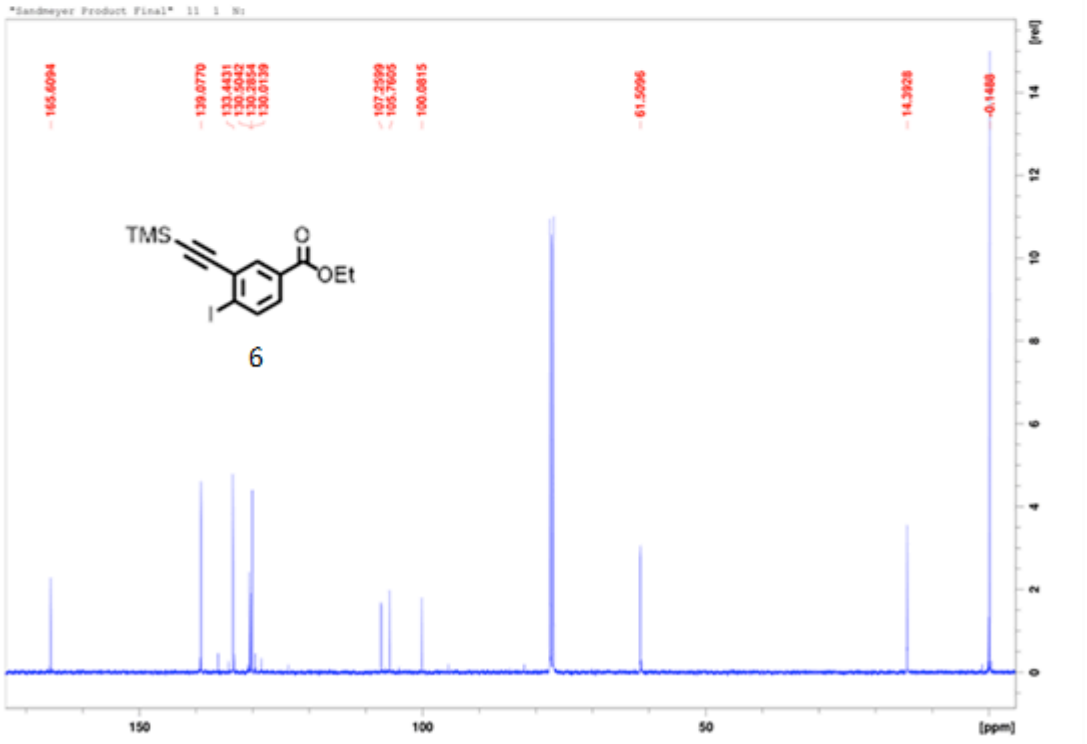
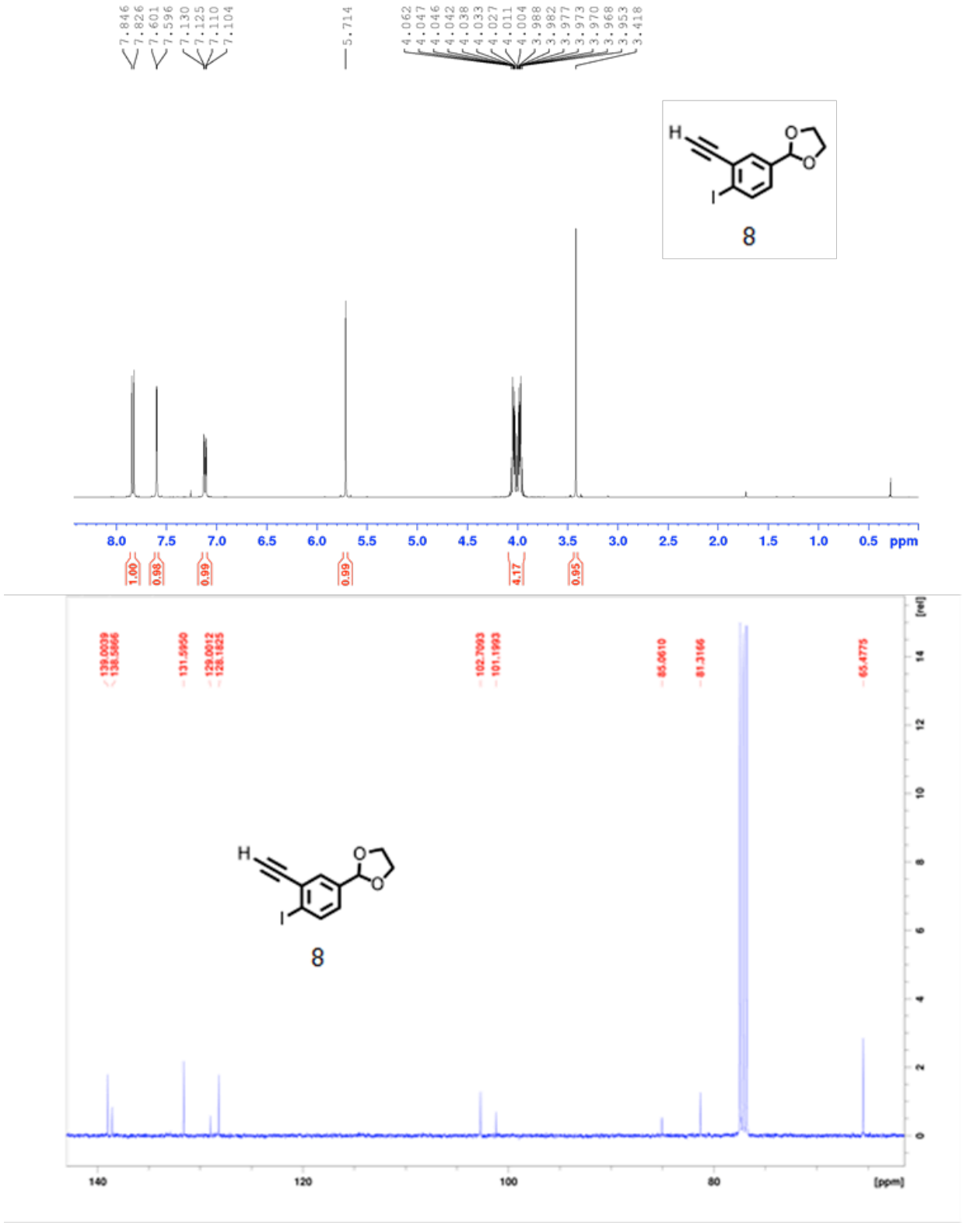


Figure S17. XPS for the C 1s region of a delithiated coin cell. The C 1s spectrum could be deconvoluted to reveal 5 peaks centered around 290.8, 288.8, 286.2, 284.6, and 283.5 eV, corresponding to the C=O, C-O, C-N, C=C, and C≡C, respectively.

