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Publisher’s note: Undertaking any experimental protocol requires adherence to local institutional guidelines for laboratory safety and ethics.
Protocol

Synthesis of 4-electron-accepting carbonyl-N-methylpyridinium species for lithium-organic batteries

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SUMMARY

Biologically derived redox-active motifs have great potential in energy storage due to their inherent functionality and availability from natural resources. In this protocol, we describe the synthesis and characterization of a class of bio-derived 4-electron-accepting carbonyl-N-methylpyridinium species for lithium-organic batteries. This protocol enables the synthesis of three small molecules and two conjugated polymers with carbonyl-N-methylpyridinium units in good quantities. We also detail the fabrication process and performance evaluation of the coin-cell-type lithium-organic batteries.

For complete details on the use and execution of this protocol, please refer to Wang et al. (2022).

BEFORE YOU BEGIN

Compared with the limited resources of inorganic materials, organic compounds have become an attractive alternative electrode for the next generation of lithium organic battery (LOB) because of their unique advantages such as lightweight, low-cost, flexible, environmentally friendly and structure diversity. Among them, new organic molecules that exhibit multiple and stable redox reactions, limited solubility and improved conductivity can compete with high-performance inorganic electrode materials.

As the key motif in NAD+/NADH couple involved in electron-transfer reaction in natural system, carbonylpyridinium redox-active unit has attracted our attention. The early basic work of Leventis et al. has proved that the benzoyl-N-methylpyridinium (BMP) part can accept two electrons per unit, and has two reversible redox events and a high theoretical capacity. Sanford et al. have certificated that BMP derivatives are very promising for redox flow batteries. However, the exploration of the application of this potential biologically derived redox active structure in lithium-ion batteries is still at an early stage, mainly due to its high solubility in common electrolytes. Recently, we reported a series of novel carbonylpyridinium-based small molecules and polymers with extended conjugation to solve the above issue. These materials show promising performance as organic anodes for LOB applications, and both cycling stability and rate performance are significantly enhanced through polymerization.

Therefore, the current protocol describes the step-by-step synthesis of the class of 4-electron-accepting carbonyl-N-methylpyridinium species (Scheme 1), with a specific focus on S3, 3 and CP2. The protocol can also be extended to the synthesis of other derivatives (S1, S2, 1, 2 and CP1). Moreover, detailed fabrication and characterization of coin-cell LOB has been described. For the same experiment performed in batch, please refer to Wang et al.
Preparation of raw materials and reaction bottles (for the synthesis of small molecules)

© Timing: 2 h

1. Prepare a 500 mL Schlenk flask, magnetic stirrer, a 16 μm syringe (for solvent) and a 12 μm syringe (for butyllithium),
   a. Place them in an air-blast drying oven and dry at 110°C for 1 h.
   b. Quickly transfer to an exchange chamber in the glove box for vacuum cooling to 25°C.
2. Take out n-BuLi from the refrigerator 30 min in advance, allowing it warm to 25°C before use.

Scheme 1. Synthetic routes
(A) Synthesis of molecular compounds 1–3
(B) Synthesis of conjugated polymers CP1 and CP2
Preparation of solutions and reagent (for the synthesis of small molecules)

**Timing:** 0.5–1 h

3. Slowly add 20 mL concentrated HCl (12 M) to 100 mL of deionized water under vigorous stirring to obtain 2 M HCl solution.

△ CRITICAL: HCl is a corrosive chemical; thus, the preparation should be handled in the fume hood and the researcher should also wear protective gloves, masks and goggles.

4. Weigh 8 g NaOH into a 250 mL beaker, and add 100 mL deionized water while stirring to obtain 2 M NaOH solution.

△ CRITICAL: NaOH is highly corrosive and tends to absorb water from the air, so weighing should be done in beakers rather than weighing paper. During the process of dissolving NaOH, a large amount of heat is released. Please pay attention to safety.

