

Supporting Information

Dihydrophenazine-derived oligomers from industrial waste as sustainable cathode materials for rechargeable lithium-ion batteries

Qimin He,^a Shaoyu Lv,^a Yuanzhu Huang,^a Jingying Guo,^a Xiangling Peng,^a Ya Du^b and Haishen Yang^{*a}

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

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

Reagents

Phenazine was obtained from Sennics CO., LTD. Shandong. Dry tetrahydrofuran (THF, 99.5%) was purchased from Greagent; Dichloromethane (DCM, anhydrous, 99.9%), 1,2-epoxypropane (99%), epoxyethane (3.0 M in THF), methylmagnesium chloride (3.0 M in THF), methacryloylchloride (95%), N-methyl-2-pyrrolidinone (NMP, 99.5%), azobisisobutyronitrile (AIBN, 98%), N-Methyl-2-Pyrrolidinone (NMP, anhydrous, 99.5%) were purchased from Amadas.

Characterization methods

Proton nuclear magnetic resonance (¹H NMR) spectrum was acquired on a Bruker AVANCE III 400M. ¹³C NMR spectrum was acquired on a JNM-ECZR. High resolution mass spectrum (HRMS) was tested on Acquity UPLC/XEVO G2-XS QTOF. Thermogravimetric analysis (TGA) was measured on the NETZSCH STA 409 PC/PG apparatus in a wide temperature range of 25-800 °C with a heating rate of 10 °C min⁻¹ under nitrogen atmosphere. Scanning electron microscopes (SEM) was detected on JEOL JSM-7810F. The Fourier transform infrared spectroscopy (FTIR) spectra were recorded on PerkinElmer Spectrum Two, and the wavenumber from 400 cm⁻¹ to 4000 cm⁻¹. Solid-state ¹³C CP/MAS NMR spectrum of **PMEPZ** was performed on BRUKER AVANCE NEO 400WB. The electronic conductivity was measured by the ST2722-SD four-point probe resistivity tester technology. MALDI-TOF Mass spectra were recorded on FLEX-PC MALDI-TOF/TOF instrument.

Synthesis

Synthesis of 5-methyl-10-(2-hydroxypropyl)-5,10-dihydrophenazine.¹ A 100 mL Schlenk tube was charged with phenazine (1 g, 5.5 mmol), then evacuated, backfilled with nitrogen, and dry THF (10 mL) was added. After dissolving, add methylmagnesium chloride (5.54 mL, 16.6 mmol) at -40 °C for 3 h. 1,2-Epoxypropane (1.36 mL, 19.4 mmol) was added at -40 °C and then gradually restored to room temperature for 0.3 h. After reaction, quenched with saturated NH₄Cl solution. Extracted with DCM to obtain a mixture, then dried, filtered and distilled under reduced pressure. Passing the crude product through a column chromatography to get the green solid in 46% yield. ¹H NMR (400 MHz, DMSO-d₆): δ 8.22 (s, 2H), 8.01 (d, J = 8 Hz, 2H), 7.92 (d, J = 8 Hz, 2H), 7.79 (t, J = 12, 8 Hz, 2H), 4.63 (s, 1H), 4.14 (d, J = 12 Hz, 1H), 1.23 (d, J = 8 Hz, 3H). ¹³C NMR (126 MHz, DMSO-d₆): δ 141.7, 141.1, 138.4, 137.8, 129.6, 129.0, 128.8, 126.5, 64.4, 63.7, 45.3 and 21.8. HRMS (ESI): m/z [M+H]⁺ calcd for [C₁₂H₁₈N₂O]⁺ 277.1317, found 277.1312.

Synthesis of 5-methyl-10-(2-methacryloxypropyl)-5,10-dihydrophenazine (MPPZ).² A 100 mL Schlenk tube was charged with 5-methyl-10-isopropyl-5,10-dihydrophenazine (440 mg, 1.7 mmol), then evacuated, backfilled with

nitrogen, and dry DCM (8 mL), DMAP (10.6 mg, 0.1 mmol), methacryloylchloride (0.2 mL, 2.1 mmol) and dry triethylamine (0.4 mL, 2.1 mmol) was added at 0 °C for 12 h. Then, extracted with DCM to obtain a mixture, then dried, filtered and distilled under reduced pressure. Passing the crude product through a column chromatography to get the greeny-yellow solid in 64% yield. ¹H NMR (400 MHz, DMSO-d₆): δ 6.55 (s, 4H), 5.86 (s, 1H), 5.57 (s, 1H), 5.16 (s, 1H), 3.56 (d, J = 84 Hz, 2H), 1.75 (s, 3H), 1.24 (d, J = 8 Hz, 3H). ¹³C NMR (126 MHz, DMSO-d₆): δ 166.7, 137.1, 136.3, 126.4, 121.6, 112.7, 68.5, 49.0, 18.4 and 17.9. HRMS (ESI): m/z [M+H]⁺ calcd for [C₂₀H₂₃N₂O₂]⁺ 323.1760, found 323.1764. FTIR v_{max} / cm⁻¹: 2928-3055 (C-H), 1710 (C=O), 1633 (C=C), 1378-1481 (C-N), 1054-1297 (C-O), 809-937 (C-H), 735 (benzene ring).

Synthesis of poly(5-methyl-10-(2-methacryloxypropyl)-5,10-dihydrophenazine) (PMPPZ).³ A 10 mL Schlenk tube was charged with monomer **MPPZ** (0.2 g, 0.62 mmol) and AIBN (10.2 mg, 0.1 mmol), then evacuated, backfilled with nitrogen, and dry THF (1.5 mL) was added. After the reaction was stirred at 60 °C for 24 h, a large amount of yellow solid appeared. Then, the precipitate was washed with methanol and acetone in turn, centrifuged and dried to obtain gray-green solid in 83% yield. ¹³C CP/MAS solid state NMR: 169.1, 142.8, 127.6, 103.8, 62.7, 47.7, 43.3, 34.5, 28.3, 25.8 ppm. FTIR v_{max} / cm⁻¹: 2820-2973 (C-H), 1723 (C=O), 1371-1485 (C-N), 1255-1254 (C-O), 736 (benzene ring).

