



# Reversible lithium storage behaviour of aromatic diimide dilithium carboxylates



M Veerababu, U.V Varadaraju, R Kothandaraman\*

Department of Chemistry, Indian Institute of Technology Madras, Chennai 600 036, India

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## ABSTRACT

Electrochemical lithiation/delithiation studies are carried out on three different aromatic diimide lithium carboxylates. Among all, naphthalene diimide based dilithium carboxylate delivers a remarkably stable capacity of  $134 \text{ mAh g}^{-1}$  at 2.24 V vs. Li/Li<sup>+</sup> over 125 cycles with a low polarization of 50 mV. A striking feature is that, the lithiation/delithiation process is biphasic with excellent plateau behaviour in the voltage-composition profile. DFT calculations confirm the lower band gap and higher electron affinity for this compound.

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## 1. Introduction

Organic materials have carved a niche for themselves not only in mature technologies such as organic light emitting diodes (OLEDs) but also in other emerging energy related technologies e.g., all organic thermoelectrics (OTEs), redox flow batteries (RFBs), photovoltaics (PVs), electrochromic devices (ECDs), to name a few [1–5]. Organic materials are environmentally benign alternatives to their inorganic counterparts, which in most cases contain toxic elements [6,7]. In addition, they offer technological advantages such as ease of processing, flexible design etc. In the context of lithium-ion batteries (LIBs) and probably sodium-ion batteries (NIBs) in the near future several organic based electrode materials such as redox active conjugated aromatic, non-aromatic carbonyl compounds (polyimides, organosulfide polymers, and carboxylates), thio-ethers, nitrosyls, and conjugated aromatic hydrocarbons were explored [7–21]. Most organic compounds react with Li in the voltage range of 1–2.5 V (vs Li/Li<sup>+</sup>) with a few exceptions wherein the reactions occur at voltages as high as 3.5 V [7,8,22,23]. Recently, the problem of dendrite formation prohibiting the use of Li metal as anode is addressed (through interfacial engineering) and the efforts hold promise [24,25]. Use of Li metal as anode could be a reality in the near future. This opens the possibility of exploring a whole range of new materials capable of intercalation/insertion reactions with Li. Organic materials fit very well into this

scheme. In the literature density functional theory (DFT) calculations, which probe the relation between the structure of the compounds with their redox potential and storage capacity, were reported [26–28].

The problems associated with the use of organic compounds in LIBs are: (i) dissolution of the compounds in the electrolyte resulting in capacity fade [7] (ii) multiple redox steps [7,8,12] (iii) large polarization due to poor electronic conductivity and (iv) the absence of well-defined plateau region in the voltage-composition profiles [7,8]. Polymerization of the redox active molecules (poly benzoquinones, polyimides and aromatic poly anhydrides) and conversion of the redox active imide functional group in to its imide lithium salt (pyromellitic diimide dilithium salt, naphthalene diimide dilithium salt) were perceived to reduce dissolution of the active material [8,29–33]. We report here a simple and elegant alternate approach. A glycine group is attached to the framework of redox active aromatic dianhydrides to yield the corresponding diimide carboxylic acids which are, in turn, converted to the lithium carboxylates.  $\pi$ - $\pi$  stacking of the aromatic core coupled with intermolecular interaction between the lithiooxycarbonyl groups is expected to enhance the electronic conductivity as well as mitigate the dissolution problem in comparison to the polymeric counterparts and simple lithium salts of diimides [34,35]. Synthesis of the aromatic diimide dilithium carboxylate is very facile and can be affected under mild conditions. Three different aromatic diimide dilithium carboxylates namely, dilithium salt of N,N'-bis (glycynyl) biphenyl diimide (Li<sub>2</sub>-BBDI), dilithium salt of N,N'-bis (glycynyl) pyromellitic diimide (Li<sub>2</sub>-BPDI) and dilithium salt of N,N'-bis (glycynyl) naphthalene diimide

\* Corresponding author.

E-mail address: [rkraman@iitm.ac.in](mailto:rkraman@iitm.ac.in) (R. Kothandaraman).

(Li<sub>2</sub>-BNDI) with three different aromatic cores, biphenyl, benzene and naphthalene, respectively were synthesized. All the phases prepared in this study are reported for the first time.

## 2. Experimental

### 2.1. Materials

Absolute ethanol 99% (Jiangsu Huaxi International Trade Co. Ltd. China), Li<sub>2</sub>CO<sub>3</sub> (Sd-fine-Chem. Ltd.), Pyromellitic dianhydride (PMDA), 3,3',4,4'-Biphenyltetracarboxylic dianhydride (BPDA) and 1,4,5,8-Naphthalenetetracarboxylic dianhydride (NTCDA) were obtained from Sigma-Aldrich, Glacial acetic acid (Alfa Aesar). All reagents were used as received.

