

*Supporting information for*

**Efficient and tunable pure organic room temperature  
phosphorescent films from selenium-containing emitters achieved by  
structural isomerism**

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## 1. Experimental details

*Measurements and Characterization:*  $^1\text{H}$ -NMR and  $^{13}\text{C}$ -NMR spectra were conducted with 500 MHz Bruker Avance NMR spectrometer using tetramethylsilane (TMS;  $\delta = 0$  ppm) as internal standard. UV/Vis absorption spectra were measured by a Perkin–Elmer Lambda 35 UV/Vis spectrometer. Photoluminescence (PL) measurements were conducted utilizing FluoroMax-4 spectrophotometer equipped with a 150 W xenon lamp as the excitation source. Fluorescence lifetimes and phosphorescence lifetimes were measured with Edinburgh fluorescence spectrometer (FLSP-980). The quantum yields were measured on an integrating sphere (Hamamatsu Photonics C9920-2). MALDI-TOF mass spectra were performed using an AXIMA CFR MS apparatus (COMPACT).

*The fabrication of doped films:* The preparation process of 1, 2 and 3 doped film is as follows: dyes/PS dissolved in toluene solution (1 mg/mL in total), and stirred for 30 min at room temperature in glovebox. Then the mixed solution was spin-coated onto the quartz substrates at 1000 rpm for 3 min to obtain the doped film. It is found that when the dye contents varied from 0.1 wt% to 5.0 wt%, these doped films exhibit the stable steady-state PL spectra. When the doping concentrations is up to 10 wt%, the doped film exhibits obviously red-shifted emission peaks with decreased RTP intensity. For better comparison, the doped films with the dye content of 1 wt% are used for various characterization.

*Theoretical Calculations:* Density functional theory (DFT) and time-dependent DFT (TD-DFT) calculations were carried out at the M062X/6-31G\* level using on Gaussian 09 package. **1**, **2**, and **3** were directly optimized to obtain the  $S_0$  geometry and the geometry of the lowest triplet ( $T_1$ ) directly optimized in gas phase. The TD-DFT calculations for all molecules are performed using the optimized  $S_0$  geometry. The orbital coupling constant (SOC) was carried out at the M062X/def2-SV(P) level using ORCA 4.2.1. The SOC is calculated using optimized  $S_0$  geometry. The Hole-Electron analysis of **1**, **2**, and **3** was carried out by Multiwfn 3.7.

*Oxygen sensing:* A series of different oxygen fractions were prepared by controlling the flow rate of high-purity oxygen and high-purity nitrogen through the flow control valve. The oxygen detection experiment was carried out at 25 °C with the humidity of 30%. PL intensity quenching experiment of the doped film was carried out by sequentially introducing ratios of different oxygen/argon mixed gas into the closed system. The radiometric oxygen sensing was analyzed quantitatively according to the Stern-Volmer equation (4) based on the data shown in Figure 4:

