Supporting Information

Fast Switching Properties and Ion Diffusion Behavior of Polytriphenylamine Derivative with Pendent Ionic Liquid Unit

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Experimental

Materials / Chemicals. Diphenylamine, 4-fluorobenzonitrile, sodium hydride, N-bromosuccinimide (NBS), bis(triphenylphosphine)palladium(II) dichloride, 2-thiophenylboric acid, potassium carbonate (K_2CO_3), sodium hydroxide, 4-dimethylaminopyridine (4-DMAP), 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDCI), 6-bromo-1-hexanol, 1-methylimidazole, silver tetrafluoroborate and tetrabutylammonium perchlorate (TBAP) were purchased from Adamas and used as received. Commercial HPLC grade acetonitrile (ACN, 99%) and dichloromethane (DCM, 99%) were purchased from Aladdin. Indium tin oxide (ITO) glass substrates (Kaivo Optoelectronic Technology Co., Ltd.) were cleaned by ultrasonic in a series of solvents including sodium hydroxide solution, distilled water, ethanol, acetone and methylbenzene for 15 minutes respectively.

Characterization. ^{1}H-NMR spectra of all these synthesized compounds was recorded by Bruker AVANCE III instrument (Bruker, Switzerland). Mass spectra (MS) was recorded by AXIMA-CFRTM plus instrument. Electrochemical polymerization of the monomers ($TTPAC_6Br$, $TTPAC_6IL\text{-}BF_4$) and electrochemical properties of their corresponding polymer films were performed by CHI660E electrochemical analyzer (Chen Hua, China). Surface morphology of polymer films was carried out by the NOVA NANOSEM 450 and AFM (Bruker Dimension, USA). Thickness measurement of polymer films was performed by the DEKTAK-XK step profiler. UV-Vis absorption spectra, spectroelectrochemical absorption spectra, optical transmittance and switching time were characterized by the Shimadzu UV-1800 spectrophotometer (Shimadzu, Japan) combined with CHI660E electrochemical analyzer. The electrochemical impedance spectroscopy (EIS) were carried out between 0.01Hz to 1 MHz by CHI660E electrochemical analyzer. Chromaticity coordinate data was collected in Japan Konica

Minolta spectrophotometer CM-3600d. The GAMESS program was used for computing parameters of the molecules. And the theoretical computations of frontier molecular orbitals as well as the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy level were based on restricted density functional theory (DFT) and were performed by using Becke's three-parameter hybrid method and the Lee-Yang-Parr exchange-correlation energy functional (B3LYP) with the 6-31G(d) basis set for all elements considered.

Synthesis of monomers.

Monomer synthesis 1: 4-(diphenylamino) benzonitrile. Sodium hydride (1.496 g) and diphenylamine (5.11 g) were firstly dissolved in N,N-Dimethylformamide (DMF) (40 mL). Then 4-fluorobenzonitrile (4.49 g) was added to the above solution. The reaction was performed under nitrogen atmosphere for 12 h at 110 ^{o}C. The resulting solution was extracted with DCM and saturated salt solution several times and dried by anhydrous $MgSO_4$. The solvent was evaporated off and the solid residue was purified by column chromatography to afford white powder with 58.2% (4.75 g) yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.43 (t, 2H), 7.35 (d, 4H), 7.18 (d, 2H), 7.16 (t, 4H), 6.97 (d, 2H) (**Figure S1**); MS (EI): m/z: 271.1.

Monomer synthesis 2: 4-(bis(4-bromophenyl)amino) benzonitrile. Monomer 1 (4 g) was firstly dissolved in DMF (30 mL). Then NBS (6.59 g) was dissolved in DMF (15 mL) and added to the solution dropwise. The reaction was performed without light for 24 h. The resulting solution was extracted with DCM and saturated salt solution several times and dried by anhydrous $MgSO_4$. The solvent was evaporated off and the solid residue was purified by column chromatography to afford white powder with 95.6% (6.0 g) yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.45 (d, 6H), 7.00 (d, 6H) (**Figure S2**); MS (EI): m/z: 428.9.

Monomer synthesis 3: 4-(bis(4-(thiophen-2-yl)phenyl)amino) benzonitrile. Monomer 2 (3.75 g), K_2CO_3 (5.4 g), bis(triphenylphosphine) palladium (II) dichloride (780 mg) and 2-thiophenylboric acid (3.9 g) were dissolved in methanol (50 mL) and toluene (50 mL). The reaction was performed under nitrogen for 24 h at 100 ^oC. The resulting solution was extracted with DCM and saturated salt solution several times and dried by anhydrous $MgSO_4$. The solvent was evaporated off and the solid residue was purified by column chromatography to afford white powder with 73.2% (2.79 g) yield. ^1H NMR (500 MHz, $CDCl_3$): δ 7.59 (m, 4H), 7.48 (d, 2H), 7.30 (d, 4H), 7.17 (d, 4H), 7.10 (d, 2H), 7.08 (d, 2H) (**Figure S3**); MS (EI): m/z: 434.8.

Monomer synthesis 4: 4-(bis(4-(thiophen-2-yl)phenyl)amino) benzoic acid. Monomer 3 (2.3 g) was dissolved in ethanol (40 mL) and 25% NaOH solution (40 mL). The reaction was performed for 14 h at 80 ^oC. The resulting solution was added with 3 M HCl (90 mL) and yellow powder was separated out. After filtrated by vacuum filtration and washed by distilled water, the product was then dried in vacuum for 24 h at 60 ^oC and afforded a yield of 91.6% (2.2 g). ^1H NMR (500 MHz, $CDCl_3$): δ 7.95 (d, 2H), 7.58 (m, 4H), 7.29 (d, 4H), 7.20 (d, 4H), 7.11 (d, 2H), 7.09 (d, 2H) (**Figure S4**); MS (EI): m/z: 454.2.

