

π - π stacking-regulated interfacial $\text{Zn}^{2+}/\text{H}^+$ co-storage in a fully conjugated organic cathode for long-life aqueous zinc-ion batteries

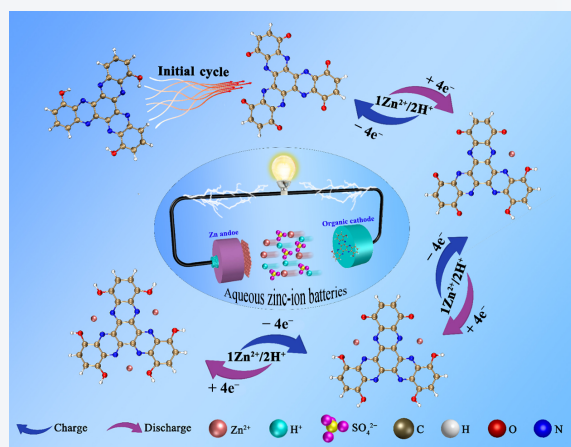
Qianqian Wang, Hongxi Li, Xuejiao Sun , Jiahao Huang, Dongmei Li , and Zhongzhen Tian 

School of Chemistry and Chemical Engineering, Inner Mongolia University of Science & Technology, Baotou 014010, China



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ABSTRACT: Regulating the molecular/electrolyte interface is crucial for improving aqueous zinc-ion batteries (AZIBs), particularly for organic cathodes that often suffer from dissolution, sluggish interfacial charge transfer, and insufficient cycling stability. Herein, inspired by the C=N zinc-storage sites in phenazine-based cathodes, a fully conjugated pyrazine-linked organic cathode, diquinoxalino[2,3-a:2',3'-c]phenazine-1,7,13-triol (DQPAT), was rationally designed to regulate molecular aggregation and cation-binding interfaces. The fully conjugated backbone integrated C=N sites and electrochemically activatable C=O groups within an extended π -conjugated framework, enabling multi-site $\text{Zn}^{2+}/\text{H}^+$ co-storage through reversible C=N/C=N and C=O/C=O redox couples. The extended π -conjugated framework promoted intramolecular electron delocalization, while ordered π - π stacking facilitated intermolecular charge transport and suppressed molecular dissolution at the electrode/electrolyte interface. Consequently, DQPAT delivered a high capacity of $561 \text{ mAh}\cdot\text{g}^{-1}$ at $0.05 \text{ A}\cdot\text{g}^{-1}$ and retained 90.3% capacity after 20,000 cycles at $10 \text{ A}\cdot\text{g}^{-1}$. Notably, the electrochemically oxidized state (o-DQPAT) reached its theoretical capacity under ultralow active-material loading, confirming nearly complete utilization of a twelve-electron redox process. *In situ/ex situ* analyses and theoretical calculations revealed a coupled $\text{Zn}^{2+}/\text{H}^+$ adsorption/desorption mechanism. This work demonstrated an interface-oriented molecular design strategy for developing high-capacity and long-life organic cathodes in AZIBs.



KEYWORDS: aqueous zinc-ion batteries, interfacial charge storage, π - π stacking, cation binding, organic cathode

1 Introduction

With the rapid development of renewable energy technologies and portable electronic devices, safe, low-cost, and environmentally benign energy-storage systems are urgently required [1]. Although lithium-ion batteries have been widely commercialized, their further development is constrained by uneven resource distribution, high cost, and safety concerns associated with organic electrolytes [2]. In this context, aqueous batteries based on multivalent metal ions have emerged as promising candidates for next-generation sustainable energy storage [3]. Among them,

aqueous zinc-ion batteries (AZIBs) have attracted considerable attention owing to the high theoretical capacity ($820 \text{ mAh}\cdot\text{g}^{-1}$), natural abundance, low cost, and intrinsic safety of zinc metal [4–6].

Cathode materials are critical to determining the capacity, rate capability, and cycling stability of AZIBs. Conventional inorganic cathodes, including manganese-based oxides [7], vanadium-based oxides [8], and Prussian blue analogs [9], generally deliver considerable capacities but often suffer from structural degradation, metal dissolution, and sluggish reaction kinetics [10, 11]. In contrast, organic cathode materials offer structural tunability [12], adjustable theoretical capacity [13], and environmental compatibility [14]. However, their practical application is strongly governed by interfacial processes, including molecular dissolution at the electrode/electrolyte interface, ion adsorption/desorption at redox-active sites, and interfacial charge transfer [15]. Therefore, developing organic cathodes with low solubility, high conductivity, accessible cation-binding interfaces, and multiple redox-active sites is essential for advancing aqueous organic zinc-ion batteries.

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✉ Address correspondence to Xuejiao Sun, sunxuejiao@163.com; Dongmei Li, 2019951@imust.edu.cn; Zhongzhen Tian, 2019952@imust.edu.cn

Recently, phenazine-based organic cathodes have received increasing attention because their nitrogen-containing conjugated frameworks and C=N active sites provide favorable interfacial binding sites for reversible Zn²⁺ storage. Previous studies have demonstrated that C=N bonds can act as Zn²⁺-binding sites, while reducing peripheral hydrophilic groups helps suppress molecular dissolution in aqueous electrolytes [16]. Moreover, molecular engineering strategies, such as extending π -conjugated frameworks [17], regulating electronic structures [18], and increasing the number of active sites [19], have effectively improved the capacity, rate performance, and cycling stability of phenazine derivatives. Nevertheless, simultaneously achieving high capacity, rapid interfacial kinetics, and long-term structural stability remains challenging.

Inspired by these advances, we designed a fully conjugated pyrazine-linked organic cathode material, diquinoxalino[2,3-a:2',3'-c]phenazine-1,7,13-triol (DQPAT), by focusing on the regulation of molecular aggregation and cation-binding interfaces. The design followed an interface-oriented logic. First, the fully conjugated pyrazine-linked backbone and extended π -conjugated framework promoted electron delocalization and interfacial charge transfer. Second, the C=N sites and electrochemically activatable C-O groups provided multiple redox-active sites for Zn²⁺/H⁺ binding. Third, the symmetric molecular configuration promoted ordered π - π stacking, which stabilized molecular packing and suppressed active-material dissolution at the electrode/electrolyte interface. Benefiting from these synergistic structural features, DQPAT delivered a high specific capacity of 561 mAh·g⁻¹ at 0.05 A·g⁻¹ and retained 90.3% of its capacity after 20,000 cycles at 10 A·g⁻¹. Furthermore, *in situ/ex situ* characterizations combined with theoretical calculations revealed that the electrochemically oxidized state (o-DQPAT) served as the effective charged state for a coupled Zn²⁺/H⁺ co-storage mechanism involving a twelve-electron redox process. These results demonstrated that regulating cation-organic interfacial interactions through molecular conjugation and π - π stacking can improve active-site utilization, reaction kinetics, and cycling stability in organic AZIB cathodes.

