Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Electronic Supplementary Information

Hyper-conjugated lithium carboxylate based on perylene unit for high-rate organic lithium-ion batteries

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1. Experimental details

Reagents and Chemicals

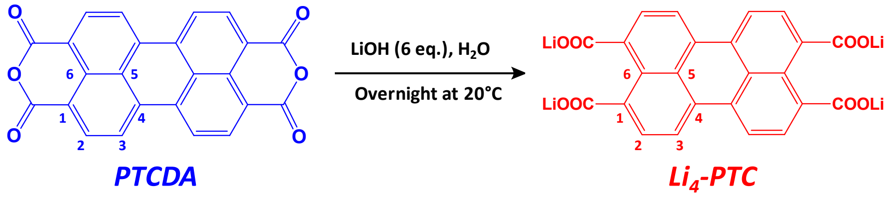
Perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA) and lithium hydroxide (LiOH) were purchased from Alfa Aesar and Sigma-Aldrich, respectively. They were used as received without further purification. De-ionized water was utilized for the synthesis of the tetra-lithium salt.

Instrumentation

FT-IR (Fourier Transform Infra-Red) spectra were recorded in transmission mode at room temperature using a Nicolet AVATAR 370 DTGS spectrometer from Thermo-Electron. ^{13}C solid-state NMR spectra were acquired on Bruker AVANCE 500 spectrometer with an executive frequency of 11.7 T using a 2.5 mm rotor. All chemical shifts were calibrated to external glycine. The particles morphology and their size were estimated by Scanning Electron Microscopy (SEM) using an environmental FEI Quanta 200 FEG-microscope. Thermogravimetric analysis (TGA) were performed on a Netzsch thermal analyzer STA 449C Jupiter equipped with a differential analysis microbalance coupled with a mass spectrometer QMS 403 Aëolos. Nitrogen adsorption/desorption isotherm was recorded using a Micromeritics ASAP 2020 porosimeter at liquid nitrogen temperature. Lithium stoichiometry was evaluated by flame emission spectrometry (Perkin-Elmer). The calibration curve was obtained by using lithium standard solutions purchased from Aldrich. The electrochemical properties were investigated using Swagelok-type cell assembled in an argon-filled glove box. The working electrode was typically composed of *ca.* 60 mg of active materials (60 %) manually grinded in a mortar with 40 mg (40 %) of Super P carbon. A lithium metal foil (Aldrich) was used as both negative and reference electrode. The negative and positive electrodes were separated by two Whatman fiberglass sheets soaked with battery grade LP30 electrolyte from Merck (1 M $LiPF_6$ in ethylene carbonate / dimethyl carbonate 1/1 volume mixture).

Hydrolysis and lithiation process

Hyper-conjugated organic lithium carboxylate is synthesized through a one-pot hydrolysis/lithiation reaction of the perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA) to yield the related tetra-lithium salt (Scheme 1).



Scheme 1: Synthesis of Tetralithium perylen-3,4,9,10-tetracarboxylate (Li_4-PTC)

A typical synthesis involves 1 g of PTCDA poured in 100 mL of D.I. water. 6 equivalents of anhydrous LiOH, prior dissolved in D.I. water, are added dropwise. After 16 hours stirring at room-temperature / ambient conditions, the red suspension turns into a deep orange color suggesting an increase of HOMO/LUMO energy gap which stems from the shorten π-conjugation backbone in Li_4-PTC. The resulting solid was retrieved by centrifugation, washed three times with D.I. water and a last time by acetone. The orange powder is then dried under vacuum at 60 °C for 3 hours before any utilization. The product was systematically stored into an argon-filled glovebox to avoid water adsorption. The aforementioned reaction leads to highly polydisperse platelet-like particles whose size lies between 50 nm to 1 µm (Figure. S5). The B.E.T. surface area is determined to *ca.* 75 $m^2.g^{-1}$ based on nitrogen adsorption (C_{BET} = 325). Water content was determined using Karl Fischer titration method. Typically, 108 mg of Li_4-PTC were dispersed in 10mL of dry hexane or THF (in a close flask) and left 2 hours in ultrasonic bath. Karl-Fischer titration was then carried out on a Metrohm 831 Karl Fischer coulometer and repeated three times for each solvent. The results indicated a water content of only 26 ppm and 29 ppm in dry hexane and in dry THF after pouring whereas it was initially 13 ppm and 16 ppm before addition of Li_4-PTC.