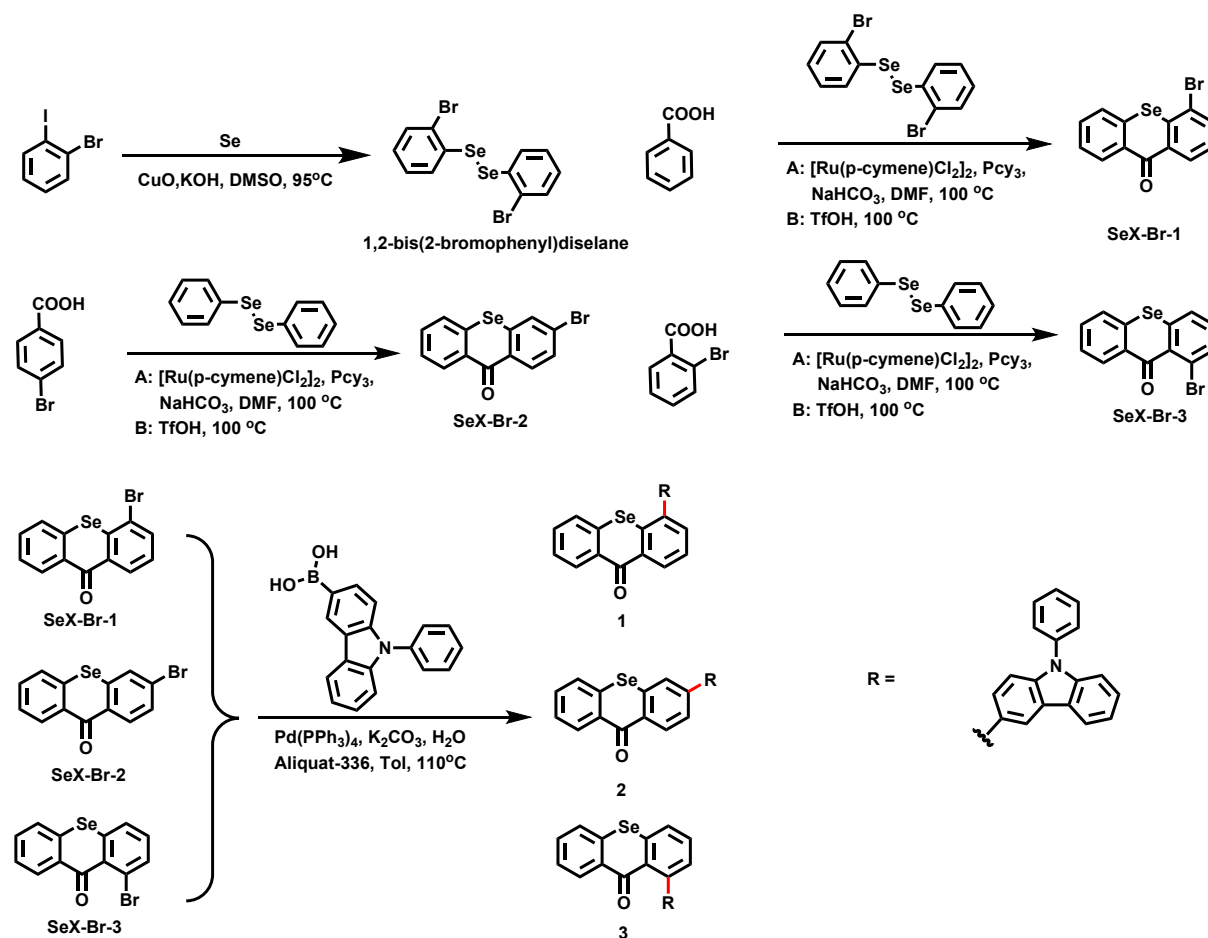
$$I_0/I - 1 = K_{SV} [\text{O}_2] \quad (1)$$

where  $I_0$  and  $I$  denote the radiometric emission intensity ratio in the fully deoxygenated and partially dope film of **1** and **2**, respectively.  $K_{SV}$  is the Stern-Volmer constant, which indicates the quenching efficiency between oxygen and the indicator;  $[\text{O}_2]$  is the oxygen fraction. LOD define as defined as the concentration at 3-fold S/N (S/N is defined as signal-to-noise ratio). 1 ppm  $\text{O}_2$  corresponds to 0.0001%  $\text{O}_2$  (ratio by volume).

*Bigaussian fitting of the steady-state PL spectra:* The fluorescence and phosphorescence peak values for fitting are fixed at the fluorescence and RTP peaks

in steady-state PL spectra, respectively, and a bigaussian function is utilized to fit until it converged to an Adj. R-Square  $\geq 0.99$ . After fitting, the population of RTP can be estimated by using the ratio of the RTP integrated area relative to the total area of the PL spectrum, which multiplies by the phosphorescence efficiency ( $\Phi_{PL}$ ) to afford RTP efficiency<sup>1</sup>.

**Synthesis:** All chemicals and reagents were used as received from commercial sources without further purification. Solvents for chemical synthesis were purified according to the standard procedures.



