Electronic supplementary information

An Air-stable Electrochromic Conjugated Microporous Polymer as an Emerging Electrode Material for Hybrid Energy Storage Systems

Yuyu Dai,[a] Weijun Li,[a,*] Zhangxin Chen,[a] Xiaogang Zhu,[a] Junlei Liu,[a] Ruiyang Zhao,[b] Dominic S. Wright,[c] Abolhassan Noori,[d] Mir F. Mousavi,[d,*] and Cheng Zhang[a,*]

[a] State Key Laboratory Breeding Base of Green Chemistry Synthesis Technology, College of Chemical Engineering, Zhejiang University of Technology, Chaowang Road, Hangzhou 310014, P. R. China

[b] College of Chemical Engineering, Qingdao University of Science and Technology, Qingdao, 266042, P.R. China

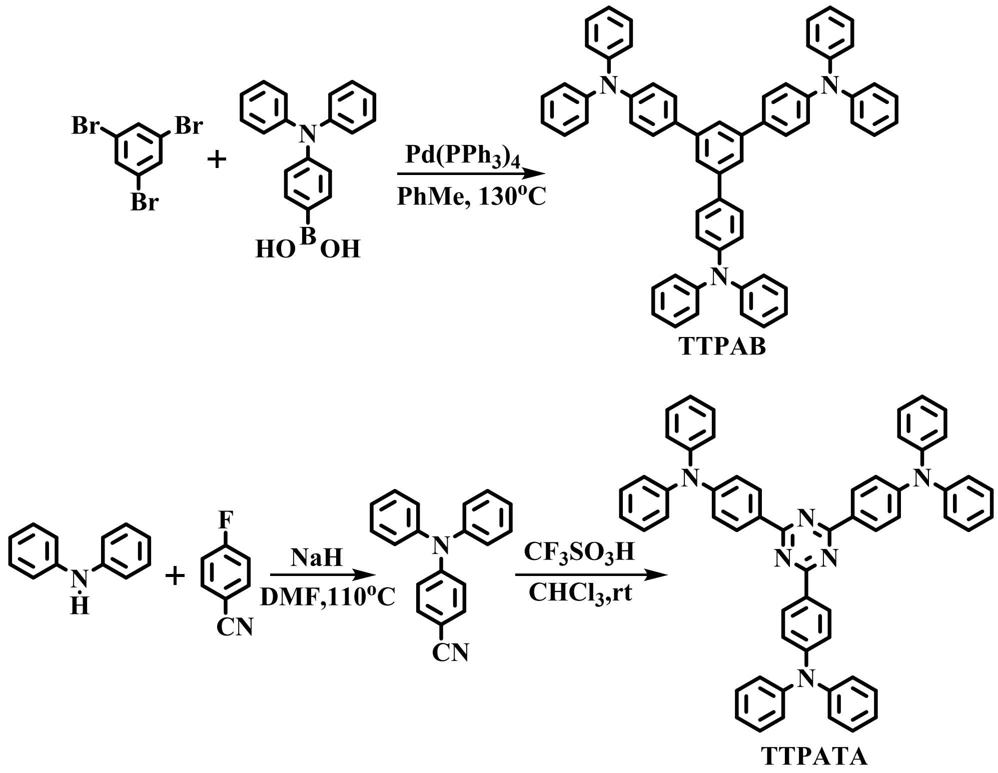
[c] Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, UK

[d] Department of Chemistry, Tarbiat Modares University, Tehran, 14115-175, Iran

Email: liwj@zjut.edu.cn; mousavim@modares.ac; czhang@zjut.edu.cn;

Contents

1. Synthesis of TTPAB and TTPATA



Scheme S1 Synthetic route of TTPAB and TTPATA

Synthesis of TTPAB

TTPAB was prepared following a modified procedure given in the literature.[1] Under a nitrogen atmosphere, 1, 3, 5-tribromobenzene (1 mmol, 0.31 g), [4-(diphenylamino) phenyl]boronic acid (3.5 mmol, 1.01 g), $Pd(PPh_3)_4$ (0.15 mmol, 0.17 g) , Na_2CO_3 (9 mmol, 0.95 g), THF (30 mL) and water (4.5 mL) were added into the flask and reflux for 24 h. During the reaction, the mixture was concentrated using a rotary evaporator. Then, dichloromethane and water were added into the resulting mixture for extraction before desiccation with anhydrous $MgSO_4$. The solvent was evaporated off, and the solid residues were purified by column chromatography to afford white product with a yield of 75%. ^1H NMR (500MHz, $CDCl_3$, 25°C, TMS, δ): 7.70 (s, 3H), 7.59 (d, J = 8.7 Hz, 6H), 7.34 – 7.28 (m, 12H), 7.16 (t, 18H), 7.06 (s, 6H). MALDI-TOF MS (mass m/z): 808.1 [M+ + H].

Synthesis of TTPATA

TTPATA was synthesized by two steps, as shown in Scheme 1. The first step was to synthesize 4-(diphenylamino)benzonitrile via Ullmann reaction; The second step was the cyclization of the intermediate product. The specific synthetic process was given as follows.

Sodium hydride (53.75 mmol, 1.29 g) was added into 100 mL N, N-Dimethylformamide solvent. After stirring with no bubble appearance, diphenylamine (26.09 mmol, 4.41 g) was added. When color of the solution changed toward green, the resulting solution was heated to 110 ^{o}C. At this temperature, 4-Fluorobenzonitrile (31.54 mmol, 3.82 g) was added slowly and the resulting solution turned to wine red. Gradually, the mixture solution became brown color and heated at 110 ^{o}C for 12 h. After cooling to room temperature, the reaction mixture was poured into water and extracted with dicholomethane. The collected organic solution was repeatedly washed with water and dried over anhydrous $MgSO_4$. The crude product was purified by column chromatography eluting with petroleum ether-dichloromethane mixtures (v/v, 2/1) to obtain 4-(diphenylamino)benzonitrile product (4.09 g) with a white color. Yield: 58%.

