**Electronic Supplementary Information**

# Insulated Donor-π-Acceptor Systems Based on Fluorene-Phosphine Oxide Hybrides for Non-Doped Deep-Blue Electroluminescent Devices

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## Content

## Experimental section

### Materials and Instruments

All the reagents and solvents used for the synthesis of the compounds were purchased from Aldrich and Acros companies and used without further purification.

4'-(9-(4-(diphenylphosphoryl)phenyl)-9H-fluoren-9-yl)-N,N-diphenylbiphenyl-4-amine (**9TPAFSPO**) was prepared according to our previous report[1].

^{1}H NMR spectra were recorded using a Varian Mercury plus 400NB spectrometer relative to tetramethylsilane (TMS) as internal standard. Molecular masses were determined by a FINNIGAN LCQ Electro-Spraying Ionization-Mass Spectrometry (ESI-MS), or a MALDI-TOF-MS. Elemental analyses were performed on a Vario EL III elemental analyzer. Absorption and photoluminescence (PL) emission spectra of the target compound were measured using a SHIMADZU UV-3150 spectrophotometer and a SHIMADZU RF-5301PC spectrophotometer, respectively. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed on Shimadzu DSC-60A and DTG-60A thermal analyzers under nitrogen atmosphere at a heating rate of 10 °C min$^{-1}$. Cyclic voltammetric (CV) studies were conducted using an Eco Chemie B. V. AUTOLAB potentiostation in a typical three-electrode cell with a platinum sheet working electrode, a platinum wire counter electrode, and a silver/silver chloride (Ag/Ag$^+$) reference electrode. All electrochemical experiments were carried out under a nitrogen atmosphere at room temperature in dichloromethane.

**Scheme SI1.** Synthetic routine of **9DEFFSPO** and **9DPNAFSPO**.

## Synthesis

*9'-(4-bromophenyl)-9,9-diethyl-9H,9'H-2,9'-bifluorene* ***1***: 9,9-bis(4-bromophenyl) fluorene (0.9524 g, 2 mmol), Pd(pph$_3$)$_4$ (0.0289 g, 0.025 mmol), TBAB (0.0081 g, 0.025

mmol), sodium hydroxide solution (1.5 mL, 3 mmol, 2 mol L$^{-1}$) in anaerobic tetrahydrofuran (10 mL) was stirred under argon avoiding light at 80-90°C. 2-(9,9-diethyl-9H-fluoren-2-yl)- 4,4,5,5- tetramethyl-1,3,2-dioxaborolane (0.3483 g, 1 mmol) in anaerobic tetrahydrofuran (5 mL) was added in batches. Subsequently stirring was continued for one day at the same temperature. The organic layer was separated and washed with ammonium chloride solution. The extract phase was dried with anhydrous sodium sulfate and the solvent was removed by distillation in *vacuum*. The crude was further purified by column chromatography (silica, petroleum ether). **1** was obtained as white powder (yield 70%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ (*ppm*): 7.789 (d, $J$ = 7.6 Hz, 2H), 7.729-7.687 (m, 2H), 7.537-7.484 (m, 4H), 7.420-7.250 (m, 13H), 7.145-7.110 (m, 2H), 2.053-1.998 (m, 4H), 0.324 (t, $J$ = 7.2 Hz, 6H); LDI-TOF (m/z, %): 617 (M$^+$, 100).

*2-(4-{9-[4-(Diphenyl-phosphinoyl)-phenyl]-9H-fluoren-9-yl},-phenyl)-9,9-diethyl-9H -fluorene (**9DEFFSPO**)*: **1** (0.6176 g, 1 mmol) in dry tetrahydrofuran (5 mL) was stirred under argon and cooled to -78 °C. *n*-Butyllithium (0.6666 mL, 2.5 mol/L, 1.6 mmol) was slowly added with vigorous stirring. Stirring was continued for two hours at the same temperature. Chlorodiphenylphosphine (0.4533 mL, 2.4 mmol) was slowly added and the mixture allowed stirring for 30 min at the same temperature. Subsequently the mixture was stirring at room temperature for 12 hours. The reaction mixture was quenched with water and the organic contents were extracted with methylene dichloride. The extract phase was dried with anhydrous sodium sulfate and the solvent was removed by distillation in a vacuum at 45 °C. The crude phoshphine was recrystallized from acetone and obtained as white powder (yield 70%). Then the crude intermediate (0.7229 g, 1 mmol) in 10 mL dichloromethane were stirred in a round-bottom flask, and then H$_2$O$_2$ (1.2 mL, 10 mmol, 30 %) was slowly added into the mixture while stirring at room temperature. The organic layer was separated and washed with water. The extract was evaporated to dryness affording a white solid, which was further purified by column chromatography (silica, ethyl acetate: petroleum ether = 1:1). The final product was obtained as white powder (yield 90 %). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ (*ppm*): 7.787 (d, $J$ = 7.6 Hz, 2H), 7.723-7.634 (m, 6H), 7.540-7.230 (m, 25H), 2.060-1.993 (m, 4H), 0.321 (t, $J$ = 7.2 Hz, 6H); ESI-MS (m/z, %): 738 (M$^+$, 100); elemental analysis (%): for calculated C$_{54}$H$_{43}$OP: C 87.78, H 5.87, O 2.17; found: C 87.84, H 5.91, O 2.37.