**Scheme S1.** Synthetic route for **1**, **2**, and **3**.

**1,2-bis(2-bromophenyl)diselane:** To a stirred solution of Se metal (3.2 g, 40 mmol) and 1-Bromo-2-iodobenzene (5.84 g, 20 mmol) in dry DMSO (15 mL) was added CuO nanoparticles (160 mg, 2 mmol) followed by KOH (2.2 g, 40 mmol) under nitrogen atmosphere at 90 °C. The progress of the reaction was monitored by TLC. After the reaction was complete, it was allowed to cool to room temperature and quenched with water. The mixture was extracted with Diethyl ether and the organic layer was dried over anhydrous NaSO<sub>4</sub> and concentrated under reduced pressure. The resulting residue was purified by silica gel column chromatography (hexane) to provide pure yellow solid (1.72 g, Yield 36.6 %).

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ (ppm): 7.59 (dd, *J* = 8.0, 1.5 Hz, 2H), 7.49 (dd, *J* = 7.9, 1.4 Hz, 2H), 7.21 (td, *J* = 7.7, 1.3 Hz, 2H), 7.08 (td, *J* = 7.6, 1.6 Hz, 2H)。

**4-(9-phenyl-9H-carbazol-3-yl)-9H-selenoxanthen-9-one (1):** Bromobenzoic acid (606 mg, 4.97 mmol), 1,2-bis(2-bromophenyl)diselane (4.67 g, 9.94 mmol), [Ru(p-cymene)Cl<sub>2</sub>]<sub>2</sub> (130 mg, 0.20 mmol), PCy<sub>3</sub> (112 mg, 0.4 mmol), and NaHCO<sub>3</sub> (420 mg, 4.97 mmol), were added to a mixture dry DMF (40 mL) under air, and the resulting mixture was heated at 100°C for 48 h. The color changes from orange to deep-red and then becomes black. After completion of the reaction, it was cooled to room temperature, quenched with AcOH when the pH < 7, and diluted with water. The mixture was extracted with ethyl acetate three times. The organic layer was washed by saturated brine three times, and the organic layer was dried over anhydrous NaSO<sub>4</sub>, and the solvent was removed under vacuum. The resulting residue was purified by silica gel column chromatography (hexane: ethyl acetate: acetic acid = 90:10:1) to get the crude product. The crude product was treated with triflic acid at 100 °C for 5 h. After that, it was allowed to cool to room temperature and quenched with water. The mixture was extracted with dichloromethane (DCM) and the organic layer was dried over anhydrous NaSO<sub>4</sub> and concentrated under reduced pressure. The resulting residue was purified by silica gel column chromatography (hexane dichloromethane = 4:1) to provide pure yellow solid (4-bromo-9H-selenoxanthen-9-one, SeX-Br-1). And then, 4-bromo-9H-selenoxanthen-9-one (500 mg, 1.48 mmol), (9-phenyl-9H-carbazol-3-yl) boronic acid (637 mg, 2.22 mmol), Pd (PPh<sub>3</sub>)<sub>4</sub> (85.47 mg, 0.074 mmol), 2 M K<sub>2</sub>CO<sub>3</sub> (5 mL), and Aliquant-336 (two drops) were added to mixture dry toluene (25 mL) under argon, and the resulting mixture was heated at 110°C for 12 h. After cooling to room temperature, the reaction mixture was diluted by water and then extracted with dichloromethane three times. The organic layer was dried over anhydrous NaSO<sub>4</sub>, and the solvent was removed under a vacuum. The resulting residue was purified by silica gel column chromatography (hexane: dichloromethane = 4: 1) to provide pure yellow solid (467 mg, Yield 63%).

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ (ppm): 8.73 (dd, *J* = 6.2, *J* = 1.5 Hz, 1H), 8.66 – 8.62 (m, 1H), 8.27 – 8.23 (m, 1H), 8.16 (d, *J* = 6.2 Hz, 1H), 7.70 – 7.63 (m, 4H), 7.62 (dd, *J* = 5.8, *J* = 1.5 Hz, 1H), 7.59 (d, *J* = 6.2 Hz, 1H), 7.57 – 7.50 (m, 3H), 7.47 (m, 5H), 7.32 (m, 1H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ (ppm): 182.82, 142.22, 141.42, 140.84, 137.42, 136.60, 136.16, 133.38, 132.08, 131.61, 131.24, 131.09, 130.24, 130.09, 129.99, 128.27, 127.74, 127.12, 127.05, 126.64, 126.47, 126.16, 123.52, 123.12, 121.19, 120.48, 120.33, 110.05, 109.96. FT-IR (cm<sup>-1</sup>): 3055, 1628, 1586, 1505, 1453, 1326, 1236, 1024, 816, 736, 631. MALDI-TOF MS (*m/z*): 501.1 [M<sup>+</sup>].

