

Electronic Supplementary Information

Quinoxalinophenazinedione covalent triazine framework for boosted aqueous zinc-ion battery

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1. Materials synthesis

Synthesis of 2,9-dicyano-5,7,12,14-tetraaza-6,13-pentacenequinone (DCTPQ). DCTPQ was synthesized by a modified method according to the previous report.^{S1} Firstly, 2,5-dihydroxy-1,4-benzoquinone (DHBQ, 1.00 g, 7.14 mmol, Energy Chemical) and 3,4-diaminobenzonitrile (DABZ, 3.80 g, 28.55 mmol, Energy Chemical) were mixed thoroughly using a pestle and mortar. The mixture was heated at 180°C for 6 h under nitrogen flow. After cooling to room temperature, the mixture was filtered and washed several times with deionized water and acetone, and then dried for 18 hours in a vacuum at 80°C. The deep purple DDTAP powder was obtained in a yield of up to 95%. Secondly, 25 mL H₂SO₄ (98%) was diluted with 100 mL deionized water, and as-prepared DDTAP (1.40 g, 4.19 mmol) was added into the solution. After gradually adding K₂Cr₂O₇ (4.93 g, 16.75 mmol) as an oxidant, the mixture was heated at 80°C for 5 h and then poured into 200 mL ice water. The product was then filtered, washed with deionized water and acetone subsequently, and dried at 80°C in vacuum for 18 h. Finally, the DCTPQ yellow powder was obtained with 70% yield. ¹H NMR (500 MHz, DMSO-d₆, δ): 9.11 (s, 1H), 8.59 (d, 2H), 8.41 (d, 2H). MALDI-TOF MS: m/z = 362.0549 [M]⁺, calcd. for C₂₀H₆N₆O₂, 362.0552.

Synthesis of Poly(triazine-5,7,12,14-tetraaza-6,13-pentacenequinone) (TTPQ). Trifluoromethanesulfonic acid and 40 mL CHCl₃ were placed in a pre-dried 2-neck flask with round bottom in N₂ atmosphere. The mixture was cooled to 0°C and DCTPQ (0.362 g, 1 mmol) in 100 mL CHCl₃ was added to the solution droplet by droplet over 30 min. The mixture was stirred at 0°C for another 2 h and then left overnight at room temperature. The solution turned dark green, forming a solid precipitate. The mixture was then poured into 200 ml of water containing 10 ml of ammonia solution and stirred for 3 hours. The precipitate was filtered and washed in sequence with water, ethanol, acetone and chloroform. TTPQ (0.224 g, 56.5% yield) is a dark brown solid. ¹³C SSNMR (125 MHz, DMSO-d₆, δ): 168.65, 164.65, 139.09, 137.10, 128.60.

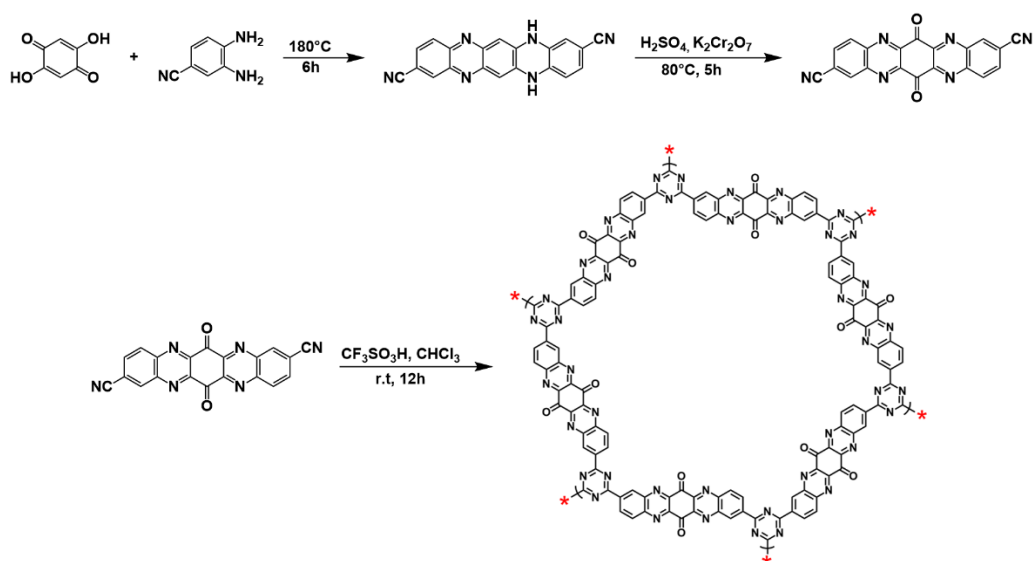


Figure S1. Synthesis route to TTPQ via DCTPQ.

2. Electrode preparation

To prepare the DCTPQ or TTPQ cathode, 60 wt% DCTPQ or TTPQ powder, 30 wt% KB conductive carbon (vinyl ketone carbon black, EC-600JD) and 10 wt% polytetrafluoroethylene (PTFE) binder were mixed and ground in a mortar. The mixture was then coated on a stainless mesh current collector and dried overnight at 60°C . The electrochemical performance of TTPQ in 1 M H_2SO_4 aqueous electrolyte was measured by three-electrode system (TTPQ working electrode, platinum as the counter electrode, Ag/AgCl electrode as the reference electrode). To test AZIBs performance, 2M ZnSO_4 aqueous electrolyte was simply prepared by dissolving zinc sulfate heptahydrate ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, 99%, Aladdin) in deionized water and assembled in a CR2032 coin cell in ambient air by using a glass fiber septum (Whatman, GF/B) to separate the zinc anodes (15 and 0.5 mm in diameter and thickness, respectively) from the DCTPQ or TTPQ cathode with 2 M ZnSO_4 aqueous solution as the electrolyte.

