Supporting Information

Effect of trace hydrofluoric acid in $LiPF_6$ electrolyte on the performance of Li-organic battery with N-heterocycle based conjugated microporous polymer as cathode

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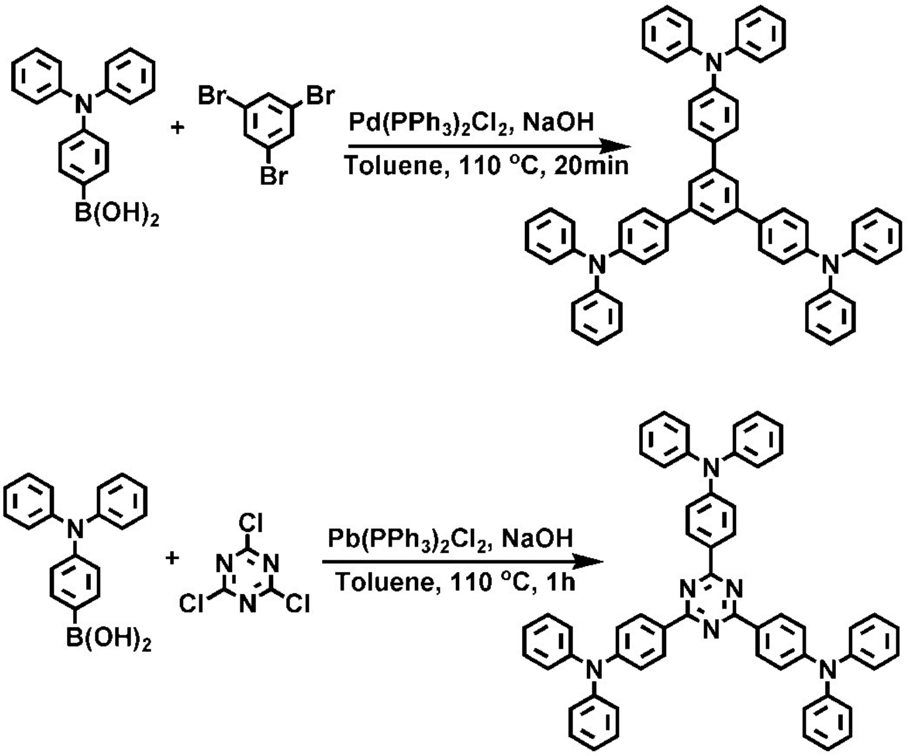
1. Synthesis

Synthesis of 1,3,5-tris(4-diphenylamino-phenyl)benzene (TTPAB) monomer.

1,3,5-tris(4-diphenylamino-phenyl)benzene was prepared simply by Suzuki coupling reaction compared to the literature (**Scheme S1**). A mixture of 1,3,5-Tribromobenzene (0.35 g), [4-(diphenylamino)phenyl] boronic acid (1.32 g), $Pd(PPh_3)_2Cl_2$ (30 mg), NaOH (0.24 g) were dissolved in toluene (20 ml), and then heated at 110 ^{o}C for only 20 minutes under nitrogen atmosphere. After cooling to room temperature, the mixture was extracted with DCM and dried by anhydrous $MgSO_4$. The obtained TTPAB was isolated by column chromatography with a 58% yield as a white solid powder. 1H NMR (500MHz, $CDCl_3$), δ 7.71 (s, 3H), 7.58 (d, J = 8.6 Hz, 6H), 7.31-7.28 (m, 12H) (overlapped with the solvent peak of CDCl3), 7.17 (t, J = 7.6 Hz, 18H), 7.05(t, J = 6.8 Hz, 6H). MS (MADLI-TOF): calculated for $C_{60}H_{45}N_3$: m/z=807.36, found m/z=807.36.

Synthesis of the 1,3,5-Tris(4-Diphenylamino-Phenyl)Triazine (TDAPTz) Monomer

The 1,3,5-tris(4-diphenylamino-phenyl)triazine was simply prepared by Suzuki coupling in a short time (**Scheme S1**). A mixture of Cyanuric chloride (0.184 g), [4-(diphenylamino)phenyl] boronic acid (1.445 g), $Pd(PPh_3)_2Cl_2$ (36 mg), and NaOH (0.4 g) was dissolved in toluene (20 ml), and then heated at 110 ^{o}C for 1 h under nitrogen atmosphere. After cooling to room temperature, the mixture was extracted with DCM and dried by anhydrous Na_2SO_4. The obtained TDAPTz was isolated by column chromatography with a 60% yield as a yellow solid powder. Mass spectrometer (MS) (ESI): calculated for $C_{57}H_{42}N_6$ m/z: 810.35, found m/z: 811.3). 1H NMR (500 MHz, $CDCl_3$) δ 8.58 (d, J = 8.8 Hz, 1H), 7.35 (t, J = 7.9 Hz, 2H), 7.22 (d, J = 7.5 Hz, 2H), 7.17 (t, J = 7.4 Hz, 1H), 7.10 (d, J = 8.8 Hz, 1H)



Scheme S1 the synthesis route of TTPAB and TDAPTz monomer

Table S1 electrochemical and Optical Parameters of the Samples: TPADTz, PTPADTz, PTPADTz-LiPF$_6$.

