

## Electronic Supplementary Information

### Semiconducting polyfluorenes with electrophosphorescent on-chain platinum-salen chromophores

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### Characterization Methods

The <sup>1</sup>H- and <sup>13</sup>C-NMR spectra were recorded on a Bruker ARX 400 spectrometer with deuterated tetrachlorethane or dimethylsulfoxide as the solvents. Low-resolution mass spectroscopy was obtained on a Varian MAT 311A operating at 70 eV (electron impact) and reported as m/z. Elemental analyses were done on a Vario EL II (CHNS) instrument. UV-vis absorption spectra were recorded on a Jasco V550 spectrophotometer. Fluorescence measurements were carried out on a Varian Cary Eclipse instrument. Gel permeation chromatographic analysis (GPC) utilized PS columns (three columns, 5 μm gel, pore widths 103, 105 and 106 Å) connected with UV-Vis and RI detection. All GPC analyses were performed on solutions of the polymer in THF or toluene at 30°C with a flow rate of 1 mL/min (concentration of the polymer ca. 1.5 g/L). The calibration was based on polystyrene standards with narrow molecular weight distribution. Microwave-assisted syntheses were performed using a CEM Discover microwave system.

### Materials and General Procedures

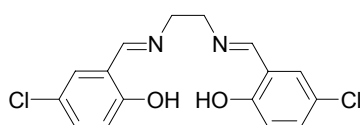
Unless otherwise indicated, all reagents were obtained from commercial suppliers and were used without further purification. All reactions were carried out under an argon atmosphere. The solvents were used as commercial p.a. quality. The reactions were carried out under

argon with the use of standard and Schlenk techniques. The vials for the microwave assisted reactions were filled in a glove box.

### OLED Fabrication Procedure

Poly (3,4-ethylenedioxythiophene) doped with poly(styrene sulfonate) (PEDT:PSS) (Baytron P purchased from H.C. Starck) was spin-coated onto pre-cleaned and O<sub>2</sub>-plasma treated indium tin oxide (ITO) substrates, yielding layers with a thickness of ca. 60 nm. The PEDT:PSS layers were baked at 80°C for half an hour to remove residual water. The PF/Pt-salen copolymers, blends of PF/Pt-salen copolymer and the monomeric Pt-salen complex in PVK/PBD (4:1 by weight) in chloroform solution were spin-coated on top of the PEDT:PSS films. The thickness of the emissive layer was ca. 80-100 nm as measured by Dektak profilometry. The devices were completed by thermal deposition of 5 nm thick Ca and 100 nm thick Al. Current-voltage characteristics were measured with a Keithley 2400 source recorded unit. The brightness of the devices was recorded with a Minolta CS-100A camera. EL spectra of the devices were measured using a charge coupled device fiber spectrometer (Ocean Optics). With the exception of the deposition of the PEDT:PSS layer, all processes were carried out in a dry nitrogen atmosphere.

### Synthesis of Bis(5-chlorosalicylidene)ethylenediamine. (L1)



To a solution of 5-chloro-2-hydroxybenzaldehyde (5.5 g, 0.04 mol) in 250 mL THF ethylenediamine (1.0 g, 0.02 mol) was slowly added. The mixture was stirred under reflux with a dean stark apparatus for eight hours. The resulting yellow precipitate was filtered and washed several times with THF and Hexane. Yield 4.9 g (87 %). <sup>1</sup>H-NMR (400 MHz, DMSO-D<sub>6</sub>, 32 °C):  $\delta$  = 13.35 (s, 2H, OH), 8.55 (s, 2H, HC=N), 7.50 (d, 2H,  $J$  = 2.0 Hz, Ph), 7.31 (ddd, 2H,  $J$  = 0.8 Hz,  $J$  = 2.7 Hz,  $J$  = 8.8 Hz, Ph), 6.86 (d, 2H,  $J$  = 8.7 Hz, Ph). <sup>13</sup>C-NMR (100 MHz, DMSO-D<sub>6</sub>, 32 °C):  $\delta$  = 165.7, 159.5, 132.0, 130.4, 121.8, 119.6, 118.5, 58.4. MS (EI, 70 eV) :  $m/z$  = 336. Anal. Calcd for C<sub>16</sub>H<sub>14</sub>Cl<sub>2</sub>N<sub>2</sub>O<sub>2</sub>: C, 56.99; H, 4.18; N, 8.31; Found: C, 57.06; H, 4.07; N, 8.30.