Under a nitrogen atmosphere, 4-(diphenylamino)benzonitrile (7.40 mmol, 2 g) was added into the anhydrous chloroform solution. When the solid was adequately dissolved, trifluoromethanesulfonic acid (11.80 mmol, 1.78 g) was added dropwise via a syringe at 0 ^{o}C. Then the reaction was warmed to room temperature and stirred for 4 d. The color of the resulting solution changed from colorless to pink, and finally atropurpureus color. After that, the mixture was poured into water and extracted with dichloromethane. Then, the reaction product was dried over anhydrous $MgSO_4$. The residue was purified by column chromatography using petroleum-dichloromethane (v/v, 1/1) as the eluent to obtain light yellow product (0.82 g). Yield: 41%. ^{1}H NMR (500MHz, $CDCl_3$, 25^{o}C, TMS, δ): 8.56 (d, J = 8.8 Hz, 6H), 7.33 (t, J = 7.8 Hz, 12H), 7.20 (d, J = 7.6 Hz, 12H), 7.14 (dd, J = 15.1, 8.0 Hz, 12H). MALDI-TOF MS (mass m/z): 808.1 [M+ + H].

2. Materials and methods

Tetrabutylammonium hexafluorophosphate $TBAPF_6$ (Bu_4NPF_6, 98%) was obtained from J&K chemicals. Dichloromethane and acetonitrile solvents at the chromatographic level were purchased from Aladdin. All the other chemical regents were used as received.

Indium tin oxide (ITO) glass substrates were cleaned by ultrasonic in a series of solvents including distilled water, ethanol, methylbenzene and acetone solutions for 15 minutes, respectively.

^1H (500MHz) NMR spectra of the synthesized compounds were recorded on Bruker AVANCE 111 instrument (Bruker, Switzerland). MALDI time-of-flight mass spectrometry (MALDI-TOF-MS) analysis was tested using an AXIMA-CFRTM plus instrument. DFT calculation of TTPATA was performed via Gaussian 09 at the B3LYP/6-311+G (d, p) level. UV-vis absorption spectra were recorded on Shimadzu UV-1800 spectrophotometer (Shimadzu, Japan). The IR spectra were carried out by Fourier transform infrared spectrometer (Thermo Fisher Nicolet, USA) with KBr pellets. The XPS spectra were carried out on an AXIS spectrometer (Kratos, England) using a monochromatic Al Ka excitation source (1486.6 eV). The film thickness was tested on DEKTAK-XK step profiler. The XRD study was performed on the pTTPATA polmer film by X' Pert PRO (PNAalytical, Netherlands) with Cu Ka radiation. The HR-TEM sample was obtained by loading pTTPATA film on micro grid support membrane and the image was recorded on a JEOL model JEM-2100F at an accelerating voltage of 200 kV. The SEM images of pTTPATA were carried out on Utral 55 (Carl Zeiss, Germany).

The pTTPATA polymer powder was prepared by chemical oxidation polymerization of TTPATA monomers in chloroform (30 ml) using ferric chloride as the oxidant. The mixture was refluxed by 40 ^oC for 24 h. After the polymerization, methanol was added to deposit the obtained polymer, which was filtrated and washed with methanol, HCl (2%) and water for several times to remove residual $FeCl_3$. Finally, the product was filtered and dried in vacuo at

60 ^{o}C for 24 h.

Electrochemical experiments were conducted by a CHI 660 E Electrochemical Workstation (Chen hua, China). Preparation of polymer films were performed with ITO-coated glass (active area, 9 mm × 20 mm) as a working electrode, platinum sheet (area, 10 mm ×40 mm) as a counter electrode, and a double-junction Ag/AgCl saturated KCl as a reference electrode. Electrochemical energy storage studies were tested in a three-electrode cell setup with two identical pTTPATA films as working and counter electrodes, and an Ag/AgCl as the reference electrode. The mass loading was measured by Mettler Toledo ultramicro balance. The monomer concentration of the obtained pTTPATA was 1 mM in dichloromethane containing 0.1 M $TBAPF_6$. All the above electrochemical tests were performed at the acetonitrile solution containing 0.1 M $TBAPF_6$.

