

ORIGINAL ARTICLE OPEN ACCESS

A Topology-Guided Design Strategy for Polymerized Naphthoquinone Cathodes in Rechargeable Aluminium-Ion Batteries

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Received: 10 October 2025 | **Revised:** 4 February 2026 | **Accepted:** 5 February 2026

Keywords: naphthoquinone | organic cathode | rechargeable aluminium-ion batteries | topology-guided design

ABSTRACT

Rechargeable aluminium-ion batteries (RAIBs) are promising candidates for sustainable energy storage owing to their low cost, safety, and resource abundance. However, the lack of durable cathode materials restricts their development. Here, we propose a topology-guided design strategy by synthesizing three thioether-bridged naphthoquinone polymers from 1,4-naphthoquinone. Structural characterization combined with density functional theory calculations confirms that polymerization reduces crystallinity, enhances thermal stability, and extends π -conjugation, with the para-topology providing the most favorable configuration and strongest AlCl_2^+ coordination. The nearly planar para-naphthoquinone polymer (*p*-PNQ) exhibits an extended conjugated backbone, reduced bandgap, and uniform electrostatic potential distribution. Electrochemical tests reveal that *p*-PNQ delivers 146 mAh g⁻¹ initially at 0.1 A g⁻¹ and a 97.2% retention after 500 cycles, surpassing pristine 1,4-NQ and *o*/*m*-isomers. Ex situ analyses confirm that redox activity originates from reversible coordination between carbonyl groups and AlCl_2^+ species. This study establishes molecular topology as a key parameter for designing organic cathodes, and demonstrates that topology-controlled strategies enable durable, high-performance cathodes for energy storage in RAIBs.

1 | Introduction

With the increasing demand for sustainable energy storage systems, rechargeable aluminium-ion batteries (RAIBs) have emerged as a promising alternative to traditional lithium-ion batteries due to their high safety, low cost, and abundant aluminum resources [1–4]. However, the development of RAIBs is hindered by the limited choice of cathode materials, particularly those capable of efficiently storing multivalent Al^{3+} ions [5–8]. Organic electrode materials, especially quinone-based compounds, have garnered significant attention owing to their

structural diversity, tunable redox properties, and environmental friendliness [9, 10]. Among these, naphthoquinone (NQ) derivatives exhibit high theoretical capacities and reversible redox reactions, making them attractive candidates for RAIBs [11, 12].

1,4-Naphthoquinone (1,4-NQ) is a widely studied precursor due to its high electrochemical activity and straightforward synthesis [13]. However, its symmetric structure and solubility in electrolytes often lead to rapid capacity decay and poor cycling stability [14]. To address these challenges, molecular engineering

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strategies, such as polymerization and spatial structure design, have been employed to enhance the performance of polymerized materials [15–17]. Recent studies have demonstrated that modifying the spatial configuration of NQ derivatives can significantly influence their electrochemical properties, including solubility, redox kinetics, and ion storage capacity [18]. For instance, thioether-linked NQ isomers with tunable spatial structures have shown remarkable improvements in specific capacity and cycling stability in aqueous zinc-ion batteries, highlighting the importance of structural design in optimizing electrode materials [19]. Yet, in the context of RAIB cathodes, most existing approaches focus on chemical modification to suppress dissolution, whereas the critical role of molecular topology—that is, the relative position of C=O on the aromatic backbone—has rarely been systematically investigated [20–22]. Similar coordination-driven redox behaviors have also been emphasized in recent organic–metal systems [23].

Inspired by these advancements, this study focuses on synthesizing three NQ-based polymers, ortho-polymerized naphthoquinone (*o*-PNQ), meta-polymerized naphthoquinone (*m*-PNQ), and para-polymerized naphthoquinone (*p*-PNQ), using 1,4-NQ as the precursor. By introducing sulfur bridges at different positions (ortho, meta, and para) on the benzene ring, we aim to tailor the spatial structures of these polymers to achieve enhanced electrochemical performance in RAIBs. The asymmetric and nonplanar configurations of *o*-PNQ and *m*-PNQ are expected to provide independent redox-active sites and reduce solubility, while the centrosymmetric structure of *p*-PNQ may offer superior electron transfer kinetics and structural stability. This design enables us to disentangle how substitution topology dictates π -conjugation, molecular planarity, steric hindrance, and ultimately ion storage capability. Unlike conventional polymerization that primarily addresses solubility, our approach directly leverages spatial configuration as a design parameter.

Among the three, the para-linked *p*-PNQ exhibits a nearly planar and extended π -conjugated backbone, reduced bandgap, and more uniform electrostatic potential distribution, which collectively facilitate faster charge transport and stronger ion coordination. By systematically comparing *o*-, *m*-, and *p*-PNQ, this study not only clarifies the structure–property relationship of naphthoquinone polymers but also establishes para-topology as an effective paradigm for designing durable organic cathodes in RAIBs.

2 | Results and Discussion

2.1 | Design Strategy and Characterization of 1,4-NQ and PNQ Samples

Figure 1 provides a comprehensive overview of the molecular engineering strategy applied to 1,4-naphthoquinone (1,4-NQ) derivatives for use as cathode materials in RAIBs. The design involves covalently linking two NQ units via thioether bonds to a benzene ring at different substitution positions, ortho (*o*-PNQ), meta (*m*-PNQ), and para (*p*-PNQ), to systematically modulate the molecular geometry, steric hindrance, and π – π stacking

behavior. The synthetic route, as shown in the upper panel, is a one-step nucleophilic substitution between 1,4-NQ and benzene dithiols, a strategy validated in previous literature for its efficiency and structural precision. Density functional theory (DFT, theoretical calculations carried out in the Gaussian 09 program package) of the molecular electrostatic potential (MESP) reveal significant differences in charge distribution among the 1,4-NQ and three PNQ isomers [24]. Notably, *p*-PNQ displays the most uniform negative potential around C=O groups, consistent with stronger ion (i.e., AlCl_2^+) coordination and a smoother electrostatic landscape for ion migration; *o*-PNQ shows localized potential and adjacent-thioether crowding that can hinder ion approach; *m*-PNQ exhibits intermediate features, reflecting a balance between steric demand and charge delocalization. The synthesis, characterization, and electrochemical testing procedures followed established protocols reported in previous studies. All products were obtained in yields above 85% (see Supporting Information for details).