3. Characterization

The FT-IR spectra were copied from ThermoFisher Nicolet iS-10. Field-emission scanning electron microscope (SEM) images were obtained from J Hitachi S-4800 at

an accelerating voltage of 3 kV. Transmission electron microscopy (TEM) images were obtained from FEI F20. ^1H NMR spectra were recorded on a Bruker ADVANCE 500 MHz spectrometer with trimethylsilane (TMS) as the internal reference. Solid state ^{13}C cross-polarization magic angle spinning nuclear magnetic resonance (CP/MAS NMR) spectra were taken on a Bruker AVANCE NEO 400 WB spectrometer (Bruker BioSpin AG, Fällanden, Switzerland) spectrometer. Mass spectra were measured using GCT-MS EI and Bruker Daltonics Biflex III MALDI-TOF Analyzer in the MALDI mode. X-ray diffraction (XRD) patterns were recorded from Bruker D8 Advance Diffractometer. X-ray photoelectron spectroscopy (XPS) analysis was carried out on a Thermo ESCALAB 250 X-ray photoelectron spectrometer. Thermogravimetric analysis was conducted by TGA/SDTA851E (Mettler Toledo). Nitrogen (N_2) adsorption-desorption curve was measured by 3Flex three-station all-purpose gas adsorber (Micromeritics, America). All DFT calculations were performed in Gaussian09 code at the B3LYP/6-31(d) level. All electrochemical measurements were conducted on a CHI 760E electrochemical workstation (Chenhua, Shanghai).

4. FT-IR data, MS and SSNMR spectra

Bond and Vibration Type	DDTAP	DCTPQ
N-H, stretching	3250–2683 cm^{-1}	
C-H, stretching	3250–2683 cm^{-1}	2988 cm^{-1}
$\text{C}\equiv\text{N}$, stretching	2219 cm^{-1}	2234 cm^{-1}
$\text{C}=\text{O}$, stretching		1714 cm^{-1}
$\text{C}=\text{N}$, stretching	1617 cm^{-1} , 1579 cm^{-1}	1620 cm^{-1} , 1531 cm^{-1}
$\text{C}=\text{C}$, stretching	1477 cm^{-1} , 1446 cm^{-1}	1483 cm^{-1} , 1434 cm^{-1}
$\text{C}-\text{CO}-\text{C}$, stretching		1056 cm^{-1}

Table S1. FT-IR spectra of DDTAP and DCTPQ

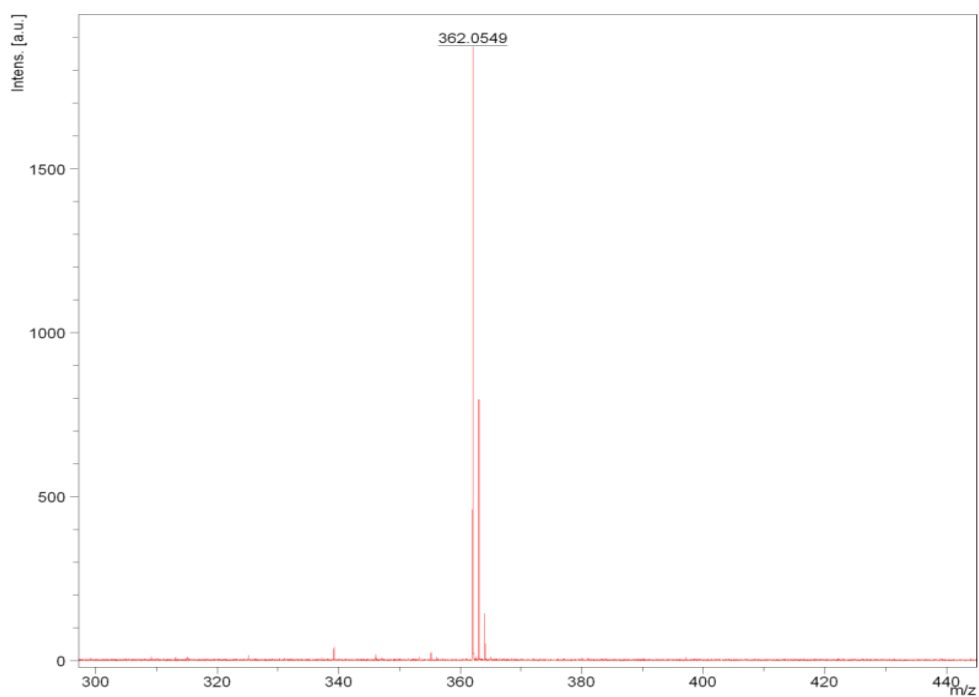


Figure S2. MADLI-TOF mass spectrum of DCTPQ.

