

Electronic Supporting Information

Diazirine-Based Photopolymerizable Materials for Defect Free Fabrication of Solution Processed Organic Light-Emitting Diodes

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Materials and Methods:

All chemicals and solvents were analytical grade and they were used without purification. ^1H and ^{13}C NMR spectra were measured with a Bruker[®] Avance IITM 500MHz UltraShield[™] (Bruker Corporation, Mass, USA) spectrometer operating at 11.7 T. The chemical shifts (δ ppm) are referenced to the respective solvent and splitting patterns are designed as s (singlet), d (doublet), t (triplet), m (multiplet). Low resolution GC/MS-spectra were recorded on a combined gas chromatograph with a Shimadzu GC-MS QP5050A mass spectrometer with a 30 m column, 0.25 mm internal diameter and 0.25 μm thickness from RESTEK. MALDI-TOF/MS spectra were obtained from a Bruker Daltonics Omnicflex spectrometer. All reactions were monitored using Whatman K6F Silica Gel 60 Å analytical TLC plates by UV detection (254 nm and 365 nm). Absorption spectra was recorded with a Hitachi U-3010 double beam spectrophotometer. Fluorescence emission spectra was recorded by using a F900 fluorimeter from Edinburgh Instruments. For column chromatography, silica gel from EMD Science (60 Å, 32-63 μm) was used. Photolysis was performed with a Spectroline ENF 280C at 365 nm, at a voltage of 115 V, working with a frequency of 60 Hz and equipped with 8W tube. Thin films were fabricated by using a Laurell WS-400B-6NPP/LITE/8K spin coater and thickness of thin films were determined by Alpha-Step IQ surface profiler (KLA Tencor). Fluorescence images were captured by the KODAK image station 4000 mm PRO system and processed by NIH ImageJ software. For device fabrication PEDOT:PSS was purchased from H.C. Starck and then used as the hole injection layer (HIL). NPB and TPBI, the hole and electron transport layer respectively, MCP, the host materials were purchased from Sigma Aldrich. $\text{Ir}(\text{mppy})_3$, the dopant material was purchased from Lumitec. The materials were used without further purification.

Cyclic Voltammetry:

Cyclic voltammetry (CV) measurements were performed on a potentiostat/galvanostat model EPP-4000 (Princeton Applied Research) using an Ag/AgNO₃ reference electrode, a platinum wire counter electrode, and a platinum disk working electrode. The working electrode was coated with a NPB (with and without cross-linker) film by drop-casting a NPB solution in chloroform. CV measurements were recorded in 0.1 M tetrabutylammonium hexafluorophosphate in dry acetonitrile at a sweeping rate of 100 mV.s⁻¹ using ferrocene/ferrocenium (Fc/Fc⁺) couple as a standard. The HOMO energy levels were calculated using the equation: $E_{\text{HOMO}} \text{ (eV)} = - (E_{\text{ox}}^{\text{onset}} - E_{\text{Fc/Fc}^+}^{\text{onset}}) - 4.80 \text{ eV}$, where $E_{\text{ox}}^{\text{onset}}$ and $E_{\text{Fc/Fc}^+}^{\text{onset}}$ are the onset oxidation potentials for the NPB sample and the ferrocene against the Ag/AgNO₃ reference electrode, while the value - 4.8 eV is the HOMO energy level of ferrocene against vacuum.¹⁻³ The LUMO energy levels were calculated with the HOMO levels obtained by CV measurements and the optical band gap ($E_{\text{g}}^{\text{opt}}$) obtained by UV-vis measurements: $E_{\text{LUMO}} \text{ (eV)} = E_{\text{g}}^{\text{opt}} + E_{\text{HOMO}}$.

It was observed that unphotolysed and an hour photolyzed NPB (0% and 10% **1**) show only irreversible oxidation peak and no reduction peak was observed. It was found that Fc/Fc⁺ has a onset oxidation potential of 6 mV, so we have calibrated all our data with respect to Fc/Fc⁺.