### **Synthesis of [N,N'-Bis(5-chlorosalicylidene)ethylenediaminato-N,N',O,O']platinum(II). (1)**

An aqueous solution of KOH (50 mL, 1M), the ligand (**L1**) (200 mg, 0.59 mmol) and K<sub>2</sub>PtCl<sub>4</sub> (246 mg, 0.59 mmol) was stirred for 8 hours at 40°C. The orange precipitate was filtered and washed extensively with aqueous KOH (1M), water and finally with methanol. The solid was recrystallized from acetonitril and filtered to give an orange powder. Yield: 0.15 g (54 %). <sup>1</sup>H-NMR (400 MHz, DMSO-D<sub>6</sub>, 80 °C): δ = 8.42 (s, 2H, <sup>3</sup>J<sub>H-Pt</sub> = 34.3 Hz, HC=N), 7.38 (d, 2H, J = 9.2 Hz, Ph), 6.2 (d, 2H, J = 9.2 Hz, Ph), 3.81 (s, 4H, CH<sub>2</sub>). <sup>13</sup>C-NMR (100 MHz, DMSO-D<sub>6</sub>, 80 °C): δ = 161.0, 155.1, 132.5, 131.3, 122.7, 122.4, 118.3, 60.7. MS (EI, 70 eV) : m/z = 530. Anal. Calcd for C<sub>16</sub>H<sub>12</sub>C<sub>12</sub>N<sub>2</sub>O<sub>2</sub>Pt: C, 36.24; H, 2.28; N, 5.28; Found: C, 35.90; H, 2.26; N, 5.33.

### **Synthesis of Statistical Copolymer PF2/6-Pt-Salen via a Microwave Assisted Yamamoto Protocol. (3a)**

To a 10 mL reaction tube containing Ni(COD)<sub>2</sub> (143 mg, 0.52 mmol), complex (**1**) (19 mg, 0.04 mmol), bipyridyl (89 mg, 0.57 mmol) and 2,7-dibrom(9,9-bis(2-ethylhexyl)fluorene (130 mg, 0.24 mmol), 5 mL of THF and COD (0.09 mL, 0.57 mmol) were added via a syringe. The tube was heated in a microwave apparatus for 12 minutes at 300 W/115°C. The solution was washed 2 times with 2N aqueous HCl, Na-EDTA solution and water. The solvent was removed and the residue was dissolved in chloroform. The polymer was precipitated into methanol and extracted with acetone to give a yellow powder. Yield 57 mg (40%). M<sub>n</sub> = 169,500, PD = 2.1. <sup>1</sup>H NMR (400 MHz, C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>, 25°C): δ = 7.08 - 8.23 (m, 6 H), 3.70 - 3.89 (m, 0.1 H), 1.59 - 2.59 (m, 2.34 H), 1.16 - 1.51 (m, 2.19 H), 0.26 - 1.14 (m, 31.82 H); (all signals are rather broad) <sup>13</sup>C NMR (100 MHz, C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>, 25°C) δ = 151.6, 140.7, 126.4, 123.3, 120.0, 55.4, 50.6, 35.3, 34.6, 29.9, 28.8, 27.6, 23.0, 14.1, 10.7.

### **Synthesis of Statistical PFO-Pt-Salen Copolymer via a Microwave Assisted Yamamoto Protocol. (3b)**

To a 10 mL reaction tube containing Ni(COD)<sub>2</sub> (110 mg, 0.4 mmol), complex (**1**) (19 mg, 0.04 mmol), bipyridyl (68 mg, 0.44 mmol) and 2,7-dibromo-9,9-bis(octyl)fluorene (100 mg, 0.18 mmol), 5 mL of a mixture of toluene/DMF (4/1) and COD (0.07 mL, 0.44 mmol) were added via a syringe. The tube was heated in a microwave apparatus for 12 minutes at

