

Supplementary Information

Maleimide-Functionalized Metal-Organic Framework for Polysulfide Tethering in Lithium-Sulfur Batteries

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Compounds and Materials

Compounds. Zirconium (IV) chloride (ZrCl₄, Strem Chemicals), 2-aminoterephthalic acid (NH₂-BDC, 99%, Aldrich), N-phenylmaleimide (NPM, Oakwood Chemical), lithium sulfide (Li₂S, Strem Chemicals), and elemental sulfur (S₈, 99.5-100.5%, Sigma Aldrich), lithium bis-(trifluoromethanesulfonyl)imide (LiTFSI, Oakwood Chemical), lithium nitrate (LiNO₃, 99 %, Strem Chemicals), and poly(vinylidene fluoride) (PVDF, Alfa Aesar) were used as received.

Solvents. 1,2-dimethoxyethane (DME, 99+%, Alfa Aesar) and 1,3-dioxolane (DOL, 99.5 %, Acros Organics) were dried with sodium metal (Sigma Aldrich) and benzophenone (99%, Sigma Aldrich) and distilled prior to use. N,N'-dimethylformamide (DMF, 99.8%, Sigma Aldrich), N-methyl-2-pyrrolidinone (NMP, Oakwood Chemical), glacial acetic acid (J.T. Baker), 1-butyl-3-methylimidazolium hexafluorophosphate ([Bmim]⁺[PF₆]⁻, Oakwood Chemical), and ethanol (200 proof, Pharmaco-Aaper) were used as received.

Coin Cell Parts. Carbon paper with 5% wet-proofing was purchased from The Fuel Cell Store. Stainless steel coin cell parts were purchased from TOB New Energy.

Experimental Details

Instrumentation. ¹H NMR and ¹³C NMR were collected with a Bruker Avance II 400 MHz Spectrometer. UV-Vis spectra were collected with an Agilent Technologies Cary 60. Fluorescence emission spectra were collected with a Thermo Scientific Lumina fluorescence spectrometer. X-ray diffraction (PXRD) patterns were collected with a Bruker D8 Focus diffractometer, Cu K α , LynxEye detector, Fourier transform infrared spectra (FT-IR) were collected with a ThermoScientific Nicolet iS FT-IR with iD 5 ATR attachment. Galvanostatic battery cycling experiments were performed using an MNT-BA-5V (MicroNanoTools). XPS measurements were performed on a Kratos Ultra DLD spectrometer using a monochromatic Al K α source operating at 150 W (1486.6 eV). The operating pressure was 2 x 10⁻⁹ Torr. High-resolution S 2p spectra were acquired at a pass energy of 20 eV and were charged referenced by adjusting the C 1s region to 284.5 eV. XPS data was processed using Casa XPS software. A Shirley background subtraction was used for the quantification of the S 2p region.

Ligand and MOF synthesis. Maleimide-benzenedicarboxylate (Mi-BDC), its methyl ester (Mi-BDOMe), and Mi-UiO-66 were synthesized as reported in literature.¹ NH₂-UiO-66 was synthesized following the same procedure with the replacement of Mi-BDC with 2-aminobenzene-1,4-dicarboxylic acid (NH₂-BDC).

MOF synthesis. $ZrCl_4$ (9.60 mg, 0.040 mmol) and the appropriate linker (0.040 mmol) were dissolved in 1.6 mL DMF with 120 μ L acetic acid. The solution was heated in an oven at 120 °C for 24 hours to form the MOF precipitate. After removal of the warm supernatant, the MOF powder washed with DMF three times with centrifugation. The powder was then immersed in fresh DMF at 80 °C overnight. The DMF was removed by centrifugation and replaced with ethanol, in which the powder was soaked at 60 °C for 2 days. The solvent was refreshed every ~6-12 hours during the 2-day period. The warm supernatant was then removed, and the MOF powder was dried in an oven at 80 °C. All MOFs were activated by heating at 160 °C under vacuum for 30 minutes prior to use in all experiments.

Lithium Polysulfides. Lithium polysulfide (Li_2S_8) solutions were made by stirring stoichiometric ratios of Li_2S and S_8 in 1:1 DOL:DME for several days until no further solids dissolved and the solution turned deep red-orange in color.

Solution-phase UV-Vis and Fluorescence Experiments. In an argon-filled glovebox, the methyl ester of the Mi-MOF linker (Mi-BDOME, white solid) was dissolved in saturated Li_2S_8 solutions (red-orange) in the ratios of 1 mg Mi-BDOME per 0.1 mL Li_2S_8 solution and 10 mg Mi-BDOME per 0.1 mL Li_2S_8 solution. The solutions underwent a noticeable color change to a deep red color immediately upon addition of Mi-BDOME. The solutions were diluted by addition of 2.5 mL 1:1 DOL:DME and transferred to sealed quartz cuvettes for absorption and fluorescence measurements. An excitation wavelength of 405 nm was used for fluorescence measurements.