Material	Eox	HOMO[a]	λ max	λ onset	E_g [b]	LUMO[c]
TPADTz	1.0 V	-5.12eV	/	/	/	/
PTPADTz	0.86V	-4.97eV	411nm	481nm	2.58 eV	-2.39 eV
PTPADTz- LiPF$_6$	0.9 V	-5.01eV	515nm	652nm	1.90 eV	-3.11 eV

[a] Estimated from the onset oxidation potential by using HOMO = $-E_{ox} - 4.8$ eV + E_{ox} Fc/Fc$^+$.

[b] Calculated by using Eg = 1240/λonset (λonset: the absorption edge of the maximum absorption).

[c] LUMO = HOMO + Eg

Table S2. Some of the detailed physical parameters of LiPF$_6$ electrolyte supplied by the company in this work

Items	**Technical standard**	**In this article**	**Dodochem**	**JH new energy**
H_2O content (ppm)	≤ 20	**8**	~5	~8
HF content (ppm)	≤ 30	**19**	~20	~15
Conductivity	≥ 8.0	**12.7**	~10	~10

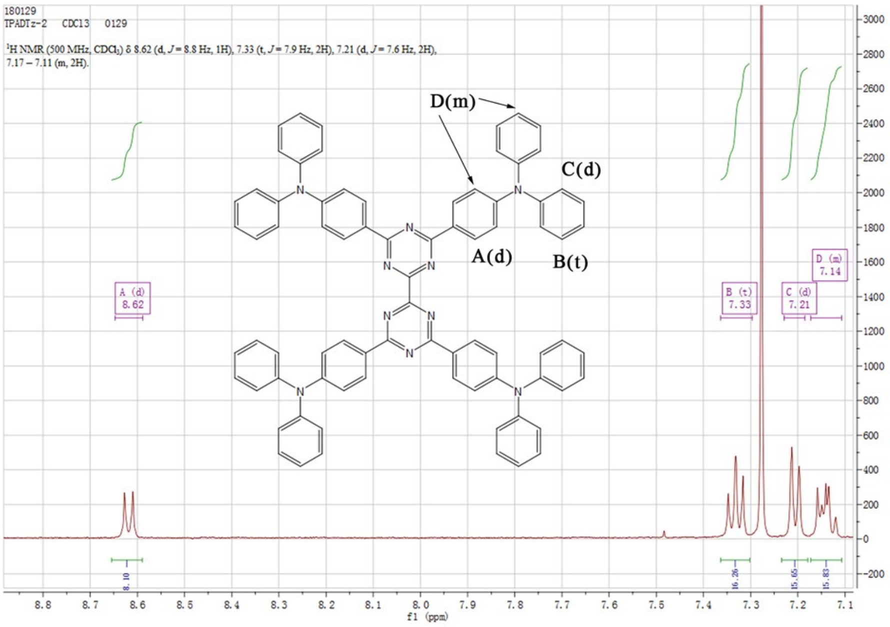


Figure S1 the ^{1}H NMR of the monomer TPADTz

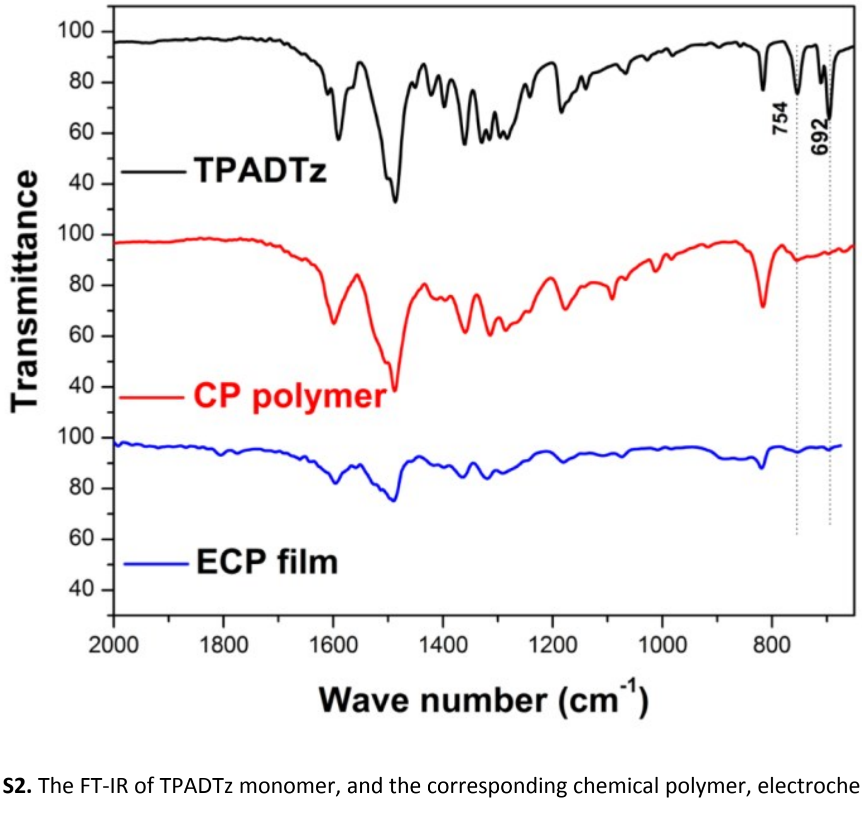


Figure S2. The FT-IR of TPADTz monomer, and the corresponding chemical polymer, electrochemical film.

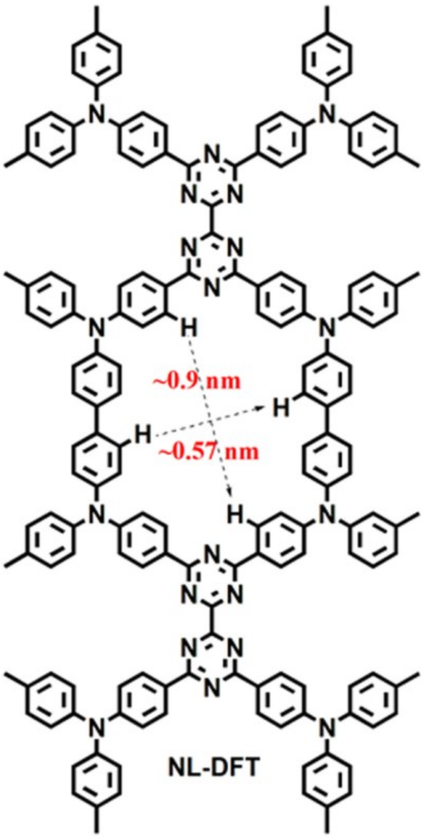


Figure S3 the length and width pore diameter of the micropore via the nonlocal density functional theory calculations (NL-DFT)

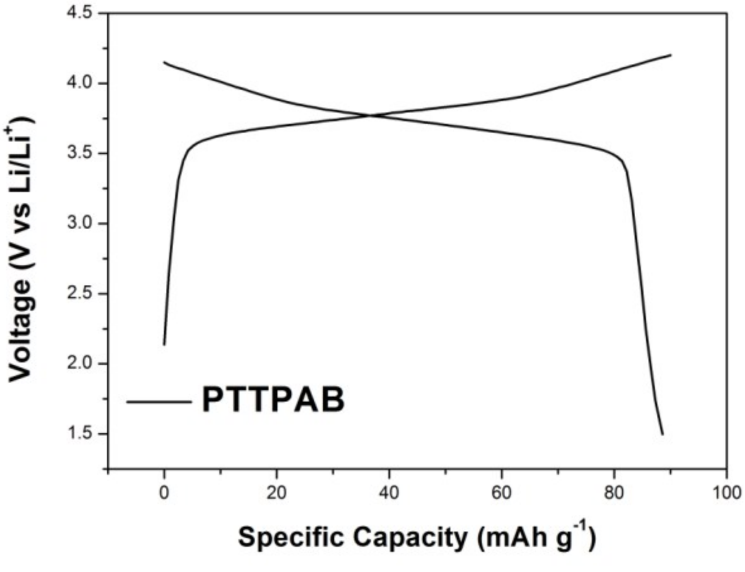


Figure S4 the 2nd charge/discharge curve of PTTPAB at 20 mA g^{-1} between 1.5-4.2V