**KEY RESOURCES TABLE**

| REAGENT or RESOURCE | SOURCE | IDENTIFIER |
|---------------------|--------|------------|
| Chemicals, peptides, and recombinant proteins | | |
| 5,5'-Dibromo-2,2'-bithiophene (98%) | Adamas | CAS: 4805-22-5 |
| 4,4'-dibromobiphenyl | Adamas | CAS: 92-86-4 |
| 3,3',5,5'-tetrabromo-2,2'-bithiophene | Adamas | CAS: 125143-53-5 |
| 4-cyanopyridine (99%+) | Adamas | CAS: 100-48-1 |
| n-Butyllithium (2.5 M solution of Hexanes, Safeseal) | Adamas | CAS: 109-72-8 |
| Iodomethane (MeI) | Energy Chemical | CAS: 74-88-4 |
| Bis(triphenylphosphine)palladium(II) chloride (Pd(PPh3)2Cl2) | AMATEK | CAS: 13965-03-2 |
| Copper iodide | Adamas | CAS: 7681-65-4 |
| Triethylamine (AR) | SCR | CAS: 121-44-8 |
| Tetrahydrofuran (Dry THF, 99.9%, Safe Dry, with molecular sieves, Water ≤ 30 ppm) | Adamas | CAS: 109-99-9 |
| N,N’-dimethylformamide (Dry DMF, 99.8%, Safe Dry, with molecular sieves) | Adamas | CAS: 68-12-2 |
| N,N’-dimethylformamide (AR, 99.5%) | SCR | CAS: 68-12-2 |
| Tetrahydrofuran (AR) | SCR | CAS: 109-99-9 |
| Hydrochloric acid (HCl) (AR, 36.0–38.0%) | SCR | CAS: 7647-01-0 |
| Sodium hydrate (NaOH) (AR) | SCR | CAS: 1310-73-2 |
| Dichloromethane (CH2Cl2) (AR) | SCR | CAS: 75-09-2 |
| Diethyl ether (Et2O) (AR) | SCR | CAS: 60-29-7 |
| Methanol (MeOH) (AR, 99.5%) | SCR | CAS: 67-56-1 |
| Polyvinylidene fluoride (PVDF) | Shenzhen Kejing Zhida Technology Co., Ltd | CAS: 24937-79-9 |
| N-methyl pyrrolidone (NMP) | Energy Chemical | CAS: 872-50-4 |
| Other | | |
| Schlenk line | Synthware Co., Ltd | N/A |
| Analytical balance | METTLER TOLEDO | ME204 |
| Stir plate | IKA | Model RCT B 5025 |
| Vacuum drying oven | Shanghai Yiheng Scientific Instrument Co., Ltd | DZF-6030A |
| Blast drying oven | Shanghai Yiheng Scientific Instrument Co., Ltd | DHG-9070A |
| Centrifuge | Sichuan Shuke Instrument Co., Ltd | TG16-WS |
| Low-constant-temperature reaction bath | Zhengzhou Greatwall Scientific Industrial and Trade Co., Ltd | DHJF-8002 |
| Rotary evaporator | IKA | RV10 |

(Continued on next page)
CRITICAL: 1) n-Butyllithium, Iodomethane, Bis(triphenylphosphine)palladium(II) chloride (Pd(PPh₃)₂Cl₂) should be stored at 4°C. 2) Dry solvents, such as dry THF and dry DMF, need to be taken in a nitrogen atmosphere for use. 3) n-Butyllithium is prone to spontaneous combustion in air. Reaction systems and solvents using butyllithium should be kept strictly free of water and oxygen.

Alternatives: In this protocol, the dry THF could be prepared by distillation over CaH₂.

