

## Electronic Supplementary Information

### Amino Group Enhanced Phenazine Derivative as Electrode Material for Lithium Storage

*Bingbing Tian*<sup>a,b</sup>, *Zijing Ding*<sup>a,b</sup>, *Guo-Hong Ning*<sup>b</sup>, *Wei Tang*<sup>b</sup>, *Chengxin Peng*<sup>b</sup>, *Bo Liu*<sup>b</sup>, *Jie Su*<sup>b</sup>, *Chenliang Su*<sup>a,b,\*</sup>, and *Kian Ping Loh*<sup>a,b,\*</sup>

<sup>a</sup> SZU-NUS Collaborative Innovation Center for Optoelectronic Science & Technology, Key Laboratory of Optoelectronic Devices and Systems of Ministry of Education and Guangdong Province, College of Optoelectronic Engineering, Shenzhen University, Shenzhen 518060, China

<sup>b</sup> Department of Chemistry, Centre for Advanced 2D Materials (CA2DM) and Graphene Research Centre, National University of Singapore, 3 Science Drive 3, Singapore 117543, Singapore

\* Corresponding author: Kian Ping Loh, E-mail: [chmlohkp@nus.edu.sg](mailto:chmlohkp@nus.edu.sg),  
Chenliang Su, E-mail: [chmsuc@szu.edu.cn](mailto:chmsuc@szu.edu.cn)

## Experimental Section and Methods

PNZ (98%) and DAP (90%) were purchased from Sigma Aldrich and directly used as active electrode materials without any further purification. The organic electrodes were fabricated using the following procedure. The organic active material, Super P and polyvinylidene fluoride (PVDF) binder were mixed in a weight ratio of 60:30:10 in N-methyl-2-pyrrolidone (NMP) to form the well-dispersed slurry by stirring overnight and then coated onto an aluminum foil substrate. The coatings were dried immediately in a blast oven at 60 °C for ~2 h, followed by activation in a vacuum oven at 60 °C for overnight to produce membranes that were then cut into circular electrode discs with a diameter of 14 mm. After weighing the electrode discs (active material loading: ~1.2 mg cm<sup>-2</sup>), the cells were assembled in a glovebox (VAC) under Ar atmosphere with H<sub>2</sub>O and O<sub>2</sub> contents lower than 1 ppm, using CR2016 coin cell hardware, with lithium foil as the counter electrode and Whatman Glass Microfibre Filter as 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).

Cyclic voltammetry (CV) was performed using an Ivium-n-Stat multi-channel electrochemical analyser. Cyclic voltammograms (CVs) were recorded over the potential range of 1.1-3.4 V at a scanning rate of 0.1 mV s<sup>-1</sup>, starting from OCP into the cathodic scan (discharge) direction. Galvanostatic discharge-charge cycling of the batteries was monitored within a voltage window of 1.1-3.4 V using a LAND Battery Tester (Wuhan, China). All potentials hereafter are given versus Li/Li<sup>+</sup>. All the Electrochemical measurements were performed at room temperature.

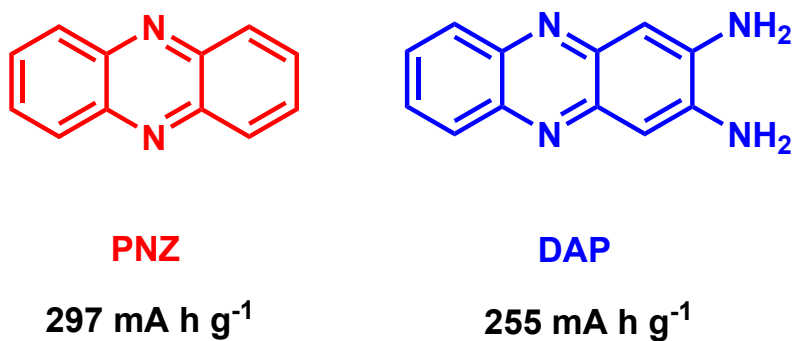
For chemical analyses, the DAP electrodes were submitted to different stages of galvanostatic discharge and charge. The electrochemical treated cells were disassembled in the glovebox and the samples were rinsed with ReagentPlus® 1,3-Dioxolane (DOL, 99%, Sigma-Aldrich) and dried with Ar flow for Fourier transform infrared spectroscopy (FTIR, transmission mode, Bruker OPUS/IR PS15

spectrometer), X-ray photoelectron spectroscopy (XPS, Omicron EAC2000-125 analyzer, Al K $\alpha$  monochromatized radiation ( $h\nu = 1486.6$  eV), base pressure during analysis was  $10^{-9}$  Torr) and Ultraviolet–visible spectroscopy (UV-Vis, UV-3600 Shimadzu UV-vis Spectrophotometer) analyses. UV-Vis analysis was performed by immersion the galvanostatic discharged or recharged samples in the anhydrous acetonitrile to obtain the test solution.