3. The first CV curves of TPA, TTPATA and TPhTA in dichloromethane.

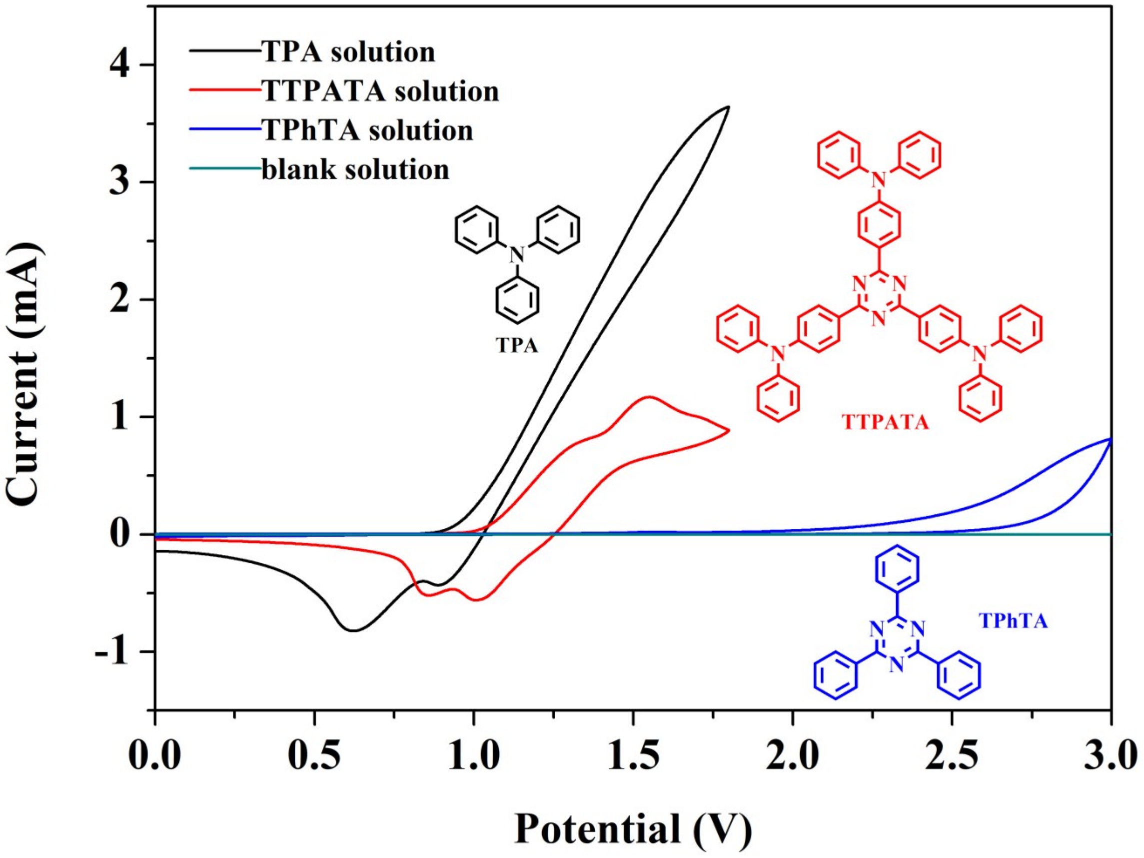


Figure S1 The first CV curves of 1.0 mM TPA (black curve), TTPATA (red curve) and TPhTA (blue curve) in dichloromethane containing 0.1 M $TBAPF_6$. CV curve of the blank electrolyte containing 0.1 M $TBAPF_6$ (green curve) is also presented.

4. Theoretical calculation of TTPATA

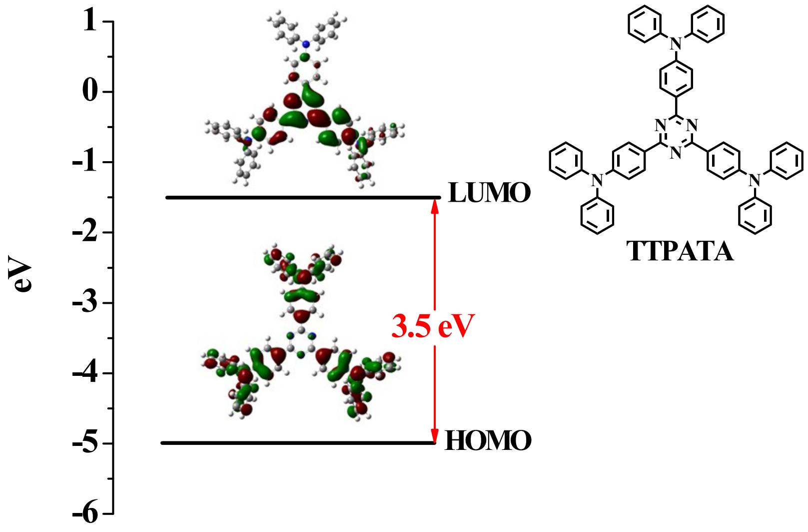


Figure S2 Theoretical calculation of TTPATA.

5. BET/BJH analyses of the pTTPATA polymers

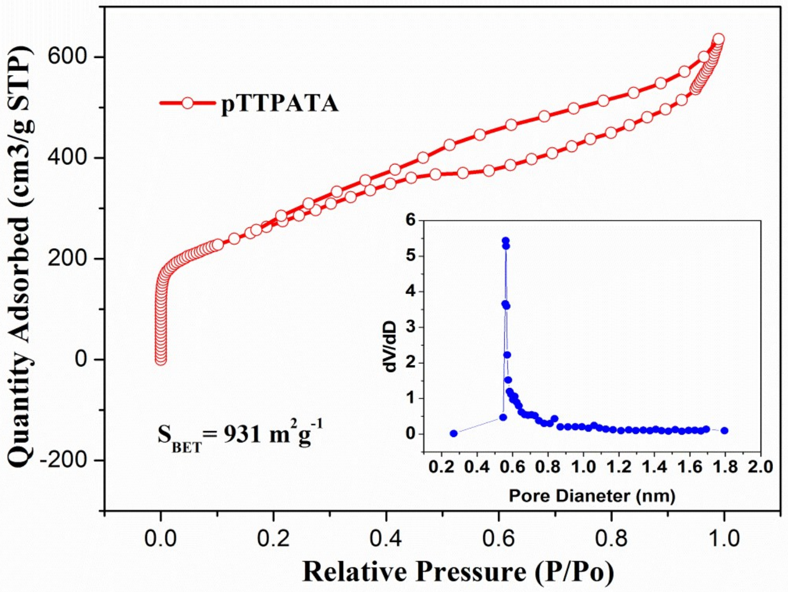


Figure S3 The N_2 adsorption-desorption (BET) isotherm of the pTTPATA polymers. The inset shows the BJH pore size distribution in the pTTPATA polymers.

