Supplementary Information

Polyquinoneimines for Lithium Storage: More than Sum of Its Parts

Bingbing Tian,a,b Guo-Hong Ning,b Wei Tang,b Chengxin Peng,b Dingyi Yu,b Zhongxin Chen,b Yinglin Xiao,a Chenliang Su,a,b and Kian Ping Loh,a,b

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

K. P. Loh E-mail: chmlohp@nus.edu.sg Fax: (+65) 67791691
**Synthesis of Polyquinoneimines (PQIs)**

All the starting materials, 2,6-diaminoanthraquinone (DAAP), 1,4,5,8-naphthalenetetracarboxylic dianhydride (NTCDA), Perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA) and pyromellitic dianhydride (PMDA) were purchased from Sigma-Aldrich. The PQIs were synthesized via a DMF (N,N-Dimethylformamide, anhydrous, 99.8%, Sigma-Aldrich) solution process. Specifically in a typical PQI-1 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-1 is obtained. The PQI-3 synthetic method is similar to PQI-1 whereas a claret-red powder obtained. We also prepared PQI-2 via the similar synthetic procedure using the low solubility PTCDA. In order to get a more fully reacted product, much longer reaction time (7 days) was implemented in this experiment. Finally, a gray-black PQI-2 powder obtained according to the above processing steps.

![Molecular structure](image)

**Scheme S1.** Molecular structure of DAAP, NTCDA, PTCDA, PMDA, PQI-1, PQI-2 and PQI-3.
**Table S1** Theoretical gravimetric capacity of DAAP, NTCDA, PTCDA, PMDA, PQI-1, PQI-2 and PQI-3. (The theoretical gravimetric capacity of DAAP and dianhydrides are calculated based on a two electrons reaction in one monomer, the theoretical gravimetric capacity of PQIs are calculated based on a four electrons reaction in one monomer).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Theoretical gravimetric capacity (mAh g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DAAP</td>
<td>225</td>
</tr>
<tr>
<td>NTCD A</td>
<td>200</td>
</tr>
<tr>
<td>PTCDA</td>
<td>137</td>
</tr>
<tr>
<td>PMDA</td>
<td>246</td>
</tr>
<tr>
<td>PQI-1</td>
<td>228</td>
</tr>
<tr>
<td>PQI-2</td>
<td>180</td>
</tr>
<tr>
<td>PQI-3</td>
<td>272</td>
</tr>
</tbody>
</table>

**FTIR characterizations of PQIs and precursors:**

The FTIR spectroscopy of PQI and their precursors are performed to confirm the successfully polymerization of PQIs. As shown in Fig. S1, the peaks around 1136 and 940 cm⁻¹ in the precursors (NTCDA, PTCDA and PMDA) are attributed to the stretch of the C-O-C band, which almost disappeared in PQIs after polymerization. All the PQIs have a new peak at the 1360 cm⁻¹ band compare with dianhydrides, which is ascribed to the C–N stretch, indicating that the polymerization is successful. Moreover, the absorbance signals at 3332 and 3423 cm⁻¹, attributed to the vibrational modes of the NH₂ bonds (primary amine) connected with benzene ring disappeared, also indicating the polycondensation reactions of dianhydrides with diamines. Furthermore, the characteristic band of C=O shifts to from 1772 cm⁻¹ to 1687 cm⁻¹. This phenomenon derives from conjugation, which leads to a shift in the band towards
lower wave number. The strong absorption at 1687 cm\(^{-1}\) also suggests that the carbonyl groups are well retained.\(^3\)\(^4\)

![FTIR curves of PQI-2 and PQI-3 with their precursors.](image)

**Fig. S1.** FTIR curves of PQI-2 and PQI-3 with their precursors.

**Table S2** Characteristic FTIR band assignments of DAAP, NTCDA, PTCDA, PMDA, PQI-1, PQI-2 and PQI-3.

<table>
<thead>
<tr>
<th>Group</th>
<th>DAAP</th>
<th>NTCDA</th>
<th>PTCDA</th>
<th>PMDA</th>
<th>PQI-1</th>
<th>PQI-2</th>
<th>PQI-3</th>
</tr>
</thead>
<tbody>
<tr>
<td>C=O, (\nu_{as})</td>
<td>1659</td>
<td>1764</td>
<td>1774</td>
<td>1857</td>
<td>1713</td>
<td></td>
<td>1770</td>
</tr>
<tr>
<td>C=O, (\nu_s)</td>
<td>1627</td>
<td>1728</td>
<td>1743</td>
<td>1771</td>
<td>1672</td>
<td>1671</td>
<td>1718</td>
</tr>
<tr>
<td>C-N, (\nu)</td>
<td>1331</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>1346</td>
<td>1361</td>
<td>1352</td>
</tr>
<tr>
<td>C=C, (\nu)</td>
<td>1572</td>
<td>1728</td>
<td>1595</td>
<td>1722</td>
<td>1593</td>
<td>1589</td>
<td>1571</td>
</tr>
</tbody>
</table>

\(^a\) broaden and overlapping.

**TGA**

TG analysis shows that the decomposition temperature of PQI-2 is \(~500\) °C in N\(_2\) atmosphere, which is higher than PQI-1 and 3. This suggests that the PTCDA and DAAP polymerized and the PQI-2 has a best thermal stability compared with its analogues and precursors. However, PQI-3 shows an even poor thermal stability than its DAAP precursors, indicating a poor polymerization process or unstable polymerization products of PQI-3. This poor thermal stability of PQI-3 is responsible for the inferior cycling performance.
Fig. S2. TGA of PQI-2 and PQI-3 with their precursors.

**Scanning Electron Microscope (SEM) images of PQIs:**

The morphologies of the synthesized PQIs are shown in Fig. S3. PQI-1 and PQI-3 form a regular lamellar structure, but PQI-2 forms irregular rod sheet due to the low solubility of its precursor PTCDA.

Fig. S3. SEM images of PQI-1, PQI-2 and PQI-3 materials.
Transmission Electron Microscope (TEM) images of PQIs:

The TEM images of the PQIs are shown in Fig. S4. The PQI-1 material possesses a nanosheets structure.

**Fig. S4.** TEM images of the PQI-1, PQI-2 and PQI-3 materials.
**Fig. S5.** (a) The second CV curves (scan rate: 0.1 mV s⁻¹) and (b) the second discharge-charge curves of the DAAP, NTCDA and PQI-1 in the 1.5-3.5 V potential range.
From the electrode photographs of DAAP, NTCDA and PQI-1 after 5 discharge-charge cycles, we can clearly see the solubility of different organic electrode materials in electrolyte. The DAAP and NTCDA have an obviously serious dissolution in the electrolyte of 1 M LiTFSI in 1:1 v/v DOL:DME.

Fig. S6. Electrode photographs of DAAP, NTCDA and PQI-1 after 5 discharge-charge cycles.
Fig. S7. (a), (b) the CV curves (scan rate: 0.1 mV s\(^{-1}\)); (c), (d) the first three discharge-charge curves; and (e), (f) cycling performance of the PQI-2 and PQI-3 in the potential range of 1.5-3.5 V.
References