2 Experimental section

2.1 Materials

Hexaketocyclohexane octahydrate (HKCO, $\geq 99\%$) was purchased from Aladdin. 2,3-Diaminophenol (DA, $\geq 97\%$) was purchased from Tansoole. Acetic acid (analytical reagent (AR)) was purchased from China National Pharmaceutical Group Corporation. All reagents were used without further purification.

2.2 Synthesis of DQPAT

The synthesis of DQPAT was carried out via a modified procedure based on previously reported methods [20]. Typically, HKCO (0.18 g, 1 mmol) was dissolved in 50 mL acetic acid under uniform stirring. After that, DA (0.22 g, 3 mmol) was added to the above solution. The resultant suspension was heated under reflux for 12 h and then collected by vacuum filtration, accompanied by washing several times with hot acetic acid, ethanol, and water, respectively. Finally, the product (yield 70%) was purified by Soxhlet extraction with ethanol and dried under vacuum at 30 °C overnight.

2.3 Characterization

The morphology of the sample was characterized by scanning

electron microscope (SEM, Regulus 8230) and transmission electron microscopy (TEM, JEM2100). The compositions and chemical structures of the samples were characterized by X-ray photoelectron spectroscopy (XPS, Axis Ultra DLD Kratos AXIS SUPRA), X-ray diffraction (XRD, D2 PHASER), Fourier-transform infrared spectroscopy (FT-IR, Thermo Scientific Nicolet IS5, 400–4000 cm⁻¹), and ¹H nuclear magnetic resonance spectroscopy (¹H NMR, Bruker Avance 400). Ultraviolet–visible (UV–vis) spectra of samples were measured using a UV–vis diffuse reflection spectrometer (SPECORD 210). Thermogravimetric analysis (TGA) was performed on a thermogravimetric analyzer (STA449 F5) at a heating rate of 5 °C·min⁻¹. Specific surface areas were calculated using the Brunauer–Emmett–Teller (BET) method, and pore-size distributions were analyzed using the Barrett–Joyner–Halenda (BJH) model. Raman spectra were collected using a Raman spectrometer (HORIBA Jobin Yvon) with an excitation wavelength of 532 nm.

2.4 Electrochemical measurements

DQPAT, Ketjen black (KB), and polyvinylidene fluoride (PVDF) were mixed at a mass ratio of 6:3:1 and ground together, and the resulting mixture was dispersed in 2–3 mL of N-methyl-2-pyrrolidone (NMP). The mixture was then uniformly coated onto a carbon cloth current collector, and the DQPAT electrode was dried at 60 °C for 2 h to prepare the working electrode. The mass loading of the active material was 1–2 mg·cm⁻². High-loading electrodes with DQPAT mass loadings of 3–7 mg·cm⁻² were fabricated using the same procedure. CR2032 coin cells were assembled using 2 M ZnSO₄ as the electrolyte, glass fiber as the separator, and a metallic zinc sheet as the counter electrode. Cyclic voltammetry (CV) measurements were carried out over a voltage range of 0.2–1.6 V vs. Zn²⁺/Zn at scan rates of 0.1–0.5 mV·s⁻¹ using a CHI660E electrochemical workstation. Electrochemical impedance spectroscopy (EIS) measurements were carried out on a PARSTAT2273 electrochemical workstation with an amplitude of 5 mV over a frequency range of 10⁻¹–10⁵ Hz. The galvanostatic charge/discharge cycling and the galvanostatic intermittent titration technique (GITT) tests were carried out using the NEWARE (5 V/10 mA, Shenzhen, China) battery test system in an appropriate voltage range.

2.5 Density functional theory (DFT) calculation

Isochemical shielding surface (ICSS), localized orbital locator- π (LOL- π), average local ionization energy (ALIE), and interaction region indicator (IRI) analyses were performed using Multiwfn. The electrostatic potential (ESP) distributions and optimized molecular geometries were calculated using Becke's three-parameter exchange functional [21] combined with the Lee–Yang–Parr correlation functional (B3LYP) [22], Grimme's DFT-D3(BJ) [23] dispersion correction, and the def2-SVP basis set. The single-point energy was calculated for the optimized geometry with B3LYP/def2-TZVP using the solvation model based on density (SMD) with water as the solvent. All molecular geometries were optimized, and frequency calculations confirmed the absence of imaginary frequencies. The DFT calculations were performed using the Gaussian 16 program.

3 Results and discussion

3.1 Physicochemical properties

The molecular structure of the fully conjugated pyrazine-linked

DQPAT was first verified to confirm the designed conjugated backbone. DQPAT was synthesized via a condensation reaction between HKCO and DA (Fig. 1(a)). High-resolution mass spectrometry showed an observed mass-to-charge ratio (m/z) value of 433.1042, which matched the calculated value of 433.10 for $[C_{24}H_{12}N_6O_3 + H]^+$ (Fig. S1 in the Electronic Supplementary Material (ESM)). FT-IR spectroscopy further verified the formation of the target structure (Fig. 1(b)). The broad band at 3500–3200 cm^{-1} was assigned to O–H stretching and adsorbed H_2O , while the peak at 1229 cm^{-1} corresponded to C–O stretching. The newly formed peak at 1617 cm^{-1} was attributed to C=N stretching, confirming the formation of the pyrazine ring [24]. Raman spectroscopy was used to further probe the conjugated framework (Fig. S2 in the ESM). The peaks at 1372 and 1404 cm^{-1} were associated with C–OH-related vibrational modes, while the peak at 1516 cm^{-1} corresponded to the G-band-like vibration of the conjugated carbon framework [25]. XPS spectrum confirms the elemental composition and bonding states of DQPAT. The survey spectrum showed the presence of C, N, and O elements (Fig. S3 in the ESM), and the high-resolution C 1s, N 1s, and O 1s spectra

confirmed the characteristic signals of C=N, C–N, and C–O bonds (Fig. S4 in the ESM) [26], verifying the successful reaction between HKCO and DA [27]. In addition, the π – π^* satellite peak at 288.6 eV further supported the aromatic conjugated structure of DQPAT [28].