6. Spectroelectrochemistry of TPA, BTPA and TTPAB spin-coated film

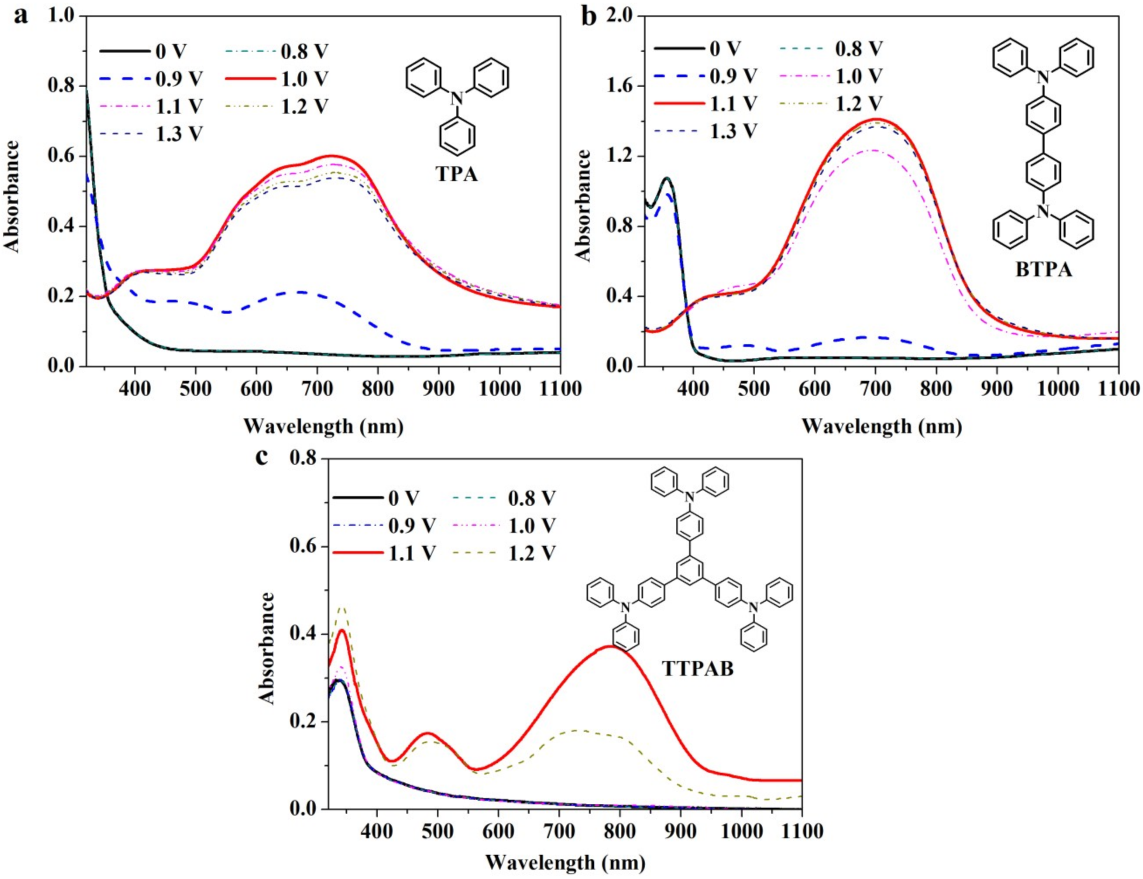


Figure S4 Spectroelectrochemistry of spin-coated film for (a) TPA and (b) BTPA at different applied voltages in H_2O containing $LiClO_4$, (c) TTPAB at different applied voltages in acetonitrile containing $TBAPF_6$.

7. The absorption-time curves of pTTPATA and BTPA spin-coated film upon removing the applied voltages.

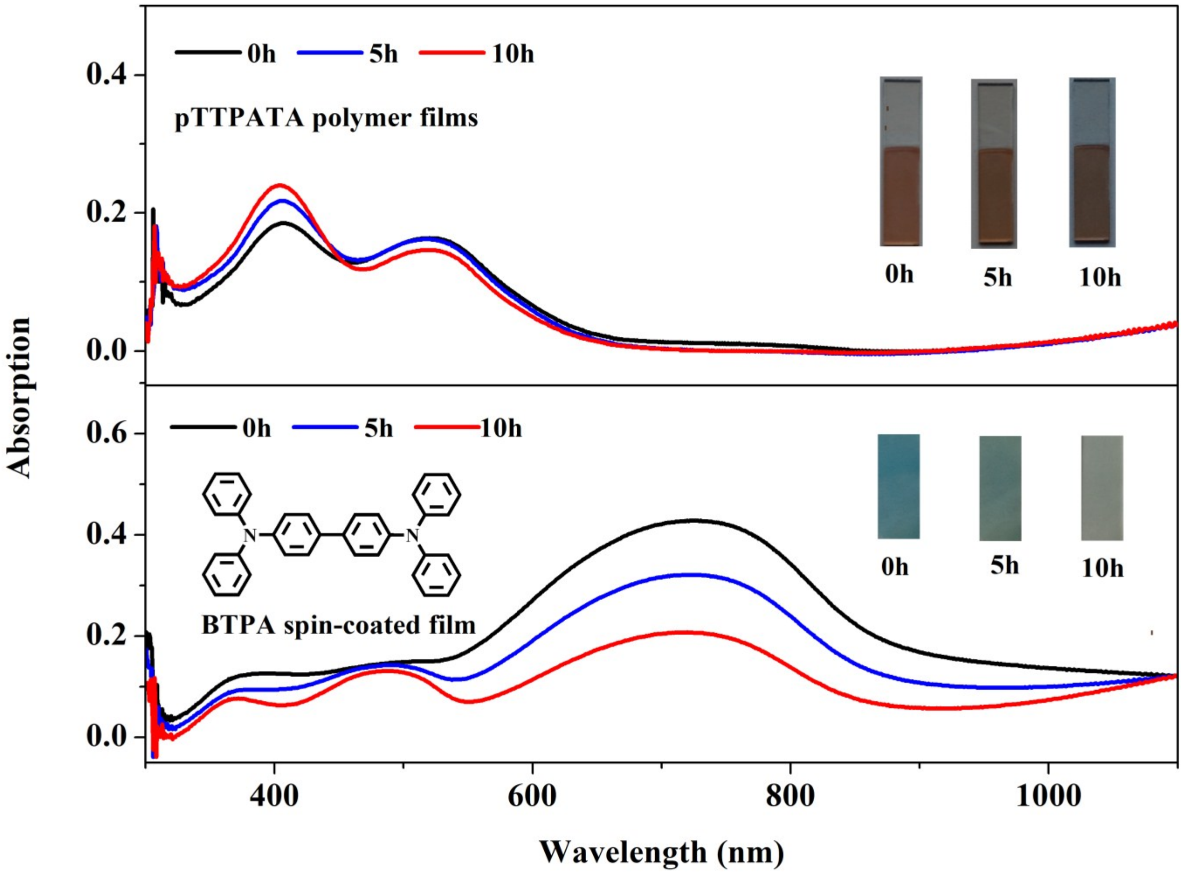


Figure S5 The UV-vis absorption curves of pTTPATA (top panel) and BTPA spin-coated film (bottom panel) at different time intervals upon removing the applied voltages. The inset images are the corresponding photographs of the electrodes taken with different exposition times from 0 to 10 h.

