Electronic Supplementary Information

Carbonyl-based polyimide and polyquinoneimide for potassium-ion batteries

Bingbing Tian,^a Ji Zheng,^b Chenxi Zhao,^{c,f} Cuibo Liu,^a Chenliang Su,^a Wei Tang,^d Xing Li^e and Guo-Hong Ning^{*b}

- ^{a.} International Collaborative Laboratory of 2D Materials for Optoelectronics Science and Technology of Ministry of Education, Engineering Technology Research Center for 2D Material Information Function Devices and Systems of Guangdong Province, College of Physics and Optoelectronic Engineering, Shenzhen University, Shenzhen 518060, China
- ^{b.} College of Chemistry and Materials Science, Jinan University, Guangzhou, Guangdong 510632, China. Email: guohongning@jnu.edu.cn
- ^{c.} Key Laboratory for Advanced Materials and Department of Chemistry, School of Chemistry and Molecular Engineering, East China University of Science and Technology, Shanghai 200237, China
- ^{d.} School of Chemical Engineering and Technology, Xi'an Jiaotong University, Xi'an, Shaanxi 710049, China
- e. Department of Chemistry, National University of Singapore, 3 Science Drive 3, Singapore 117543, Singapore
- ^{f.} Department of Chemistry and Materials Innovation Factory, University of Liverpool, Liverpool, UK

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1. General procedure

All the commercially available chemicals were purchased from Sigma Aldrich and TCI, and used without further purification. All the NMR spectra were collected at 300 K, and chemical shifts were reported as the detal scale in parts per million (ppm) relative to an internal standard, tetramethylsilane ($\delta = 0.00$ ppm for ¹H NMR). Thermal gravimetric analysis (TGA) was performed on a Discovery TGA Thermo-Gravimetric Analyzer (TA Instruments).

The organic cathode was composed of the active material (PI, PQI and PI-CMP), conductive carbon (Super P), and the polyvinylidene fluoride (PVDF) binder in a ratio of 60:30:10 (60 wt% active material). Such mixtures were suspended in N-methyl-2-pyrrolidone (NMP) to form a slurry and then coated onto an aluminum foil substrate. Coating were dried in a blast oven at 80 °C for ~ 2 hours, followed by activation in a vacuum oven for more than 24 h to give the film that were cut into circular electrode discs with a diameter of 14 mm and active material loading of ~ 1 mg cm⁻². The cells were were assembled in a glovebox under an Ar atmosphere with H₂O and O₂ contents lower than 1 ppm, using CR2016 coin cell hardware, with postassium foil as the counter electrode and Whatman Glass Microfibre Filter as the separator. The electrolyte contains 1 M lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) in a mixed solvent of 1,3-dioxolane (DOL) and 1,2-dimethoxyethane (DME) (1:1 v/v).

Electrochemical performance: CR2016-type coin cell batteries were assembled to analyze the electrochemical behaviors. The separator was Whatman Glass Microfibre Filter. The cells were assembled in a glovebox filled with highly pure argon gas, and charge/discharge tests were performed in the voltage range of 1.5 to 3.5 V (vs. K/K⁺) at different current densities on a Land batteries tester.

Cyclic voltammetry (CV) was performed using an Ivium-n-Statmulti-channel electrochemical analyzer. Cyclic voltammograms were recorded over the potential range of 1.5-3.5 V (*vs.* K/K⁺) at a scanning rate of 0.1 mV s⁻¹, starting from OCP to the cathodic scan (discharge) direction. Galvanostatic discharge–charge cycling of the batteries was monitored within a voltage window of 1.5-3.5 V using a LAND Battery Tester. All potentials hereafter are given versus K/K⁺. All the electrochemical measurements were performed at room temperature.