*N-(4'-(9-(4-bromophenyl)-9H-fluoren-9-yl)biphenyl-4-yl)-N-phenylnaphthalen-1-amine* **2**: 9,9-bis(4-bromophenyl)-9H-fluorene (0.9524 g, 2 mmol), Pd(pph$_3$)$_4$ (0.0289 g, 0.025 mmol), TBAB (0.0081 g, 0.025 mmol), sodium hydroxide solution (1.5 mL, 3 mmol, 2 mol/L) in anaerobic tetrahydrofuran (10 mL) was stirred under argon avoiding light at 80-90°C. N-phenyl-N-(4-(4,4,5,5-tetramethyl-1,3,2- dioxaborolan- 2-yl) phenyl) naphthalen-1- amine (0.4213 g, 1 mmol) in anaerobic tetrahydrofuran (5 mL) was added in batches. Subsequently stirring was continued for 24 hours at the same temperature. The organic layer was separated and washed with ammonium chloride solution. The extract phase was dried with anhydrous sodium sulfate and the solvent was removed by distillation in a vacuum. The crude was further purified by column chromatography (silica, petroleum ether). **2** was obtained as white powder (yield 66 %). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ (*ppm*): 7.928 (d, $J$ = 8.4 Hz, 1H), 7.877 (d, $J$ = 8.4 Hz, 1H), 7.766 (d, $J$ = 7.2 Hz, 3H), 7.488-7.428 (m, 2H), 7.391-7.314 (m, 12H), 7.284 (d, $J$ = 6.8 Hz, 2H), 7.197 (t, $J$ = 8.2 Hz, 4H), 7.100-7.054 (m, 4H), 7.018 (d, $J$ = 8.4 Hz, 2H), 6.941 (t, $J$ = 7.4 Hz, 1H); LDI-TOF (m/z, %): 689 (M$^+$, 100).

*N-(4'-(9-(4-(diphenylphosphoryl)phenyl)-9H-fluoren-9-yl)biphenyl-4-yl)-N-phenylnaphthalen-1-amine (**9DPNAFSPO**)*: **2** (0.6907 g, 1 mmol) in dry tetrahydrofuran (5 mL) was stirred under argon and cooled to -78 °C. *n*-Butyllithium (0.6666 mL, 2.5 mol/L, 1.6 mmol) was slowly added with vigorous stirring. Stirring was continued for two hours at the same temperature. Chlorodiphenylphosphine (0.4533 mL, 2.4 mmol) was slowly added and the mixture allowed stirring for 30 min at the same temperature. Subsequently the mixture was stirring at room temperature for 12 hours. The reaction mixture was quenched with water and the organic contents were extracted with methylene dichloride. The extract phase was dried with anhydrous sodium sulfate and the solvent was removed by distillation in a vacuum at 45 °C. The crude phoshphine was recrystallized from acetone and obtained as white powder (yield 64%). Then the crude intermediate (0.7960 g, 1 mmol) in 10 mL dichloromethane were stirred in a round-bottom flask, and then H$_2$O$_2$ (1.2 mL, 10 mmol, 30 %) was slowly added into the mixture while stirring at room temperature. The organic layer was separated and washed with water. The extract was evaporated to dryness affording a white solid, which was further purified by column chromatography (silica, ethyl acetate: petroleum ether = 1:1). The final product was

obtained as white powder (yield 92 %). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ (*ppm*): 7.924 (d, *J* = 8.4 Hz, 1H), 7.875 (d, *J* = 8 Hz, 1H), 7.767 (d, *J* = 7.6 Hz, 3H), 7.674-7.626 (m, 4H), 7.530-7.272 (m, 24H), 7.215-7.157 (m, 4H), 7.061 (d, *J* = 8 Hz, 2H), 7.013 (d, *J* = 8.4 Hz, 2H), 6.939 (t, *J* = 7.4 Hz, 1H); ESI-MS (m/z, %): 811 (M$^+$, 100); elemental analysis (%): for calculated C$_{59}$H$_{42}$NOP: C 87.28, H 5.21, N 1.73, O 1.97; found: C 87.35, H 5.23, N 1.84, O 2.11.

