Supplementary Information

Polyquinoneimines for Lithium Storage: More than Sum of Its Parts

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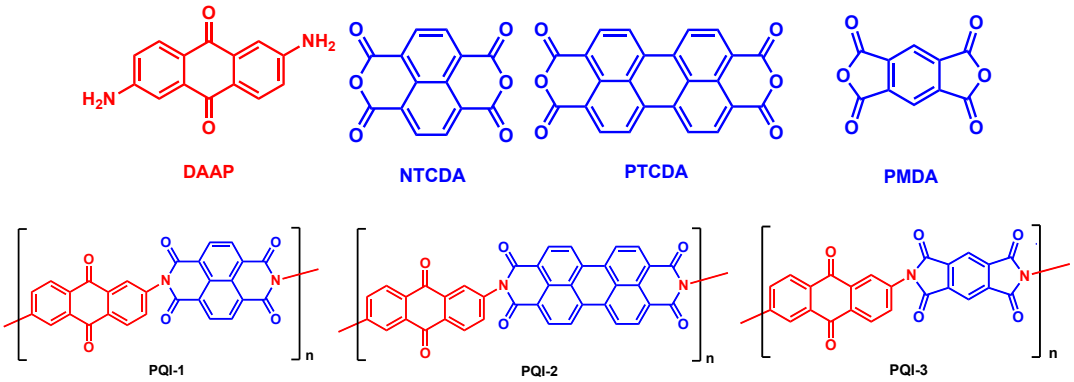
Synthesis of Polyquinoneimines (PQIs)

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. [1-2] 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 ^{o}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 N_2 gas at 140 ^{o}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.



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).

Sample	Theoretical gravimetric capacity (mAh g^{-1})
DAAP	225
NTCDA	200
PTCDA	137
PMDA	246
PQI-1	228
PQI-2	180
PQI-3	272

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 NH_2 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]

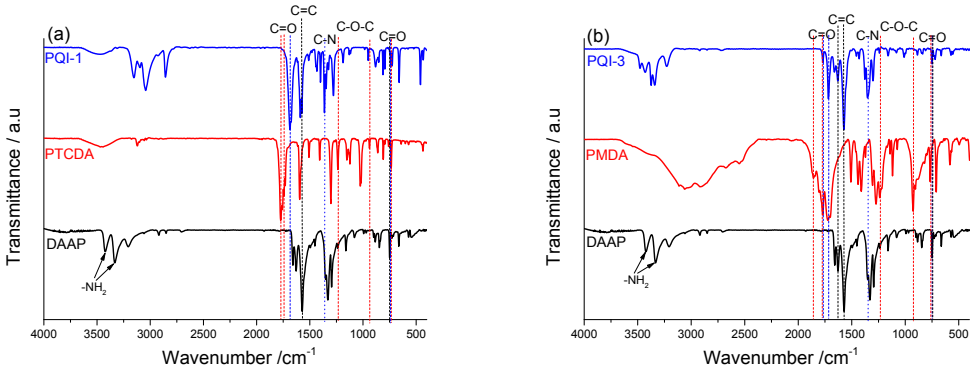


Fig. S1. FTIR curves of PQI-2 and PQI-3 with their precursors.

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

Group	DAAP	NTCDA	PTCDA	PMDA	PQI-1	PQI-2	PQI-3
C=O, ν_{as}	1659	1764	1774	1857	1713	1686[a]	1770
C=O, ν_{s}	1627	1728	1743	1771	1672		1718
C-N, ν	1331	–	–	–	1346	1361	1352
C=C, ν	1572	1728	1595	1722	1593	1589	1571

a, broaden and overlapping.

TGA

TG analysis shows that the decomposition temperature of PQI-2 is ~500 ^{o}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.

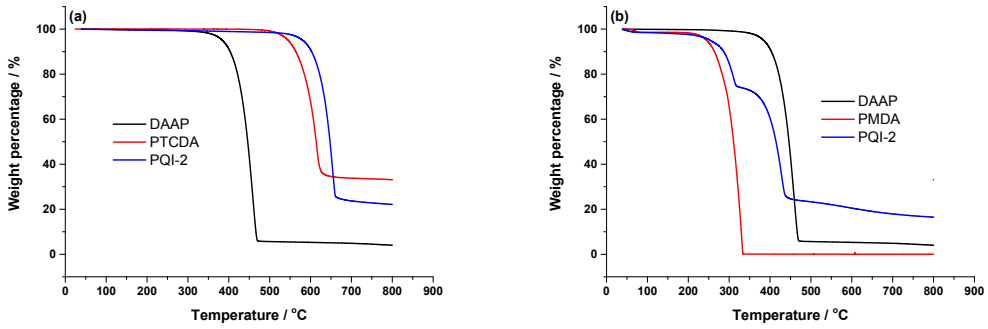


Fig. S2. TGA of PQI-2 and PQI-3 with their precursors.