Monomer synthesis5: 6-bromohexyl 4-(bis(4-(thiophen-2-yl)phenyl)amino) benzoate (TTPAC_6Br) . Monomer 4 (1 g), 4-DMAP (0.14 g), EDCI (1.27 g) and 6-bromo-hexanol (0.60 g) were dissolved in DCM (25 mL). The reaction was performed for 15 h at 30 ^oC. The resulting solution was extracted with DCM and saturated salt solution several times and dried by anhydrous $MgSO_4$. The solvent was evaporated off and the solid residue was purified by column chromatography to afford yellow viscous liquid with 87.8% (1.19 g) yield. ^1H NMR (500 MHz, $CDCl_3$): δ 7.91 (d, 2H), 7.56 (m, 4H), 7.29 (d, 4H), 7.17 (d, 4H), 7.10 (d, 2H), 7.09 (d, 2H), 4.31

(t, 2H), 3.43 (t, 2H), 1.90 (m, 2H), 1.77 (m, 2H), 1.55 (m, 2H), 1.51 (m, 2H) (**Figure S5**); MS (EI): m/z: 617.2.

Monomer synthesis 6: 1-(6-((4-(bis(4-(thiophen-2-yl)phenyl)amino)benzoyl)oxy)hexyl)-3-methyl-imidazolium bromate (TTPAC$_6$IL-Br). Monomer 5 (690 mg) and 1-methylimidazole (83.3 mg) were dissolved in ACN (15 mL). The reaction was performed for 32 h at 70 ^{o}C. ACN in the resulting solution was evaporated off and ice ethyl acetate was added dropwise into the solution. The viscous liquid was kept and washed with ice ethyl acetate for several times. It was dried in vacuum for 24 h at 60 ^{o}C and yellow viscous liquid with 88.9 % (630 mg) yield was obtained. ^{1}H NMR (500 MHz, DMSO): δ 9.11 (s, 1H), 7.85 (d, 2H), 7.77 (d, 1H), 7.70 (d, 1H), 7.68 (m, 4H), 7.55 (d, 2H), 7.49 (d, 2H), 7.17 (d, 4H), 7.15 (d, 2H), 7.05 (d, 2H), 4.23 (t, 2H), 4.16 (t, 2H), 3.84 (s, 3H), 1.81 (m, 2H), 1.70 (m, 2H), 1.42 (m, 2H), 1.30 (m, 2H) (**Figure S6**), FTIR spectra was shown in **Figure S8**.

Monomer synthesis 7: 1-(6-((4-(bis(4-(thiophen-2-yl)phenyl)amino)benzoyl)oxy)hexyl)-3-methyl-imidazolium tetrafluoroborate (TTPAC$_6$IL-BF$_4$). Monomer 6 (296 mg) and silver tetrafluoroborate (108 mg) were dissolved in methanol (20 mL). The reaction was performed without light for 3 h at room temperature. In order to prevent sliver salt decomposed in the light, the resulting solution was filtrated in the dark and the orange-yellow solution was kept. The solvent was evaporated off and remained yellow powder with 80.6% (240 mg) yield. ^{1}H NMR (500 MHz, DMSO): δ 9.11 (s, 1H), 7.85 (d, 2H), 7.77 (d, 1H), 7.70 (d, 1H), 7.68 (m, 4H), 7.55 (d, 2H), 7.49 (d, 2H), 7.17 (d, 4H), 7.15 (d, 2H), 7.05 (d, 2H), 4.23 (t, 2H), 4.16 (t, 2H), 3.84 (s, 3H), 1.81 (m, 2H), 1.70 (m, 2H), 1.42 (m, 2H), 1.30 (m, 2H) (**Figure S7**) , FTIR spectra was shown in **Figure S8**.

Preparation of polymer films. The PTTPAC_6IL-BF_4 and PTTPAC_6Br films were prepared via cyclic voltammetry polymerization between 0 V to 1.4 V according to **Scheme 2** in a conventional three-electrode cell with an ITO-coated glass as working electrode, a platinum (Pt) sheet as auxiliary electrode and a Ag/AgCl electrode (silver wire coated with AgCl in saturated KCl solution) as reference electrode. The concentration of two monomers were 2 mM containing 0.1 M TBAP in DCM/ACN solutions (3: 7, by volume). The subsequent cyclic voltammetry curves of TTPAC_6Br and TTPAC_6IL-BF_4 were carried out at a scan rate of 0.1 V/s from 0 V to 1.4 V. The electrochemical behavior of monomer TTPAC_6IL-BF_4 and TTPAC_6Br were also tested using the glassy carbon electrode instead of the ITO glass as the working electrode with the same conditions. The electrochemical measurements of polymer films on ITO glasses were performed in 0.1 M TBAP/ACN solutions. Spectroelectrochemical experiments of polymer films on ITO glasses were carried out in 0.1 M TBAP/ACN solution as applied potentials between 0 V and 1.2 V. Optical contrast and switching time of polymer films were monitored in 0.1 M TBAP/ ACN solution between 0 V and 1.2 V with a residence of 5 s at 1100 nm and 420 nm.