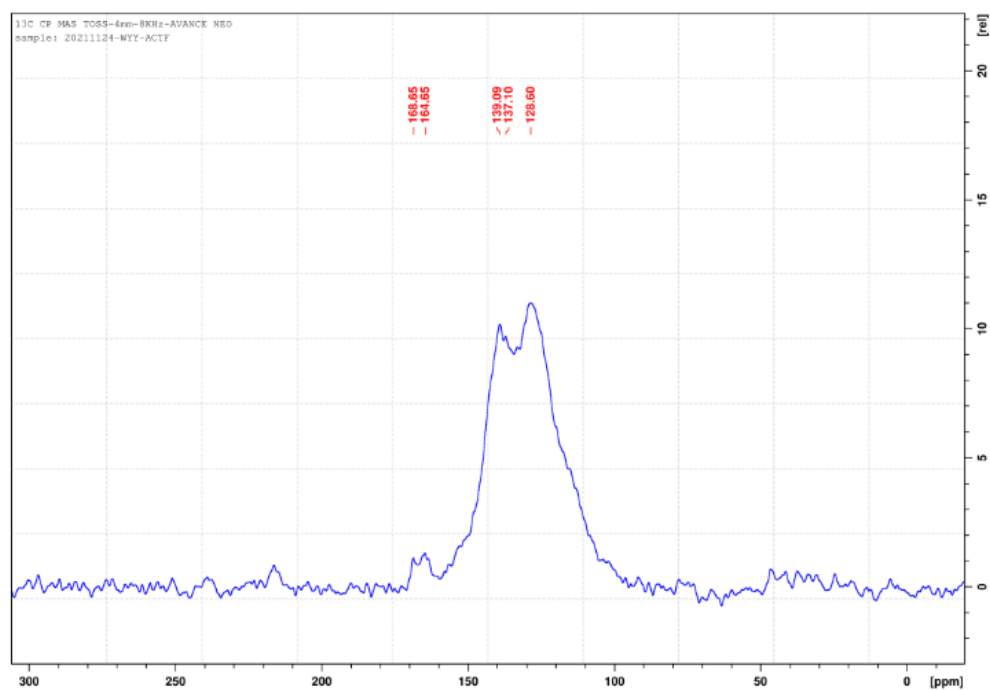


Figure S3. ¹³C SSNMR spectrum of TTPQ.

5. SEM images

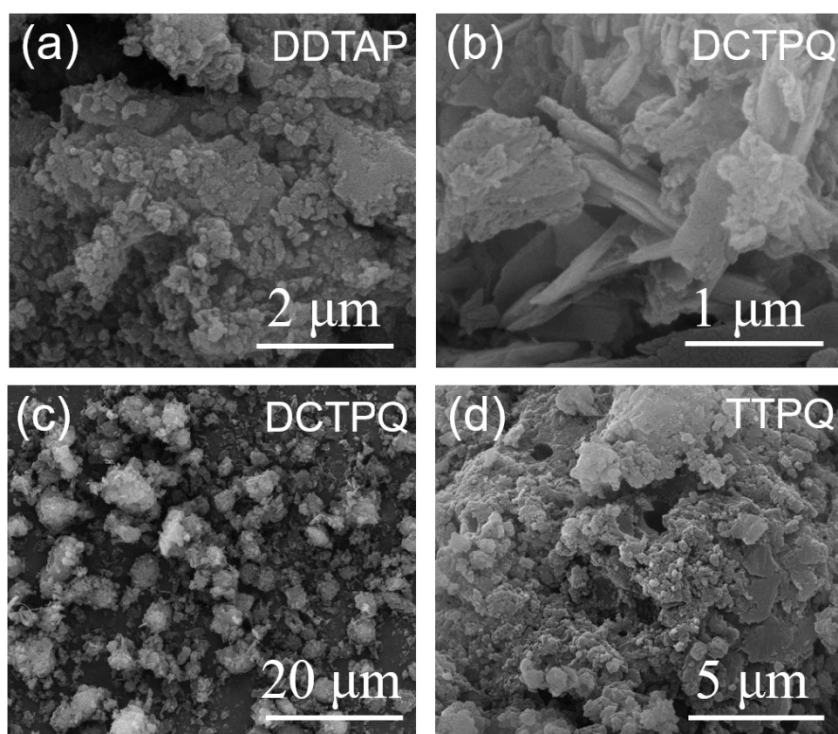


Figure S4. SEM image of (a) DDTAP, (b, c) DCTPQ, (d) TTPQ.

6. TGA and isothermal desorption

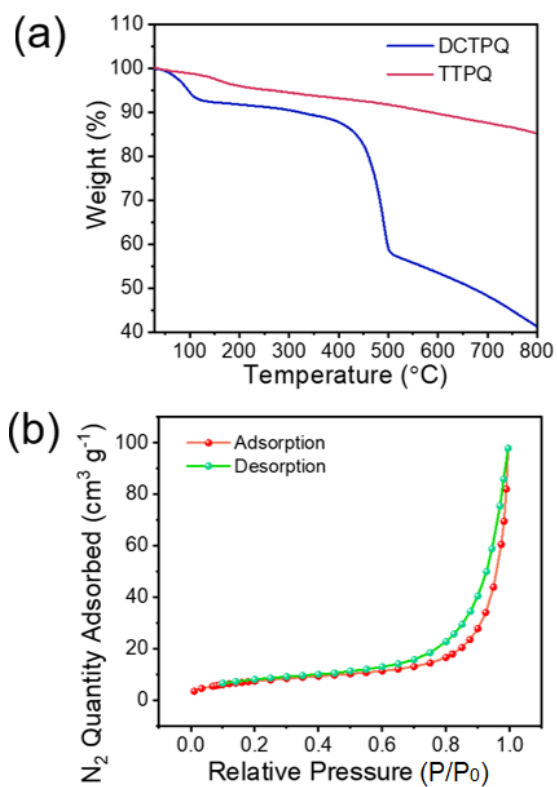


Figure S5. (a) TGA curves of DCTPQ and TTPQ. (b) Nitrogen (N₂) adsorption-desorption curves of TTPQ.