Synthesis of 5-methyl-10-(2-hydroxyethyl)-5,10-dihydrophenazine.¹ A 100 mL Schlenk tube was charged with phenazine (1 g, 5.5 mmol), then evacuated, backfilled with nitrogen, and dry THF (10 mL) was added. After dissolving, add methylmagnesium chloride (5.54 mL, 16.6 mmol) at -40 °C for 3 h. Epoxyethane (6.47 mL, 19.4 mmol) was added at -40 °C and then gradually restored to room temperature for 20 h. After reaction, quenched with saturated NH₄Cl solution. Extracted with DCM to obtain a mixture, then dried, filtered and distilled under reduced pressure. Passing the crude product through a column chromatography to get the green solid in 47% yield. ¹H NMR (400 MHz, DMSO-d₆): δ 4.94 (s, 1H), 3.57 (s, 2H). ¹³C NMR (126 MHz, DMSO-d₆): δ 142.4, 139.3, 135.1, 132.1, 131.1, 130.1, 127.2, 127.1, 65.6, 61.3 and 48.3. HRMS (ESI): m/z [M+H]⁺ calcd for [C₁₂H₁₈N₂O]⁺ 263.1160, found 263.1169.

Synthesis of 5-methyl-10-(2-methacryloxyethyl)-5,10-dihydrophenazine (MEPZ).² A 100 mL Schlenk tube was charged with 5-methyl-10-(2-hydroxyethyl)-5,10-dihydrophenazine (1 g, 4.2 mmol), then evacuated, backfilled with nitrogen, and dry DCM (10 mL), DMAP (25.4 mg, 0.2 mmol), methacryloylchloride (0.6 mL, 6.2 mmol) and dry triethylamine (0.9 mL, 6.2 mmol) was added at 0 °C for 12 h. Then, extracted with DCM to obtain a mixture, then dried, filtered and distilled under reduced pressure. Passing the crude product through a column chromatography to get the greeny-yellow solid in 66% yield. ¹H NMR (400 MHz, DMSO-d₆): δ 6.56 (s, 4H), 5.99 (s, 1H), 5.66 (s, 1H), 4.28 (s, 2H), 3.78 (s, 3H), 1.84 (s, 3H). ¹³C NMR (126 MHz, DMSO-d₆): δ 154.6, 136.1, 126.8, 103.9, 100.0, 81.5, 50.4 and 18.5. HRMS (ESI): m/z [M+H]⁺ calcd for [C₁₂H₁₈N₂O]⁺ 309.1603, found 309.1597. FTIR v_{max} / cm⁻¹: 2858-3052 (C-H), 1720 (C=O), 1604-1634 (C=C), 1384-1493 (C-N), 1033-1265 (C-O), 818-942 (C-H), 714 (benzene ring).

Synthesis of poly(5-methyl-10-(2-methacryloxyethyl)-5,10-dihydrophenazine) (PMEPZ).³ A 10 mL Schlenk tube was charged with monomer **MEPZ** (0.2 g, 0.6 mmol) and AIBN (9.7 mg, 0.1 mmol), then evacuated, backfilled with nitrogen, and dry THF (1 mL) was added. After the reaction was stirred at 60 °C for 24 h, a large amount of yellow solid appeared. Then, the precipitate was washed with methanol and acetone in turn, centrifuged and dried to obtain gray-green solid in 89% yield. ¹³C CP/MAS solid state NMR: 177.2, 137.4, 121.7, 112.4, 61.0, 55.9, 44.8, 30.5, 25.0, 18.3 ppm. FTIR v_{max} / cm⁻¹: 2944-3059 (C-H), 1725 (C=O), 1389-1481 (C-N), 1026-1259 (C-O), 728 (benzene ring).

Synthesis of PMEPEZ-MWCNTs. A 10 mL Schlenk tube was charged with monomer **MEPZ** (0.2 g, 0.6 mmol) and MWCNTs (0.02 g, 10 wt%), then evacuated, backfilled with nitrogen, and added dry THF (1 mL). Sonicated the mixed solution for 1 h, and then put it overnight. After sonicated for another 1 h, added AIBN (9.7 mg, 0.1 mmol) treated under ultrasonic for 1 h. Then, put the Schlenk tube in 60 °C oil bath with stirring for 24 h. The precipitate

was washed with methanol and acetone in turn, centrifuged and dried to obtain black solid in 89% yield. FTIR ν_{max} / cm^{-1} : 2890-2992 (C-H), 1719 (C=O), 1381-1480 (C-N), 1050-1260 (C-O), 728 (benzene ring).

Electrochemical measurements

The electrochemical properties of the polymers were studied by using CR-2016 coin-type Li metal half cells. This cathode consists of 50 wt% active material (0.4-0.5 mg), 40 wt% conductive agent (MWCNTs or KB), and 10 wt% PVDF binder in NMP. For the high active mass ratio cells, 50 wt% active material was mixed with 5 wt% MWCNTs, 35 wt% KB, and 10 wt% PVDF binder in NMP. Ball milling for two hours to mix the slurry evenly. Then, coat uniform mixture on aluminum foil (16 μm thick) using doctor blade method, and put it into a vacuum oven at 80 $^{\circ}\text{C}$ overnight. After drying, the electrodes are cut into disks (14 mm diameter) with a manual punching machine. The half cell was assembled in a glove box in which water and oxygen values less than 0.01 ppm. Li metal foil (14 mm diameter) as the anode, 1 M LiPF_6 dissolved in ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1 by volume) as the electrolyte and polypropylene film as the separator. After assembly, take it out of the glove box for electrochemical test at room temperature. The charge-discharge cycle test of the cell was tested on a NEWARE CT-4008 cell test. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were both recorded on the electrochemical workstation system. All of the electrochemical tests were completed at 25 $^{\circ}\text{C}$.