After confirming the molecular structure, the aggregation behavior and interface-stabilizing features of DQPAT were investigated. N_2 adsorption–desorption analysis showed an average pore diameter of 18.2 nm, confirming the mesoporous structure of DQPAT (Fig. S5 in the ESM). SEM images revealed a hierarchical flower-like micro/nanostructure assembled from one-dimensional rod-like units (Fig. 1(c)), which provided accessible ion-transport pathways, improved electrolyte wettability, and enhanced active-site accessibility. XRD patterns show distinct diffraction peaks (Fig. S6 in the ESM), suggesting a certain degree of molecular ordering in DQPAT [29]. This ordered structure was likely associated with the planar extended π -conjugated backbone and intermolecular π – π stacking interactions, which promoted molecular ordering. TEM images revealed locally layered aggregation but no clear lattice fringes (Fig. S7 in the ESM), suggesting ordered molecular

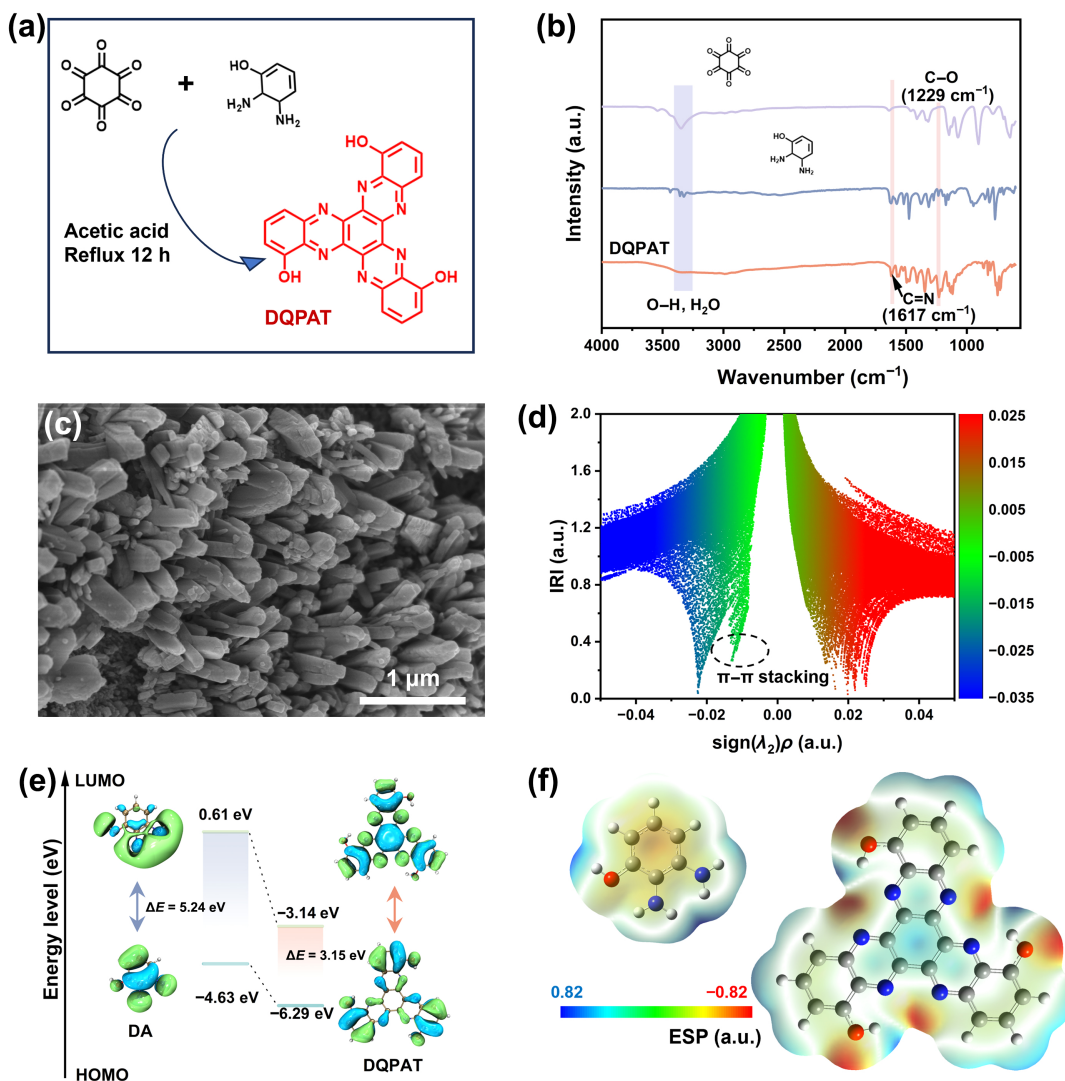


Figure 1 (a) Synthesis process of DQPAT. (b) The FT-IR spectra of DQPAT sample. (c) SEM images of DQPAT. (d) Plot of the density gradient decreasing with $\text{sign}(\lambda_2)\rho$. Here, λ_2 is the second eigenvalue of the Hessian matrix of the electron density, ρ is the electron density, and $\text{sign}(\lambda_2)\rho$ is the electron density multiplied by the sign of λ_2 . (e) LUMO/HOMO energy levels. (f) Simulated ESP distributions of DA and DQPAT.

aggregation in DQPAT. The IRI isosurface displayed multiple sharp peaks between -0.01 and 0 (Fig. 1(d)), confirming π - π interactions between DQPAT molecules [30]. Together, the XRD, TEM, and IRI results indicated that π - π interactions were considered to contribute to locally ordered molecular packing, which helped stabilize the electrode framework and facilitate charge/ion transport. Energy dispersive X-ray spectroscopy (EDS) mapping showed a uniform elemental distribution (Fig. S8 in the ESM). TGA showed that DQPAT possessed good thermal stability under both air and nitrogen atmospheres (Fig. S9 in the ESM), with only 12.6% mass loss at 400°C in air. Solubility tests and UV absorption spectra confirmed the low dissolution of DQPAT in the electrolyte, which was attributed to its extended π -conjugated framework and strong intermolecular π - π stacking interactions (Figs. S10 and S11 in the ESM) [31]. This suppressed dissolution further supported the improved cycling stability.

To further clarify the structure-performance relationship, DFT calculations were performed for DQPAT and DA. As shown in Fig. 1(e), DQPAT (-3.14 eV) showed a much lower lowest unoccupied molecular orbital (LUMO) energy level than DA (0.61 eV), indicating stronger electron affinity and electron-accepting ability [19]. Its highest occupied molecular orbital (HOMO)-LUMO gap (3.15 eV) was also smaller than that of DA

(5.24 eV), suggesting more favorable electronic transitions and charge transport [32]. Consistently, UV-vis diffuse reflectance spectra showed a narrower optical bandgap for DQPAT (2.31 eV) than DA (2.82 eV, Fig. S12 in the ESM). ESP analysis revealed electron-rich regions around the N and O atoms of DQPAT (Fig. 1(f)), which provided favorable sites for cation interaction and redox reactions [33]. These results suggested that the extended π -conjugated framework endowed DQPAT with a favorable electronic structure, improved charge-transport capability, and enhanced redox activity, thereby supporting its excellent electrochemical performance [34].