N. NMR Spectroscopy



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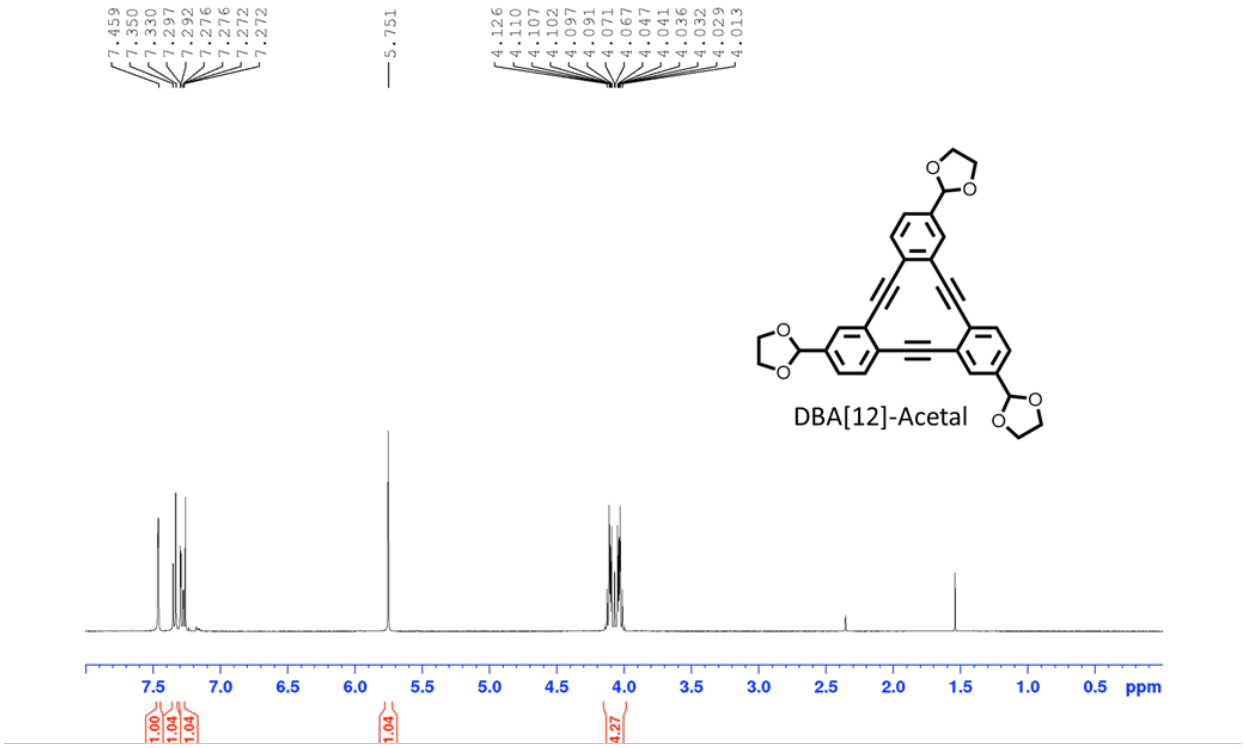
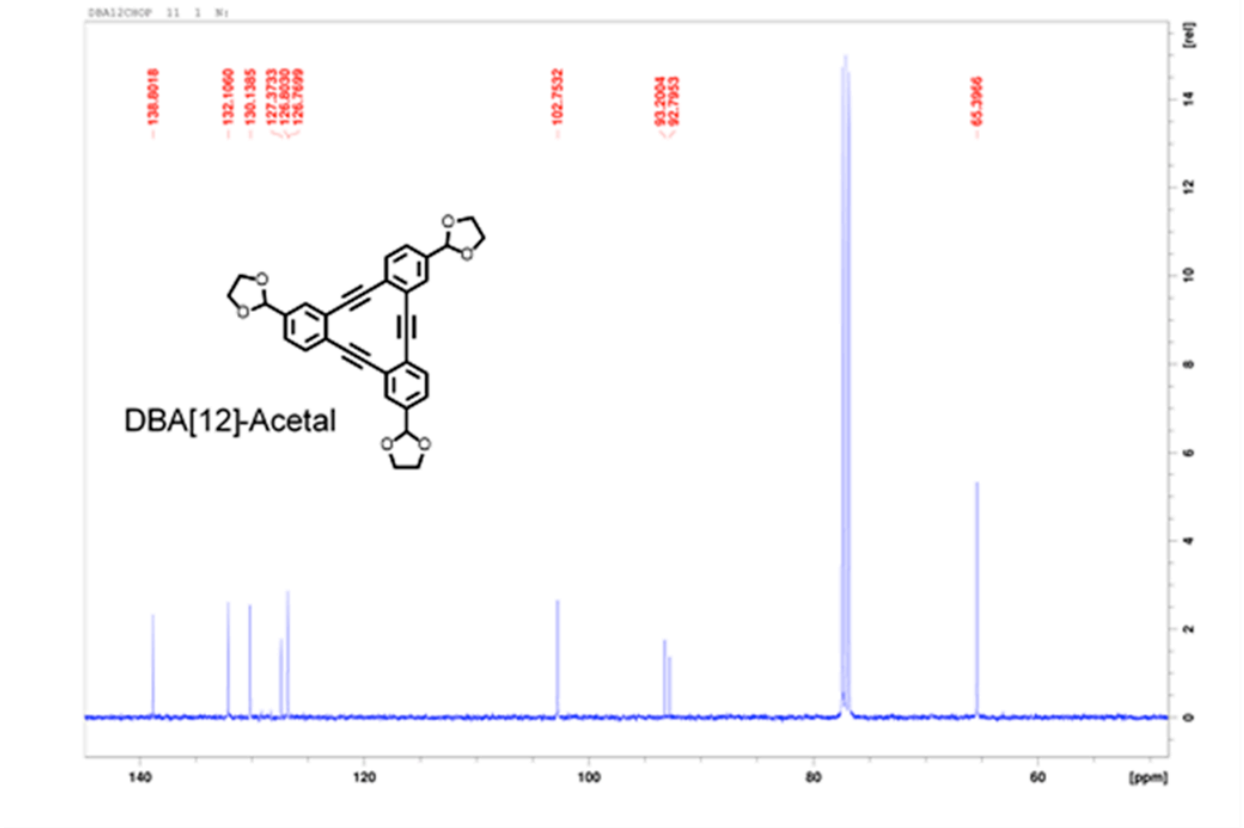
7.826
7.601
7.596
7.130
7.125
7.110
7.104
5.714
4.062
4.047
4.046
4.042
4.038
4.033
4.027
4.011
4.004
3.988
3.982
3.977
3.973
3.970
3.968
3.953
3.418
8
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.00
0.98
0.99
0.99
4.17
0.95
139.0039
138.5866
131.5950
129.0012
128.1625
102.7093
101.1993
85.0610
81.3166
65.4775
8
140
120
100
80
[ppm]