Capacity contribution of PMPZ-MWCNTs cathode electrode calculation

The composite capacity of **PMPZ-MWCNTs** cathode electrode can be regarded as the contribution of two components, as described by the following equation:

$$C_{\text{cathode}} = C_{\text{PMPZ-MWCNTs}} + C_{\text{conductive additives}} \times R_{\text{conductive additives}} / R_{\text{PMPZ-MWCNTs}}$$

Where C_{cathode} , $C_{\text{PMPZ-MWCNTs}}$ and $C_{\text{conductive additives}}$ represent the capacities of cathode electrode of **PMPZ-MWCNTs**, **PMPZ-MWCNTs** and conductive additives, respectively. $R_{\text{conductive additives}}$ and $R_{\text{PMPZ-MWCNTs}}$ correspond to the mass percent of cathode electrode of **PMPZ-MWCNTs**.

Supporting Figures

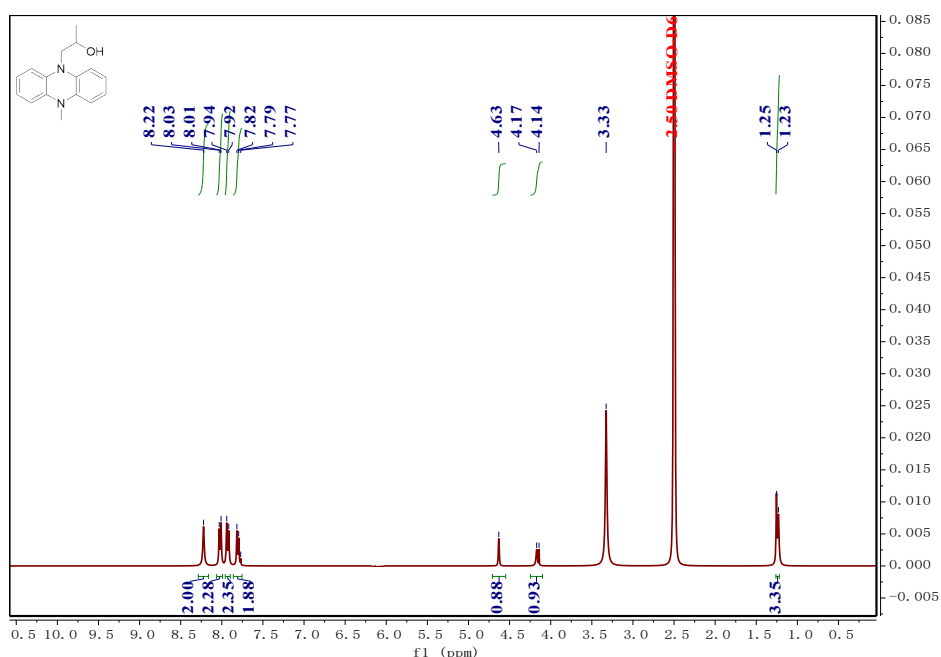


Fig. S1 ^1H NMR spectrum of 5-methyl-10-(2-hydroxypropyl)-5,10-dihydrophenazine in DMSO-d_6 .

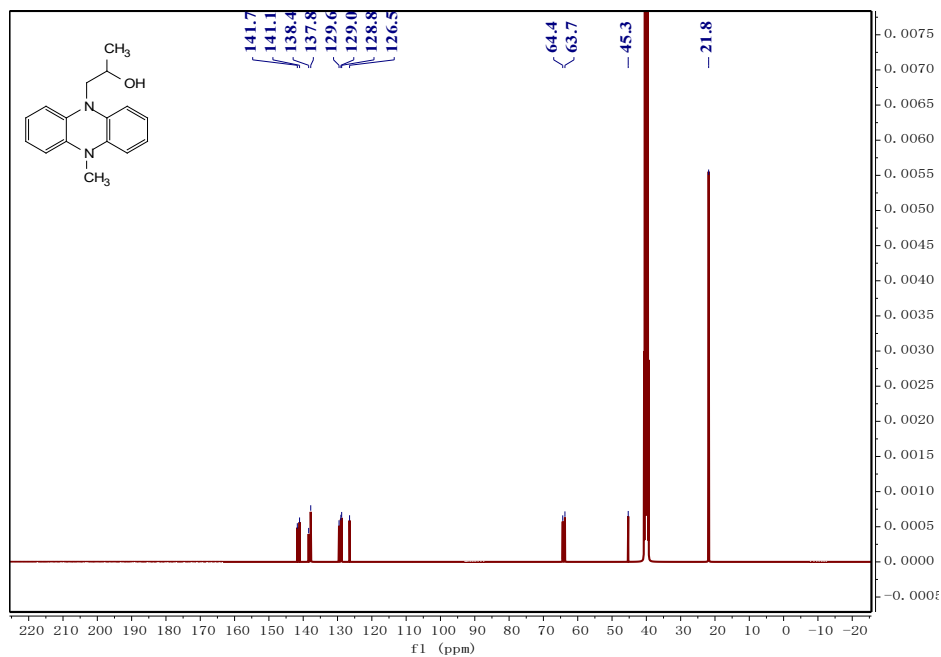


Fig. S2 ¹³C NMR spectrum of 5-methyl-10-(2-hydroxypropyl)-5,10-dihydrophenazine in DMSO-d₆.