Nuclear Magnetic Resonance. 1H NMR and ^{13}C NMR samples pertaining to the synthesis of Mi-BDOME and Mi-BDC were dissolved in $DMSO-d_6$ (99.9%, Cambridge Isotope Labs). Samples containing Li_2S_x and N-phenylmaleimide were dissolved in CD_3CN (99.8%, Cambridge Isotope Labs). Digested MOF and linker NMR samples were prepared by soaking ~5 mg of Mi-BDC, Mi-UiO-66, and NH_2 -UiO-66 in separate 1 mL solutions of 10 vol% D_2SO_4 (98 wt% in D_2O , Cambridge Isotope Labs) in D_2O (99.9 atom%, Aldrich) for 24 hours. The supernatant solutions were transferred to NMR sample tubes for measurement.

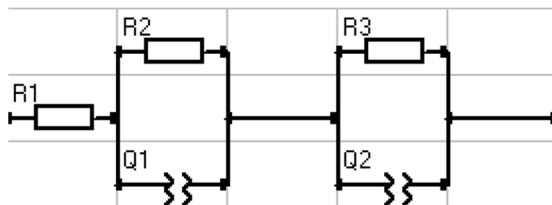
X-ray Photoelectron Spectroscopy. MOF samples were prepared by immersing ~5 mg of solid in 2 mL saturated Li_2S_8 solutions overnight in a nitrogen-filled glovebox. The supernatant solutions were removed and the solids quickly dried in the glovebox atmosphere. The dried powders were removed from the glovebox and quickly inserted into the spectrometer for the measurements. The samples were pumped down to a pressure of 2×10^{-9} torr before XPS measurements were acquired.

Battery Assembly and Cycling. MOF composite cathodes were prepared by casting N-methyl-2-pyrrolidinone (NMP) slurries containing 45% sulfur, 30% MOF, 10% PVDF, and 15% Super-P by weight on carbon paper disks. The MOF was either Mi-UiO-66 or a control MOF, NH_2 -UiO-66. The cathodes were dried in an oven at 80 °C and pressed prior to assembly into Li-S coin cells in an argon-filled glovebox. Coin cells were assembled using CR 2032 casings and contained a cathode, polished Li metal anode, two Celgard separators, two stainless steel spacers, a conical spring, and the appropriate amount of electrolyte. The electrolyte solution consisted of 1 M LiTFSI and 2 wt% $LiNO_3$ in 1:1 DOL-DME and was added to cells in the amount of 60 μ L/mg S_8 . The

values used for sulfur content and ratio of electrolyte volume to sulfur mass were selected based on optimization in our previous MOF studies.

All coin cells were allowed to rest for 8 hours following assembly before being cycled at a C-rate of $C/10$ ($168 \text{ mA g}^{-1} \text{ S}$) for one cycle followed by 100 cycles at $C/2$ (840 mA g^{-1}). For variable C-rate experiments, cells were cycled 5 times at the following series of C-rates: $C/10$ ($168 \text{ mA g}^{-1} \text{ S}$), $C/5$ ($336 \text{ mA g}^{-1} \text{ S}$), $C/2$ ($840 \text{ mA g}^{-1} \text{ S}$), $1C$ ($1680 \text{ mA g}^{-1} \text{ S}$), $2C$ ($3360 \text{ mA g}^{-1} \text{ S}$). Following cycling at $2C$ ($3360 \text{ mA g}^{-1} \text{ S}$), the cells were allowed to rest for 1 week before being cycled again at $C/10$ ($168 \text{ mA g}^{-1} \text{ S}$) for 20 cycles. At least 3 coin cells of each variety were tested for each cycling experiment.

Electrochemical Impedance Spectroscopy (EIS). EIS spectra were collected with an Ivium-n-STAT multichannel electrochemical analyzer on cells in the discharged state following completion of galvanostatic discharge experiments. Data were collected at the cell's open circuit potential with an amplitude of 10 mV in the frequency range of 10^{-1} - 10^6 Hz. Nyquist plots were produced and fit with the equivalent circuit shown below in IviumSoft software.



Supplemental Figures

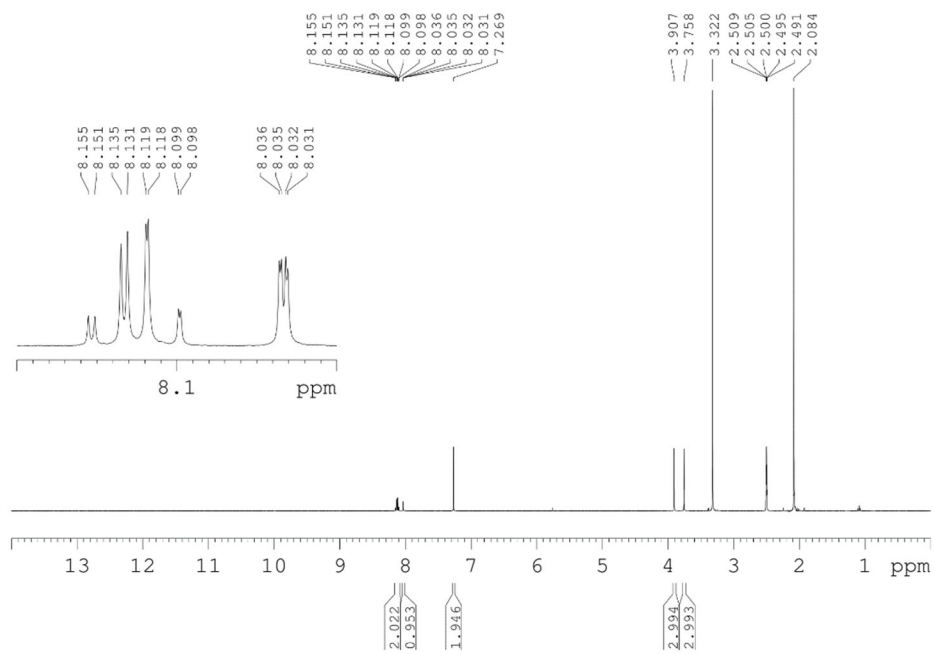


Figure S1. Mi-BDOME ^1H NMR in DMSO-d^6 .