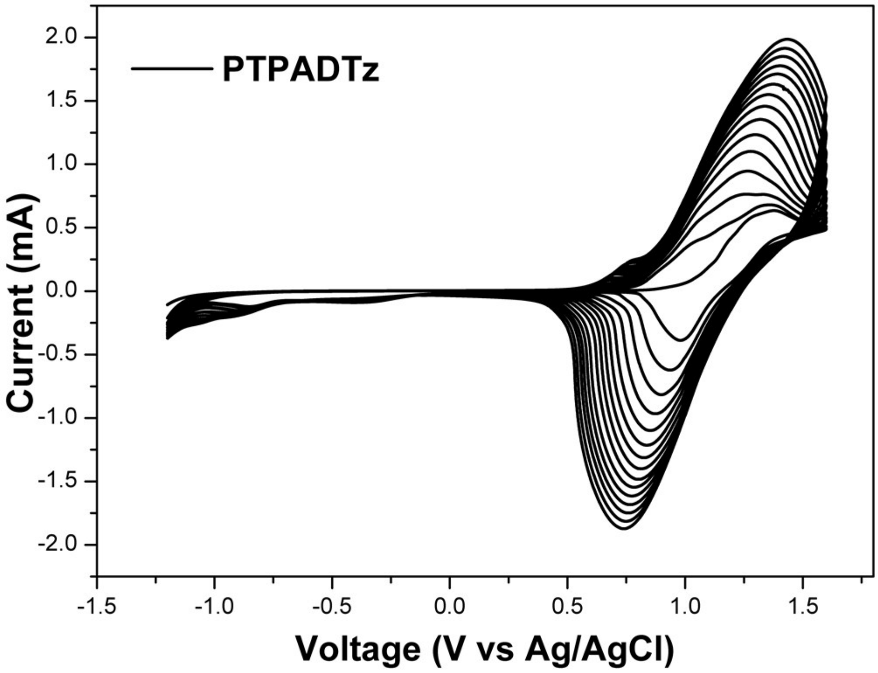


Figure S5 The electro-synthesis of PTPADTz by repeated CV scans from -1.2 to 1.6 V at a scan of 100 mV S^{-1} and 0.1 M TBAP in DCM solution with a monomer concentration of 10^{-3} M L^{-1}

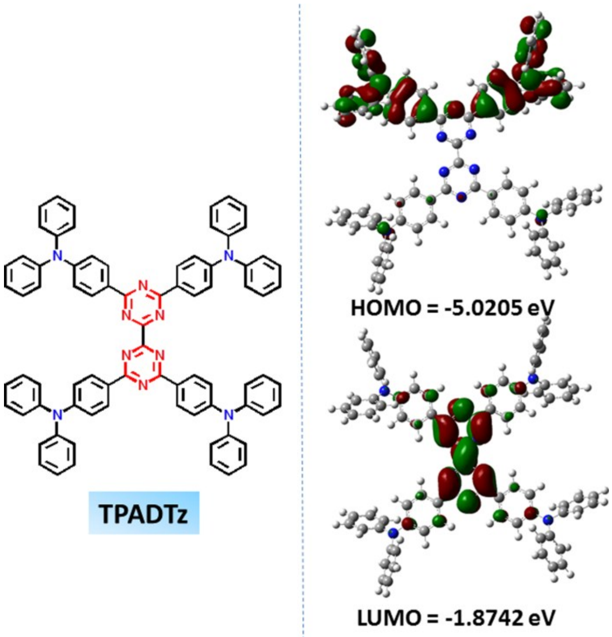


Figure S6. the energy level of TPADTz using the DFT calculation at the B3LYP/6-31 g level performed via Gaussian 09

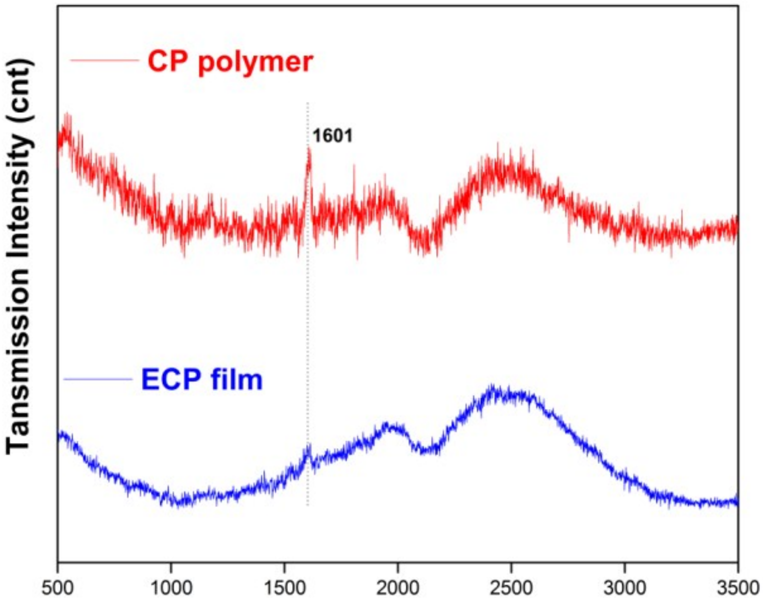


Figure S7 the Raman of CP polymer and ECP film (polymer PTPADTz)