Table S1. Electrochemical and optical properties of thin film of NPB (0% and 10% **1**)

Material	$E_{\text{ox}}^{\text{onset}}$ (V) vs. Fc/Fc ⁺	E_{HOMO} (eV)	$E_{\text{g}}^{\text{opt}}$ (eV)	E_{LUMO} (eV)
NPB	0.629	5.429	2.932	2.496
NPB_photolysed	0.636	5.436	2.899	2.536
NPB_10% 1 _photolysed	0.613	5.413	2.895	2.518

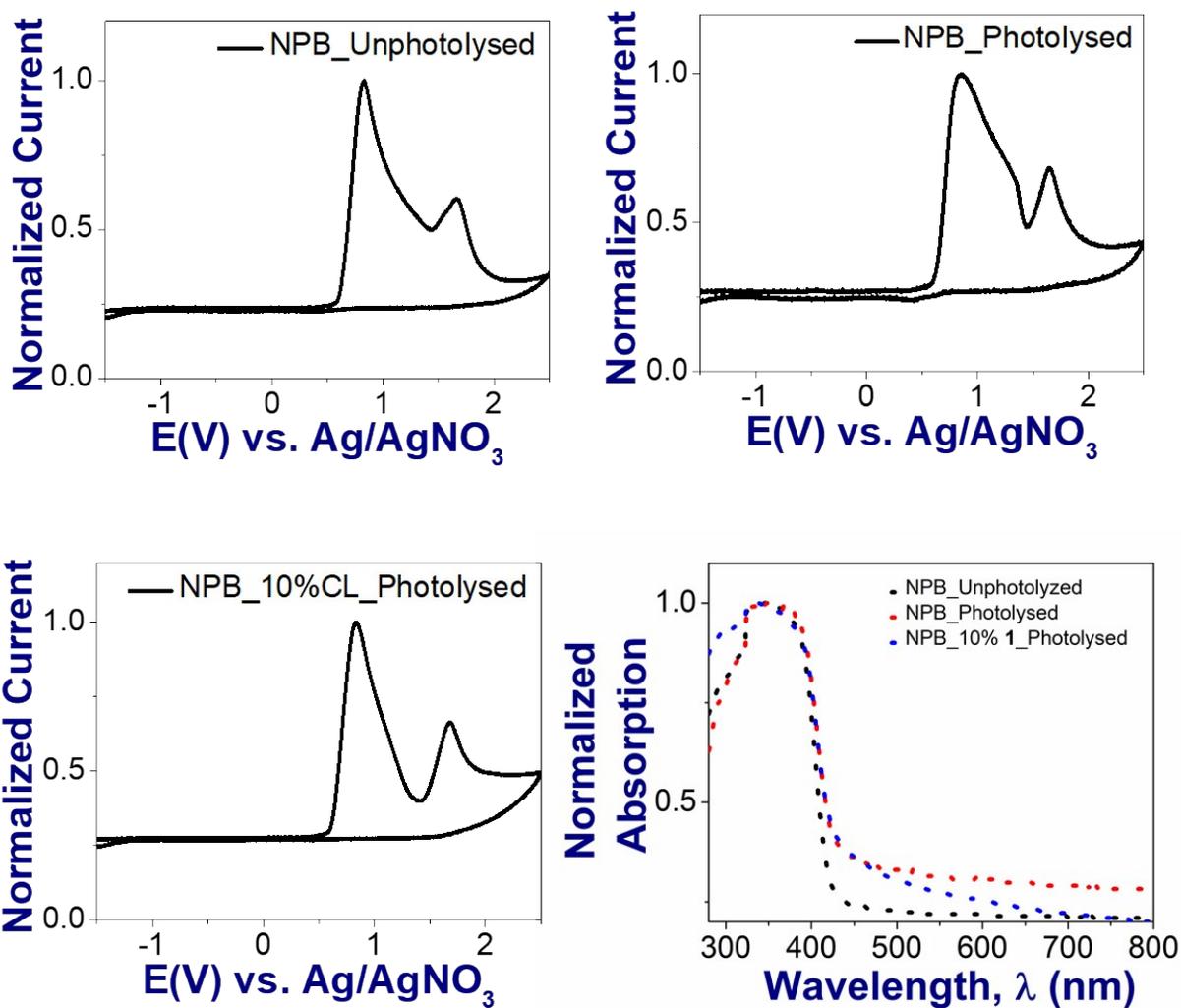
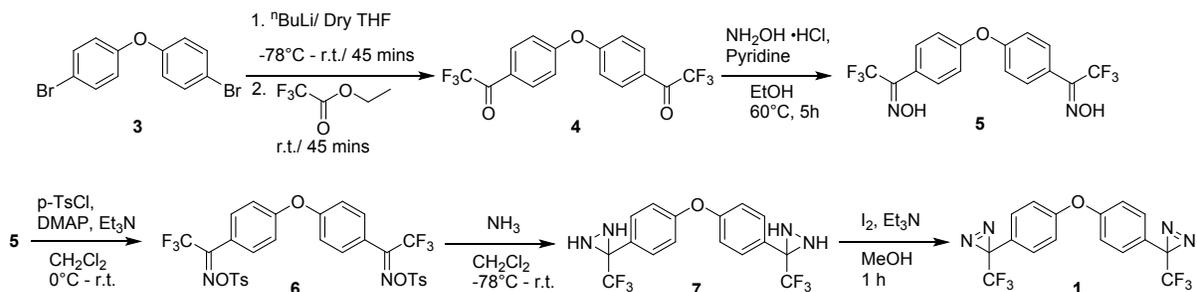


