# Supporting information

## Synthesis and Tunable Electrical Behaviors of Polyfluorene Functionalized with Triphenylamine and (3-Methyl-1-imidazolium-yl) hexyl Side Chains

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#### EXPERIMENTAL

**Measurements and Instruments**: 2,7-bis(4,4,5,5-tetramethyl-1,3,2- dioxab- orolan-2-yl)- 9,9dioctylfluorene (**M2**) and other analytically pure chemicals were purchased from Aldrich and used without further purification. All organic solvents were redistilled under dry nitrogen. All the operations were performed under purified nitrogen. 2,7-Dibromo-9,9- di(triphenylamine) fluorene (**M1**)<sup>[1]</sup>, and 2,7-dibromo-9,9-bis(6-bromohexyl) fluorene (**M3**)<sup>[2]</sup> were synthesized according to the literatures.

A Shimadzu UV-2450 spectrophotometer was employed to measure UV/Vis absorption spectral. A HORIBA JOBIN YVON Fluoromax-4 spectrofluorometer was used to record the steady-state fluorescence spectra. Fourier transform infrared (FTIR) spectra were recorded using Spectrum 100 spectrophotometer (Perkin Elmer, Inc., USA). An atomic force microscopy (Dimension V, Veeco) equipped with a conducting cantilever coated with Pt was employed for the C-AFM measurements of the device. Molecular weights [number-average (Mn) and weight-average (Mw)] were determined with a Waters 2690 gel permeation chromatography (GPC) using a polystyrene standards eluting with tetrahydrofuran. <sup>1</sup>Hnuclear magnetic resonance (NMR) spectra were recorded on a Bruker 400 spectrometer in deuterated solution with a tetramethylsilane (TMS) as a reference for the chemical shifts. For a cyclic voltammetry experiment, a CH instrument (CHI650D) electrochemical workstation was used at 298 K. Tetrabutylammonium perchlorate (n-Bu4NClO₄) in acetonitrile (0.1M) was used as the supporting electrolyte. An Ag/AgCl electrode was used as reference. Polymer film was deposited onto a Pt disk electrode (0.3 mm<sup>2</sup>) by drop-casting from THF solution. The Pt disk electrode was completely cleaned and dried before use.

**Device Fabrication:** A 50  $\mu$ L of polymer solution (10 mg·mL<sup>-1</sup>) in cyclohexanone was spincoated on the pre-cleaned ITO sheet at 800 rpm for 10 s and then at 2000 rpm for 40 s. Afterwards, the obtained device was thoroughly vacuum-dried at 60 °C for 10 h. The thickness of the film was estimated as 100 nm by step-profile. To complete fabricating the device, Ta top electrodes (90 nm in thick, 0.4×0.4 mm2 in area) were thermally deposited on the surface of active layer through a shadow mask at 10<sup>-7</sup> Torr. All electrical measurements in this work were performed on a Keithley 4200 semiconductor parameter analyzer in ambient condition without any protection.

#### General Procedures for Suzuki Polymerization Taking PTOBF-2 as an Example:

To a 25 mL Schlenk tube charged with **M1** (405 mg, 0.5 mmol), **M2** (642 mg, 1 mmol), **M3** (325 mg, 0.5 mmol), and tetrabutylammonium bromide (30.72 mg, 0.10 mmol) and K<sub>2</sub>CO<sub>3</sub> (552 mg, 4 mmol) was added Pd(PPh<sub>3</sub>)<sub>4</sub> (10 mg) in glove-box. Degassed toluene (8 mL) and distilled water (2 mL) were added into the mixture by syringe under nitrogen protection. After heating the mixture at 85 °C under nitrogen atmosphere for 36 h, excess phenylboronic acid and bromobenzene were added as end-capping reagents. The mixture was extracted with chloroform for three times, and the combined organic extracts were washed with water, brine and dried over sodium sulfate. The salt was filtered off and the filtrate was concentrated into a small volume. The polymer solution was added dropwise into stirred methanol. After filtration, the collected solid was purified by reprecipitating into methanol and then Soxhlet extraction with acetone. The polymer was dried under vacuum to give 689 mg of light yellow solid with a yield of 71.8%. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$ /ppm= 7.55-7.87 (m), 6.85-7.20 (m), 3.24-3.36 (br), 2.02-2.25 (br), 1.03-1.37 (m), 0.65-0.78 (m). GPC (THF): M<sub>n</sub> = 1.25 ×10<sup>4</sup>, M<sub>w</sub>/M<sub>n</sub> = 1.78

**PTOF: M1** (810 mg, 1 mmol), **M2** (642 mg, 1 mmol). 841 mg of light yellow solid, yield 81.3%. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$ /ppm= 7.55-7.87 (m), 6.85-7.20 (m), 2.02-2.25 (br), 1.03-1.37 (m), 0.65-0.78 (m). GPC (THF): M<sub>n</sub> = 1.42 ×10<sup>4</sup>, M<sub>w</sub>/M<sub>n</sub> = 1.72

