

Supporting Information

Fine-tuning emission properties of the 9*H*-phenoselenazine core through substituents engineering for high efficiency purely organic room-temperature phosphorescence

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Experimental section

General information

All the reagents and solvents were procured from commercial sources and used without further purification. The chromatographic separations were performed using silica gel (200-300 nm). The purification of all the compounds was done by column chromatography and for the final products further purification was done by temperature gradient vacuum sublimation process. The final products were confirmed by ^1H , ^{13}C nuclear magnetic resonance (NMR), and mass spectrometry. The ^1H and ^{13}C NMR data of the final products were recorded on 500 and 300 MHz spectrometers by using deuterated chloroform (CDCl_3) as a solvent and chemical shift is expressed in parts per million (ppm), with tetramethylsilane (TMS) as an internal standard. The instrumental tools used are Fourier transform-nuclear magnetic resonance 500 MHz (Unity Inova), Fourier transform-nuclear magnetic resonance 300 MHz (Oxford 300 NMR), cyclic-voltammetry (CV) (Ivium Tech., Iviumstat), UV-Visible absorption spectroscopy (JASCO, V-730), fluorescence spectroscopy (PerkinElmer, LS-55), mass spectrometry (Advion, Expression LCMS spectrometer in APCI mode), and thermogravimetric analyzer (TGA) [Seiko Exstar 6000 (TG/DTA6100)].

Synthetic procedures

Synthesis of 10*H*-phenoselenazine

The 10*H*-phenoselenazine was synthesized as per the procedure reported in the literature.

Synthesis of 10-(4-(*tert*-butyl)phenyl)-10*H*-phenoselenazine (**I-1**)

10*H*-phenoselenazine (3.00 g, 12.2 mmol, 1 equiv.), 1-bromo-4-(*tert*-butyl)benzene (3.1 g, 14.6 mmol, 1.2 equiv.), and sodium *tert*. butoxide (3.5 g, 36.6 mmol, 3 equiv.) was stirred in 25 mL of dry toluene under a nitrogen atmosphere for 10 min. A mixture of Tris(dibenzylideneacetone)dipalladium (0) [Pd₂(dba)₃] (0.56 g, 0.6 mmol, 0.05 equiv.) and tri-*tert*-butylphosphine [P(*t*Bu)₃] in 10 mL of dry toluene was added to the above mixture under nitrogen atmosphere. The reaction mixture was refluxed for 12 h under a nitrogen atmosphere. After completion, the solvent was evaporated under a vacuum. The crude product obtained was purified by column chromatography using hexane (100%) as eluent to give **I-1** as white solid. Yield: 2.3 g (74%). MS (APCI) *m/z*: found 379.89 [(M+H)⁺]. Calculated for C₂₂H₂₁NSe: 378.38.

Synthesis of 3-bromo-10-(4-(*tert*-butyl)phenyl)-10*H*-phenoselenazine (**I-2**)

10-(4-(*tert*-butyl)phenyl)-10*H*-phenoselenazine (**I-1**) (2.3 g, 6.1 mmol, 1 equiv.), and *N*-bromo succinimide (NBS) (1.1 g, 6.1 mmol, 1 equiv.) were stirred in 10 mL of *N,N*-dimethylformamide (DMF) at 40 °C for 12 h. The reaction mass was poured in 50 mL of water and the solid obtained was filtered and washed with water twice. The crude product was purified by column chromatography using hexane (100%) as eluent to give (**I-2**) as white solid. Yield: 1.1 g (39%). MS (APCI) *m/z*: found 459.55 [(M+2)⁺]. Calculated for C₂₂H₂₀BrNSe: 457.27.

Synthesis of 10-(4-(*tert*-butyl)phenyl)-3-(dibenzo[*b,d*]furan-2-yl)-10*H*-phenoselenazine (PSeDBF)

3-bromo-10-(4-(*tert*-butyl)phenyl)-10*H*-phenoselenazine (**I-2**) (0.5 g, 10.9 mmol, 1 equiv.), dibenzo[*b,d*]furan-2-ylboronic acid (0.28 g, 13.1 mmol, 1.2 equiv.), potassium phosphate tribasic (K₃PO₄) (0.7 g, 32.7 mmol, 3 equiv.), 2-dicyclohexylphosphino-2', 6'-dimethoxybiphenyl (S-phos) (0.45 g, 1.1 mmol, 0.1 equiv.), and bis(dibenzylideneacetone)palladium (0) [Pd(dba)₂] (0.05 g, 0.06 mmol, 0.05 equiv.) were refluxed in toluene: water (20: 2 mL) mixture for 6 h. After completion of reaction, the reaction mass was cooled to room temperature and diluted with dichloromethane (DCM) (50 mL). The solvent was evaporated under vacuum. The crude product was purified by column chromatography using hexane: DCM (90:10). The PSeDBF obtained as off-white solid. Yield: 53%. ¹H NMR (500 MHz, CDCl₃) δ 8.03 (s, 1H), 7.95 (d, *J* = 7.6 Hz, 1H), 7.56 (dd, *J* = 8.1, 3.3 Hz, 6H), 7.45 (t, *J* = 7.7 Hz, 1H), 7.34 (dd, *J* = 14.4, 7.9 Hz, 3H), 7.28 – 7.23 (m, 2H), 6.98 (t, *J* = 7.6 Hz, 1H), 6.88 (t, *J* = 6.8 Hz, 1H), 6.59 (dd, *J* = 24.1, 8.4 Hz, 2H), 1.40 (s, 9H). ¹³C NMR (126 MHz, CDCl₃) δ 156.84 (s), 155.81 (s), 150.51 (s), 135.35 (s), 129.85 (s), 128.84 (s), 127.56 (d, *J* = 10.6 Hz), 126.32 (t, *J* = 10.1 Hz), 124.94 (s), 124.43 (s), 123.48 (s), 123.00 (s), 120.91 (s), 119.12 (s), 118.96 (s), 118.69 (s), 111.98 (s), 34.95 (s), 31.69 (s). MS (APCI) *m/z*: found 545.1263 [(M)⁺]. Calculated for C₃₄H₂₇N₂OSe: 545.1258.