2. Supplemental figures and discussion.

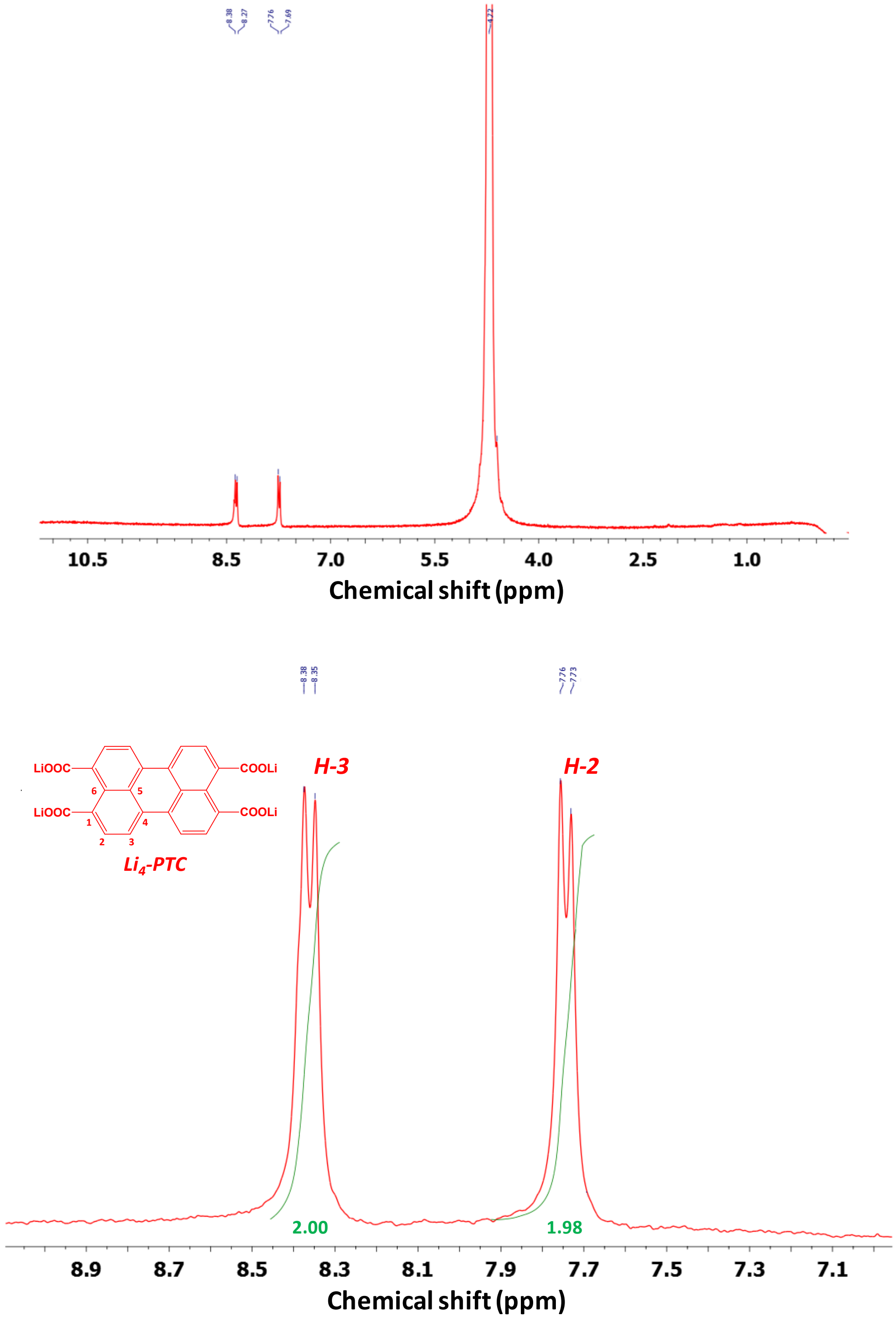


Fig S1 ^{1}H liquid NMR spectrum of Li_4-PTC performed in D_2O (a) full spectrum and (b) zoomed on aromatic region.

