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Supporting Information

A Novel Ambipolar Polymer: From Organic Thin-Film Transistors to Enhanced Air-Stable Blue Light Emitting Diodes

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Device Fabrication Materials and Methods:

***Fabrication and Characterization of FET Devices* :** Transistors were fabricated in the bottom-gate, bottom-contact configuration on heavily doped n-type Si substrates as the gate and thermally grown 200 nm silicon dioxide as the dielectric layer (Silicon Quest, dry oxide). The source and drain electrodes were patterned using standard photolithography and formed on SiO 2 with electron-beam evaporation of 3 nm of nickel and 47 nm of gold. Prior to casting, devices were cleaned in acetone and isopropyl alcohol and dried in an oven at 120 ° C for 15 min. The samples were then surface-activated with acid hydrolysis, dried, and then exposed for 30 min to UV light in air. The devices were surface-treated with DTS for 30 min by immersion in 1% by volume DTS in toluene. The devices were then cleaned by rinsing with toluene and dried under nitrogen flow followed spin-coating of the polymer. Polymer films were spin-cast at 4000–5000 Rpm in a glove box from a 10 mg mL − 1 solution in chloroform. Samples were dried at 60 ºC for 30 min and then annealed at the desired temperature for 10 min in a glove box. FET mobility measurements were performed in a glove box using a Keithley 4200 Semiconductor Parametric Analyzer and a Signotone Micromanipulator S-1160 probe station. Samples measured had channel lengths of 5 μ m and channel widths of 1mm.

Preparation of PEDOT:PSS:GO composite: For preparation of thin films comprising PEDOT:PSS and GO, we synthesized and characterized GO based on previous reports and blended it with different molar ratios (0.01, 0.03 and 0.06 wt. %) into the PEDOT:PSS dispersion.[i,ii] After sonicating the blend for 15 min and preparing spin-coated films (3000rpm, 30sec), PEDOT:PSS:GO thin films were annealed up to 120°C. GO will be reduced in this temperature to some extent.

Preparation of PFO/ PNDIT-alt-DTP binary blend: We prepared our binary blend of PFO and PNDIT-alt-DTP in the ratio of 95:5 wt. %, respectively. The solutions were sonicated for an hour before spin-coating. The prepared polymer solution exhibit absorption maxima in the region of 360 nm, which is almost consistent with the absorption peak for PFO homopolymer. It suggests that most of the absorption was caused by the fluorene units since a small amount of ambipolar polymer is added (As shown in Figure S10). However the DA polymer absorption peaks around 750 nm is also observable in the blends spectra. Thin films were prepared from chloroform solution (5 mg/mL) by spin-coating on a glass substrate for 30 s at 2000 rpm. Thin films show an absorption maximum at about 389 nm, which is attributed to a π-π* transition of the polymer. This main absorption band peaks at 3.2 eV with an onset at ~ 2.95 eV.

Fabrication and Characterization of PLEDs: Indium tin oxide (ITO)-coated glass substrates (Sigma Aldrich) were cleaned sequentially in ultrasonic bathes of phosphate-free detergent, water, isopropanol, water, and acetone, and then dried at 60 °C in a vacuum oven for an hour. After drying, the substrates were exposed to UV ozone, and the spin-coating process followed immediately after the UV ozone cleaning. Indium tin oxide (ITO) is used as the anode in the PLEDs due to its high electrical conductivity and high transparency. A 55 nm PEDOT:PSS (Φ= 5.2 eV) hole injection layer or PEDOT:PSS:GO was spin-coated on top of ITO layer and dried at 120 °C for 20 minutes under vacuum. By doping GO into PEDOT:PSS, with increasing the conduction of this layer, the injection barrier will be decreased. The doping of graphene can effectively enhance the conductivity in the hole-injection layer and reduce the turn-on voltage and higher overall device efficiency.