7.459
7.350
7.330
7.297
7.292
7.276
7.276
7.272
7.272
5.751
4.126
4.110
4.107
4.102
4.097
4.091
4.071
4.067
4.047
4.041
4.036
4.032
4.029
4.013
DBA[12]-Acetal
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
ppm
1.00
1.04
1.04
1.04
4.27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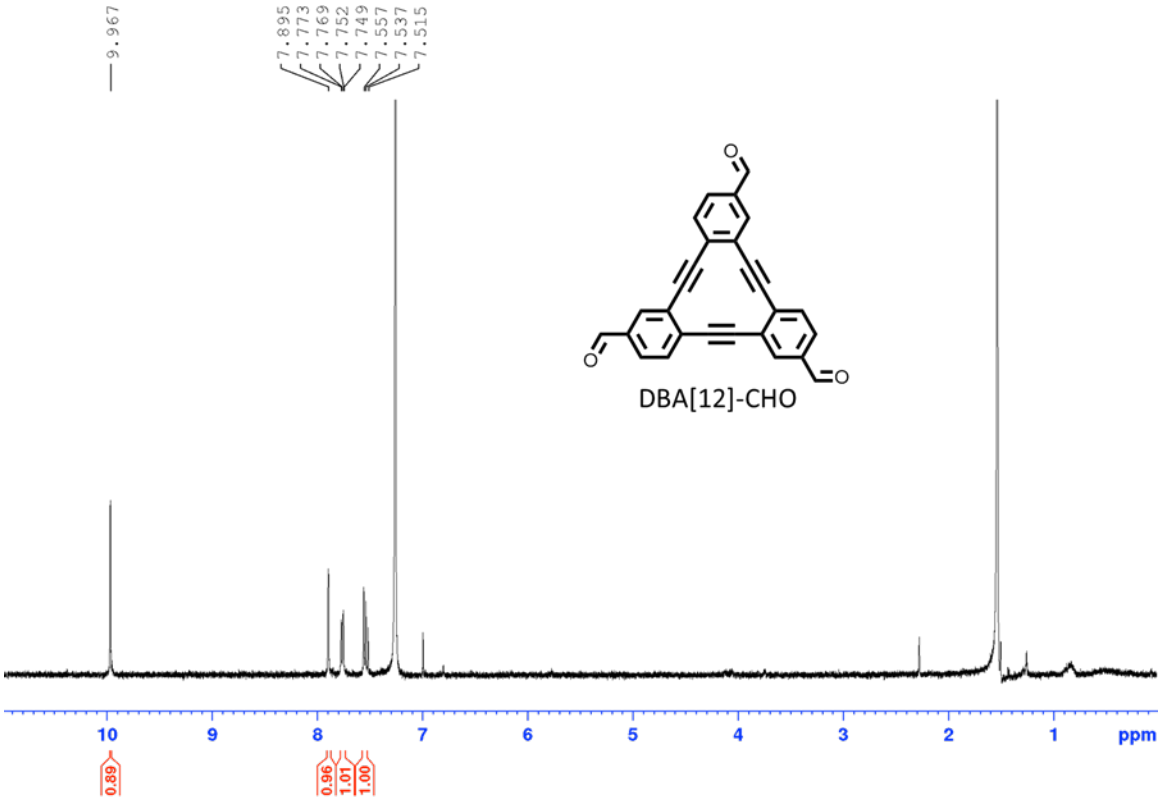
132.1060
130.1385
127.3733
126.6030
126.7699
102.7532
93.2004
92.7953
65.3966