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.

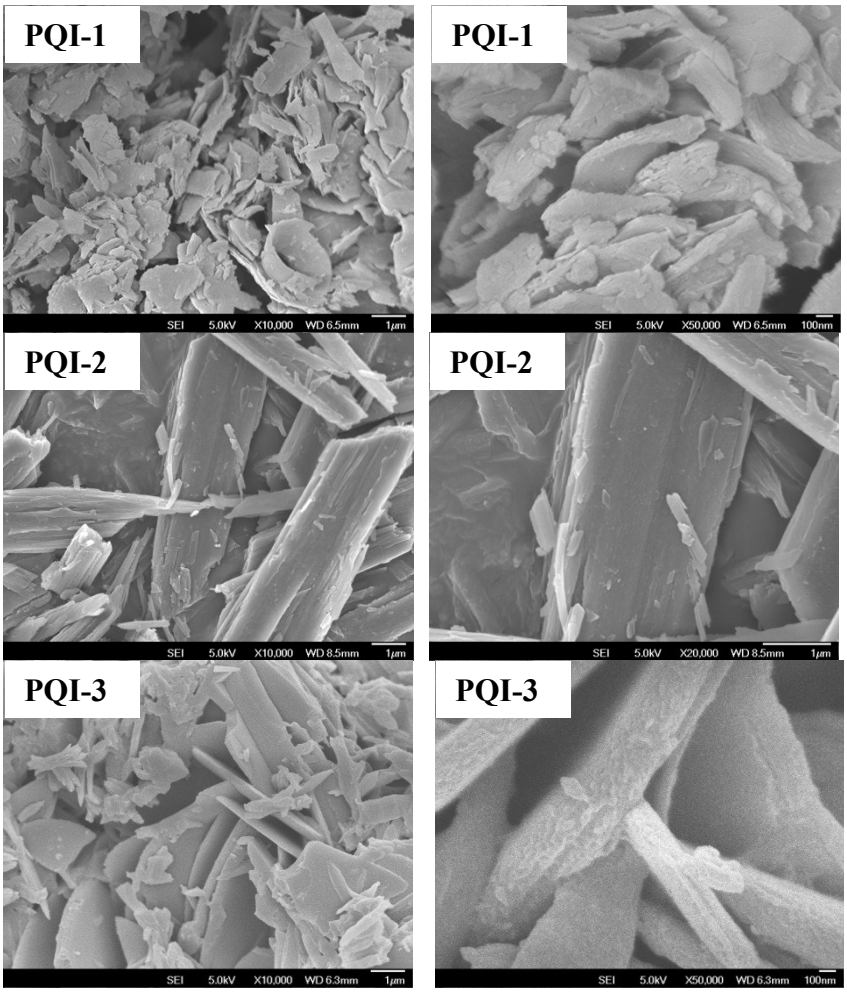


Fig. S3. SEM images of PQI-1, PQI-2 and PQI-3 materials.

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.