Figure S1: Cyclic voltammetry of thin films of photolyzed NPB (0% and 10% **1**) and unphotolyzed NPB recorded in 0.1 M tetrabutylammonium hexafluorophosphate in dry acetonitrile at a sweeping rate of 100 mV.s⁻¹ using a Ag/AgNO₃ reference electrode.

Synthesis:



Scheme 1: Synthesis of bis-diazirine cross-linker **1**.

Synthesis of 1,1'-(oxybis(4,1-phenylene))bis(2,2,2-trifluoroethan-1-one) (**4**): To a stirring solution of 4,4'-oxybis(bromobenzene) (1 g, 3 mmol) in dry THF (80 ml) under argon atmosphere at -78° C, *n*-Butyllithium (2.4 ml, 6 mmol, 2.5M) was slowly added and the resulting solution was kept stirring for an hour. Then ethyl trifluoroacetate (1.2 ml, 9 mmol) was added dropwise and the reaction mixture was kept stirring for another 45 minutes and warmed up to room temperature. By adding 1 ml of ethanol the reaction mixture was quenched, then THF was removed by evaporation under reduced pressure and the residue was extracted with water (50 ml) and diethyl ether (50 ml×3) and dried over MgSO₄. Filtration and followed by evaporation under reduced pressure and finally a flash column chromatography on silica gel using Hexane:Ethyl acetate (4:1 v/v) as eluent yielded 926 mg (85%) of pure compound **4** as colorless oil. ¹H NMR of **4** (500 MHz, CDCl₃): δ = 7.20 (d, *J* = 10 Hz, 4H), 8.15 (d, *J* = 10 Hz, 4H). ¹³C NMR of **4** (125 MHz, CDCl₃): δ = 116.66 (q, *J* = 288.75 Hz), 119.43, 126.01, 132.92 (q, *J* = 2.12 Hz), 161.41, 179.54 (q, *J* = 35 Hz). MS (GCMS): *m/z* = 362 (M⁺).

Synthesis of 1,1'-(oxybis(4,1-phenylene))bis(2,2,2-trifluoroethan-1-one) dioxime (**5**): A mixture of ketone **4** (340 mg, 0.93 mmol), hydroxylamine hydrochloride (0.23 g, 3.58 mmol), pyridine (3.5 ml) and ethanol (10 ml), was stirred and heated at 70° C for 12 hrs. After cooling down to room