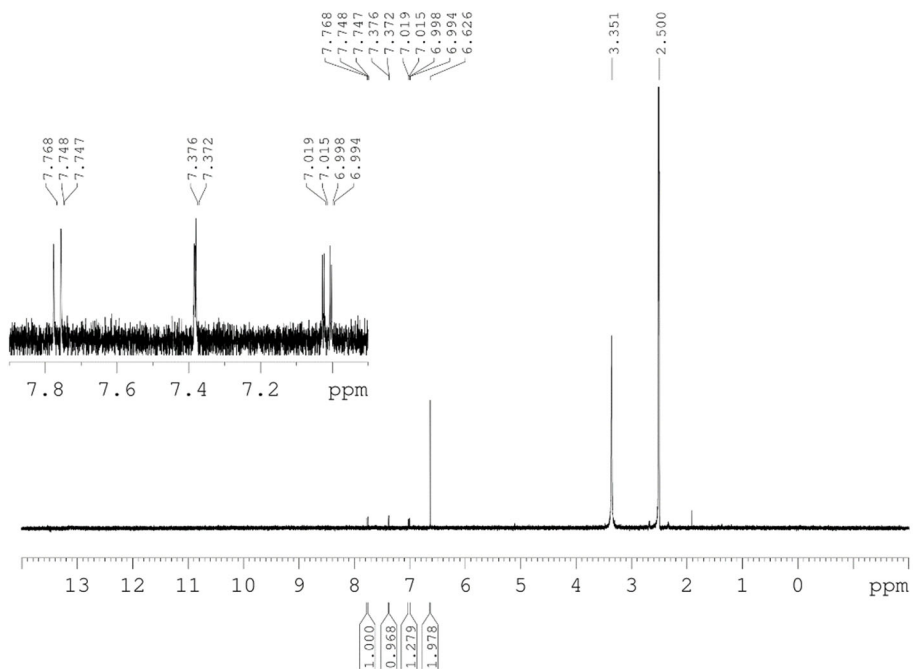


Figure S2. Mi-BDC ^1H NMR in DMSO-d^6 .

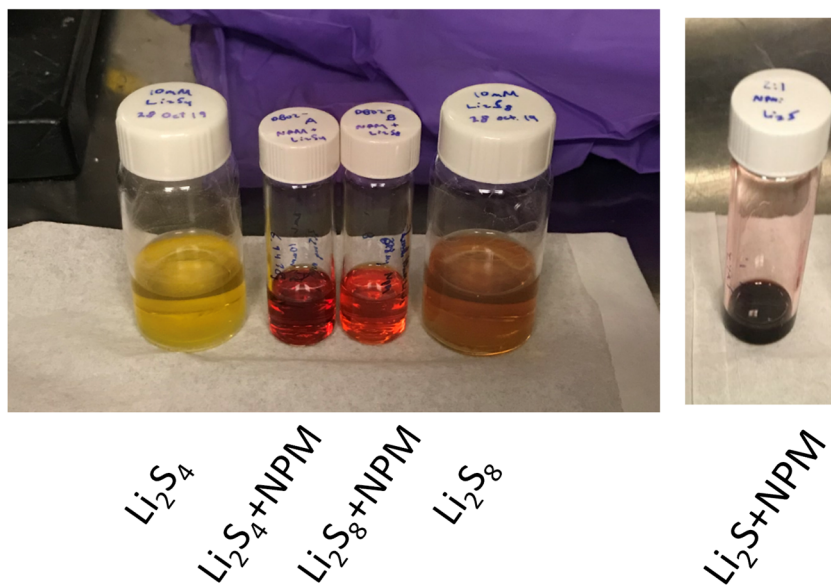


Figure S3. Color changes observed upon addition of lithium polysulfide solutions Li_2S_4 and Li_2S_8 to N-phenyl maleimide (NPM) in DOL/DME (left). Color observed upon addition of NPM solutions in DOL/DME to solid Li_2S (right).