Before spin-coating, the as-received PEDOT:PSS solution was placed in ultrasonic bath for 15 minutes and then filtered through 0.45 μm poly(vinylidenefluoride) (PVDF) syringe filters. The film thickness was measured with a Dektak 8000 surface profiler. For emitting layer, we used PFO 4g L^{-1} dissolved in chloroform and stirred all solutions over night. The spin coating rate and time of deposition changed in each section to spin coat a thin film of around 45 nm. In those devices using PVK as HTL, a thickness of 65 nm were used. A 150 nm thick aluminum layer were then sequentially deposited through a shadow mask on top of the emissive layer thin film layer to form active diode areas of about 30-40 mm^2. The resulting architecture of the diodes was ITO/PEDOT:PSS/PFO:DA molecule blend/Al.

EL and PL of fabricated PLEDs were performed by USB2000 and HR4000 Ocean Optics. The *J*-*V* characteristics of the devices were measured using a computer controlled Keithley 2400 source measure unit for the electrical characteristics. The maximum luminous measurements were checked by optical meter Mastech-MS6612. All the device fabrication and characterization steps were done under ambient laboratory air.

The devices were prepared as below:

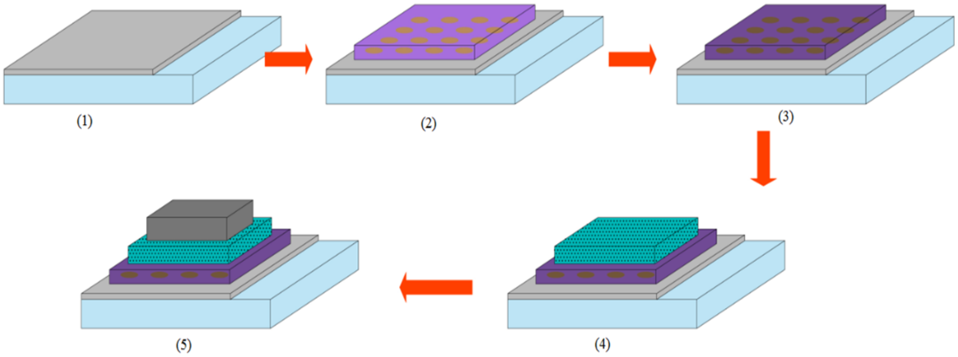


Figure S1. Schematic process of preparation of PLED device. (1) Etched ITO on top of glass substrate, (2) spin-coated PEDOT:PSS:GO, (3) annealed PEDOT:PSS:GO, (4) spin-coated polymer blend, (5) vacuum thermal deposited Aluminum on top of the emissive layer.

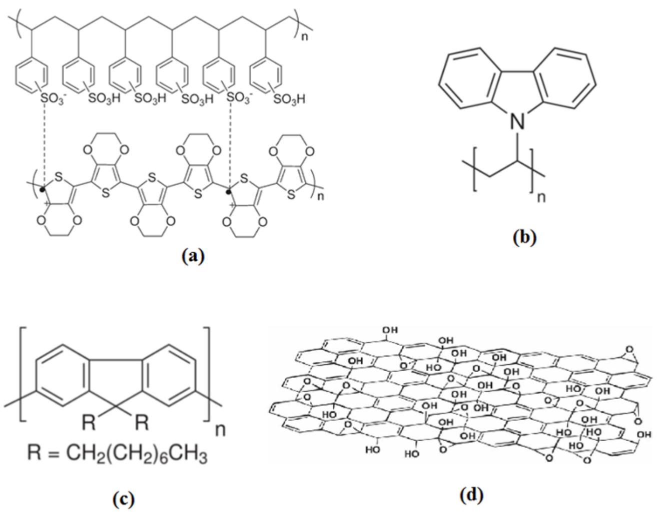


Figure S2. Chemical structure of the polymers considered in this study: (a) PEDOT:PSS, (b) PVK, (c) PFO (d) Graphene oxide.

