

## Supporting Information for

# Anion- $\pi$ Interactions in Lithium-Organic Redox Flow Batteries

Lei Li,<sup>a</sup> Yu-Jian Hong,<sup>a</sup> Dong-Yang Chen<sup>b</sup>, Wang-Chuan Xiao,<sup>c</sup> and Mei-Jin Lin<sup>a\*</sup>

<sup>a</sup> College of Chemistry, Fuzhou University, China, 350116, E-mail: meijin\_lin@fzu.edu.cn, Tel: 0086 591 2286 6143

<sup>b</sup> College of Materials Science and Engineering, Fuzhou University, China, 350116

<sup>c</sup> School of Resources and Chemical Engineering, Sanming Institute of Fluorochemical Industry, Sanming University, China, 365004

### Table of Contents:

1. Materials and measurement	S2
2. Fabrication of organic-lithium flow batteries and electrochemical measurements	S3
3. Battery performances	S4
4. Electrochemical redox reaction Mechanism	S6
5. TGA curves	S7
6. Viscosities and conductivities	S7
7. References	S7

## 1. *Materials and measurements*

Perylene 3,4,9,10-tetracarboxylic acid dianhydride (PTCDA, 98%), 2,6-diisopropylaniline (97%), ethanol (analytical reagent grade), propionic acid (analytical reagent grade), dimethyl sulfoxide (DMSO, analytical reagent grade), iodoethane ( $C_2H_5I$ , analytical reagent grade), cuprous iodide (98%), L(-)-proline (98%), maleic anhydride, *p*-chloranil, hydrochloric acid (HCl) and graphite felt were obtained from commercial suppliers. All chemicals and reagents were used as received unless otherwise stated. Potassium carbonate ( $K_2CO_3$ ) and graphite felt was dried under vacuum at 100 °C for 24 h. In addition, synthesis of **1** and benzo[ghi]perylene-3,4,6,7,9,10-hexacarboxylic 3,4:6,7:9,10-tri(2,6-diisopropyl phenyl)imide (**2**) and *N,N'*-bis(2,6-diisopropylphenyl)-3,4:9,10-perylenetetracarboxdiimide (**3**) were prepared according to the literatures [S1].

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance 400 and 500 spectrometer, with working frequencies of 400 and 500 MHz. Chemical shifts are given in parts per million (ppm) and referred to TMS as internal standard.  $^1H$  coupling constants *J* are given in Hertz (Hz). High-resolution mass spectra (HRMS) were acquired on the Thermo Scientific Exactive Plus Mass spectrometer equipped with electrospray ionization (ESI) source. The UV/Vis/NIR spectra were recorded on a Perkins Elmer Lambda 900 spectrometer equipped with a PTP-1 Peltier temperature controller.

## 2. Fabrication of organic-lithium flow batteries and electrochemical measurements

The non-aqueous electrolyte preparation and organic-lithium redox flow cell assembly were completed inside an argon-filled glove box (H<sub>2</sub>O content: 0.35 ppm; O<sub>2</sub> content: 0 ppm) and under an Ar atmosphere into half lithium batteries using CR2032 coin cell hardware. The RFBs electrolyte was prepared by dissolving **1** or **2** or **3** and lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) (battery grade) in a mixture of 1,3-dioxacyclopentane/ 1,2- dimethoxyethane (DOL/DME, 1:1 by volume) [or lithium hexafluorophosphate (LiPF<sub>6</sub>) (battery grade) in a mixture of ethylene carbonate / dimethyl carbonate (EC/DMC, 1:1 by volume)] at room temperature, with concentrations of 0.03 M **1** or **2** and 1.0 M LiTFSI. The battery was assembled with a 0.25 cm thick graphite felt disk (SGL Carbon Group, Germany) soaked with 0.05 mL of the above electrolyte as a working electrode and a piece of lithium disk as a counter electrode, with a porous polypropylene film as the separator (Celgard 2400, USA) in between. [S2] The whole assembly was subsequently sealed in the battery compartment. The current rates for galvanostatic measurements were calculated based on the theoretical specific capacity of each compound.