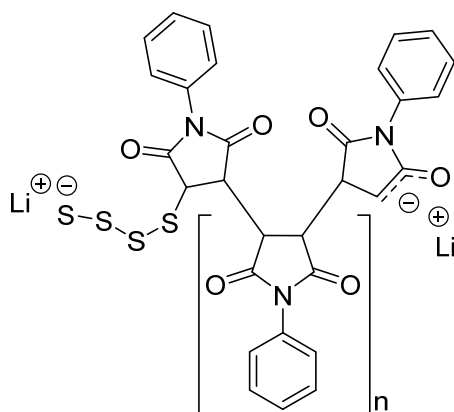


Figure S4. Example of NPM homopolymer initiated by Li_2S_x addition.²

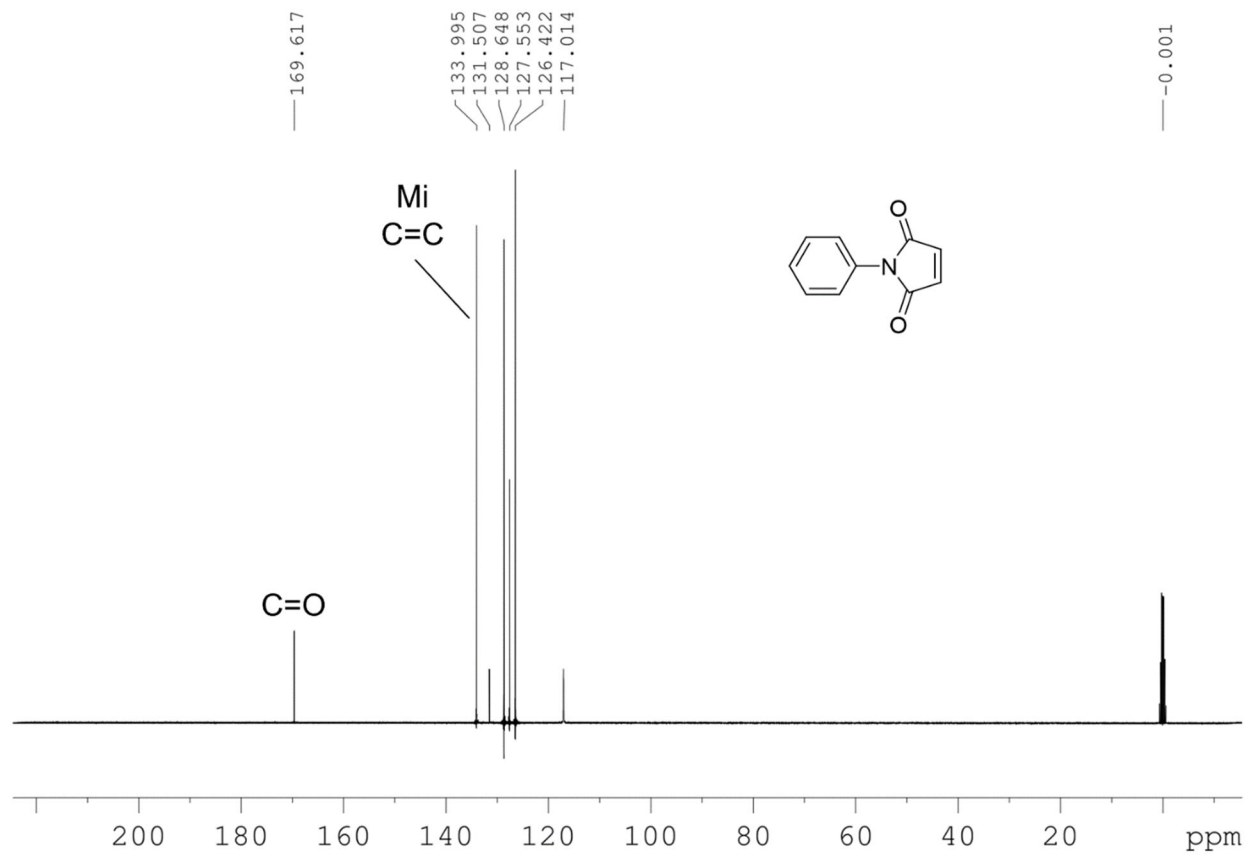


Figure S5. ^{13}C NMR spectrum of NPM in CD_3CN .