Synthesis of 10-(4-(*tert*-butyl)phenyl)-3-(9,9-dimethyl-9*H*-fluoren-3-yl)-10*H*-phenoselenazine (PSeFL)

The PSeFL synthesized using same procedure as used for the synthesis of PSeDBF using (9,9-dimethyl-9*H*-fluoren-2-yl)boronic acid (0.31 g, 1.31 mmol, 1.2 equiv.). The PSeFL obtained as yellow solid. Yield: 0.38 g (61%). ¹H NMR (500 MHz, CDCl₃) δ 7.73 – 7.69 (m, 2H), 7.58 –

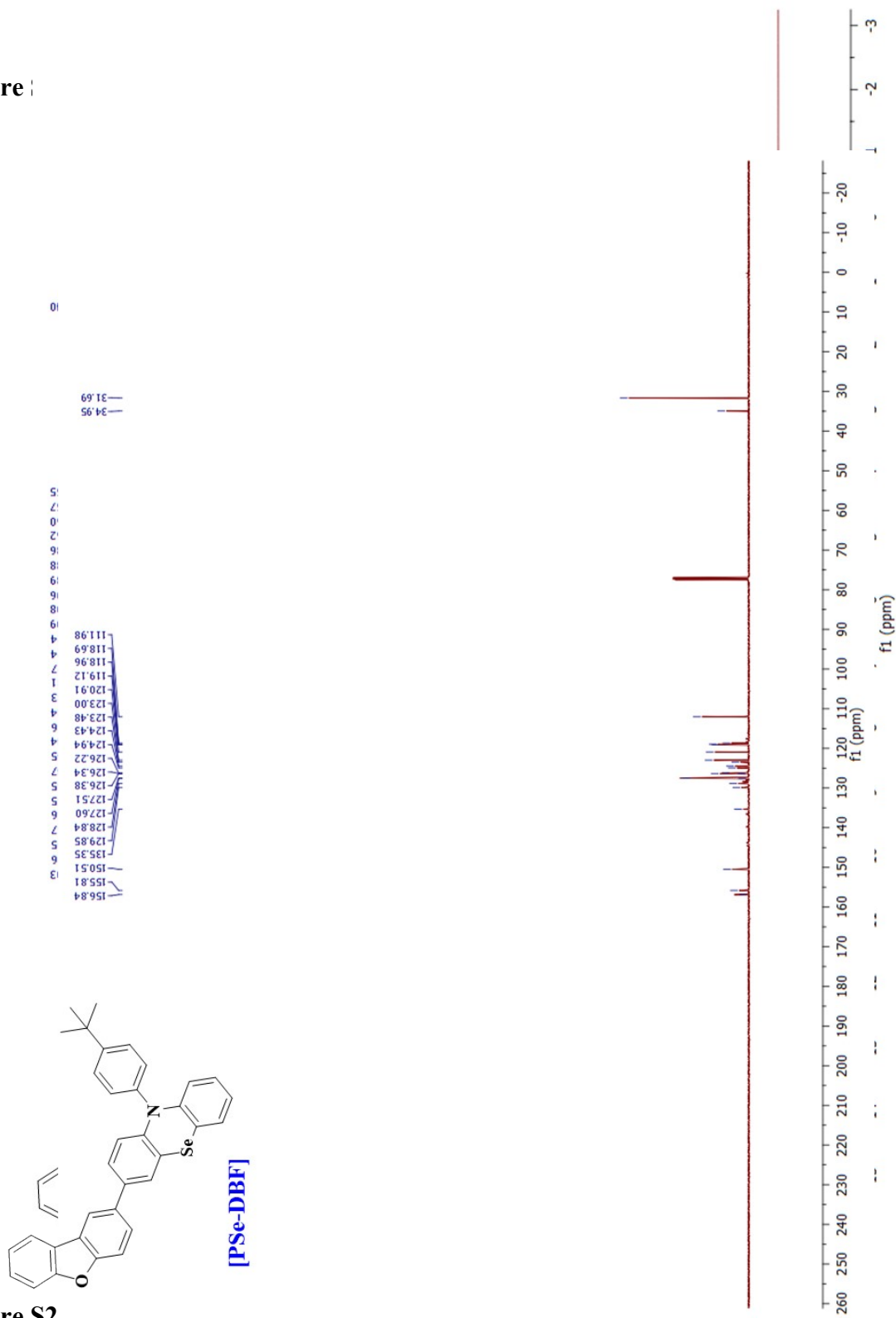
7.52 (m, 4H), 7.45 (dd, $J = 19.8, 7.4$ Hz, 2H), 7.35 – 7.28 (m, 4H), 7.26 (d, $J = 6.2$ Hz, 2H), 6.97 (t, $J = 7.6$ Hz, 1H), 6.88 (d, $J = 6.6$ Hz, 1H), 6.57 (dd, $J = 16.3, 8.4$ Hz, 2H), 1.50 (s, 6H), 1.40 (s, 9H). ^{13}C NMR (126 MHz, CDCl_3) δ 154.47 (s), 154.03 (s), 150.48 (s), 144.50 (s), 143.84 (s), 139.81 (s), 139.16 (d, $J = 22.5$ Hz), 139.07 – 138.93 (m), 138.40 (d, $J = 7.5$ Hz), 136.81 (s), 129.83 (s), 128.89 (s), 128.49 (d, $J = 95.1$ Hz), 127.44 (d, $J = 10.7$ Hz), 127.22 (s), 126.17 (s), 125.68 (s), 123.45 (s), 122.80 (s), 120.95 (s), 120.47 (s), 120.21 (s), 118.97 (d, $J = 19.3$ Hz), 118.23 (s), 117.54 (s), 47.13 (s), 34.94 (s), 31.69 (s), 27.50 (d, $J = 12.9$ Hz). MS (APCI) m/z : found 571.1777 [(M) $^+$]. Calculated for $\text{C}_{37}\text{H}_{33}\text{NSe}$: 571.1778.

Device fabrication

The OLED devices were fabricated by using a transparent glass substrate with 50 nm thick ITO. The cleaning of the ITO glass substrate was done using acetone and deionized water by ultrasonic treatment. The deposition of all the layers was carried out by vacuum thermal evaporation under the pressure of 3.0×10^{-7} torr. The deposition rates for the organic layers, LiF, and Al were controlled at 0.1, 0.01, and 0.5 nm/s, respectively. The encapsulation on glass was performed under the inert atmosphere (N_2 atmosphere) to protect the device from O_2 . All the device measurements were performed at ambient temperature. The electrical and optical characterizations of the devices were carried out by using Keithley 2400 Source Meter and CS 2000 spectroradiometer, respectively.