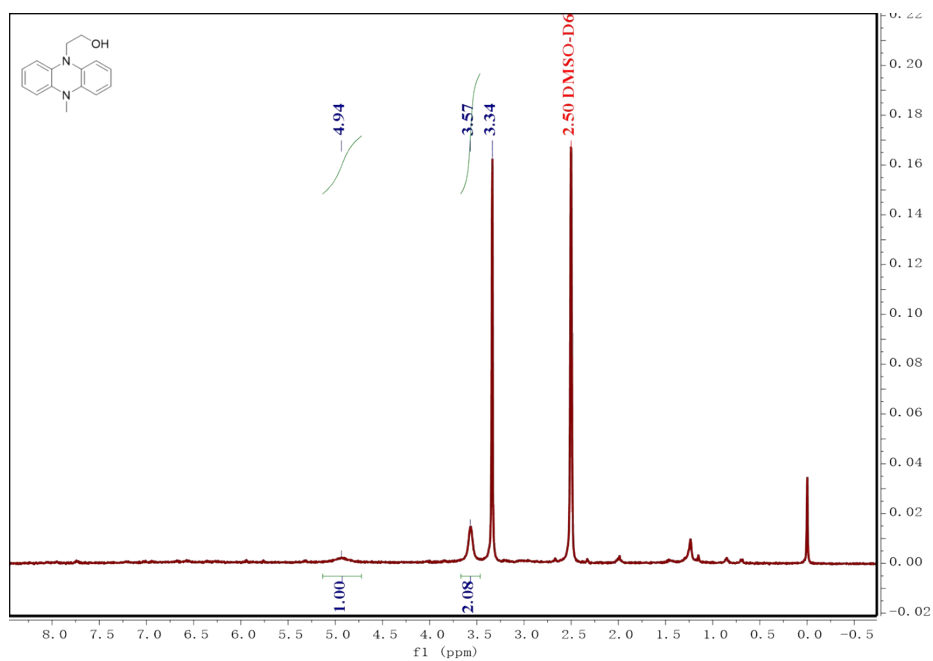


Fig. S3 ¹H NMR spectrum of 5-methyl-10-(2-hydroxyethyl)-5,10-dihydrophenazine in DMSO-d₆.

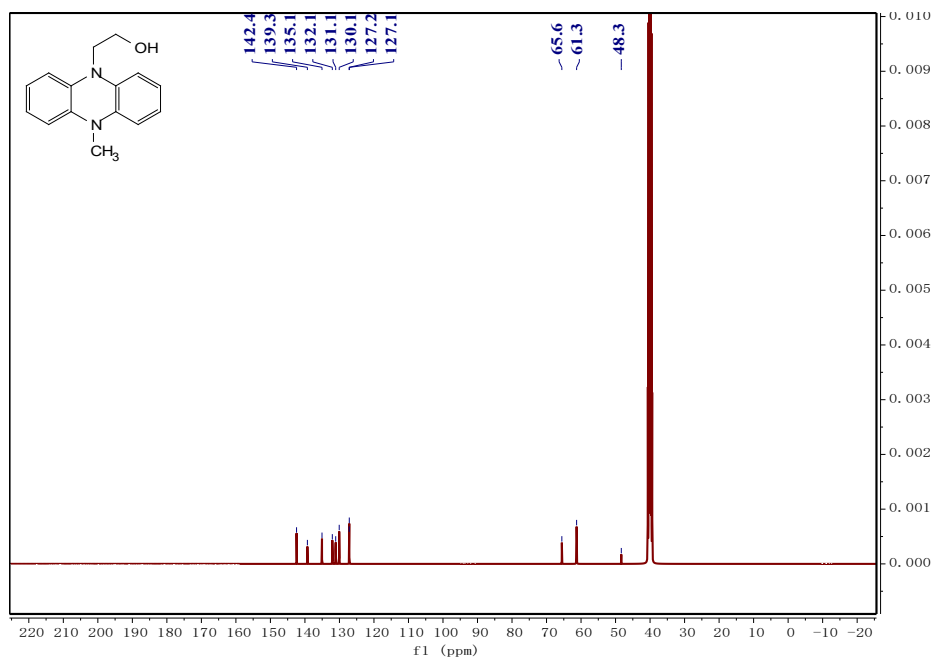


Fig. S4 ^{13}C NMR spectrum of 5-methyl-10-(2-hydroxyethyl)-5,10-dihydrophenazine in DMSO-d_6 .

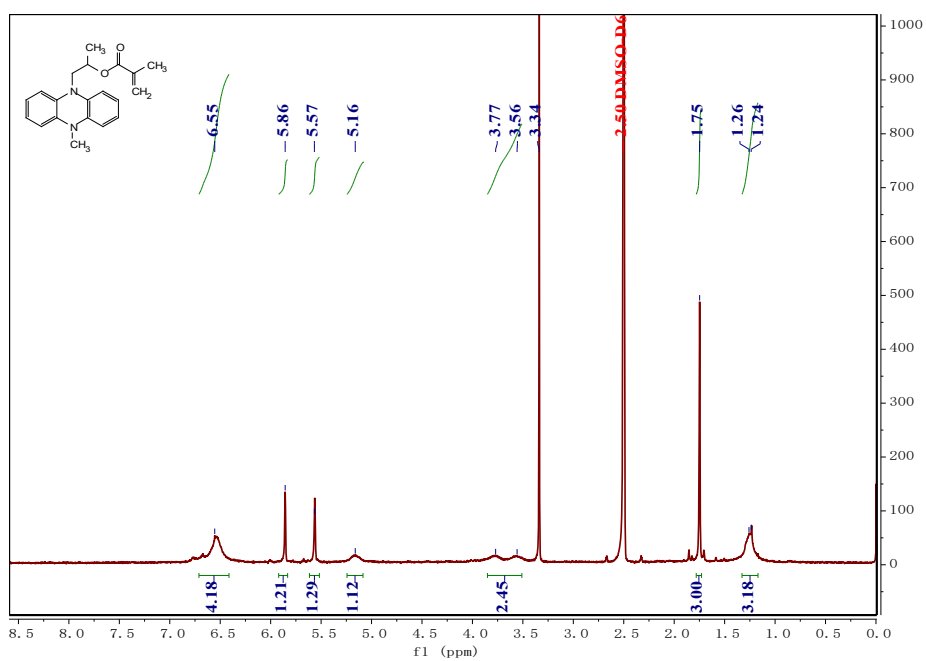


Fig. S5 ^1H NMR spectrum of MPPZ in DMSO-d_6 .

