Supporting information

Enhancing Organic Cathodes of Aqueous Zinc-Ion Batteries via Nitro Group Modification

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Experimental procedures

All chemicals and solvents were purchased from Shanghai Kaiyulin Pharmaceutical Technology Co., Ltd, Jilin Province Yanshen Technology Co., Ltd., Adamas-beta® including Pyrene-4,5,9,10-tetraone, 2,7-dibromopyrene-4,5,9,10-tetraone, fuming nitric acid, 98% sulfuric acid, and directly employed without further purification.

Synthesis of 2-dinitropyrene-4,5,9,10-tetraone (PTO-NO₂): Pyrene-4,5,9,10-tetraone (0.786 g, 3.0 mmol) was added to fuming nitric acid (10 mL) in a 100 mL round-bottom flask.

The mixture was heated at 80 °C for 1.5 h. The reaction mixture was poured into ice water (300 mL). The resulting yellow precipitate was collected by filtration, washed with water, and dried under reduced pressure. The compound PTO-NO₂ was obtained as yellow powder (0.85 g). Yield: 93%. Chemical shifts are reported using the signal of DMSO-d₆ at δ 2.50 for ¹H NMR. ¹H NMR (400 MHz, DMSO-d₆): δ (ppm) 8.83 (s, 2 H), 8.41 (d, *J* = 7.6 Hz, 2 H), 7.87 (t, *J* = 7.6 Hz, 1 H).



Scheme S1. Synthetic route of 2-nitropyrene -4,5,9,10-tetraone.

Synthesis of 2,7-dinitropyrene-4,5,9,10-tetraone (PTO-2NO₂): Pyrene-4,5,9,10-tetraone (1.0 g, 3.8 mmol) was added to 98% sulfuric acid (12 mL) in a 100 mL round-bottom flask, then the fuming nitric acid (12 mL) was added to the above mixture dropwise in an ice bath. The mixture was heated at 90 °C for 2 h. The reaction mixture was poured into ice water (500 mL). The resulting yellow precipitate was collected by filtration, washed with water, and dried under reduced pressure. The compound PTO-2NO₂ was obtained as yellow powder (1.1 g). Yield: 82%. ¹H NMR (400 MHz, DMSO-d₆): δ (ppm) 8.89 (s, 4H).



Scheme S2. Synthetic route of 2,7-dinitropyrene -4,5,9,10-tetraone.

Materials characterization

Solution nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AV-III 400 spectrometer (¹H: 400 MHz, ¹³C: 100 MHz) in dimethyl sulfoxide-d₆ (DMSO-d₆). ¹H NMR spectra were referenced internally using the residual solvent resonances ($\delta = 2.50$ ppm for DMSO-d₆) relative to SiMe₄ (TMS, $\delta = 0$ ppm). Powder X-ray diffraction (PXRD) patterns

were collected at room temperature on a D/Max–2500C X-ray diffractometer (Rigaku Co., Japan). Fourier transform infrared spectra (FT-IR) were recorded as KBr pellets using a Thermo Scientific iN10. X-ray photoelectron spectroscopy (XPS) data were conducted on Thermo Fisher Scientific 250XI/K-Alpha. Al K α X-ray (6 mA × 12 KV) was utilized as the irradiation source. All measurements were performed in the CAE mode with the reference of C 1s (284.8 eV).

Electrolyte preparation

Aqueous metal ion solutions were prepared by dissolving a certain amount of metal ion salt in 100 mL deionized water, the final concentration of the metal ion was controlled at 2 M. 0.5 M H_2SO_4 electrolyte was prepared by adding a certain amount of concentrated H_2SO_4 in deionized water under stirring. 0.5 M $Zn(CF_3SO_3)_2$ organic electrolyte was prepared by dissolving 0.5 mol $Zn(CF_3SO_3)_2$ in acetonitrile (ACN).

Electrochemical measurements

Cathode preparation: Cathode was prepared by mixing PTO, PTO-NO₂ or PTO-2NO₂ (60 wt%), Ketjen Black (30 wt%), and polytetrafluoroethylene (10 wt%) in isopropanol to form a slurry after grinding. The slurry was cast on a Ti mesh current collector and dried at 80 °C for 12 h under vacuum to form the PTO, PTO-NO₂ or PTO-2NO₂ electrode. For electrochemical tests in typical three-electrode systems and coin cells, the mass loading of the cathode is about 2-3 mg.