3.2 Electrochemical performance

On the basis of the above structural advantages, the electrochemical performance of DQPAT was evaluated as an organic cathode for AZIBs. AZIBs were assembled using DQPAT as the cathode, Zn foil as the anode, and 2 M ZnSO_4 as the electrolyte. No additional pre-activation treatment was applied to the DQPAT electrode before routine electrochemical testing. As shown in Fig. 2(a), DQPAT exhibited a higher redox current response and a larger CV area than DA at $0.5\text{ mV}\cdot\text{s}^{-1}$, indicating enhanced interfacial redox activity and charge-storage capability. At a current density of $0.05\text{ A}\cdot\text{g}^{-1}$, DQPAT delivered a high initial discharge capacity of

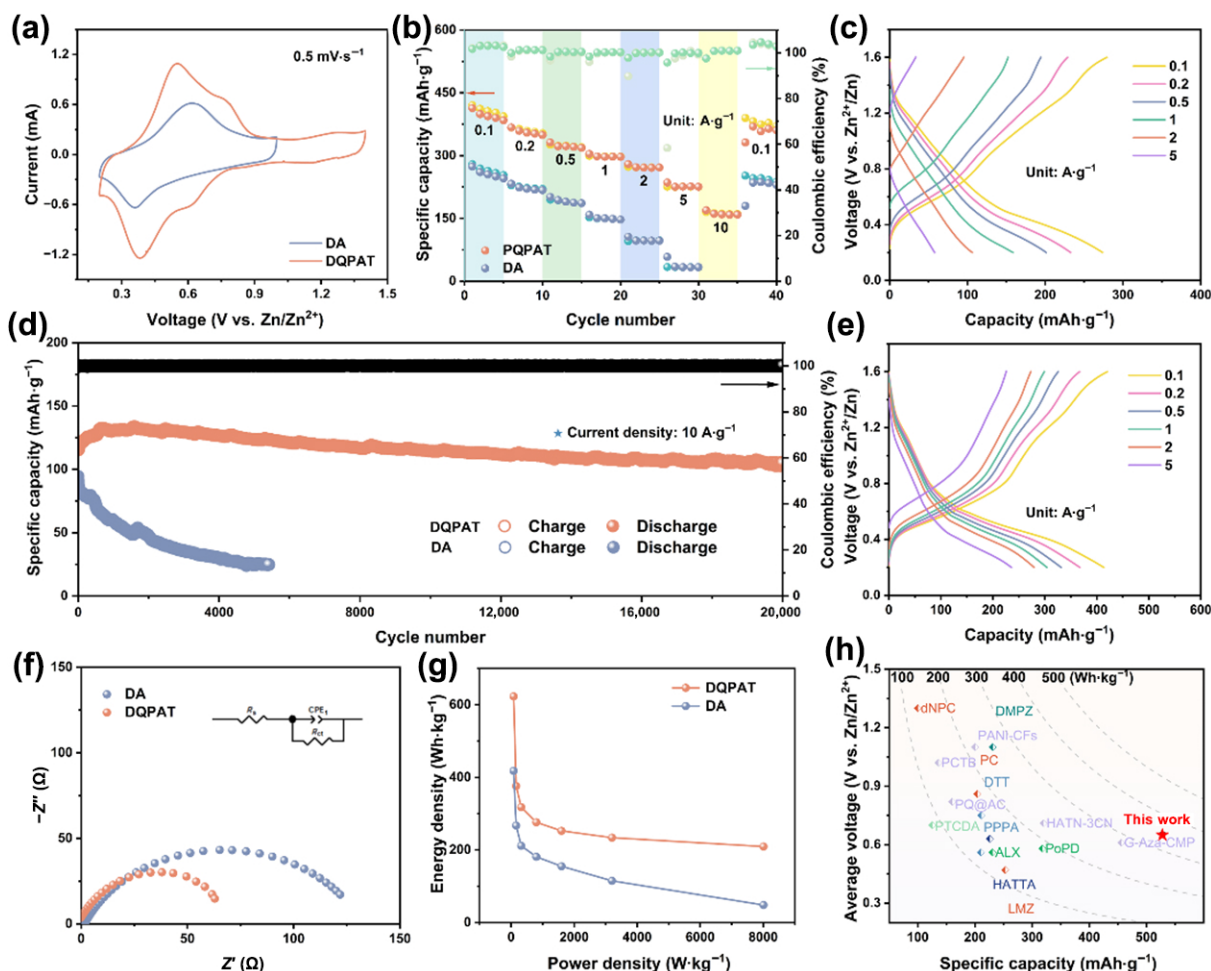


Figure 2 (a) CV curves of the DQPAT and DA cathodes at $0.5\text{ mV}\cdot\text{s}^{-1}$. (b) Rate capability of the DQPAT and DA cathodes. (c) GCD curves of the DA cathode. (d) Long-term cycling stability of the DQPAT and DA cathodes at $10\text{ A}\cdot\text{g}^{-1}$. (e) GCD curves of the DQPAT cathode. (f) EIS plots of the DQPAT and DA cathodes (inset represents the equivalent circuit). (g) Ragone plots of energy density and power density. (h) Comparison of the capacities and energy densities between the DQPAT electrode and recently reported organic cathodes.

561 $\text{mAh}\cdot\text{g}^{-1}$, which was markedly superior to that of DA (Fig. S13 in the ESM). The charge/discharge profiles of DQPAT remained well preserved with gradual capacity decay and no obvious voltage drop, whereas DA showed lower capacity and more pronounced fading (Fig. S14 in the ESM). The improved performance was attributed to the integrated effects of the extended π -conjugated framework, multiple redox-active sites, and ordered π -stacked molecular packing, which jointly facilitated charge transport, cation storage, and structural stability during cycling.

The rate and long-term cycling results further confirmed the effectiveness of this interface-oriented molecular design. As shown in Fig. 2(b), DQPAT delivered higher capacities than DA at all tested current densities, with discharge capacities of 413, 367, 331, 304, 280, 234, and 169 $\text{mAh}\cdot\text{g}^{-1}$ from 0.1 to 10 $\text{A}\cdot\text{g}^{-1}$. When the current density was returned to 0.1 $\text{A}\cdot\text{g}^{-1}$, the capacity recovered to its initial level, indicating good reversibility and consistent charge-storage behavior (Figs. 2(c) and 2(e)). At 10 $\text{A}\cdot\text{g}^{-1}$, DQPAT retained 105.48 $\text{mAh}\cdot\text{g}^{-1}$ after 20,000 cycles from an initial capacity of 116.86 $\text{mAh}\cdot\text{g}^{-1}$, corresponding to 90.3% capacity retention and nearly 100% Coulombic efficiency (Fig. 2(d)), whereas DA showed rapid fading after 5500 cycles. To exclude the contribution from conductive carbon, a KB/PVDF control electrode was tested under the same conditions. As shown in Fig. S15 in the ESM, after subtracting the contribution from KB, DQPAT still delivered high specific capacities of 400, 356, 321, 294, 271, 226, and 161 $\text{mAh}\cdot\text{g}^{-1}$ at current densities of 0.1, 0.2, 0.5, 1, 2, 5, and 10 $\text{A}\cdot\text{g}^{-1}$, respectively. The superior cycling stability was mainly attributed to the strong π - π stacking of DQPAT, which suppressed active-material dissolution and stabilized the electrode/electrolyte interface. EIS measurements were performed at open-circuit voltage before cycling, and the fitted charge transfer resistance (R_{ct}) values of DQPAT and DA were 82 and 130 Ω , respectively (Fig. 2(f)). The lower R_{ct} of DQPAT confirmed its faster interfacial charge-transfer behavior (Table S1 in the ESM). This improved charge-transfer