The optimized multilayer device structure is, ITO (50 nm)/ PEDOT: PSS (60 nm)/ TAPC (10 nm)/ TCTA (10 nm)/ PCzAC (5 nm)/ *m*CP (5 nm)/ *m*CP:TSPO1: PSeDBF and PSeFL (25:50%:X%)/ TSPO1 (5 nm)/ TPBi (40 nm)/ LiF (1 nm)/ Al (200 nm). Where, 1,1-Bis[(di-4-tolylamino)phenyl]cyclohexane (TAPC): tris(4-carbazoyl-9-ylphenyl)amine (TCTA) as hole transporting layer, 9,9-dimethyl-10-(9-phenyl-9*H*-carbazol-3-yl)-9,10-dihydroacridine (PCzAC): 1,3-di(9*H*-carbazol-9-yl)benzene (*m*CP) as hole type exciton blocking layer. The *m*CP:TSPO1: PSeDBF and PSeFL used as the emitting layer (EML) Where, *m*CP as hole-type (*p*-type) host and diphenyl(4-(triphenylsilyl)phenyl) phosphine oxide (TSPO1) as electron-type (*n*-type) host. Each of the hosts was taken in a 50 wt% ratio to develop a mixed host system. TSPO1 was also used as a hole-type exciton blocking layer, 1,3,5-tris(1-phenyl-1*H*-benzo[*d*]imidazol-2-yl)benzene (TPBi) was electron transporting layer.