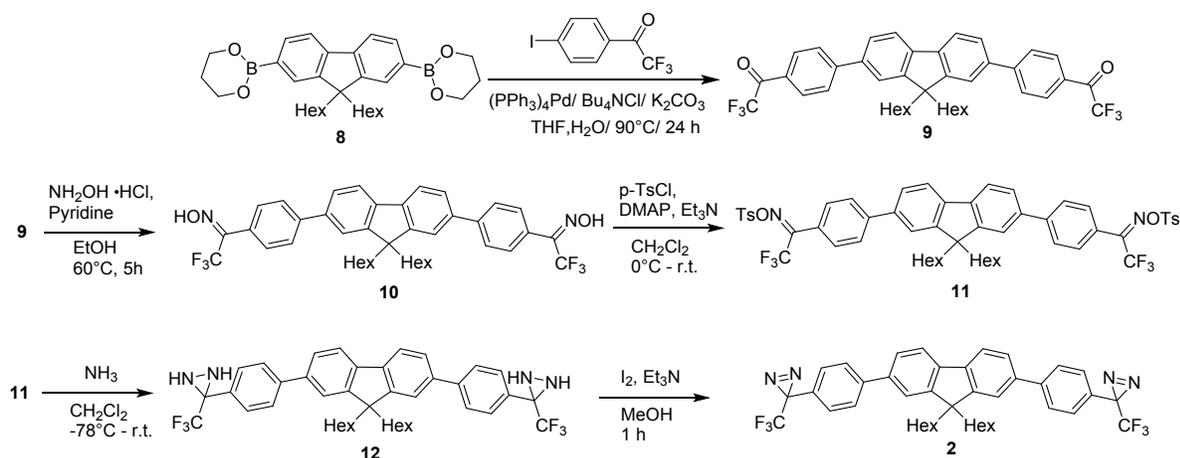
temperature, the reaction mixture was concentrated by evaporation under reduced pressure and then extracted with citric acid (50 ml, 10% in water) and diethyl ether (50 ml×3) and dried over MgSO₄. Filtration followed by evaporation under reduced pressure and finally a flash column chromatography on silica gel using DCM as eluent yielded 253 mg (69%) of pure compound **5** as white solid. ¹H NMR of **5** (500 MHz, CDCl₃): δ = 7.15 (d, *J* = 10 Hz, 4H), 8.61 (d, *J* = 10 Hz, 4H), 9.16 (s, 2H). ¹³C NMR of **5** (125 MHz, CDCl₃): δ = 119.01, 120.61 (q, *J* = 272.5 Hz), 121.13, 130.89, 146.80 (q, *J* = 32.5 Hz), 158.08. MS (GCMS): *m/z* = 392 (M⁺).

Synthesis of 1,1'-(oxybis(4,1-phenylene))bis(2,2,2-trifluoroethan-1-one) O,O-ditosyl dioxime (6):
A mixture of oxime **5** (158 mg, 0.40 mmol), triethylamine (0.17 ml, 1.2 mmol), and DMAP (0.010 gm, 0.079 mmol) was stirred in DCM (25 ml) at 0°C for an hour and then *p*-toluenesulfonyl chloride (0.23 gm, 1.2 mmol) was added and the reaction mixture was kept stirring for overnight at room temperature. The complete consumption of the starting materials was confirmed by TLC and the reaction mixture was evaporated under reduced pressure and extracted with water (50 mL) and diethyl ether (50 mL x 3) and dried over MgSO₄. Filtration and followed by evaporation and finally a flash column chromatography on silica gel using Hexane:EtAc (1:2 v/v) as eluent yielded 250 mg (88%) pure compound **6** as yellow solid. ¹H NMR of **6** (500 MHz, CDCl₃): δ = 2.49 (s, 6H), 7.13 (d, *J* = 5 Hz, 4H), 7.40 (d, *J* = 10 Hz, 4H), 7.47 (d, *J* = 5 Hz, 4H), 7.91 (d, *J* = 10 Hz, 4H). ¹³C NMR of **6** (125 MHz, CDCl₃): δ = 21.83, 119.29, 119.62 (q, *J* = 276.25 Hz), 119.97, 127.06, 129.32, 129.94, 130.24, 130.92, 131.05, 146.26, 152.97 (q, *J* = 33.75 Hz), 158.61. MS (GCMS): *m/z* = 700 (M⁺).

Synthesis of 3,3'-(oxybis(4,1-phenylene))bis(3-(trifluoromethyl)diaziridine) (7): In a solution of Compound **6** (500 mg, 0.72 mmol) in DCM (20 ml) at -78° C, liquid ammonia (10 ml) was added and the resulting mixture was kept stirring for 24 hours while it was warmed up to room

temperature. The reaction mixture was concentrated by carefully evaporating DCM and excess ammonia and extracted with water (50 ml) and DCM (50 mL×3) and dried over MgSO₄. Filtration and followed by evaporation under reduced pressure and finally a flash column chromatography on silica gel using EtOH:CHCl₃ (1:99 v/v) as eluent yielded 200 mg (68%) pure compound **7** as colorless solid. ¹H NMR of **7** (500 MHz, CDCl₃): δ = 7.61 (d, *J* = 10 Hz, 4H), 7.06 (dd, *J* = 2.1, 9 Hz, 4H), 2.81 (d, *J* = 10, 2H), 2.23 (d, *J* = 10, 2H). ¹³C NMR of **7** (125 MHz, CDCl₃): δ = 57.62 (q, *J* = 36.25 Hz), 119.14, 123.48 (q, *J* = 276.25 Hz), 126.97, 130, 157.99. MS (GCMS): *m/z* = 389 ((M-H)⁺).

