Supporting Information

Mesoporous conjugated polymer based on high free radical density polytriphenylamine derivative: its preparation and electrochemical performance as cathode material for Li-ion batteries

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1. ^{1}H NMR of TDATA monomer

For verifying the TDATA being successfully synthesized, the ^{1}H NMR of TDATA monomer has been measured at 75 ^{o}C with DMSO as solvent, and the results have been shown in the following Fig. S1. According to the Figure, there are two groups of peaks presented in the ^{1}H NMR, in which the chemical shift at 7-8 ppm belongs to the

hydrogen atoms vibration of DMSO (solvent) and the chemical shift at 2-3 ppm is due to that of the TDATA monomer. After the integration of the two groups of peaks between 7-8 ppm, it is found that the ratio of peak area is 2:5, corresponding to the 12 hydrogen atoms at the inner benzene ring of the TDATA monomer and the 30 hydrogen atoms at the outer benzene ring, which is consistent with the hydrogen atoms on the TDATA monomer. The results indicate that TDATA monomer has been successfully synthesized.^{1}H NMR (500 MHz, DMSO-d_6), δ=7.32-7.25 (m, 12H), 7.07-6.96(m,30H).

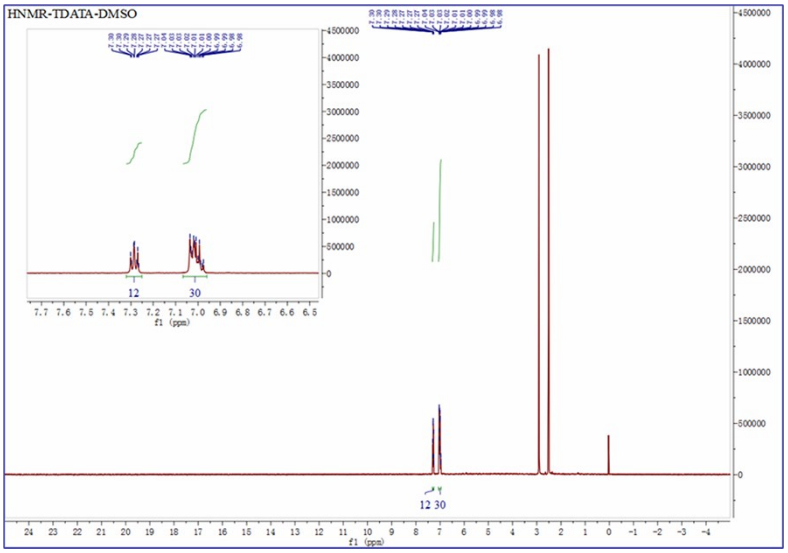

Fig. S1 The ^{1}H NMR figure of TDATA

2. ESI-MS of TDATA monomer

The electron spray ionization mass spectrometry (ESI-MS) was used to analyze the TDATA sample. And the results of ESI-MS testing have been shown in the Fig. S2, in which both molecular ion at 746.3298 m/e and 747.3298 m/e correspond to the $[M]^{+}$ and $[M-H]^{+}$ (M= 4,4′,4″-tris(N,N-diphenyl-amino) triphenylamine (TDATA),

respectively, indicating that TDATA has been successfully synthesized. MS (ESI): calculated $C_{54}H_{42}N_4$ m/z: 746.4, found m/z: 746.4.