7. XPS of TTPQ

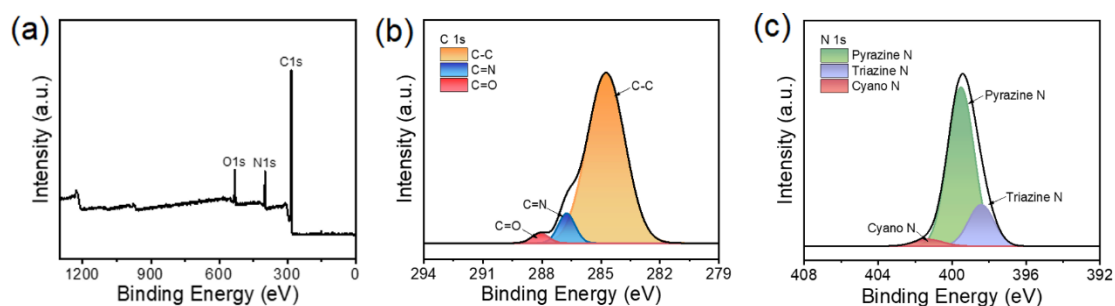


Figure S6. XPS spectra of TTPQ for (a) full spectrum, (b) C 1s, and (d) N 1s. XPS

8. AZIBs tests

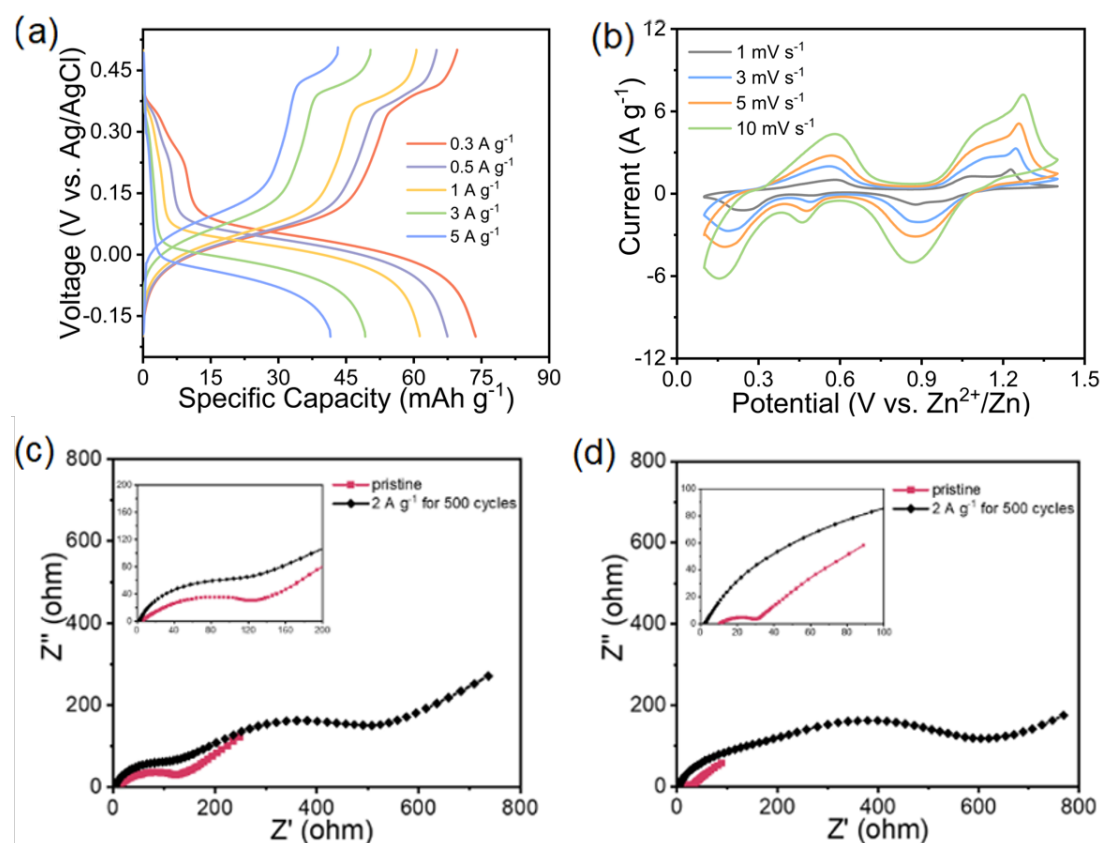


Figure S7. (a) GCD curves of TTPQ from 0.3 A g⁻¹ to 5 A g⁻¹ in 1 M H₂SO₄ electrolyte. (b) Typical CV curves of DCTPQ at a series scan rate of 1, 3, 5, 10 mV s⁻¹ in 2 M ZnSO₄ electrolyte in the voltage range of 0.1-1.4 V vs. Zn²⁺/Zn. Electrochemical impedance spectra of (c) DCTPQ and (d) TTPQ at pristine state and 500 cycles at 2 A g⁻¹, respectively.