DBA[12]-Acetal
[rel]
[ppm]
140
120
100
80
60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7.895
7.773
7.769
7.752
7.749
7.557
7.537
7.515
DBA[12]-CHO
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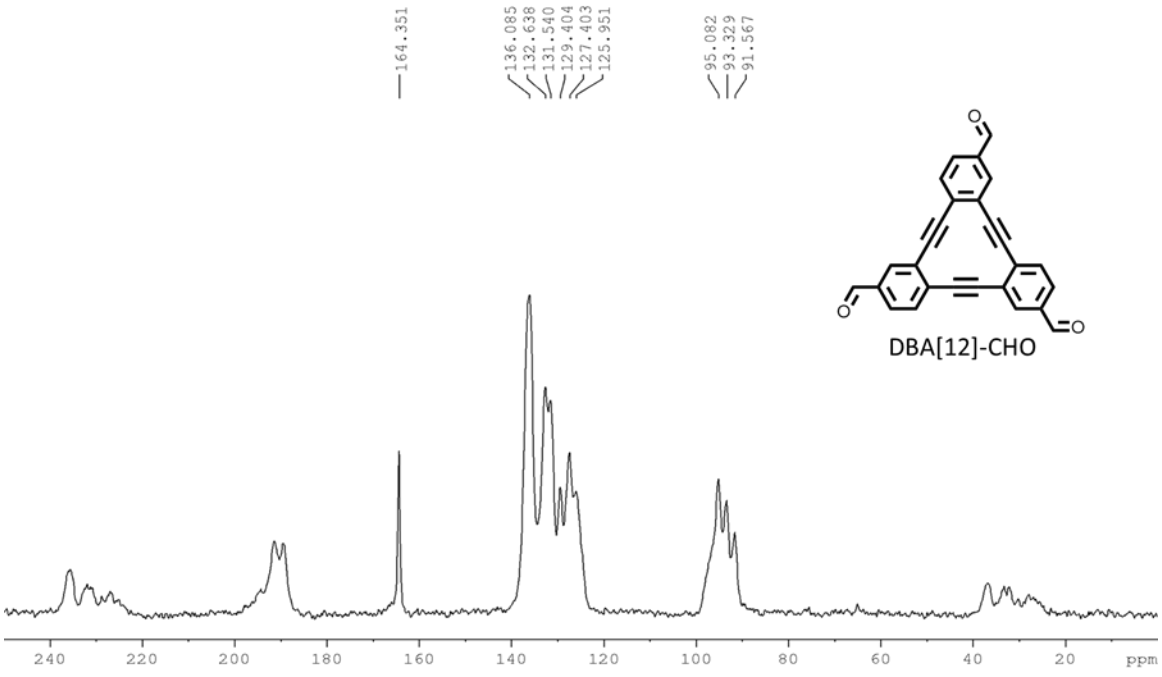
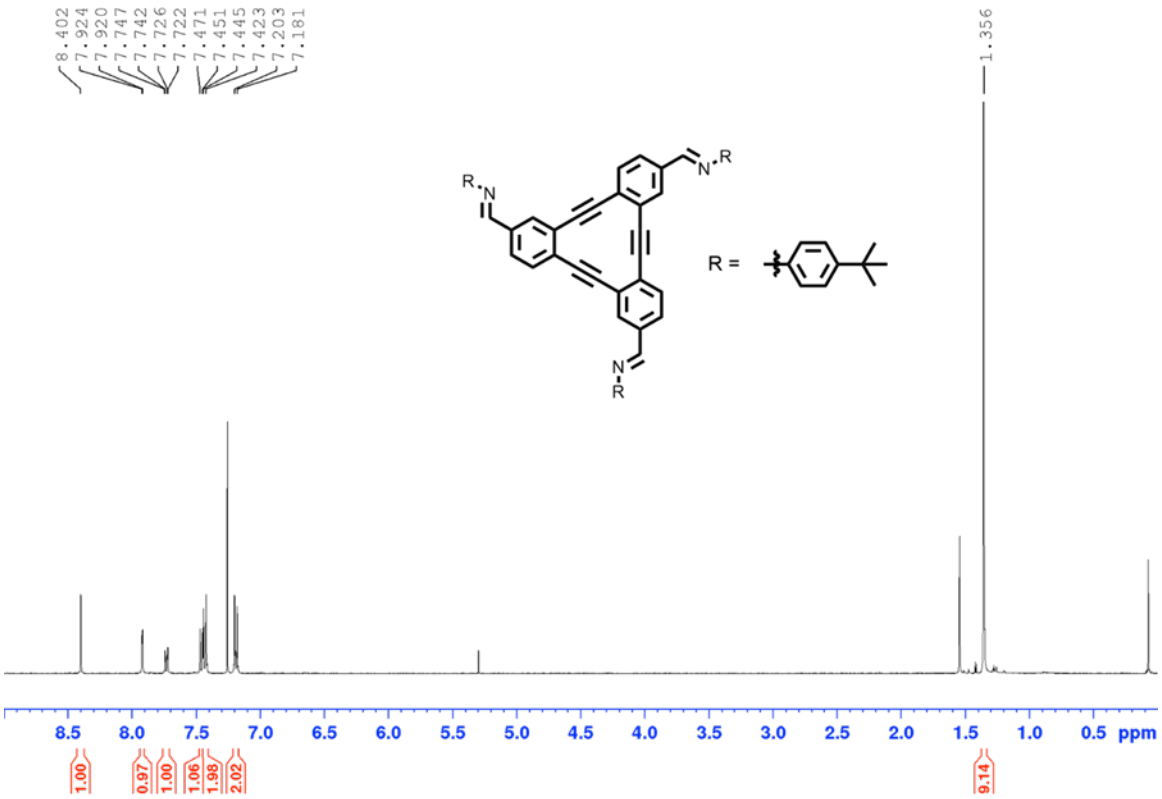
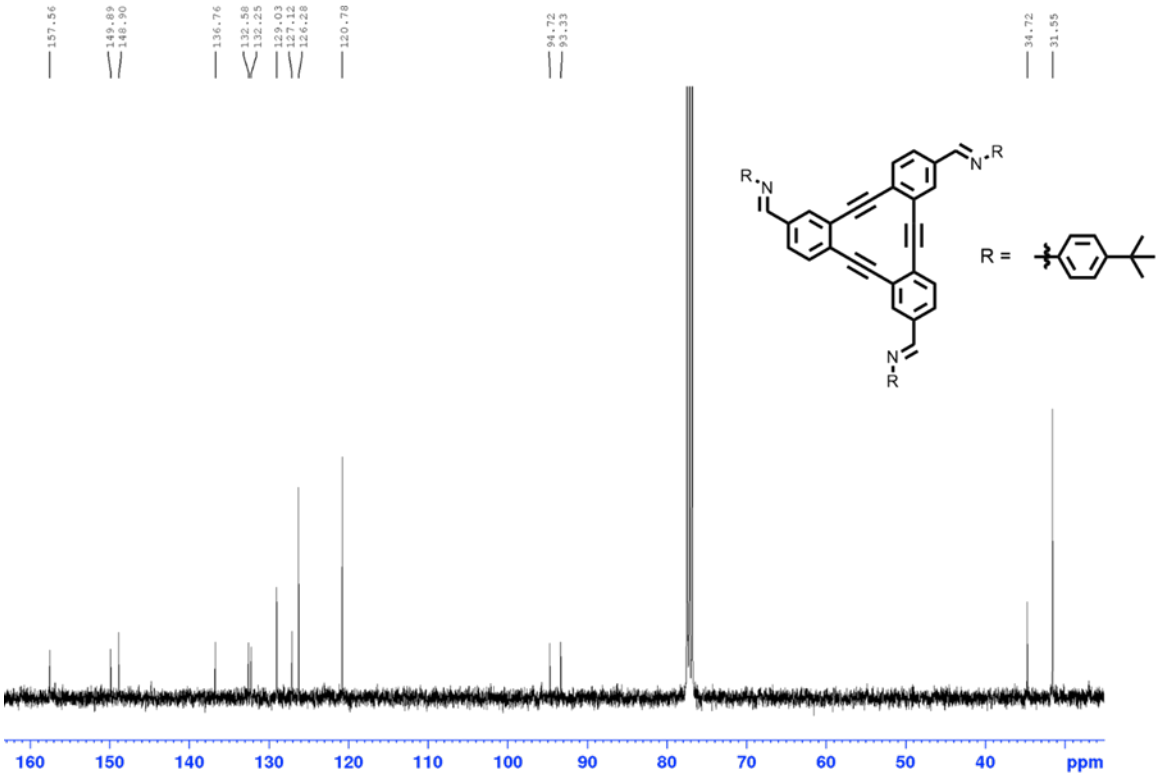
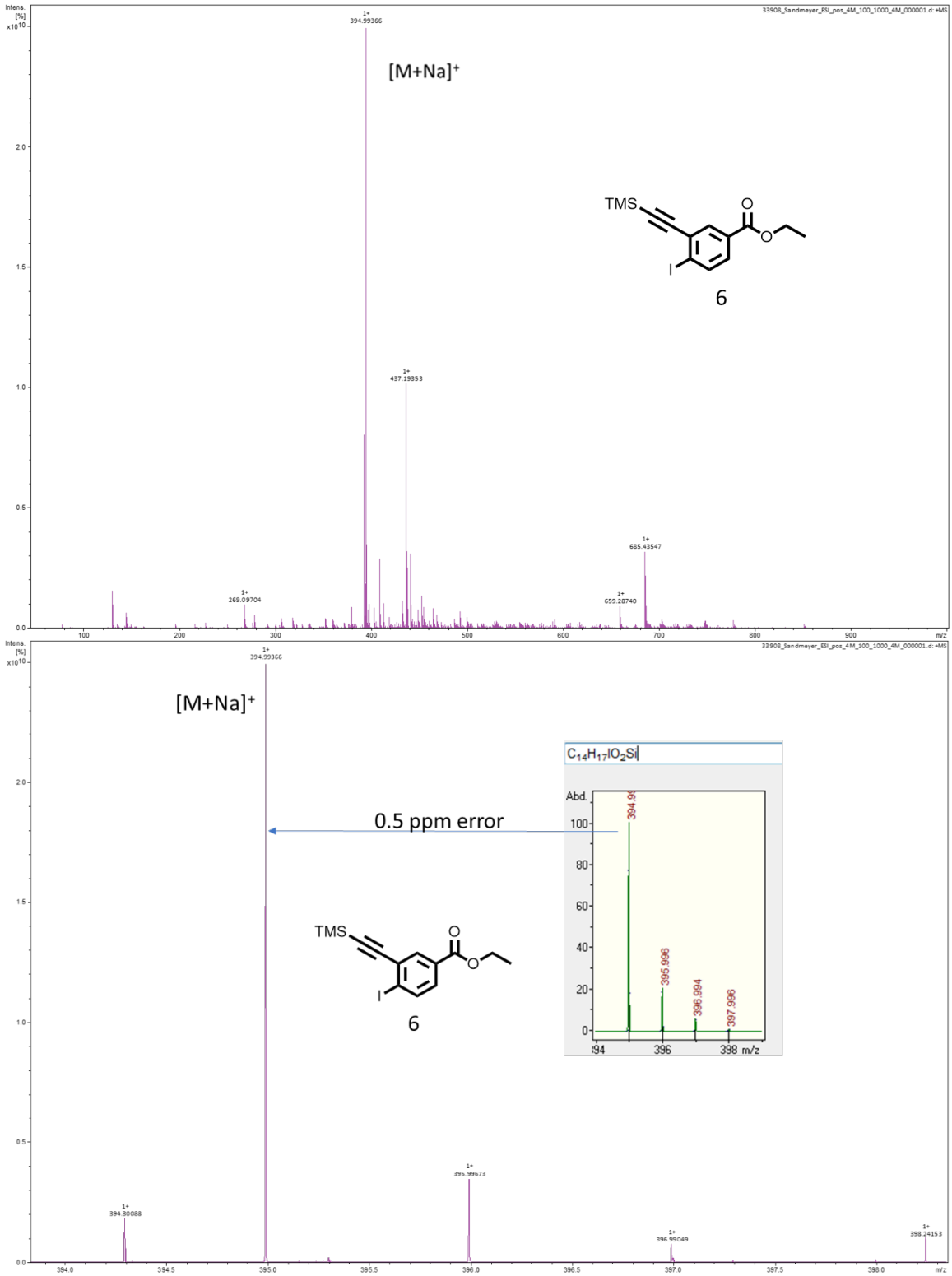
9
8
7
6
5
4
3
2
1
ppm
0.89
0.96
1.01
1.00