### 2.2. Synthesis of diimide dicarboxylic acids

N,N'-bis (glyciny)l pyromellitic diimide (H<sub>2</sub>BPDI) was synthesized according to the reported procedure [36]. Pyromellitic dianhydride (1.635 g, 7.5 mmol), glycine (1.125 g, 15 mmol) were dissolved in glacial acetic acid (40 mL) and refluxed for 4 h. The product was filtered and washed with de-ionized water several times followed by drying overnight in oven at 70 °C. Same procedure was followed for the synthesis of N,N'-bis (glyciny)l biphenyl diimide (H<sub>2</sub>BBDI) and N,N'-bis (glyciny)l naphthalene diimide (H<sub>2</sub>BNDI) with the corresponding dianhydride as starting material (Scheme 1). The structural formulae of the three imide carboxylates are shown in Fig. 1.

NMR spectra: (a). H<sub>2</sub>BPDI. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 500 MHz): δ 8.36 (s, 2H, ArH), δ 4.40 (s, 4H, CH<sub>2</sub>). <sup>13</sup>C NMR (DMSO-d<sub>6</sub>, 500 MHz): δ 168.22 (-COOH), δ 165.89 (-N-C=O), δ 137.39 (Ar-C), δ 118.82 (Ar-C), δ 53.11 (-CH<sub>2</sub>-). (b). H<sub>2</sub>BBDI. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 500 MHz): δ 8.38 (s, 2H, ArH), δ 8.34 (d, 2H, 8 Hz, ArH), δ 8.06 (d, 2H, 8 Hz, ArH), δ 4.36 (s, 4H, -CH<sub>2</sub>-). <sup>13</sup>C NMR (DMSO-d<sub>6</sub>, 500 MHz): δ 169.31 (-COOH), δ 167.33 (-N-C=O), δ 145.01 (Ar-C), δ 134.40 (Ar-C), δ 132.96 (Ar-C), δ 131.68 (Ar-C), δ 124.60 (Ar-C), δ 122.95 (Ar-C), δ 39.53 (-CH<sub>2</sub>-). (c). H<sub>2</sub>BNDI. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 500 MHz): δ 8.72 (s, 4H, ArH), δ 4.76 (s, 4H, -CH<sub>2</sub>-). <sup>13</sup>C NMR (DMSO-d<sub>6</sub>): δ 169.48 (-COOH), δ 162.69 (-N-C=O), δ 131.51 (Ar-C), δ 126.76 (Ar-C), δ 126.47 (Ar-C), δ 41.98 (-CH<sub>2</sub>-).