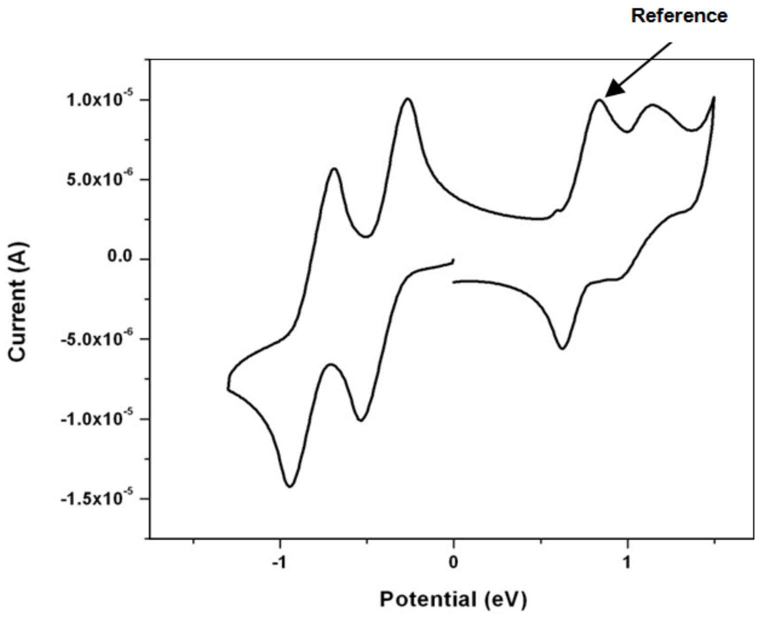


Figure S3. Cyclic voltammograms of the P(NDIT-DTP) in chlorobenzene, 0.1 $TBBF_4$. Scan rate = 100 mV/s. Platinum as working electrode, wave at ca 0.7 eV is the internal Fc/Fc^+ Reference.