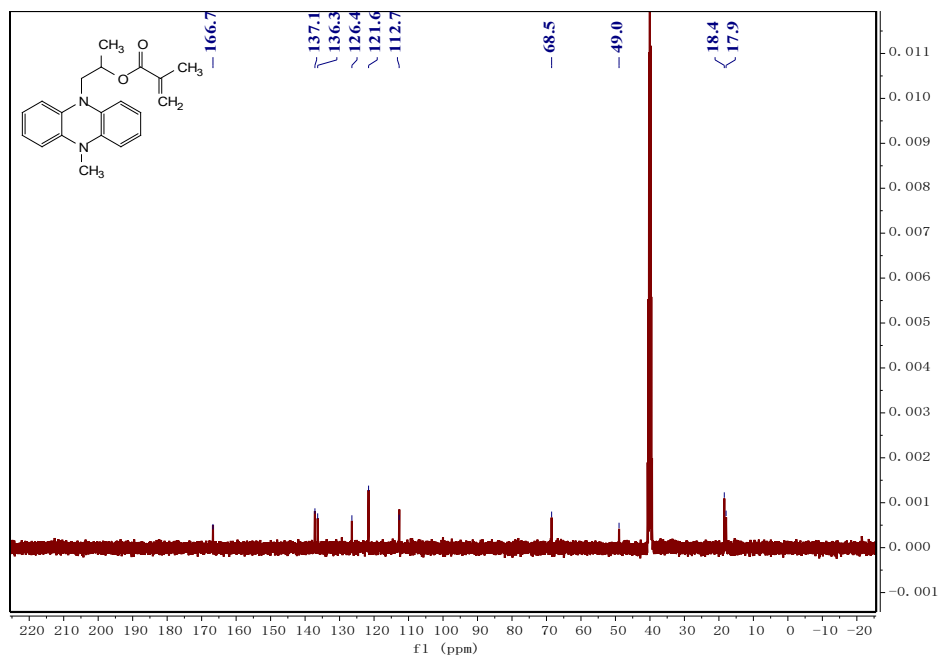


Fig. S6 ^{13}C NMR spectrum of MPPZ in DMSO-d_6 .

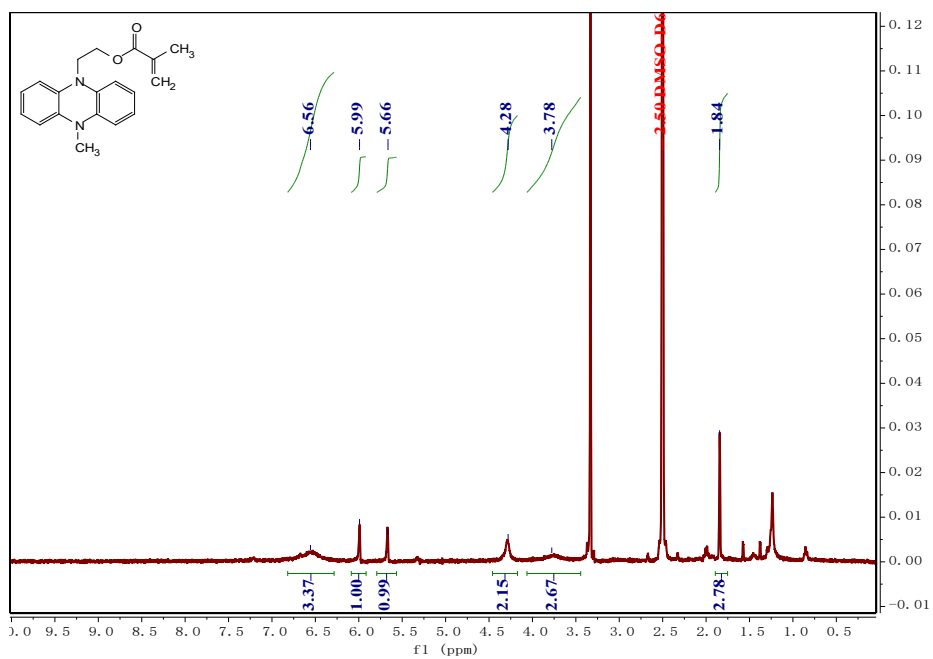


Fig. S7 ^1H NMR spectrum of MEPZ in DMSO-d_6 .

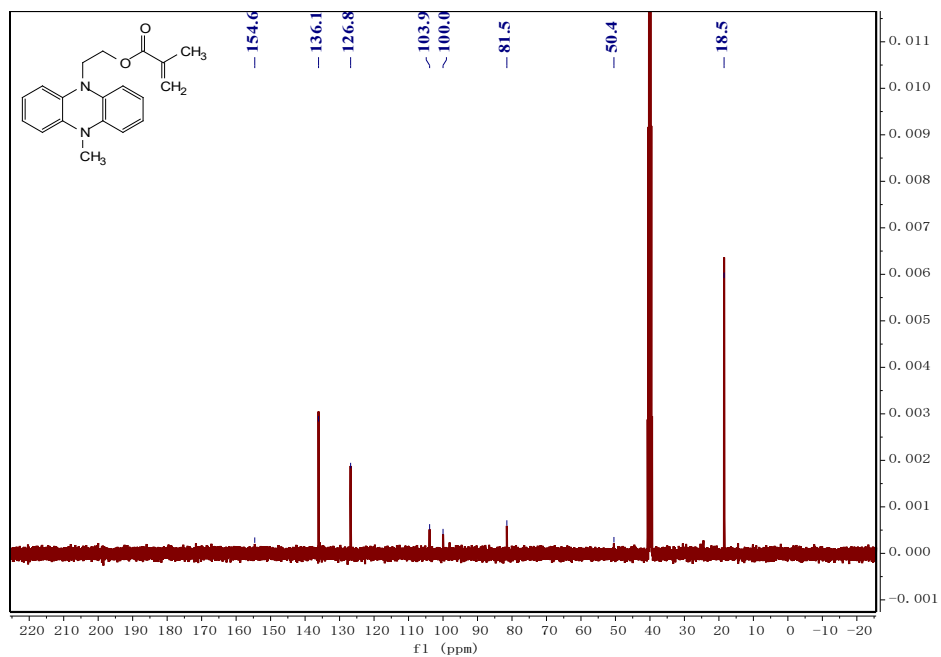


Fig. S8 ^{13}C NMR spectrum of MEPZ in DMSO-d_6 .