8. The fitting parameters of the nitrogen spectra

Table S1. The fitting parameters including name, peak type, position, FWHM, lorentzian-gaussain and residual error $\sum{}^2$ of the XPS curves in Fig. 3

Figure 3	Name	Peak Type	Position (eV)	FWHM	% Lorentzian-Gaussian (0%：G, 100%：L)	$\sum{}^2$
3a	C-N$^{\cdot+}$-C	s	400.9	0.93	0	1.05
	C-N-C	s	400.0	0.93	0	
	C-N$^{\cdot+}$=C	s	399.0	0.93	0	
	C-N=C	s	398.6	0.92	0	
3b	C-N$^{\cdot+}$-C	s	400.9	0.93	0	0.79
	C-N-C	s	400.0	0.93	0	
	C-N$^{\cdot+}$=C	s	399.0	0.93	0	
	C-N=C	s	398.6	0.93	0	
3c	C-N$^{\cdot+}$-C	s	400.9	0.94	0	0.77
	C-N-C	s	400.0	0.94	0	
	C-N$^{\cdot+}$=C	s	399.0	0.93	0	
	C-N=C	s	398.6	0.89	0	

9. C1s XPS spectra of pTTPATA film

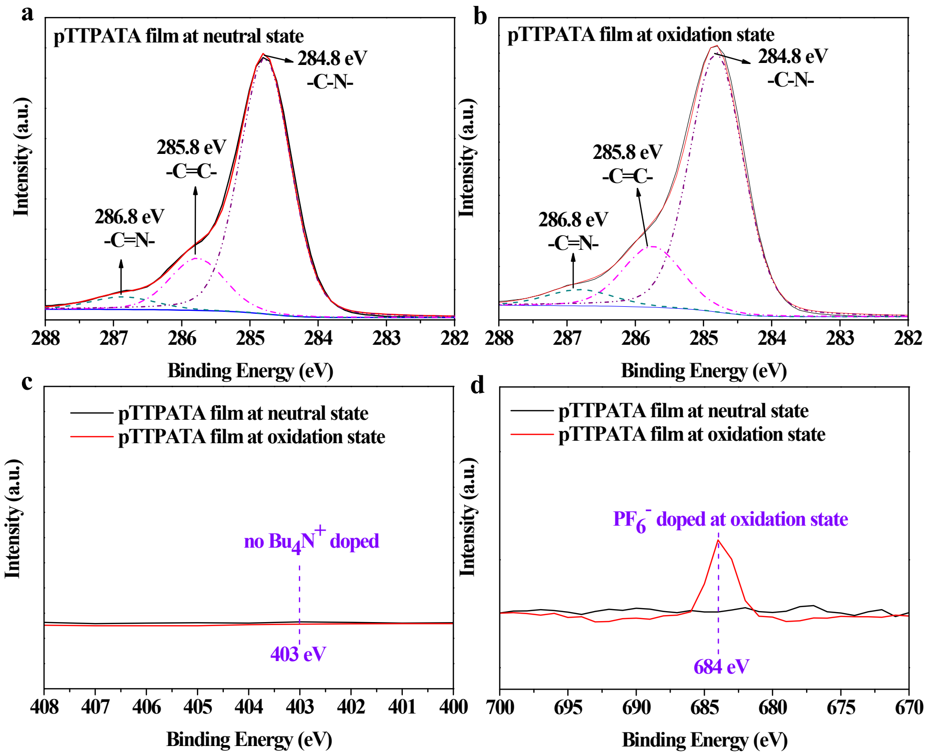


Figure S6 Core level C1s XPS spectra of pTTPATA film at (a) neutral state (applied voltage of 0 V) and (b) oxidized at 1.0 V. XPS spectra of the polymeric films at neutral and oxidized states between (c) 400 eV to 408 eV; and (d) 670 eV to 700 eV.