Scanning electron microscopy (SEM) images reveal that the three PNQ isomers exhibit distinct particle morphologies. Although these differences do not alone establish a direct topology–morphology causation, they provide useful qualitative insight into how molecular configuration may influence aggregation and assembly behavior. Although pristine 1,4-NQ forms smooth, platelet-like crystals with irregular macroporosity, the polymeric PNQ derivatives display distinct morphological architectures: *o*-PNQ predominantly appears as porous microspheres, *m*-PNQ as layered flakes, and *p*-PNQ as interconnected nanosheet-like assemblies. These morphologies likely arise from differences in intermolecular interactions and packing tendencies among the isomers, although additional studies would be required to unambiguously determine the structural origin of these features. The nanosheet-like assemblies of *p*-PNQ provide a more open and accessible architecture compared with the other isomers. Although morphology alone cannot determine electrochemical behavior, such features are generally considered favorable for electrolyte wetting and ion accessibility and may contribute, together with the molecular-scale electronic advantages, to the improved performance observed experimentally [25]. Additional SEM images at higher magnification for the PNQ isomers are shown in Supporting Information S1: Figure S1.

Structurally, *p*-PNQ forms an extended π -conjugated framework composed of five aromatic rings. This architecture enhances electron delocalization and increases the density of redox-active sites. This extended framework arises from para-substitution and the associated linear geometry, which facilitates efficient π – π stacking, enhances charge carrier mobility, and stabilizes structural integrity upon repeated Al-based ion insertion/extraction.

Figure 2A shows the DFT-optimized geometries and frontier orbital energy levels of 1,4-NQ and the three PNQ isomers. Compared with 1,4-NQ (HOMO–LUMO gap of 4.01 eV), all PNQ derivatives exhibit substantially narrowed gaps (2.99–3.13 eV), indicating enhanced electronic delocalization after thioether linking. Notably, although the HOMO–LUMO gaps of these three are close, their absolute LUMO levels differ in a clear order (*o*-PNQ: -3.08 eV; *m*-PNQ: -3.27 eV; *p*-PNQ: -3.34 eV). The

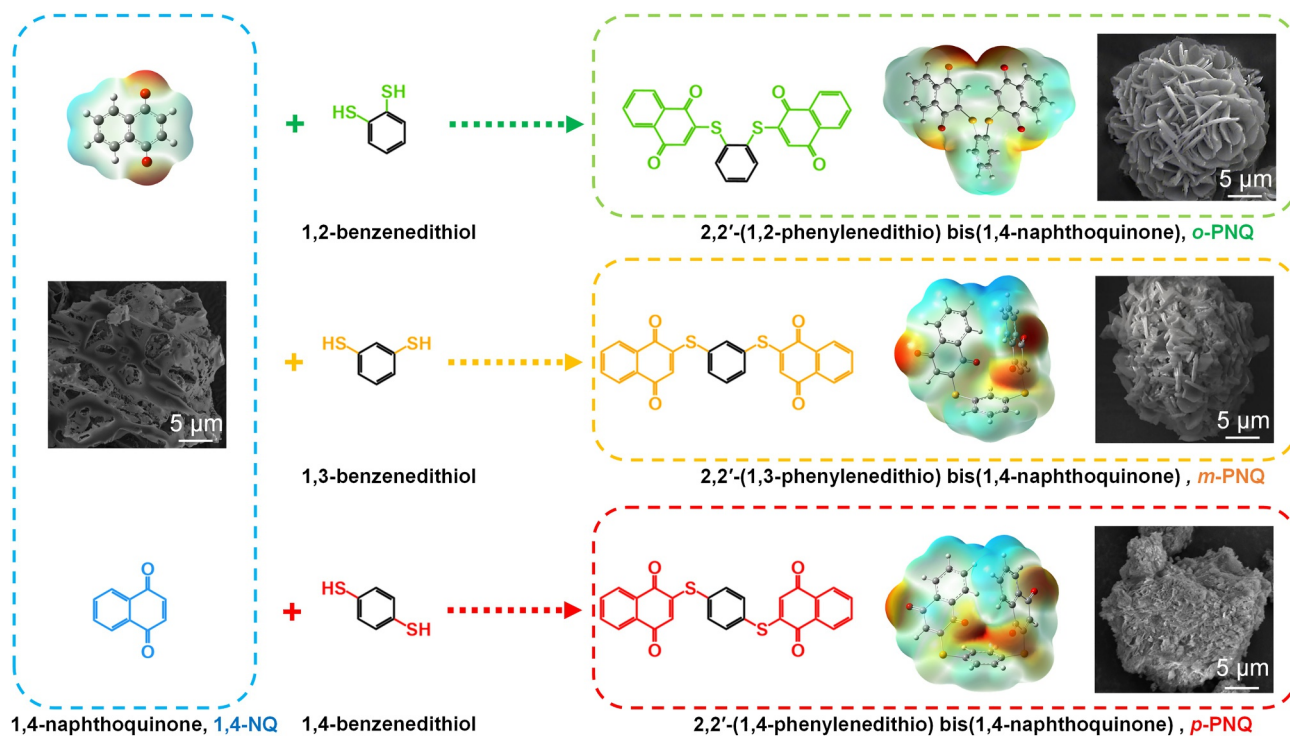


FIGURE 1 | Molecular design strategy, synthetic route, DFT calculation of MESP distribution and SEM images of 1,4-NQ, *o*-PNQ, *m*-PNQ and *p*-PNQ.

progressively lowered LUMO suggests an increased electron-accepting tendency for *p*-PNQ, which is beneficial for facilitating the reduction of carbonyl groups and the subsequent co-ordination with chloroaluminate species. Therefore, the topology-dependent electrochemical hierarchy is attributed primarily to the combined effects of frontier-orbital energetics and carbonyl accessibility/coordination thermodynamics, rather than only to the small difference in bandgap magnitude alone.

As shown in Figure 2B, *p*-PNQ exhibits a strongly co-operative two-step AlCl_2^+ binding process (-106.91 and -165.41 kcalmol $^{-1}$), consistent with a bidentate coordination mechanism involving both carbonyl groups. Although only *p*-PNQ is explicitly evaluated in Figure 2B, the large and co-operative binding energies support the interpretation that topology-controlled steric accessibility—rather than the HOMO–LUMO gap—is the primary contributor to its favorable redox kinetics. These topology-dependent structural and electronic features form the mechanistic basis of the improved electrochemical performance observed for *p*-PNQ.