behavior arose from the highly conjugated π -electron system within the DQPAT molecular framework, which promoted electron delocalization and accelerated redox reaction kinetics [35]. Moreover, DQPAT achieved a maximum energy density of 623 $\text{Wh}\cdot\text{kg}^{-1}$ at 80 $\text{W}\cdot\text{kg}^{-1}$, exceeding that of DA under the same conditions (418 $\text{Wh}\cdot\text{kg}^{-1}$, Fig. 2(g)).

High-loading electrodes were typically limited by sluggish electron/ion transport and increased internal resistance, leading to inferior electrochemical performance [36]. Therefore, achieving high performance at high mass loading was crucial for practical AZIB applications and requires favorable conductivity and reaction kinetics [37]. Since DQPAT outperformed most reported organic cathodes under conventional loading (Table S2 in the ESM and Fig. 2(h)), its performance was further evaluated at higher mass loadings of 3–7 $\text{mg}\cdot\text{cm}^{-2}$. As shown in Fig. S16 in the ESM, DQPAT electrodes maintained good cycling stability at different mass loadings and current densities. Notably, at 7 $\text{mg}\cdot\text{cm}^{-2}$, DQPAT delivered 249 $\text{mAh}\cdot\text{g}^{-1}$ at 0.5 $\text{A}\cdot\text{g}^{-1}$ and retained 78% of its initial capacity after 100 cycles, corresponding to 195 $\text{mAh}\cdot\text{g}^{-1}$. At a mass loading of 7 $\text{mg}\cdot\text{cm}^{-2}$, the DQPAT electrode delivered an initial areal capacity of approximately 1.74 $\text{mAh}\cdot\text{cm}^{-2}$ and retained approximately 1.37 $\text{mAh}\cdot\text{cm}^{-2}$ after 100 cycles, demonstrating its favorable performance under high-loading conditions. These results indicated that the conjugation- and stacking-regulated interface design remained effective even under practical high-loading conditions.

3.3 Redox kinetics

As discussed above, the excellent electrochemical performance of DQPAT was closely related to its favorable interfacial charge-transfer kinetics. To verify this relationship, CV curves were recorded at scan rates of 0.1–0.5 $\text{mV}\cdot\text{s}^{-1}$ (Fig. 3(a)). The redox peaks showed only slight potential polarization, suggesting favorable redox kinetics and charge-transfer behavior. Further calculations were performed based on the relationship between the peak current

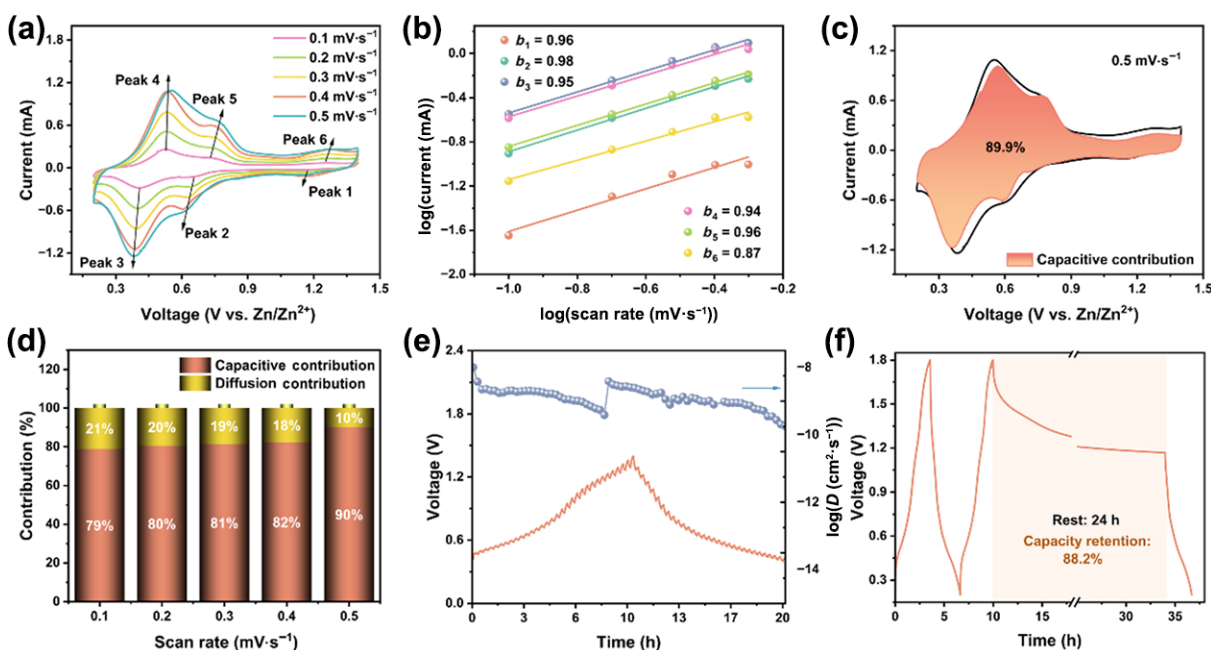


Figure 3 (a) CV curves of the Zn//DQPAT battery at different scan rates. (b) b values of DQPAT were calculated by linearly fitting the log current versus the log scan rate. (c) Capacitance contribution at different scan rates. (d) Current separation due to capacitance (yellow area) and diffusion (white area) for the Zn//DQPAT battery at a scan rate of 0.5 $\text{mV}\cdot\text{s}^{-1}$. (e) GITT of the Zn//DQPAT battery. (f) Self-discharge behavior of the Zn//DQPAT battery.

(i) and the scan rate (ν) according to Eq. (S4) in the ESM. The fitted kinetic parameter (b) values were 0.96, 0.98, 0.95, 0.94, 0.96, and 0.87, respectively (Fig. 3(b)), indicating that charge storage was mainly governed by surface-controlled capacitive behavior. This pseudocapacitive-dominated process was consistent with the accessible cation-binding interface and promoted fast $\text{Zn}^{2+}/\text{H}^+$ storage kinetics.