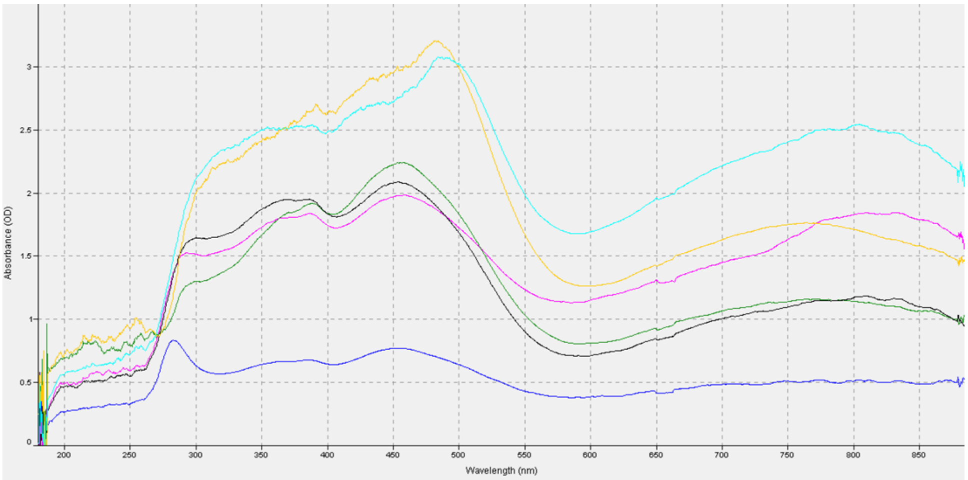


Figure S4. UV-Vis of P(NDIT-DTP) in chloroform in different concentrations

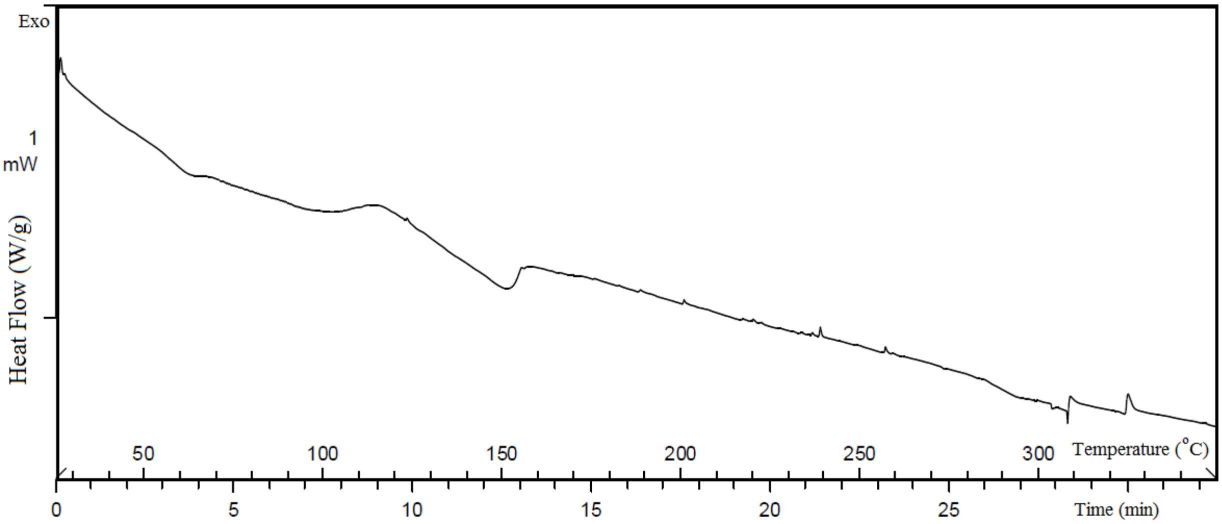
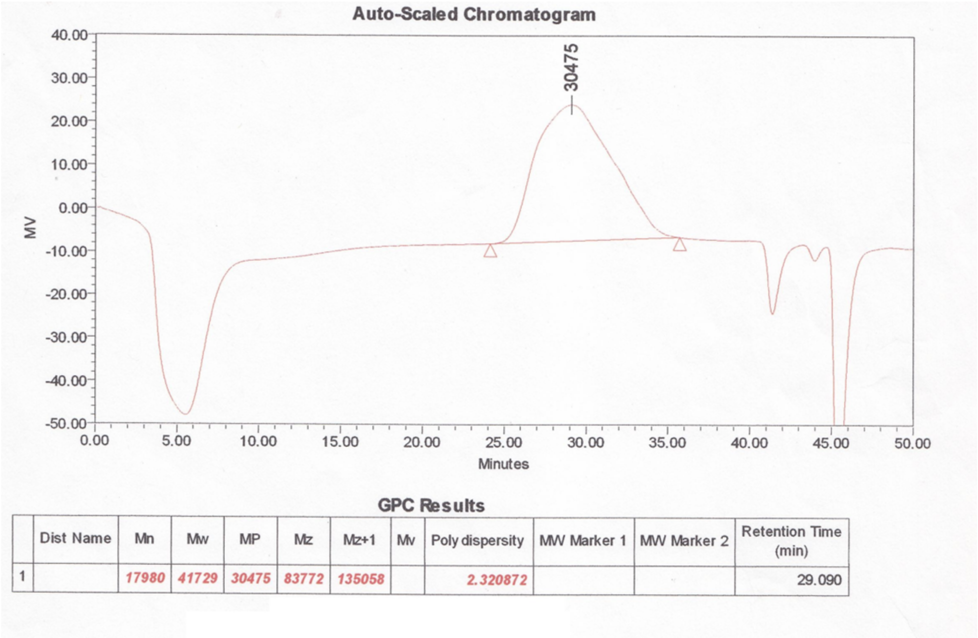


Figure S5. DSC curve for PFO used, the second transition around 100 was chosen for annealing.



GPC Results

	Dist Name	Mn	Mw	MP	Mz	Mz+1	Mv	Poly dispersity	MW Marker 1	MW Marker 2	Retention Time (min)
1		17980	41729	30475	83772	135058		2.320872			29.090

Figure S6. GPC elution curves and molecular weights of P(NDIT-DTP)

