

# *Supporting Information*

## **Cation- $\pi$ induced Lithium-doped conjugated microporous polymer with remarkable hydrogen storage performance**

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## Main materials and Measurements

2-indolinone was purchased from J & K Technology Co., Ltd., and used without further purification. Phosphorus oxychloride and anhydrous FeCl<sub>3</sub> were purchased from Xiya reagent (Chengdu) and used without further purification.

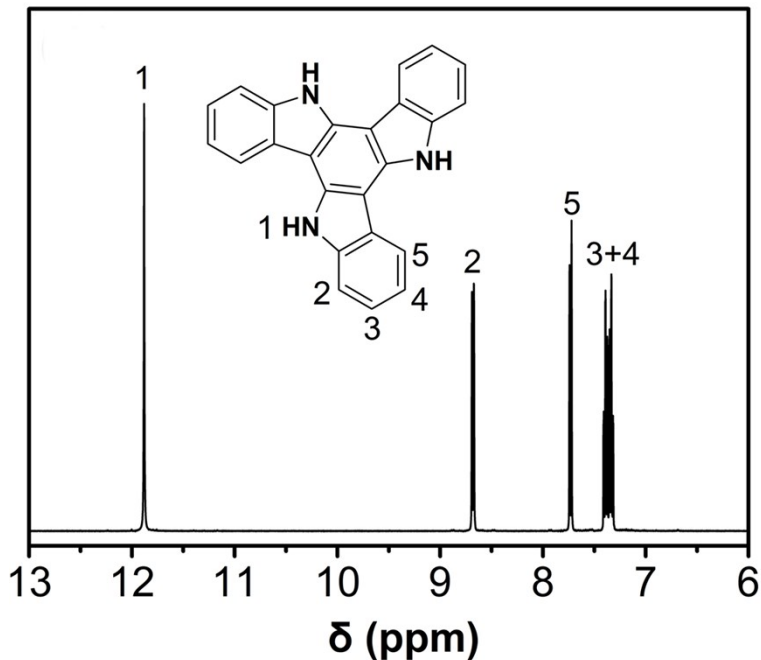
FT-IR spectra were recorded on a Nicolet 6700 FTIR spectrometer. <sup>1</sup>H NMR were performed on Bruker AV-400 spectrometer at 400 MHz while solid-state cross-polarization magic-angle-spinning (CP/MAS) NMR spectrum was recorded on a Bruker Avance III 400 NMR spectrometer. The elemental analysis characterization technique was performed using a Vario EL III apparatus. The ICP-MS experiment was performed on a Perkin Elmer ELAN® DRC II. And thermogravimetric analysis (TGA) was performed on a Setarma TG-92 at a heating rate of 10 °C/min under nitrogen atmosphere. The microscopic features of the samples were carried out on a field-emission scanning electron microscopy (SEM) (S-4800 (Hitachi Ltd)) and high-resolution transmission electron microscopy (HRTEM) (Tecnaï G2 F20 S-TWIN). XRD measurements were carried out on X-ray diffractometer (X'Pert PRO). The UV resonance Raman (UVR) experiments were carried out on LABRAM HR EVO (Horiba) with a 532-nm laser line with the spectrometer pinhole. The objective lens is magnified 100 times and the acquisition time is 100 seconds. UV-vis absorption spectra were detected on a SHIMADZU UV-3150 UV-vis-NIR spectrophotometer. The stoichiometric triazatruxene (TAT) monomer was dissolved in N,N-Dimethylformamide (DMF) (1.0 × 10<sup>-5</sup> M), after the first testing, drop 50μL of 1 equivalent LiCl in distilled water into