300 W/220°C. The solution was washed 2 times with 2N aqueous HCl, Na-EDTA solution and water. The solvent was removed and the residue was dissolved in chloroform. The polymer was precipitated into methanol and extracted with ethyl acetate to give a yellow powder. Yield 45 mg (41%).  $M_n=24,300$ , PD = 2.7.  $^1\text{H-NMR}$  (400 MHz,  $\text{C}_2\text{D}_2\text{Cl}_4$ , 25°C):  $\delta=7.45 - 7.89$  (bm, 6 H), 3.75 - 3.88 (m, 0.30 H), 1.9-2.2 (m, 3.26 H), 1.38-1.45 (m, 1.07 H), 1.05-1.25 (m, 22.4 H), 0.85-0.95 (m, 2.88 H), 0.75-0.8 (m, 7.04 H); (all signals are rather broad)  $^{13}\text{C-NMR}$  (100 MHz,  $\text{C}_2\text{D}_2\text{Cl}_4$ , 25°C)  $\delta = 152.1, 140.4, 140.1, 126.2, 121.7, 120.1, 55.4, 40.3, 31.9, 30.2, 29.4, 24.1, 22.8, 14.3$ .

### Synthesis of Poly([9,9-bis(2-ethylhexyl)fluorene]). (PF2/6)

To a 100 mL flame dried Schlenk tube containing  $\text{Ni}(\text{COD})_2$  (3.6 g, 1.3 mmol), bipyridyl (1.9 g, 1.2 mmol) and 2,7-dibrom(9,9-bis(2-ethylhexyl)fluorene) (3 g, 0.55 mmol), THF (70 mL) and COD (1.3 g, 1.2 mmol) were added via a syringe. The tube was heated for 3 d at 80°C. The reaction was quenched with HCl in 1,4-dioxane and extracted with chloroform. The solution was washed 2 times with 2N aqueous HCl, Na-EDTA solution and water. The solvent was removed and the residue was dissolved in chloroform. The polymer was precipitated into methanol and extracted with ethylacetate to give a white powder. Yield 1.8 g (50%).  $M_n = 125,700$ , PD = 1.7.  $^1\text{H-NMR}$  (400 MHz,  $\text{C}_2\text{D}_2\text{Cl}_4$ , 25°C):  $\delta = 7.26 - 8.05$  (m, 6H), 1.74 - 2.51 (m, 2H), 0.12 - 1.08 (m, 32 H); (all signals are rather broad)  $^{13}\text{C-NMR}$  (100 MHz,  $\text{C}_2\text{D}_2\text{Cl}_4$ , 25°C)  $\delta = 151.5, 140.6, 140.4, 126.4, 123.3, 120.0, 55.4, 45.1, 35.3, 34.6, 28.8, 27.6, 23.0, 14.2, 10.7$ .

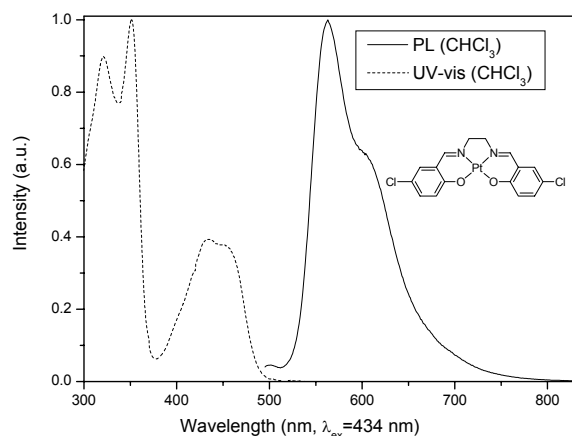


Fig. S1 UV-vis and PL spectrum of **1** in chloroform solution ( $\lambda_{\text{ex}}=434$  nm)