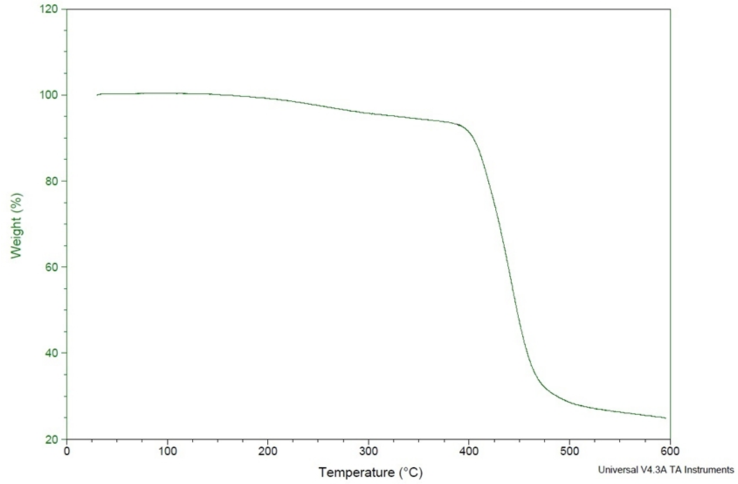


Figure S7. Thermogravimetric analysis (TGA) of PNDIT-alt-DTP

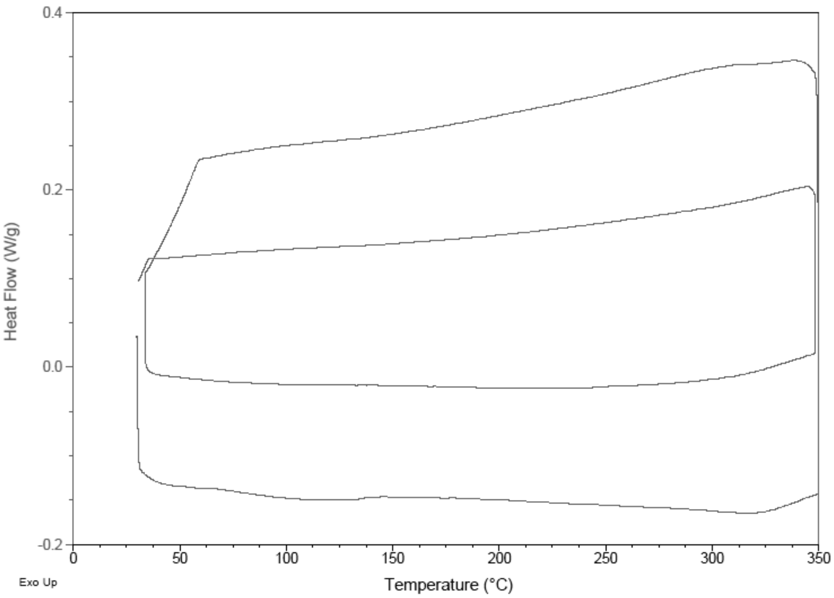


Figure S8. The first and second DSC scan curves of P(NDIT-DTP) with a scan rate of 5 °C/min under nitrogen.

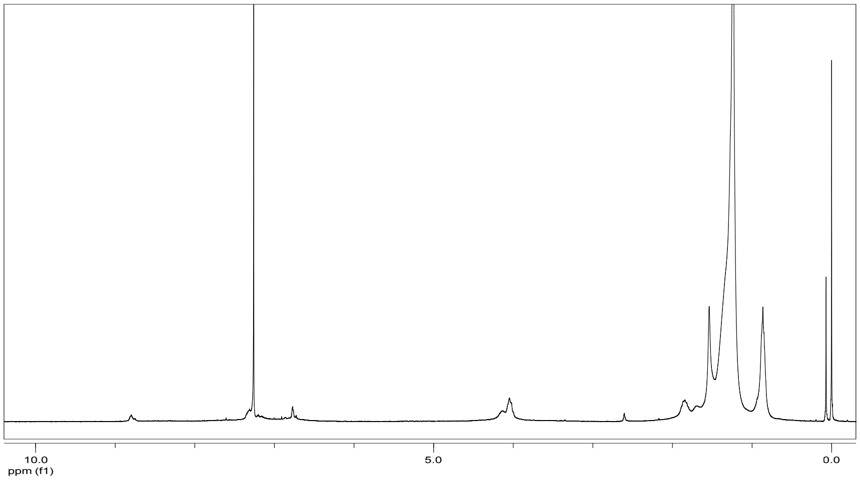


Figure S9. ^1H NMR (600 MHz) spectrum of polymer P(NDIT-DTP) in $CDCl_3$

		X	Y
1	**PFO PL Sol.**	0.1734	0.1087
2	**PFO PL film**	0.3236	0.2392
3	**PFO blend PL**	0.2089	0.1233
4	**PFO no GO turn on V**	0.2238	0.332
5	**PFO no GO 10 V**	0.2432	0.3581
6	**PFO no GO 15 V**	0.3185	0.4406
7	**PFO GO turn on V**	0.2553	0.346
8	**PFO GO 10 V**	0.2589	0.3853
9	**PFO GO 15 V**	0.2725	0.4026
10	**PFO blend no GO**	0.2254	0.2406
11	**PFO blend 0,01 GO**	0.1744	0.1626
12	**PFO blend 0,03 GO**	0.1622	0.1826
13	**PFO blend 0,06 GO**	0.1896	0.2511