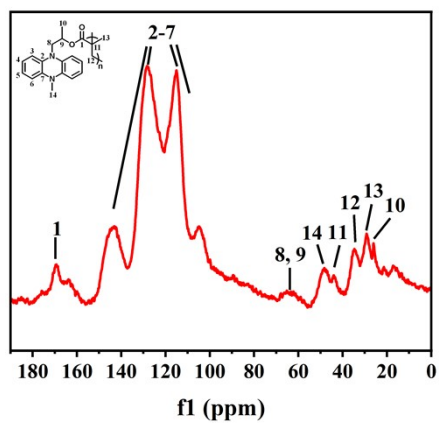


Fig. S9 ^{13}C CP/MAS solid state NMR spectrum of PMPPZ.

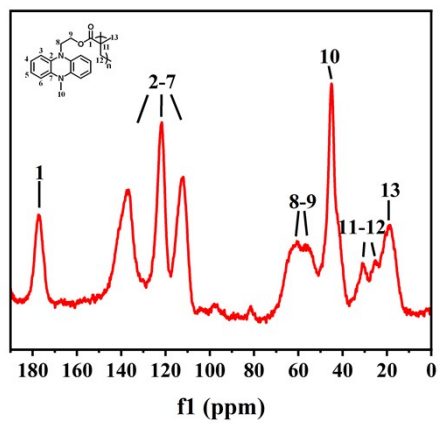


Fig. S10 ^{13}C CP/MAS solid state NMR spectrum of PMEPPZ.

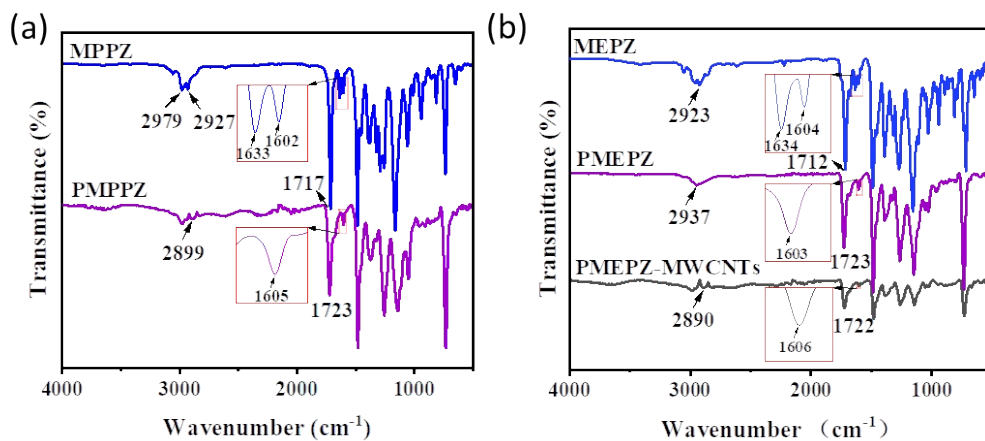


Fig. S11 FTIR spectra of (a) MPPZ and PMPPZ; (b) MEPZ, PMEPEZ and PMEPEZ-MWCNTs.

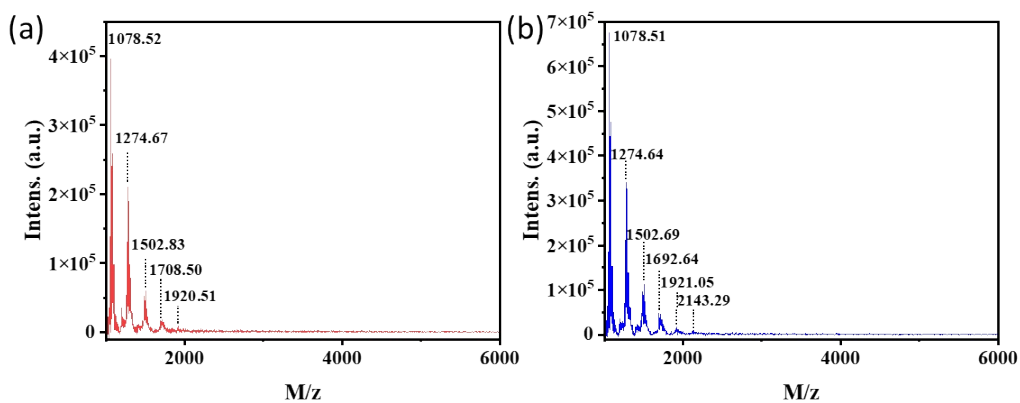


Fig. S12 MALDI-TOF Mass spectrum of PMPPZ (a) and PMEPEZ (b).