10. FT-IR spectra of pTTPATA film at the neutral and oxidative state

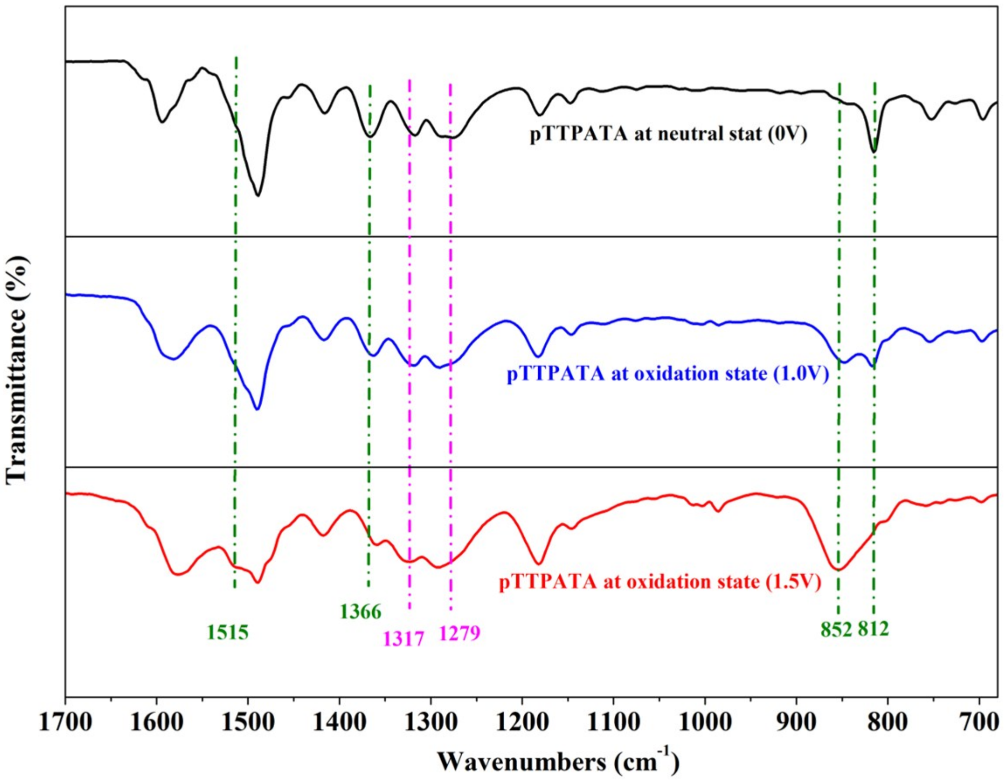
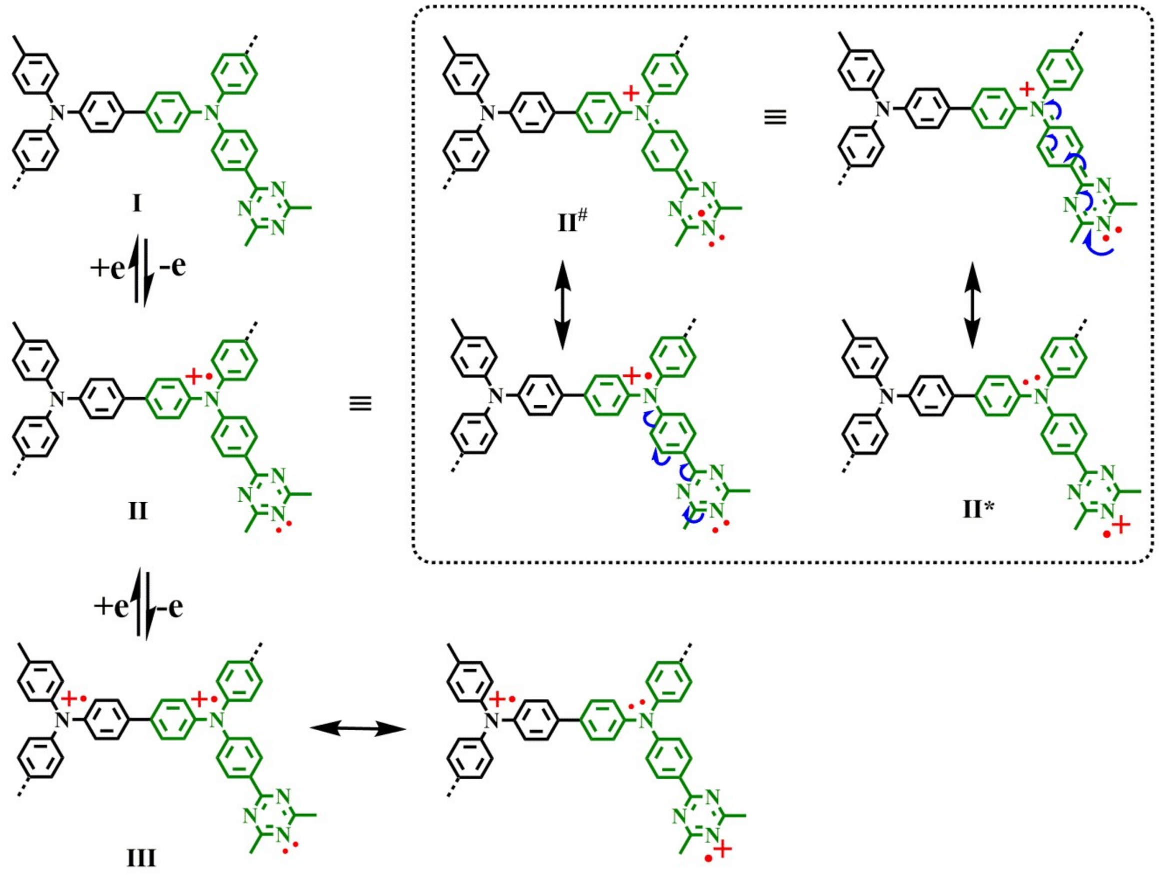


Figure S7 FT-IR spectra of pTTPATA film at neutral state (applied voltage of 0 V), oxidized at 1.0 V, and oxidized at 1.5 V.

11. The oxidation mechanism of pTTPATA



Scheme S2 The proposed oxidation mechanism of pTTPATA along with the resonance of the delocalized electrons in the structure of pTTPATA.

