# **Supporting Information**

# Polydiaminoanthraquinones with Tunable Redox Properties as High Performance Organic Cathodes for K-ion batteries

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# 2. Experimental

### 2.1 Material synthesis

All the polymers are synthesized via chemical oxidation polymerizations.

Poly (1, 5 - diaminoanthraquinone) (PQ-1,5): PQ-1, 5 is synthesized according to

the previous report [29]. 1.19 g 1.5-diaminoanthraquinone monomers (15DAAQ) and 1.2 g  $CrO_3$  were dissolved in 50 mL and 20 ml 1 M  $H_2SO_4$  N, N-dimethylformamide (DMF) solution, respectively. Then the  $CrO_3$  solution was added into the solution containing 15DAAQ by dropwise, and the reaction was carried out under stirring for 25 °C for 24 h.

Poly (1, 4 - diaminoanthraquinone) (PQ-1, 4) and poly (1,4-diamino-2,3dicyanoquinone) (PQ-CN): the typical experimental procedure was to dissolve 0.01 mol PQ-1,4 (or 1,4-diamino-2,3-dicyanoquinone) and 0.02 mol Ce(NH<sub>4</sub>)<sub>2</sub>(NO<sub>3</sub>)<sub>6</sub> in 100 mL and 20 mL DMF. Then add the DMF solution of Ce(NH<sub>4</sub>)<sub>2</sub>(NO<sub>3</sub>)<sub>6</sub> dropwise into the solution of PQ-1,4 (or PQ-CN). The reaction was carried out at 25 °C for 24 h.

All the products were washed with deionized water and ethanol and reduced to emeraldine states by ammonia. The precipitates were finally dried in vacuum at 120 °C for 12 h.



Scheme S1. The synthesis process of PQ-1,5, PQ-1,4 and PQ-CN

### 2.2 Structural characterization

The morphology of the samples were examined by field-emission scanning electron microscopy (SEM, Zeiss SIGMA FESEM, USA). The structure of the polymer (PQ-1,4, PQ-1,5 and PQ-CN) were determined by X-ray diffraction (XRD) using a PANalytical Multi-Purpose Diffractometer equipped a Cu K<sub> $\alpha$ </sub> Radiation ( $\lambda$ =1.5406Å). The chemical structures were determined by Fourier transform infrared spectroscopy (FTIR, Bruker VERTEX 70, USA). The thermal stability of the products were performed on thermogravmetric analyzer (TGA) / differential scanning calorimetry (DSC) analyzer (Netzsch Instruments, STA 449 F5) at a heating of 10 °C min<sup>-1</sup> in N<sub>2</sub> from room temperature to 800 °C. Molecular weight of the polymers are tested by gel permeation chromatography (GPC) using Agilent PL-GPC50 at 30 °C.

### 2.3 Electrochemical characterization

Working electrodes were a film cast onto carbon-coated Al foil containing 60 wt% PQ, 30 wt% Ketjenblack and 10 wt% polyvinylidene fluoride (PVdF) with active mass  $\sim$ 2 mg/cm<sup>2</sup>. 2025-type coin cells were assembled with potassium foil as an anode and 1 M potassium bis(trifluoromethane sulfonyl) imide (KTFSI) in mixed dimethoxyethane and dioxolane solution (DOL:DME = 1:1 by volume) as electrolyte in an argon-filled glovebox. The electrochemical performances were conducted on a LAND system at room temperature. The cyclic voltammetry (CV) was examined by an electrochemical workstation (CHI604E, Chenhua, China) at a constant scanning rate of 0.2 mV s<sup>-1</sup>.

### 2.4 Computational details

All calculations were done using Gaussian 09 package [1]. Geometries were first optimized at the level of theory B3LYP/6-31G(D). Then single point energy calculations were carried out based on the optimized geometries at the same level of theory. HOMO/LUMO energies were obtained after the self-consistent-field (SCF) cycles converged.

## 1. SEM images



Fig. S1. SEM images of the PQs (a) PQ-1, 5; (b) PQ-1, 4.

## 2. XRD patterns of PQ-1,4 and PQ-1,5



Fig. S2. XRD patterns of PQ - 1, 4 (a) and PQ - 1, 5 (b)

# 3. FT-IR spectra



Fig. S3. FT-IR spectra of the PQ - 1, 5 and PQ - 1, 4

In the FT-IR spectra of PQ-1, 5 and PQ- 1, 4, the peaks located at 812, 770, and 713 cm<sup>-1</sup> can be ascribed to the out-plane bending of the benzene ring, while the bands at 1260 and 1494 cm<sup>-1</sup> are attributed to the deformation vibration of C-N and N-H bonds. The strong absorption peak at 1602 cm<sup>-1</sup> reflects C=O stretching in the benzoquinone structures. Noteworthy, for PQ - 1, 4, the strong peak located at 1021cm<sup>-1</sup> can be ascribed to the out-plane bending of the –NH<sub>2</sub> groups.