Overall, the para-linked topology endows *p*-PNQ with a nearly planar and extended π -framework that minimizes steric congestion around the carbonyl groups and enables more favorable AlCl_2^+ coordination. These topology-governed structural advantages—not the small differences in the HOMO–LUMO gaps—play the dominant role in determining the redox kinetics and capacity. Furthermore, as shown in the electrode-immersion experiment (Figure 4G), the *p*-PNQ electrode exhibits markedly suppressed dissolution compared to pristine 1,4-NQ, providing additional stability during long-term cycling. Together, these features explain the performance hierarchy observed experimentally (*p*-PNQ > *m*-PNQ > *o*-PNQ).

Consistent with these structural and morphological advantages, electrochemical tests (shown in Figure 4) reveal that *p*-PNQ outperforms *o*-PNQ and *m*-PNQ in specific capacity, cycling stability, and rate performance. These results underscore the critical role of rational molecular design—particularly symmetry—in governing the electrochemical behavior of organic cathode materials. Therefore, *p*-PNQ exemplifies an effective design paradigm wherein para-linked π -conjugated architectures simultaneously balance redox activity, structural robustness, and ion transport efficiency.

The structural and compositional characterization differences between 1,4-NQ and *p*-PNQ were comprehensively investigated through multiple analytical techniques. X-ray diffraction (XRD) analysis in Figure 3A revealed distinct crystalline characteristics, with 1,4-NQ exhibiting prominent peaks at 13.6° , 25.1° , and 27.6° whereas *p*-PNQ showed characteristic peaks at 11.1° , 13.6° , and 23.8° . All PNQ isomers display broadened peaks at lower angles, confirming successful synthesis and indicating reduced crystallinity with partially amorphous features. Such structural disorder is expected to improve ion diffusion [26, 27]. Fourier-transform infrared spectroscopy (FTIR) in Figure 3B demonstrated significant structural modifications in *p*-PNQ through the appearance of new absorption bands at 1560 and 701 cm^{-1} , attributed to additional C=O functional groups and C-H out-of-plane bending vibrations. These features are observed consistently in all PNQs, suggesting that the bonding environment is similar across the isomers. Thermogravimetric analysis (TGA) in Figure 3C highlighted enhanced thermal stability in all PNQ derivatives compared to NQ. Although minor differences exist, *p*-PNQ exhibits the highest onset temperature, followed by *m*-PNQ and *o*-PNQ, exhibiting decomposition onset at 154°C with less than 50% mass loss at 600°C , compared to

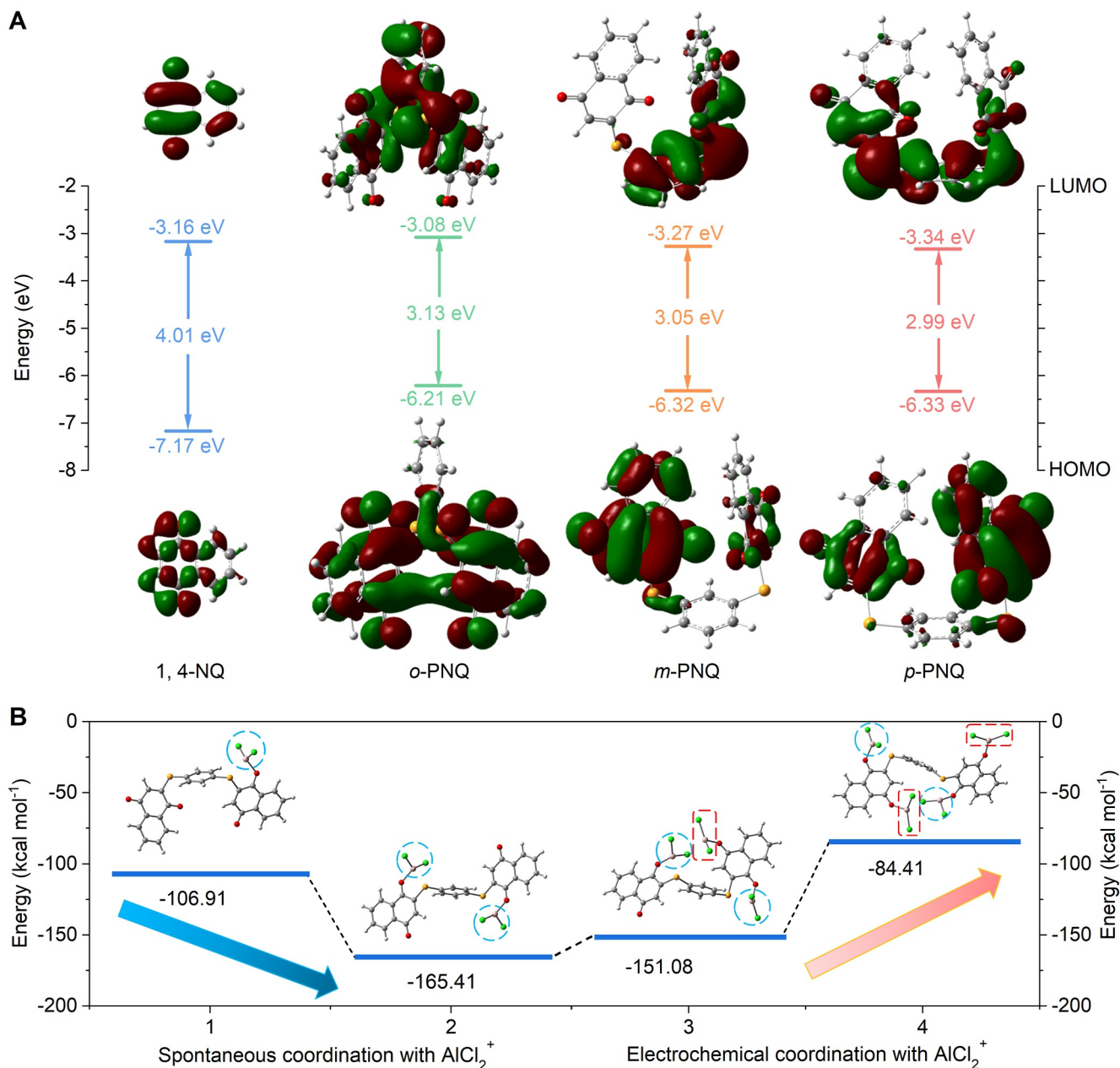


FIGURE 2 | DFT calculation of 4 samples. (A) Optimized structure and calculated molecular orbital energy levels of 1,4-NQ, o-PNQ, m-PNQ and p-PNQ; (B) binding energy for p-PNQ with the most stable structure at each AlCl_2^+ complexation stage.