**3-(9-phenyl-9H-carbazol-3-yl)-9H-selenoxanthen-9-one (2):** 4-bromobenzoic acid (1 g, 4.97 mmol), 1,2-diphenyldiselane (3.12 g, 9.94 mmol), [Ru(p-cymene)Cl<sub>2</sub>]<sub>2</sub> (130 mg, 0.20 mmol), PCy<sub>3</sub> (112 mg, 0.4 mmol), and NaHCO<sub>3</sub> (420 mg, 4.97 mmol), were added to a mixture dry DMF (40 mL) under air, and the resulting mixture was heated at 100°C for 48 h. The color changes from orange to deep-red and then becomes black. After completion of the reaction, it was cooled to room temperature, quenched with AcOH when the pH < 7, and diluted with water. The mixture was extracted with ethyl

acetate three times. The organic layer was washed by saturated brine three times, and the organic layer was dried over anhydrous NaSO<sub>4</sub>, and the solvent was removed under vacuum. The resulting residue was purified by silica gel column chromatography (hexane: ethyl acetate: acetic acid = 90:10:1) to get the crude product. The crude product was treated with triflic acid at 100 °C for 5 h. After that, it was allowed to cool to room temperature and quenched with water. The mixture was extracted with dichloromethane (DCM) and the organic layer was dried over anhydrous NaSO<sub>4</sub> and concentrated under reduced pressure. The resulting residue was purified by silica gel column chromatography (hexane dichloromethane = 4:1) to provide pure yellow solid (3-bromo-9H-selenoxanthen-9-one, SeX-Br-2). And then, 3-bromo-9H-thioxanthen-9-one (500 mg, 1.71 mmol), (9-phenyl-9H-carbazol-3-yl)boronic acid (500 mg, 1.74 mmol), Pd (PPh<sub>3</sub>)<sub>4</sub> (99 mg, 0.086 mmol), 2 M K<sub>2</sub>CO<sub>3</sub> (5 mL), and Aliquant-336 (two drops) were added to mixture dry toluene (25 mL) under argon, and the resulting mixture was heated at 110°C for 12 h. After cooling to room temperature, the reaction mixture was diluted by water, and then extracted with dichloromethane three times. The organic layer was dried over anhydrous NaSO<sub>4</sub>, and the solvent was removed under vacuum. The resulting residue was purified by silica gel column chromatography (hexane dichloromethane = 6: 1) to provide pure yellow solid (503 mg, Yield 68%).

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ (ppm): 8.75 (d, *J* = 6.7 Hz, 1H), 8.71 – 8.67 (m, 1H), 8.46 (d, *J* = 1.1 Hz, 1H), 8.23 (d, *J* = 6.2 Hz, 1H), 7.97 (d, *J* = 1.2 Hz, 1H), 7.85 (dd, *J* = 6.7 Hz, *J* = 1.3 Hz, 1H), 7.74 (dd, *J* = 6.7 Hz, *J* = 1.3 Hz, 1H), 7.66 (m, 3H), 7.60 (d, *J* = 5.7 Hz, 2H), 7.58 – 7.54 (m, 1H), 7.50 (q, *J* = 6.7, 6.2 Hz, 3H), 7.47 – 7.42 (m, 2H), 7.37 – 7.32 (m, 1H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ (ppm): 145.66, 141.47, 141.08, 137.36, 135.68, 135.11, 132.07, 131.85, 131.35, 130.93, 129.99, 128.29, 127.75, 127.06, 126.74, 126.46, 126.10, 125.93, 125.44, 124.07, 123.26, 120.46, 120.38, 119.29, 110.33, 110.08. FT-IR (cm<sup>-1</sup>): 3046, 1643, 1590, 1505, 1444, 1321, 1226, 930, 811, 720, 631. MALDI-TOF MS (*m/z*): 501.1 [M<sup>+</sup>].