### 2.3. Synthesis of diimide dilithium carboxylates

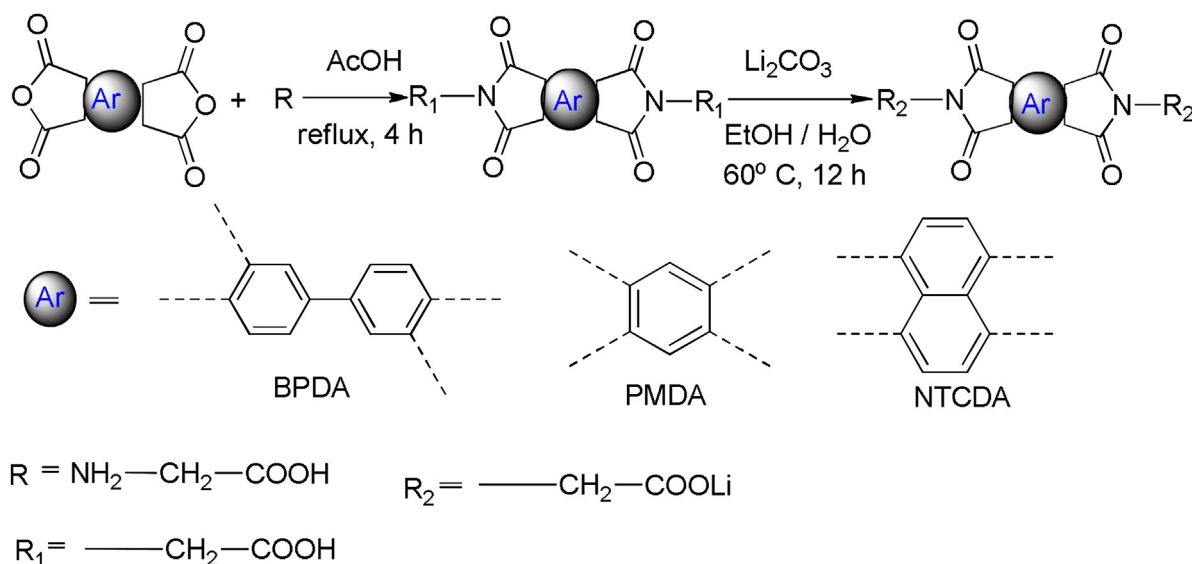
(i). Dilithium salt of N,N'-bis (glyciny)l biphenyl diimide (Li<sub>2</sub>-BBDI): Stoichiometric amounts of H<sub>2</sub>BBDI (0.5 mmol) and Li<sub>2</sub>CO<sub>3</sub> (0.5 mmol) were added to 15 mL of 1:4 v/v water and ethanol mixture followed by stirring at 60 °C for 12 h. The precipitate obtained was washed with absolute ethanol several times and dried at 70 °C in vacuum oven for 24 h. White crystalline powder of Li<sub>2</sub>-BBDI was obtained in 92% yield with respect to H<sub>2</sub>BBDI. <sup>1</sup>H NMR (D<sub>2</sub>O, 500 MHz): δ 8.19 (s, 2H, ArH), δ 8.15 (d, 2H, 8 Hz, ArH), δ 8.01 (d, 2H, 8 Hz, ArH), δ 4.28 (s, 4H, -CH<sub>2</sub>-). <sup>13</sup>C NMR (D<sub>2</sub>O, 500 MHz): δ 174.44 (COOLi), δ 169.58 (-N-C=O), δ 169.45 (-N-C=O), δ 145.22 (Ar-C), δ 133.76 (Ar-C), δ 132.40 (Ar-C), δ 131.12 (Ar-C), δ 124.15 (Ar-C), δ 122.46 (Ar-C), δ 41.11 (-CH<sub>2</sub>-).

(ii). Dilithium salt of N,N'-bis (glyciny)l pyromellitic diimide (Li<sub>2</sub>-BPDI): Stoichiometric amounts of H<sub>2</sub>BPDI (0.66 mmol) and Li<sub>2</sub>CO<sub>3</sub> (0.66 mmol) were added to 25 mL of 1:4 v/v water and ethanol mixture, stirred at 60 °C for 12 h. The precipitate obtained was washed with absolute ethanol several times and dried at 70 °C in vacuum oven for 24 h. White crystalline powder of Li<sub>2</sub>-BPDI was obtained in 90% yield with respect to H<sub>2</sub>BPDI. <sup>1</sup>H NMR (D<sub>2</sub>O, 500 MHz): δ 8.40 (s, 2H, ArH), δ 4.35 (s, 4H, CH<sub>2</sub>). <sup>13</sup>C NMR (D<sub>2</sub>O, 500 MHz): δ 174.03 (COOLi), δ 167.82 (-N-C=O), δ 137.29 (Ar-C), δ 118.53 (Ar-C), δ 41.40 (-CH<sub>2</sub>-).

(iii). Dilithium salt of N,N'-bis (glyciny)l naphthalene diimide (Li<sub>2</sub>-BNDI): Stoichiometric amounts of H<sub>2</sub>BNDI (0.5 mmol) and Li<sub>2</sub>CO<sub>3</sub> (0.5 mmol) were added to 15 mL of 1:4 v/v water and ethanol mixture, stirred at 60 °C for 12 h. The final product was washed with absolute ethanol several times and dried at 70 °C in vacuum oven for 24 h. Brown crystalline powder of Li<sub>2</sub>-BNDI was obtained in 95% yield with respect to H<sub>2</sub>BNDI. <sup>1</sup>H NMR (D<sub>2</sub>O, 500 MHz): δ 8.64 (s, 4H, ArH, δ 4.71) (s, 4H, -CH<sub>2</sub>-). <sup>13</sup>C NMR (D<sub>2</sub>O, 500 MHz): δ 174.74 (COOLi), δ 163.93 (-N-C=O), δ 131.14 (Ar-C), δ 126.21 (Ar-C), δ 126.07 (Ar-C), δ 43.96 (-CH<sub>2</sub>-).

### 2.4. Material characterization and electrochemical measurements

The IR spectra of samples were recorded on JSCO 4100-FT-IR spectrometer. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded at Bruker AVANCE 500 MHz spectrometer. The working electrodes were prepared by 50 wt% of active material, 40 wt% of acetylene black



Scheme 1. General synthesis of imide carboxylates.

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