Figure 1



Figure

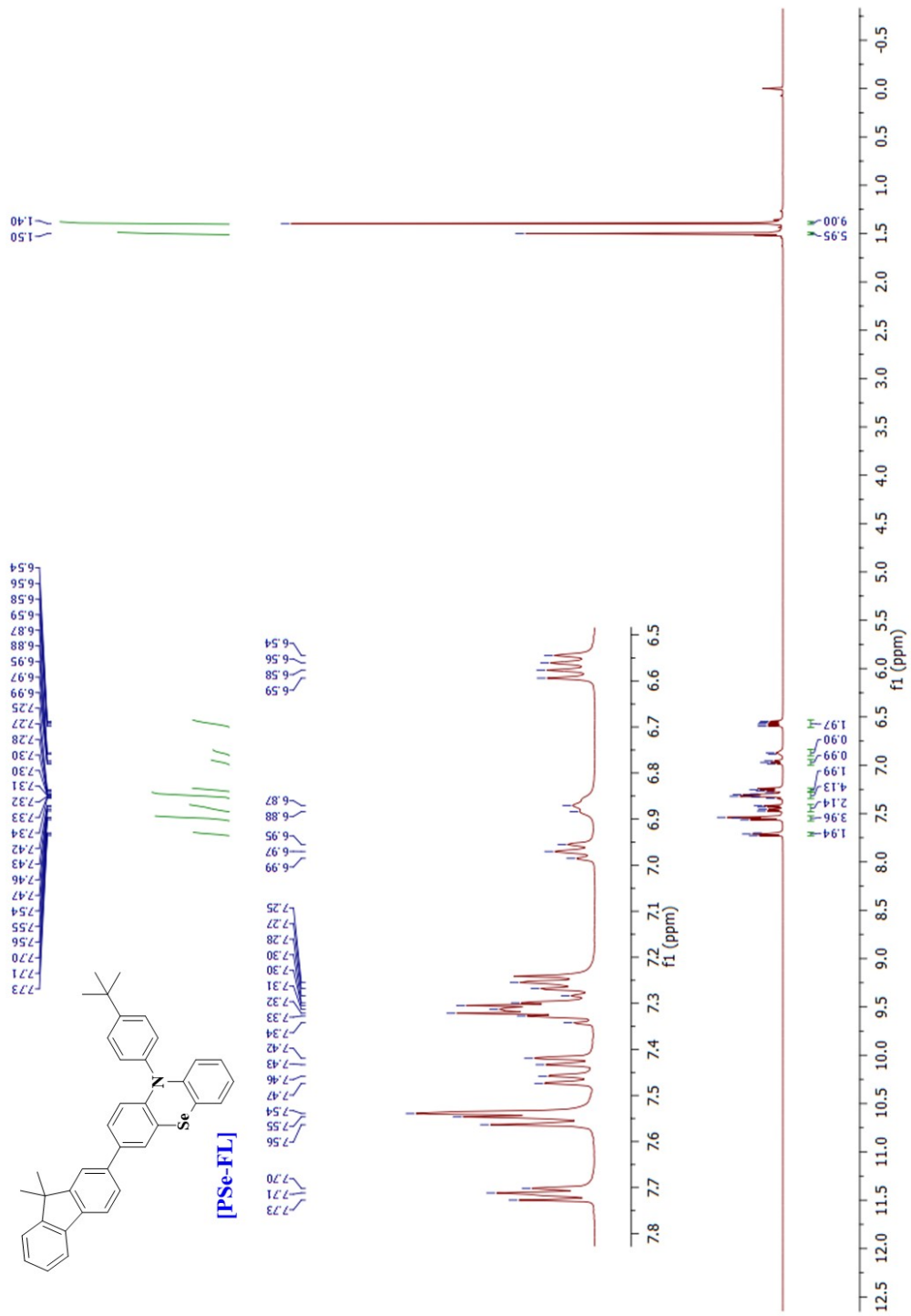


Figure S4. T

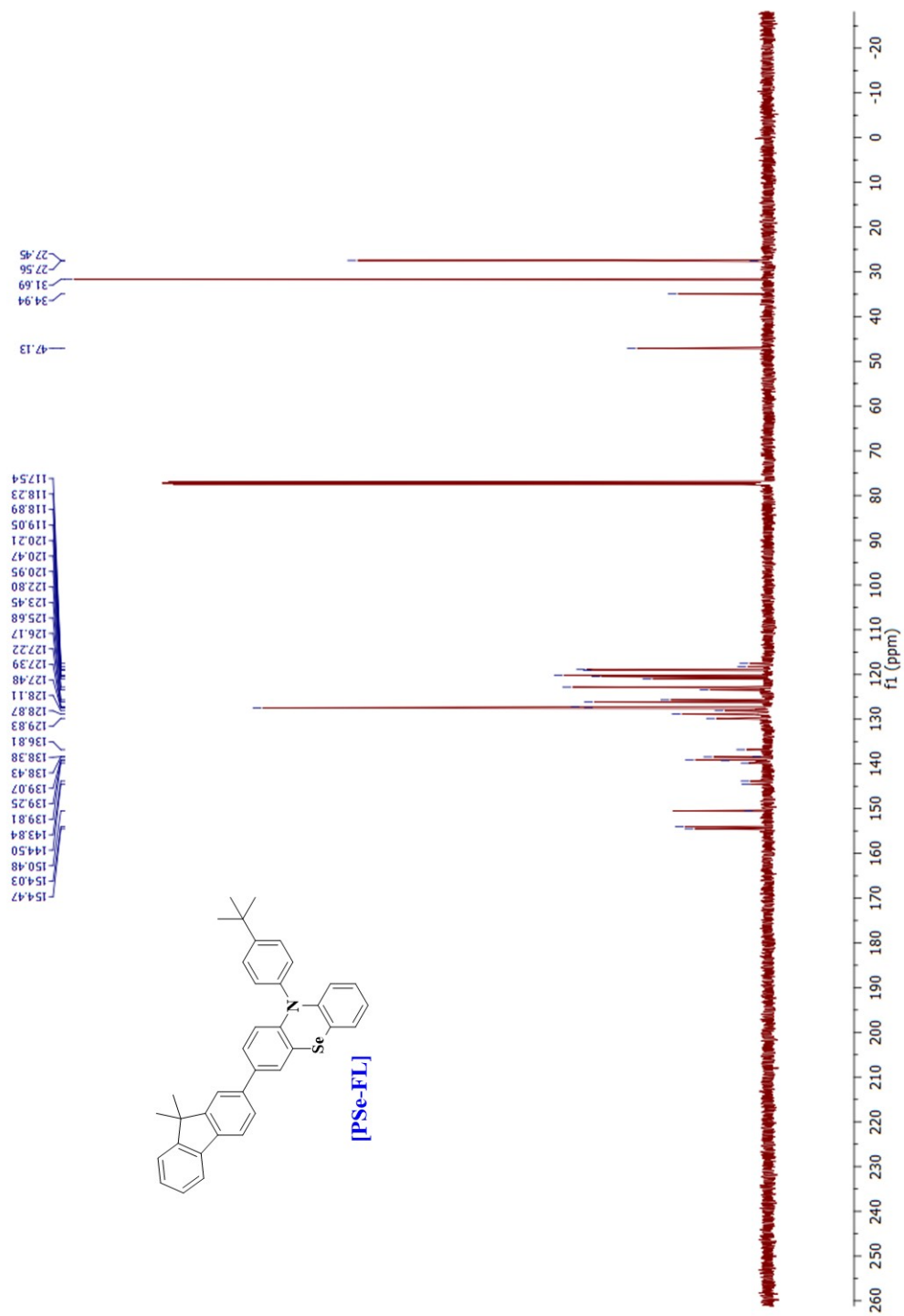


Figure S5. Tl

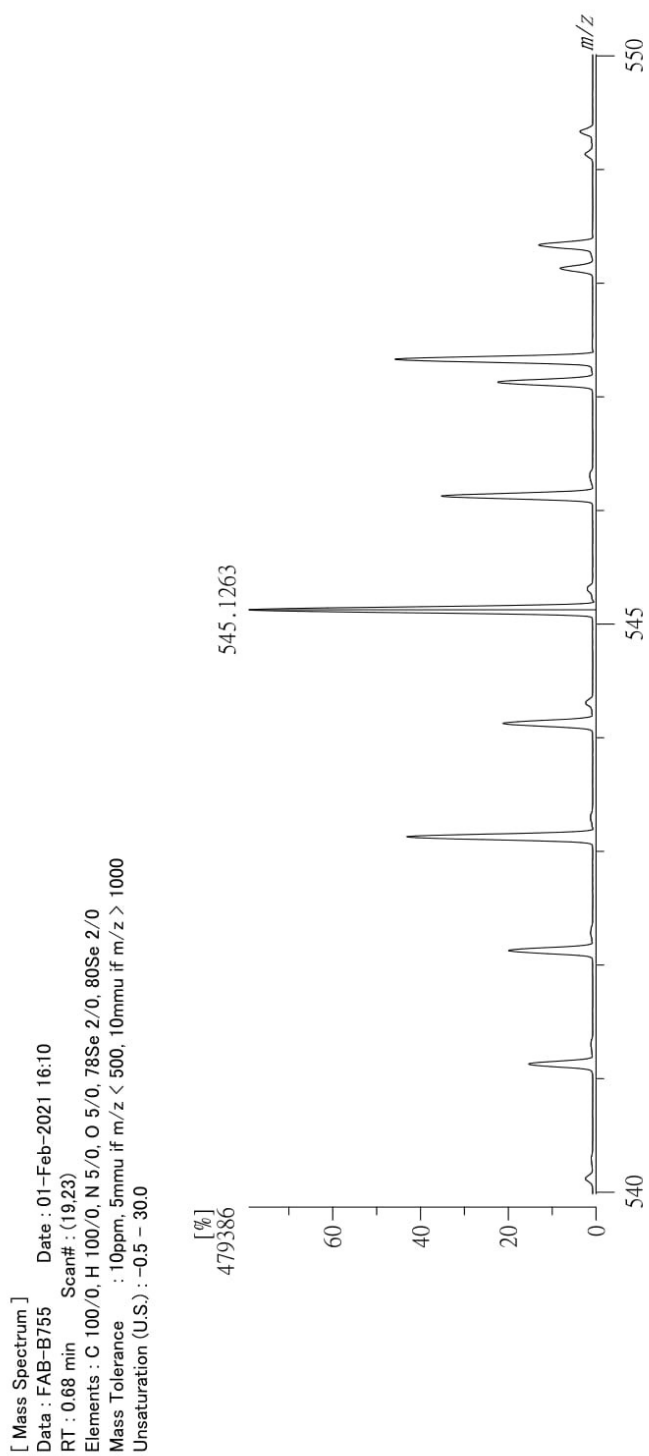
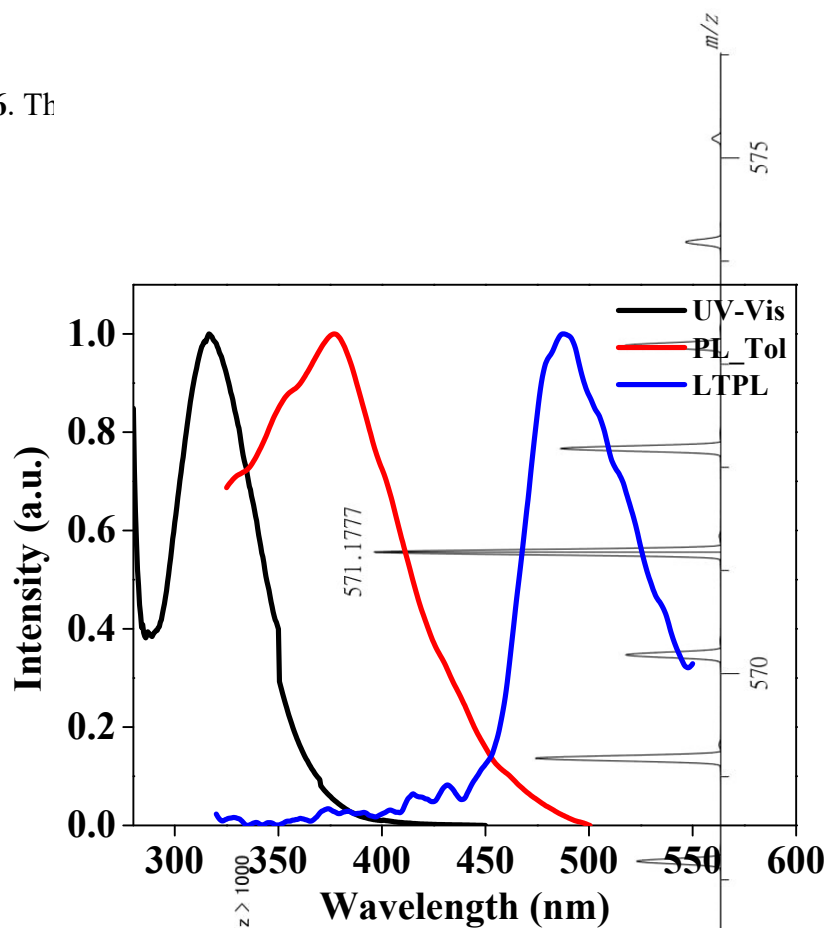