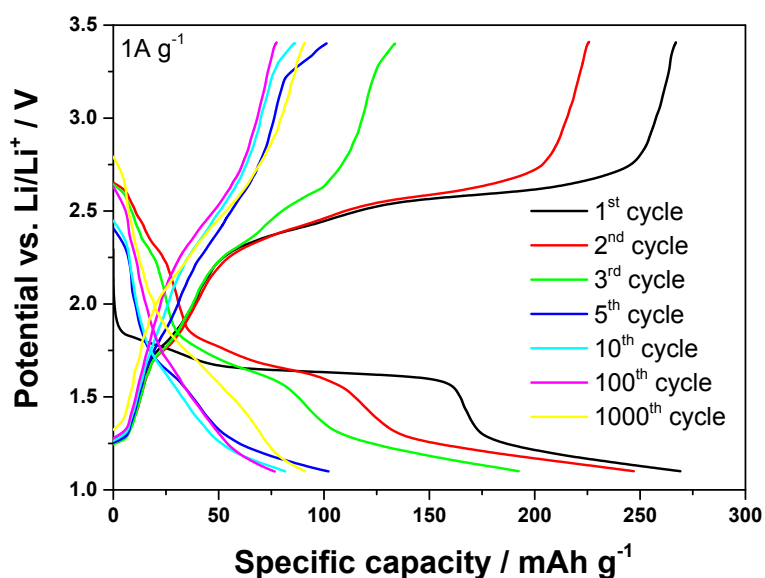
The glovebox used in this study is directly interfaced to a XPS. In this work, the electrode samples were disassembled and washed with DOL in an argon-atmosphere glovebox directly connected to the XPS to ensure that the samples were not exposed to air. UV-Vis analysis was performed by immersing the galvanostatic discharged or recharged samples in anhydrous acetonitrile in the argon-filled glovebox to obtain the test solution. For FTIR measurement, the cells were disassembled and the samples were rinsed with DOL, and dried with Argon flow in glovebox to prepare test KBr pellets. Then the test pellet was transferred in a sealed glass vessel to perform FTIR in a vacuum FTIR machine.

### **Computational Method**

The first-principles calculations were carried out based on density functional theory (DFT), employing Projector augmented wave pseudopotentials and the Perdew-Burke-Ernzerhof (PBE) form of the exchange-correlation functional, as implemented in the Vienna *ab initio* simulation package code. We employed an energy cutoff of 400 eV for plane waves, and the criterion for total energy convergence was set to  $10^{-4}$  eV. All atoms are relaxed during geometry optimization until the magnitude of forces is less than 0.01 eV/Å.



**Scheme S1.** Molecular structures of the PNZ and DAP; The theoretical specific capacity is based on a two-electron reaction.

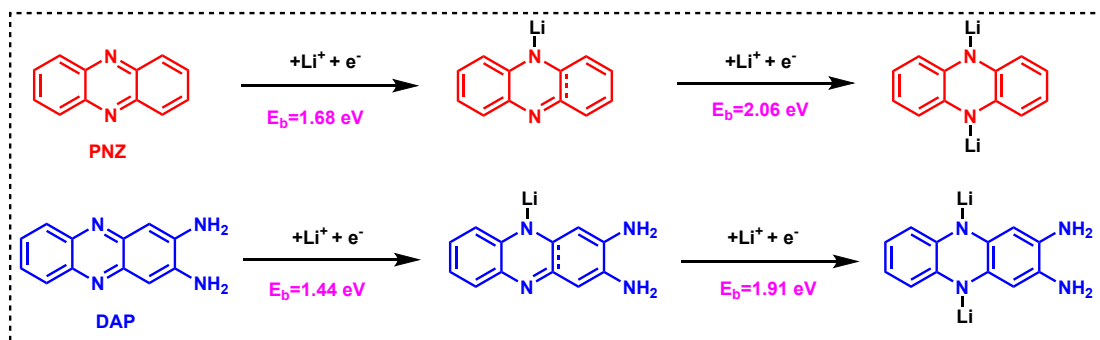


**Fig. S1.** Galvanostatic charge/discharge profiles of DAP electrode at the current density of 1 A g<sup>-1</sup>.

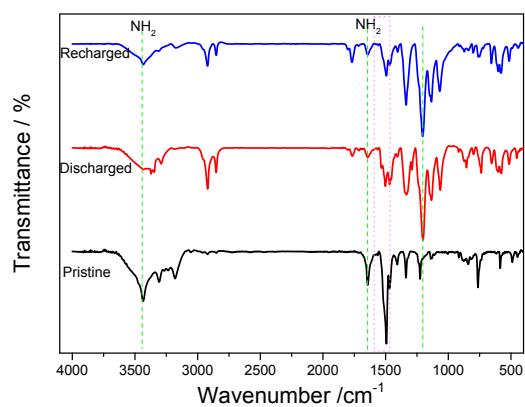
**Table S1.** Energy levels of PNZ and DAP molecule based on DFT.

	LUMO (eV)	HOMO (eV)	Gap (eV)
PNZ	-5.67	-3.47	2.20
DAP	-5.19	-3.05	2.14

Using B3LYP/6-31+G(d,p) exchange-correlation functional, the energy gap of PNZ and DAP is 3.61 eV and 3.50 eV, respectively.