## Gaussian Calculation

Computations on the electronic ground states of the single molecules of the compounds were performed using Becke's three-parameter density function in combination with the nonlocal correlation functional of Lee, Yang, and Parr (B3LYP).[2] 6-31G(d) basis sets were employed. The ground-state geometries were fully optimized at the B3LYP level. All computations were performed using the Gaussian 03 package.[3]

## Device Fabrication and Testing

The OLEDs with configurations of ITO|MoO$_3$ (5 nm)|NPB (50 nm)|TCTA (5 nm)| **9ArFSPO** (20 nm)|TPBi (30 nm)|LiF (1 nm)|Al were fabricated, where MoO$_3$ and LiF served as hole- and electron-injecting layers, NPB is N,N-bis(naphthylphenyl)-4,4'-biphenyldiamine as the hole-transporting layer (HTL), TPBI is 1,3,5-tris(1-phenyl-1H-benzo[d]imidazol-2-yl)benzene as electron-transporting hole-blocking layer, and TCTA is tris(4-(9H-carbazol-9-yl)phenyl)amine as exciton-blocking layer, respectively. Before loading into a deposition chamber, the ITO substrate was cleaned with detergents and deionized water, dried in an oven at 120 °C for 4 h, and treated with UV-ozone for 20 min. Devices were fabricated by evaporating organic layers at a rate of 0.1-0.3 nm s$^{-1}$ onto the ITO substrate sequentially at a pressure below $1\times10^{-6}$ mbar. Onto the TPBI layer, a layer of LiF with 0.5 nm thickness was deposited at a rate of 0.1 nm s$^{-1}$ to improve electron injection. Finally, a 100-nm-thick layer of Al was deposited at a rate of 0.6 nm s$^{-1}$ as the cathode. The emission area of the devices was 0.14 cm$^2$ as determined by the overlap area of the anode and the cathode. The EL spectra and CIE coordinates were measured using a PR650 spectra colorimeter. The current-density-voltage and brightness–voltage curves of the devices were measured using a Keithley 2400/2000 source meter and a calibrated silicon photodiode. All the experiments and measurements were carried out at room temperature under ambient conditions.
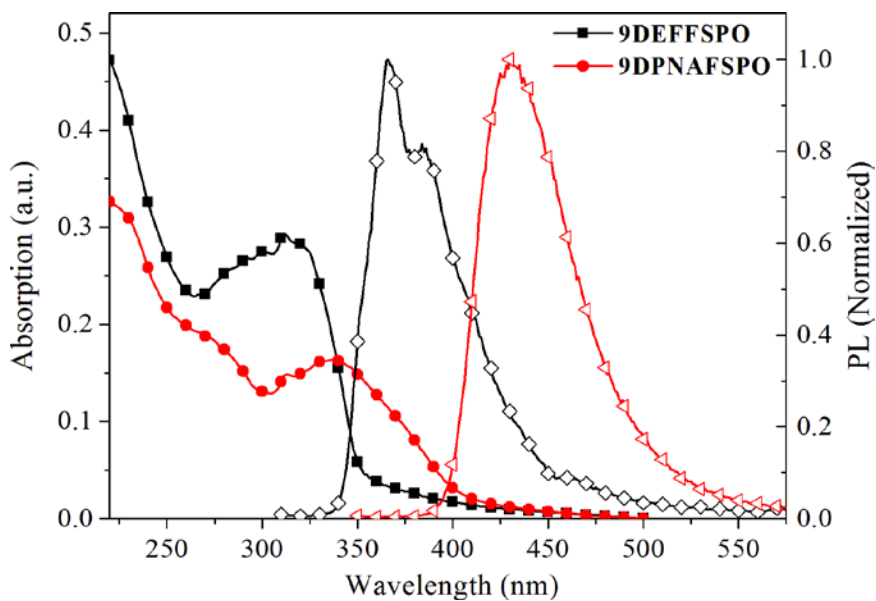
## Thermal Properties
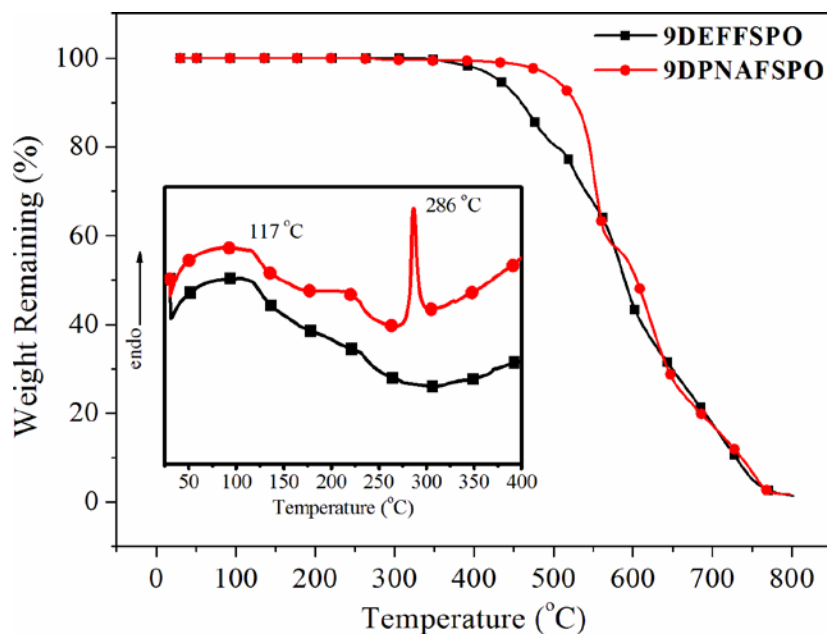