quartz cuvette and continue to the second test. Cyclic voltammetry (CV) measurements were carried out on a CHI660E electrochemical workstation (Chenhua Co., Ltd., Shanghai, China) at scan rates of  $0.1 \text{ mV s}^{-1}$  at room temperature. The CR2032 coin-type cells were assembled in an argon-filled glovebox, where both moisture and oxygen levels were less than 1 ppm. The electrodes were fabricated by mixing of 50 wt% active material with Super P (40 wt%), polyvinylidene fluoride (PVDF, 10 wt%) and the polymer PTAT or  $\text{Li}^+$ -PTAT in N-methyl-2-pyrrolidone (NMP) solvent, and then pasted onto the copper foils. Lithium foils were used as counter electrodes and macroporous polypropylene film (Celgard 2400) as the separator. The electrolyte solution was made of 1 M  $\text{LiPF}_6$  in ethylene carbonate (EC)/diethyl carbonate (DEC) (1/1, w/w). Surface areas and pore size distributions were measured by nitrogen adsorption and desorption at 77 K using a static nitrogen adsorption analyzer (JW-BK112). The sample was treated at 120 °C for 24 h before the measurement. The surface area was calculated by Brunauer-Emmett-Teller (BET) equation ( $0.01 < P/P_0 < 0.1$ ). The pore-size-distribution (PSD) curve was obtained from the adsorption branch using non-local density functional theory (NL-DFT) method.

### **Synthesis of triazatruxene**

A mixture of 2-indolinone (4 g, 30 mmol) and  $\text{POCl}_3$  (20 mL) was heated at 100 °C for 8 h. Then, the reaction mixture was poured into ice and neutralized carefully with KOH. After neutralization, the precipitate was filtered to give the crude product as a brown solid. The crude solution in MeOH was absorbed on silica-gel, dried, loaded and eluted

through a thick silica-gel pad with a DCM as a mobile phase. After evaporation of eluate at reduced pressure and recrystallization from DMAc, pure pale yellow solid was obtained. Yield: 48%;  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ )  $\delta$  = 11.88 (1s, 3H, N-H), 8.67 (1d, 3H,  $J=7$  Hz, aromatic H), 7.72 (1d, 3H,  $J=7.4$  Hz, aromatic H), 7.35 (1m, 6H, aromatic H) ppm;  $^{13}\text{C}$  NMR(100 MHz,  $(\text{CD}_3)_2\text{S=O}$ ):  $\delta$  = 138.94, 134.13, 122.86, 122.64, 120.27, 119.50, 111.40, 100.9 ppm; FT-IR spectrum (KBr pellet,  $\text{cm}^{-1}$ ): 3435, 1607, 774. Anal. Calcd. For  $\text{C}_{24}\text{H}_{15}\text{N}_3$ : C, 83.46; H, 4.38; N, 12.17; Found: C, 82.58; H, 4.19; N, 12.39.



**Figure S1.**  $^1\text{H}$  NMR spectrum of triazatruxene.

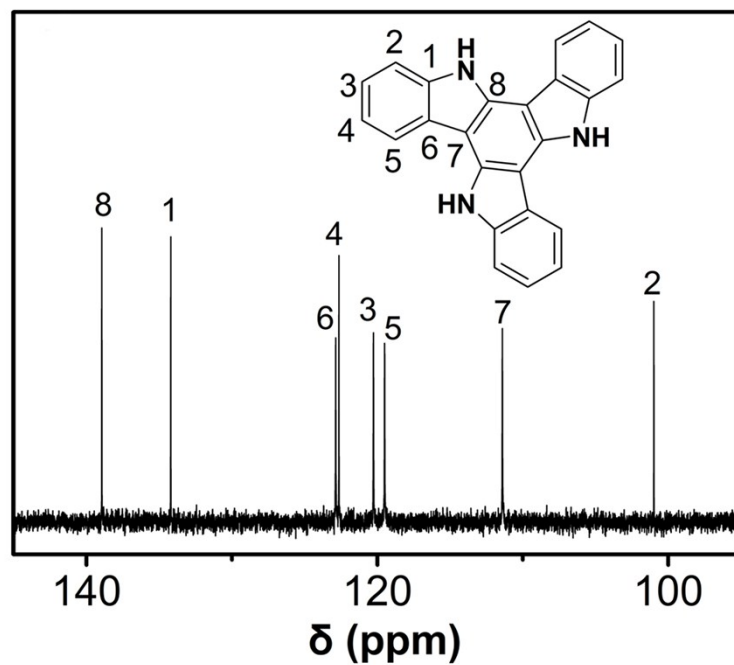


Figure S2.  $^{13}\text{C}$  NMR spectrum of triazatruxene.

