

## Electronic Supplementary Information

### Dual functions of a novel low-gap polymer for near infra-red photovoltaics and light-emitting diodes

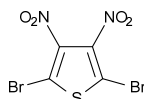
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#### Materials and methods

All reagents and starting materials were purchased from commercial sources and used as received, unless otherwise noted. The distannylated cyclopentadithiophene (CPDT) monomer was synthesized according to the literature.<sup>1, 2</sup> The synthesis of the pyrazine monomer was carried out following the procedure described below.<sup>3, 4</sup>

<sup>1</sup>H NMR and <sup>13</sup>C NMR data were collected on a Bruker AVANCE 400 or a Bruker Avance III 600 NMR spectrometer. Chemical shifts are expressed in parts per million ( $\delta$ ) using residual solvent protons as internal standards. Gel permeation chromatography (GPC) was performed using an Agilent 1200 Series equipped with MZ Plus linear 300 mm (5 $\mu$ ) columns connected with UV/Vis and RI detection using THF as eluent. The calibration was based on polystyrene standards with narrow molecular weight distribution. FD mass spectrometry was performed at MPIP Mainz by Stefan Türk using a Fisions Instruments Sectorfield Mass Spectrometer (VG Instrument ZAB 2-SE-FPD).

#### Synthesis



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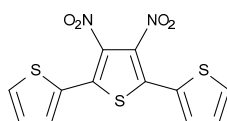
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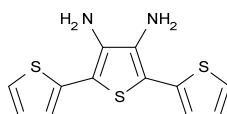
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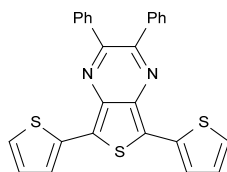
**2,5-Dibromo-3,4-dinitrothiophene.** 120 g (49.6 mmol) of 2,5-dibromothiophene were slowly added to a ice-cold solution of 330 ml of concentrated sulphuric acid and 110 ml of concentrated nitrous acid in a 1L flask in such a way that the inside temperature does not exceed 20 °C. After complete addition the solution was stirred over night at room temperature and then slowly poured into 800 g of ice. The precipitated product was filtered off and washed with water several times. Recrystallisation from methanol gave the product as light yellow crystals. Yield 72 g (21.7 mmol, 43.7 %).  $^{13}\text{C}$ -NMR (100MHz,  $\text{C}_2\text{D}_2\text{Cl}_4$ ):  $\delta$  ppm 159.5; 113.3. FD-mass  $m/z = 332$  ( $\text{M}^+$ ).



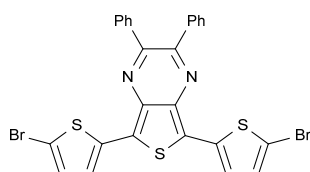
**2,5-Bis(2-thienyl)-3,4-dinitrothiophene.** Under inert atmosphere 16 g (48.2 mmol) of 2,5-dibromo-3,4-dinitrothiophene, 45 g (116 mmol) of 2-tributylstannyl thiophene, 350 mg (6.0 mmol) potassium fluoride and 250 mg (0.4 mmol) of  $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$  were dissolved in 100 ml of dry THF. The reaction mixture was heated for 18 h at 80 °C. Then the solution was poured into 200 ml of water and extracted several times with diethyl ether. The combined organic phases were then dried over  $\text{MgSO}_4$ , filtered and the solvent was removed. The product was purified by column chromatography using hexane/chloroform (7:3, v:v) as eluent. Yield 12.5 g (36.9 mmol, 76.6 %).  $^1\text{H}$ -NMR (400MHz,  $\text{C}_2\text{D}_2\text{Cl}_4$ ):  $\delta$  ppm 7.66 (d, 2H), 7.56 (d, 2H), 7.20 (dd, 2H).  $^{13}\text{C}$ -NMR (100MHz,  $\text{C}_2\text{D}_2\text{Cl}_4$ ):  $\delta$  ppm 135.8, 134.6, 131.9, 131.6, 128.9, 128.1. FD-mass  $m/z = 338$  ( $\text{M}^+$ ).



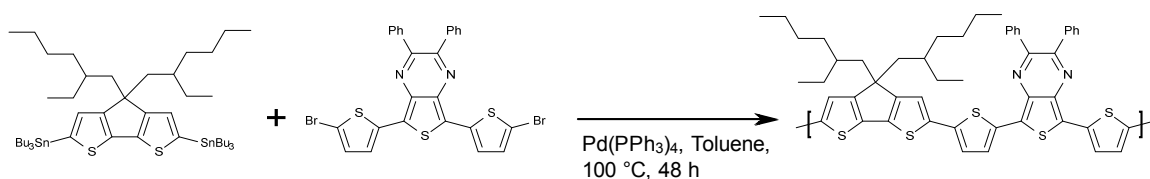
**2,5-Bis(2-thienyl)-3,4-diaminothiophene.** 1.35 g (4.0 mmol) of 2,5-bis(2-thienyl)-3,4-dinitrothiophene were dissolved in a mixture of 50 ml ethanol and 35 ml concentrated hydrochloric acid. 34,3 g (152 mmol) of tin(II)-chloride dihydrate were added in small portions and the mixture was stirred for 18 h at ambient conditions. The reaction mixture was basified with 6 M aqueous sodium hydroxide solution and extracted several times with toluene. The combined organic phases were dried over  $\text{MgSO}_4$ , filtered and the solvent was evaporated. The product was used without any further purification.