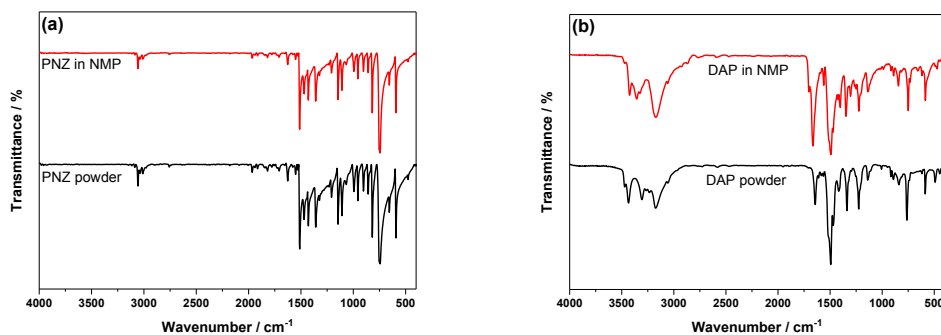


**Fig. S2.** Lithiation and binding energies of PNZ and DAP with lithium atoms.



**Fig. S3.** FTIR spectra of C=N and NH<sub>2</sub> bonds at different states of discharge and charge during battery cycling.

We added PNZ/DAP in the NMP and they are soluble in NMP (Solubility: ~120mg/mL for PNZ and ~50mg/mL for DAP, respectively, at room temperature). After drying, similar FTIR curves are observed before and after immersion in NMP for the PNZ and DAP, indicating no reaction occurred between PNZ/DAP and NMP (Fig. S4).



**Fig. S4.** FTIR curves of theC PNZ and DAP before and after immersion in NMP.

We also evaluated the electrochemical properties of PNZ and DAP in a commercial electrolyte [1 M LiPF<sub>6</sub> in a 1:1:1 (volume ratio) mixture of ethylene carbonate (EC), ethylene methyl carbonate (EMC) and dimethyl carbonate (DMC), which is commonly used as electrolyte in lithium ion batteries]. However, the electrochemical performances are inferior for both PNZ and DAP in the commercial carbonate type electrolyte (Fig. S5) due to the higher solubility and the poor possible compatibility issues. So, in this work, we use an ethers electrolyte to ensure the electrochemical performances of the phenazines.

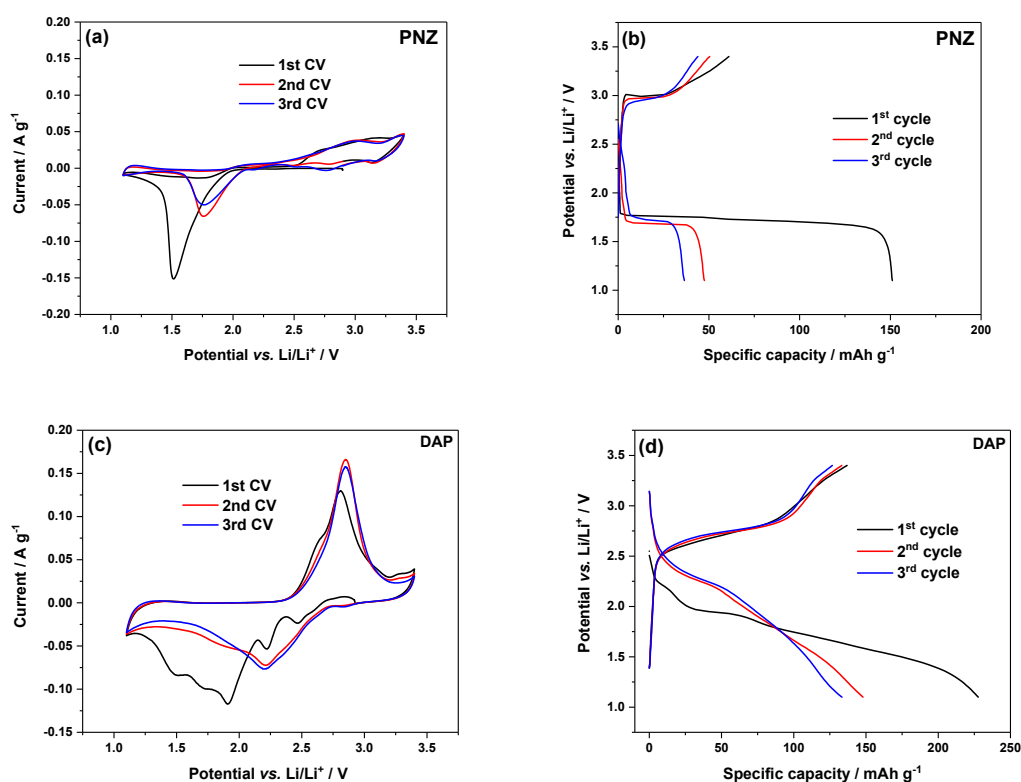


Fig. S5. Electrochemical performances (CVs and discharge/charge curves) of the PNZ and DAP in a commercial electrolyte of 1 M LiPF<sub>6</sub> in a 1:1:1 (volume ratio) of mixture of EC, EMC and DMC.