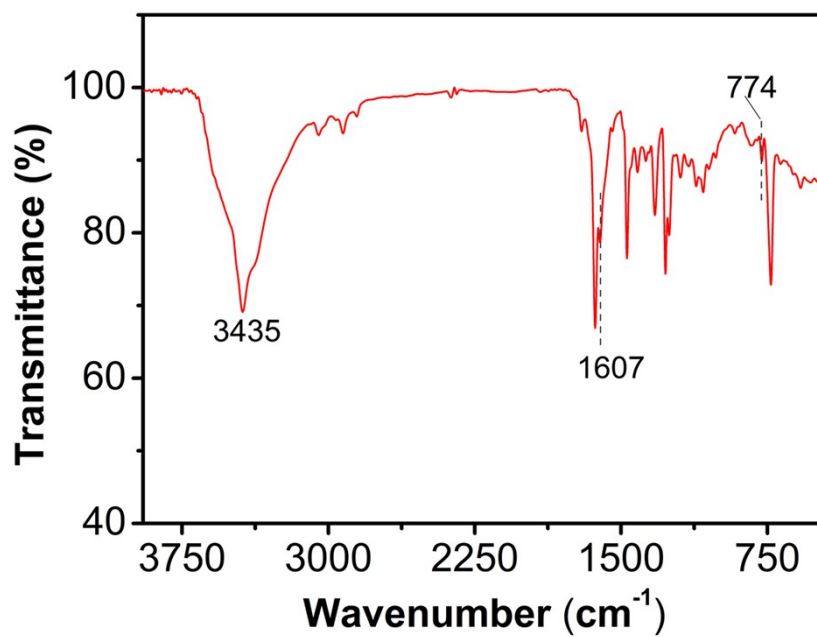
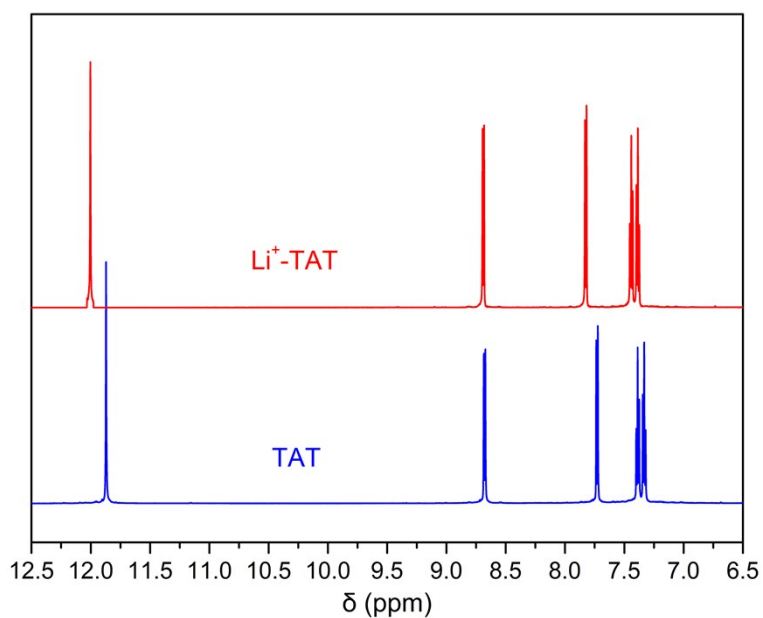


Figure S3. FT-IR spectrum of triazatruxene.