Figure S6. Th



[Mass Spectrum]
Data : FAB-B751 Date : 01-Feb-2021 15:26
RT : 0.41 min Scan# : (13,20)
Elements : C 100/0, H 100/0, N 5/0, 78Se 2/0, 80Se 2/0
Mass Tolerance : 10ppm, 5mmu if m/z < 500, 10mmu if m/z > 1000
Unsaturation (U.S.) : -0.5 - 50.0

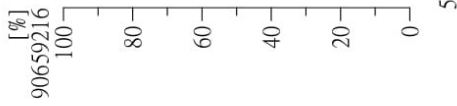


Figure S7. Th

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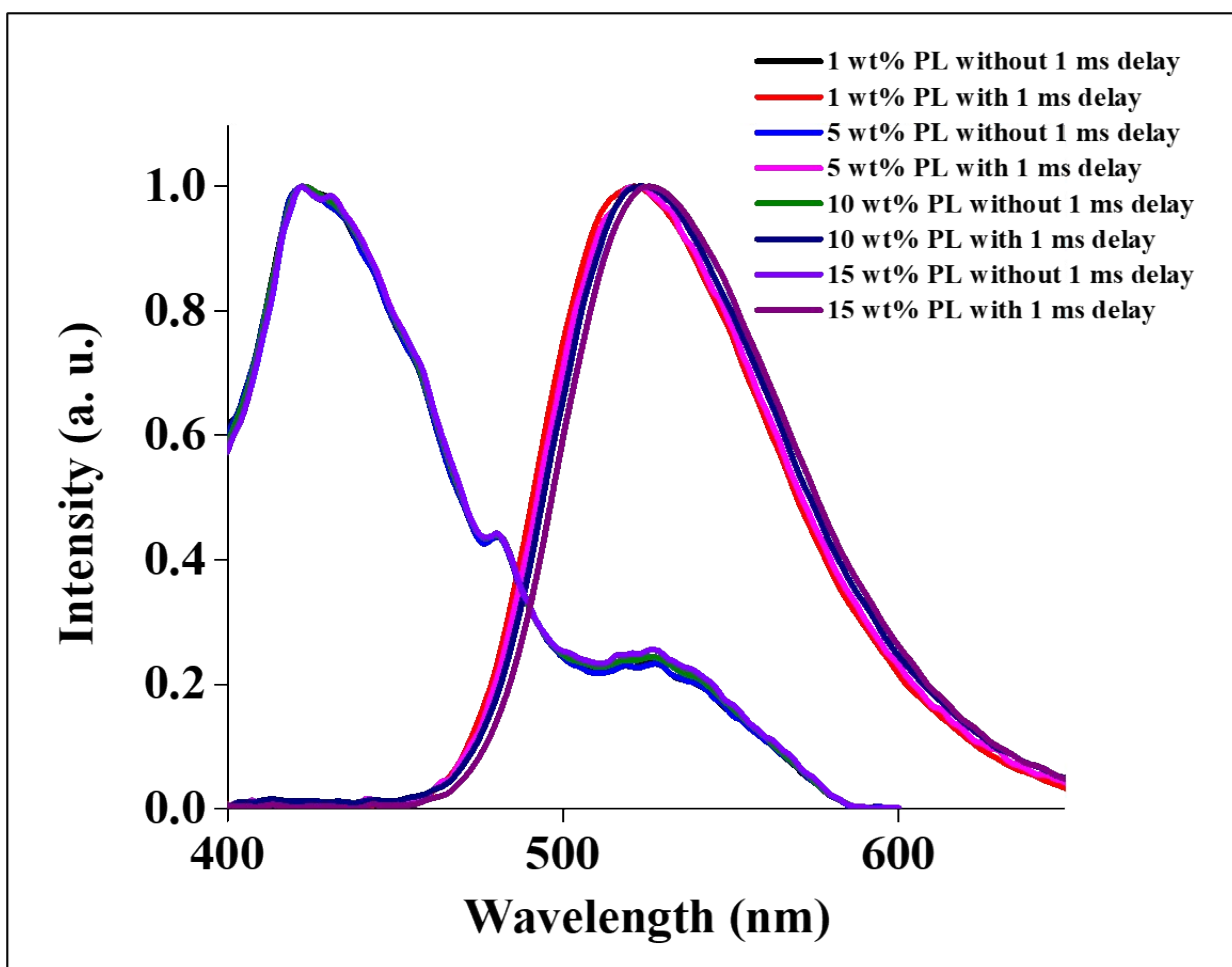


Figure S8. The photoluminescence measured using different doping concentrations of PSeDBF (1, 5, 10, and 15 wt%) in *m*-CP/TSPO-1 host matrix without and with 1.0 ms delay.