MATERIALS AND EQUIPMENT

| REAGENT or RESOURCE | SOURCE | IDENTIFIER |
|---------------------|--------|------------|
| Glassy carbon working electrode | Shanghai Chenhua Instrument Co., Ltd | CHI1102 |
| Pt wire counter electrode | Shanghai Chenhua Instrument Co., Ltd | CHI111 |
| Ag/AgNO₃ reference electrode | Shanghai Chenhua Instrument Co., Ltd | CHI112 |
| Nickel wafer | Shenzhen Kejing Zaida Technology Co., Ltd | 350 |
| Conductive carbon black (ECP-600JD) | Shenzhen Kejing Zaida Technology Co., Ltd | ECP-600JD |
| Electrochemical workstation | Shanghai Chenhua Instrument Co., Ltd | CHI740E |
| Glove box | Vigor | SG1200/750TS-F |
| Battery packaging machine | HF-Kejing | MSK-160E |
| Constant temperature incubator | DHP-4208S | Beijing Yongguangming Medical Instrument Co., Ltd |
| LANHE CT3001A | Wuhan Lantian Electronics Co., Ltd | BT2016A |
| 400 MHz/600 MHz Bruker NMR spectrometers | Bruker | Ascend TM 400 |
| JEOL RESONANCE ECZ 400R NMR spectrometer | JEOL | JNM-ECZ400R/S1 |
| Bruker maxis UHR-TOF mass spectrometer | Bruker Daltonics | Maxis Ultimate 300hplc |
| Fourier-transform infrared spectrometer (FTIR) | Bruker | TENSOR27 |
| X-ray Photoelectron Spectrometer | Shimadzu | Axis UltraDLD |
| Scanning electron microscope (SEM) | HITACHI | SU8220 |
| X-ray powder diffractometer | Bruker | Bruker D8 Discover |
| Physical adsorption instrument | Micromeritics | ASAP2460 |
| Thermogravimetric analyzer | TA Instruments | Q-600/Q1000 |
| UV-vis spectrometer | Agilent | Cary 3500 |

Stock solution of 2 M HCl solution

| Reagent | Final concentration | Amount |
|---------|---------------------|--------|
| Concentrated HCl | 12 M | 20 mL |
| Deionized water | N/A | 100 mL |
| Total | 2 M | 120 mL |

Note: The HCl solution can be stored at 25°C for 3 months.

Stock solution of 2 M NaOH solution

| Reagent | Final concentration | Amount |
|---------|---------------------|--------|
| NaOH | N/A | 8 g |
| Deionized water | N/A | 100 mL |
| Total | 2 M | 100 mL |

Note: The NaOH solution can be stored at 25°C for one month.
STEP-BY-STEP METHOD DETAILS

Part 1: Synthesis of small molecules

© Timing: 3 days

In this part, we take 4,4’-(3,3’-dibromo-[2,2’-bithiophene]-5,5’-dicarbonyl)bis(1-methylpyridinium) iodide (3) as an example to describe the synthesis in detail. This protocol has also been extended to the synthesis of 4,4’-(1,1’-biphenyl)-4,4’-dicarbonyl)bis(1-methylpyridinium) iodide (1) and 4,4’-([2,2’-bithiophene]-5,5’-dicarbonyl)bis(1-methylpyridinium) iodide (2). The overall synthetic route is presented in Scheme 1.

1. Synthesis of (3,3’-dibromo-[2,2’-bithiophene]-5,5’-diyl)bis(pyridin-4-ylmethanone) (S3, step i in Scheme 1).
   a. Weigh 3,3’,5,5’-tetrabromo-2,2’-bithiophene (5 g, 10.4 mmol) on the analytical balance and add it into the 500 mL flame-dried Schlenk flask.
   b. Place the glass stopper in the neck of the flask, and take the reaction flask to fume hood setup, fit it to Schlenk line.
   c. The flask was vacuum treated and back filled with nitrogen for 3 times.
   d. Replace the glass stopper with septum, and add 150 mL of dry THF to the reaction bottle using syringe under N2.
   e. Stir the suspension for 15 min at 25°C.
   f. Place the reaction bottle into 0°C–78°C cooling bath and stir for 30 min.
   g. Add n-butyl lithium (2.5 M, 8.7 mL, 22 mmol) slowly to the reaction bottle using syringe for 30 min. The mixture was stirred at 0°C for 1 h.