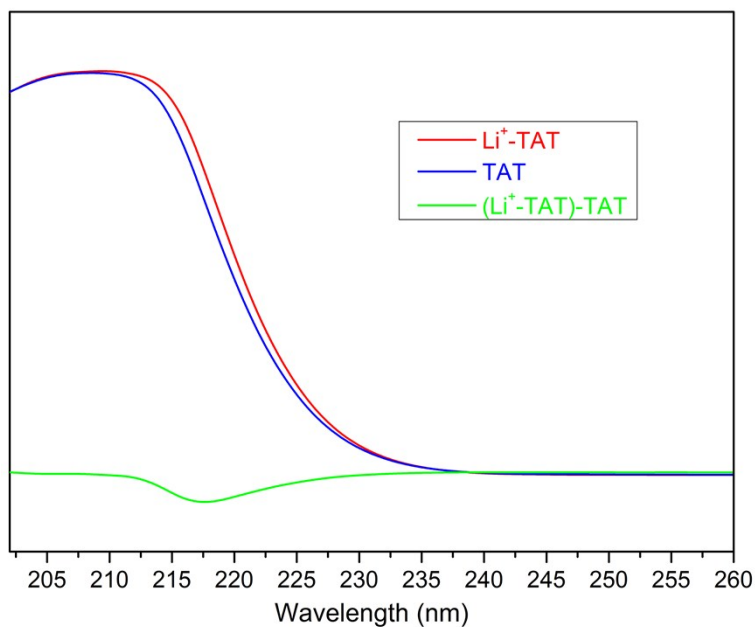
### Prepare of Li<sup>+</sup>-TAT

The TAT monomer was firstly dispersed into deionized water to form a stable suspension with the help of ultrasonication. The concentration was 1 mg mL<sup>-1</sup>. Then, an inorganic salt LiCl was added to the suspension under continuous stirring. The salt concentration was 0.25 mol L<sup>-1</sup>. After steeping 24 hours, the product was filtrated and washed deionized water, and dried.

### The characterization of the cation- $\pi$ interaction mechanism in Li<sup>+</sup>-TAT complex



**Figure S4.** <sup>1</sup>H NMR spectra of TAT and Li<sup>+</sup>-TAT.



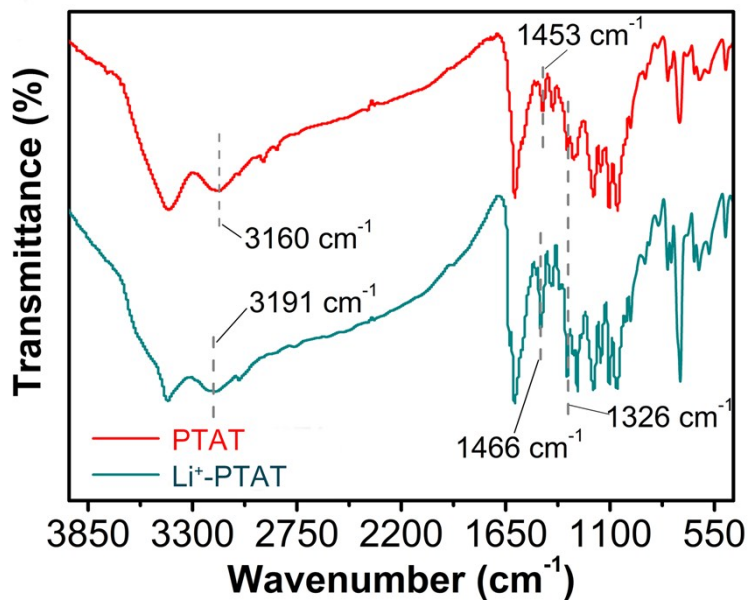
**Figure S5.** UV-vis absorption spectra of TAT and Li<sup>+</sup>-TAT.

