## **Supporting information**

# A series of blue supramolecular polymers with different counterions for polymer light-emitting diodes

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#### 1. Measurement and characterization.

<sup>1</sup>H and <sup>13</sup>C NMR were recorded using a bruker-300 and 600 spectrometer operating at 300 or 600 and 150 MHz at 298K. Chemical shifts were reported as  $\delta$  values (ppm) relative to an internal tetramethylsilane (TMS) standard.Time-of-flight mass spectrometry (TOF-MS) was performed in the positive ion mode with matrix of dithranol using bruker-autoflex III smartbean. Differential scan calorimetry (DSC) measurements were carried out with a Netzsch DSC 204 under N<sub>2</sub> flow at heating and cooling rates of 10 °C min<sup>-1</sup>.The viscosity was measured with a digital viscometer from Brookfield Engineering Laboratories, Inc. (model LVDV-I+). UV-vis absorption spectra was performed on a HP 8453 spectrophotometer. PL spectra were recorded on an Hitachi F-4500 fluorescence spectrophotometer.

### 2. Device fabrication and measurement

The device was fabricated according to the configuration indium tin oxide (ITO)/poly(3,4-ethylenedioxythiophene):poly(styrene sulfonic acid) (PEDOT:PSS)/ FSO-FX/aluminium. The ITO-coated glass substrates were ultrasonically cleaned with deionized water, acetone, detergent, deionized water, isopropyl alcohol. Then a layer of 40 nm thick PEDOT:PSS (H.C.Stack, 4083) was spin-coated onto the precleaned and O<sub>2</sub>-plasma-treated ITO substrates. After that, the PEDOT:PSS layer was baked at 150 °C for 20 min to remove residual water, and then the devices were moved into glove box under the nitrogen-protected environment. FSO-FX was later spin-coated from chlorobenzene solution onto the PEDOT:PSS layer. The samples were transfer into chamber and kept under vacuum  $(3.0 \times 10^{-4} \text{ Pa})$  for 2 h. Aluminum with thickness of 100 nm were subsequently deposited on top of the FSO-FX to form cathode. The current density (*J*) and brightness (*L*) versus voltage (*V*) data were collected using a Keithley 236 source meter and silicon photodiode. After typical encapsulation with UV epoxy and cover glass, the devices were taken out from dry box and the luminance was calibrated by a PR-705 SpectraScan Spectrophotometer (Photo Research) with simultaneous acquisitions of the EL spectra.

3. Synthesis of the monomers FSO and FX.



Scheme S1. Synthesis of the monomers FSO.

3,7-Dibromodibenzothiophene-S,S-dioxide  $(1)^1$ , 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene  $(2)^2$ , 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-dibenzo-24-crown-8  $(5)^3$ , and N,N'-(((2,2':7',2''-ter(9,9-dioctylflourene)-7,7"-diyl)bis(4,1-phenylene))bis(methylene))bis(1-

phenylmethanaminium) hexafluorophosphate(V)  $(FPF_6)^3$  were prepared according to the reported procedures. All chemicals and reagents were purchased from commercial

sources (Adrich, Acros, and Alfa Aesar) and used without further purification unless stated otherwise.

#### Synthesis of 3,7-di(9,9-dioctylflourene-2-yl)-dibenzothiophene-S,S-dioxide (3)

3,7-Dibromodibenzothiophene-S,S-dioxide (1) (0.75g, 2mmol), 2-(4,4,5,5tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene (2) (2.27g, 4.2 mmol), and tetrakis(triphenylphosphine)palladium [Pd(PPh<sub>3</sub>)<sub>4</sub>](40 mg)were added in a 100 mL two-necked round-bottomed flask.Toluene (40 mL), THF (20 mL) and 20% aqueous tetraethylammonium hydroxide (6 mL)were added to the flask under argon.The mixture was refluxed for 24 h under argon atmosphere. After the mixture had been cooled to the room temperature, the mixturewas poured into brine.Then the mixture was extracted with dichloromethane, the two phases was separated, and the water phase was extracted twice with dichloromethane. The combined organic extracts were washed three times with water, dried over MgSO<sub>4</sub>, evaporated, and purified with column chromatography (silica gel, petroleum ether/dichloromethane (4/1) as eluent) to yield1.62 g (82%) of **1** as a light yellow solid.<sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  (ppm): 8.15 (s, 2H), 7.97~7.88 (m, 4H), 7.78 (d, *J* = 7.9 Hz, 2H), 7.66~7.58 (m, 6H), 7.51~7.45 (m, 6H), 2.05~1.97 (m, 8H), 1.33~1.27 (m, 8H), 1.25~1.07 (m, 32H), 0.86~0.77 (m, 12H), 0.73~0.70 (m, 8H).