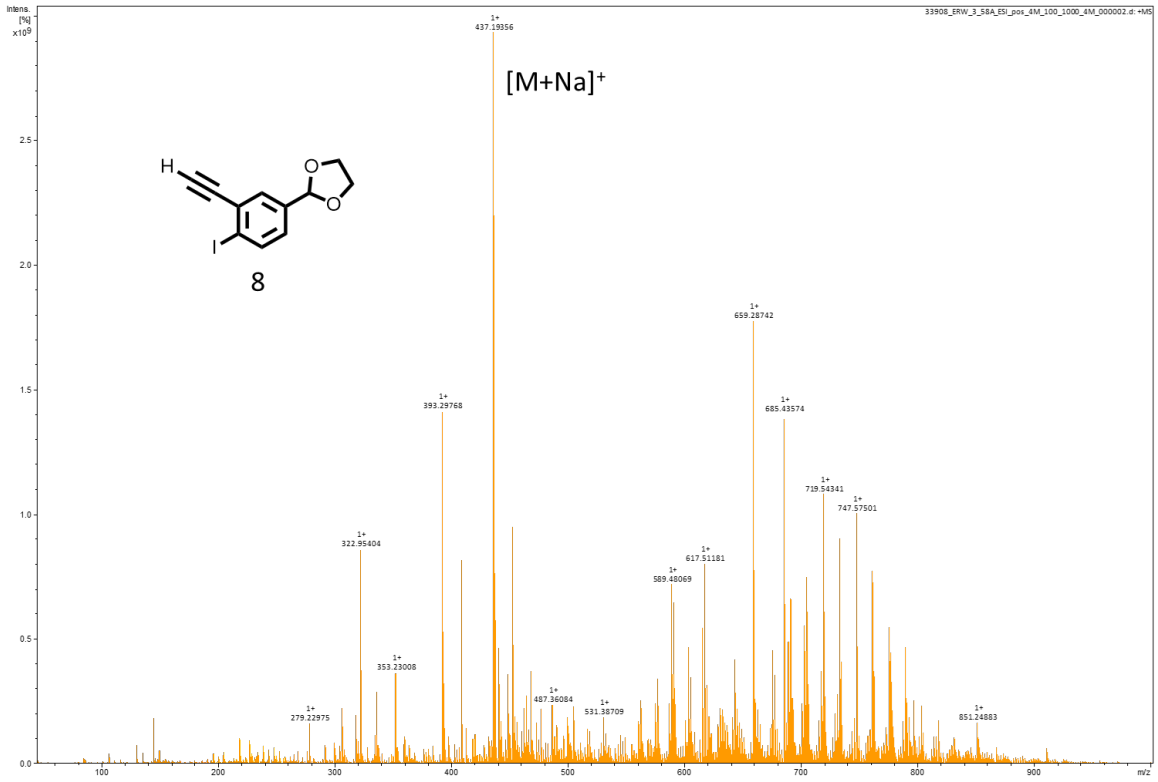

164.351
136.085
132.638
131.540
129.404
127.403
125.951
95.082
93.329
91.567
DBA[12]-CHO
240
220
200
180
160
140
120
100
80
60
40
20
ppm

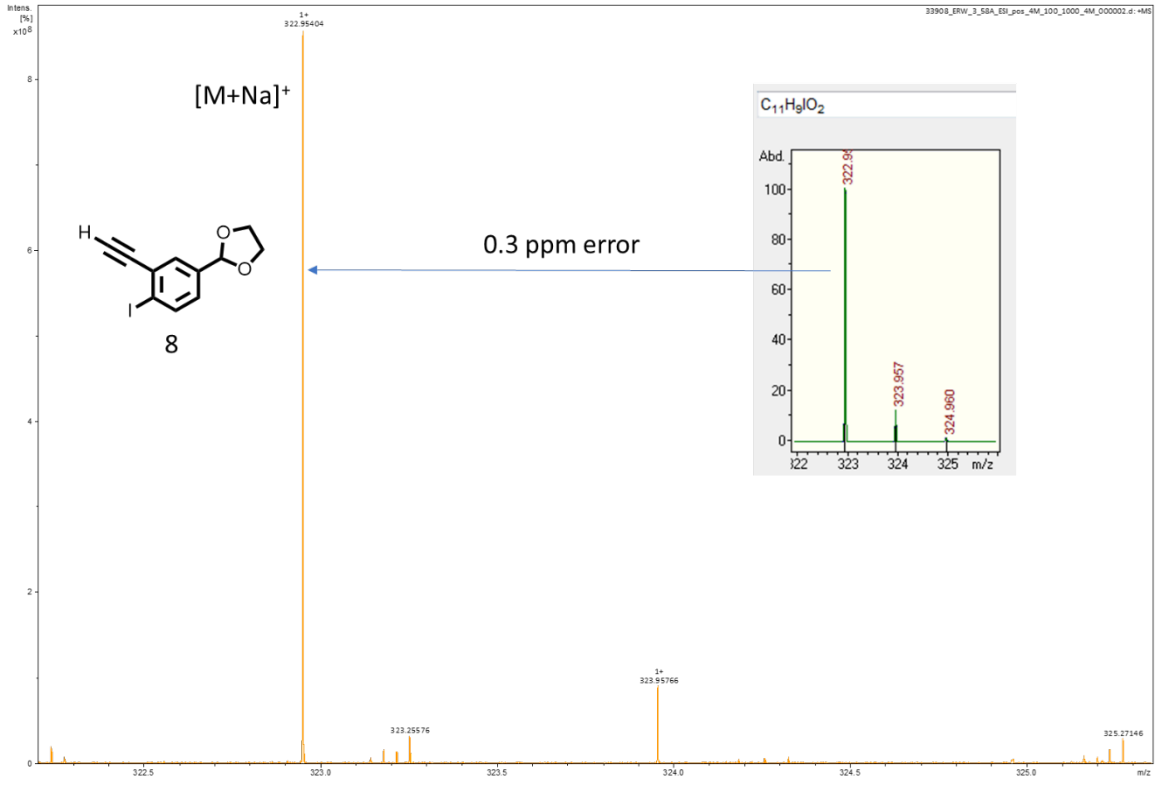

8.402
7.924
7.920
7.747
7.742
7.726
7.722
7.471
7.451
7.445
7.423
7.203
7.181
1.356
R =
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.00
0.97
1.00
1.06
1.98
2.02
9.14