The cyclic voltammograms of the batteries composed of **1**, **2** and **3** were conducted on two-electrode cells with a lithium disk as the counter electrode and cycled within a voltage window of 1.65–3.5 V (vs. Li/Li<sup>+</sup>) under a scan rate of 0.1 mV s<sup>-1</sup> on an electrochemical workstation (IVIUM, Netherlands). The galvanostatic charging/discharging experiments were measured on a Neware battery testing system (BTS7.5.6, Shenzhen, China) in the potential range of 1.65-3.2 V vs. Li/Li<sup>+</sup> for **1-3** batteries at varies current densities. The reversibility of the redox reactions were validated by UV-Vis-NIR spectroscopy. Samples were prepared in a glove-box under the protection of Ar. Electrolyte was used as solvent to dissolve both the discharged and recharged forms of active materials for UV-Vis-NIR measurements. Conductivity of the electrolyte solutions were measured using conductivity meter (INESA, DDSJ-308F, Shanghai, China). Viscosities of all the electrolyte solutions were measured using a rotary viscometer (CNSHP, NDJ-5S, Shanghai, China). All electrochemical testing was conducted at room temperature.

The theoretical volumetric capacity of the electrolyte can be calculated by the following formula:

$$C = \frac{m \cdot n \cdot F}{M \cdot V}$$

In the formula, C, m, n, F, M and V respectively mean the theoretical volumetric capacity (Ah L<sup>-1</sup>), mass (g), the transferred electron number in each structural unit (number), Faraday's constant (C mol<sup>-1</sup>), molar mass (g mol<sup>-1</sup>) and volume (L).

### 3. Battery performances

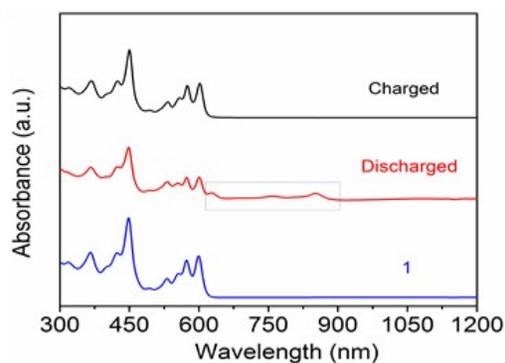


Figure S1. UV-Vis-NIR spectra of pristine, discharged, and recharged **1** in the electrolyte.