12. The coulombic efficiency of pTTPATA polymer films

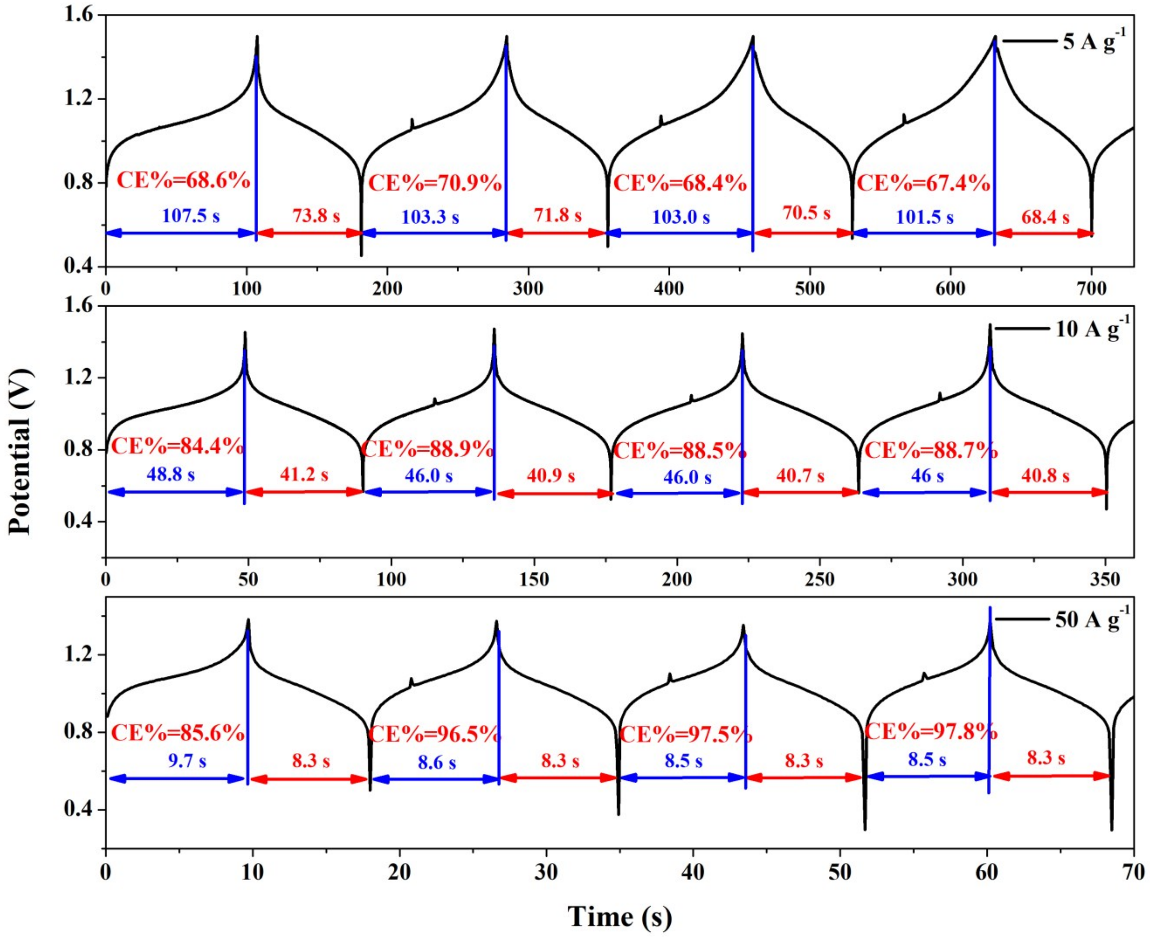


Figure S8 The coulombic efficiency of pTTPATA films at different specific current values of 5 A g^{-1}, 10 A g^{-1} and 50 A g^{-1}.

13. Estimations and test of pTTPATA film mass for energy storage application

The mass of the ultrathin pTTPATA film was estimated by the mass Lamber-Beer's law.[2] The final mass of a 57 nm thick film with active area of 1.6 cm^2 is about 8.35 μg, which is consistent with the results measured by Mettler Toledo ultramicro balance.

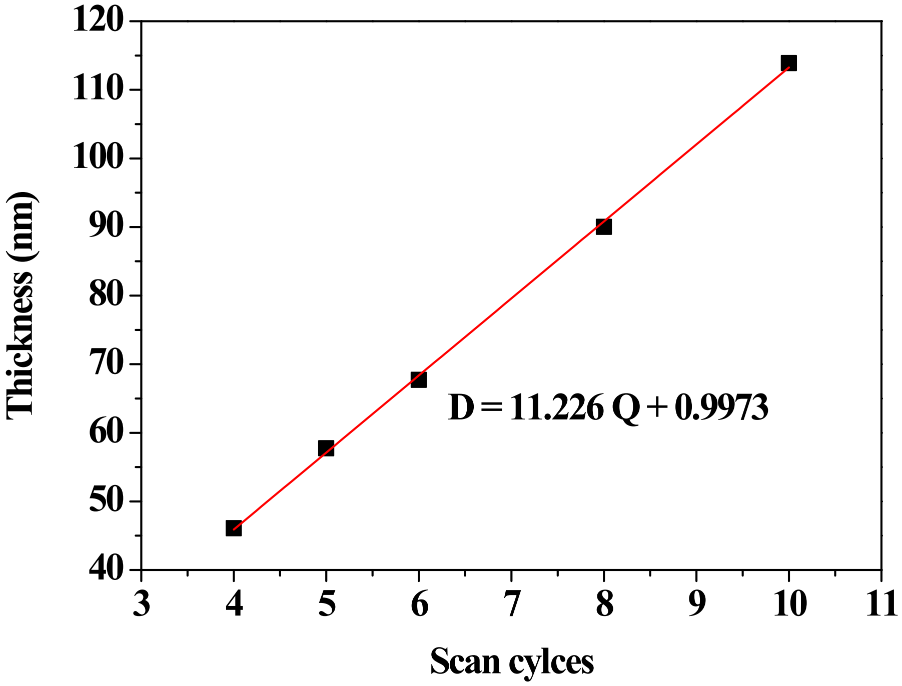


Figure S9 The relationship between film thickness and scan cycles.