Coin-type (CR 2032) cells were assembled using the as-prepared PTO, PTO-NO₂, or PTO-2NO₂ electrodes as the cathode and Zn foil as the anode. A 2 M ZnSO₄ solution served as the electrolyte, prepared by dissolving 1.61 g of ZnSO₄ in 5 mL of water. The electrochemical performance of the PTO-2NO₂ electrode materials in other metal-ion electrolytes was evaluated using a three-electrode system, with Pt and Ag/AgCl as the counter and reference electrodes, respectively. Galvanostatic charge/discharge (GCD) and galvanostatic intermittent titration technique (GITT) measurements were conducted using the LAND CT3002A battery testing device. The GITT was recorded through a series of galvanostatic discharge pulses lasting 120 seconds at a current density of 200 mA g^{-1} , followed by a 30-minute relaxation period. The CHI 760E multichannel electrochemical workstation was employed to record cyclic voltammetry (CV) and electrochemical

impedance spectroscopy (EIS). Specific capacities were calculated based on the mass of the active components (PTO, PTO-NO₂, PTO-2NO₂).

The PTO-Azo electrodes were acquired by disassembling the $Zn||PTO-2NO_2$ cells after they had been discharged four times. The electrochemical performance of PTO-Azo in a 0.5 M H₂SO₄ electrolyte was evaluated using a three-electrode system, with Pt and Hg/Hg₂SO₄ serving as the counter and reference electrodes, respectively, and the PTO-Azo cathode functioning as the working electrode. Additionally, the performance of PTO-Azo in an organic zinc electrolyte was assessed using coin cells, with 0.5 M Zn(OTF)₂/ACN as the electrolyte.

Calculation of the electron transfer number



Molecular weight (M) is 262.2, 307.2, 353.2, respectively. According to the formula: Specific capacity = $F \times n/M = 26.8 \times n/M$ (S1) F is the Faraday constant (96,500 C or 26.8 Ah) n is the number of electrons involved in stoichiometric reaction.

As the specific capacity of PTO, PTO-NO₂ and PTO-2NO₂ is 330.2, 694.6, 904.8 mAh

g⁻¹, the number of electrons is 3.23, 7.96 and 11.92, respectively (Table S1).

The increased electron transfer number resulting from the incorporation of nitro groups can be attributed to the enhanced activity of carbonyl groups, which facilitated an approximately 4-electron transfer reaction, along with a 4-electron transfer reaction per nitro group.

| Sample | Molecular weight (g mol ⁻¹) | Specific capacity (mAh g ⁻¹) | Electron transfer |
|-----------------------|--|--|----------------------|
| РТО | 262.2 | 330.2 | 3.23 |
| PTO-NO ₂ | 307.2 | 694.6 | 7.96 |
| PTO-2 NO ₂ | 353.21 | 904.8 | 11.92 |

Table S1. Molecular weight, specific capacity and electron transfer number of the three different cathode materials.

Calculation based on Nernst Equation

In order to explore the effect of hydrogen ion concentration, the electrochemical reaction of PTO-Azo can be simplified as the hydrogen ion intercalation process in $0.5 \text{ M H}_2\text{SO}_4$ electrolytes:

 $PTO-Azo + n H^+ + n e^- \rightleftharpoons H_n PTO-Azo$

According to the Nernst Equation:

$$\varphi = \varphi^{\theta} + \frac{2.303RT}{nF} \log_{10} \frac{[PTO - Azo][H^+]n}{[H^-PTO - Azo]} = \varphi^{\theta} + \frac{0.0592}{n} \log_{10} \frac{[PTO - Azo][H^+]n}{[H^-PTO - Azo]}$$
(S2)

Where, the φ , φ^{θ} , R, T, n, F present the electrode potential (V), the standard potential (V), gas constant (8.314 J K⁻¹ mol⁻¹), temperature (298.15 K), electron transfer numbers and Faraday constant (96500 C mol⁻¹) respectively.

Since the activity of solid electrode is considered as 1, the equation can be simplified as:

$$\varphi = \varphi^{\theta} + 0.0592 \log_{10} [H^+] = \varphi^{\theta} - 0.0592 pH$$
(S3)

Since the pH values of 0.5 M H_2SO_4 and 2 M $ZnSO_4$ are 0 and 4.45, respectively. The potential of H⁺ intercalation in 2 M $ZnSO_4$ is

$$\varphi^{\mathscr{C}} = \varphi^{\mathscr{C}} + 0.0592(pH1 - pH2) = \varphi^{\mathscr{C}} - 0.26344$$
(S4)

Here, φ^{er} is the potential obtained in 0.5 M H₂SO₄.