The capacitive and diffusion-controlled contributions were further quantified from CV curves at different scan rates. The capacitive contribution increased with scan rate and reached 89.9% at $0.5 \text{ mV}\cdot\text{s}^{-1}$ (Figs. 3(c) and 3(d)), explaining the excellent rate capability of DQPAT. GITT was then used to evaluate the apparent ion-transport kinetics in the DQPAT electrode, and the ion diffusion coefficients calculated from Eq. (S5) in the ESM were 10^{-8} – $10^{-10} \text{ cm}^2\cdot\text{s}^{-1}$ (Fig. 3(e)), indicating rapid ion transport within the electrode. In addition, the Zn//DQPAT battery retained 88.2% of its capacity after being charged and rested for 24 h (Fig. 3(f)), demonstrating good structural stability and low solubility, consistent with the UV-vis results. These kinetic results linked the molecular design to fast interfacial redox reactions and stable charge storage.

3.4 Charge storage mechanism

To elucidate the interfacial charge-storage mechanism of DQPAT, *in situ/ex situ* characterizations were performed at different charge/discharge states (Fig. 4(a)). *Ex situ* FT-IR spectra showed that the intensities of C=N and C=O decreased during discharge, while those of C–N and C–O increased, indicating cation insertion and binding at redox-active sites (Fig. 4(b)). In the O 1s XPS spectra, pristine DQPAT showed C–O (532.5 eV) and weak C=O (531.1 eV) signals (Fig. 4(c)), the latter suggesting slight oxidation [38]. Some C–OH groups in DQPAT could be oxidized to C=O groups through electron transfer, similar to the electrochemical oxidation behavior of phenols reported previously [39]. After discharge, the O 1s peaks shifted to lower binding energies, which was attributed to increased electron density around oxygen atoms induced by cation binding [40]. The mass spectrometry results after electrochemical activation also supported the formation of oxidized DQPAT-related species, providing additional evidence for the oxidation/activation process (Fig. S17 in the ESM). After charging, the C=O component became dominant, indicating the formation of the oxidized DQPAT state (o-DQPAT). To clarify the activation of C–OH groups, differential capacity (dQ/dV , where Q is the charge

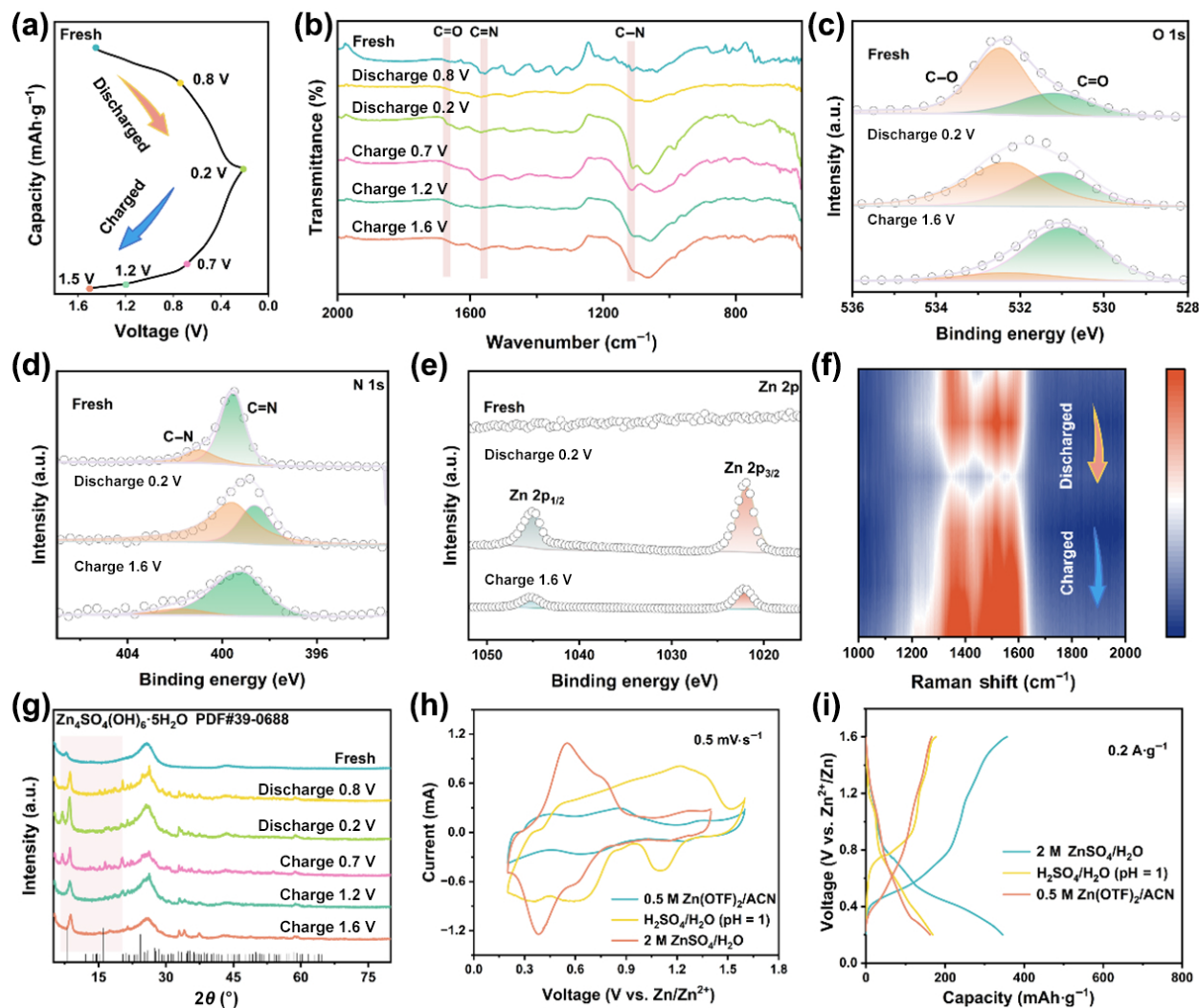


Figure 4 (a) Charge/discharge voltage profiles of DQPAT cathode. (b) *Ex situ* FT-IR of the DQPAT cathode during the charge/discharge processes. *Ex situ* high-resolution XPS spectra of (c) O 1s, (d) N 1s, and (e) Zn 2p for the DQPAT electrode at different charge/discharge states. (f) *In situ* Raman spectra of the DQPAT cathode during the charge/discharge processes. (g) *In situ* XRD patterns. (h) CV curves and (i) charge/discharge profiles.

capacity and V is the cell voltage) testing was performed using DA alone (Fig. S18 in the ESM). A strong oxidation peak appeared at 1.3 V during the first cycle and gradually weakened in the subsequent cycles, confirming an irreversible electrochemical activation process involving the conversion of C–OH groups into C=O groups. The initial oxidation of C–OH to C=O served as an *in situ* activation process, generating additional C=O/C–O redox sites and enhancing the subsequent reversible capacity; this process was also responsible for the slight fluctuations in the initial capacity and Coulombic efficiency. After this activation, o-DQPAT was regarded as the effective charged state, and the generated C=O/C–O redox couple participated reversibly in the subsequent charge-storage process. Similarly, the C=N/C–N signals in the N 1s spectra exhibited reversible changes comparable to those of C=O/C–O (Fig. 4(d)). After charging to 1.6 V, both C=N/C–N and C=O/C–O signals recovered, confirming the reversible evolution of C=N and C=O as cation-storage sites [41, 42]. The reversible variation of Zn 2p signals further confirmed reversible Zn storage in DQPAT (Fig. 4(e)) [43].