**1-(9-phenyl-9H-carbazol-3-yl)-9H-selenoxanthen-9-one (3):** 2-bromobenzoic acid (1 g, 4.97 mmol), 1,2-diphenyldiselenane (3.12 g, 9.94 mmol), [Ru(*p*-cymene)Cl<sub>2</sub>]<sub>2</sub> (130 mg, 0.20 mmol), PCy<sub>3</sub> (112 mg, 0.4 mmol), and NaHCO<sub>3</sub> (420 mg, 4.97 mmol), were added to a mixture dry DMF (40 mL) under air, and the resulting mixture was heated at 100°C for 48 h. The color changes from orange to deep-red and then becomes black. After completion of the reaction, it was cooled to room temperature, quenched with AcOH when the pH < 7, and diluted with water. The mixture was extracted with ethyl acetate three times. The organic layer was washed by saturated brine three times, and the organic layer was dried over anhydrous NaSO<sub>4</sub>, and the solvent was removed under vacuum. The resulting residue was purified by silica gel column chromatography (hexane: ethyl acetate: acetic acid = 90:10:1) to get the crude product. The crude product was treated with triflic acid at 100 °C for 5 h. After that, it was allowed to cool to room temperature and quenched with water. The mixture was extracted with dichloromethane (DCM) and the organic layer was dried over anhydrous NaSO<sub>4</sub> and concentrated under reduced pressure. The resulting residue was

purified by silica gel column chromatography (hexane dichloromethane = 4:1) to provide pure yellow solid (1-bromo-9H-selenoxanthen-9-one, SeX-Br-3). And then, 1-bromo-9H-thioxanthen-9-one (500 mg, 1.71 mmol), (9-phenyl-9H-carbazol-3-yl) boronic acid (500 mg, 1.74 mmol), Pd (PPh<sub>3</sub>)<sub>4</sub> (99 mg, 0.086 mmol), 2 M K<sub>2</sub>CO<sub>3</sub> (5 mL), and Aliquant-336 (two drops) were added to mixture dry toluene (25 mL) under argon, and the resulting mixture was heated at 110°C for 12 h. After cooling to room temperature, the reaction mixture was diluted by water and then extracted with dichloromethane three times. The organic layer was dried over anhydrous NaSO<sub>4</sub>, and the solvent was removed under a vacuum. The resulting residue was purified by silica gel column chromatography (hexane dichloromethane = 6: 1) to provide pure yellow solid (229 mg, Yield 31%).

<sup>1</sup>H NMR (500 MHz, DMSO)  $\delta$  (ppm): 8.26 (d,  $J$  = 6.1 Hz, 1H), 8.20 (d,  $J$  = 1.3 Hz, 1H), 7.94 (m, 3H), 7.75 – 7.60 (m, 6H), 7.60 – 7.54 (m, 1H), 7.52 – 7.35 (m, 5H), 7.29 (td,  $J$  = 6.0 Hz,  $J$  = 5.4 Hz,  $J$  = 1.0 Hz, 2H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 185.60, 146.92, 141.21, 139.93, 137.74, 135.01, 134.88, 134.87, 132.95, 131.48, 131.29, 130.54, 130.33, 130.28, 129.81, 127.58, 127.35, 127.11, 127.03, 126.79, 126.61, 125.86, 123.60, 123.38, 120.31, 119.86, 119.50, 109.80, 109.39. FT-IR (cm<sup>-1</sup>): 3051, 1628, 1590, 1496, 1450, 1364, 1226, 1156, 905, 749, 698, 622. MALDI-TOF MS (m/z): 501.1 [M<sup>+</sup>].