Synthesis of 3,3'-(oxybis(4,1-phenylene))bis(3-(trifluoromethyl)-3H-diazirine) (**1**): Within a stirring solution of diaziridine **7** (1.47gm, 3.8 mmol), triethylamine (6.32 ml, 45 mmol) in methanol (30 ml); a solution of iodine (1.92 gm, 7.568 mmol) in methanol (10 ml) was dropwise added for 30 mins at room temperature in dark condition. After checking TLC the complete consumption of compound **7** was confirmed, then the reaction mixture was carefully concentrated by evaporation of solvents under reduced pressure and extracted with water (50 ml) and diethyl ether (50 mL×3) and dried over MgSO₄. Filtration, followed by evaporation under reduced pressure and finally a flash column chromatography on silica gel using Hexane:Ethyl acetate (9:1) as eluent yielded 742 mg (51%) pure bis-diazirine **1** as a colorless liquid. ¹H NMR of **1** (500 MHz, CDCl₃): δ = 7.20 (d, *J* = 10 Hz, 4H), 7.01 (dd, *J* = 2, 10 Hz, 4H). ¹³C NMR of **1** (125 MHz, CDCl₃): δ = 28.19 (q, *J* = 40 Hz), 119.30, 122.10 (q, *J* = 272.5 Hz), 124.37, 128.51, 157.64. MS (GCMS): *m/z* = 332 ((M-2N₂+2H)⁺).



Scheme 2: Synthesis of bis-diazirine cross-linker 2.

Synthesis of 1,1'-((9,9-dihexyl-9H-fluorene-2,7-diyl)bis(4,1-phenylene))bis(2,2,2-trifluoroethan-1-one) (**9**): 9,9-Dihexylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester (3.8 gm, 7.67 mmol) and 2,2,2-trifluoro-1-(4-iodophenyl)ethanone (5.75 gm, 19.17 mmol) were dissolved in THF (90 ml) and argon was bubbled through the solution for 30 min also separately in a solution of potassium carbonate in water (2M, 30 ml) argon was bubbled for 30 mins. The water solution was added in THF solution and under the argon atmosphere tetrakis(triphenylphosphine)-palladium(0) (0.03 gm, 0.03 mmol) was added and the flask was sealed and stirred at 90° C for 72 hrs. Then THF was removed by evaporation under reduced pressure and the residue was extracted with water (50 mL) and diethyl ether (50 mL×3) and dried over MgSO₄. Filtration and followed by evaporation under reduced pressure and finally a flash column chromatography on silica gel using Hexane:Ethyl acetate (6:1 v/v) as eluent yielded 4.28 gm (83%) of pure compound **9** as a yellow solid. ¹H NMR of **9** (500 MHz, CDCl₃): δ = 8.19 (d, *J* = 5 Hz, 4H), 7.87-7.85 (m, 6H), 7.68 (dd, *J* = 1.65, 10 Hz, 2H), 7.63 (d, *J* = 1.2 Hz, 2H), 2.09-2.06 (m, 4H), 1.13-1.04 (m, 12H), 0.76-0.67 (m, 10H). ¹³C NMR of **9** (125 MHz, CDCl₃): δ = 14, 22.57, 23.83, 29.64, 31.46, 40.36, 55.58, 116.81

(q, $J = 288.75$ Hz), 120.75, 121.75, 126.64, 127.69, 128.44, 130.83 (d, $J = 1.25$ Hz), 138.43, 141.24, 148.52, 152.21, 180.08 (q, $J = 35$ Hz). MS (GCMS) $m/z = 678$ (M^+).