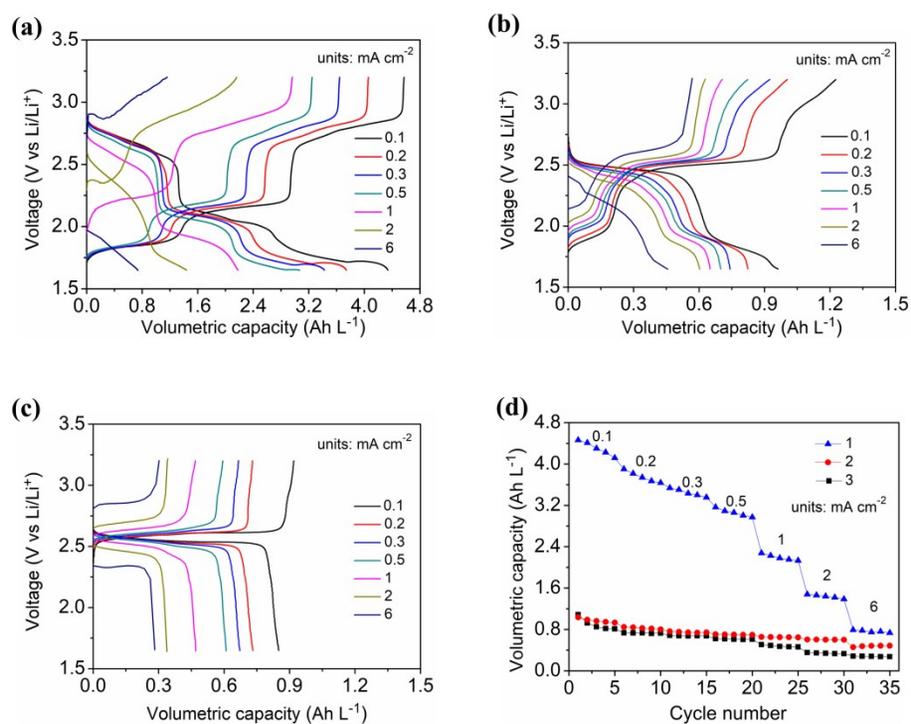
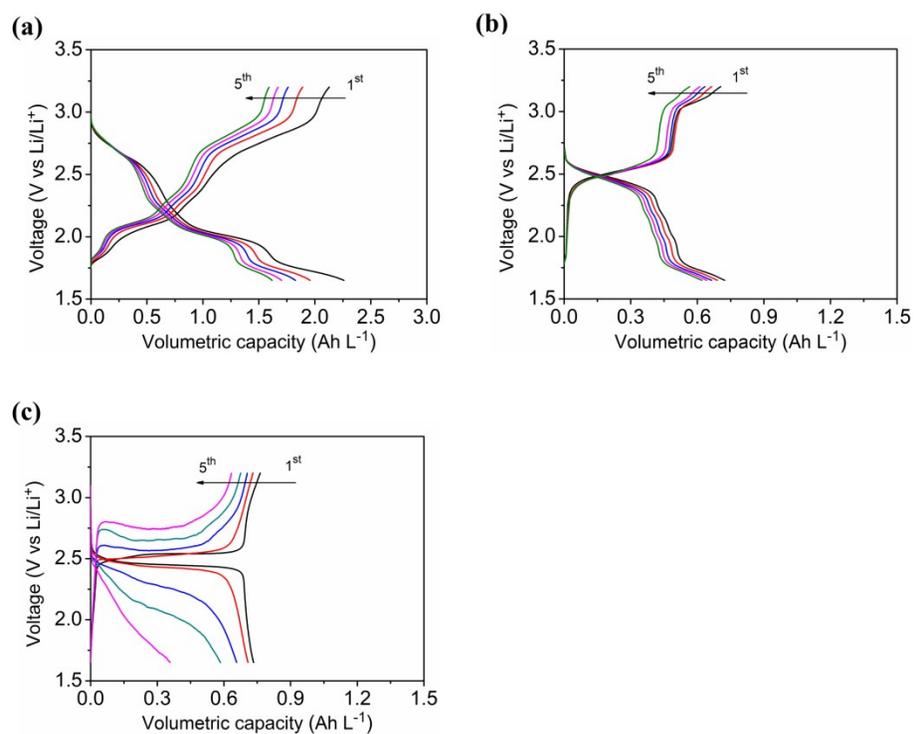
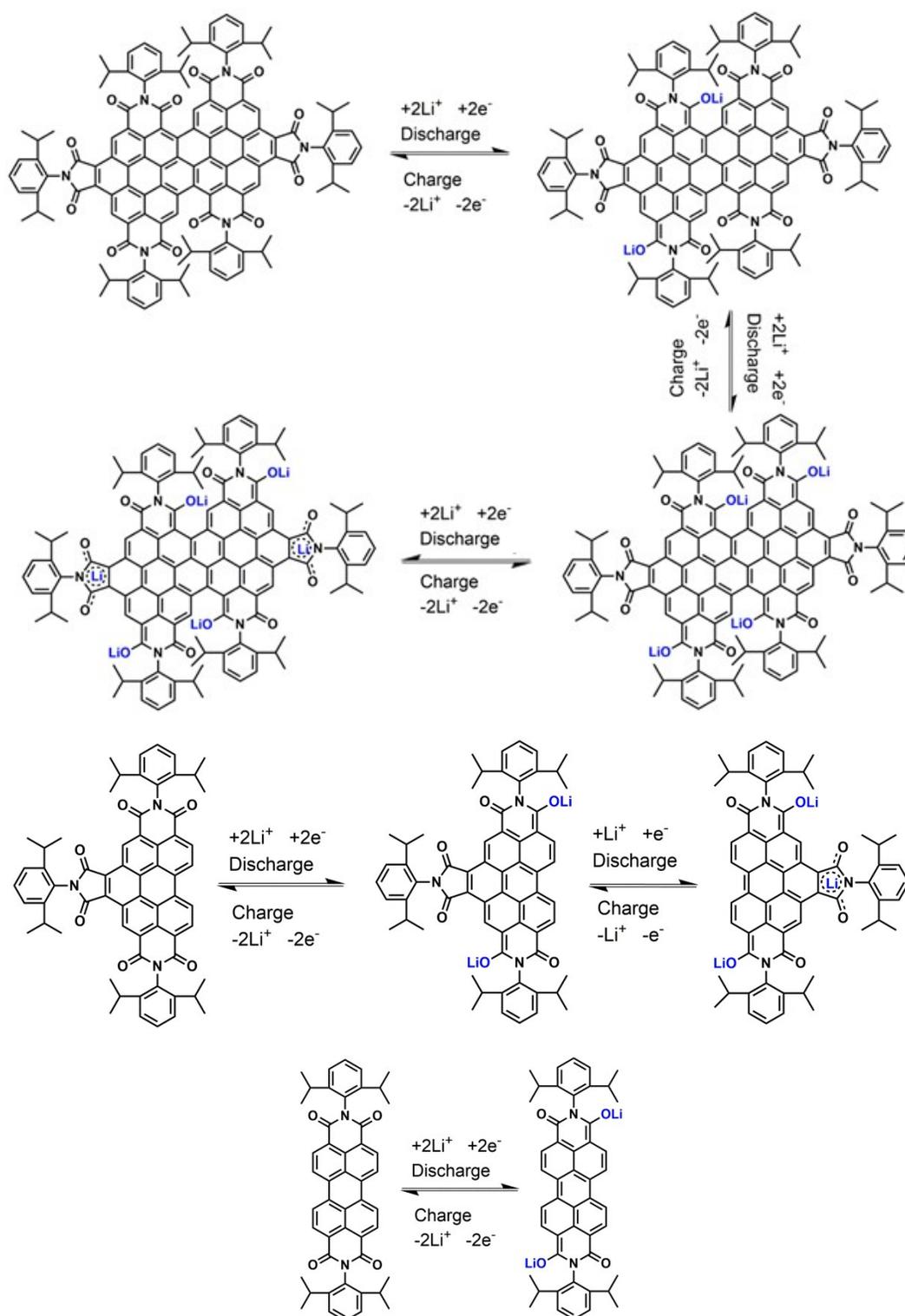