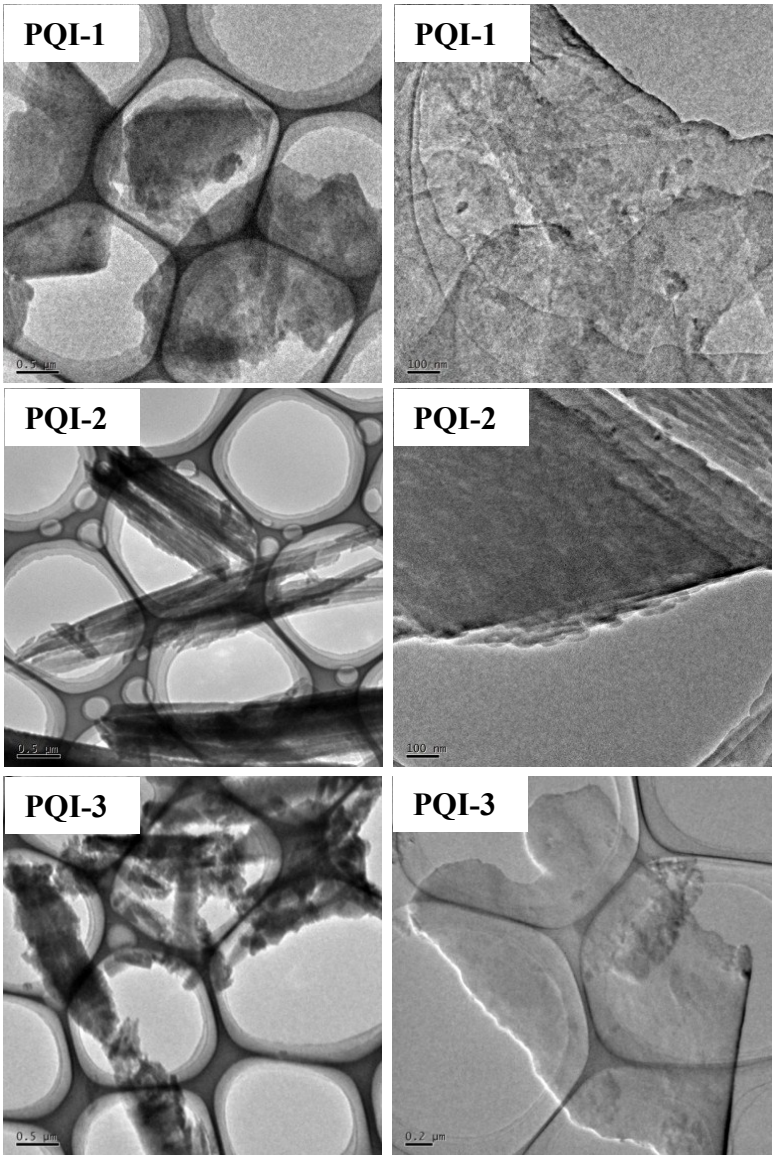


Fig. S4. TEM images of the PQI-1, PQI-2 and PQI-3 materials.

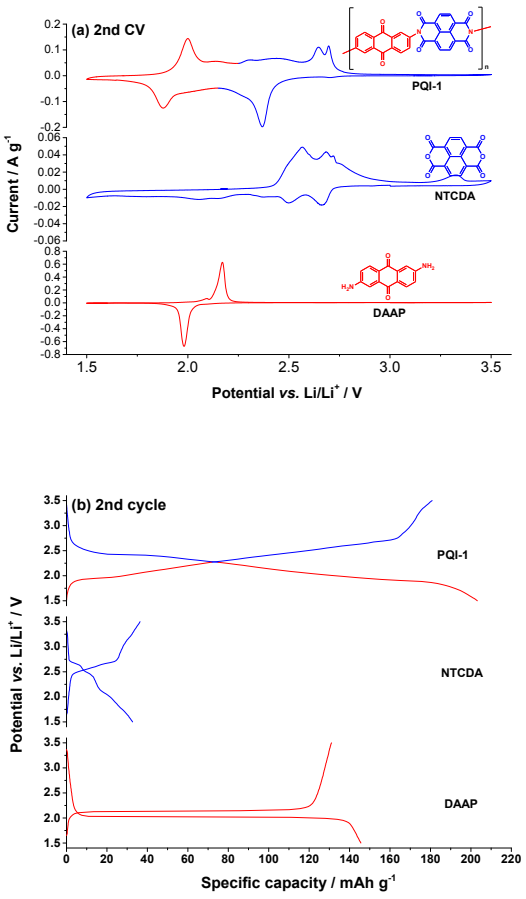


Fig. S5. (a) The second CV curves (scan rate: 0.1 mV s^{-1}) and (b) the second discharge-charge curves of the DAAP, NTCDA and PQI-1 in the 1.5-3.5 V potential range.

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.

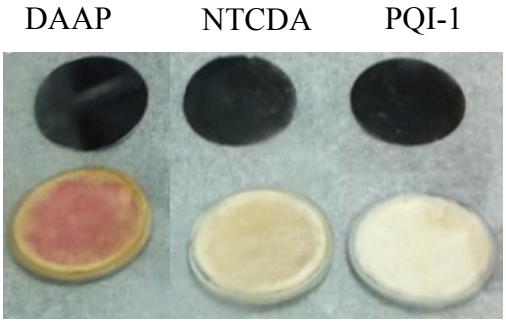


Fig. S6. Electrode photographs of DAAP, NTCDA and PQI-1 after 5 discharge-charge cycles.