Synthesis of 1,1'-((9,9-dihexyl-9H-fluorene-2,7-diyl)bis(4,1-phenylene))bis(2,2,2-trifluoroethanol-1-one) dioxime (**10**): A mixture of ketone **9** (4.9 gm, 7.2 mmol), hydroxylamine hydrochloride (2 g, 28.8 mmol), pyridine (40 ml) and ethanol (60 ml), was stirred and heated at 70° C for 12 hrs. After cooling down to room temperature, the reaction mixture was concentrated by evaporation under reduced pressure and then extracted with citric acid (100 ml, 10% in water) and diethyl ether (100 ml×3) and dried over MgSO₄. Filtration followed by evaporation under reduced pressure and finally a flash column chromatography on silica gel using DCM as eluent yielded 4.59 gm (90%) of pure compound **10** as colorless solid. ¹H NMR of **10** (500 MHz, CDCl₃): $\delta = 8.86$ (s, 1H), 8.74 (s, 1H), 7.81-7.78 (m, 4H), 7.75-7.73 (m, 2H), 7.67-7.66 (m, 2H), 7.63-7.58 (m, 6H), 2.07-2.03 (m, 4H), 1.14-1.02 (m, 12H), 0.77-0.70 (m, 10H). ¹³C NMR of **10** (125 MHz, CDCl₃): $\delta = 13.99$, 22.56, 23.80, 29.66, 31.45, 40.42, 55.38, 118.4 (q, $J = 282.5$), 120.33, 121.56 (d, $J = 11.25$ Hz), 121.65 (q, $J = 273.75$), 124.49, 126.21 (d, $J = 6.25$ Hz), 127.28, 128.64, 128.82, 129.19, 138.99 (q, $J = 2.5$ Hz), 140.55 (d, $J = 6.25$ Hz), 147.69 (q, $J = 32.5$ Hz), 147.79 (q, $J = 30$ Hz), 151.90. MS (GCMS) $m/z = 709$ (($M+H$)⁺).

Synthesis of 1,1'-((9,9-dihexyl-9H-fluorene-2,7-diyl)bis(4,1-phenylene))bis(2,2,2-trifluoroethanol-1-one) O,O-ditosyl dioxime (**11**): A mixture of oxime **10** (5.065 gm, 7.2 mmol), triethylamine (3 ml, 21.6 mmol), and DMAP (0.04 gm, 0.36 mmol) was stirred in DCM (450 ml) at 0°C for an hour and then p-toluenesulfonyl chloride (4.1 gm, 21.6 mmol) was added and the reaction mixture was kept stirring for overnight at room temperature. The complete consumption of the starting materials was confirmed by TLC and the reaction mixture was evaporated under reduced pressure and extracted with water (50 ml) and diethyl ether (50 ml×3) and dried over MgSO₄. Filtration and

followed by evaporation and finally a flash column chromatography on silica gel using Hexane:EtAc (1:4 v/v) as eluent yielded 6.81 gm (93%) pure compound **11** as yellow solid. ^1H NMR of **11** (500 MHz, CDCl_3): δ = 7.94-7.92 (m, 4H), 7.83-7.69 (m, 6H), 7.63-7.54 (m, 8H), 7.42-7.39 (m, 4H), 2.49 (d, J = 10Hz, 6H), 2.07-2.02 (m, 4H), 1.14-1.05 (m, 12H), 0.75-0.68 (m, 10H). ^{13}C NMR of **11** (125 MHz, CDCl_3): δ = 153.72 (q, J = 32.5 Hz), 151.99, 146.80, 146.20, 146.01, 144.96 (dd, J = 11.25, 3.75 Hz), 142.91, 140.75, 138.71 (d, J = 3.75 Hz), 138.62 (d, J = 5 Hz), 137.38, 131.45, 131.15, 130.23, 129.92, 129.59, 129.36 (d, J = 7.5 Hz), 129.14 (d, J = 12.5 Hz), 127.42 (d, J = 11.25 Hz), 127.04 (d, J = 3.75 Hz), 126.09, 121.55 (d, J = 13.75 Hz), 120.47, 119.68 (q, J = 282.5 Hz), 55.44, 40.41, 31.47, 29.66, 23.80, 22.56, 21.84, 13.99. MALDI-TOF m/z = 1016.6 ((M-H) $^+$).