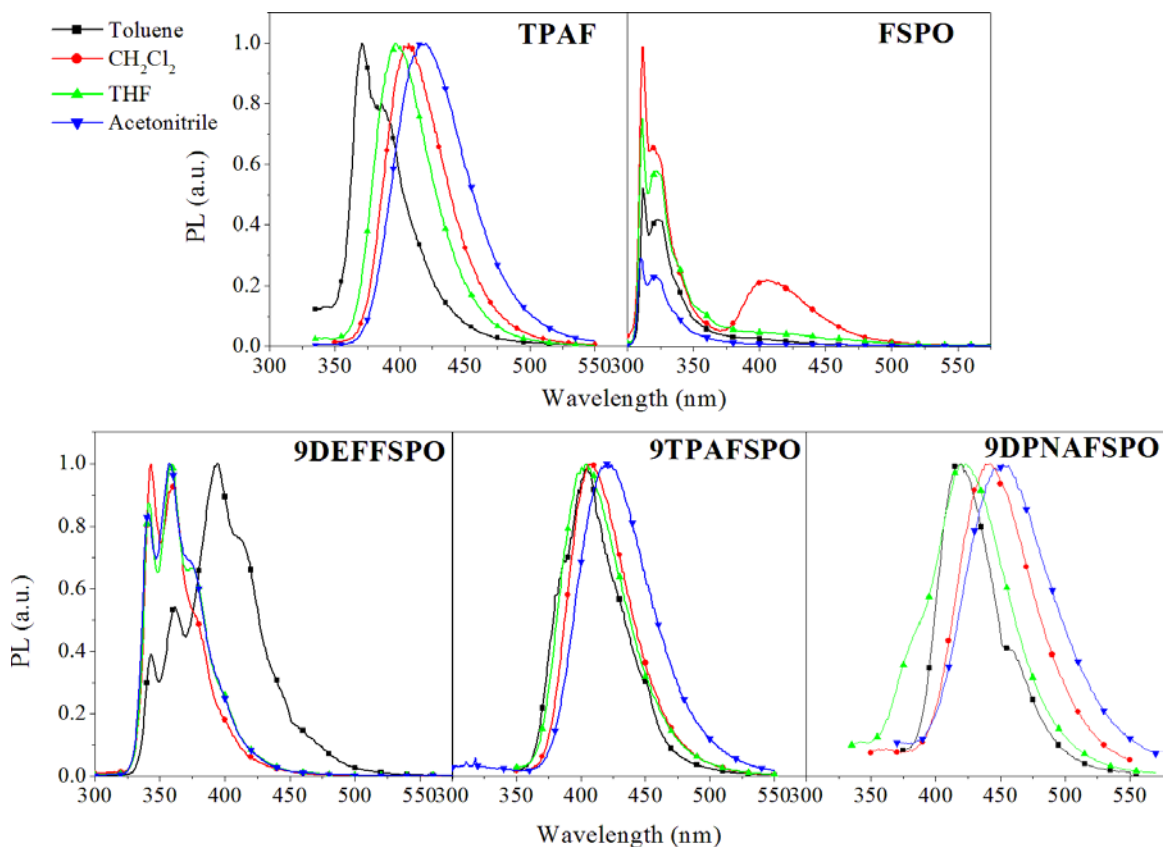**Figure SI1**. DSC (inserted) and TGA curves of **9DEFFSPO** and **9DPNAFSPO**.