### **Synthesis and characterizations of PTAT and Li<sup>+</sup>-PTAT**

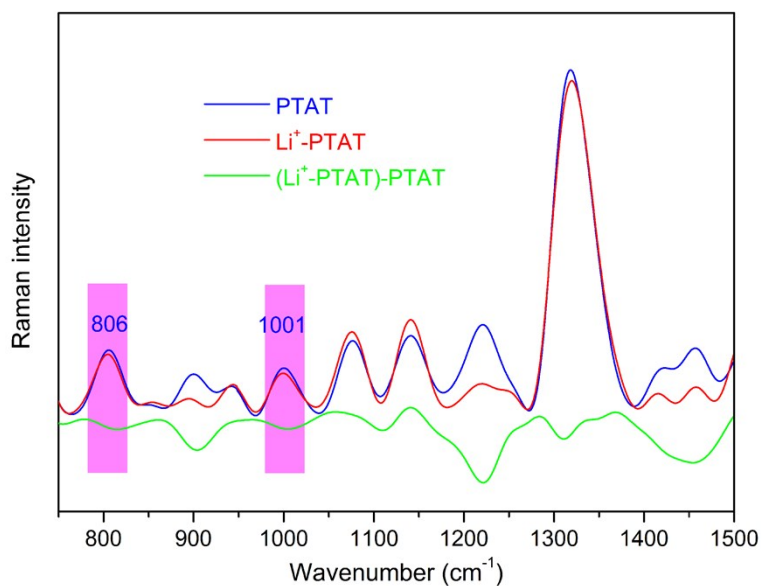
A solution of the monomer triazatruxene (4 mmol) in anhydrous CHCl<sub>3</sub> (80 mL) was dropwise added into a suspension of FeCl<sub>3</sub> (12 mmol) in anhydrous CHCl<sub>3</sub> (40 mL) under nitrogen atmosphere. The mixture was stirred at room temperature for 24 h, and then 100 mL of methanol was added. The resulting precipitate was collected by filtration and washed with methanol and 2 M HCl solution. After extracted in a Soxhlet extractor with methanol for 24 hours at reflux, the product was collected and dried in vacuum oven at 80 °C for 24 hours (yield, 80%).

The PTAT polymer powder was firstly dispersed into deionized water to form a stable suspension with the help of ultrasonication. The concentration was 1 mg mL<sup>-1</sup>. Then, an inorganic salt LiCl was added to the suspension under continuous stirring. The

salt concentration was 0.25 mol L<sup>-1</sup>. After steeping 24 hours, the product was filtrated and washed deionized water, and dried.