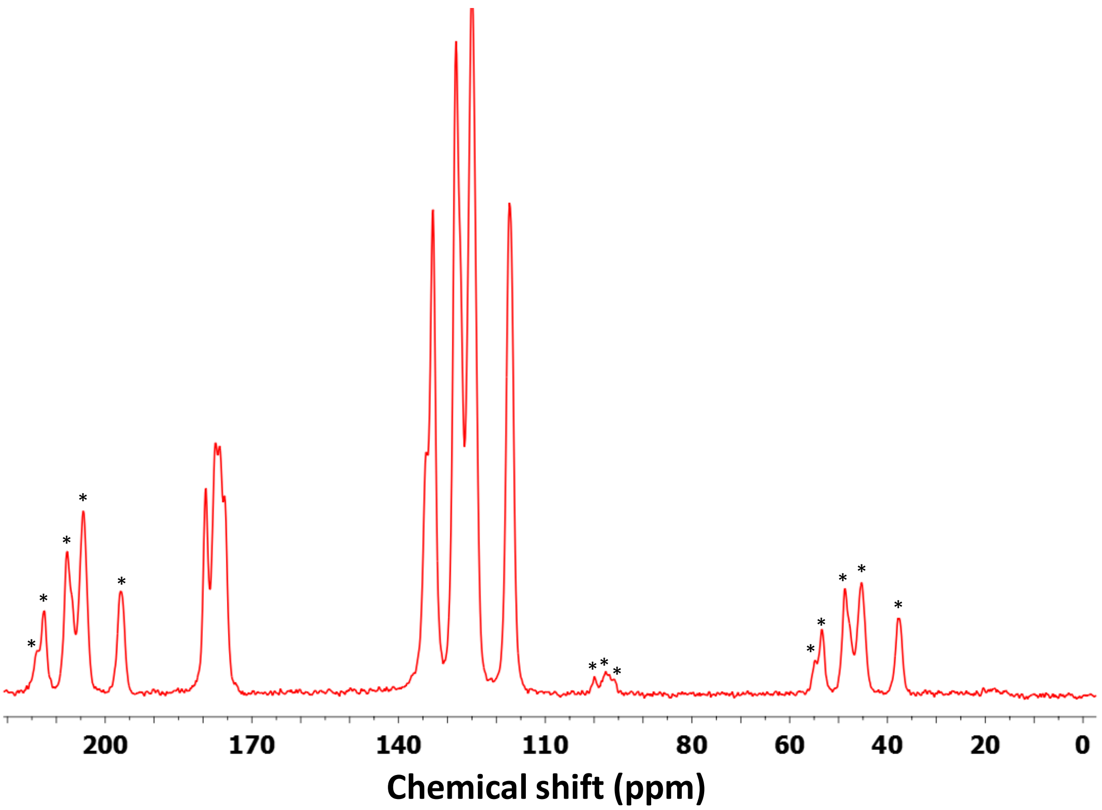


Fig S2 Solid-State NMR ^{13}C spectrum of Li_4-PTC using CP MAS sequence. Rotation bands are marked with an asterisk.