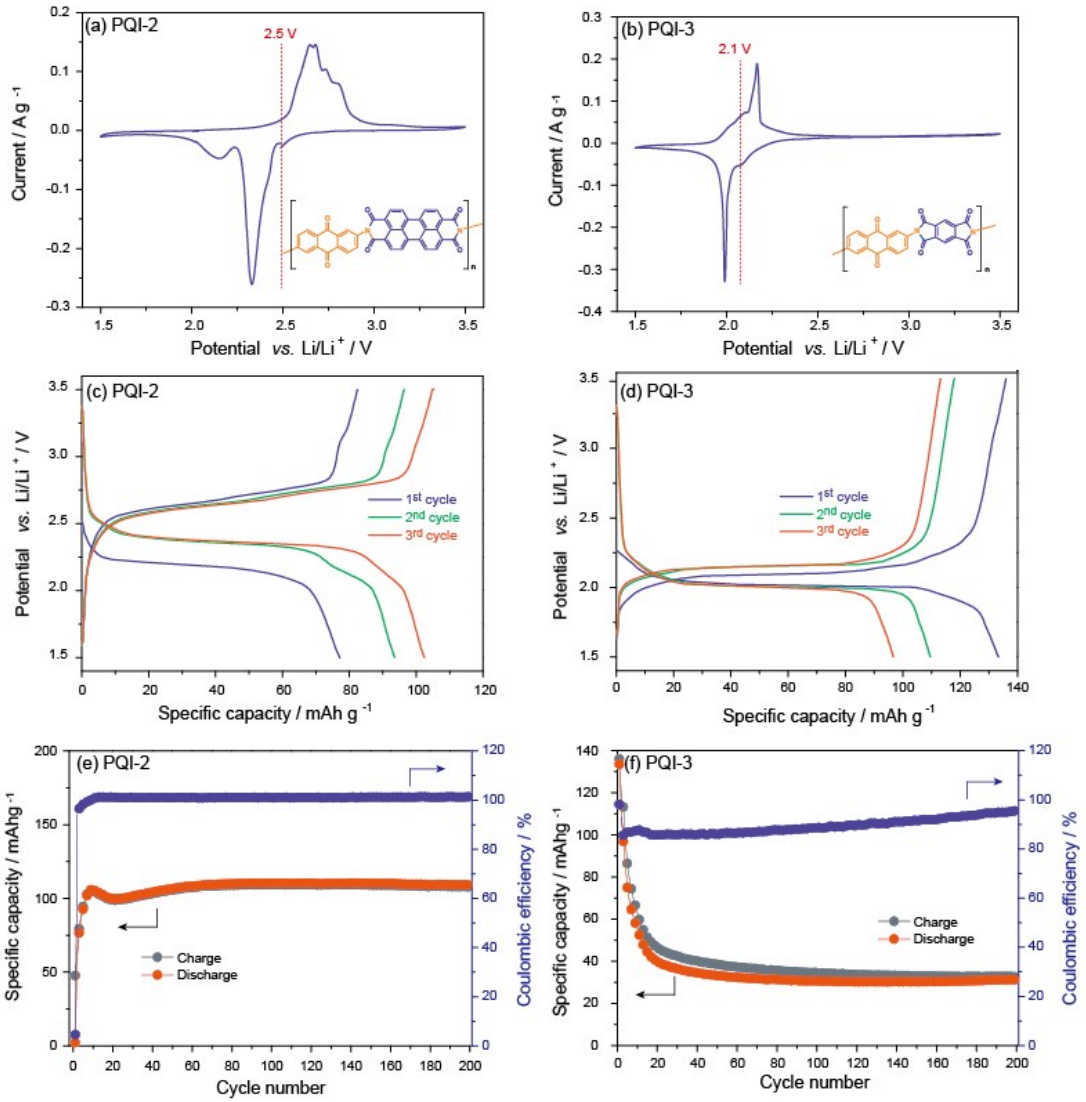


Fig. S7. (a), (b) the CV curves (scan rate: 0.1 mV s^{-1}); (c), (d) the first three discharge-charge curves; and (e), (f) cycling performance of the PQI-2 and PQI-3 in the potential range of 1.5-3.5 V.

References

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