For chemical analysis, the **PI-CMP** electrodes were subjected to different states of galvanostatic discharge–charge. The cells were disassembled and the samples were rinsed with ReagentPluss 1,3-dioxolane (DOL, 99%, Sigma-Aldrich) and dried under an Ar flow for Fourier transform infrared spectroscopy (FTIR, transmission mode, OPUS/IR PS15

spectrometer, Bruker) analyses and X-ray photoelectron spectroscopy (XPS, Omicron EAC2000-125 analyzer, Al K α monochromatized radiation (hv = 1486.6 eV,), base pressure during analysis was 10⁻⁹ Torr, directly conected with the glovebox). SEM and TEM imaging of the **PI-CMP** pristine materials were performed using a JEOL JSM-6701F Field-Emission Scanning Electron Microscope (FESEM) and a JEOL JEM-3011 Transmission Electron Microscope (TEM).

2. Synthesis section

2.1 Synthesis of Naphthalene-N,N'-bis(imido-amine) (NDI) ligand 1



The compound **1** was prepared according to the reported procedure¹ with some modification. 1,4,5,8-naphthalenetetracarboxylic dianhydride (NTCDA) (500 mg, 1.87 mmol) was stirred in 25 mL DMF and heated to 140 °C until all the solids are dissolved. After then hydrazine monohydrate (234 mg, 4.75 mmol) was added to NTCDA solution in DMF, and the yellow precipitation was formed immediately. The mixture was heated at 140 °C for overnight, and then cooled down to the room temperature. The resultant solid was filtered, washed with acetone and dried up in vacuo to give the compound **1** as brown-yellow solids (450 mg) in 82% yield based on the NTCDA. IR (KBr): 3337-3038 (br, -NH₂-), 1690 (s, C=O), 1636 (s, C=O), 1553 (s), 1411 (s), 1361 (s), 1247 (s), 1184 (s), 1101 (m), 1066 (m) and 942 cm⁻¹ (s). ¹H NMR (DMSO, 500 MHz, 300 K): δ (ppm) 8.69 (s, aromatic hydrogen, 4H), 5.86 (s, -NH₂-, 4H).

2.2 Synthesis and characterization of PI, PQI and PI-CMP polymer

The PI and PQI were synthesized *via* a DMF (*N*,*N*-Dimethylformamide, anhydrous, 99.8%, Sigma-Aldrich) solution process.²⁻⁵ Specifically in a typical PQI composite procedure, NTCDA (268 mg, 1 mmol) was added into DMF solution (40 mL). Then the as prepared mixture was heated to 140 °C until all the NTCDA dissolved in the solution. After DAAP (238 mg, 1 mmol) was added to the solution, the reaction mixture was refluxed and stirred under N₂ gas at 140 °C, then product precipitated gradually. After 3 days, the as-obtained powder was filtrated and washed with methanol and acetone. After dried at 60 °C overnight,

the brown powder of PQI is obtained. The PI synthetic method is similar to PQI. For more details, please see previously report.⁶

A solution of 1,3,5-Triformylbenzene TFB (23 mg, 0.167 mmol) in DMSO (1 mL) was added drop-wise to a 25 mL round flask with a pre-heated (120 °C) solution of ligand **1** (60 mg, 0.2 mmol) in 9 mL DMSO. The mixture were stirred and heated at 120 °C for 7 days, during this time, the green powders were formed. After then, the reaction was cooled to room temperature, the solids filtered and washed with DMSO, THF, and dried at 120 °C under vacuum overnight to give the PI-CMP conjugated porous polymer as green solids (45 mg) in 60 % yield. IR (KBr): 3500 (br, H₂O), 1704 (s, C=O), 1680 (s, C=O), 1581 (m), 1443 (m), 1361 (m), 1314 (s), 1243 (s), 1203 (m), and 976 cm⁻¹ (m). Elemental analysis: calculated for $[C_{60}H_{24}N_{12}O_{12}]_n$: C 65.22, H 2.19, N 15.21 %; found : C 60.43, H 3.97, N 12.64 %.