# Synthesis of 3,7-di(7-bromo-9,9-dioctylflourene-2-yl)-dibenzothiophene-S,Sdioxide (4)

A flask was charged with 3 (0.99g, 1.0 mmol) and 3.37g CuBr<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>. 100 mL CCl4 were added and the suspension was stirred at 70 °C for two weeks. The CuBr<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> was filtered off. The organic extracts were evaporated, and purified with column chromatography (silica gel, petroleum ether/dichloromethane (4/1) as eluent) to yield0.75 g (65%).<sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  (ppm): 8.14 (s, 2H), 7.96~7.89 (m, 4H), 7.77 (d, *J* = 7.9 Hz, 2H), 7.64~7.59 (m, 6H), 7.50~7.47 (m, 4H), 2.06~1.96 (m, 8H), 1.33~1.28 (m, 8H), 1.23~1.07 (m, 32H), 0.85~0.77 (m, 12H), 0.72~0.70 (m, 8H).

# Synthesis of 3,7-di((7-dibenzo-24-crown-8)-9,9-dioctylflourene-2-yl) dibenzothiophene-S,S-dioxide (FSO)

4 (2.30 g, 2.0 mmol), 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)- dibenzo-24-crown-8 (5) (3.32 g,5.8 mmol), and Pd(PPh<sub>3</sub>)<sub>4</sub>(60 mg)were added in a 100 mL two-necked round-bottomed flask. Toluene (20 mL), THF (20 mL) and 20% aqueous tetraethylammonium hydroxide (8 mL)were added to the flask under argon. The mixture was refluxed for 36 h under argon atmosphere. After the mixture had been cooled to the room temperature, the mixturewas poured into brine. Then the mixture was extracted with dichloromethane, the two phases was separated, and the water phase was extracted twice with dichloromethane. The combined organic extracts were washed three times with water, dried over MgSO<sub>4</sub>, evaporated, and purified with column chromatography (alumina, petroleum ether/ethyl acetate/dichloromethane (4/3/1) as eluent) to yield2.75 g (72%) of 1as a light yellow solid.<sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz)  $\delta$  (ppm):8.16 (s, 2H), 7.96 (d, J = 7.8 Hz, 2H), 7.91 (d, J = 7.8 Hz, 2H), 7.81 (d, J = 7.8 Hz, 2H), 7.77 (d, J = 7.8 Hz, 2H), 7.63(d, J = 7.8 Hz, 2H), 7.61 (s, 2H), 7.53 (d, J = 7.8 Hz, 2H), 7.51 (s, 2H), 7.23~7.21 (m, 4H), 6.97 (d, J = 7.8 Hz, 2H), 6.91~6.85 (m, 8H), 7.50~7.47 (m, 4H), 4.31~4.30 (m, 4H), 4.25~4.24 (m, 4H), 4.19~4.18 (m, 8H), 4.00~3.96 (m, 16H), 3.89 (s, 16H), 2.10~2.07 (m, 8H), 1.26~1.18 (m, 8H), 1.14~1.10 (m, 32H), 0.83~0.80 (m, 12H), 0.72~0.70 (m, 8H).<sup>13</sup>C NMR (CDCl<sub>3</sub>, 150 MHz) δ (ppm):152.1, 151.8, 149.2, 149.0, 148.7, 148.0, 147.1, 144.3, 141.7, 140.3, 138.7, 137.3, 135.1, 132.6, 129.9, 126.0, 125.9, 121.9, 121.5, 121.3, 121.2, 120.6, 120.4, 120.3, 120.2, 114.2, 113.8, 71.3, 71.2, 70.0, 69.9, 69.5, 69.8, 69.6, 69.4, 31.8, 30.0, 29.2, 23.9, 22.6, 14.0. MALDI-TOF (m/z): calcd1886.04, found [M]<sup>+</sup>1886.18, [M + Na]<sup>+</sup>1909.01.

#### General procedure for counterion exchange.

N,N'-(((2,2':7',2"-Ter(9,9-dioctylflourene)-7,7"-diyl)bis(4,1phenylene))bis(methylene))bis(1-phenylmethanaminium) hexafluorophosphate(V) (300 mg, 0.16 mmol) was dissolved in 10 mL methanol/THF. Subsequently, a solution with an excess of a salt containing the desired anion of interest in 10 mL water was added. The mixture was stirred for two days at room temperature. The mixture was poured into a 1000 molecular weight cutoff symmetric cellulose ester membrane sealed with closures, and immersed into a 2L beaker filled with deionized water. The water inside the membrane was filtered after dialysis for two days. The product was obtained by drying under vacuum.