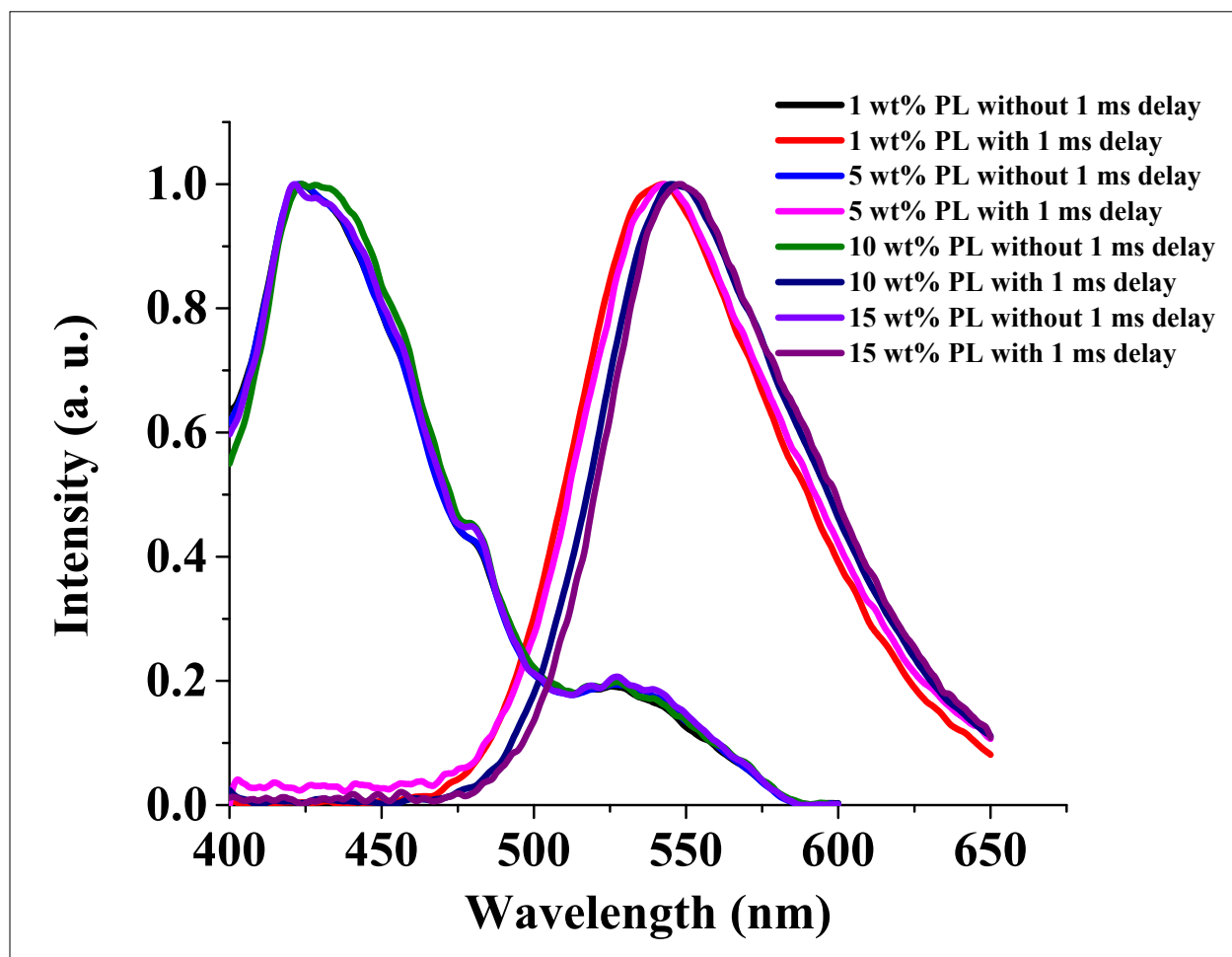


Figure S9. The photoluminescence measured using different doping concentrations of PSeFL (1, 5, 10, and 15 wt%) in *m*-CP/TSPO-1 host matrix without and with 1.0 ms delay.