   △ CRITICAL: A dry needle should be used to access the butyllithium and a sealing film should be wrapped around the connection between the syringe and the needle. In detail, first extend the nitrogen-passed needle above the liquid level; then aspirate the butyllithium and transfer it quickly to the reaction flask, pushing it in gradually and without venting. The whole process should preferably be completed within three minutes. An ethanol wash bottle should be prepared to clean the used needles.

   h. Add 4-cyanopyridine (2.2 g, 22 mmol) dissolved in 15 mL dry THF to the reaction flask using syringe in 5 min. Allow the mixture stir at –78°C for 2 h and then warm up to 25°C slowly for a further 2 h.

   Note: The reaction mixture changes from off-white to yellow, then to brown and finally to black.

   i. Add 2 M HCl (80 mL) to quench the reaction, and the mixture was stirred for 2 h at 25°C.
   j. Basicify the mixture to pH 9–10 by adding 2 M NaOH solution (80 mL).
   k. Collect the solid by vacuum filtration using a Buchner funnel, wash it with H2O (3 × 20 mL), CH3OH (3 × 20 mL) and CH2Cl2 (3 × 20 mL).
   l. Purify the product by washing with hot THF.

   Note: The crude product was suspended in 100 mL THF, heated to 70°C for 4 h. After cooling down, the pure product was collected by vacuum filtration and dried in vacuo. The desired product was obtained yellow solids in 55%.

   m. Analyze S3 by 1H NMR (600 MHz, CDCl3): δ = 8.89 (d, J = 5.9 Hz, 4H), 7.68 (d, J = 6.0 Hz, 4H), 7.63 (s, 2H) ppm; HRMS (APCI): m/z calculated for C20H11Br2N2O2S2 * [M+H]⁺ 534.8603, found 534.8600.
Note: No well-resolved $^{13}$C NMR spectrum of S3 could be obtained due to its extremely limited solubility.

Note: The synthesis of [1,1'-biphenyl]-4,4'-diylbis(pyridin-4-ylmethanone) (S1) and [2,2'-bithiophene]-5,5'-diylbis(pyridin-4-ylmethanone) (S2) was similar to that used to prepare S3, except 4,4'-dibromobiphenyl (3.2 g, 10.4 mmol) or 5,5'-tetrabromo-2,2'-bithiophene (3.4 g, 10.4 mmol) was used in place of 3,3',5,5'-tetrabromo-2,2'-bithiophene (5 g, 10.4 mmol). Analytical data for S1: Yield: 86%; white solid. $^1$H NMR (600 MHz, CDCl$_3$): δ (ppm) = 8.85 (d, J=5.9 Hz, 4H), 7.96 (d, J = 8.2 Hz, 4H), 7.80 (d, J = 8.3 Hz, 4H), 7.63 (d, J = 6.1 Hz, 4H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ (ppm) = 194.53, 150.47, 144.56, 144.24, 135.56, 130.90, 127.58, 122.80; HRMS: m/z calculated for C$_{24}$H$_{17}$N$_2$O$_2$ $^+$ [M+H]$^+$ 365.1285, found 365.1284. Analytical data for S2: Yield: 65%; yellow solid. $^1$H NMR (300 MHz, CDCl$_3$): δ (ppm) = 8.85 (d, J = 5.4 Hz, 4H), 7.66 (d, J = 5.4 Hz, 4H), 7.60 (d, J = 4.1 Hz, 2H), 7.42 (d, J = 4.1 Hz, 2H); No well-resolved $^{13}$C NMR spectrum could be obtained due to its extremely limited solubility; HRMS (APCI): m/z calculated for C$_{20}$H$_{13}$N$_2$O$_2$S$_2$ $^+$ [M+H]$^+$ 377.0413, found 377.0408.