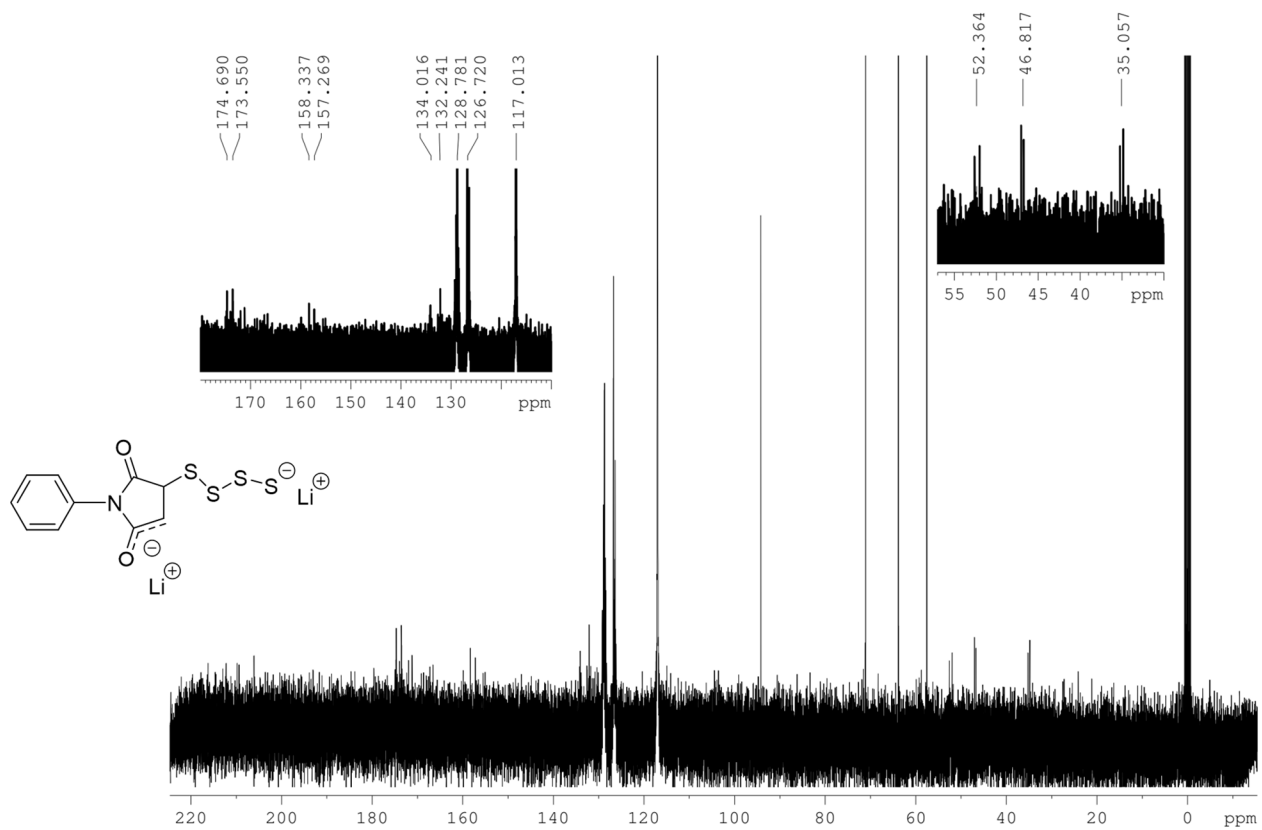


Figure S6. ^{13}C NMR spectrum of NPM+Li₂S in CD₃CN.

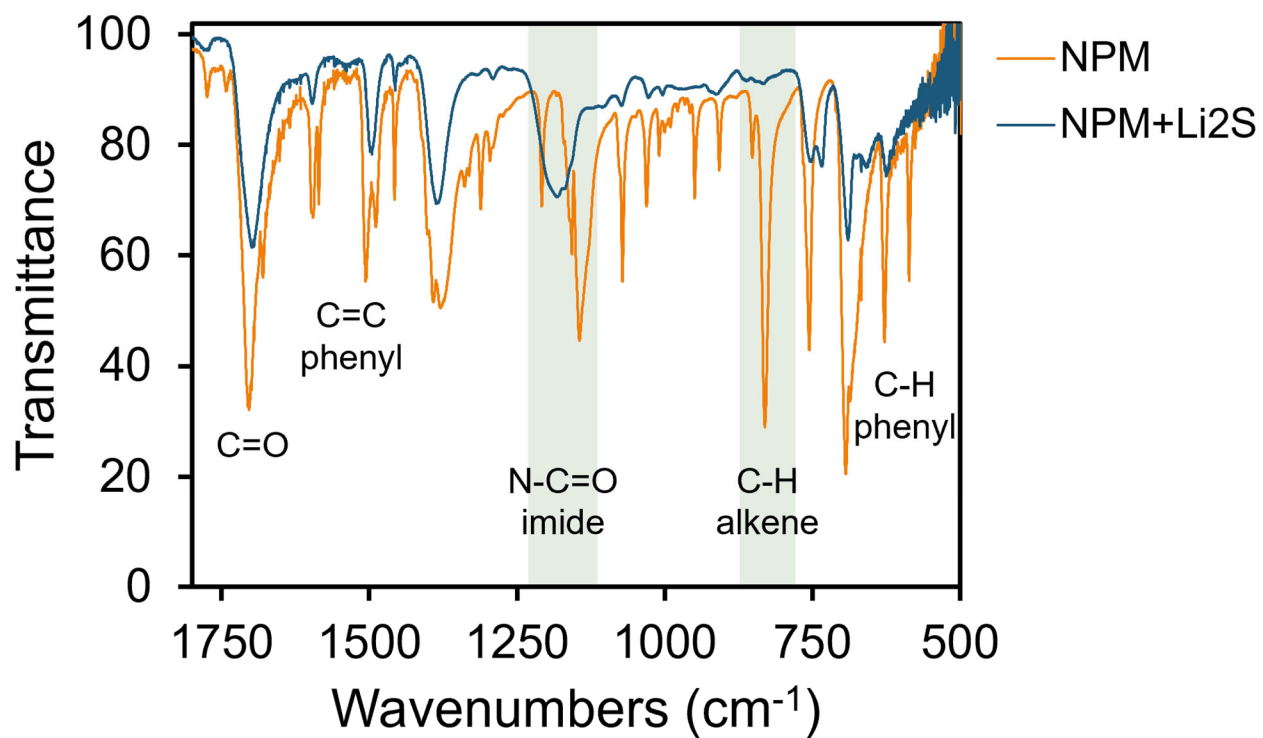


Figure S7. FTIR spectra of NPM (orange) and NPM+Li₂S (blue). Highlighted peaks: C-H alkene 829 cm⁻¹, imide 1144 cm⁻¹ (NPM) and imide 1179 cm⁻¹ (NPM+Li₂S).