1,4-NQ which showed substantial mass loss beginning at 113°C, reflecting subtle topology-dependent stability differences. Such stability is beneficial during electrode processing steps—including slurry drying and vacuum sealing—which typically involve a high temperature. In addition, a thermally more stable backbone helps suppress heat-induced structural degradation during long-term cycling, contributing to the superior capacity retention of the p-PNQ electrode. ¹H NMR spectroscopy further revealed structural changes in the aromatic region (6–8 ppm), where p-PNQ not only maintained characteristic peaks at 7.7 and 8.1 ppm with increased intensity but also displayed new resonances at 7.3 and 6.2 ppm, indicating the formation of additional benzene ring structures. Raman spectroscopy in Figure 3E further confirmed structural modifications, with attenuation of

the near 1642 cm⁻¹ band and the emergence of a new band near 1574 cm⁻¹ across all PNQ derivatives, reflecting altered quinone vibrations. Besides, liquid chromatography-mass spectrometry (LC-MS) in Figure 3F conclusively verified the molecular differences, with a diagnostic peak at *m/z* 158 confirming 1,4-NQ and a prominent signal cluster at *m/z* 455 matching the theoretical molecular mass of all PNQ isomers. Collectively, these results demonstrate the successful preparation of PNQ derivatives with reduced crystallinity, improved thermal stability, and expanded conjugation frameworks. Importantly, although all isomers share these structural advantages, the degree of stabilization varies with substitution topology, with p-PNQ showing the most favorable combination, in line with its superior electrochemical performance.

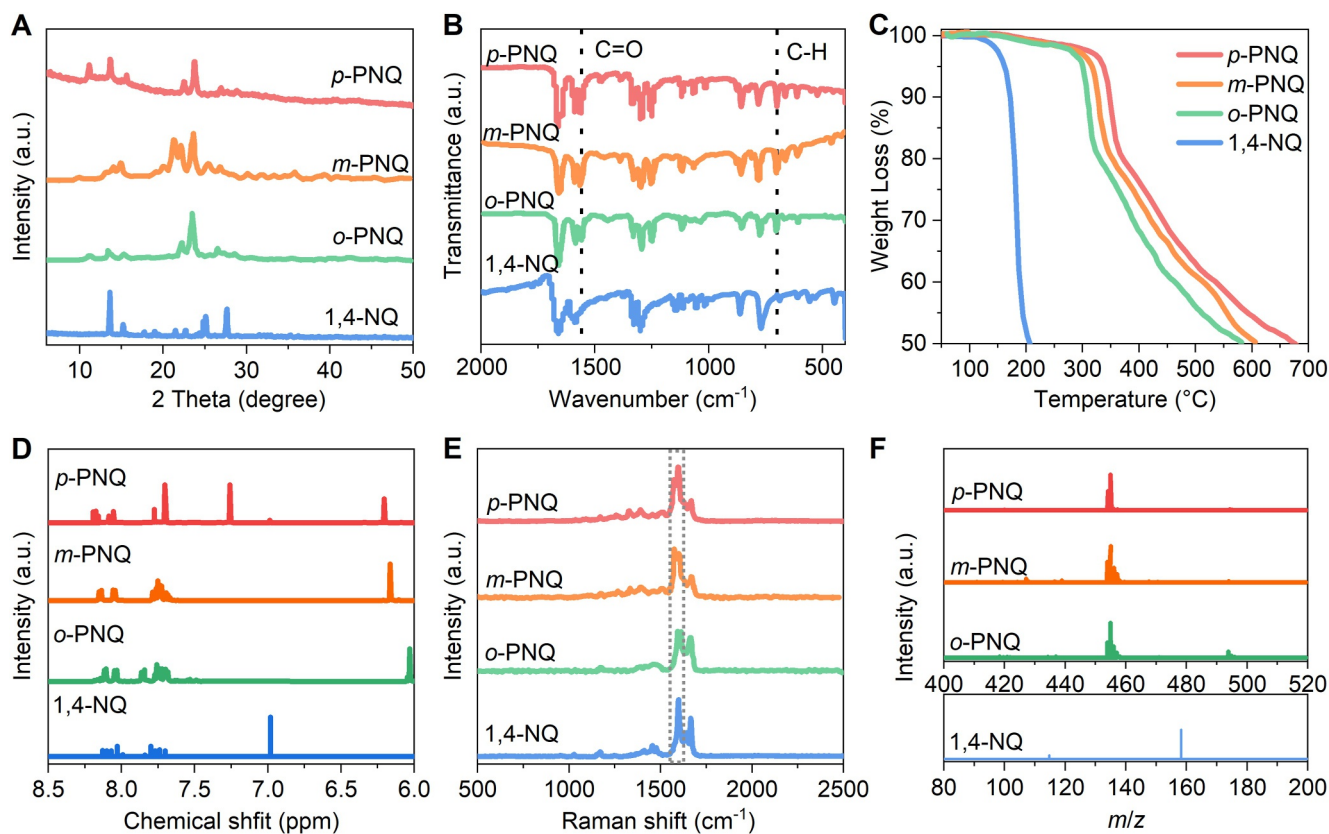


FIGURE 3 | Structure characterization results of 1,4-NQ, *o*-PNQ, *m*-PNQ and *p*-PNQ: (A) XRD patterns; (B) FTIR spectra; (C) TG curves (N_2 , $10^\circ C\ min^{-1}$); (D) ^1H NMR spectra; (E) Raman spectra; (F) LC-MS spectra.

2.2 | Electrochemical Performance of 1,4-NQ and PNQ Samples

A direct comparison of the electrochemical properties between 1,4-NQ and *p*-PNQ cathodes reveals significant performance enhancements attributable to structural modifications. As shown in the cyclic voltammetry (CV) profiles (Figure 4A), all electrodes exhibit characteristic redox peaks corresponding to the reversible redox transitions of the quinone carbonyl groups. Notably, *p*-PNQ delivers the strongest and most symmetric redox peaks, reflecting its highly reversible electrochemical behavior, whereas pristine NQ displays weak and broad peaks, indicative of sluggish kinetics and limited utilization of active sites. The enhanced peak intensity of *p*-PNQ can be attributed to its extended π -conjugated structure and uniform molecular electrostatic potential distribution, which collectively facilitate more efficient electron delocalization and ion coordination.