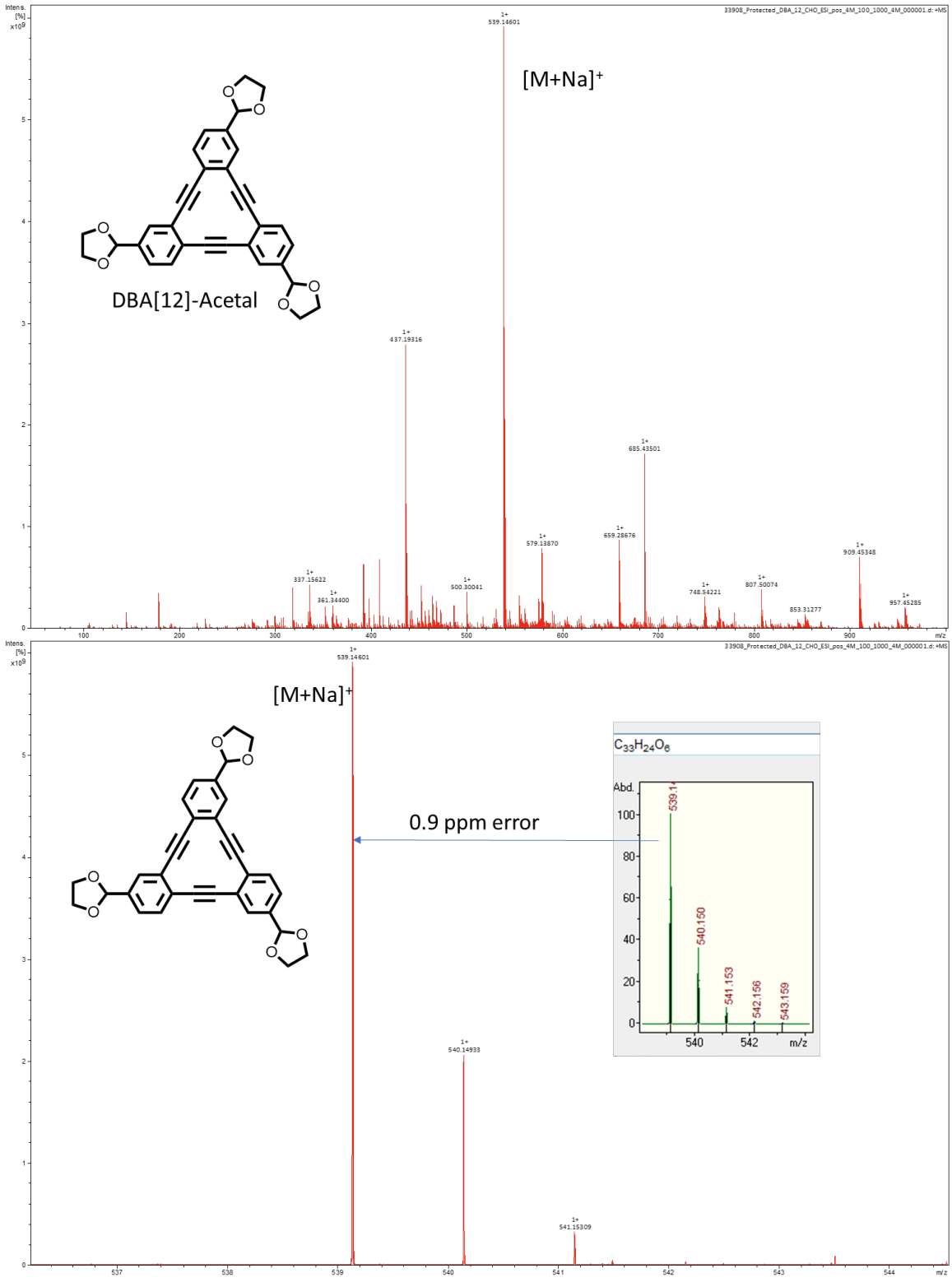

157.56
149.89
148.90
136.76
132.58
132.25
129.03
127.12
126.28
120.78
94.72
93.33
34.72
31.55
R =
160 150 140 130 120 110 100 90 80 70 60 50 40 ppm