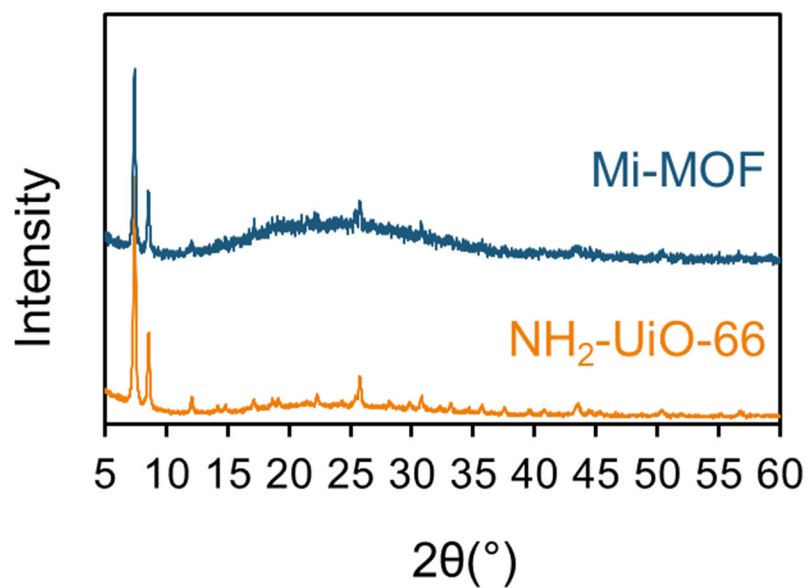


Figure S8. XRD of MOFs as synthesized.

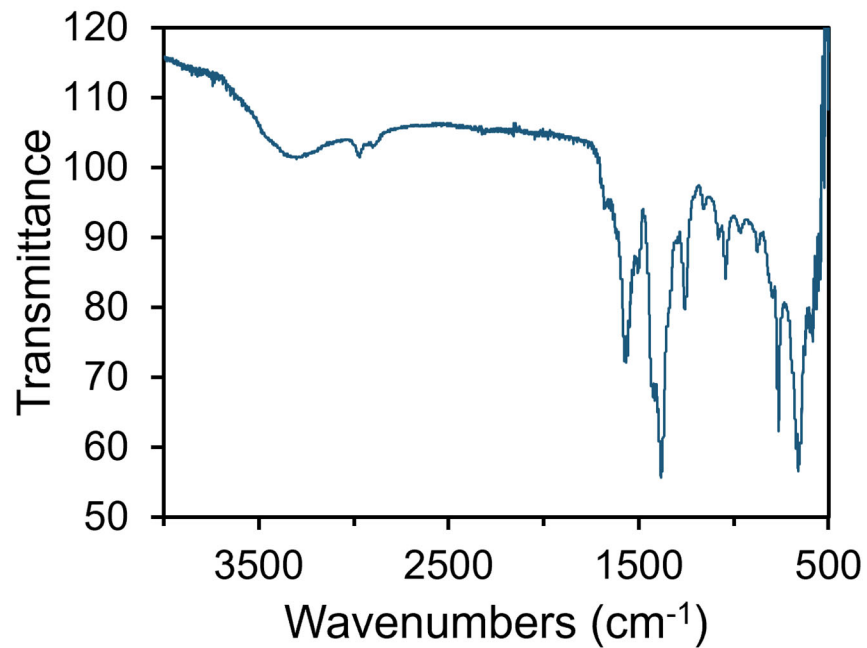


Figure S9. FTIR spectrum of Mi-MOF as synthesized.