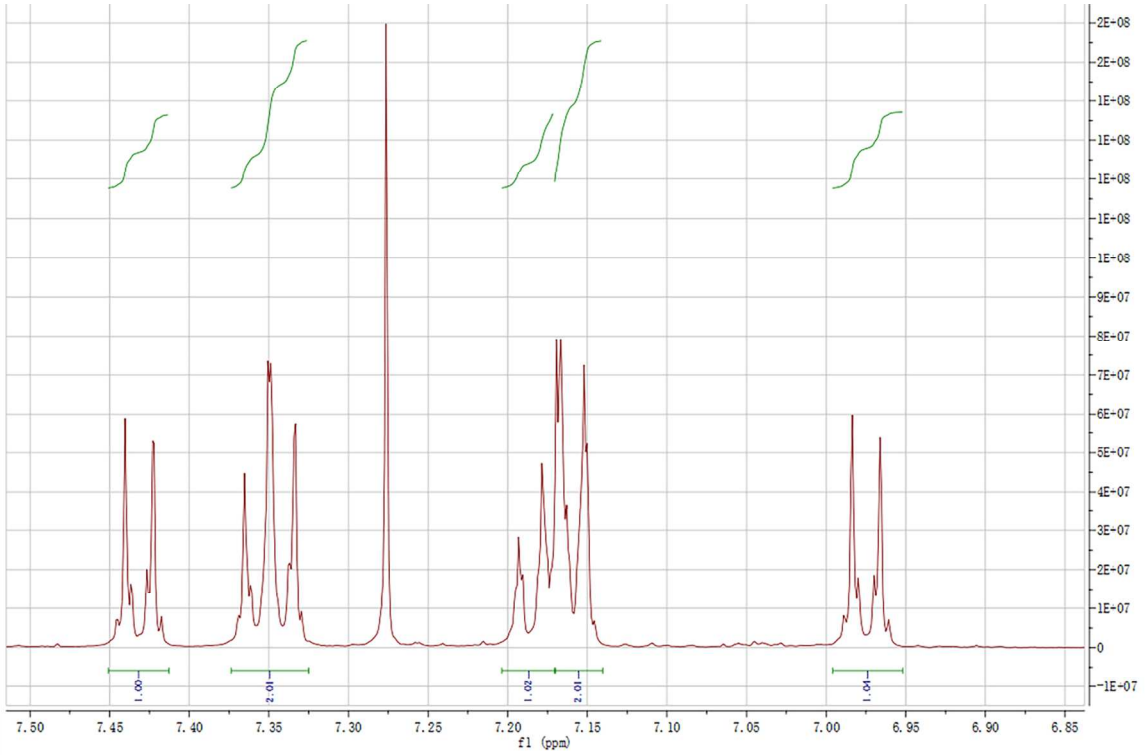

Figure S1 ^{1}H NMR spectra of 1 in $CDCl_3$

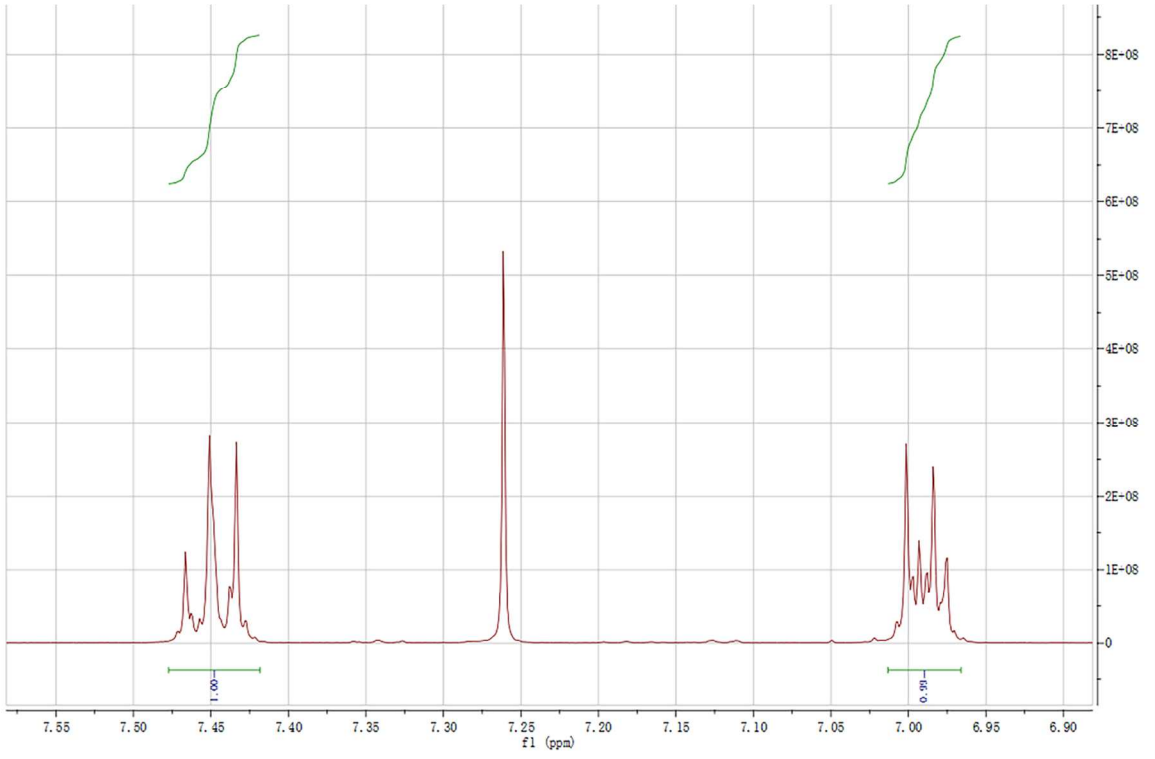

Figure S2 ^{1}H NMR spectra of 2 in $CDCl_3$