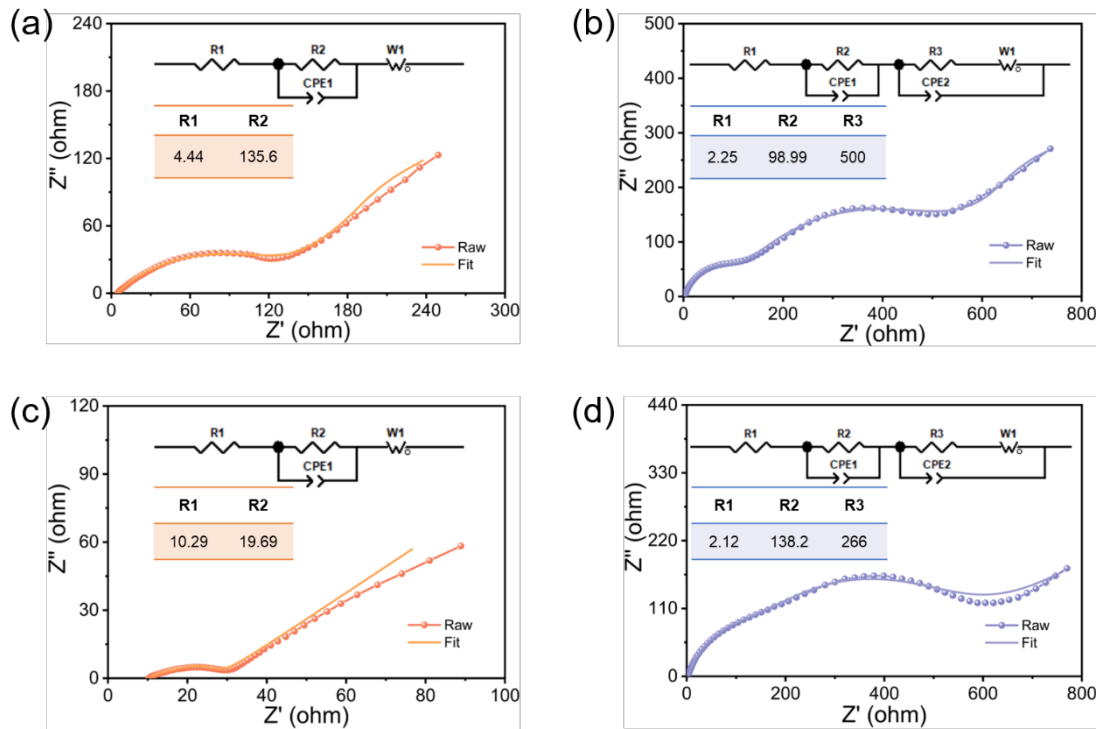


Figure S8. EIS plots and fitted spectra of DCTPQ (a, b) and TTPQ (c, d) at pristine state and 500 cycles at 2 A g^{-1} , respectively. The corresponding equivalent circuit models fitted and the values of each resistor are shown as inset figures. The series resistance (R_1) includes the resistance of the electrolyte, separator and electrode materials. R_2 represents the interface resistance between the electrolyte and electrode after 500 cycles, and the charge transfer resistance (R_{ct} : R_2 at pristine state and R_3 after 500 cycles) is associated with the semicircle at high-frequency region. Warburg impedance (Z_w) is shown as a straight diagonal line at the low-frequency end, which is related to the diffusion process.

Table S2. Fitted parameters of the elements in the below equivalent circuit for the EIS data in Figure S7c&7d and Figure S8.

Sample	State	R_1	R_2	R_3	CPE_{1-T}	CPE_{1-P}	W_{1-R}	W_{1-T}	W_{1-P}	CPE_{2-T}	CPE_{2-P}
DCTPQ	Pristine	4.44	135.6		1.23×10^{-3}	0.544	433.4	92.69	0.582		
	500 th	2.25	98.99	500	7.28×10^{-5}	0.853	900	93	0.606	9.94×10^{-4}	0.677
TTPQ	Pristine	10.29	19.69		2.52×10^{-3}	0.528	209.7	94.38	0.582		

	500 th	2.12	138.2	266	1.57×10^{-4}	0.770	405	49.38	0.169	5.77×10^{-4}	0.752
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Table S3. Electrochemical performance comparison of reported n-type organic cathode materials for aqueous rechargeable zinc batteries, corresponding to Figure 2(f).

Material	Electrolyte	Voltage Range (Average Voltage)	Capacity (Current density)	Capacity retention @current density (Cycle number)	Reference
C4Q	3 M Zn(CF ₃ SO ₃) ₂	0.2–1.8 V (1.0 V)	335 mA h g ⁻¹ (0.02 A g ⁻¹)	87%@0.5 A g ⁻¹ (1000 cycles)	S2
PTO	2 M ZnSO ₄	0.36-1.46 V (0.8 V)	336 mA h g ⁻¹ (0.04 A g ⁻¹)	70%@3 A g ⁻¹ (1000 cycles)	S3
DTT	2 M ZnSO ₄	0.3-1.4 V (0.76 V)	205 mA h g ⁻¹ (0.043 A g ⁻¹)	70%@0.217 A g ⁻¹ (200 cycles)	S4
PQ-Δ	3 M Zn(CF ₃ SO ₃) ₂	0.25-1.6 V (0.78 V)	203 mA h g ⁻¹ (0.03 A g ⁻¹)	99.9%@0.15 A g ⁻¹ (500 cycles)	S5
HATN	2 M ZnSO ₄	0.3-1.1 V (0.53 V)	370 mA h g ⁻¹ (0.11 A g ⁻¹)	93%@5 A g ⁻¹ (5000 cycles)	S6
HATN-3CN	2 M ZnSO ₄	0.1-1.6 V (0.64 V)	320 mA h g ⁻¹ (0.05 A g ⁻¹)	91%@5 A g ⁻¹ (5800 cycles)	S7
TAPQ	1 M ZnSO ₄	0.5-1.6V (0.84 V)	270 mA h g ⁻¹ (0.05 A g ⁻¹)	94%@0.05 A g ⁻¹ (260 cycles)	S1
PTCDA	2 M ZnCl ₂	0.05-1.0 V (0.5 V)	123 mA h g ⁻¹ (0.2 A g ⁻¹)	81%@8 A g ⁻¹ (500 cycles)	S8
PA-COF	1 M ZnSO ₄	0.2-1.8 V (0.7V)	247 mA h g ⁻¹ (0.1 A g ⁻¹)	74%@1 A g ⁻¹ (10000 cycles)	S9
TTPQ	2M ZnSO ₄	0.1-1.4 V (1.07 V)	404 mA h g ⁻¹ (0.3 A g ⁻¹)	94%@0.5 A g ⁻¹ (250 cycles)	This work