In situ Raman spectroscopy was used to evaluate the structural stability of DQPAT (Fig. 4(f)). During discharge, the increased intensity ratio (I_D/I_G , where I_D represents D-band intensity and I_G represents G-band intensity) indicated reduced structural ordering after $\text{Zn}^{2+}/\text{H}^+$ insertion (Fig. S19 in the ESM). Upon charging, the I_D/I_G ratio recovered to its initial value, indicating restoration of the conjugated framework. The reversible change in the I_D/I_G ratio suggested reversible modulation of the local conjugated structure during $\text{Zn}^{2+}/\text{H}^+$ insertion/extraction [44]. These reversible structural changes demonstrated the robust electrochemical stability of DQPAT during cycling. The optical photographs and UV–vis spectra of the electrolytes collected at different charge/discharge states showed no obvious color change or characteristic absorption peaks (Fig. S20 in the ESM), indicating negligible dissolution of DQPAT during cycling and further confirming its structural stability.

SEM-EDS was performed to track the elemental evolution of DQPAT at different charge/discharge states (Fig. S21 in the ESM). Only C, N, and O were detected in the pristine electrode, whereas Zn and S signals appeared after full discharge and weakened after charging, confirming reversible Zn^{2+} storage, consistent with the XPS results. Together with the pH monitoring and XRD results, the reversible S signal was associated with the reversible formation/decomposition of basic zinc sulfate, supporting the involvement of proton storage [45]. To further verify H^+ involvement, the pH near the DQPAT cathode was monitored *in situ* (Fig. S22 in the ESM). The pH increased during discharge and recovered during charge, supporting reversible proton insertion/extraction. *In situ* XRD patterns further confirm the formation of $\text{Zn}_4\text{SO}_4(\text{OH})_6 \cdot 5\text{H}_2\text{O}$ during discharge, which almost disappeared after charging (Fig. 4(g)), consistent with the SEM results and indicating reversible proton storage [46]. These results demonstrated a synergistic $\text{Zn}^{2+}/\text{H}^+$ storage mechanism in DQPAT. CV measurements in different electrolytes were further conducted to distinguish the Zn^{2+} and H^+ contributions. DQPAT showed clear redox peaks in 0.5 M $\text{Zn}(\text{OTF})_2/\text{ACN}$ (OTF: trifluoromethanesulfonate and ACN: acetonitrile), $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$, and 2 M $\text{ZnSO}_4/\text{H}_2\text{O}$ electrolytes, while the largest CV area was obtained in 2 M $\text{ZnSO}_4/\text{H}_2\text{O}$ (Fig. 4(h)), confirming the synergistic contribution of Zn^{2+} and H^+ . To exclude the possible influence of Zn^{2+} generated from Zn corrosion in H_2SO_4 electrolyte, a Zn-free

three-electrode CV measurement was further performed using Pt as the counter electrode (Fig. S23 in the ESM). The DQPAT electrode still exhibited clear redox responses in H_2SO_4 , confirming that H^+ participation was not caused by Zn^{2+} generated from the Zn anode. The corresponding dQ/dV profiles further indicated that both Zn^{2+} and H^+ participated in the three redox steps (Fig. S24 in the ESM). The charge–discharge curves obtained in Zn^{2+} -dominated and H^+ -dominated electrolytes suggested that both Zn^{2+} and H^+ were involved in the charge-storage process (Fig. 4(i)). To estimate the capacity contributions of Zn^{2+} and H^+ , inductively coupled plasma optical emission spectroscopy (ICP-OES) was performed on the discharged DQPAT electrode to analyze the Zn and S contents. Based on the quantitative analysis, the estimated capacity contributions of Zn^{2+} and H^+ were 43.4% and 56.6%, respectively (see the ESM for details). Thus, the experimental mechanism analysis connected the activated C=N/C=O redox sites with the coupled $\text{Zn}^{2+}/\text{H}^+$ interfacial storage process.

3.5 Theoretical calculation

As discussed above, the *in situ* and *ex situ* characterization results confirmed the n-type interfacial storage mechanism of DQPAT, involving reversible $\text{Zn}^{2+}/\text{H}^+$ co-storage during discharge/charge. Considering that pristine DQPAT was electrochemically activated to o-DQPAT during the initial charging process, o-DQPAT was regarded as the effective charged state for the subsequent reversible discharge reaction. To quantify the electron-transfer number in each step, DQPAT//Zn batteries were assembled under an ultralow current density and low active-material loading. Based on the molecular weight of o-DQPAT, the theoretical capacity for a twelve-electron transfer process was calculated to be $679 \text{ mAh}\cdot\text{g}^{-1}$. Under ultralow active-material loading, the activated o-DQPAT cathode reached this theoretical capacity, confirming nearly complete twelve-electron utilization. Analysis of the dQ/dV and galvanostatic charge–discharge (GCD) curves revealed three consecutive reduction processes during discharge (Fig. S25 in the ESM). These processes contributed approximately one-third of the total discharge capacity each, corresponding to three successive four-electron transfer steps and a total twelve-electron reaction. The well-resolved redox peaks indicated that multiple redox-active sites in o-DQPAT were effectively activated and participated in reversible cation storage.

The n-type storage mechanism was further evaluated by calculating the Gibbs free energy changes (ΔG) associated with cation binding during discharge [47]. For clarity, the discharged products derived from o-DQPAT were denoted as $\text{DQPAT}_x\text{H}_y\text{Zn}_z$, where x and y represent the numbers of bound H^+ and Zn^{2+} , respectively. These species were optimized to identify the energetically favorable intermediates and final product. ICSSzz analysis showed a pronounced shielding region around the C=N bonds, indicating enhanced electron delocalization and structural stability (Fig. 5(a)). The LOL- π map further confirmed the highly conjugated framework and efficient π -electron delocalization of DQPAT (Fig. 5(b)), which favored rapid electron transfer [48].