Table S1. x, y of chromaticity diagram (the CIE 1931 color space diagram)

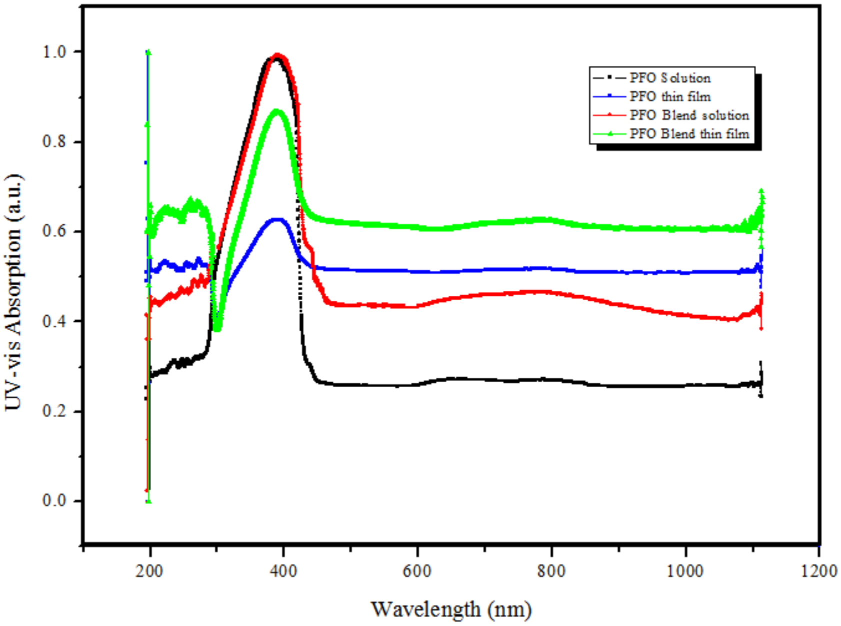


Figure S10. UV-visible absorption spectra of chloroform solution of pristine PFO and blend solution, annealed PFO and blend thin films.

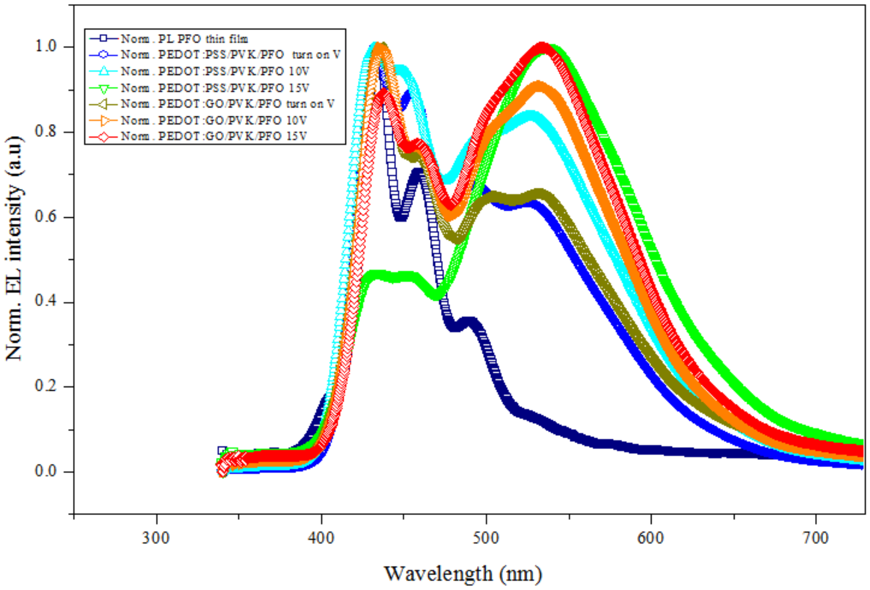


Figure S11. All Normalized EL intensity of device ITO/PEDOT:PSS:GO/PVK/PFO/Al and ITO/PEDOT:PSS/PVK/PFO/Al for comparison. The PL spectra of amorphous PFO exhibit emission peaks at around 430 (0-0 band), 455 (0-1 band), and 489 nm (0-2 band) with a shoulder around 525 nm (0-3).