Galvanostatic charge–discharge (GCD) curves (Figure 4B) further support these observations. *p*-PNQ exhibits the highest discharge capacity with well-defined and stable voltage plateaus, confirming its superior redox reversibility and structural robustness. In contrast, NQ shows a rapid voltage decay and low capacity, a reflection of its poor structural stability and limited active site accessibility. Both *o*-PNQ and *m*-PNQ electrodes demonstrate intermediate performance, underscoring the influence of substitution topology on the extent of conjugation and steric hindrance.

Electrochemical Impedance Spectroscopy (EIS) in Figure 4C further highlights the kinetic differences among the four

electrodes. *p*-PNQ exhibits the smallest semicircle diameter in the high-frequency region, reflecting the lowest charge-transfer resistance and the most efficient electron transport [28]. In contrast, pristine 1,4-NQ shows a much larger semicircle, indicating sluggish interfacial kinetics. The *o*-PNQ and *m*-PNQ electrodes display intermediate semicircle sizes, which can be attributed to their non-linear linkages that hinder extended π -conjugation and limit charge delocalization. In the low-frequency region, the Warburg slopes of *o*- and *m*-PNQ are also steeper than that of *p*-PNQ, suggesting more restricted ion diffusion. Together, these results demonstrate that the para-linked configuration provides the most favorable pathways for both electron conduction and ion transport, whereas the ortho- and meta-substituted structures offer only partial improvements over pristine NQ.

Rate performance measurements (Figure 4D) highlight the kinetic advantages of the polymeric derivatives over pristine NQ. When cycled at increasing current densities, *p*-PNQ retains a high specific capacity. It also recovers well when the current returns to a lower value, indicating efficient ion diffusion and minimal polarization. In comparison, NQ suffers from severe capacity fading at high rates, with only partial recovery upon rate reduction. The intermediate behaviors of *o*-PNQ and *m*-PNQ suggest that spatial configuration dictates the balance between redox activity and ion transport, with the para-linked structure offering the most favorable transport channels.

Long-term cycling stability (Figure 4E) provides further evidence of the structural benefits imparted by molecular engineering.

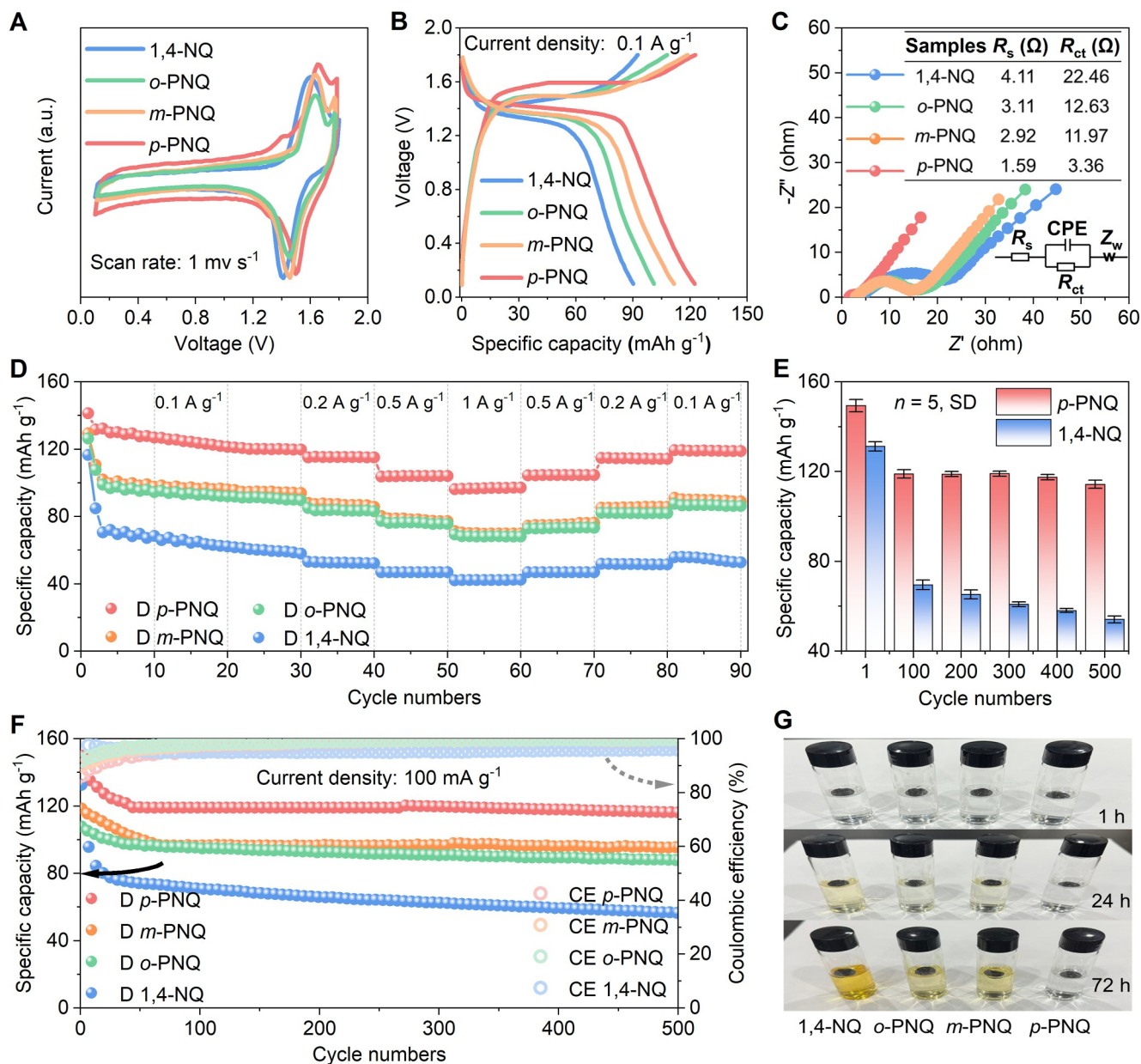


FIGURE 4 | Electrochemical performance of 4 samples. (A) Typical CV curves at a scan rate of 1 mV s^{-1} , (B) typical charge-discharge voltage profiles at current density of 0.1 A g^{-1} , (C) Nyquist plots, (D) specific capacities at different current densities from 0.1 to 1 A g^{-1} , (E) mean cycling specific capacity from five independent cells ($n = 5$), and error bars represent the standard deviation (SD), and (F) cycling performance and the CE at a current density of 0.1 A g^{-1} with the cut-off voltage of 1.8 V for 1,4-NQ, o-PNQ, m-PNQ and p-PNQ; (G) visual immersion solubility test of four cathodes in electrolyte, photographs were taken after 1, 24, and 72 h of static soaking at room temperature.