Calculation details

The Density Functional Theory (DFT) calculations were performed using the Vienna Ab

Initio Simulation Package (VASP).^{1,2} The Generalized Gradient Approximation (GGA), specifically the Perdew–Burke–Ernzerhof (PBE) functional, was used to describe exchange-correlation interactions.³ The core electrons were treated with the projector-augmented wave (PAW) method, while the valence electrons were represented by plane-wave basis sets.⁴ To include dispersion forces, the DFT-D3 correction with Becke–Johnson (BJ) damping was applied.^{5,6} A plane-wave energy cutoff of 450 eV was set, and the force convergence criterion was established at 0.05 eV/Å.



Figure S1. X-ray diffraction patterns of the PTO, PTO-NO₂ and PTO-2NO₂.



Figure S2. FT-IR spectra of the PTO, PTO-NO₂ and PTO-2NO₂.



Figure S3. ¹H NMR (400 MHz, DMSO-d₆, 298 K) spectrum of PTO.



Figure S4. ¹H NMR (400 MHz, DMSO-d₆, 298 K) spectrum of PTO-NO₂.



Figure S5. ¹H NMR (400 MHz, DMSO-d₆, 298 K) spectrum of PTO-2NO₂.



Figure S6. FT-IR spectra of PTO-NO₂ electrode after cycling for 100 cycles.



Figure S7. Illustrations of the molecular structures for the discharged products from PTO- NO_2 (a) and PTO- $2NO_2$ (b).



Figure S8. GCD curves of PTO-2NO₂ in different zinc salt electrolytes.



Figure S9. GCD curve of PTO-2NO₂ in aqueous MgSO₄ solution.



Figure S10. GCD curve of PTO-2NO₂ in aqueous Na₂SO₄ solution.



Figure S11. Electrochemical performance of $PTO-2NO_2$ and PTO within a voltage range of 0.80 V-1.5 V and 0.85 V-1.5 V: (a, b) GCD curves, with PTO-2Br used as a comparison; (c) Cycling stability and Coulombic efficiency at 0.2 A g⁻¹.



Figure S12. Ex-situ XPS spectra of O element during the first discharge process.

The results indicate an initial formation of C–O–H, followed by the successive conversion of C=O to O–Zn. Upon discharge to 0.8 V, the C=O groups disappeared, indicating complete coordination of carbonyl groups with H⁺ and Zn²⁺ ions. The calculated ratio of C–O–H to O–Zn was 1.7, highlighting a proton-dominated intercalation process.



Figure S13. CV curves of PTO at various scan rates.



Figure S14. CV curves of 2PTO-Azo at various scan rates.



Figure S15. CV curves of PTO-Azo at various scan rates.



Figure S16. Cycling stability and Coulombic efficiency of PTO, 2PTO-Azo and PTO-Azo, at 0.2 A g^{-1} .



Figure S17. Self-discharge performance of PTO, 2PTO-Azo and PTO-Azo.



Figure S18. Cycling stability and Coulombic efficiency of PTO, 2PTO-Azo and PTO-Azo at 0.5 A g⁻¹.



Figure S19. Comparison with previously reported organic materials with quinone units¹⁻⁸ at small current densities ($\leq 1 \text{ A g}^{-1}$).



Figure S20. Rate performance of PTO and PTO- $2NO_2$. (a) Specific capacity at different current densities and the corresponding Coulombic efficiency; (b, c) GCD curves at different current densities.



Figure S21. Comparison with previously reported quinone materials.



Figure S22. GITT curves of a coin cell with PTO cathode at a current density of 0.2 A g^{-1} .



Figure S23. O1s and N1s XPS spectra of the PTO-NO₂ at the 4th discharge and 5th charge stages.

The recoverable C=O groups and the stably present N=N groups certified the stable structure of the PTO-Azo sample.



Figure S24. GCD curves of PTO-Azo in different Zn^{2+} electrolytes.



Figure S25. GCD curves of PTO-Azo in 0.5 M H_2SO_4 solution.

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