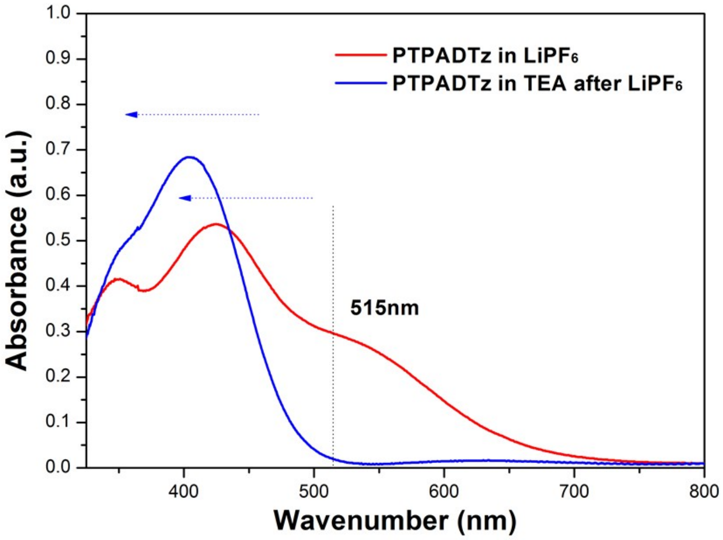


Figure S8 the UV-vis of PTPADTz film in $LiPF_6$ electrolyte and then in TEA solvent under the same film test

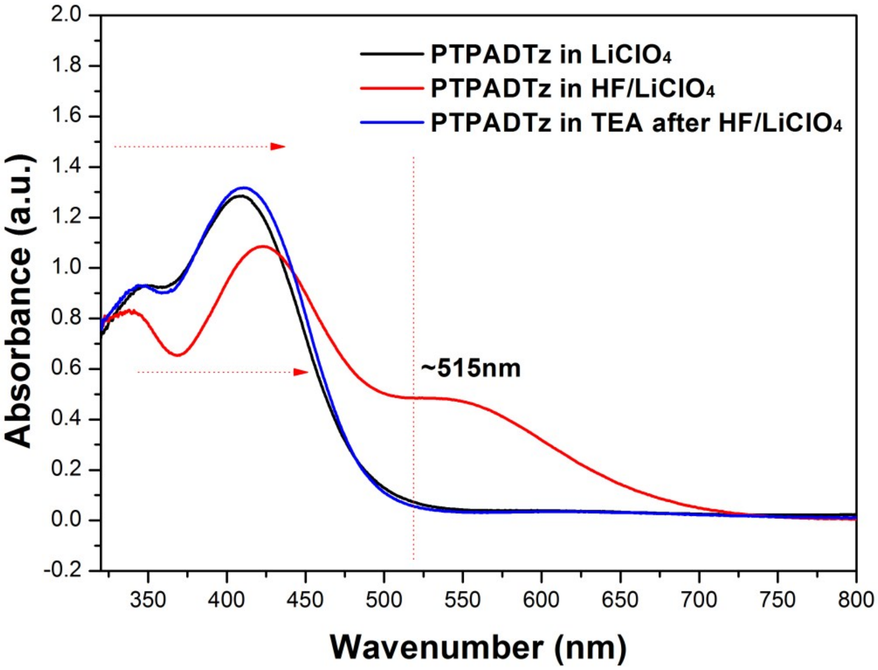


Figure S9 the UV-vis of PTPADTz film in $LiClO_4$, in $HF/LiClO_4$ (the ratio of HF is ~25ppm) electrolyte and then in TEA solvent under the same film test

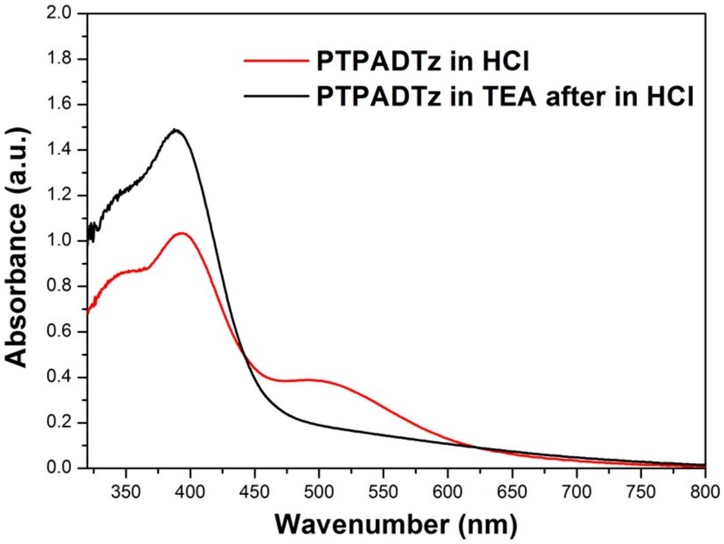


Figure 10 the UV-vis of PTPADTz film in HCl solution (~36%) and then in TEA solvent under the same film test