After 500 cycles, p-PNQ maintains the highest capacity with the slowest fading over extended cycling (from 119.6 to 116.2 mAh g^{-1} with a capacity retention rate of 97.2% based on stabilized region), indicating that the rigid, linear para-linked backbone not only accommodates repeated Al-based ion insertion/extraction but also resists dissolution and structural collapse [29]. By contrast, pristine NQ undergoes rapid degradation (from 77.1 to 56.5 mAh g^{-1} , with a retention rate of 73.28%), highlighting its intrinsic instability in chloroaluminate electrolytes. The improved retention in o-PNQ and m-PNQ arises from the incorporation of thioether linkages, yet their non-linear configurations hinder the formation of extended conjugation and stable π - π stacking, resulting in lower performance compared to p-PNQ. The long-

term cycling data in Figure 4E represent the average performance of five independently assembled samples, whose consistent behavior demonstrates the excellent reproducibility of the p-PNQ cathode. To evaluate the dissolution behavior under realistic conditions, we performed an immersion test using fully fabricated electrode films rather than raw materials. As shown in Figure 4G, the p-PNQ electrode displays almost no coloration of the electrolyte even after 72 h, whereas 1,4-NQ exhibits severe dissolution and o-PNQ and m-PNQ show moderate levels. This confirms that polymerization greatly reduces the tendency of the active material to dissolve from the electrode. As summarized in Supporting Information S1: Table S1, p-PNQ exhibits competitive cycling stability among recently reported organic cathodes for RAIBs.

The charge/discharge plateau of 1,4-NQ and *p*-PNQ can be seen in Figure 5A,B. Consistent with the cycling performance, *p*-PNQ has a specific capacity of 146, 122, 120, 118 and 116 mAh g⁻¹ at the 2nd, 50th, 100th, 200th and 500th cycle, respectively, whereas the number of 1,4-NQ is 132, 74, 71, 66 and 56 mAh g⁻¹. As can be seen in Figure 5C, the retention rate of *p*-PNQ decreases much slower than 1,4-NQ with a satisfying percentage from the cycling of 50–500. Based on these measured capacities, the corresponding electron-transfer number (*n*) and the estimated number of coordinated AlCl₂⁺ per repeat unit are summarized in Supporting Information S1: Table S2, supporting an approximately two-electron coordination process in the stabilized cycling region.

And these situations are consistent with the CV curves at different scan rates in Figure 5D–F, the *b* values of peak 1 and

peak 2 are 0.56 and 0.69 for 1,4-NQ, and of peak 3 and peak 4 are 0.65 and 0.79 for *p*-PNQ. The leading rate of *p*-PNQ is higher than 1,4-NQ, showing a lower voltage drop and better energy efficiency after the polymerization process. This observation is consistent with its improved capacity retention at high rates, highlighting the role of the polymeric architecture in modulating charge storage dynamics.

Compared in Figure 5G–I, as the scan rate increased from 0.1 to 2 mV s⁻¹, the pseudocapacitive contribution of 1,4-NQ rose significantly as 32%, 66%, 72% and 81%, demonstrating dominant surface-controlled behavior. In contrast, *p*-PNQ exhibited a more moderate increase from 31% to 48%, 57% and 66% in its pseudocapacitive contribution. This distinct behavior suggests that unlike conventional surface modification approaches that primarily enhance pseudocapacitive characteristics, the