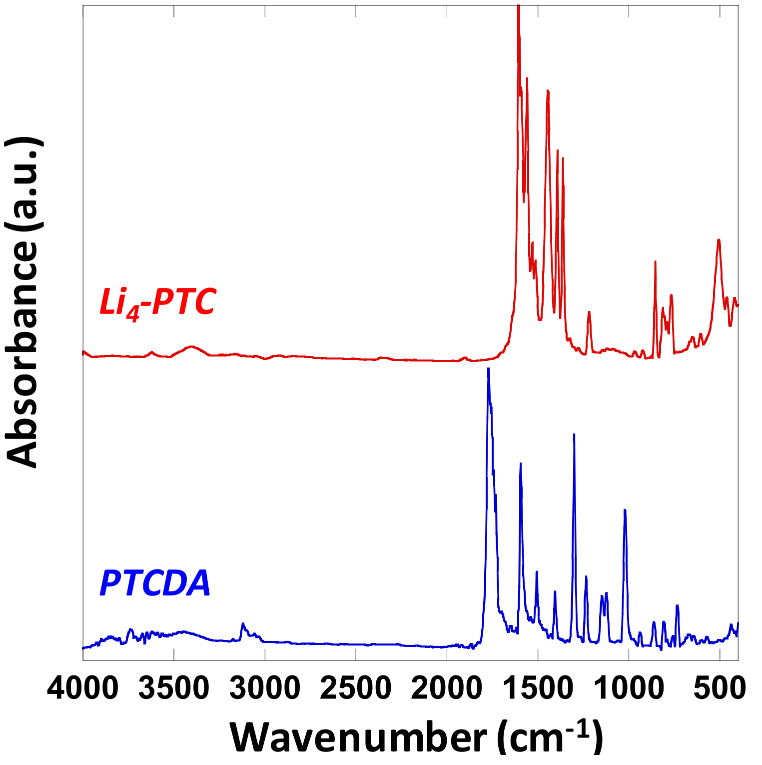


Fig S3 Comparison between pristine PTCDA (blue curve) and precipitated Li_4-PTC solid (red curve) by FT-IR in transmission mode.

	Wavenumber in cm^{-1}									
PTDCA	1772	1594	1506	1405	1300	1236	1122	862	808	733
Li_4-PTC	1598 1447	1560	1533	1510	1393 1362	1218	-	856	813	767
Attribution	$\upsilon_{C=O}$	υ_{C-C} δ_{C-H}	υ_{C-C}	υ_{C-C} δ_{C-C}	δ_{C-H} υ_{C-C}	υ_{C-C} δ_{C-H}	υ_{C-O}	δ_{C-H}	δ_{C-H} δ_{C-C-C}	$\delta_{O=C-C}$ δ_{C-O-C}

Table S1: FT-IR bands attribution based on complete description of PTDCA spectra in the reference 14 of the manuscript.

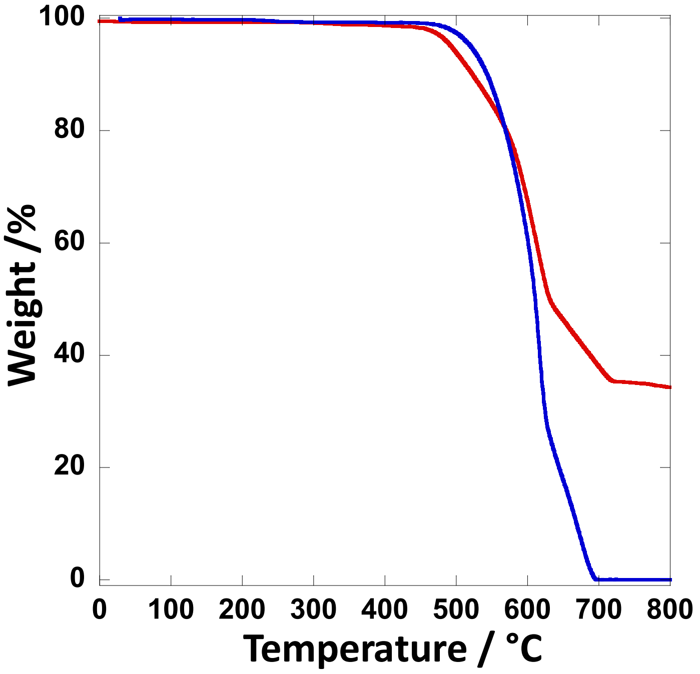


Fig. S4 Comparison between pristine PTCDA (blue curve) and precipitated Li_4-PTC solid (red curve) by thermogravimetric analysis under air.

Their thermal degradation onset at 450 °C. It proceeds in one step leading to a weight loss of 67 % for Li_4-PTC and a total loss for PTCDA. This mass loss arises from the degradation of the hydrocarbon backbone leading to CO, CO_2 and H_2O. The residual solid left in the crucible for Li_4-PTC corresponds to the lithium carbonate (Li_2CO_3) whose amount of 33 % is in excellent consistency with the four lithium stoichiometry. This emphasizes once again on the advantage held by such organic electrode materials in terms of recyclability because of their easier retrieval process of the initial lithium content. Worth mentioning, although stored into a glove box, the material does not show hygroscopic features. The content of adsorbed water was determined to be almost insignificant (0.6 % in mass).