# Synthesis of N,N'-(((9,9,9',9'',9'',9''-hexaoctyl-9H,9'H,9''H-[2,2':7',2''terfluorene]-7,7''-diyl)bis(4,1-phenylene))bis(methylene))bis(1phenylmethanaminium) bromide(FBr)

**FPF**<sub>6</sub> (300 mg, 0.16 mmol) and NaBr (2.06 g, 20 mmol) were used to yield 220 mg (80%) of **FBr**.<sup>1</sup>H NMR (DMSO, 600 MHz)  $\delta$  (ppm): 7.96~7.95 (m, 8H), 7.86~7.72 (m, 16H), 7.61~7.59 (m, 4H), 7.52~7.47 (m, 8H), 4.24 (s, 4H), 4.19 (s, 4H), 2.13~2.10 (m, 12H), 0.99 (m, 60H), 0.67 (m, 30H). MADLI-TOF (m/z): calcd [M – 2 Br]<sup>+</sup> 1560.18, found [M – 2 Br]<sup>+</sup> 1556.86.

# Synthesis of N,N'-(((9,9,9',9',9'',9''-hexaoctyl-9H,9'H,9''H-[2,2':7',2''terfluorene]-7,7''-diyl)bis(4,1-phenylene))bis(methylene))bis(1phenylmethanaminium)tetrakis(1-imidazolyl)borate (FBIm<sub>4</sub>)

**FPF**<sub>6</sub> (300 mg, 0.16 mmol) and sodiumtetrakis(1-imidazolyl)borate (3.04 g, 10 mmol) were used to yield 250 mg (74%) of **FBIm**<sub>4</sub>.<sup>1</sup>H NMR (CDCl<sub>3</sub>/CD<sub>3</sub>CN, 600 MHz)  $\delta$  (ppm): 7.91~7.82 (m, 6H), 7.71~7.52 (m, 16H), 7.47~7.45 (m, 4H), 7.39~7.33 (m, 8H), 7.27~7.24 (m, 2H),3.85 (s, 4H), 3.82 (s, 4H), 1.97~1.95 (m, 12H), 1.19 (m, 60H), 0.78 (m, 30H). MADLI-TOF (m/z): calcd [M – 2 BIm<sub>4</sub>-]<sup>+</sup> 1560.18, found [M – 2 BIm<sub>4</sub>-]<sup>+</sup> 1556.85.

## 4. The stacked <sup>1</sup>H NMR spectra of FPF<sub>6</sub> and FBr, FBIm<sub>4</sub>.



Fig. S1 The stacked 1H NMR spectra (600 MHz, CDCl<sub>3</sub>/CD<sub>3</sub>CN 1/1, v/v, 25°C) of a) FPF<sub>6</sub>andb) FBr, c) FBIm<sub>4</sub>.

## 5. <sup>1</sup>H NMR spectra of equimolar of FSO and FPF<sub>6</sub>, FBIm<sub>4</sub>.



**Fig.S2** The stacked <sup>1</sup>H NMR spectra (600 MHz,  $CDCl_3/CD_3CN$  1/1, v/v, 25 °C) of solutions of **FSO** and **FPF**<sub>6</sub> at different concentrations: a) **FSO**, h) **FPF**<sub>6</sub>, and equimolar solutions b) 1, c) 2, d) 5, e) 10, f) 20, and g) 30mM. u: uncomplexed monomer, c: cyclic polymer, and l: linear supramolecular polymer.



**Fig.S3** The stacked <sup>1</sup>H NMR spectra (600 MHz,  $CDCl_3/CD_3CN$  1/1, v/v, 25 °C) of solutions of **FSO** and **FBIm**<sub>4</sub> at different concentrations: a) **FSO**, h) **FBIm**<sub>4</sub>, and equimolar solutions b) 1, c) 2, d) 5, e) 10, f) 20, and g) 30mM. u: uncomplexed monomer, c: cyclic polymer, and l: linear supramolecular polymer.

#### 6. DSC measurement of the supramolecular polymers FSO-FX.



Fig. S4 DSC plots of the supramolecular polymers FSO-FX.

#### 7. Viscosity measurement of the supramolecular polymers FSO-FX.



Fig.S5 Specific viscosity of equimolar mixtures of host FSO and guest FX in  $CHCl_3/CH_3CN$  (1/1, v/v) solution.

# 8. Photophysical properties of host FSO, guest FX and upramolecular polymers FSO-FX.



**Fig.S6** (a) UV-visible absorption and (b) PL spectra of  $10^{-5}$  M solution for host FSO, guest FX and FSO-FX in CHCl<sub>3</sub>/CH<sub>3</sub>CN (1/1, v/v) solution.

## 10. Electroluminescence properties of the supramolecular polymers FSO-FX.



Fig.S7 EL spectra of FSO-FPF6 at different current densities.



Fig.S8 Photovoltaic characteristics of devices with configuration of ITO/PEDOT/FSO-FX/Al