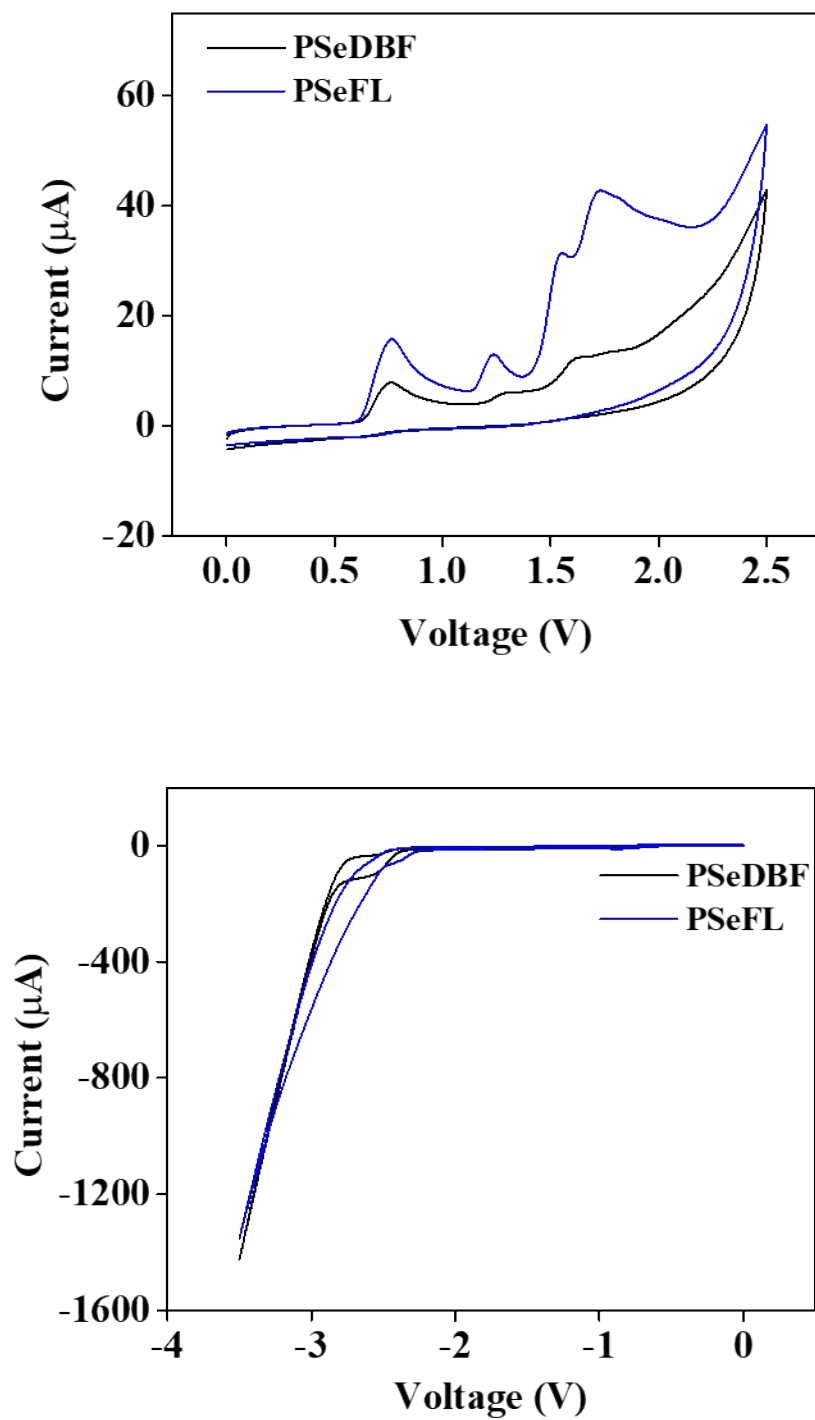


Figure S10. The CV curves of PSeDBF and PSeFL

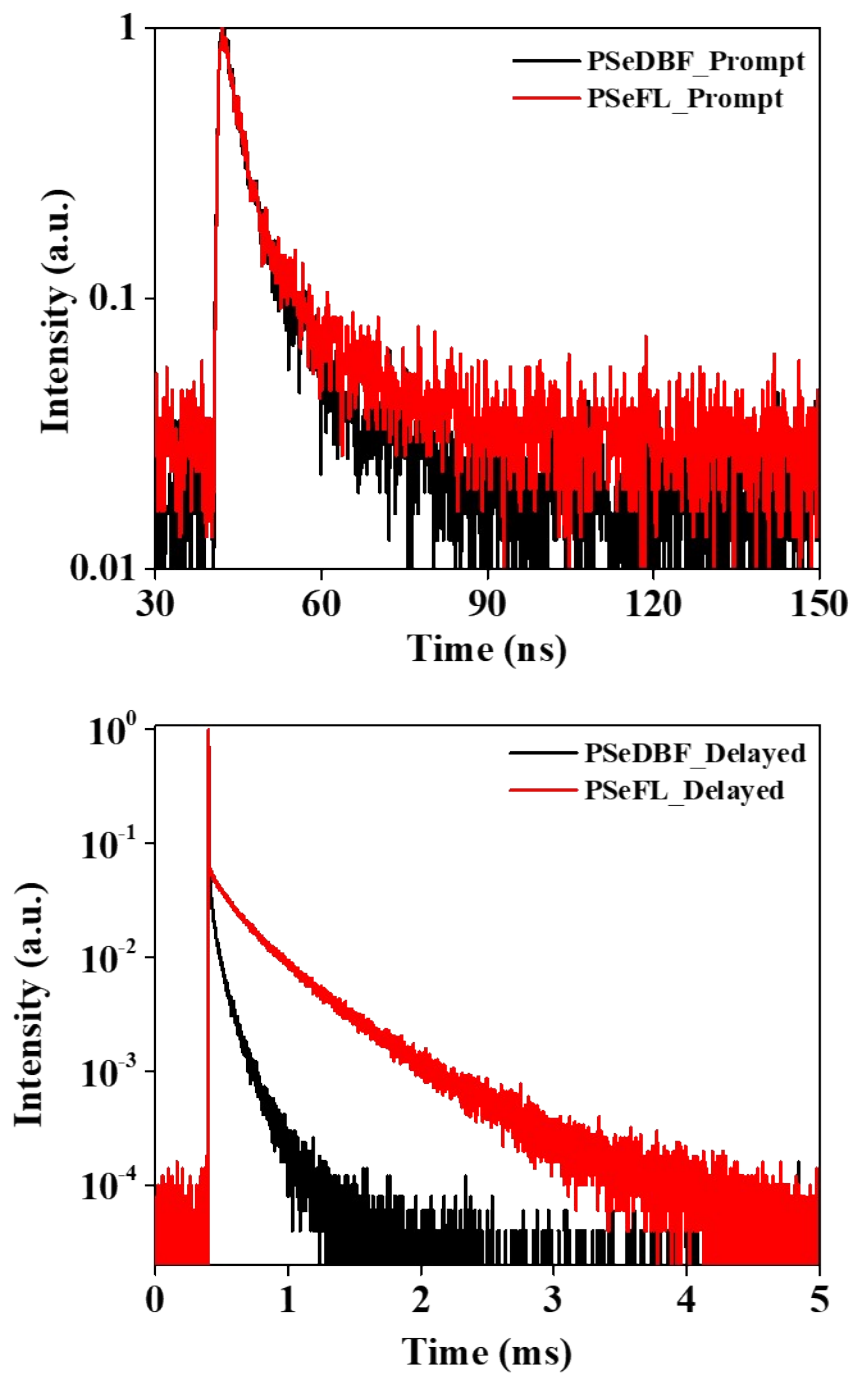


Figure S11. The Transient PL curves of PSeDBF and PSeFL

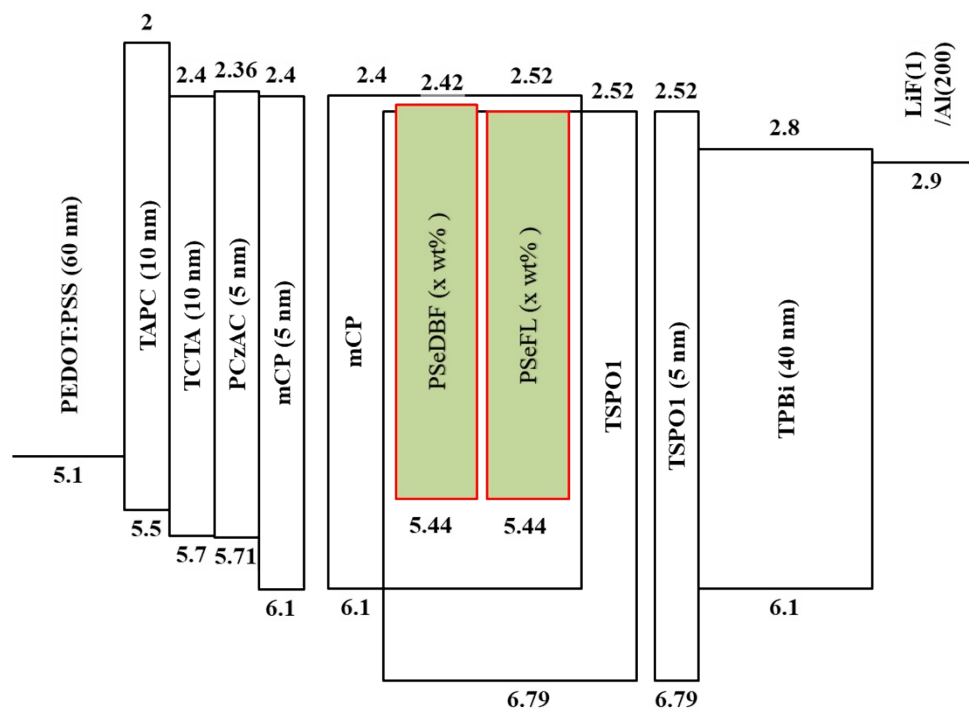
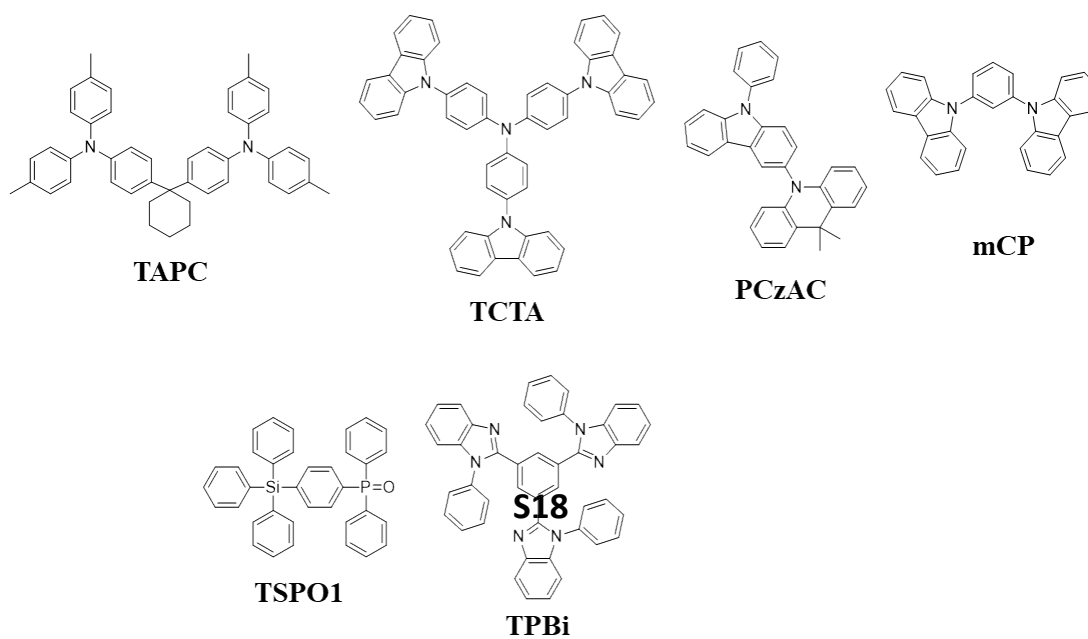