**PTOBF-1: M1** (607.5 mg, 0.75 mmol), **M2** (642 mg, 1 mmol), **M3** (162.5 mg, 0.25 mmol). 800 mg of light yellow solid, yield 87.0%. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$ /ppm= 7.55-7.87 (m), 6.85-7.20 (m), 3.24-3.36 (br), 2.02-2.25 (br), 1.03-1.37 (m), 0.65-0.78 (m). GPC (THF): M<sub>n</sub> = 1.33 ×10<sup>4</sup>, M<sub>w</sub>/M<sub>n</sub> = 1.92

**PTOBF-3: M1** (202.5 mg, 0.25 mmol), **M2** (642 mg, 1 mmol), **M3** (487.5 mg, 0.75 mmol). 788 mg of light yellow solid, yield 78.8%. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$ /ppm= 7.55-7.87 (m), 6.85-7.20 (m), 3.24-3.36 (br), 2.02-2.25 (br), 1.03-1.37 (m), 0.65-0.78 (m). GPC (THF): M<sub>n</sub> = 1.14 ×10<sup>4</sup>, M<sub>w</sub>/M<sub>n</sub> = 1.83

**POBF: M2** (642 mg, 1 mmol), **M3** (650 mg, 1 mmol). 810 mg of light yellow solid, yield 92.0%. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz): δ/ppm= 7.55-7.87 (m), 3.24-3.36 (br), 2.02-2.25 (br), 1.03-1.37 (m), 0.65-0.78 (m). GPC (THF): Mn = 1.07 ×10<sup>4</sup>, M<sub>w</sub>/M<sub>n</sub> = 1.64

General Procedures for the Synthesis of Polyelectrolytes Taking PTOIF-2 as an Example:

Four polyelectrolytes (PTOIF-1, PTOIF-2, PTOIF-3 and POIF) were synthesized according to the method reported in the literatures.<sup>[3]</sup> In a typical synthesis procedure, for example, **PTOBF-2** (100 mg) was dissolved in dry chloroform (10 mL). On addition of acetonitrile (5 mL) and 1 mL of N-methyl imidazole (12.5 mmol), the stirred mixture was refluxed for 24 h and then was allowed to cool to room temperature. A concentrated solution was added dropwise into stirred ice ether. The collected crude solid after filtration was further purified by re-precipitating into ice ether, and then subjected to Soxhlet extraction with ether for 24 h. 116mg of **PTOIF-2** was obtained. <sup>1</sup>H-NMR (DMSO-d6, 400 MHz):  $\delta$ /ppm= 9.00 (br), 7.60-8.02 (m), 6.85-7.44 (m), 4.03-4.14 (br), 3.82-3.92 (m), 2.05-2.40 (br), 1.05-1.35 (m), 0.65-0.95 (m).

**PTOIF-1:** <sup>1</sup>H-NMR (DMSO-d6, 400 MHz): δ/ppm= 9.01 (br), 7.60-8.14 (m), 6.85-7.25 (m), 4.03-4.14 (br), 3.82-3.92 (m), 2.05-2.40 (br), 1.05-1.35 (m), 0.65-0.95 (m).

**PTOIF-3:** <sup>1</sup>H-NMR (DMSO-d6, 400 MHz): δ/ppm= 9.04 (br), 7.60-8.04 (m), 6.85-7.45 (m), 4.03-4.14 (br), 3.82-3.92 (m), 2.05-2.40 (br), 1.05-1.35 (m), 0.65-0.95 (m).

**POIF:** <sup>1</sup>H-NMR (DMSO-d6, 400 MHz): δ/ppm= 9.06 (br), 7.50-8.02 (m), 4.03-4.14 (br), 3.82-3.92 (m), 2.05-2.40 (br), 1.05-1.35 (m), 0.65-0.95 (m).

	PTOF	PTOIF-1	PTOIF-2	PTOIF-3	POIF
T <sub>d</sub> (°C)	324	254	251	258	274
$T_g(^{\circ}C)$	133				

**Table S1.** The glass transition temperature  $(T_g)$  and decomposition temperature  $(T_d)$  of the polymers.







**ure S1.** <sup>1</sup>H-NMR spectra of (a) PTOIF-1, (b) PTOIF-2, (c) PTOIF-3, and (d) PTOIF in DMSO-d6.



Figure S2. UV/Vis absorption spectra of PTOF in dilute THF (—) and toluene (—) solutions.



**Figure S3.** The UV-Vis absorption (a) and photoluminescence (b) spectra of the polymer thin films.



**Figure S4.** Cyclic voltammograms of the polymer films coated on platinum plate electrode in deaerated acetonitrile solution containing 0.1M <sup>*n*</sup>Bu<sub>4</sub>NClO<sub>4</sub> at room temperature. Scan rate: 100 mV/s.



Figure S5. AFM images of the polymer film with a scanning size of  $8 \times 8 \ \mu m^2$ : (a) PTOF, (b) PTOIF-1, (c) PTOIF-2, (d) PTOIF-3, and (e) POIF.



**Figure S6.** Effect of operation time on the ON and OFF state currents of the ITO/polymer/Ta devices under a constant stress of -0.1 V



**Figure S6.** Effect of read pulses of -0.1 V on the ON and OFF state currents of the ITO/polymer/Ta devices. Pulse width =  $1\mu$ s; Pulse period =  $2\mu$ s.

### References

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