### 4. Ex-situ FT-IR spectra of PQ-1,5



Fig. S4. Ex-situ FI-IR spectra of the PQ-1,5 electrode (right) collected at the marked points in the 1st potassiation/depotassiation curve (left). (I: Fresh; II: discharge to 1.7 V; III: discharge to 1.2V; IV: charge to 3.2 V)

During the first discharge process, the peak intensity of the C=O peak (~1601 cm<sup>-1</sup>) reduce, the intensity of C- O…K bond (1346 cm<sup>-1</sup>) increase and recover during the charge process. Moreover, the absorption peak at 801 cm<sup>-1</sup> (C=C) gradually decreased and a new peak at 620 cm<sup>-1</sup> (C…K) emerged, which cannot be totally recover during the reversed charge process, suggesting irreversible K<sup>+</sup> trapping in the aromatic rings in the first cycle. 5. The coulombic efficiency of the PQ-1,5 and PQ-1,4.



Fig. S5. The coulombic efficiency of PQ-1,5 and PQ-1,4 at a constant current density of 50  $$\rm mA~g^{-1}$$ 



## 6. The solubility of the electrode in the electrolytes

Fig. S6. Digital image of the PQ-1,5 (a) and PQ-1,4 (b) electrodes dipped in the electrolytes of KIBs (1 M KTFSI in DOL/DME) after 10 h

### 7. The rate performances of the PQ-1,4 and PQ-1,5



Fig. S7. Charge-discharge profiles of the PQs at different current densities: (a) PQ-1,5; (b) PQ-1,4

### 8. The coulombic efficiency of the PQ-1,5 for the long-term cycling



Fig. S8. The coulombic efficiency of PQ-1,5 at a constant current density of 250 mA g<sup>-1</sup>

As shown in Fig. S6, for the PQ-1, 5 electrode, the coulombic efficiency (charge capacity/discharge capacity) increase dramatically to  $\sim$ 120% after charging/discharging for 120 cycles. The large charge capacity above 3.0 V in the following cycles (after 120) may be ascribed to two main reasons: 1. the decomposition of the electrolytes at high potential; 2. the irreversible

insertion of anions (PF<sub>6</sub><sup>-</sup>) into the polyaniline backbones (p-doping reactions).



#### 9. The morphology and structural characteristics of PQ-CN



The as-prepared PQ-CN appear as rod-like particles with average length of ~  $1.5 \mu$  m and diameter of ~280 nm. As shown in Fig.S5(c), similar with the FT-IR spectra of PQ-1,5 and PQ-1,4, all the absorption peaks can be ascribed to characteristics of polyaniline and benzoquinone moieties. Noteworthy, the strong bands located at 2224 cm<sup>-1</sup> is the characteristic of –CN groups. The as-prepared PQ-CN show high thermal stability up to 350 °C (Figure S5d).

#### 10. The electronic structure of PQ-CN, PQ-1, 4 and PQ-1, 5

Table S1. The HOMO, LUMO energy levels and the energy gaps (Eg) of the PQs

Polymer	PQ-1, 5	PQ-1, 4	PQ-CN
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HOMO(eV)	-5.54	-5.01	-5.82
LUMO (eV)	-2.43	-2.38	-3.53
<i>E</i> g (eV) (HOMO-LUMO	3.11	2.62	2.29

energy gaps)

# 11. The XRD patterns of PQ-CN



Fig. S10. XRD patterns of PQ-CN

### 12. The cycling performances of PQ-CN



Fig. S11. The cycling performances of PQ-CN at a constant current density of 50 mA g<sup>-1</sup>



Fig. S12. The long-term cycling performances of PQ-CN at a constant current density of 250 mA g<sup>-1</sup>

As shown in Fig. S10, after a few cycles of activation, the reversible capacity of PQ-CN increase to a steady value of ~165 mAh g<sup>-1</sup>. The capacity retention of PQ-CN over 200 cycles is 52.2% (relative to the 5<sup>th</sup> cycle). After charging-discharging for 300 cycles, a reversible capacity of 71.2 mAh g<sup>-1</sup> can be obtained.



Fig. S13. Digital image of the PQ-CN electrodes dipped in the electrolytes of KIBs (1 M KTFSI in DOL/DME) after 10 h