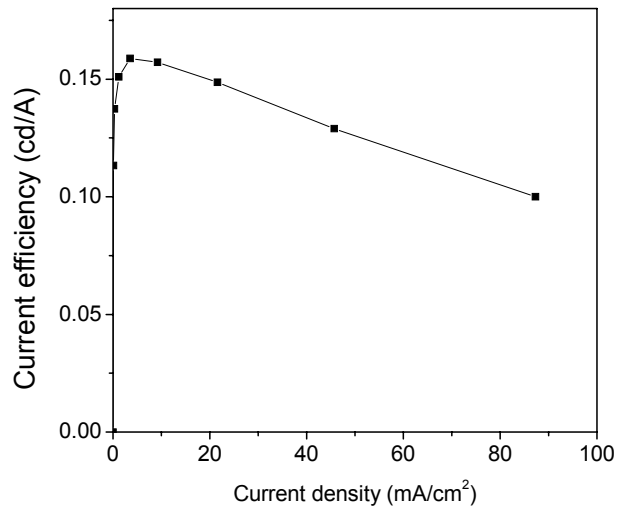


Fig. S2 EL Efficiency as a function of current density for a device in the configuration ITO/PEDT:PSS/3a/Ca/Al.

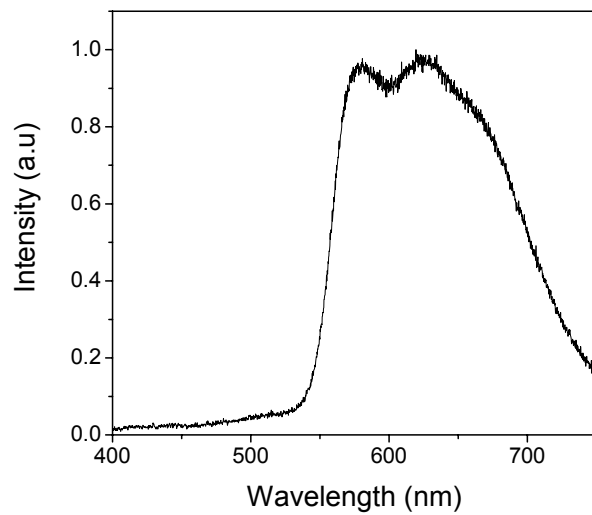


Fig. S3 EL spectra of the device in the configuration ITO/PEDT:PSS/3a/Ca/Al.

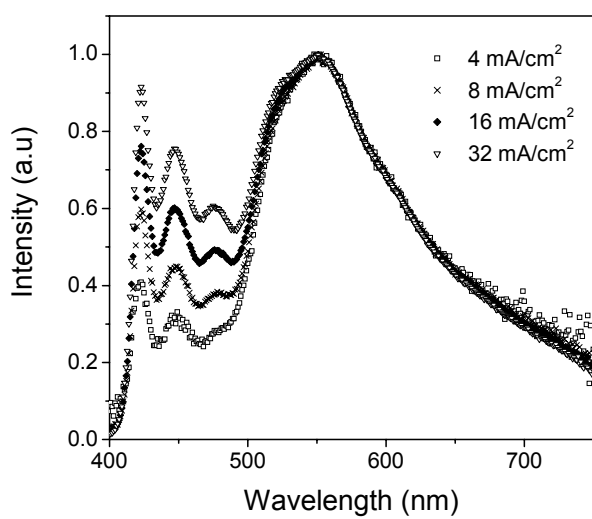


Fig. S4 EL spectra of ITO/PEDT:PSS/PF2/6-3b/Ca/Al-devices (5% 3b in PF2/6 w/w)

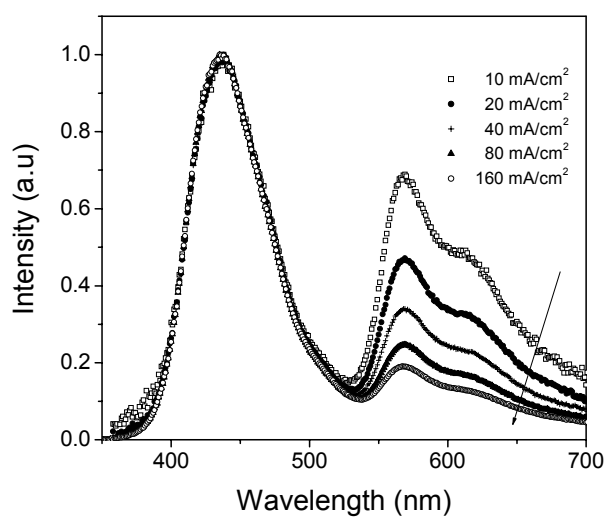


Fig. S5 EL spectra of ITO/PEDT:PSS/PVK-3b/Ca/Al-devices (5% 3b in PVK w/w)