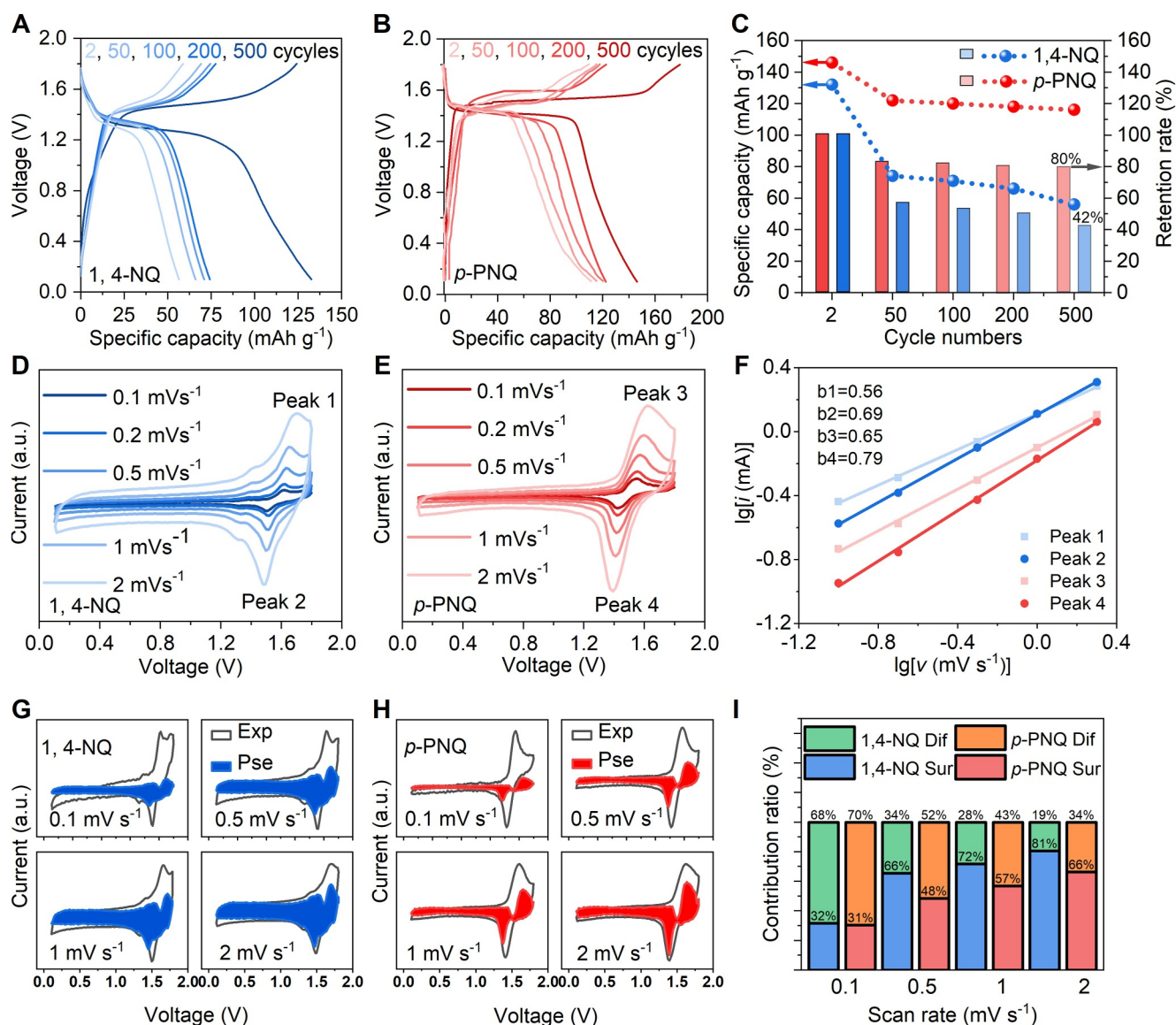


FIGURE 5 | Typical charge-discharge voltage profiles of (A) 1,4-NQ, (B) *p*-PNQ and (C) specific capacity and retention rate of two cathodes after a cycling from 2 to 500; typical CV curves of (D) 1,4-NQ and (E) *p*-PNQ cathodes at a scan rate from 0.1 to 2 mV s⁻¹; (F) linear fitting of $\lg i$ versus $\lg v$ plots to extract the *b*-values of two cathodes; experimental (Exp) and Pseudo-Capacitive (Pse) ratio in CV curves of (G) 1,4-NQ, (H) *p*-PNQ cathodes and (I) a comparison between two cathodes diffusion (Dif) and surface control (Sur) at various scan rates from 0.1 to 2 mV s⁻¹.

polymeric long-chain architecture of *p*-PNQ promotes more diffusion-controlled processes, thereby maintaining a greater proportion of bulk redox activity even at higher scan rates.

2.3 | Working Mechanism of *p*-PNQ Cathode

The ex-situ EDX mapping analysis (Figure 6A,B) provides critical insights into the working mechanism of the *p*-PNQ cathode. Notably, the intensity of Al and Cl elemental signals shows significant potential-dependent variation: weak Al and Cl signals are observed in the discharged state of 0.1 V, whereas a substantial enhancement with a uniform distribution is detected after charging to 1.8 V. These results indicate a potential-

dependent uptake of Al/Cl-containing chloroaluminate complexes, which accumulate in the cathode at the charged state and are largely released upon discharge. These species then undergo coordination reactions with the carbonyl groups (C=O) at the active sites, forming new complex structures. EDX spectra (Figure 6C) further corroborate this mechanism, demonstrating markedly increased Al and Cl signal intensities after charge compared to the discharged state.

The reaction mechanism of *p*-PNQ was examined by correlating its charge–discharge behavior with ex-situ FTIR spectra collected at different voltages (Figure 6D–E). The C=O stretching band at $\sim 1660\text{ cm}^{-1}$ shows clear intensity changes during charging (1.2–1.7 V, points a–c) and discharging (1.7–0.9 V, points d–e). In contrast, the C–O stretching vibration band near 1400 cm^{-1} was

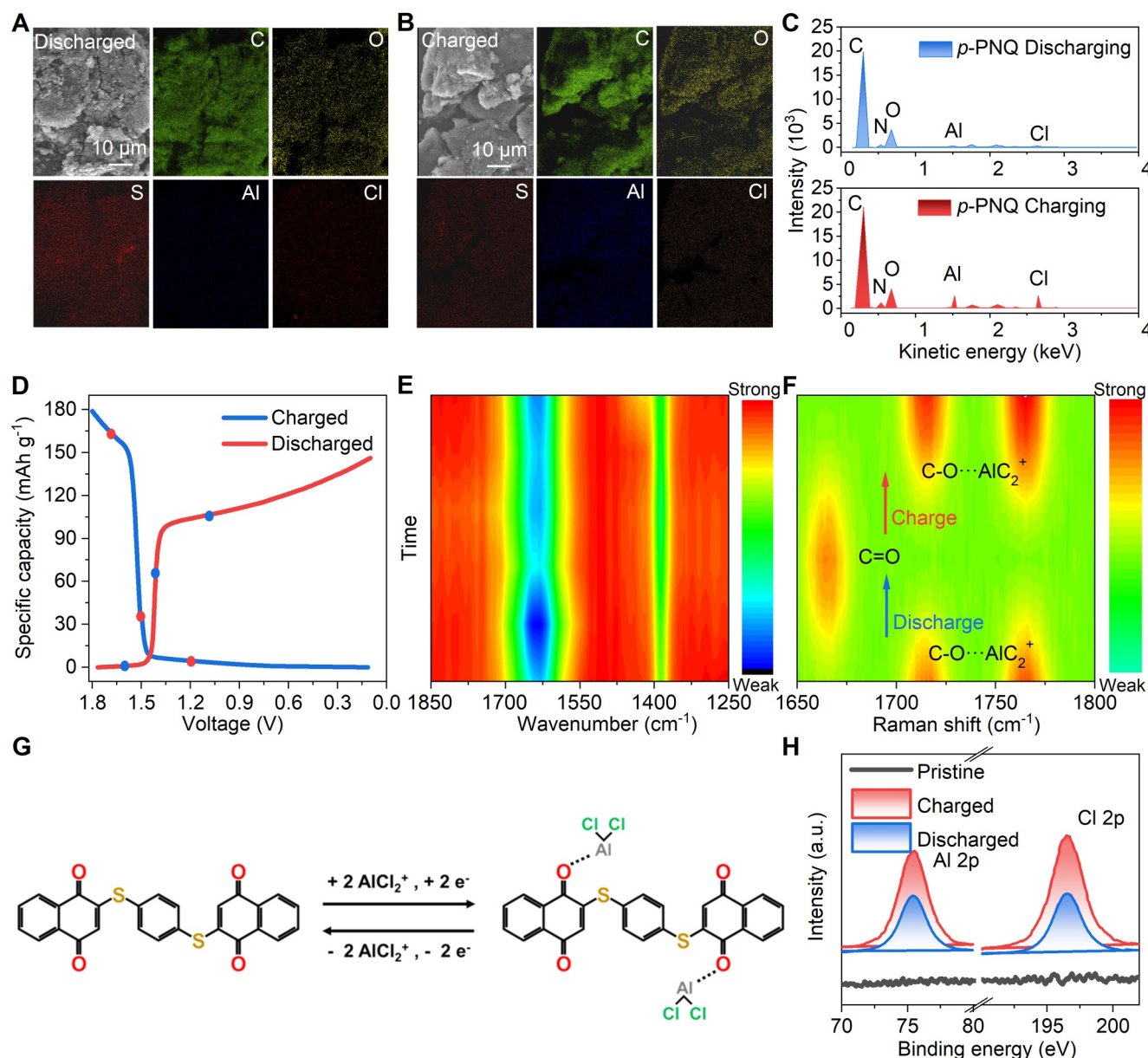
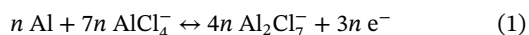
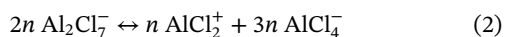
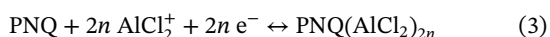