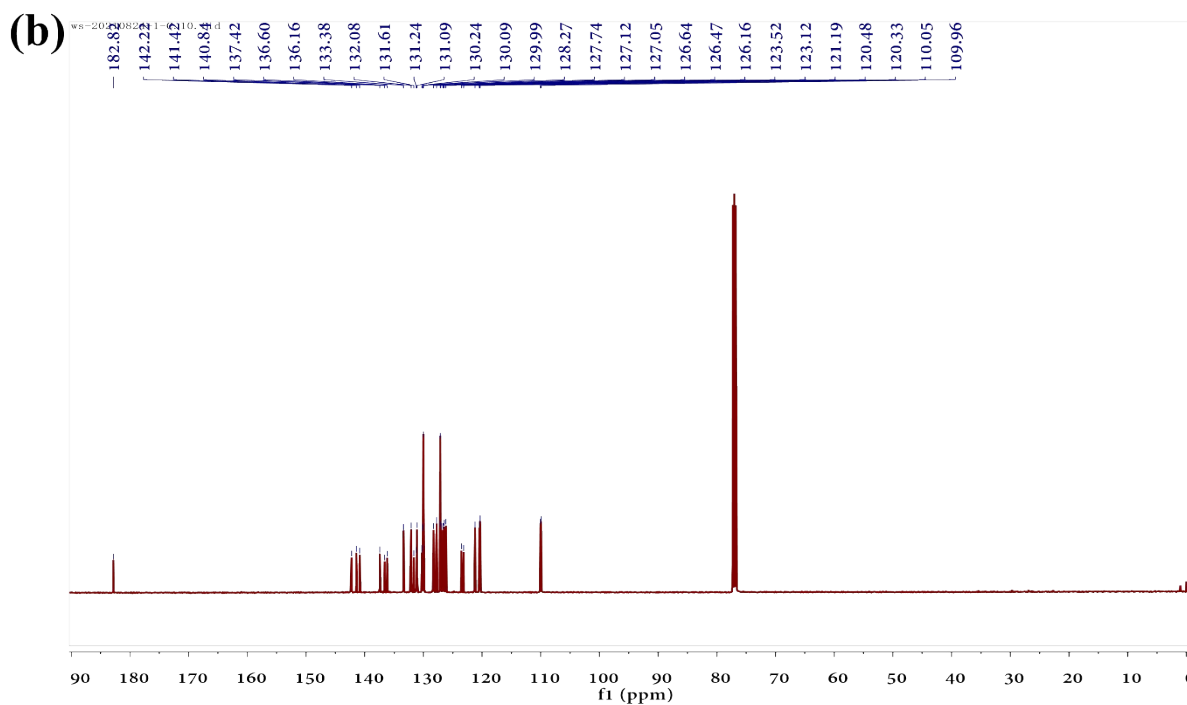