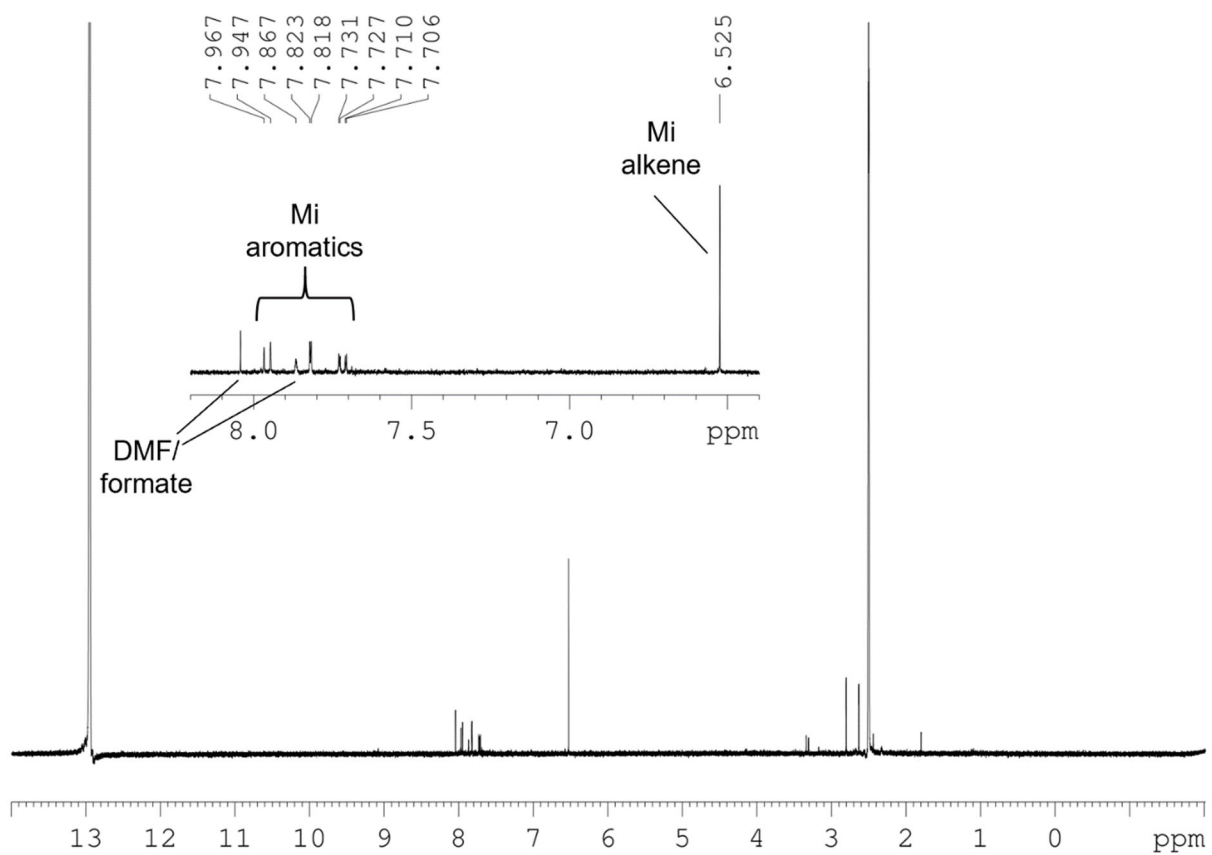


Figure S10. ^1H NMR spectrum of Mi-BDC after MOF digestion in 10% D_2SO_4 in D_2O .

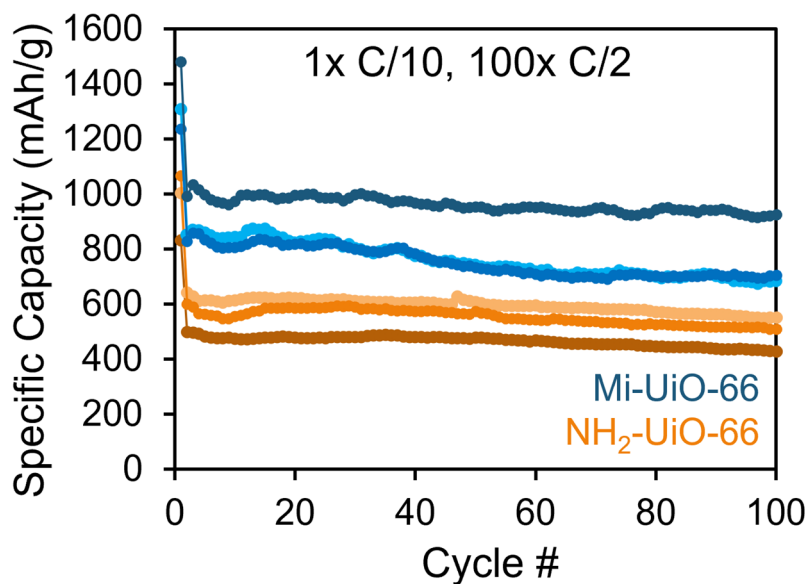


Figure S11. Capacity retention curves for 3 cells each of Mi-UiO-66 (blues) and NH₂-UiO-66 (oranges) cycled once at C/10 followed by 100 cycles at C/2.

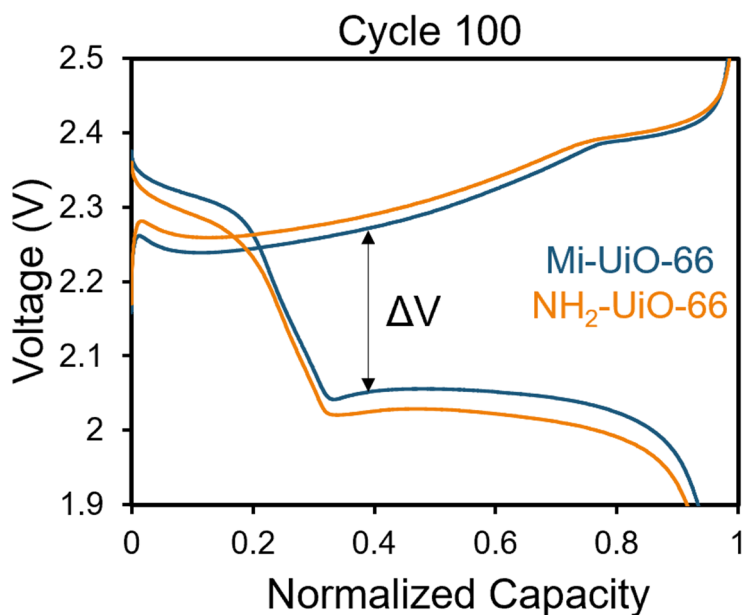


Figure S12. Polarization differences in normalized galvanostatic curves of Mi-UiO-66 (blue) and NH₂-UiO-66 (orange) after 100 cycles at C/2.