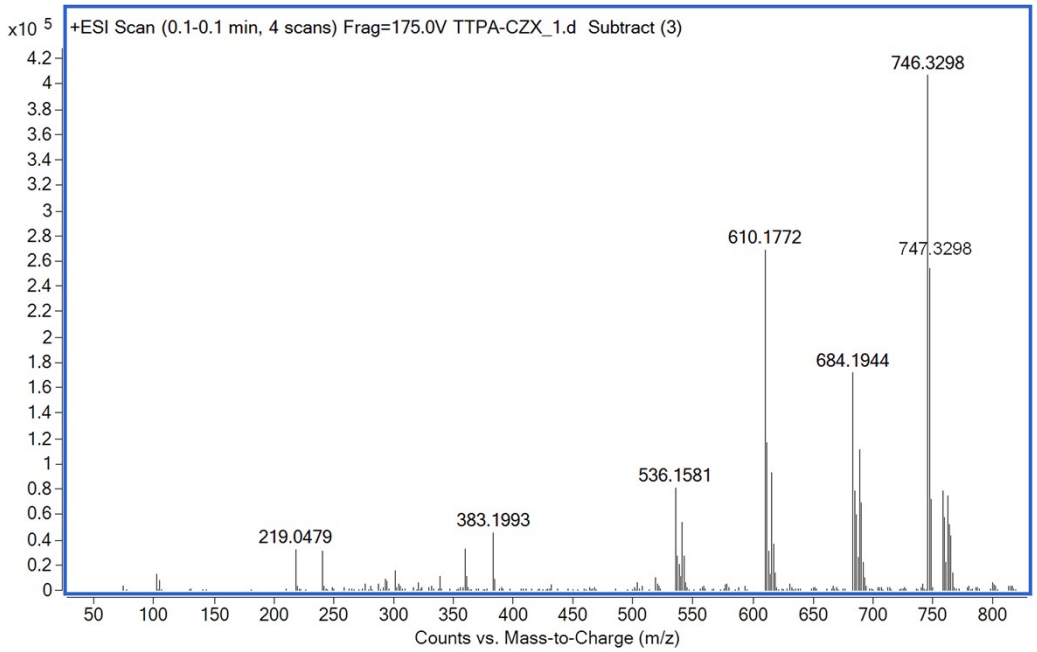

Fig. S2 ESI-MS of TDATA monomer

3. Resonance Raman spectra of PTDATA and PTPA samples

As showed in the Fig. S3, Resonance Raman spectroscopy of the as-prepared PTPA and PTDATA has been made in order to verify the structure of the polymer. The main characteristic peaks of TPA moiety have been displayed in the two samples, involving the C–H in-plane stretching at 1170 cm^{-1}, the C–C inter-ring stretching at 1284 cm^{-1}, the C-N-C stretching at 1498cm^{-1} and the C–C ring stretching at 1602 cm^{-1}. Compared to the PTPA, the some new bands at 1327 and 1349 cm^{-1} appears in the spectrum of PTDATA, which are attributed to the symmetric N-Ar-Ar-N stretching and N-Ar-N stretching respectively. The N-Ar-Ar-N and N-Ar-N moieties contained in the PTDATA polymer indicate that the polymer have been successfully prepared.

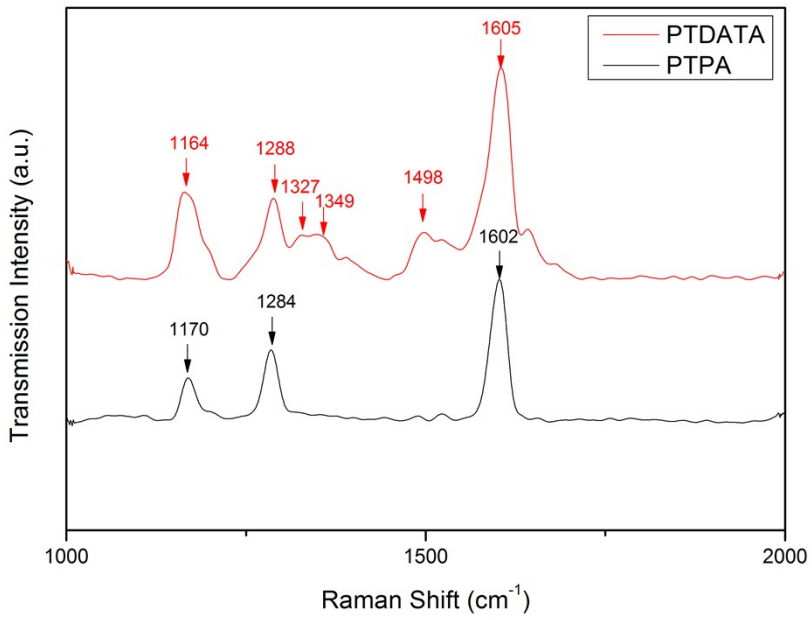

Fig. S3. Resonance Raman spectra of the (a) PTDATA and (b) PTPA samples.

4. Thermogravimetric analysis of PTDATA and PTPA samples

The thermal stability of TPA, TDATA, PTPA and PTDATA samples are also measured by thermogravimetric analysis (TGA), and the measurement is carried out from room temperature to 800 °C with a heating rate of 10 °C/min in a N_2 atmosphere. As shown in the Fig. S4, the small weight loss before about 150 °C for all samples is mainly attributed to the loss of the residue water and solvent molecules remained in the polymers. Specially, the related higher weight loss for PTDATA (about ~4-5 wt %) can be attributed to the produced micro-/mesoporous structure and the high specific surface, which benefits to the absorption of residue water and solvent molecules on the material. With the further temperature programming, both TPA and TDATA monomers show one obvious narrow thermal degradation process with the almost thorough weight loss, which start to thermal degradation at ~150 and ~400 °C and end at ~250 °C and ~520 °C, respectively. This can be attributed to the monodisperse molecular

weight feature for the monomers. Compared to the monomers, the corresponding polymers show the obviously improved thermal-stability and a multi-step mass loss occurred during the temperature-rise period; specially for PTDATA, it stars the remarkably thermal degradation until about 560 ^{o}C, and the polymer still remains a about 70 wt% at the end of 800 ^{o}C. Generally, PTDATA with the improved thermal stability will be beneficial to its practical application as the safe cathode of lithium ion battery in the future.