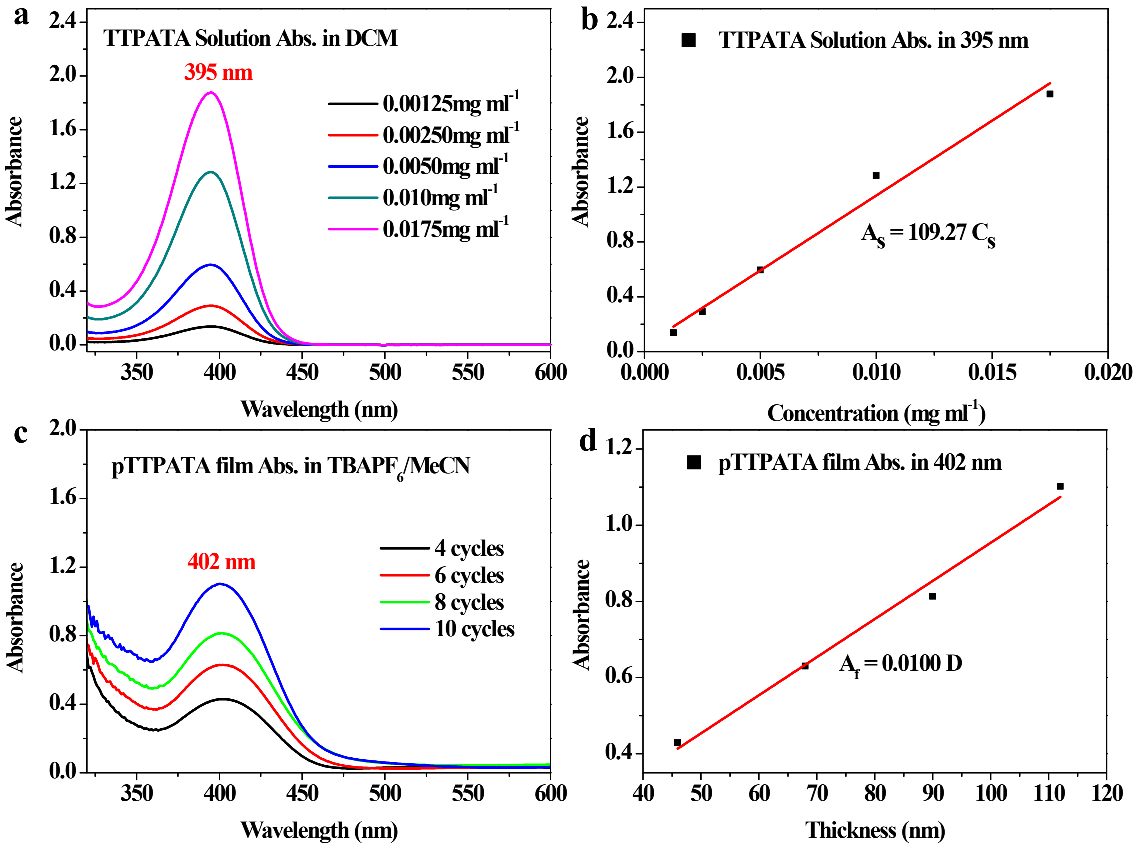


Figure S10 (a) The UV-vis absorption spectra of TTPATA at different concentrations of 0.00125 mg ml^{-1}, 0.00250 mg ml^{-1}, 0.0050 mg ml^{-1}, 0.010 mg ml^{-1} and 0.0175 mg ml^{-1}. (b) The relationship between the absorption intensity and concentration in 395 nm. (c) The absorption spectra of pTTPATA films at different scan cycles of 4, 6, 8, and 10. (d) The relationship between the absorption intensity and thickness in 402 nm.

Lambert-Beer's law:

$$A = K\,C\,L \qquad \text{Equation S1}$$

(A: absorption, K: absorption coefficient, C: concentration, L: optical length)

For TTPATA solution:

$$A = K_s\,C_s\left(\mathrm{mg\,ml^{-1}}\right)L_s\left(\mathrm{cm}\right) \qquad \text{Equation S2}$$

The L_S refers to the thickness of colorimetric cell, which is 1cm in our experiment.

From the Figure S4 (b), we get $K_s = 109.27$ ml mg^{-1} cm^{-1}

For pTTPATA film:

$$A_f = K_f C_f (mg\ ml^{-1}) L_f (cm) = K \rho (g\ cm^{-3}) D (nm) \qquad \text{Equation S3}$$

(ρ: film density, D: film thickness)

From the Figure 4 (d), we get $K_f \rho$ (g cm^{-3}) = 0.0100 nm^{-1}

For this experiment, we suppose that the absorption coefficient of TTPATA is not changed, i.e.

$$K_f \approx K_s = 109.27\ ml\ mg^{-1}\ cm^{-1}$$

Therefore, we get the ρ value

$$\rho = 0.0100\ nm^{-1}/109.27\ ml\ mg^{-1}\ cm^{-1} \approx 0.915\ g\ cm^{-3}$$

In this experiment, all pTTPATA films were prepared by cyclic voltammetry for 5 cycles. From the Figure S10, we got the relationship between the thickness and scan cycles: D = 11.226 Q + 0.9973. For 5 scan cycles, the thickness should be: D = 11.226 × 5 +0.9973 ≈ 57 nm. The active area of all pTTPATA films for utilization in an energy storage system was about 1.6 cm^2. So, the volume of pTTPATA films is estimated to be V = 57 nm × 1.6 cm^2 = 9.12×10^{-6}cm^3.

With the density and volume of pTTPATA films, the mass can be calculated to be:

$$m = \rho \times V = 0.915\ g\ cm^{-3} \times 9.12\times10^{-6}\ cm^3 \approx 8.35\ \mu g.$$

Test Experiment of pTTPATA film mass

The pTTPATA films, which were used for the mass measurement test, were prepared by cyclic voltammetry for 5 cycles. The active area of pTTPATA film for the measurement of mass was about 0.7 cm^2. The mass of pTTPATA film tested by Mettler Toledo ultramicro balance and the average value of mass was about 4 μg. From the Figure S10, we got the relationship between the thickness and scan cycles: D = 11.226 Q + 0.9973. The thickness of pTTPATA obtained by cyclic voltammetry over 5 scan cycles can be calculated to be D = 11.226 × 5 + 0.9973 = 57 nm. Using the above estimation method, the mass 57 nm-thick and

0.7 cm^2-area film was estimated to be m = 0.915 g cm^{-3}×57 nm×0.7 cm^2 ≈ 4 μg, which was consistent with the test experiment by Mettler Toledo ultramicro balance. Therefore, the mass test experiment proved the feasibility of the above estimation method.

14. References

1. L. F. Zhao, Y. L. Lin, T. Liu, H. X. Li, Y. Xiong, W. Z. Yuan, H. H.-Y. Sung, L. D. Williams, Y. M. Zhang, and B. Z. Tang, *J. Mater. Chem.,* 2015, **3,** 4903.
2. H. H. Zhang, Y. N. Zhang, C. Gu , and Y. G. Ma*, *Adv. Energy. Mater.,* 2015, **5,** 1402175.