3. IR spectrum and TGA analysis



Fig. S1. (a) FTIR spectra and (b) TGA profiles of PI, PQI and PI-CMP.



Fig. S2. IR spectra of PI-CMP and their ligands.

4. BET analysis of PI-CMP



Fig. S3. (a) Representative N_2 adsorption (closed circles) and desorption (open circles) isotherms of PI-CMP polymer synthesized in DMSO (cyan, SBET = 110 m² g⁻¹). (b) Pore size distribution for PI-CMP polymer.



Fig. S4. Powder XRD curve of a) NDI; b) TFB and c) **PI-CMP** polymer indicating the complete reaction between NDI and TFB.

6. TGA profiles of ligands



Fig. S5. TGA profiles of the NTCDA, PPD, DAAP and TFB.

7. SEM and TEM images of PI, PQI, and PI-CMP



Fig. S6. SEM images of (a) PI; (c) PQI; and (e) PI-CMP; and TEM images of (b) PI; (d) PQI; and (f) PI-CMP.

8. Electrochemical properties of ligand 1, PI, PQI and PI-CMP



Fig. S7. (a) Charge-discharge performance of ligand 1 (1st cycle, black; 2nd cycle, blue; 3rd cycle, orange; 10th cycle, green); (b) cycling performance of ligand 1.



Fig. S8. Potassium storage ability of PI-CMP at deep discharge (discharged to 0.6 V). (a) the first three galvanostatic discharge and charge cycles, (b) the first two CV curves at a scan rate of 0.2 mV s^{-1} .



Fig. S9. CV curves of PI, PQI and PI-CMP at different scan rates (0.2, 0.4 and 0.8 mV s⁻¹).

9. DFT calculation.



Fig. S10 ESP surface of the PI molecule under study, orange balls represent $V_{s,max}$ and cyan balls represent $V_{s,min}$. Energy are given in kcal/mol.



Fig. S11 NCI iso-surface of PI polymers combined with six potassium ions. Pink balls represent to the K atom, red for O atom, blue for N atom, cyan for C atom and white for H atom.



Fig. S12 The predicted potassium structures of PI during the discharging process. Pink balls represent to the K atom, red for O atom, blue for N atom, cyan for C atom and white for H atom.



Fig. S13 ESP surface of the PQI molecule under study, orange balls represent $V_{s,max}$ and cyan balls represent $V_{s,min}$. Energy are given in kcal/mol.



Fig. S14 NCI iso-surface of PQI polymers combined with six potassium ions. Pink balls represent to the K atom, red for O atom, blue for N atom, cyan for C atom and white for H atom.



Fig. S15 The predicted potassium structures of PQI during the discharging process. Pink balls represent to the K atom, red for O atom, blue for N atom, cyan for C atom and white for H atom.

10. Solubility test.



250 mg/L in electrolyte solvent

Fig. S16 Solubility of the precursors (DAAP, NTCDA) and polymers (PI, PQI, PI-CMP) in electrolyte solvents.

Material	Discharge	Current	Cycle Life	Reference
	Capacity (mAh/g)	Density		
PI	152	0.05 A/g	200	This work
PQI	221	0.05 A/g	200	This work
PI-CMP	155	0.05, 1 A/g	200, 1000	This work
PTCDA	131	0.01 A/g	200	[7]
PTCDA	122	20,10 mA/g	55, 300	[8]
PAQS	200	20 mA/g	50	[9]
$K_2C_6O_6$	212, 164	0.2, 10 C	10, 100	[10]
PTCDA@450 °C	2 mAh/cm^2	1 A/g	1000	[11]
Polyaniline	138	10 mA/g	100	[12]
ADAPTS	109, 77	1, 2 C	500, 1000	[13]
PPTS	260, 163	0.1, 10 A/g	100, 1000	[14]

 Table S1. Comparison of the organic materials for KIBs.

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