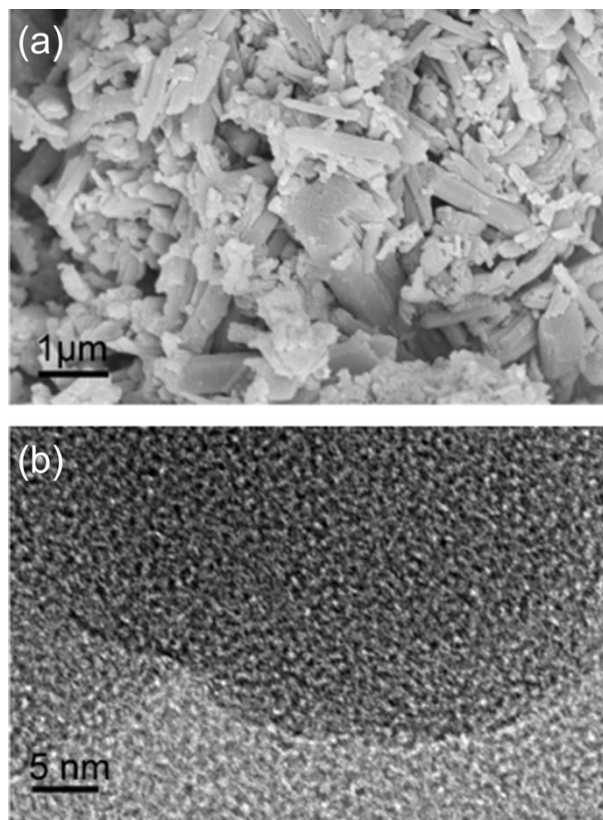


**Figure S6.** FT-IR spectra of PTAT and Li<sup>+</sup>-PTAT.

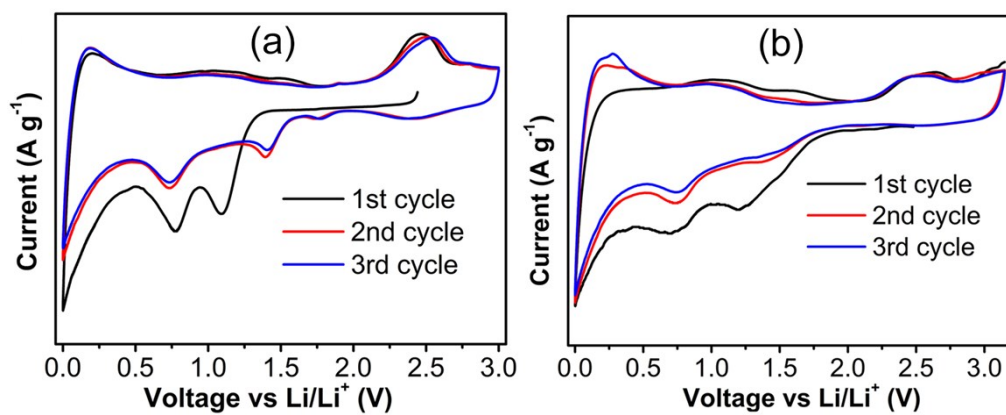


**Figure S7.** FT-IR spectra of PTAT and Li<sup>+</sup>-PTAT.



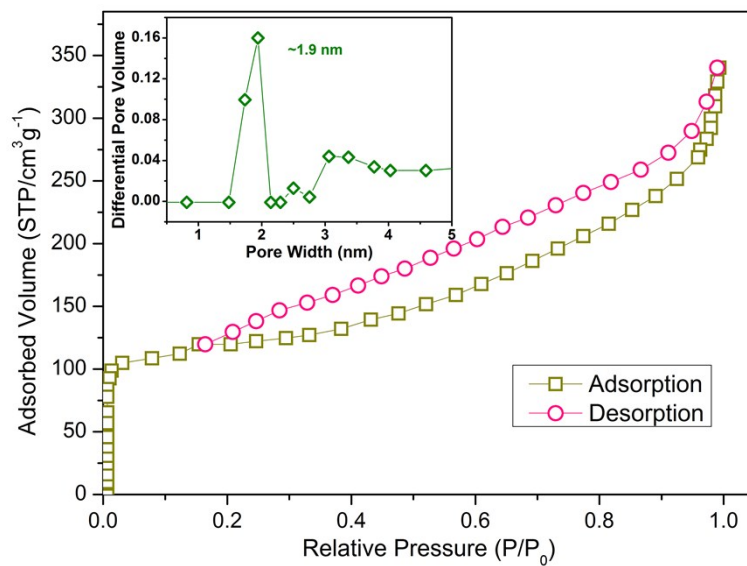


**Figure S8.** The SEM (a) and HRTEM (b) of PTAT.



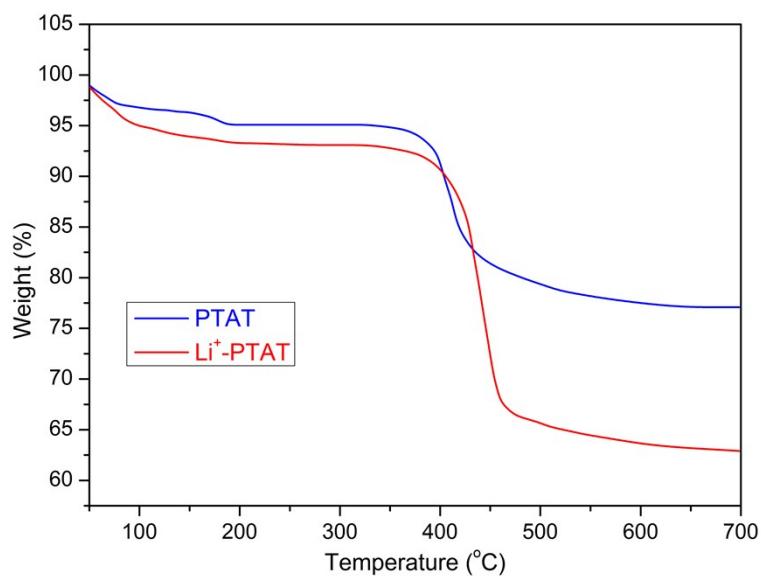
**Figure S9.** Cyclic voltammetry (CV) profiles of Li<sup>+</sup>-PTAT (a) and PTAT (b).