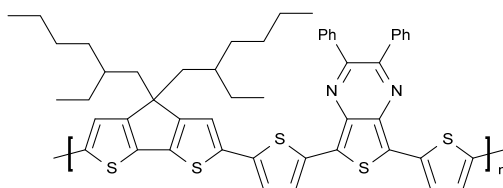


**2,3-Diphenyl-5,7-di(thiophen-2-yl)thieno[3,4-*b*]pyrazine.** 250 mg (0.9 mmol) of 2,5-bis(2-thienyl)-3,4-diaminothiophene and 400 mg (1.9 mmol) of 1,2-diphenylethane-1,2-dione were dissolved in 50 ml methanol under inert atmosphere and stirred for 2 h at 70 °C. The solvent was evaporated and the product was purified by column chromatography using hexane/dichloromethane (v:v, 6:4) as eluent. Yield 120 mg (0.3 mmol, 29.5 %). <sup>1</sup>H-NMR (400MHz, CDCl<sub>3</sub>): δ ppm 7.73 (dd, 2H), 7.60 (dd, 4H), 7.41 (d, 2H), 7.39 (d, 2H), 7.35 (t, 4H), 7-14 (dd, 2H). <sup>13</sup>C-NMR (100MHz, CDCl<sub>3</sub>): δ ppm 153.2, 139.3, 137.9, 134.9, 130.3, 129.3, 128.3, 127.7, 126.9, 125.4, 125.3. FD mass: m/z = 452 (M<sup>+</sup>)



**5,7-Bis(5-bromothiophen-2-yl)-2,3-diphenylthieno[3,4-*b*]pyrazine.** 1.25 g (2.8 mmol) of 2,3-diphenyl-5,7-di(thiophen-2-yl)thieno[3,4-*b*]pyrazine were dissolved in 75 ml of dry THF under inert atmosphere and then cooled to -78 °C in an acetone/dry ice bath. 983 mg (5.5 mmol) of NBS in 50 ml of dry THF were slowly added maintaining the temperature. After addition the solution was stirred at room temperature over night. The reaction mixture was poured into 200 ml of water and extracted with chloroform several times. The combined organic phases were dried over MgSO<sub>4</sub>, filtered and the solvent was evaporated. The product was purified by column chromatography with hexane/chloroform (v:v, 7:3) as eluent. Yield 850 mg (1.4 mmol, 50.4 %). <sup>1</sup>H-NMR (400MHz, CDCl<sub>3</sub>): δ ppm 7.58 (d, 4H), 7.39-7.44 (m, 8H), 7.12 (d, 2H). <sup>13</sup>C-NMR (100MHz, CDCl<sub>3</sub>): δ ppm 153.7, 139.0, 137.9, 136.3, 130.4, 130.3, 129.5, 128.4, 124.8, 124.6, 114.9. FD-mass m/z = 610 (M<sup>+</sup>).





**Poly[5,7-bis(5-thiophen-2-yl)-2,3-diphenyl-thieno[3,4-b]pyrazine-*alt*-2,6(4,4-bis(2-ethylhexyl))-4*H*-cyclopenta[2,1-*b*;3,4-*b'*]dithiophene] (PPy3T).** 981 mg (1 mmol) of the distannylated CPDT monomer, 610 mg (1 mmol) of 5,7-Bis(5-bromothiophen-2-yl)-2,3-diphenylthieno[3,4-*b*]pyrazine and 57.8 mg (0.05 mmol) of Pd(PPh<sub>3</sub>)<sub>4</sub> were dissolved in 60 ml of toluene under inert atmosphere and refluxed for 48 h. After cooling to room temperature, 250 ml of chloroform was added and the solution was washed with water, saturated aqueous EDTA solution and saturated aqueous brine solution. The combined organic phases were then dried over MgSO<sub>4</sub>, filtered and the solvent was evaporated. The polymer was redissolved in chloroform and precipitated from cold methanol. The product was soxhlet extracted by acetone, hexane, ethyl acetate and chloroform. The chloroform fraction was concentrated and reprecipitated again into cold methanol. Yield 60%. <sup>1</sup>H-NMR (600MHz, C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>): δ ppm 7.64 (s, 6H), 7.38 (s, 6H), 7.18 (d, 4H), 1.96 (s, 4H), 1.07-1.11 (m, 18H), 0.80 (s, 6H), 0.75 (s, 6H). <sup>13</sup>C-NMR (100MHz, C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>): δ ppm 159.2, 153.2, 139.8, 139.4, 138.3, 137.7, 136.9, 133.5, 130.3, 129.3, 128.3, 126.3, 125.2, 123.8, 119.6, 54.6, 43.9, 36.1, 34.8, 30.8, 29.1, 27.9, 23.0, 14.1, 10.9. GPC (THF): M<sub>n</sub> 5 kDa; M<sub>w</sub> 8 kDa; PDI 1.6.