## Photophysical Properties
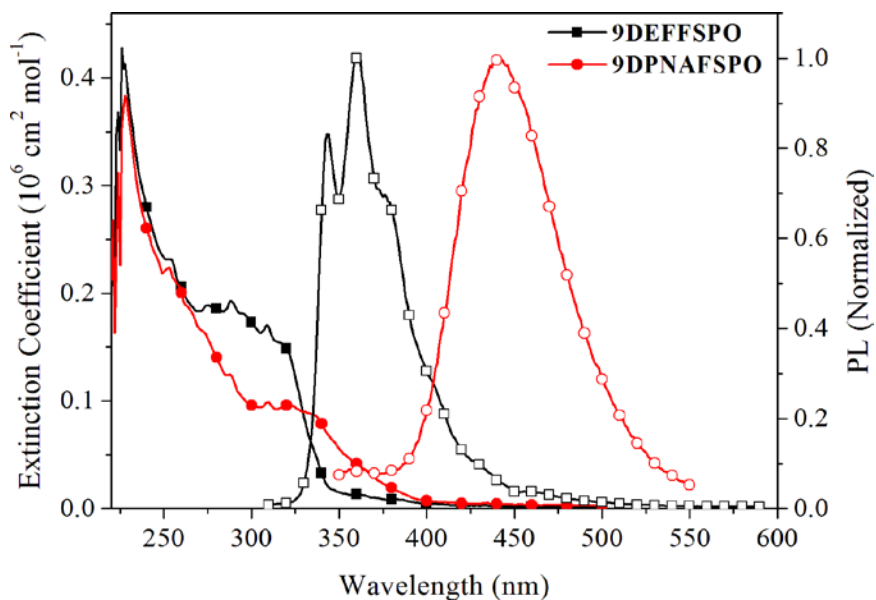


**Figure SI2**. Absorption and PL spectra of **9ArFSPO** in $CH_2Cl_2$.



**Figure SI3**. Absorption and PL spectra of **9ArFSPO** in film.

**Figure SI4**. PL spectra of N,N-diphenyl-4'-(9-phenyl-9H-fluoren-9-yl)biphenyl-4-amine (**TPAF**), **FSPO** and **9ArFSPO** in different solvents ($10^{-6}$ mol L$^{-1}$).
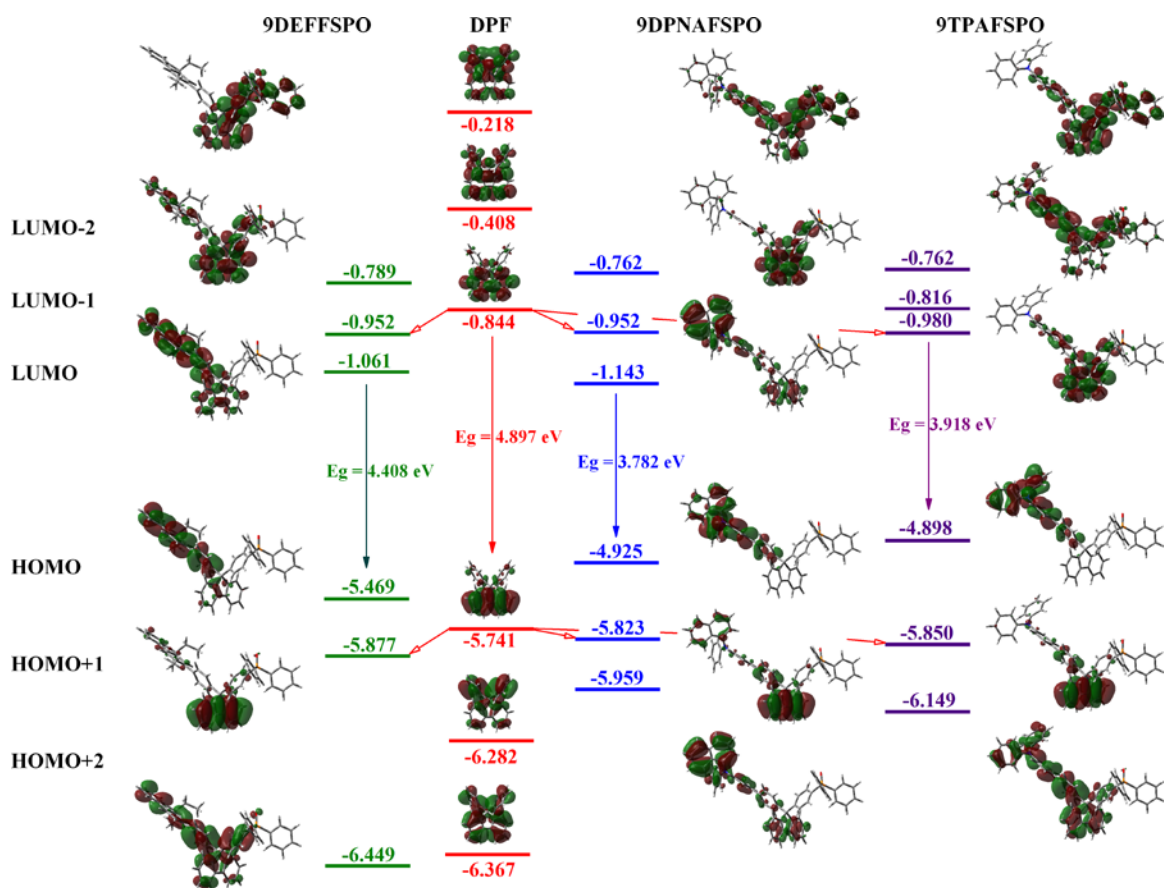
The emission spectra of **9TPAF**, **FSPO**, and **9ArFSPO** in toluene, DCM, THF and acetonitrile were added in revision as Fig. SI4 to figure out the suppressed ICT by indirect linkage. It is showed that the emissions of **9TPAF** slightly shift to red with an interval of about 10 nm. This small bathochromic shift can be attributed to the stabilization effect of polar solvents on the excited states. Different with its 2,7-substituted analog[4], the emissions of **FSPO** are almost unchanged except for the new aggregation emission in its toluene solution. The same characteristic is inherited by **9DEFFSPO**. The suppressed ICT is directly demonstrated by the emissions of **9TPAFSPO** that in toluene, THF and DCM the shape and peak of the emissions are nearly the same. Although in acetonitrile its emission shows a red shift of 13 nm, the very stable emissions still indicate the suppressing effect of indirect linkage. **9DPNAFSPO** also reveals the stable emissions along with increasing solvent polarity.