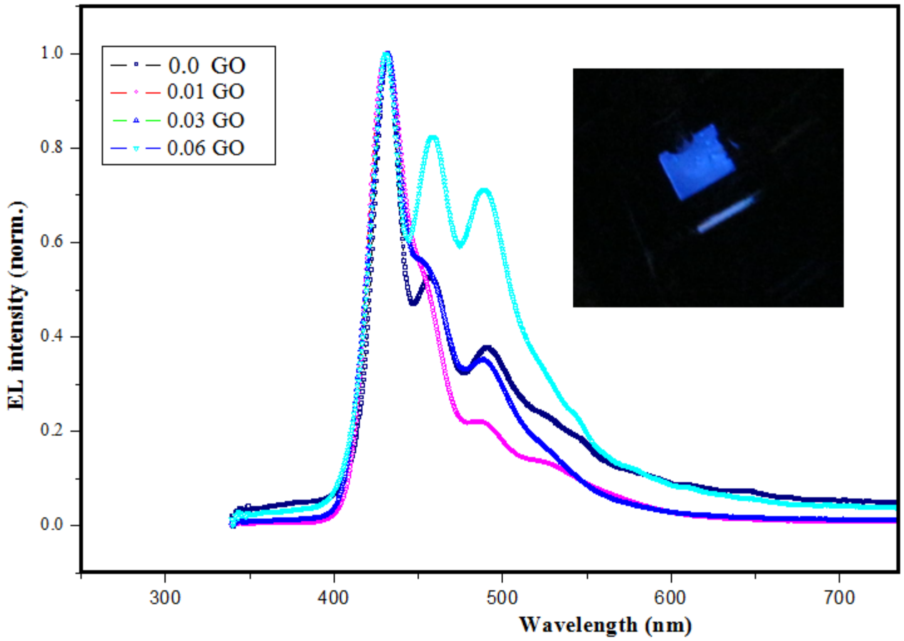


Figure S12. Normalized Electroluminescence intensity of blend system of ITO/PEDOT:PSS:GO/PFO blend/Al. Inset: The device fabricated by PEDOT:PSS:0.03GO.