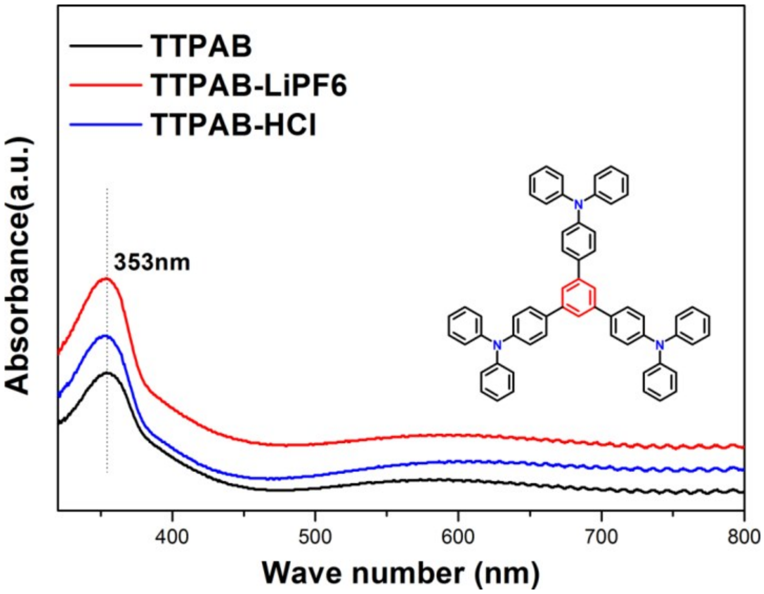


Figure S11 the UV-vis of the TTPAB; TTPAB film in $LiPF_6$ electrolyte; TTPAB film in HCl solution