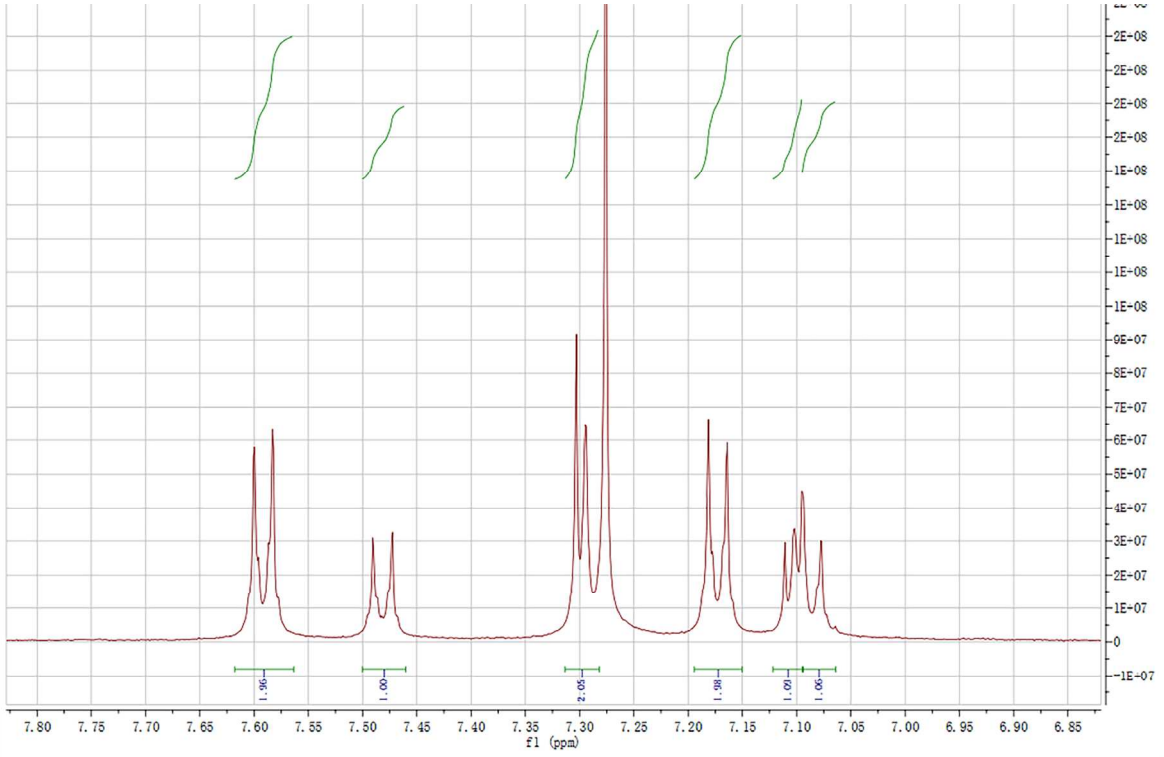

Figure S3 ^{1}H NMR spectra of 3 in $CDCl_3$

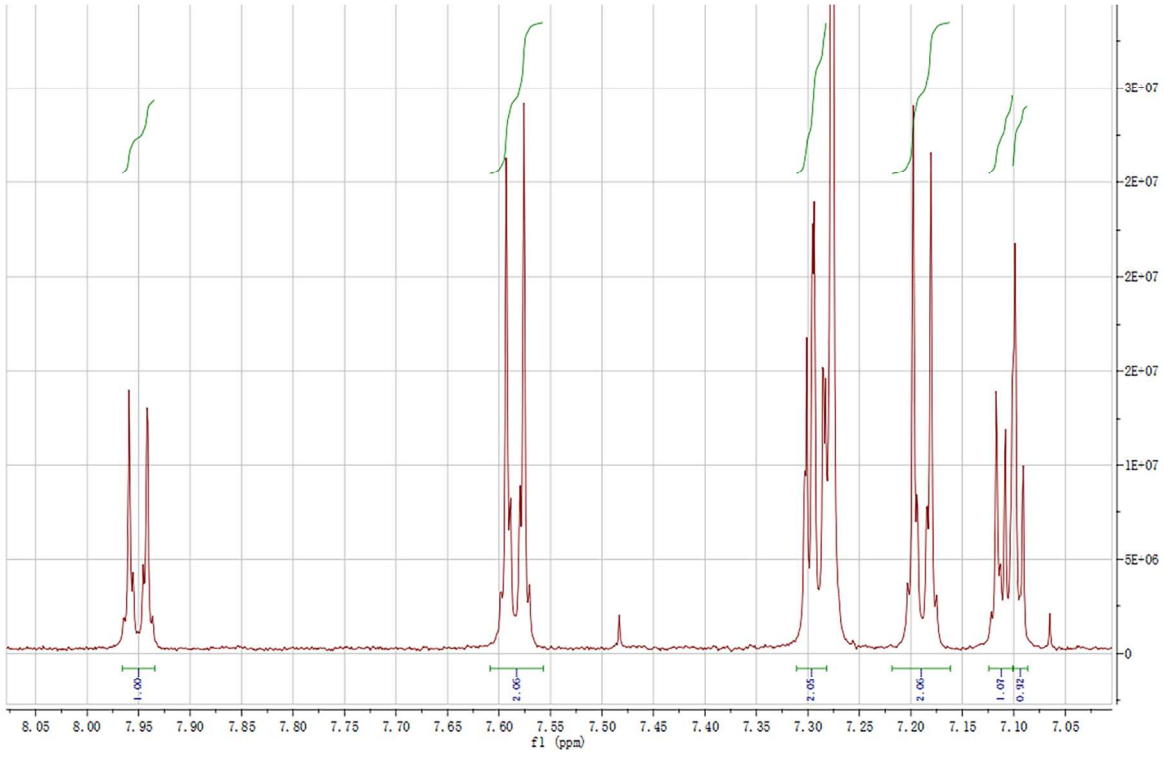

Figure S4 ^{1}H NMR spectra of 4 in $CDCl_3$