### Polymer photovoltaics fabrication

All the commercial chemicals were from Sigma Aldrich unless otherwise specified. Solutions of PPy3T, [6,6]-phenyl C<sub>71</sub>-butyric acid methylester (PC<sub>71</sub>BM) and poly-3(hexylthiophene) (P3HT) (M<sub>w</sub>~90 kDa) in dichlorobenzene<sup>5</sup> were prepared separately, with a concentration of 20 mg/ml each, and then mixed together in different ratios. Indium tin oxide (ITO) substrates were ultrasonically cleaned, using acetone and isopropanol for 15 min each before O<sub>2</sub> plasma treatment<sup>6, 7</sup>. Poly(3,4-ethylenedioxylenethiophene) (PEDOT:PSS) was immediately spin-coated on top at a speed of 5000 rpm (revolutions per minute) to form an 80 nm thick film which was then annealed in a nitrogen glovebox for 20 min at 150°C. The PPy3T:PC<sub>71</sub>BM blends were subsequently spin-coated in the glovebox at 800 rpm, yielding films with thickness ~120 nm. Two samples were annealed at 40 °C for 30 min and 100 °C

for 10 min, respectively. For PPy3T:P3HT blends, the spin-coating speed was 1500 rpm and the thickness of the films was around 160 nm. The PPy3T:P3HT samples were baked at 140 °C for 15 min in the glovebox. The devices were completed by thermally evaporating 120 nm Al as the top metal electrode. The active electrode areas are 0.14 cm<sup>2</sup>

### **Polymer LED fabrication**

Three different devices with a structure of ITO/ PEDOT:PSS /active layer/Ca/Al were fabricated, where the active layers were: pristine poly(9,9-dioctylfluorene-co-benzothiadiazole) (F8BT) (from American Dye Source), pristine PPy3T and the blend F8BT: PPy3T =19:1 (by weight). F8BT and PPy3T were separately dissolved in toluene, to prepare 2% solutions by weight. The PPy3T solution was heated at 80 °C for 2 hours to aid solubilisation. Both solutions were kept overnight and filtered using 0.45 µm filters. Then F8BT:PPy3T =19:1 was prepared by mixing the two master solutions. The procedure for cleaning ITO substrates and preparing PEDOT:PSS were the same as described for the PVs fabrication. Active layers were prepared by spin-coating the polymer solutions in a nitrogen glovebox. Finally, 50 nm calcium and 150 nm aluminium were thermally evaporated as top electrodes. The active electrode areas are 3.5 mm<sup>2</sup>. The thicknesses of the active layers were approximately 120 nm (F8BT), 135 nm (F8BT:PPy3T) and 70 nm (PPy3T), respectively.

### **Polymer PV and LED characterisation**

Absorption measurements were obtained using an Agilent 8453 spectrophotometer.

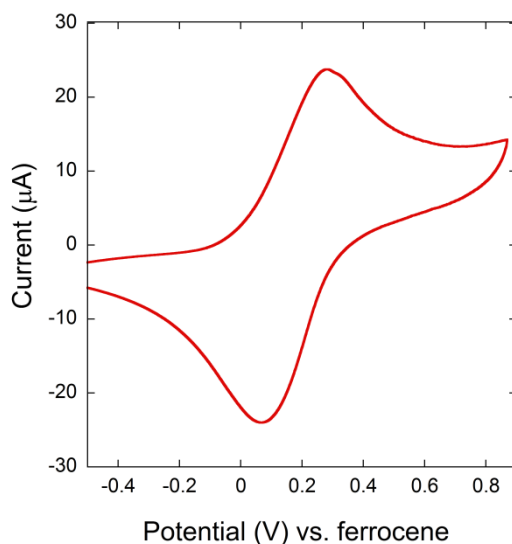
Film thicknesses were measured using a Dektak surface profilometer.

For PVs, current-voltage (*J-V*) measurements were carried out under vacuum using a Keithley 2400 source unit. Irradiation was provided by an AM1.5 solar simulator (Sun 3000, Abet technologies) with illumination of 100 mW/cm<sup>2</sup>. The incident photon-to-current conversion efficiency (IPCE) was measured by means of a Xenon lamp coupled to a monochromator, with the device under short-circuit condition.