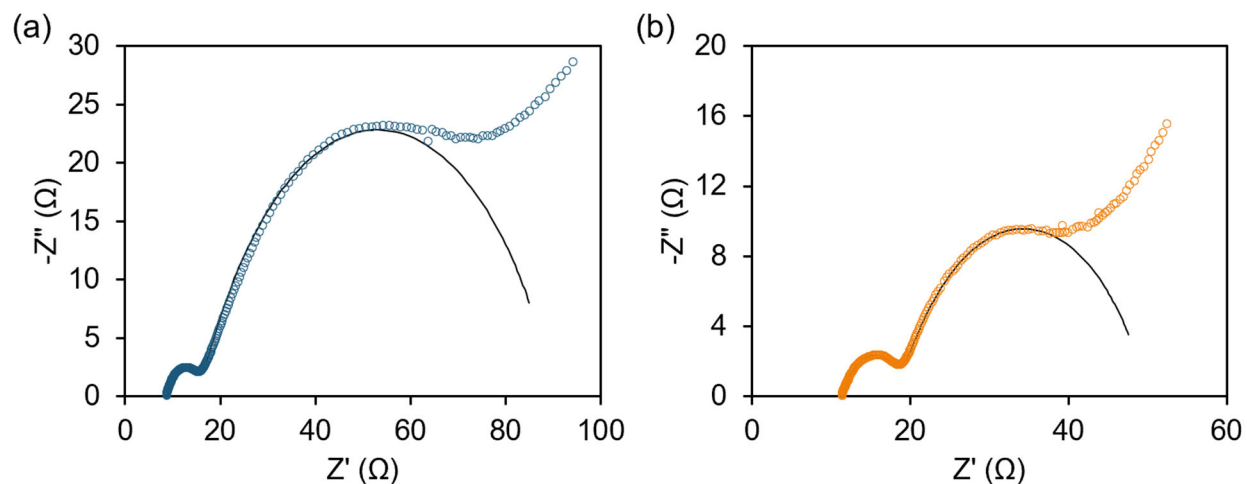


Figure S13. Electrochemical impedance spectra of representative cells containing (a) Mi-UiO-66 and (b) NH₂-UiO-66 collected in the discharged state. Black solid lines represent curves fit to the collected data points.

	Mi-UiO-66	NH ₂ -UiO-66
R1 (Ω)	8.82	11.5
R2 (Ω)	7.08	7.29
R3 (Ω)	74.4	31.1

Table S1. Components of electrochemical impedance spectra derived from the modeled curves in the Nyquist plots in Figure S12. R3 corresponds to charge transfer resistance and is represented in the second semicircle of the Nyquist plots.

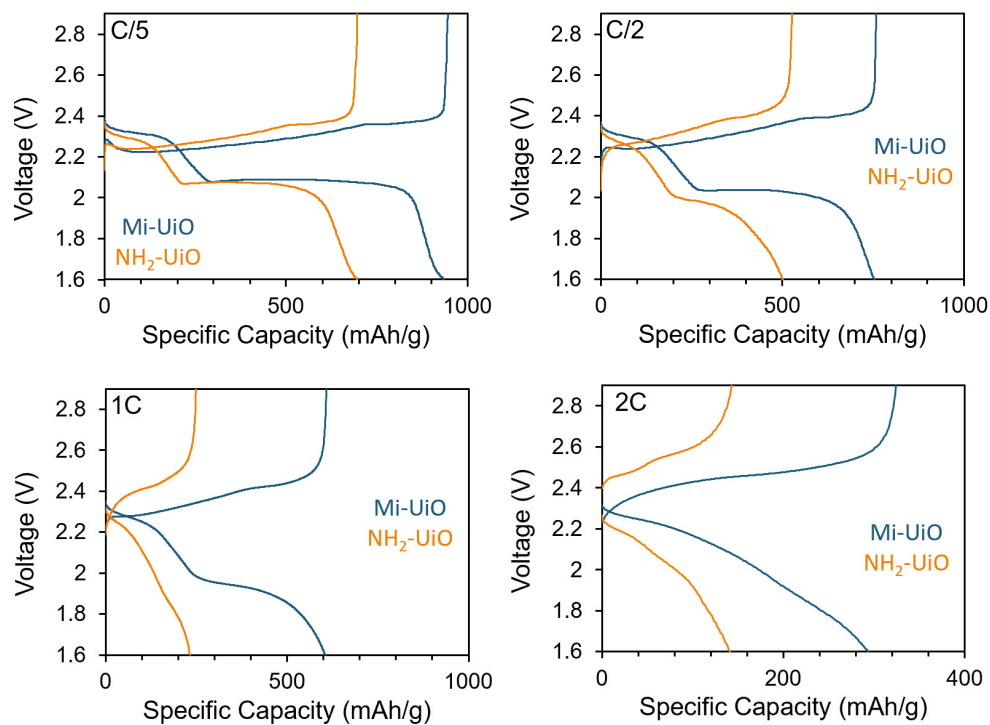


Figure S14. Galvanostatic curves rate performance of Mi-UiO-66 (blue) and NH₂-UiO-66 (orange) cells cycled at C/5, C/2, 1C and 2C. Each curve was taken from the 5th cycle at each rate.

References

- 1 Y.-A. Li, C.-W. Zhao, N.-X. Zhu, Q.-K. Liu, G.-J. Chen, J.-B. Liu, X.-D. Zhao, J.-P. Ma, S. Zhang and Y.-B. Dong, *Chem. Commun.*, 2015, **51**, 17672–17675.
- 2 J. Wu, S. Sun and B. M. Novak, *J. Appl. Polym. Sci.*, 2019, **48909**, 48909.