Synthesis of 3,3'-((9,9-dihexyl-9H-fluorene-2,7-diyl)bis(4,1-phenylene))bis(3-(trifluoromethyl)diaziridine) (**12**): In a solution of Compound **11** (1.2gm, 1.1 mmol) in DCM (50 ml) at -78°C , liquid ammonia (20 ml) was added and the resulting mixture was kept stirring for 24 hours while it was warmed up to room temperature. The reaction mixture was concentrated by carefully evaporating DCM and excess ammonia then extracted with water (50 ml) and DCM (50 ml \times 3) and dried over MgSO_4 . Filtration and followed by evaporation under reduced pressure and finally a flash column chromatography on silica gel using DCM:Ethyl acetate (10:1 v/v) as eluent yielded 466 mg (60%) pure compound **12** as pale yellowish solid. ^1H NMR of **12** (500 MHz, CDCl_3): δ = 7.80 (d, J = 10 Hz, 2H), 7.73 (s, 8H), 7.6-7.56 (m, 4H), 2.85 (d, J = 10Hz, 2H), 2.28 (d, J = 10Hz, 2H), 2.06-2.03 (m, 4H), 1.12-1.05 (m, 12H), 0.76-0.70 (m, 10Hz). ^{13}C NMR of **12** (125 MHz, CDCl_3): δ = 151.85, 143.50, 140.45, 139.06, 130.38, 128.56, 127.51, 126.20, 123.57 (q, J = 276.25 Hz), 121.55, 120.28, 57.90 (q, J = 36.25 Hz), 55.37, 40.39, 31.44, 29.65, 23.78, 22.55, 13.99. MS (GCMS) m/z = 706 (M^+).

Synthesis of 3,3'-((9,9-dihexyl-9H-fluorene-2,7-diyl)bis(4,1-phenylene))bis(3-(trifluoromethyl)-3H-diazirine) (**2**): Within a stirring solution of diaziridine **12** (308 mg, 0.436 mmol), triethylamine (0.730 ml, 5.232 mmol) in methanol (30 ml); a solution of iodine (220 mg, 0.872 mmol) in methanol (20 ml) was dropwise added for 30 mins at room temperature in dark condition. After checking TLC, the complete consumption of compound **12** was confirmed, then the reaction mixture was carefully concentrated by evaporation of solvents under reduced pressure and extracted with water (50 ml) and diethyl ether (50 ml×3) and dried over MgSO₄. Filtration followed by evaporation under reduced pressure and finally a flash column chromatography on silica gel using Hexane:Ethyl acetate (9:1) as eluent yielded 256 mg (83%) pure bis-diazirine **2** as a pale yellow solid. ¹H NMR of **2** (500 MHz, CDCl₃): δ = 7.80-7.77 (m, 2H), 7.71-7.68 (m, 4H), 7.58-7.54 (m, 4H), 7.31-7.28 (m, 4H), 2.06-2 (m, 4H), 1.13-1.05 (m, 12H), 0.76-0.69 (m, 10H). ¹³C NMR of **2** (125 MHz, CDCl₃): δ = 151.94, 142.97, 140.53, 138.83, 129.07, 128.26, 127.87, 127.56, 126.93, 126.19, 122.22 (q, *J*= 273.75 Hz), 121.53, 120.36, 55.41, 40.39, 31.46, 29.67, 28.48 (q, *J*= 40 Hz), 28.32, 22.57, 13.99, impurity= DCM. MS (GCMS) *m/z* = 703 ((M+H)⁺), 675 ((M-N₂+H)⁺), 647 ((M-2N₂+H)⁺).

Supplementary Figures:

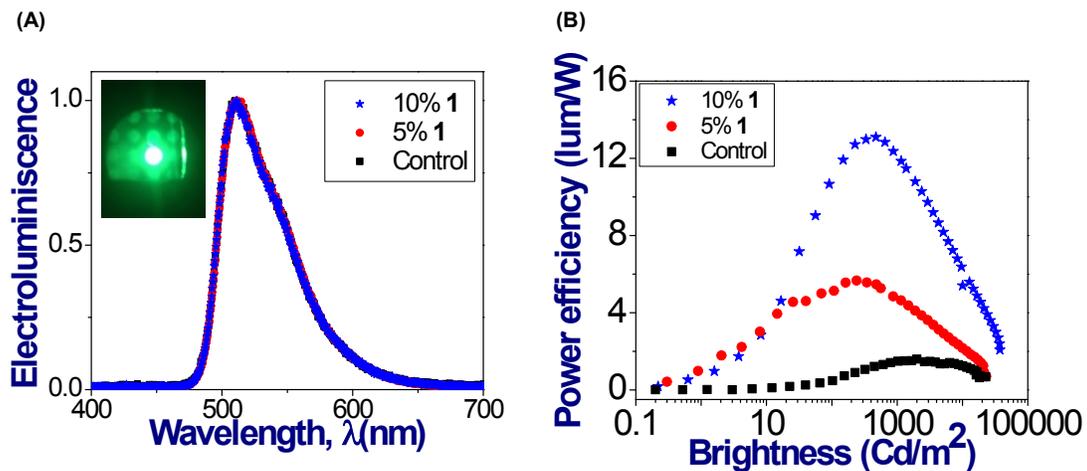


Figure S2. Comparison of electroluminescence (A) and maximum power efficiency vs Brightness (Cd/m^2) for the solution processed green OLEDs based on the different amount of **1** concentrations in the NPB. (B)

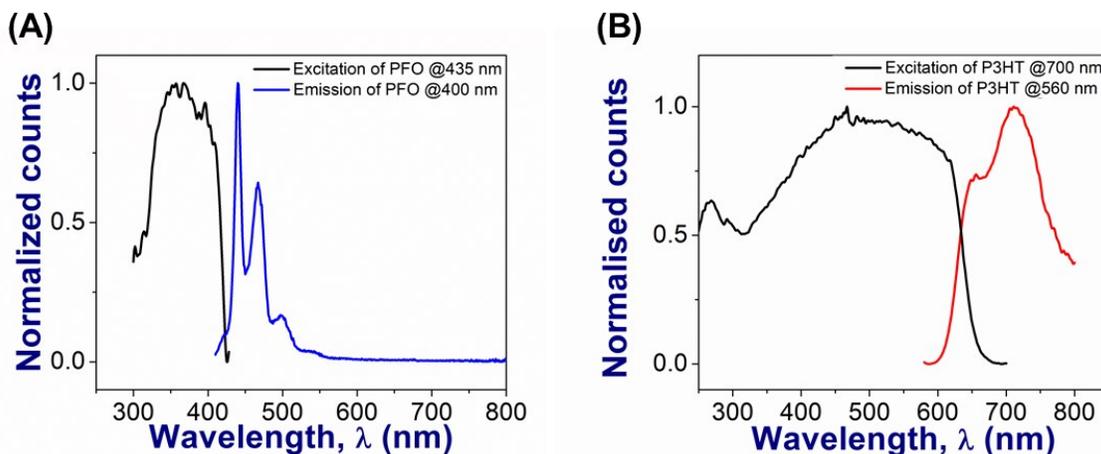


Figure S3. Excitation and Emission spectra of thin film of PFO (A) and P3HT (B) drop-casted on a quartz glass slide from a 1 mg/ml solution of Chloroform.

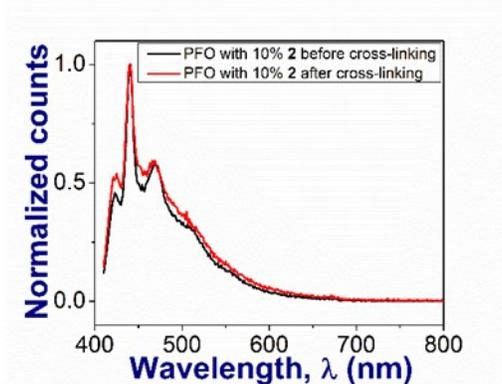


Figure S4. Emission spectra of thin film of PFO with 10% **2** (before and after cross-linking) drop-casted on a quartz glass slide from a 1 mg/ml solution of Chloroform.

Reference:

- 1 J. Pommerehne, H. Vestweber, W. Guss, R. F. Mahrt, H. Bässler, M. Porsch and J. Daub, *Adv. Mater.*, 1995, **7**, 551–554.
- 2 B. Dandrade, S. Datta, S. Forrest, P. Djurovich, E. Polikarpov and M. Thompson, *Org. Electron.*, 2005, **6**, 11–20.
- 3 F. M. Pasker, M. F. G. Klein, M. Sanyal, E. Barrena, U. Lemmer, A. Colsmann and S. Höger, *J. Polym. Sci. Part Polym. Chem.*, 2011, **49**, 5001–5011.