Figure S12. The schematic device diagram of PSeDBF and PSeFL doped devices and structures of layers used to fabricate the device



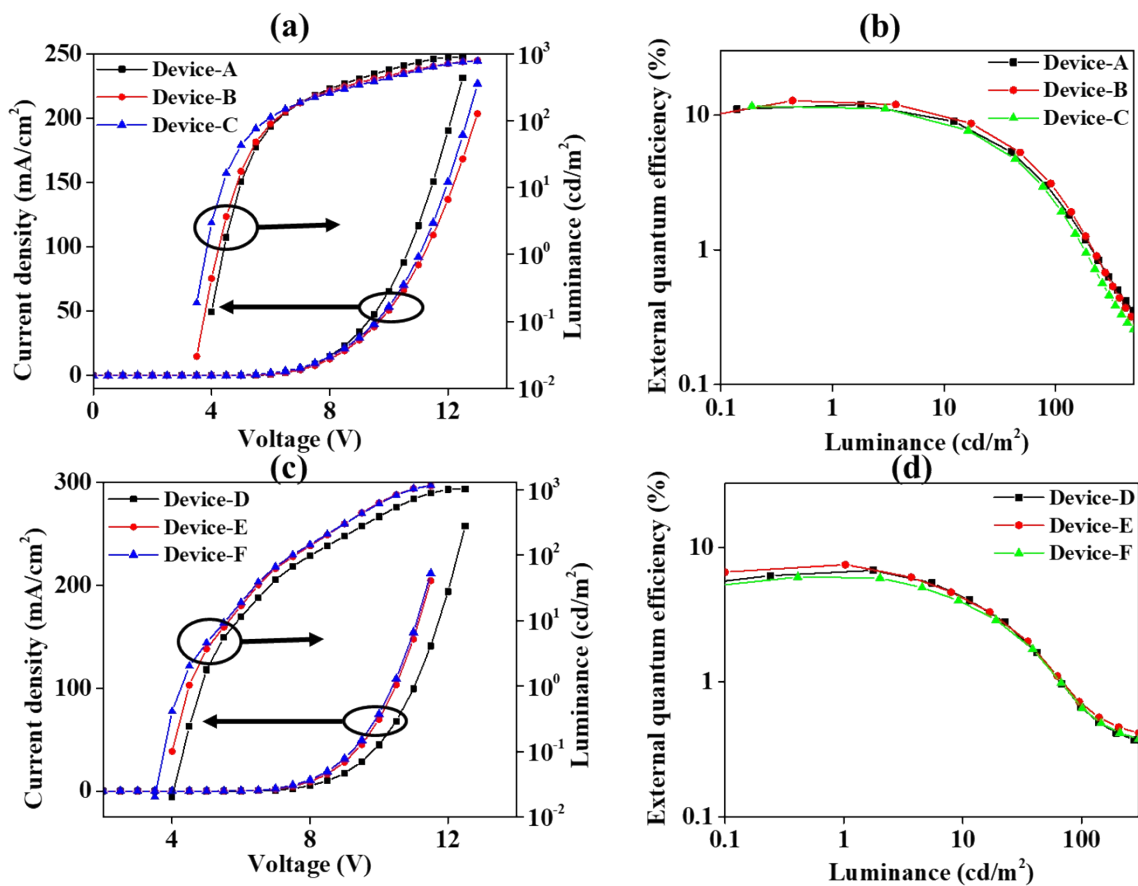


Figure S13. The current density-voltage-luminance (J-V-L), external quantum efficiency-luminance (EQE-L) of PSeDBF (a and b) and PSeFL (c and d) doped devices.

Table S1. The SOCME's and energy levels of PSeDBF and PSeFL

PSeDBF	SOCMEs (cm⁻¹)	Energy difference (ΔE_{ST}) eV
S ₁ \longrightarrow T ₁	3.75	0.42
S ₁ \longrightarrow T ₂	4.40	0.27
S ₁ \longrightarrow T ₃	3.21	0.03
T ₁ \longrightarrow S ₀	142.00	-
T ₂ \longrightarrow S ₀	3.12	-
T ₃ \longrightarrow S ₀	131.00	-

PSeFL	SOCMEs (cm⁻¹)	Energy difference (ΔE_{ST}) eV
S ₁ \longrightarrow T ₁	2.05	0.02
S ₁ \longrightarrow T ₂	2.51	0.44
T ₁ \longrightarrow S ₀	11.00	-
T ₂ \longrightarrow S ₀	12.1	-

Table S2. Photophysical data of PSe core

$\lambda_{\text{abs}}(\text{nm})^{\text{a}}$	$\lambda_{\text{em}}(\text{nm})^{\text{b}}$	$\lambda_{\text{em}}(\text{nm})^{\text{c}}$
315	377	488

^aAbsorption measured in 10^{-5} M toluene solution. ^bEmission maximum in 10^{-5} M toluene solution without delay. ^cEmission maximum in in frozen 10^{-5} M toluene solution under N_2 at 77 k with 1.0 ms delay (LTPL).