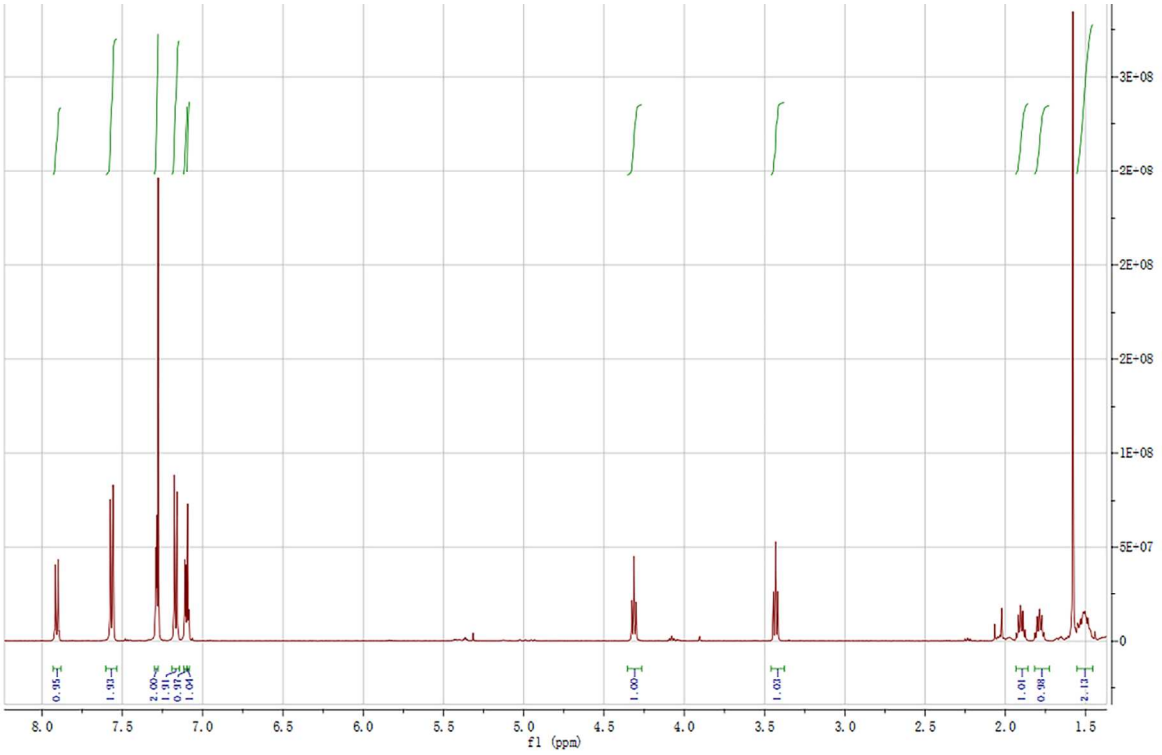

Figure S5 ^{1}H NMR spectra of 5 in $CDCl_3$

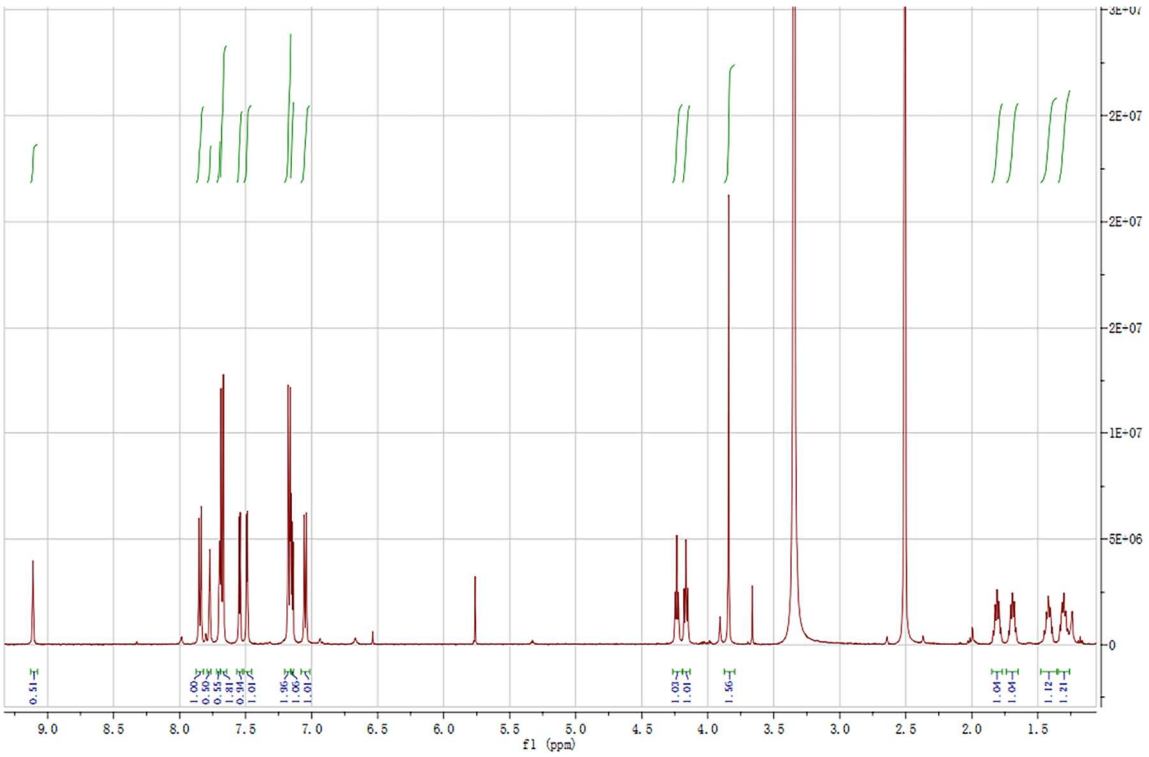

Figure S6 ^{1}H NMR spectra of 6 in DMSO-d6