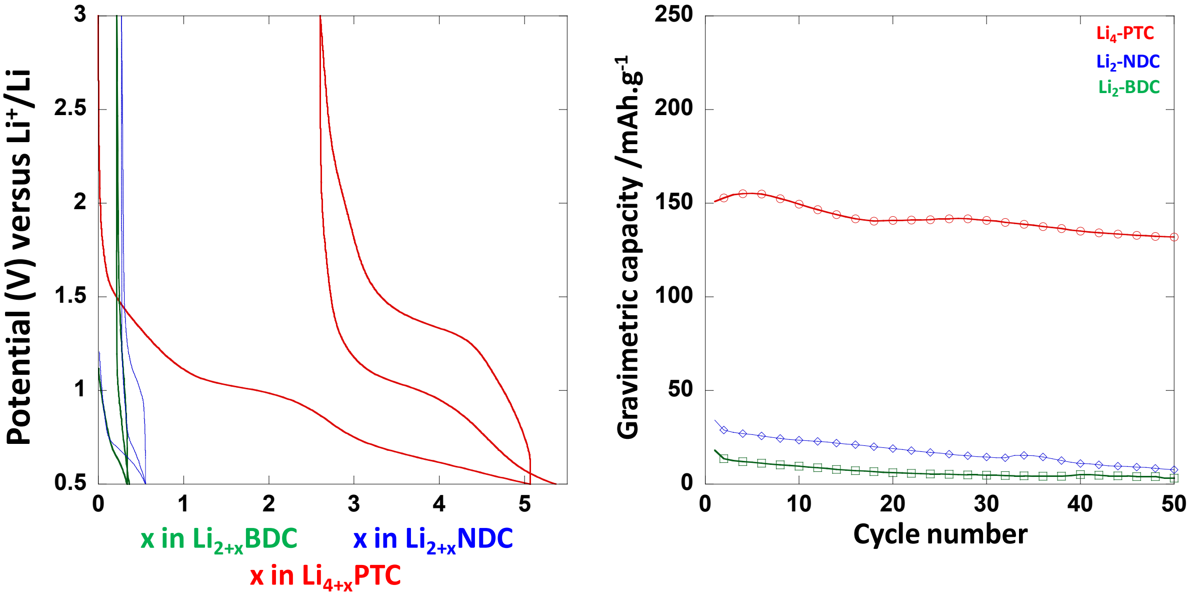


Fig. S5 (a) Potential-composition profiles and (b) corresponding gravimetric capacity as function of cycle number over 50 cycles of Dilithium Benzene-1,4-diCarboxylate (Li_2-BDC, green curve), Dilithium Naphthalene-2,6-diCarboxylate (Li_2-NDC, blue curve) and Tetralithium Perylen-3,4,9,10-tetraCarboxylate (Li_4-PTC, red curve) galvanostatically cycled at 5 Li^+/1h rate.

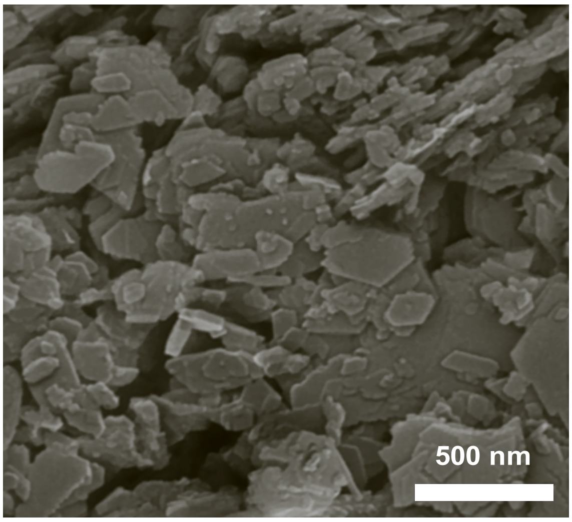


Fig. S6 Scanning Electron Micrograph of Li_4-PTC.