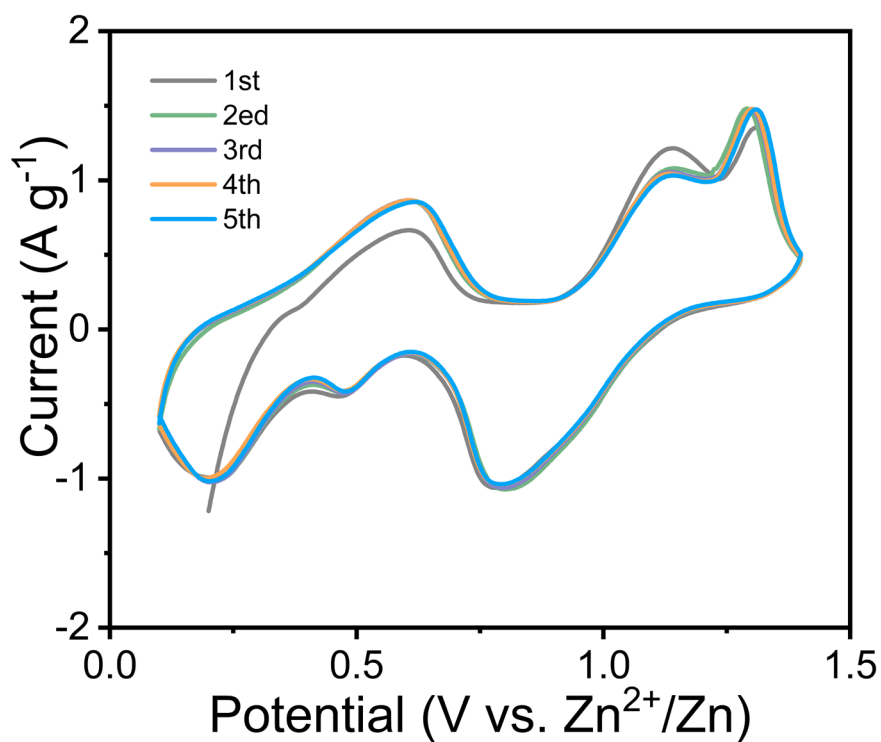


Figure S9. The first five CV curves of TTPQ in 2M ZnSO₄ electrolyte at 1 mV s⁻¹.

9. SEM of TTPQ

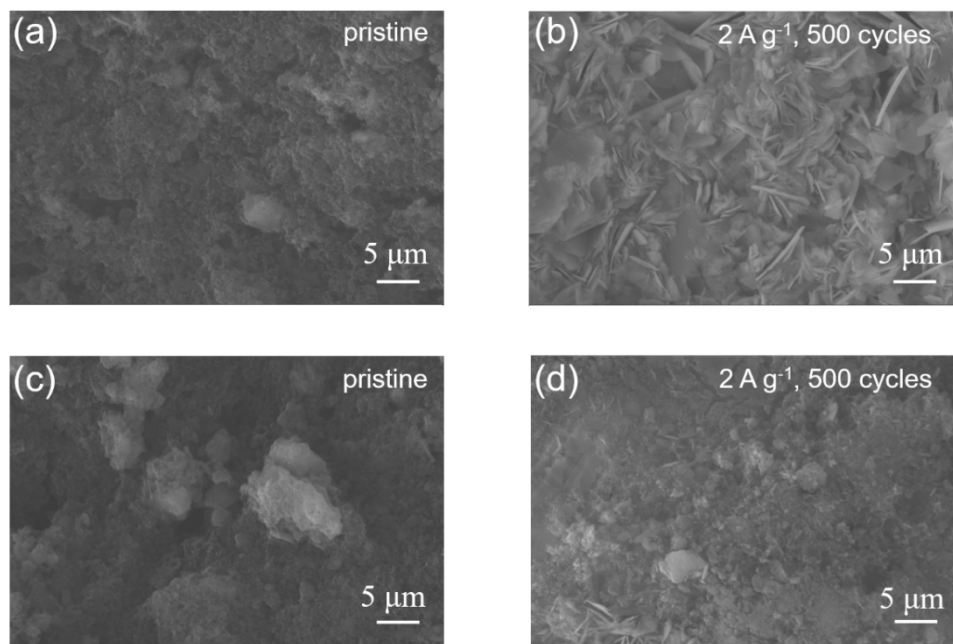


Figure S10. SEM images for (a, b) DCTPQ and (c, d) TTPQ electrode before and after 500 GCD cycles in AZIBs.