Figure S2. Charge/discharge curves at 0.1, 0.2, 0.3, 0.5, 1, 2 and 6 mA cm<sup>-2</sup> for the batteries of **1** (a), **2** (b) and **3** (c), and their cycling performances at different current rates (d) in DOL/DME (1:1 in volume) with 1.0 M LiTFSI as the electrolyte.



**Figure S3.** The galvanostatic charge/discharge curves of **1** (a), **2** (b) and **3** (c) (0.03M) in EC/DMC (1:1 in volume) with 1.0 M LiPF<sub>6</sub> for the first five cycle under a current density of 0.2 mA cm<sup>-2</sup> at room temperature.

#### 4. Electrochemical redox reaction Mechanism



**Scheme S1:** Schematic diagram for the proposed reversible electrochemical redox mechanisms of the batteries 1-3.

## 5. TGA curves

Thermal stabilities were analyzed using a TGA/DSC analyzer (METTLER TOLEDO, TGA/DSC 3+). The thermal properties of the compounds of **1-3** were tested in Ar atmosphere from 120 °C to 800 °C at a heating rate of 10°C min<sup>-1</sup>. As shown in Figure S4, the thermogravimetric analysis (TGA) curves show that **1** is thermally stable up to 450 °C, while **2** and **3** starts to decompose at 180 °C and 200 °C, respectively, somewhat indicating the high stability and safety of **1** as a redox-active electrode material in organic-lithium redox-flow batteries. [S3]

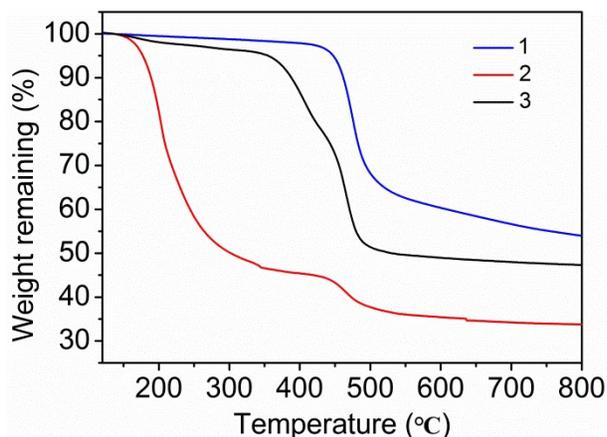


Figure S4. Thermogravimetric analysis curves of **1**, **2** and **3**.

## 6. Viscosities and conductivities

In order to get a further insight some basic parameters of the electrolytes contained ROMs **1-3** (DOL/DME electrolyte of LiTFSI), the viscosities and conductivities of these electrolyte systems were measured at room temperature. The viscosities of ROMs **1-3** are 1.43, 1.46 and 1.52 mPa s, respectively, and the conductivities of ROMs **1-3** are 12.90, 12.92 and 12.86 mS cm<sup>-1</sup>, respectively. These results indicate that the improvements of ROM **1** may not be due to the viscosity and conductivity of the electrolyte.

## 7. References

- [S1] a) L. Li, Y. J. Hong, D. Y. Chen, M. J. Lin, *Electrochim. Acta*, 2017, **254**, 255–261; b) L. Li, Y. J. Hong, Y. Lin, W. C. Xiao, M. J. Lin, *Chem. Commun.*, 2018, **54**, 11941–11944.
- [S2] a) W. Wang, W. Xu, L. Cosimbescu, D. Choi, L. Li, Z. Yang, *Chem. Commun.*, 2012, **48**, 6669–6671; b) Y. Ding, Y. Li, G. Yu, *Chem*, 2016, **1**, 790–801.
- [S3] Z. Luo, L. Liu, Qing Zhao, F. Li, J. Chen, *Angew. Chem., Int. Ed.*, 2017, **56**, 12561–12565.