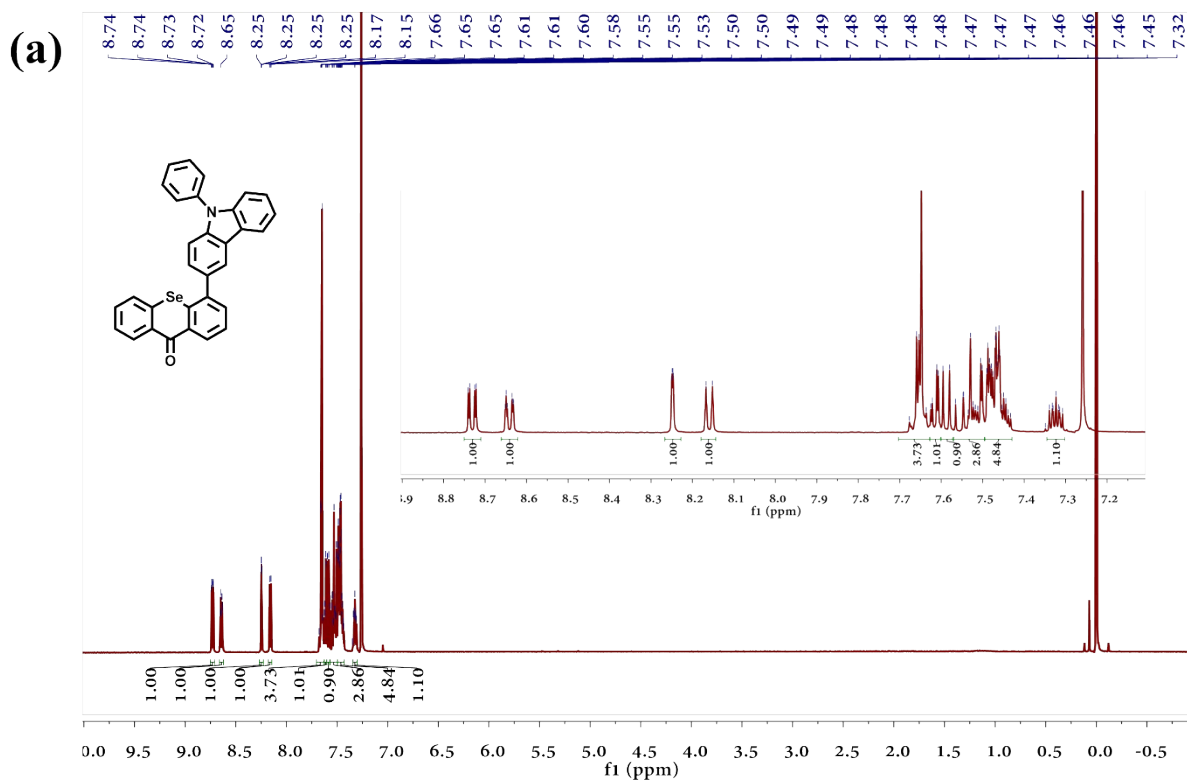
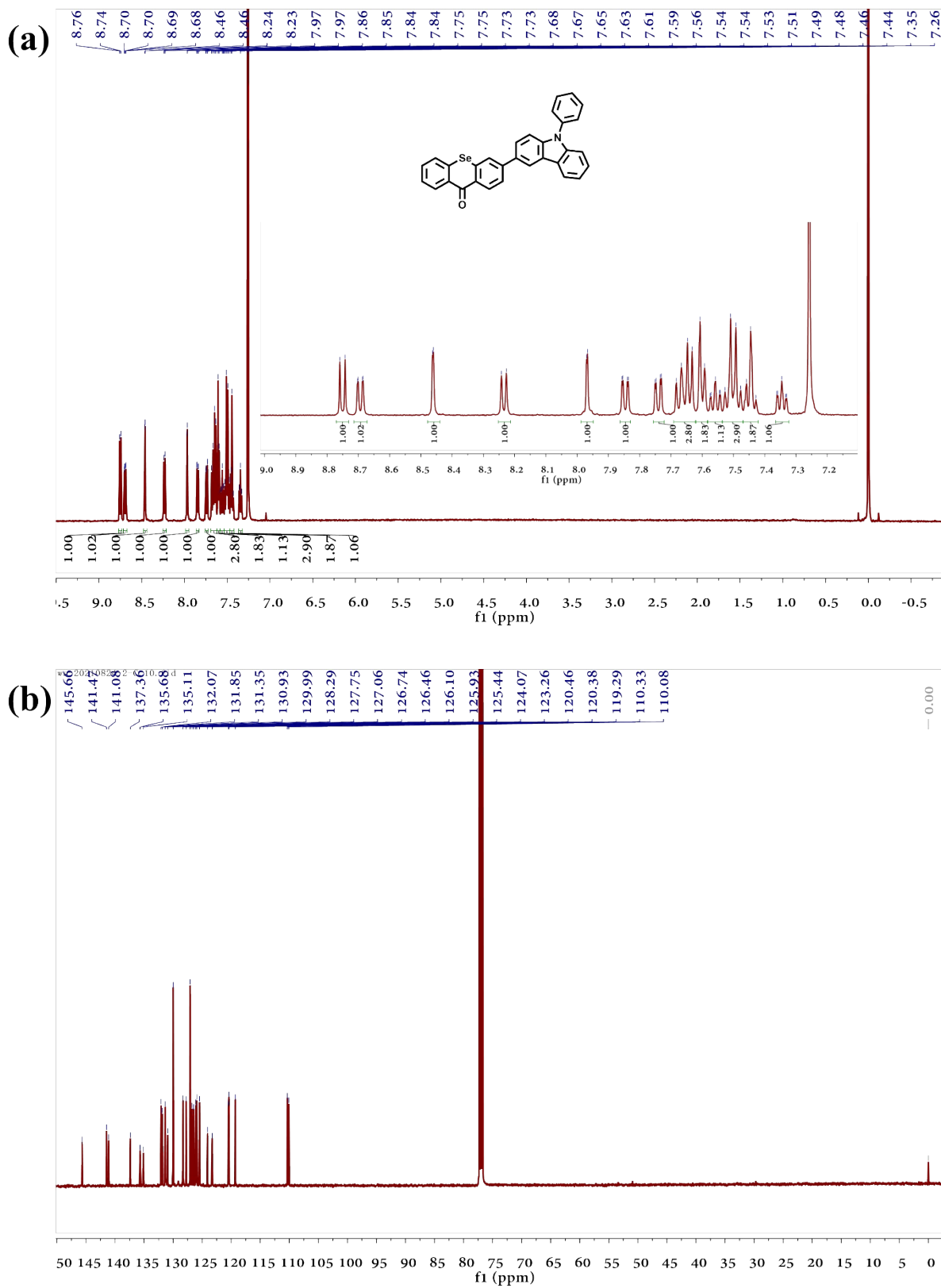