10. Ex-situ characterization during charge/discharge process

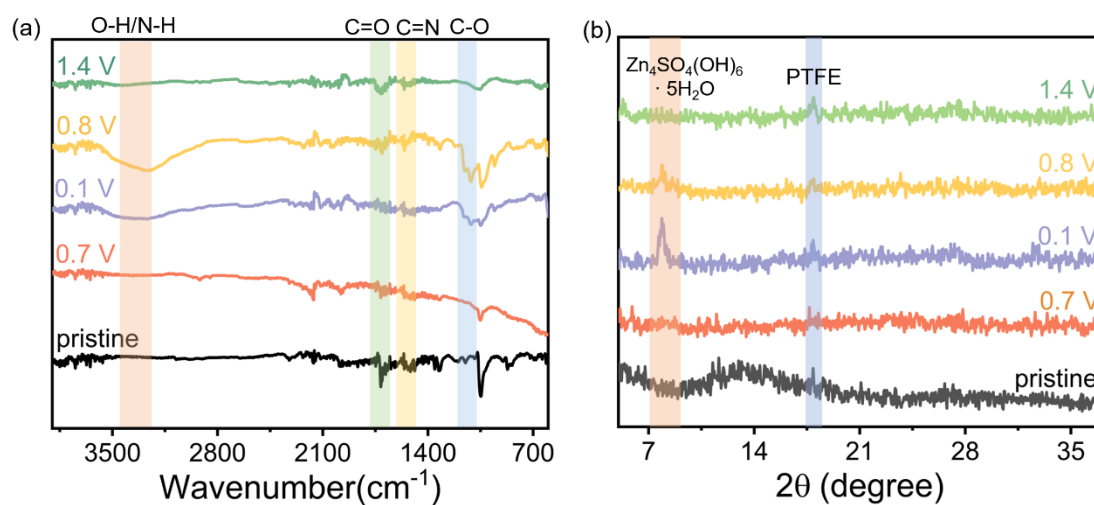


Figure S11. Ex-situ XRD patterns and FT-IR spectra of TTPQ electrodes during charge/discharge process.

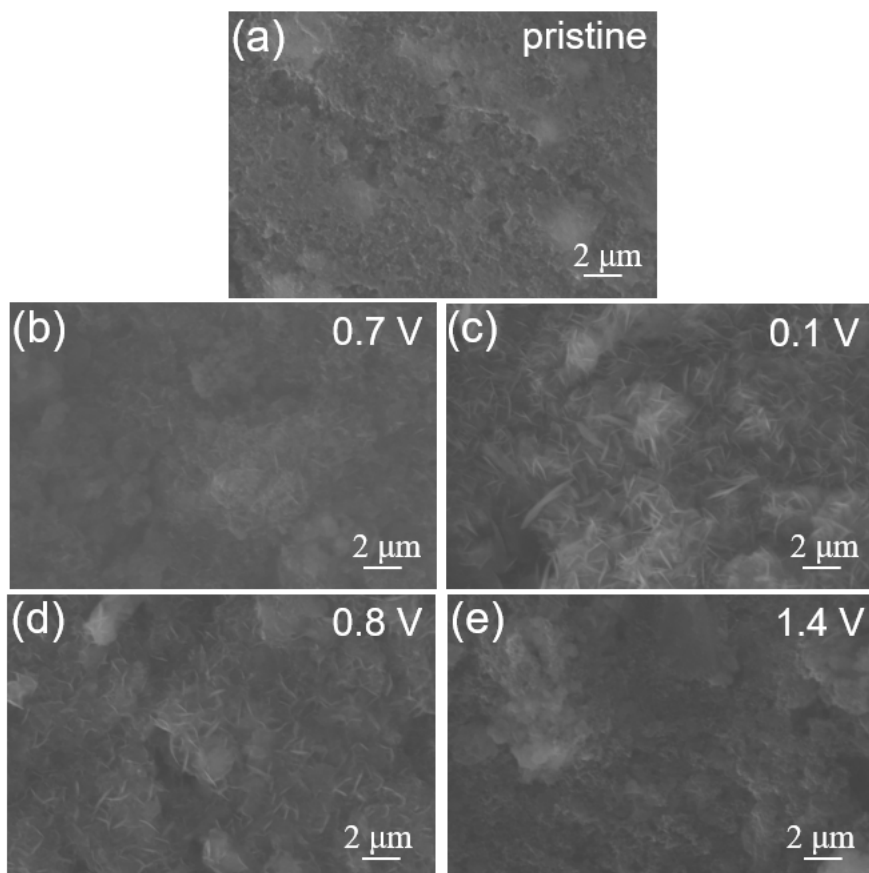


Figure S12. Ex-situ SEM images of TTPQ electrodes during charge/discharge process.