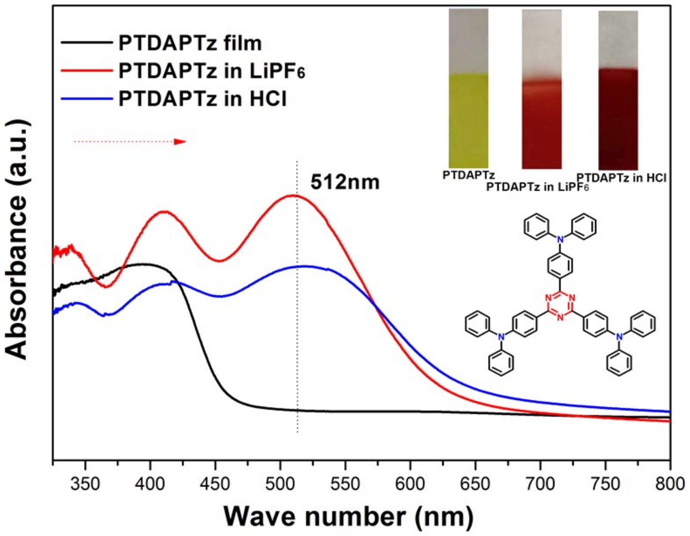


Figure S12 the UV-vis and the color change of PTDAPTz in different electrolyte

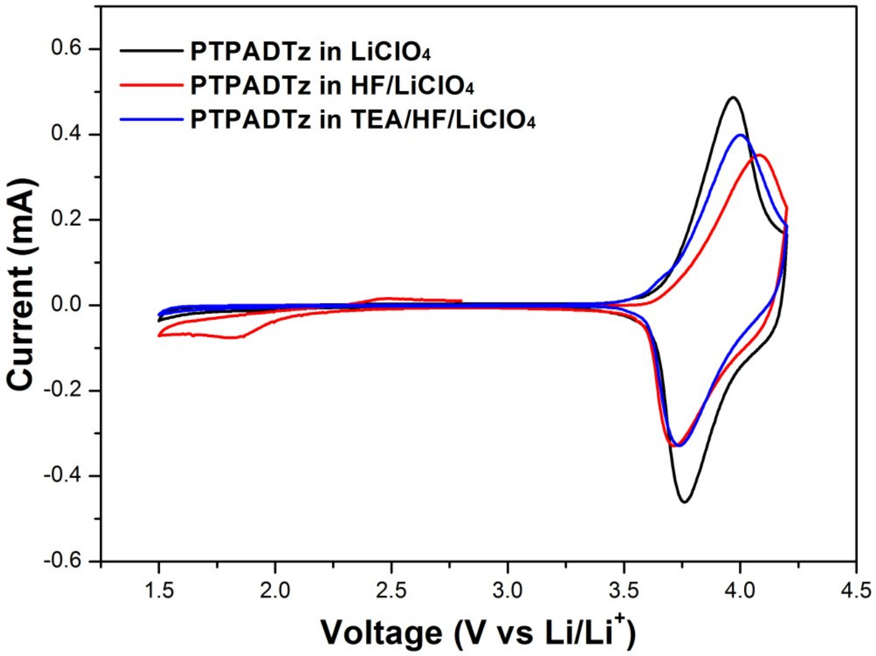


Figure S13 the CV curve of PTPADTz film in $LiClO_4$, in $HF/LiClO_4$ electrolyte (the ratio of HF is ~15 ppm) and then in $TEA/HF/LiClO_4$ (the ratio of TEA is ~20 ppm) under the same film test.

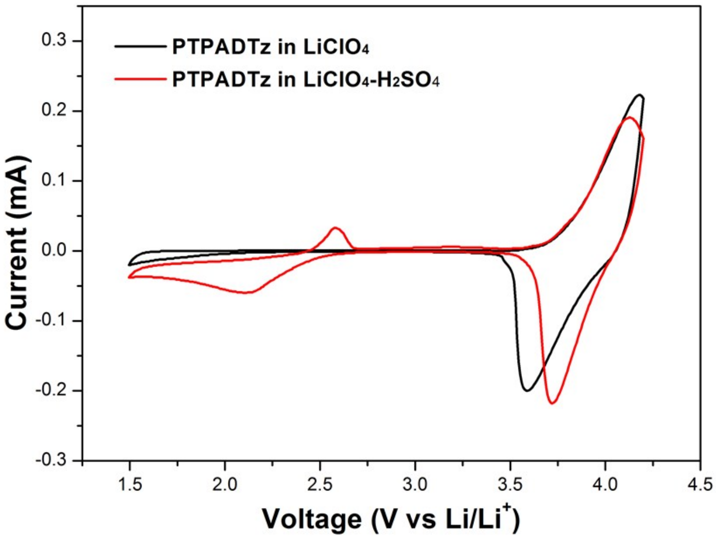


Figure S14 the CV curve of as-prepared PTPADTz film in the $LiClO_4$ and then added trace H_2SO_4 (~10 ppm) with a scan rate of the 20 mV/s under the same film test