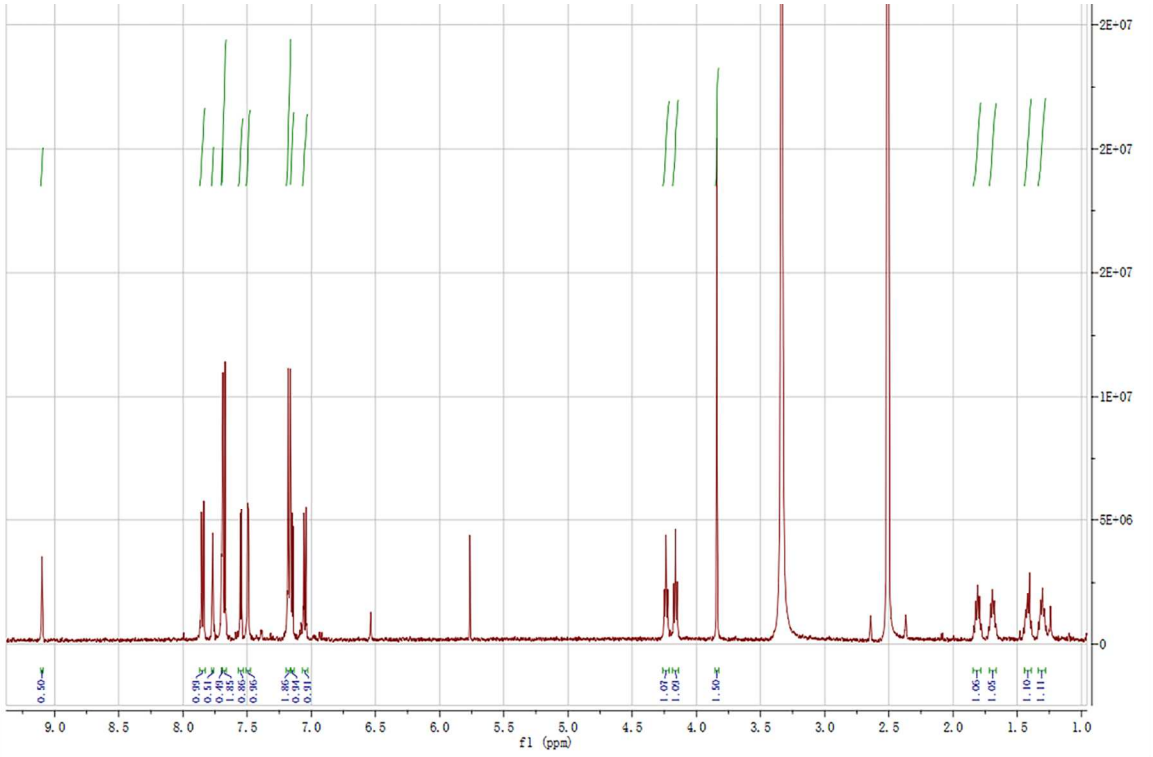

Figure S7 ^{1}H NMR spectra of 7 in DMSO-d6

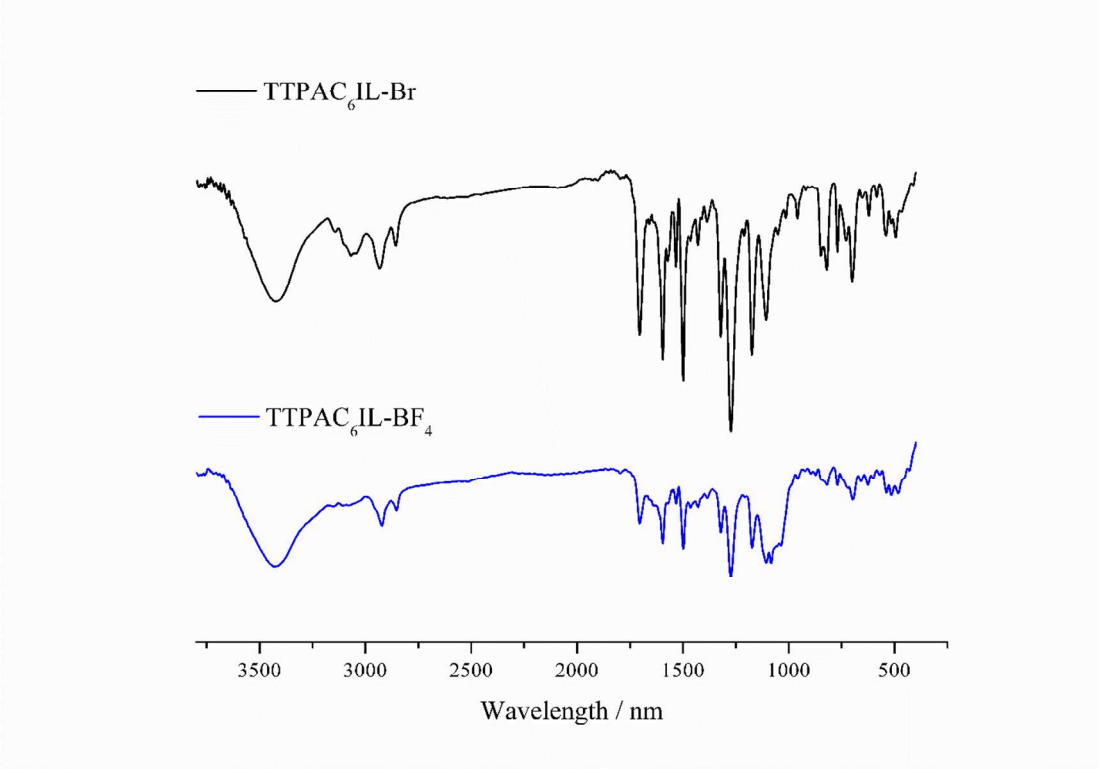

Figure S8 FTIR spectra of $TTPAC_6IL$-Br