## The porosity parameters of PTAT



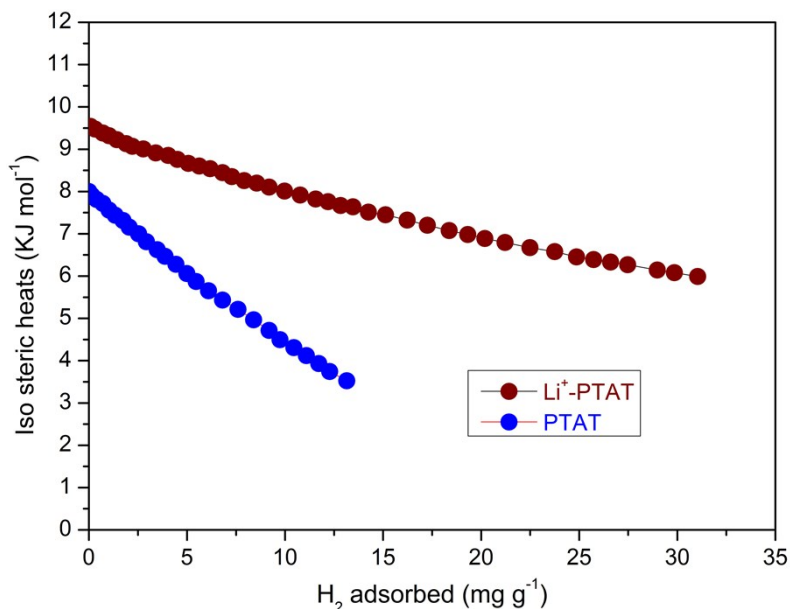
**Figure S10.** The nitrogen adsorption-desorption isotherms and the pore size distribution (inset) of PTAT.

## The thermal behaviors of the PTAT and $\text{Li}^+$ -PTAT



**Figure S11.** The TGA curves of PTAT and  $\text{Li}^+$ -PTAT.

## Isosteric heats of H<sub>2</sub> adsorption for PTAT and Li<sup>+</sup>-PTAT



**Figure S12.** The isosteric heats of hydrogen adsorption of PTAT and Li<sup>+</sup>-PTAT.

## Simulation Method

MD simulation was performed using the amorphous cell module of Materials Studio (MS, version 8.0, Accelrys Software Inc., USA) with a “Compass force field” whose intermolecular parameters were optimized.<sup>1,2</sup> A single parent chain with 10 repeat units was generated originally. Then, periodic boundary conditions were imposed and an initial density of 0.9 g cm<sup>-3</sup> was used to simulate the bulk aggregation structure for model PTAT. Each initial structure was optimized by a molecular mechanics technique. Because this optimized structure might, however, be still in a local energy minimum state, it was relaxed through NPT molecular dynamics (MD) (In the canonical ensemble, mole (M), pressure (P), and temperature (T) are conserved), the time evolution of chain

conformations up to 1000 ps with time steps of 0.0002 ps.

The radial distribution function,  $g_{AB}(r)$ , was introduced to describe how density of designated particles varies as a function of distance from a reference particle. Usually,  $g_{AB}(r)$  is determined by measuring the ensemble averaged distance between all particle pairs, as follows,  $g_{AB}(r) = \langle n_{AB}(r) \rangle / 4\pi r^2 \Delta\rho_{AB}$ , where,  $n_{AB}(r)$  is the distance of each pair between A (triazatruxene groups) and B (Lithium ions) in the simulation box.  $\langle \dots \rangle$  represents an ensemble average.  $\Delta\rho_{AB}$  is the rate of change in the average number density of Lithium ions over distance from triazatruxene groups.

## References

- [1] C. F. Fan, T. Cagin, Z. M. Chen, K. A. Smith, *Macromolecules*, 1994, 27, 2383.
- [2] K. J. Lee, W. L. Mattice, R. G. Snyder, *J. Chem. Phys.*, 1992, 96, 9138.