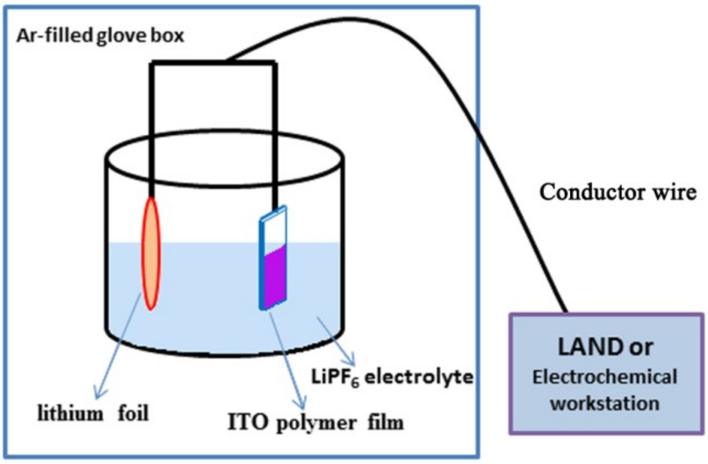


Figure S15 the schematic diagram of open lithium battery test

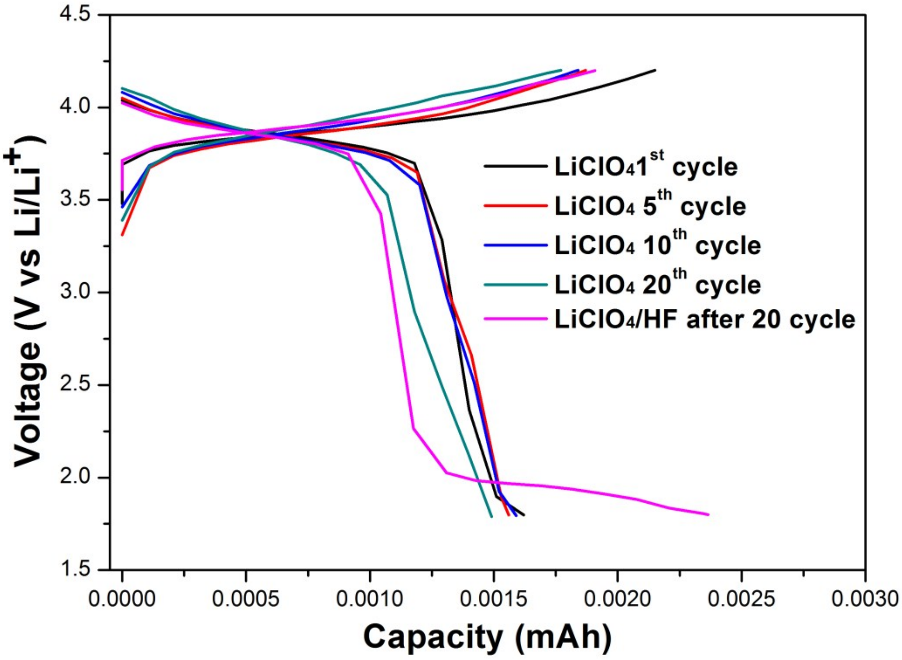


Figure S16 the charge/discharge process at a current of 20 mA of PTPADTz film in a) LiClO$_4$ electrolyte in the first 20 cycles. b) The additional HF (~15 ppm) added into the LiClO$_4$ electrolytes after 20 cycles under the same film test.

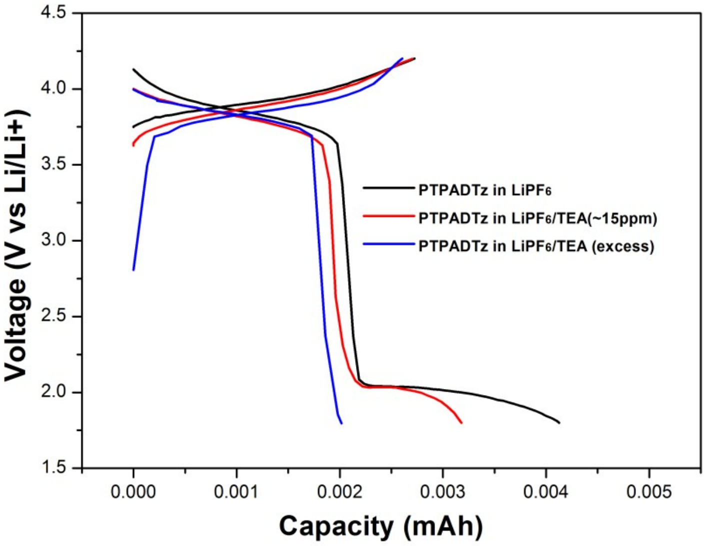


Figure S17 the charge/discharge process at a current of 20 mA of PTPADTz film in a) $LiPF_6$ electrolyte, b) The additional TEA (~15ppm) added into the $LiPF_6$ electrolytes c) The excess TEA added into the $LiPF_6$ electrolytes.

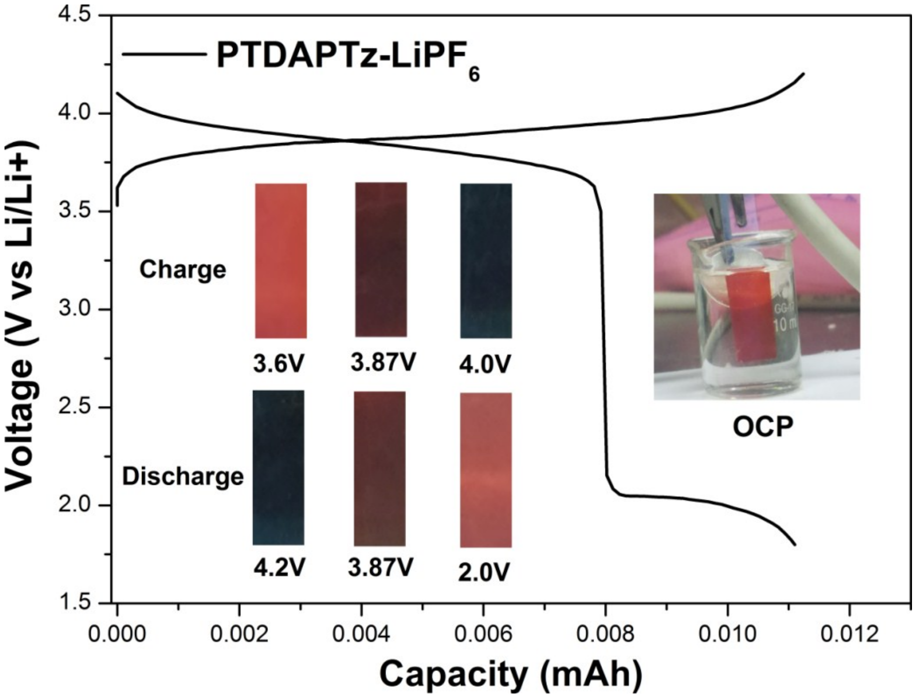


Figure S18 the relationship of color change and charge discharge curve of PTDAPTz-$LiPF_6$