ALIE analysis identified the C=N sites as the most reactive regions, as they corresponded to the minimum values on the ALIE surface (Fig. 5(c)). These sites therefore served as preferred $\text{Zn}^{2+}/\text{H}^+$ binding sites [49]. Based on these results, Fig. 5(d) summarizes the optimized stepwise $\text{Zn}^{2+}/\text{H}^+$ co-storage pathway during the multistep redox process. As shown in Fig. 5(e), the calculated ΔG values for cation binding were negative throughout discharge,

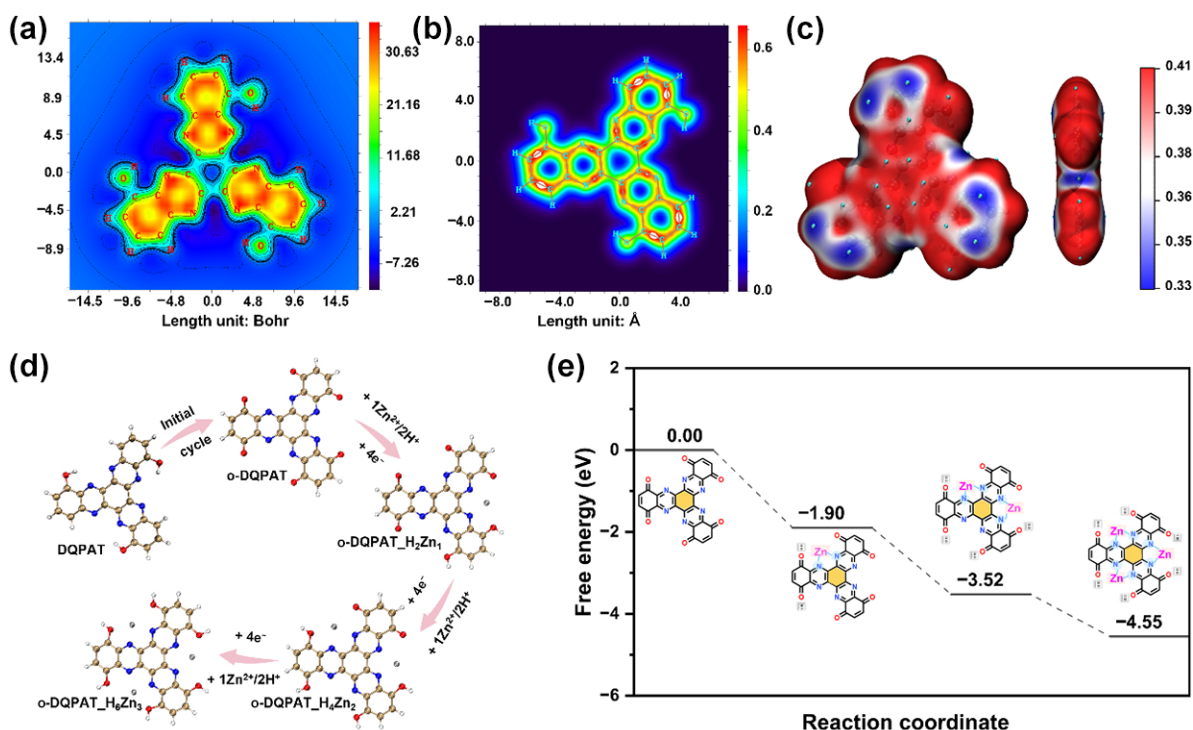
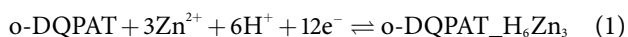


Figure 5 (a) Color-filled contour map of ICSSzz in the slice plane perpendicular to the symmetry plane of the DQPAT molecule. (b) LOL-π color-filled map. (c) ALIE analysis on the molecular surface of DQPAT. (d) Zn²⁺/H⁺ synergistic storage pathway obtained from simulations of DQPAT in the redox process. (e) Calculated Gibbs free energy diagrams of o-DQPAT during stepwise Zn²⁺/H⁺ binding.

confirming the thermodynamic feasibility of the process [50]. Starting from o-DQPAT, the discharged intermediates o-DQPAT_H₂Zn₁, o-DQPAT_H₄Zn₂, and o-DQPAT_H₆Zn₃ were successively formed with increasing electron transfer, with Δ*G* values of −1.90, −3.52, and −4.55 eV, respectively. The continuous decrease in free energy indicated stable Zn²⁺/H⁺ binding and efficient utilization of the active sites, with o-DQPAT_H₆Zn₃ being the most favorable discharged product. The overall discharge process can be expressed as



Therefore, o-DQPAT underwent an n-type redox reaction with a Zn²⁺/H⁺ co-storage mechanism. The extended π-conjugated framework enabled rapid intramolecular electron delocalization, while the planar configuration and π–π-stacked molecular packing stabilized cation binding and interfacial charge transfer. Together with the twelve-electron redox reaction, these features accounted for the high-capacity and long-life electrochemical performance of DQPAT.

4 Conclusions

In this work, a fully conjugated pyrazine-linked organic cathode material, DQPAT, was designed from an interface-oriented molecular perspective for high-performance AZIBs. The molecular design linked three key functions into one framework: The extended π-conjugated backbone promoted electron delocalization and charge transport; the C=N sites and electrochemically activatable C–O groups provided multiple cation-binding redox sites; and the ordered π–π stacking interactions stabilized molecular packing, suppressed active-material dissolution, and improved the electrode/electrolyte interface. Benefiting from these synergistic

advantages, DQPAT delivered a high specific capacity of 561 mAh·g^{−1} at low current density and stable cycling over 20,000 cycles at high current density. More importantly, after electrochemical activation to o-DQPAT, the cathode reached the theoretical capacity associated with a twelve-electron transfer under ultralow active-material loading. Kinetic and mechanistic analyses revealed fast pseudocapacitive-dominated behavior, favorable ion transport, and a synergistic Zn²⁺/H⁺ co-storage mechanism involving a twelve-electron redox process. This work provided an effective strategy for regulating cation–organic interfacial interactions through molecular conjugation and π–π stacking, offering guidance for developing high-capacity and long-life organic cathodes for AZIBs.

Electronic Supplementary Material: Supplementary material (further details on the calculation of theoretical capacity, solid-state UV–vis spectroscopy measurements, TEM measurements, and Raman spectroscopy measurements) is available in the online version of this article at <https://doi.org/10.26599/NR.2026.94909070>.

Data availability

All data needed to support the conclusions in the paper are presented in the manuscript and the Electronic Supplementary Material. Additional data related to this paper may be requested from the corresponding author upon request.

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Declaration of competing interest

All the contributing authors report no conflict of interests in this work.

Author contribution statement

Q. Q. W.: Data curation, writing – original draft, writing – review & editing. H. X. L.: Methodology, validation, formal analysis. X. J. S.: Data curation. J. H. H.: Software. D. M. L.: Funding acquisition, supervision. Z. Z. T.: Funding acquisition, project administration. All the authors have approved the final manuscript.

Use of AI statement

None.

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