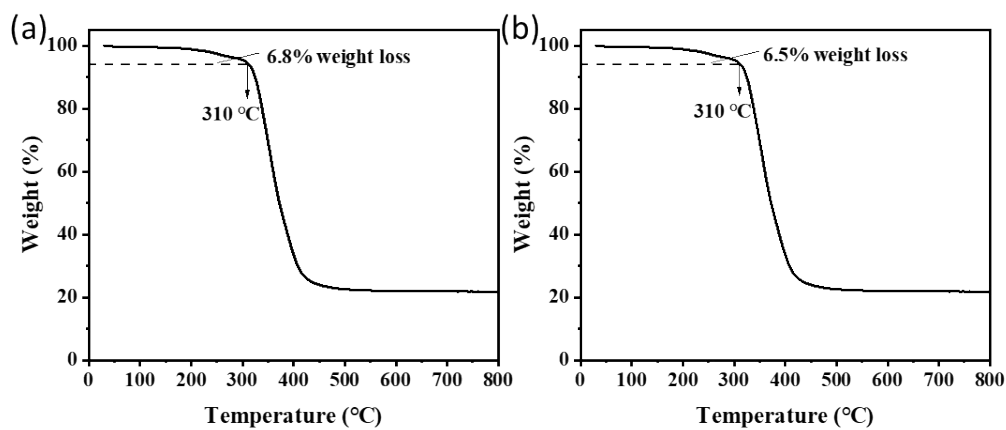


Fig. S13 TGA curve of (a) PMEPEZ and (b) PMEPEZ-MWCNTs in N_2 atmosphere at a heating rate of $10\text{ }^\circ\text{C min}^{-1}$.

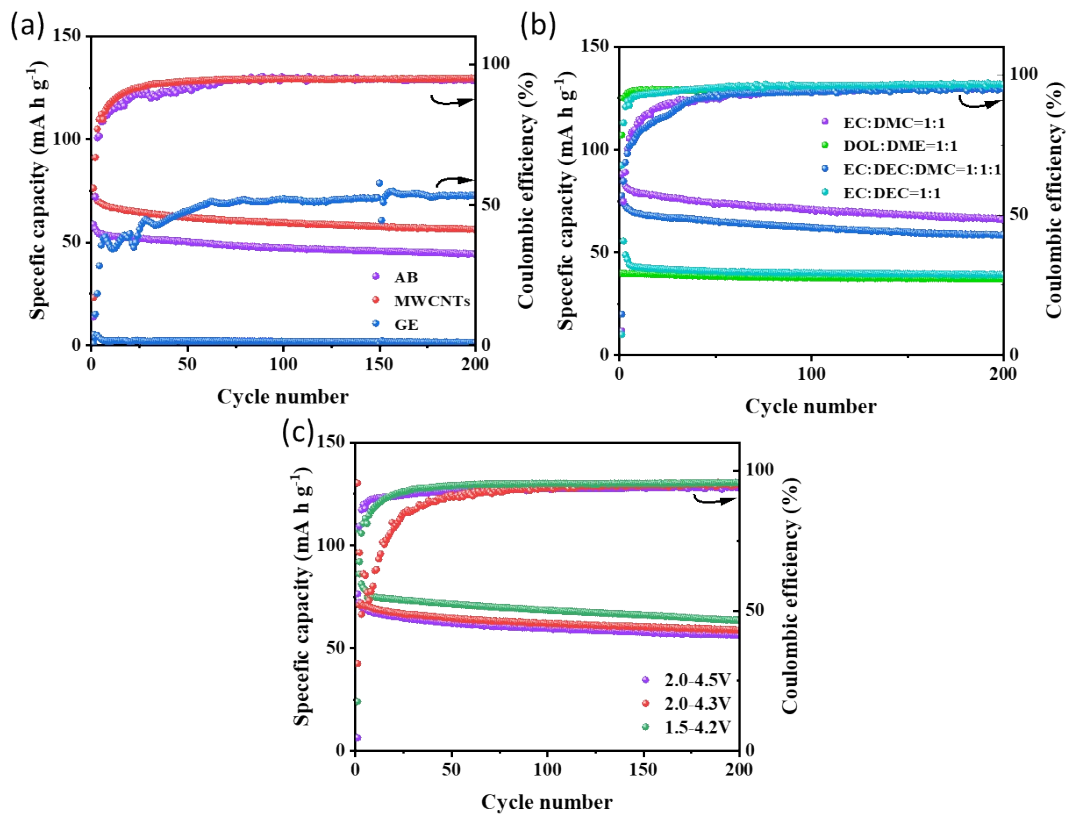


Fig. S14 The electrochemical performance of PMPPZ at 0.2 A g⁻¹. (a) different conductive carbon materials; (b) different electrolytes; (c) different voltage ranges.

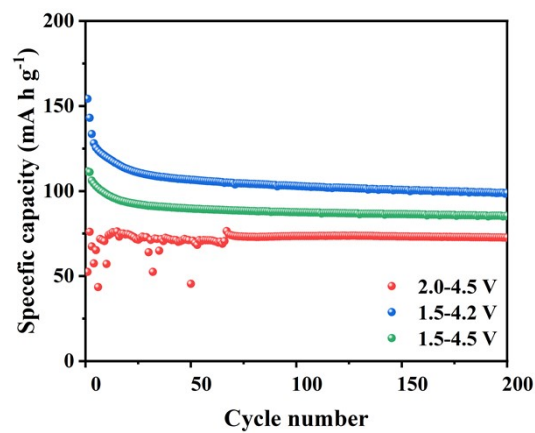


Fig. S15 The electrochemical performance of PMEPPZ in various voltage ranges at 0.2 A g⁻¹.

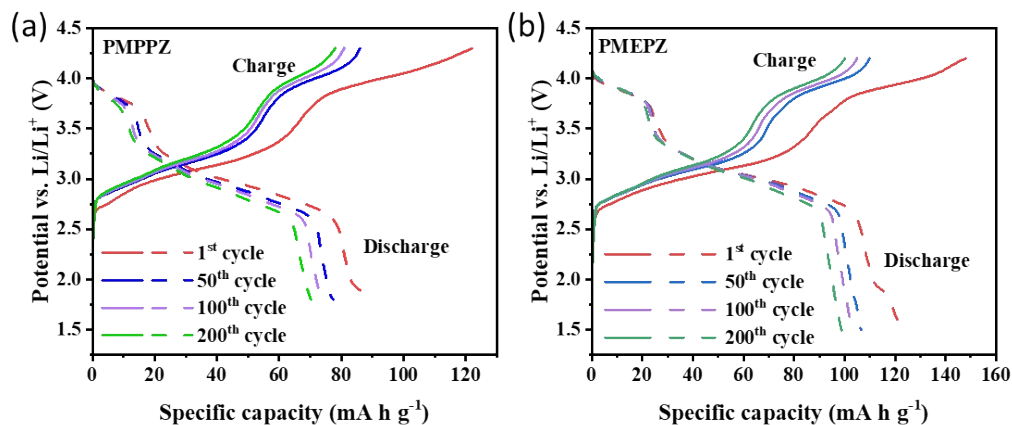


Fig. S16 Galvanostatic charge-discharge tests of PMPPZ (a) and PMPZ (b).