2. Synthesis of 4,4'-(3,3'-dibromo-[2,2'-bithiophene]-5,5'-dicarbonyl)bis(1-methylpyridinium) iodide (3, step ii in Scheme 1).
   a. Assemble the 100 mL two-neck round bottom flask, the condenser, the gas inlet adaptor and magnetic stirrer onto the oil bath.
   b. Purge the flask with nitrogen for 10 min.
   c. Load the reaction flask with S3 (1.5 g, 2.8 mmol) and dry DMF (15 mL). The mixture was stirred for 10 min at room temperature.
   d. Add iodomethane (4.0 g, 28 mmol) to the flask, and heat the reaction mixture to 90°C for 16 h.
   e. Allow the solution to cool down to room temperature and add diethyl ether (40 mL) to precipitate out the product.
   f. Filter the obtained solids using Buchner funnel, and wash with diethyl ether (3×20 mL) and CH$_2$Cl$_2$ (20 mL).
   g. Dry the solid under vacuum (-0.1 MPa) at 40°C for 2 h in the vacuum drying oven. The desired product was obtained as brown solids in 98%.
   h. Analyze 3 by $^1$H NMR (400 MHz, DMSO-d$_6$): δ (ppm) = 9.23 (d, J = 6.7 Hz, 4H), 8.50 (d, J = 6.7 Hz, 4H), 8.00 (s, 2H), 4.46 (s, 6H); $^{13}$C NMR (100 MHz, DMSO-d$_6$): δ (ppm) = 188.48, 154.44, 152.00, 147.20, 145.38, 142.08, 131.94, 119.67, 53.51. HRMS (ESI): m/z calculated for C$_{22}$H$_{16}$Br$_2$N$_2$O$_2$S$_2$ $^{2+}$ [M-2I]$^{2+}$ 281.9494, found 281.9492.

Note: The two-step synthesis of 4,4'-([1,1'-biphenyl]-4,4'-dicarbonyl)bis(1-methylpyridinium) iodide (1) and 4,4'-([2,2'-bithiophene]-5,5'-dicarbonyl)bis(1-methylpyridinium) iodide (2) was similar to that used to prepare 3, except S1 (500 mg, 1.4 mmol) or S2 (500 mg, 1.3 mmol) was used in place of S3 (1.5 g, 2.8 mmol). Analytical data for I: Yield: 95%; yellow solid. $^1$H NMR (400 MHz, DMSO-d$_6$): δ (ppm) = 9.21 (d, J = 6.7 Hz, 4H), 8.40 (d, J = 6.7 Hz, 4H), 8.39 (d, J = 6.7 Hz, 4H), 8.07 (d, J = 8.5 Hz, 4H), 7.97 (d, J = 8.5 Hz, 4H), 7.92 (d, J = 8.5 Hz, 4H), 7.91 (d, J = 8.5 Hz, 4H), 7.89 (d, J = 8.5 Hz, 4H), 7.81 (d, J = 4.2 Hz, 2H), 4.45 (s, 6H); $^{13}$C NMR (100 MHz, DMSO-d$_6$): δ (ppm) = 192.17, 151.59, 147.04, 147.04, 145.38, 144.56, 134.58, 131.55, 128.26, 127.02, 48.71; HRMS: m/z calculated for C$_{24}$H$_{17}$N$_2$O$_2$ $^+$ [M-I]$^+$ 521.0720, found 521.0723.

Part 2: Synthesis of conjugated polymers

@ Timing: 3 days
Polymerization of 3 via Sonogashira coupling by reacting it with the corresponding arylethynlenes (4,7-diethynyl-2,1,3-benzothiadiazole or 1,4-diethynylbenzene) in the presence of Pd(PPh3)2Cl2, copper iodide (CuI) in DMF/Et3N (1:1, v/v) afforded poly(1,2'-bithiophene)-5,5'-dicarboxyl)bis(1-methylpyridinium)-3,3'-diynyl-alt-phenyl)iodide (CP1) and poly((1,2'-bithiophene)-5,5'-dicarboxyl)bis(1-methylpyridinium)-3,3'-diynyl-alt-benzothiadiazole)iodide (CP2), respectively (Scheme 1). Due to the similar procedure, the synthesis of CP2 is described in detail in this part.