For LEDs, EL spectra were detected by an Andor spectrograph coupled with an Andor Newton CCD (charge-coupled device) unit. The current-light-voltage (*J-L-V*) measurements were obtained out using a Keithley 2400 sourcemeter to drive the device, and a calibrated silicon photodetector connected to a Keithley 2000 multimeter to detect the light.

### Cyclic voltammery (CV) measurements

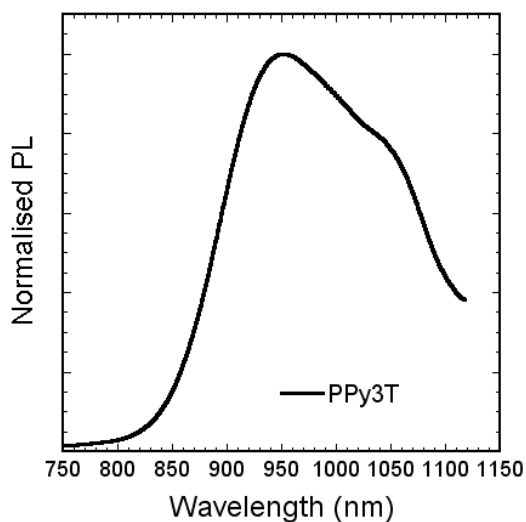
The highest occupied molecular orbital (HOMO) of PPy3T was determined to be  $-5.0$  eV ( $\pm 0.1$  eV) by cyclic voltammery (CV).<sup>8</sup> The measurement was carried out in acetonitrile using  $0.05$  M tetrabutylammonium hexafluorophosphate as electrolyte and ferrocene as internal standard (Supplementary Figure 1).



**Supplementary Figure 1** Cyclic voltammery trace for PPy3T in acetonitrile using  $0.05$  M tetrabutylammonium hexafluorophosphate as electrolyte, ferrocene as internal standard.

### Photoluminescence of PPy3T film

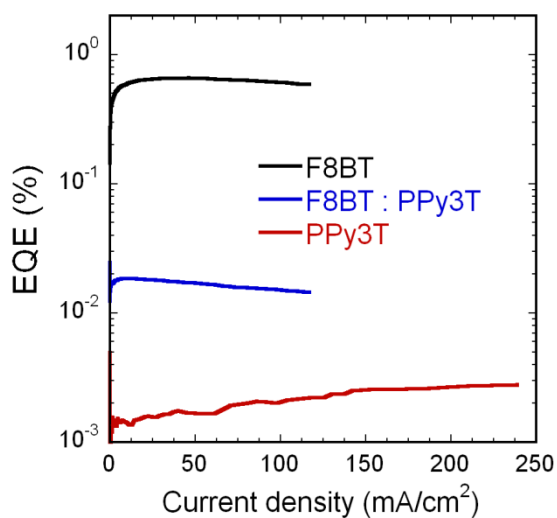
Photoluminescence spectrum: PPy3T film on fused silica was excited with a HeCd laser ( $\lambda = 325$  nm), and collected with an Andor Newton EMCCD camera coupled to an Andor SHAMROCK 163 spectrograph.



**Supplementary Figure 2** PL spectrum of PPy3T in film.

### External quantum efficiency of LED devices

The external quantum efficiency of the LEDs reported in the main paper is plotted in Supplementary Figure as a function of current density, demonstrating stable emission for all devices across a large current range.



**Supplementary Figure 3** External quantum efficiency of LEDs with the structure ITO / PEDOT:PSS / active layer / Ca / Al plotted as a function of current density.

### Performance of photovoltaic devices

**Table 1** Photovoltaic performance parameters of PPy3T : PC<sub>71</sub>BM devices.

|                                       | PPy3T : PC <sub>71</sub> BM |       |         |       |                         |                           |
|---------------------------------------|-----------------------------|-------|---------|-------|-------------------------|---------------------------|
|                                       | 1.5 : 1                     | 1 : 1 | 1 : 1.5 | 1 : 3 | 1 : 1.5<br>40°C, 30 min | 1 : 1.5<br>100 °C, 10 min |
| J <sub>sc</sub> (mA/cm <sup>2</sup> ) | 1.73                        | 2.94  | 4.28    | 1.23  | 3.91                    | 3.72                      |
| V <sub>oc</sub> (V)                   | 0.56                        | 0.55  | 0.54    | 0.48  | 0.50                    | 0.49                      |
| FF                                    | 0.31                        | 0.33  | 0.33    | 0.29  | 0.33                    | 0.33                      |
| PCE (%)                               | 0.30                        | 0.53  | 0.76    | 0.17  | 0.65                    | 0.60                      |

## References

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