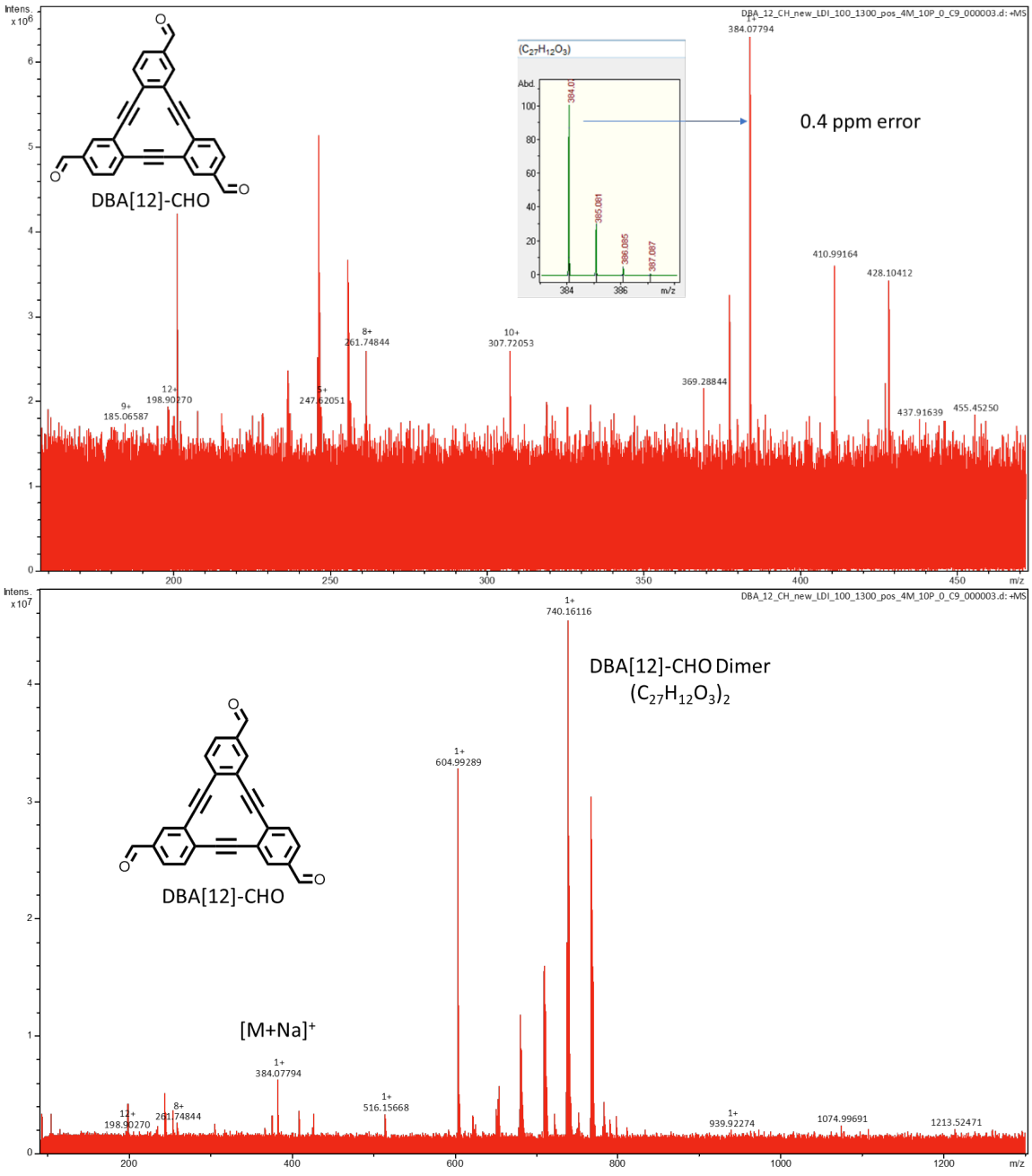
O. Mass Spectrometry

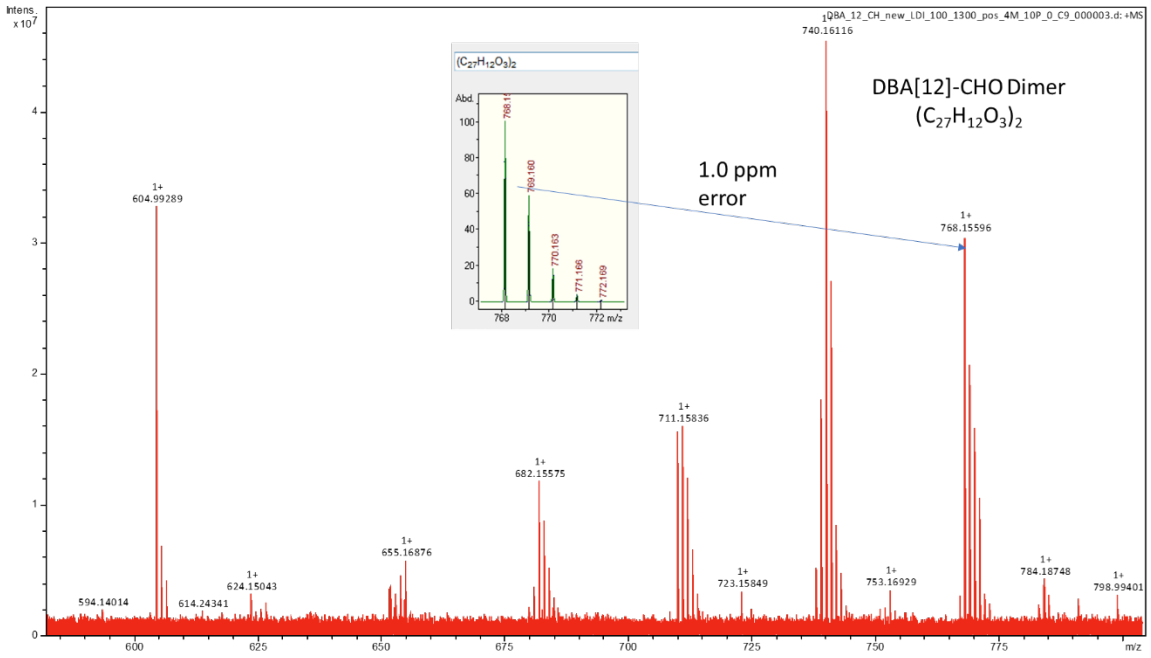


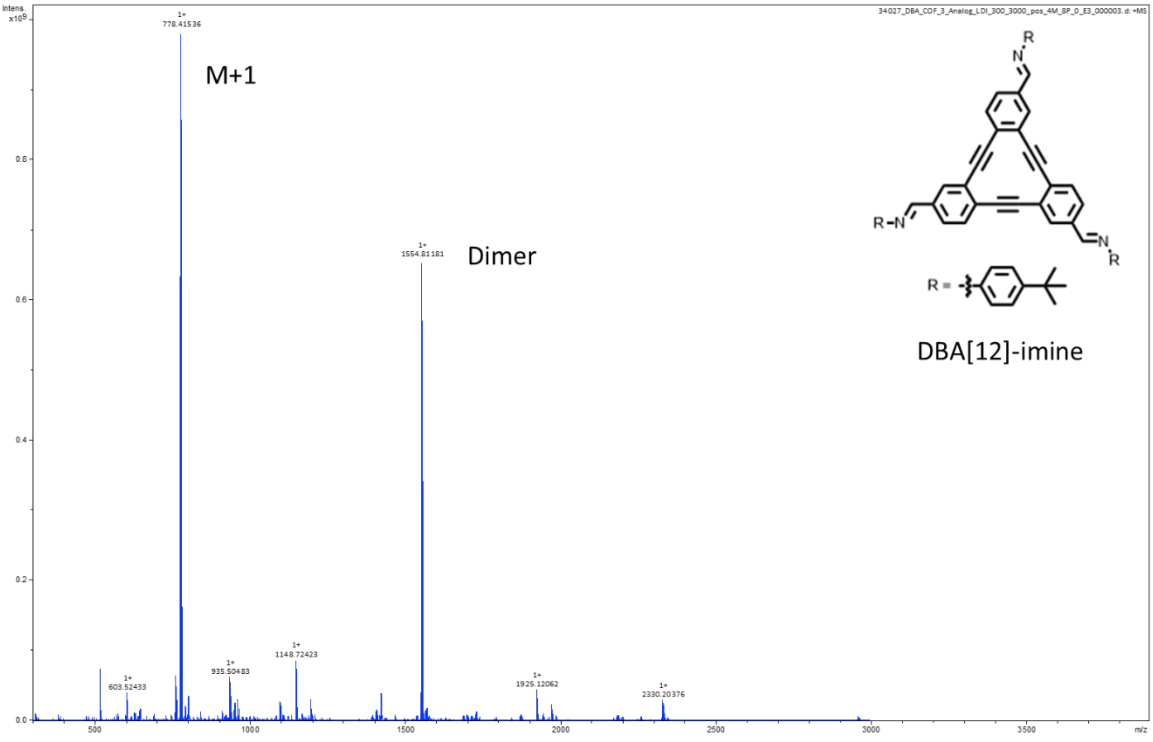

[M+Na]+
8

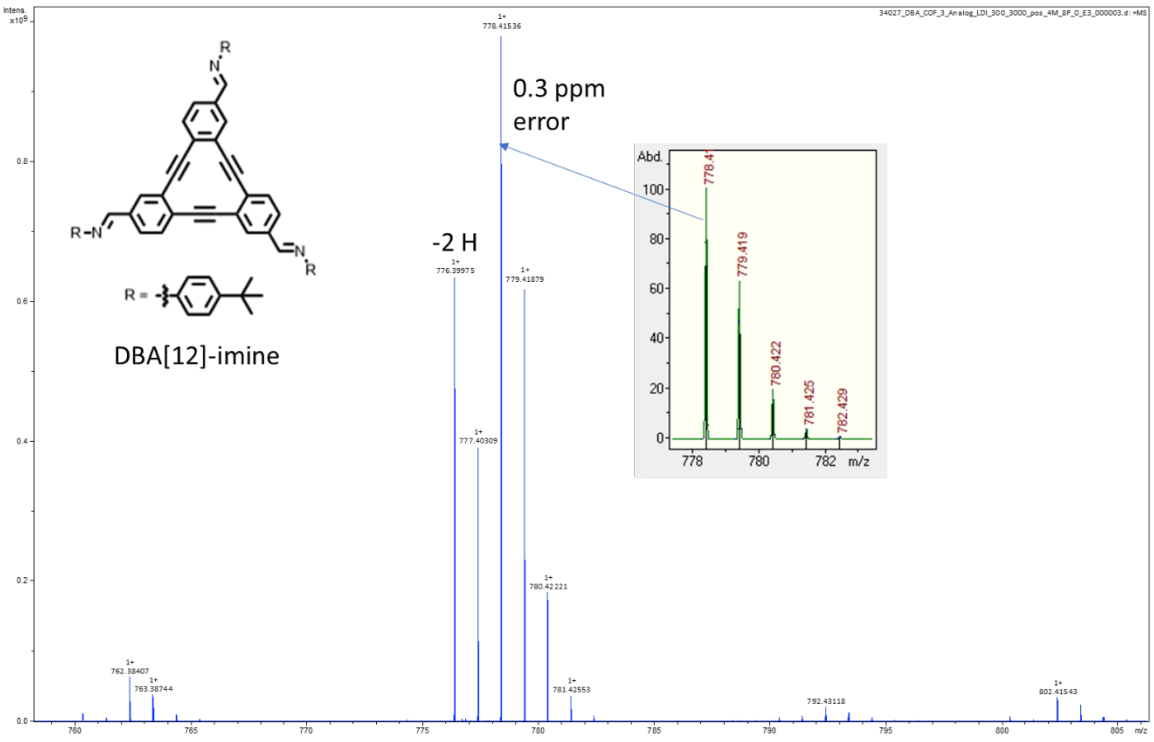

[M+Na]+
8
0.3 ppm error
C11H9IO2

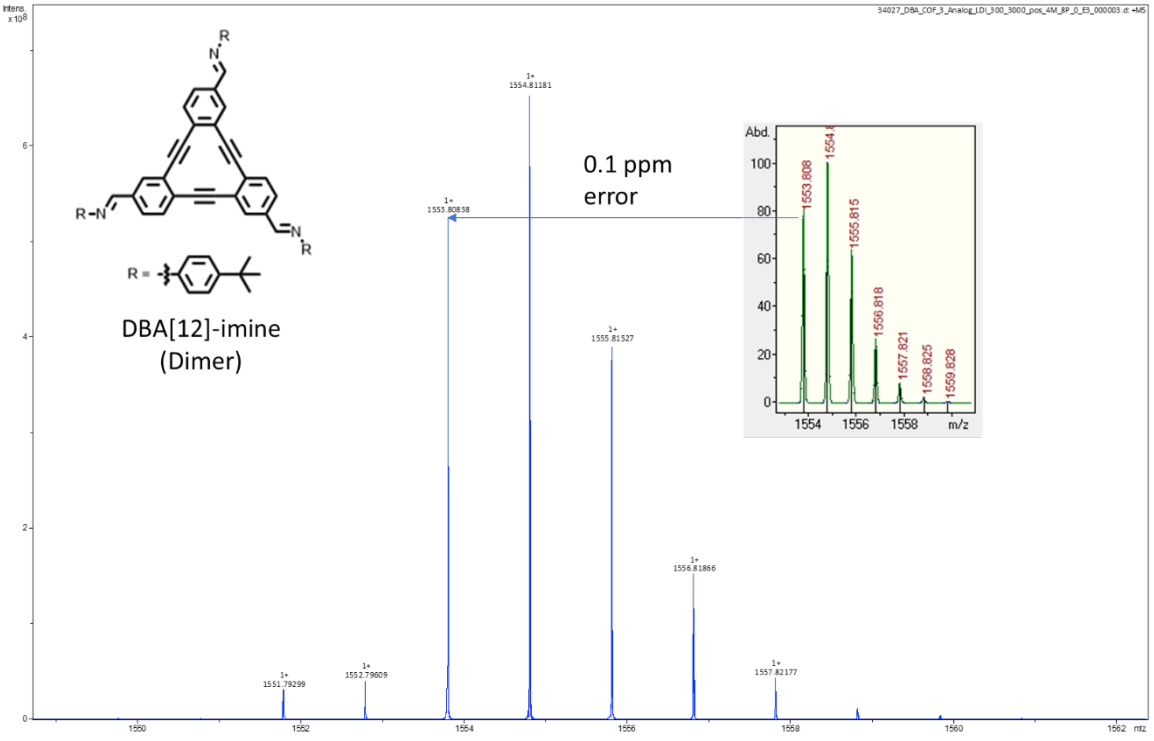

[M+Na]+
DBA[12]-Acetal
[M+Na]+
0.9 ppm error
C33H24O6


DBA[12]-CHO
0.4 ppm error
DBA[12]-CHO Dimer
$(C_{27}H_{12}O_3)_2$
DBA[12]-CHO
[M+Na]+


DBA[12]-CHO Dimer
$(C_{27}H_{12}O_3)_2$
1.0 ppm
error
740.16116
768.15596
604.99289
711.15836
682.15575
655.16876
624.15043
723.15849
753.16929
784.18748
798.99401
594.14014
614.24341


M+1
778.41536
Dimer
1554.81181
DBA[12]-imine
R =
603.52433
935.50483
1148.72423
1925.12062
2330.20376


DBA[12]-imine
0.3 ppm
error
-2 H
778.41536
776.39975
777.40309
779.41879
780.42221
781.42553
762.38407
763.38744
792.43118
802.41543
Abd.
778.4
779.419
780.422
781.425
782.429
m/z


DBA[12]-imine
(Dimer)
0.1 ppm
error
1554.81181
1555.80838
1555.81527
1556.81866
1551.79299
1552.79609
1557.82177
Abd.
1553.808
1554.8
1555.815
1556.818
1557.821
1558.825
1559.828
m/z

References

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