3. Synthesis of CP2 (step iii in Scheme 1).
   a. Assemble the 100 mL two neck round bottom flask, the condenser, the gas inlet adaptor and magnetic stirrer on to the oil bath.
   b. Charge the reaction flask with 3 (409 mg, 0.5 mmol), 4,7-diethynyl-2,1,3-benzothiadiazole (92 mg, 0.5 mmol), Pd2(PPh3)2Cl2 (18 mg, 0.025 mmol), CuI (10 mg, 0.05 mmol).
   c. The flask was vacuum treated and back filled with nitrogen for 3 times under Schlenk line.
   d. Add degassed solvent mixture of DMF/Et3N (15 mL, 2:1, v/v) by syringe bubbling method. The reaction mixture was stirred at 90°C for 48 h in the atmosphere of nitrogen.
   e. After being cooled to room temperature, the polymer was collected by centrifugation with 4000 rpm and washed the solids in turn with excess DMF, methanol, THF and finally diethyl ether. After drying under vacuum, the resultant product appears as tawny solids with a yield of 78%.

Note: The synthesis of CP1 was similar to that used to prepare CP2, except 1,4-bis(ethynyl) benzene (63 mg, 0.5 mmol) was used in place of 4,7-diethynyl-2,1,3-benzothiadiazole. The resulting two polymers are not soluble in water, organic solvents, or organic carbonates (electrolyte), indirectly affirming their polymeric structure. The chemical structures of the polymers were verified by Fourier transform infrared spectroscopy (FTIR) and solid-state 13C NMR spectroscopy.

Part 3: Measurement of electrochemistry

© Timing: 4 h

To confirm the four-electron accepting property, Cyclic voltammograms (CV) and differential pulse voltammograms (DPV) were conducted on a 1 mM 1 or 2 solution in degassed DMF containing 0.1 M TBAPF6 as a supporting electrolyte (Figure 1).

4. Prepare three electrodes (Figure 1A).
   a. Working electrode: glassy carbon disk electrode with 4 mm diameter.
   b. Counter electrode: Pt wire.
   c. Reference electrode: Ag/AgNO3 (0.01 M) pesudo-reference electrode in fritted compartment.

5. Clean working electrode (Figure 1B).

△ CRITICAL: Polish the glassy carbon disk electrode on a cloth polishing pad in a water-alumina slurry with figure-eight motions. When using circular motions, the polishing is often uneven, leading to a slanted surface.

6. Assemble the electrochemical cell, and add 5 mL DMF solution of small molecules (1 mM) containing 0.1 M TBAPF6 as a supporting electrolyte (Figure 1C).

△ CRITICAL: Make sure the selected solvents in which the tested compounds have certain solubility.

△ CRITICAL: Prior to each experiment the solution was deaerated by bubbling nitrogen gas for about 2 min so that any interference due to dissolved oxygen could be avoided. For
getting oxygen free signals of the analytes, nitrogen atmosphere was kept over the solution during electrochemical experiments.

7. Record the CV and DPN (Figures 1C and 1D).

△ CRITICAL: For trusted comparison, the scan rate must be kept the same. Changing the scan rates often leads to the shifts of the redox peaks.

Part 4: Assembly of Li-organic batteries

● Timing: 3 days

The overall preparation of the working electrodes is illustrated in Figure 2.

8. Fabrication of working electrode.
   a. Material Preparation.
      i. The materials: active material (CP2), conductive carbon black (ECP-600JD), the binder (polyvinylidene fluoride, PVDF) and the solvent (N-methyl pyrrolidone, NMP).
      ii. The utensils: the foam nickel wafer with a diameter of 12 mm (weigh and record the mass of each disk), a weighing spoon, a scraping spoon and an agate mortar.
b. Weighing and Mixing.
   i. Weigh 18 mg CP2 into the agate mortar and grind it into delicate powder (5 min);
   ii. Weigh 9 mg ECP-600JD and continue grinding (30 min);
   iii. Weigh 3 mg PVDF and continue grinding (10 min).

\[\text{\textcolor{red}{CRITICAL}}: \text{Grind the slurry in one direction scraping solids off of the agate mortar walls and push them back to the center every five minutes before continuing to grind.}\]

c. Adding NMP.