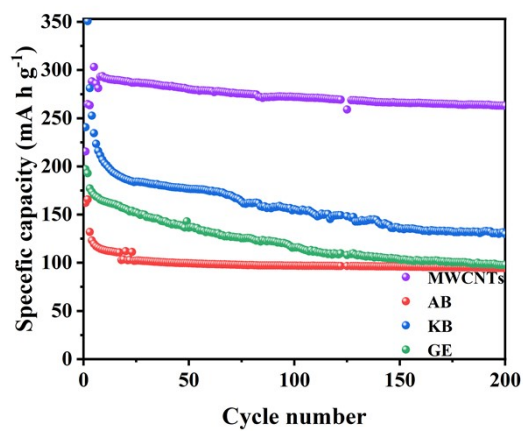


Fig. S17 Electrochemical properties of PMPZ composite with different conductive carbon materials at 0.2 A g⁻¹.

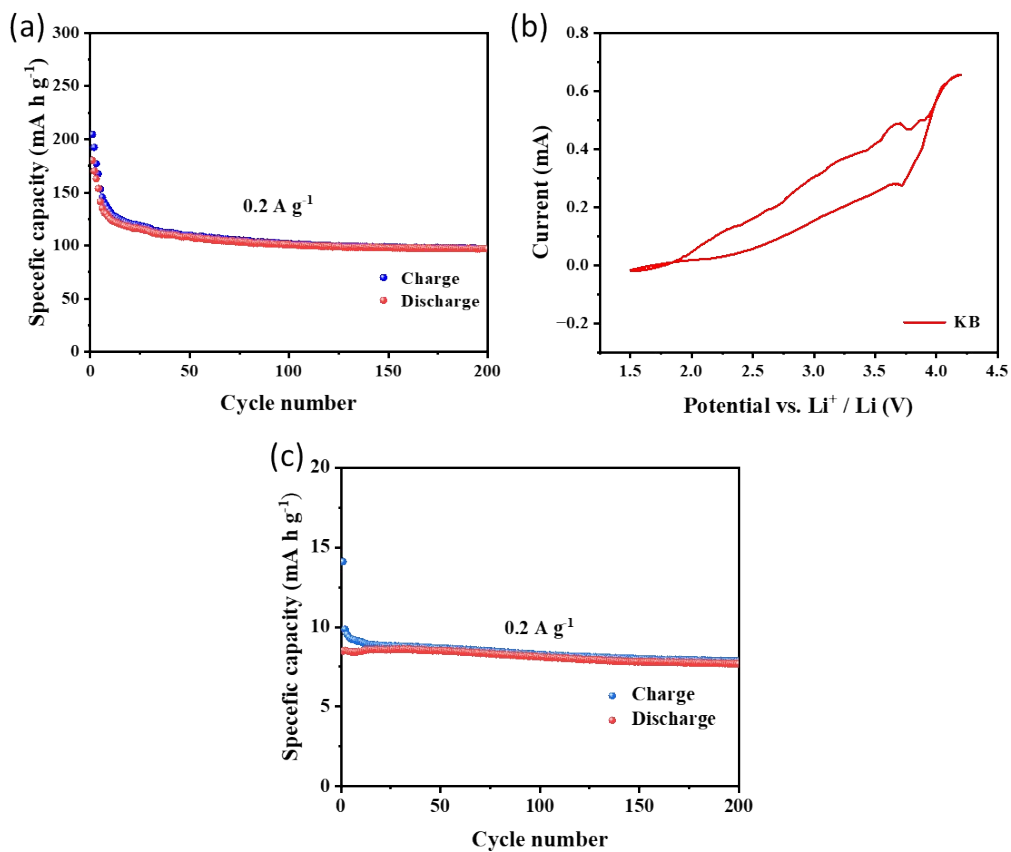


Fig. S18 (a) Capacity contribution of KB at 1.5-4.2 V; (b) cyclic voltammograms of KB at a scan rate of 2 mV s⁻¹; (c) capacity contribution of MWCNTs at 1.5-4.2 V.

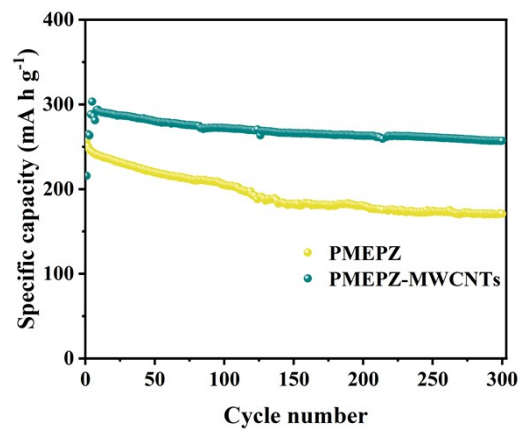


Fig. S19 Comparison of PMEPPZ and PMEPPZ-MWCNTs at 0.2 A g⁻¹.

References

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- 2 Y. Wang, Y. Huang, Y. Hua, Y. Du and H. Yang, *New Journal of Chemistry*, 2022, 46, 14314-14317.
- 3 F. Otteny, M. Kolek, J. Becking, M. Winter, P. Bieker and B. Esser, *Advanced Energy Materials*, 2018, 8, 1802151.