The comparison on the emission spectra of **PhF$_{Py2}$DPV**, **POAPF** and **9TPAFSPO** in solvents with different polarities clearly shows that for the fluorene-based ternary systems,

the direct bonding of electron-donating arylamine (DPA in **PhF$_{Py2}$DPV**) or electron-withdrawing DPPO (in **POAPF**) on fluorene moieties can still induce ICT with the red shifts about 40-60 nm, however, ICT was more effectively suppressed for **9TPAFSPO** and **9TPAFSPO** with much smaller red shifts of ~10 nm. Therefore, the indirect linkage at 9-position of fluorene effectively restrains the interplay between electron-donating arylamine, electron-withdrawing DPPO and chromophore fluorene so that the electronic communications between them are further suppressed.

## DFT Calculation Results



|  | 9DEFFSPO | DPF | 9DPNAFSPO | 9TPAFSPO |
|---|---|---|---|---|
|  |  | -0.218 |  |  |
| LUMO-2 |  | -0.408 |  |  |
| LUMO-1 | -0.789 | -0.844 | -0.762 | -0.762 |
|  | -0.952 |  | -0.952 | -0.816 |
| LUMO | -1.061 |  | -1.143 | -0.980 |

$E_g = 4.408$ eV  $E_g = 4.897$ eV  $E_g = 3.782$ eV  $E_g = 3.918$ eV

| HOMO |  |  | -4.925 | -4.898 |
|---|---|---|---|---|
|  | -5.469 |  |  |  |
| HOMO+1 | -5.877 | -5.741 | -5.823 | -5.850 |
|  |  |  | -5.959 | -6.149 |
| HOMO+2 |  | -6.282 |  |  |
|  | -6.449 | -6.367 |  |  |