and $TTPAC_6IL$-BF_4

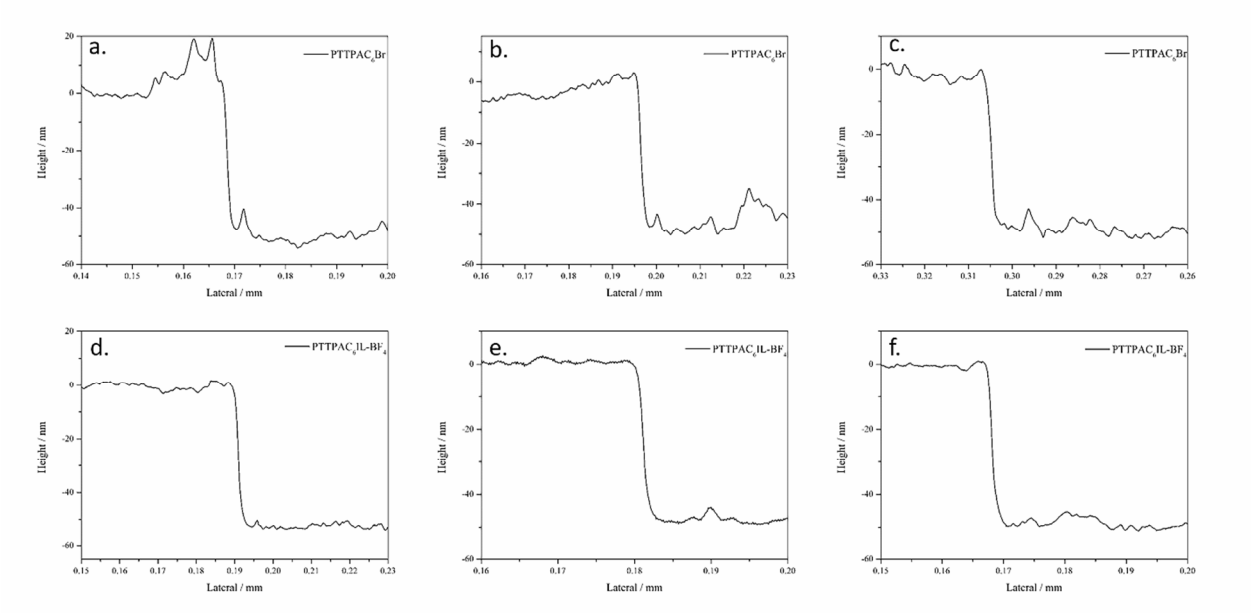

Figure S9 Thickness measurements of $PTTPAC_6Br$ (a, b, c) and $PTTPAC_6IL\text{-}BF_4$ (d, e, f) films