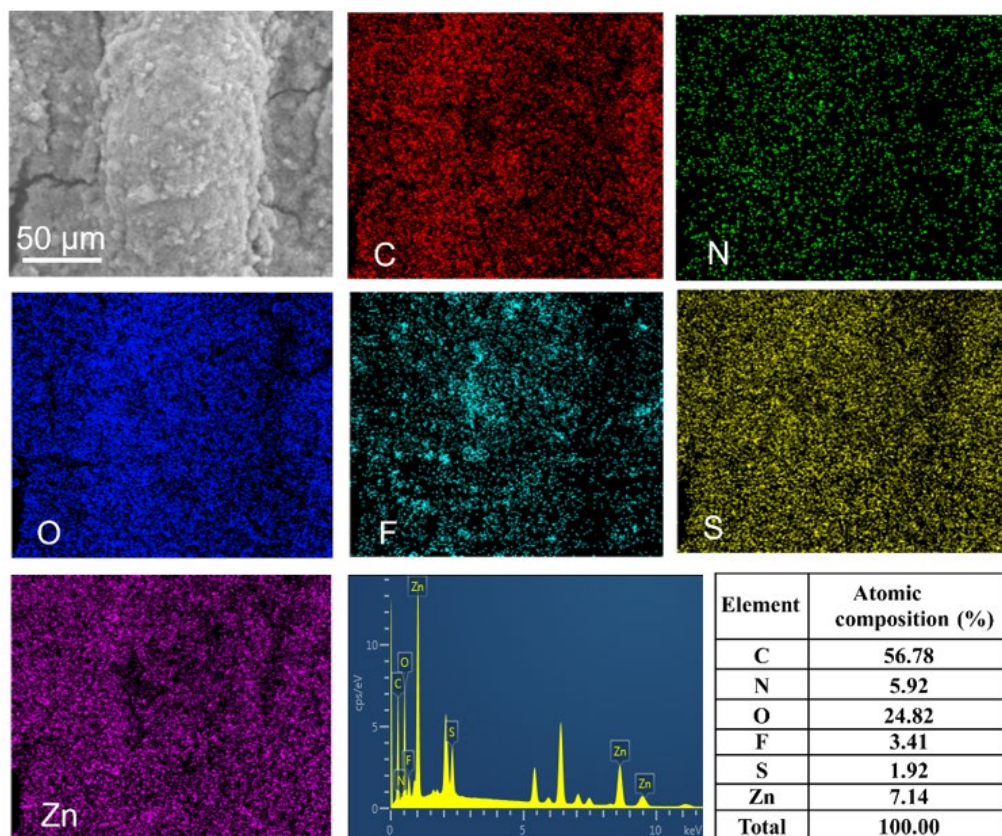


Figure S13. SEM image of TTPQ electrode and elemental mapping for C, N, O, F (from PTFE), S (from electrolyte ZnSO_4) and Zn at the discharged state of 0.1 V.

11. DFT calculation

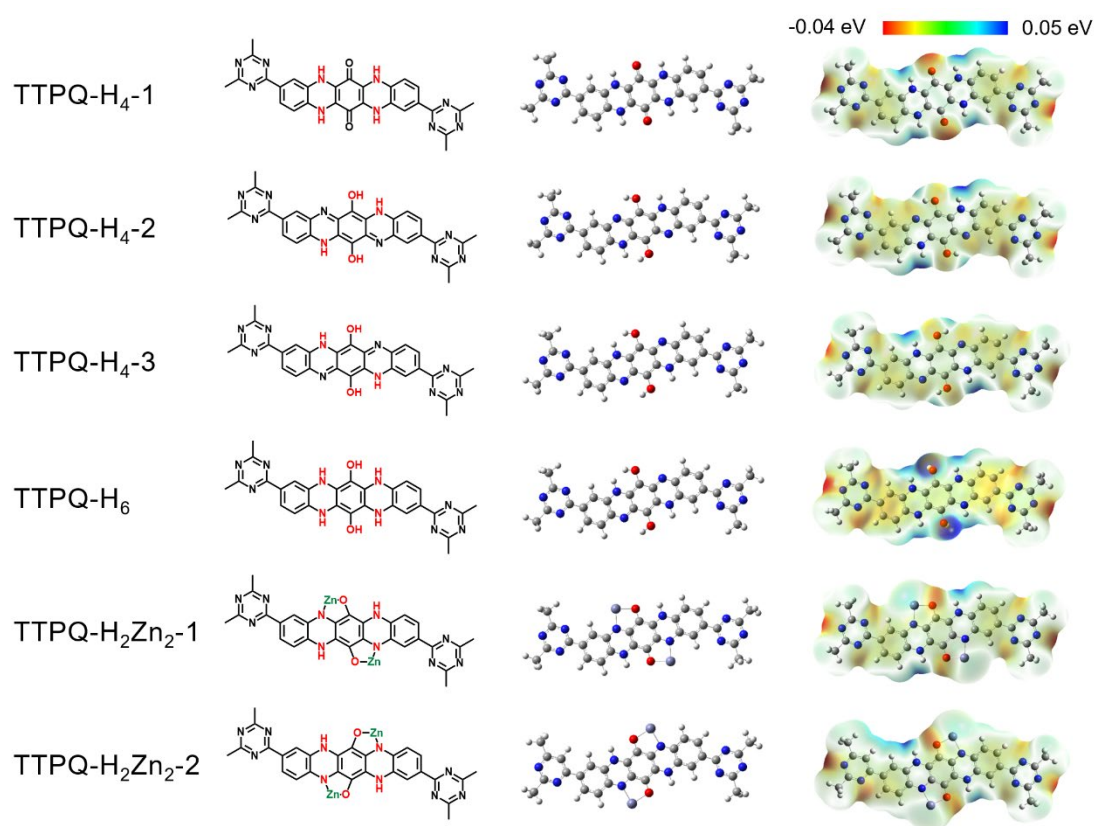


Figure S14. Possible geometric configurations of TTPQ molecules bonding H⁺ and (or) Zn²⁺ and the calculated molecular electrostatic potential (MESP).

References

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