**Figure SI5**. Molecular configurations, FMO energy levels and electron cloud distributions of **9ArFSPO** and diphenylfluorene calculated by DFT method.
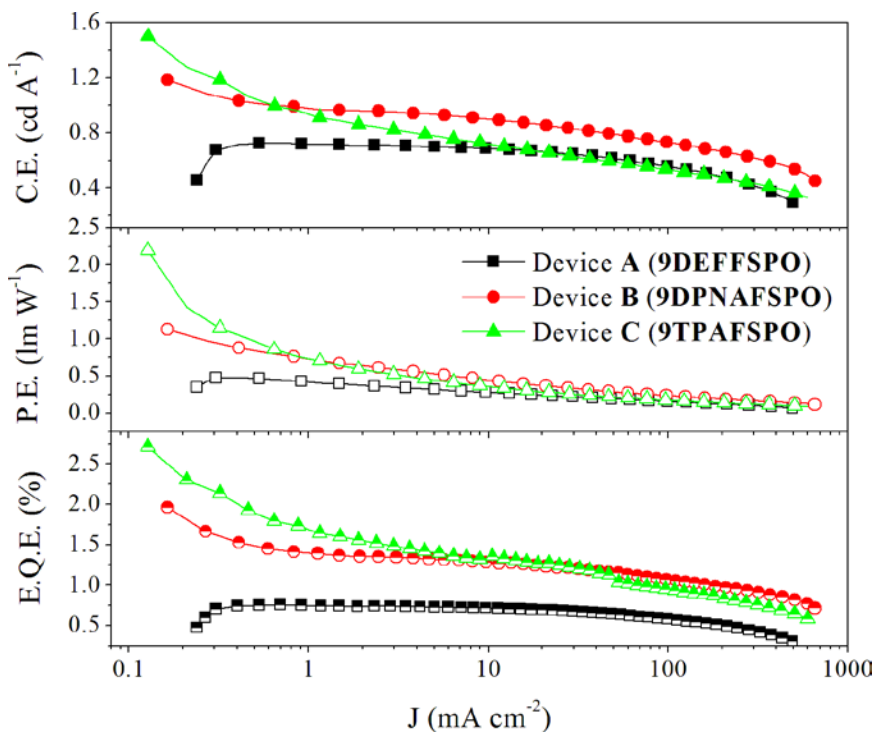
## CV Curves
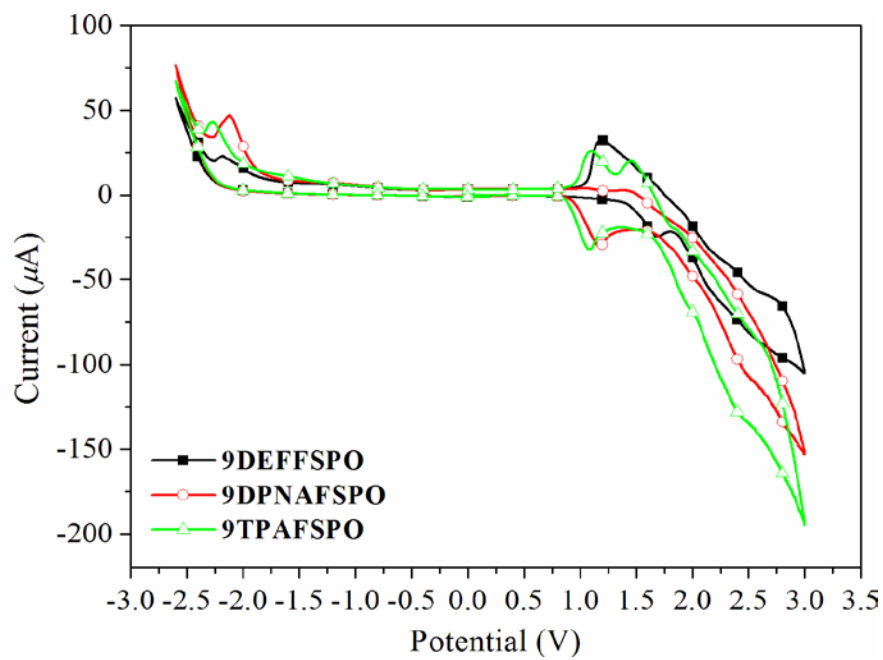