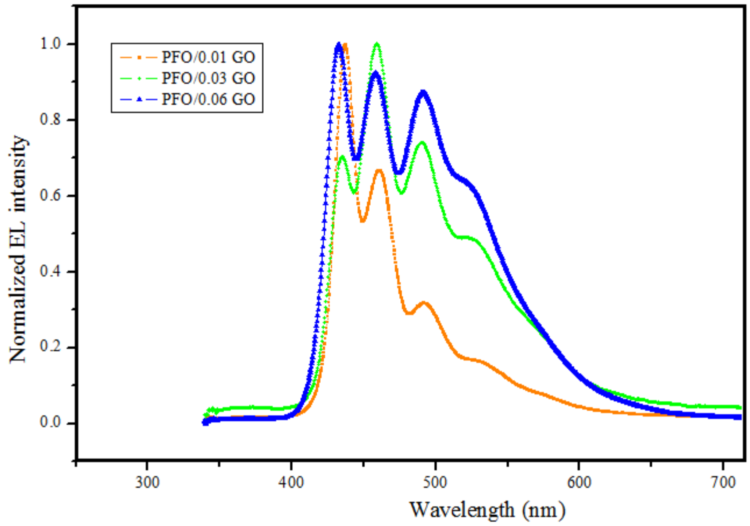
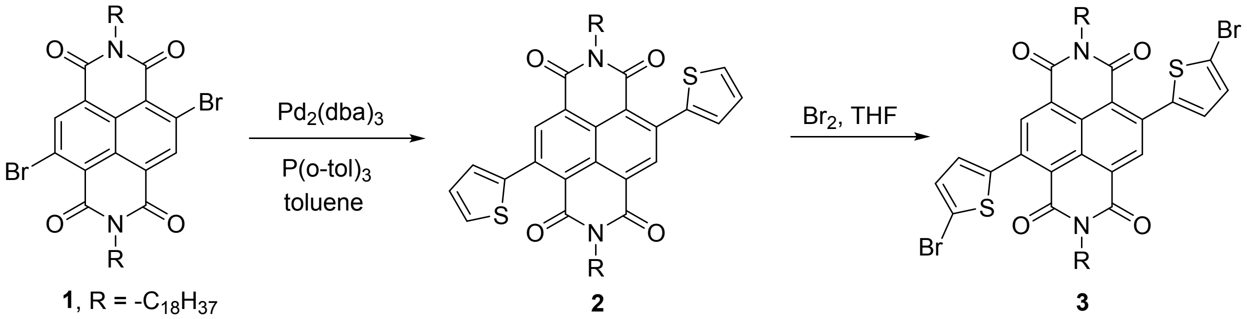
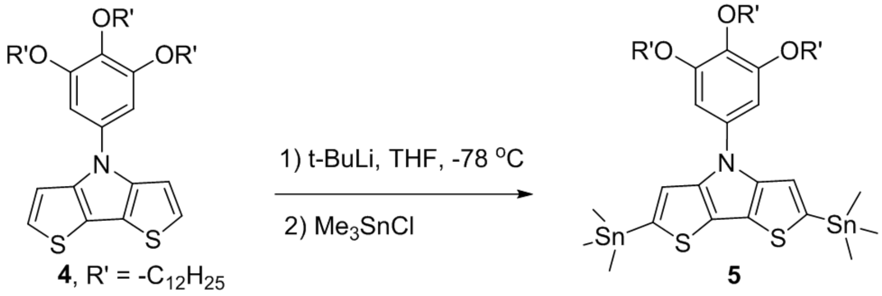


Figure S13. Normalized Electroluminescence of system: ITO/PEDOT:PSS:GO/PFO/Al.



Scheme S1. Schematic synthesis of 2,6-Bis (2-thienyl) naphthalene- 1,4,5,8- tetracarboxylic- N,N’- bis (2-octyldodecyl) diimide TNDIT (2) and 2,6-Bis(2-bromothien-5-yl) naphthalene- 1,4,5,8- tetracarboxylic- N,N’-bis (2-octyldodecyl) diimide Br-TNDIT-Br (3).



Scheme S2. Synthesis of 2,6-Bis (tri- methylstannyl) -N- (3,4,5- tris(n-dodecyloxy) phenyl)- dithieno [3,2-b:2',3'-d] pyrrole (5).

Table 1. Summary of device performance with different emitting and HI layers.

Active layer	HIL (PEDOT: PSS + wt.%GO)	0-0 Peak emission (nm)	Turn-on voltage (V)	Current Density (mA/cm^2)	Luminance$_{Max}$[a] (cd m^{-2})	Current efficiency$_{max}$[b] (cd A^{-1})	Power efficiency (lm W^{-1})
PFO	0	0	0	0	0	0	0
PFO	0.01	437	6.5	90.88	97	0.20	0.05
PFO	0.03	435	7	77.17	161	0.25	0.06
PFO	0.06	433	7	79.3	129	0.16	0.03
PFO blend	0	430	6	133.64	901	0.68	0.16
PFO blend	0.01	430	3.9	145	5510	3.8	0.97
PFO blend	0.03	430	4.5	255	5100	2	0.52
PFO blend	0.06	431	3.5	330	2430	0.73	0.15

[a] Maximum brightness.
[b] Maximum luminescence efficiency.

References:

(i) a) S. Pan, I. A. Aksay, *ACS nano* **2011**, *5*, 4073; b) W. S. Hummers, R. E. Offeman, *J. Am. Chem. Soc.* **1958**, *80*, 1339.
(ii) Y. Zhu, S. Murali, W. Cai, X. Li, J. W. Suk, J. R. Potts, R. S. Ruoff, *Adv. Mater.* **2010**, *22*, 3906.