\[\text{\textcolor{red}{CRITICAL}}: \text{NMP should be added drop by drop during the grinding process, avoiding adding a lot of NMP at one time. Slowly add about } 200 \mu \text{L NMP with continuous grinding to form a well-dispersed slurry in } 15-30 \text{ min.}\]

d. Electrode coating.

\[\text{\textcolor{red}{CRITICAL}}: \text{Evenly coat the slurry on the foam nickel wafer using a brush one by one.}\]

e. Dry the electrodes.

\[\text{\textcolor{red}{CRITICAL}}: \text{Make sure to fully dry the prepared working electrodes in a vacuum drying oven at } 80^\circ \text{C for } 12 \text{ h to remove any solvent residues.}\]

f. Flatten the electrodes.

\[\text{\textcolor{red}{CRITICAL}}: \text{Use a Manual infrared tablet press to tablet the electrodes at a pressure of 4 MPa to prevent the foam nickel wafer from penetrating the separator.}\]

g. Calculate the mass loading.

\[\text{Note: Weigh the mass of the dried electrode sheet and calculate the mass of the coated active substance. The mass loading of active material in this protocol is } 0.8-1.0 \text{ mg cm}^{-2}\].
9. Assemble CR2032 coin cells in the argon-filled glove box (Figure 3).
   a. Transfer the prepared electrodes into a glove box under an Ar atmosphere (<0.01 ppm of oxygen and water).

   **Note:** Foam nickel wafer pasted active materials was used as the working electrode, 1 mol/L LiPF_6+EC/EMC/DMC (1:1:1, v/v, 1% vinyl carbonate as additive) as the electrolyte, Celgard2400 as the separator, and lithium foil of the corresponding size as the counter electrode. These materials are commercially available and stored in glove box.

   b. Assembly the coin cells.

   **Note:** Put the positive plate, working electrolyte, separator, lithium plate, spacer (0.8 mm) and gasket into the positive shell in order, and cover the negative shell of the battery.

   c. Use the battery sealing machine to pressurize the battery to ~8.5 MPa for sealing. Place the assembled battery in a box and place it in a 30°C incubator for 8 h to be tested.

**Part 5: Li-ion battery tests**

For the characterization of the battery performance, the coin cells were connected to the LANHE CT3001A battery test system to record the galvanostatic charge/discharge behaviors, cycling performance at constant current and rate performance at different current densities. In addition, the CV and electrochemical impedance spectra were tested by an electrochemical workstation (CHI760E). The key parameter setting and results of the battery test are presented in Figures 4 and 5.
10. Test lithium battery performance by the electrochemical workstation and the LANHE CT3001A battery test system.
   a. Measure the CV over a voltage range of 0.005–3.0 V versus Li/Li⁺ at 0.2 mV s⁻¹ (Figure 5A).
      The program setting is displayed in Figure 4D.
   b. Record the galvanostatic charge-discharge (GCD) curves at a current density of 0.5 A g⁻¹ (Figure 5B).

   Note: Firstly discharge to 0.05 V and then charge to 3.00 V at a constant current of 0.5 A g⁻¹. It can also be used to test the GCD curves at other current densities.

   c. Measure the long-term cycling performance at the lower current density of 0.5 A g⁻¹ and 0.2 A g⁻¹ (Figures 5C and 5D). The program setting is presented in Figure 4B.
   d. Measure the rate performance at different current densities (Figure 5E). The program setting is displayed in Figure 4C.
   e. Analyze the electrochemical impedance spectroscopy (EIS).

   Note: It was carried out using an electrochemical workstation (CHI760E) at a frequency range between 100 kHz to 0.1 MHz. The detailed program settings are displayed in Figure 4E.