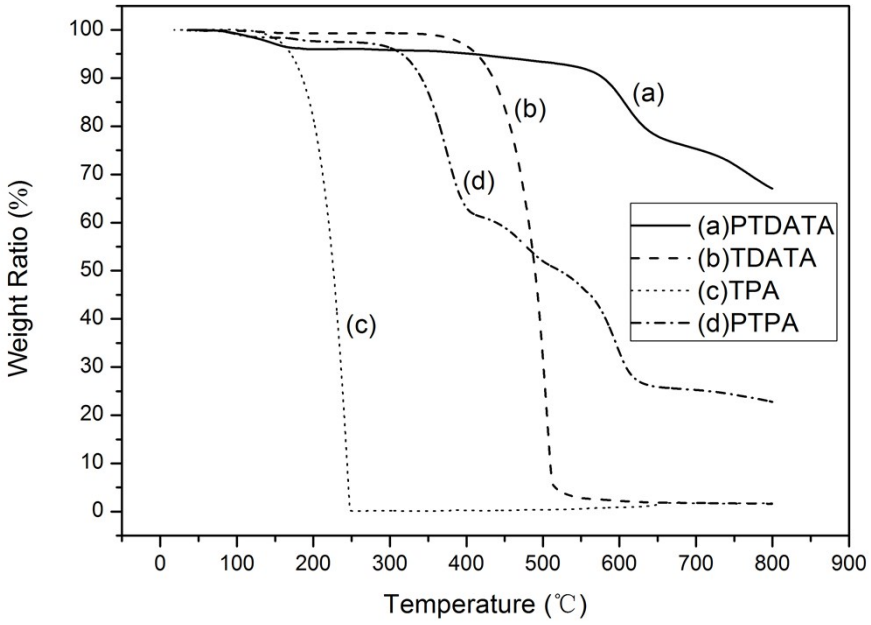

Fig. S4 Thermogravimetric analysis diagram of TDATA and TPA monomers and PTDATA and PTPA polymers

5. Differential molecular isomerism for TDATA and TPA

The monomers of 1- N,1-N,4-N-triphenyl-4-N-[4-(N-[4-(N-phenylanilino)phenyl]anilineo) phenyl]benzene-1,4-diamine) (FTP), and 4,4′,4″-tris(N,N-diphenyl-amino) triphenylamine) (TDATA) have the same monomer molecular formula, belonging to isomers. However, both monomers have different conformational isomers, in which FTP has a more conformational

isomers than TDATA, as shown in Fig. S5. Correspondingly, the PFTP polymer molecular should exhibit much flexibility compared to that of PTDATA, which will affect the morphology of the obtained polymers. Therefore, the presented different morphologies can be considered due to different molecular flexibility of PFTP and PTDATA, in which the rigid structure of PTDATA polymer molecular is benefit to the formation of the organic micro-/mesoporous polymer with with obviously improved surface area of 560.58 m^2/g, while the relatively flexible structure of PFTP results in the a serious aggregated morphology.

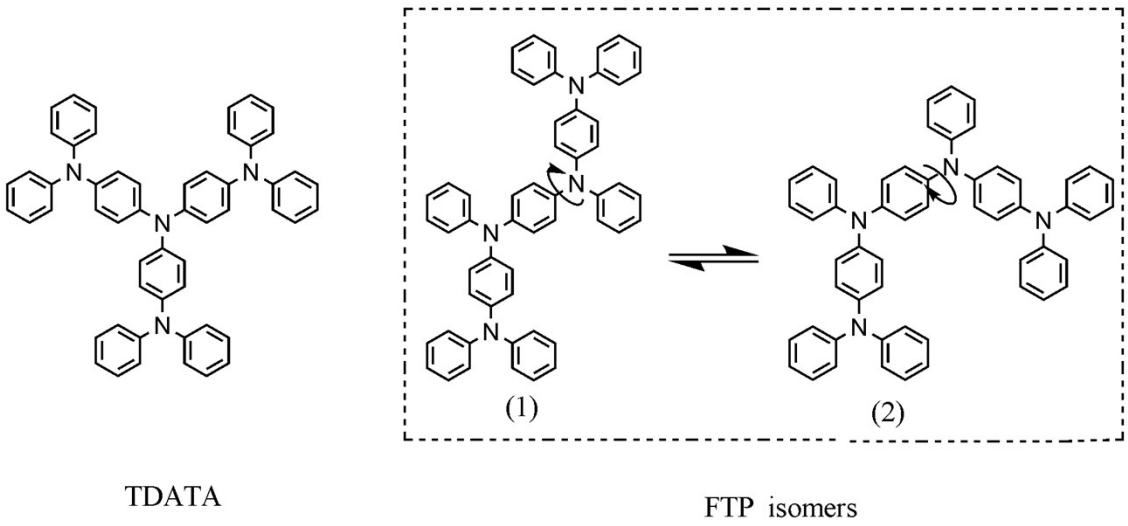

Fig. S5 Differential molecular isomerism for TDATA and TPA monomers