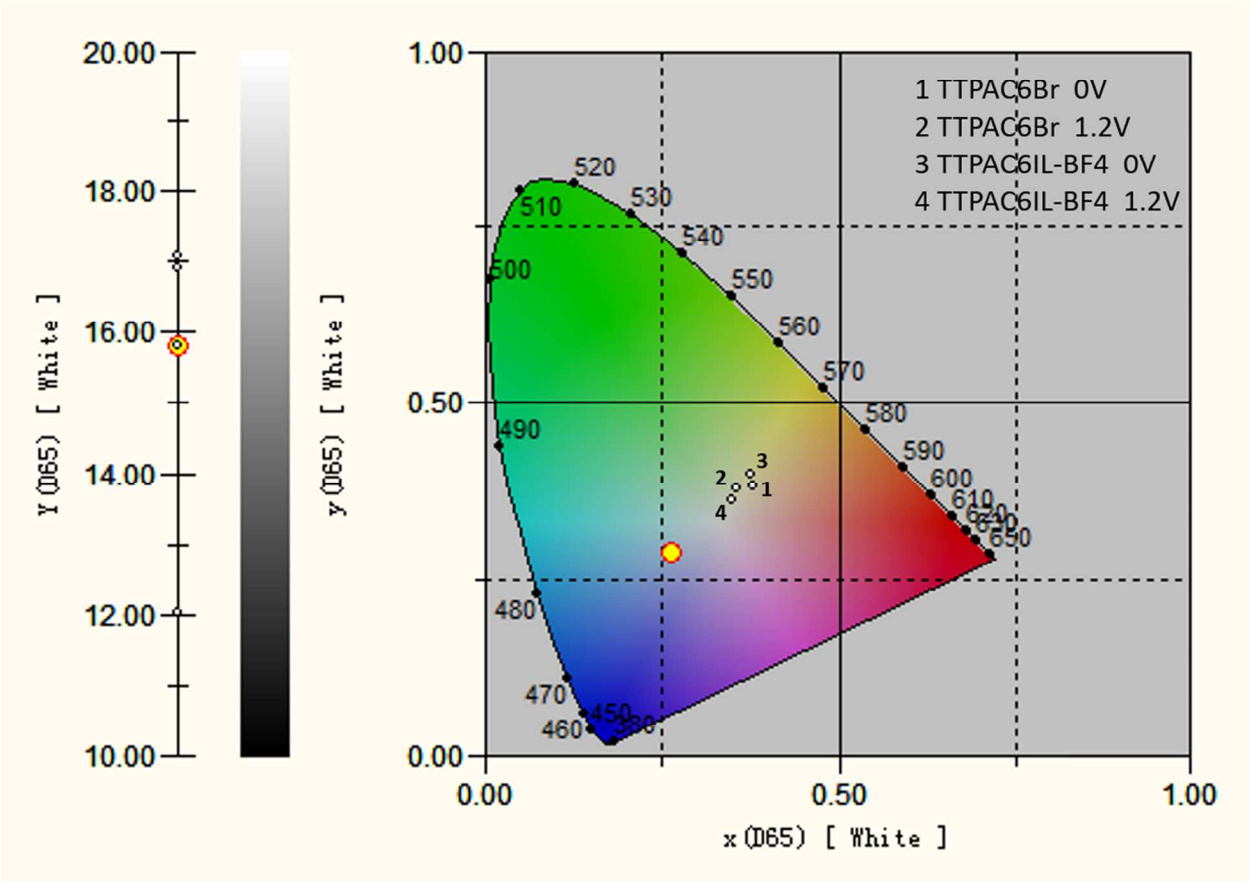

Figure S10 Chromaticity coordinate of $PTTPAC_6Br$ and $PTTPAC_6IL\text{-}BF_4$ films

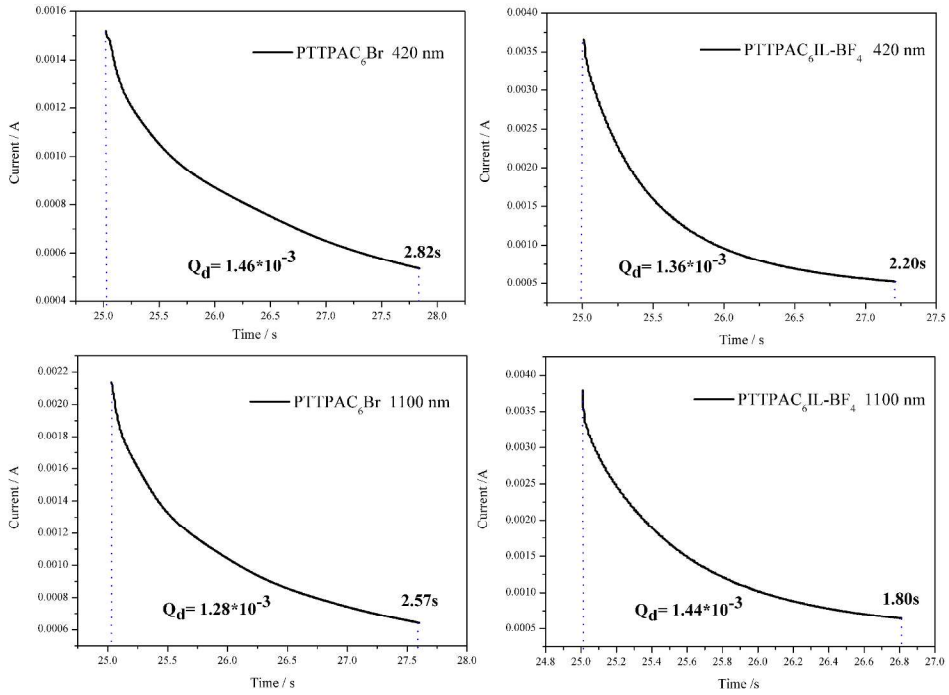

Figure S11 Chronoamperometry curve of $PTTPAC_6Br$ and $PTTPAC_6IL\text{-}BF_4$ films at 420 nm and 1100 nm

Table S1 Thickness data of $PTTPAC_6Br$ and $PTTPAC_6IL\text{-}BF_4$ films

Polymer	Film Thickness (nm)			Average Thickness (nm)
$PTTPAC_6Br$	51.83	50.30	51.32	51.15
$PTTPAC_6IL\text{-}BF_4$	51.69	49.98	48.74	50.14