**Figure SI6**. CV curves of **9ArFSPO** in CH$_2$Cl$_2$.

## IV Curves of Single-Carrier Transporting Devices
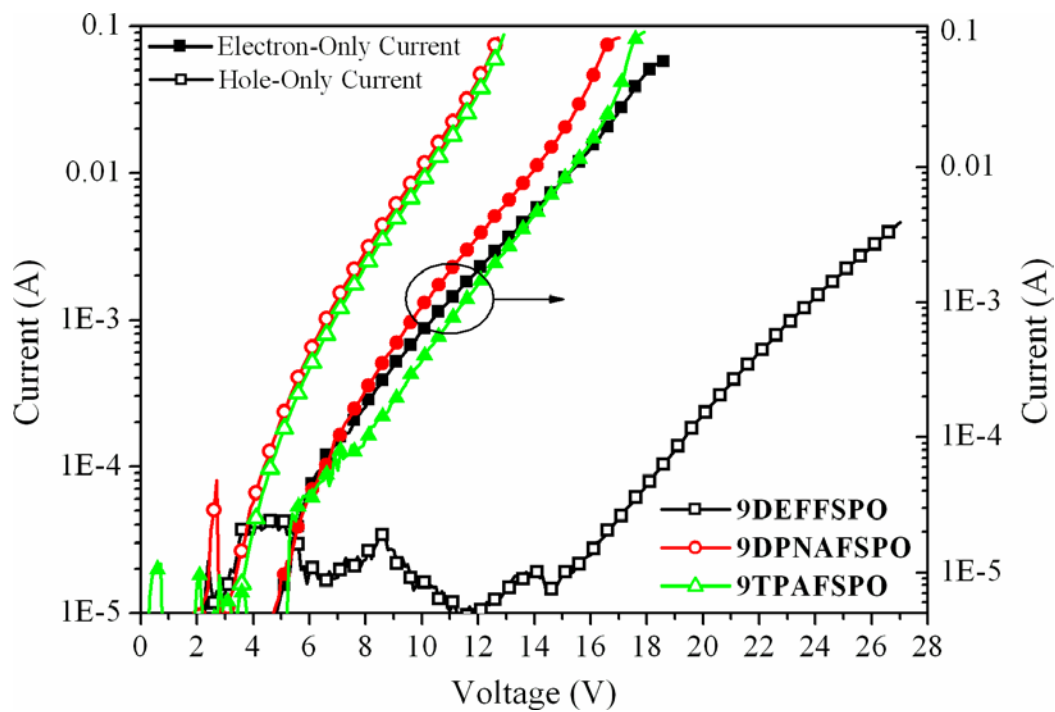


**Figure SI7**. V-*J* curves of the single-carrier transporting devices based on **9ArFSPO**.

## Efficiency-*J* Curves of the Devices



**Figure SI8**. Efficiency-*J* curves of the blue-emitting devices **A**-**C**.

**Table SI1** Physical properties of the representative blue emitters

| Emitter | PLQY (%) | HOMO/ LUMO (eV) | EL Emission Peak (nm)/CIE Coordinates | Driving Voltage (V)[a] | Max. Efficiencies[b] | $\gamma$ | Ref. |
|---|---|---|---|---|---|---|---|
| 9DPNAFSPO | 19 | -5.32/-2.58 | 424/(0.15, 0.07) | 3.1, 6.5 | 1.18, 1.13, 1.96 | 1 | This work |
| TCDqC | 99 | -5.4/-2.74 | 448/(0.15, 0.10) | 4.0, -- | 0.7, 0.4, -- | -- | [5] |
| OF(3)-NPh | 93 | -5.15/-- | 432/(0.15, 0.08) | ~4, ~6 | 2.24, 1.01, 3.1 | 0.33 | [6] |
| CzPhB | 54 | -5.92/-2.91 | 449/(0.15, 0.09) | 6.5, -- | 3.2, 1.1, 4.1 | 0.76 | [7] |
| POAn | 71 | -5.60/-2.50 | 444/(0.15, 0.07) | 3.0, ~4 | 2.9, 2.9, 4.3 | 0.61 | [8] |
| NAF1 | 70 | -5.52/-2.62 | 448/(0.15, 0.09) | 3.8, -- | 2.10, 3.56, 4.02 | 0.57 | [9] |
| TPAAnF(1) | 73 | -5.32/-- | 457/(0.14, 0.13) | 4.5, -- | 1.28, --, 0.26 | 0.04 | [10] |
| T2 | 66 | -5.55/-- | 433/(0.15, 0.10) | 3.75, -- | 1.80, 1.35, -- | -- | [11] |
| P8-OVS | 48 | - | --/(0.27, 0.57) | 3.1, -- | 8.28, --, 2.63 | 0.55 | [12] |
| PhF$_{Py2}$DPV | 48 | -5.44/-2.66 | 486/(0.15, 0.31) | --, -- | 6.4, 5.7, 3.2 | 0.67 | [13] |
| 10[c] | 85 | -5.56/-2.64 | 456/(0.15, 0.14) | 5.0, -- | 3.70, 1.98, 3.47 | 0.41 | [14] |
| BTSA | -- | -- | 436/(0.15, 0.10) | 6.7[d] | 1.3[d], --, -- | -- | [15] |

[a] in the order of onset and at 100 cd m$^{-2}$; [b] in the order of C.E. (cd A$^{-1}$), P.E. (lm W$^{-1}$) and E.Q.E. (%); [c] doped in MADN; [d] at 10 mA cm$^{-2}$.

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