FIGURE 6 | EDX mapping images for C, O, S, Al and Cl of *p*-PNQ in different states. (A) Discharged to 0.1 V, (B) charged to 1.8 V, (C) EDX spectra of *p*-PNQ in two states, (D) corresponding to the marked galvanostatic discharge/charge curve, (E) ex-situ FTIR spectra of the *p*-PNQ at various discharged and charged states, (F) in situ Raman spectra of *p*-PNQ during discharge and charge process, (G) schematic diagram of charge–discharge mechanism of *p*-PNQ in RAIBs, and (H) XPS spectra of the *p*-PNQ at various discharged and charged states.

found to remain essentially unchanged throughout the electrochemical cycling. These spectral observations provide clear verification that the electrochemical activity is predominantly localized at the carbonyl (C=O) functional groups, whereas the C-O moieties remain electrochemically inactive [30]. To further elucidate the carbonyl redox mechanism, Figure 6F presents Raman spectra collected at a series of well-defined potentials during discharge and charge. The C=O stretching band ($\sim 1670\text{ cm}^{-1}$) gradually decreases during charge, whereas two higher-frequency bands at ~ 1715 and $\sim 1760\text{ cm}^{-1}$ (corresponding to AlCl_2^+ -coordinated carbonyls) appear and intensify. During discharging, these coordinated-state bands diminish and the original C=O band is fully restored, indicating a highly reversible coordination and de-coordination process. In parallel, Figure 6H shows XPS spectra of pristine, discharged, and charged electrodes. Al 2p and Cl 2p signals are negligible in the pristine electrode, appear with moderate intensity in the discharged state, and become the strongest after charging. The reversible increase upon charging and decrease upon discharging confirm the reversible coordination-decoordination of AlCl_2^+ with the carbonyl groups.

Based on the discussion above and reported works, the reaction mechanism of RAIBs in Figure 6G could be comprehensively described as follows: At the anode side, $\text{Al}/\text{AlCl}_4^-$ and Al_2Cl_7^- species undergo reversible conversion during the charge/discharge process in Reaction (1). These species can further transform into AlCl_2^+ ions, as described in Reaction (2). Simultaneously, at the cathode side, coordination occurs between carbonyl (C=O) groups in *p*-PNQ and AlCl_2^+ cations, resulting in the formation of a *p*-PNQ (AlCl_2^+)_{2n} complex in Reaction (3). The detailed electrode reactions are presented below.



3 | Conclusions

This study presents three thioether-bridged naphthoquinone polymers (*o*-PNQ, *m*-PNQ, and *p*-PNQ) designed based on 1,4-NQ, and investigates their electrochemical behavior in RAIBs. We demonstrate that the substitution topology of polymerized naphthoquinones significantly impacts their electrochemical performance. The polymerization strategy reduces crystallinity, enhances thermal stability, and extends π -conjugation, with para-topology offering the most favorable balance of structure and function. Specifically, the para-linked *p*-PNQ achieves an initial capacity of 146 mAh g^{-1} and retains 97.2% of its capacity after 500 cycles at 0.1 A g^{-1} . Its extended π -conjugated backbone and symmetrical structure enable efficient charge transfer, stable voltage profiles, and superior rate capability compared to the *o*-/*m*-PNQ isomers and pristine 1,4-NQ. In-depth analyses confirm that the dominant redox activity originates from the reversible coordination of carbonyl groups with AlCl_2^+ species. Overall, these results validate the enhanced performance of *p*-PNQ and highlight molecular topology as a key factor in the

design of organic cathodes for RAIBs. This topology-guided approach provides new opportunities for the design of advanced organic materials for RAIBs and potentially extends to other multivalent-ion systems, such as Mg^{2+} and Ca^{2+} , offering broad application potential in large-scale energy storage.

Author Contributions

Jia Qiao: conceptualization, writing – reviewing and editing, supervision, project administration. **Yanfang Wang:** formal analysis, methodology. **Jiming Peng:** methodology, project administration. **Guokang Wei:** conceptualization, data curation, investigation, writing – original draft preparation. **Xinqi Xu:** formal analysis, investigation. **Borui Wang:** data curation, formal analysis. **Zhenhua Luo:** supervision, writing – reviewing and editing. **Aichun Dou:** supervision, writing – reviewing and editing. **Sijiang Hu:** methodology, writing – reviewing and editing.

Acknowledgments

This work was financially supported by Project entrusted by enterprise (Grant Nos. HX20210521 and HX20230264) and the China Scholarship Council program (Grant No. 202508690003).

Conflicts of Interest

The authors declare no conflicts of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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Supporting Information

Additional supporting information can be found online in the Supporting Information section.

Supporting Information S1: rar270292-sup-0001-suppl-data.doc.



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A topologyguided design strategy for polymerized naphthoquinone cathodes in rechargeable aluminiumion batteries

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2026-05

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<https://doi.org/10.1002/rar2.70292>

Qiao J, Wang Y, Peng J, et al., (2026) A topologyguided design strategy for polymerized naphthoquinone cathodes in rechargeable aluminiumion batteries. Rare Metals, Volume 45, Issue 5, May 2026, Article number e70292