EXPECTED OUTCOMES

This protocol provides the synthesis of a class of 4-electron-accepting carbonyl-N-methylpyridinium species, with a focus on the procedure of 3 and CP2. Other materials (1, 2 and CP1) can be obtained following the similar protocol. It also describes the detailed procedure for battery
assembly and analysis of the battery performance. The designed molecular compounds 1–3 can reversibly store up to four electrons, which is highly beneficial to increase the charge-storage capacity in battery. Both cycling stability and rate performance are further enhanced through polymerization, as a result of high electrochemical activity and effective suppression of dissolution. Impressively, polymer CP2 delivers not only the highest capacity but also the best cycling stability, reaching up to 574 mAh g⁻¹ after 400 cycles at 0.5 A g⁻¹, and even as high as 807 mAh g⁻¹ after 300 cycles at 0.2 A g⁻¹.

LIMITATIONS

There are several limitations to this protocol. First, n-butyllithium is extremely sensitive to water. When using it for synthesis, it is necessary to ensure that the reaction solvents and glassware used are dried; otherwise the yield of the reaction will be low. Secondly, the quality of polymers may slightly vary from different batches, and therefore strictly keep the reaction conditions as same is important. If available, we would recommend to synthesize polymers in sufficient quantities at one time to ensure that all characterizations use the same batch of polymer. Thirdly, the slurry must be ground evenly when fabricating the working electrodes; otherwise the mass distribution of the active material will be uneven, resulting in a large difference in battery performance.

TROUBLESHOOTING

Problem 1
Low yield of S3 arising from air and water sensitivity of n-BuLi (step 1g in part 1: synthesis of small molecules).
Potential solution
Butyllithium is highly sensitive to water and air. Therefore, the reaction bottle, solvents and the needle for solvent transfer must be dried in advance before the experiment. We recommend using the fresh distilled tetrahydrofuran.

Problem 2
Polymerization reactions may not occur or polymer yields are low (step 3c in part 2: synthesis of conjugated polymers).

Potential solution
Remove oxygen in the solvent during the polymerization, which plays a crucial role in the occurrence and yield of the polymerization reaction. During the synthesis of conjugated polymers CP1 and CP2, the solvents are measured with help of syringes and must contain no air. It is necessary to remove the air inside by bubbling the solvent-filled syringe for 2 min before injection.

Problem 3
Different batches of polymers may lead to differences in cell performance due to differences in polymerization (part 2: synthesis of conjugated polymers).

Potential solution
Because of the variation in compounds synthesized from batch to batch, we need to synthesize enough polymers for all characterizations at once to ensure that the same batch is used for all characterizations.

Problem 4
Spurious peaks may appear during the CV test (part 3: measurement of electrochemistry).

Potential solution
Oxygen is electroactive and can be reduced quite easily, interfering with the CV testing. Before measuring the reduction processes for 1–3 by CV, it is better to bubbling an inter gas (e.g., N2) through the solution for about 2 min.

Problem 5
There are differences in the electrochemical properties of cells made from the same batch (part 4: assembly of Li-organic batteries and part 5: Li-ion battery tests).

Potential solution
In the process of making battery cathode sheets, the unevenness of the ground slurry may lead to differences in battery performance. Care should be taken to always grind in one direction throughout the process of grinding the slurry. Also, scrape it to the bottom of the mortar after every five minutes of grinding before continuing to grind. In the process of grinding the active material and carbon black, it should be ground for at least 30 min to ensure full contact between the active material and carbon black. In addition, differences mass loading of active material pasted onto the foam nickel wafer can lead to differences in battery performance. The best approach is to apply a uniform coating and select working electrodes with a similar mass of mass loading of active material (difference of no more than 0.05 mg) for the fabrication of cell.

RESOURCE AVAILABILITY
Lead contact
Further information and requests for resources and reagents should be directed to and will be fulfilled by the lead contact, Xiaoming He (xmhe@snnu.edu.cn).
Materials availability
All reagents generated in this study are available from the lead contact.

Data and code availability
No unique datasets or codes were generated in this study.

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AUTHOR CONTRIBUTIONS
Q.L. and L.C. repeated the experiments, made the figures, and wrote the manuscript. X.W. performed the experiments and data analysis. X.H. conceived and supervised the project.

DECLARATION OF INTERESTS
The authors declare no competing interests.

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