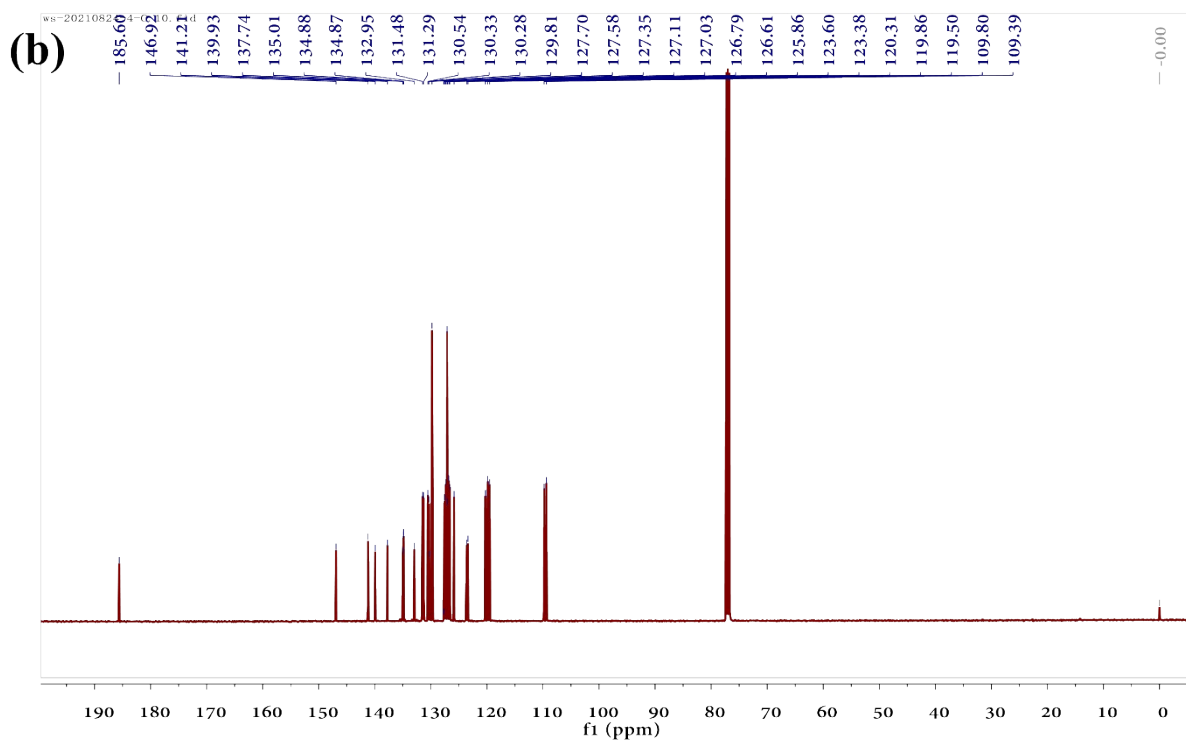
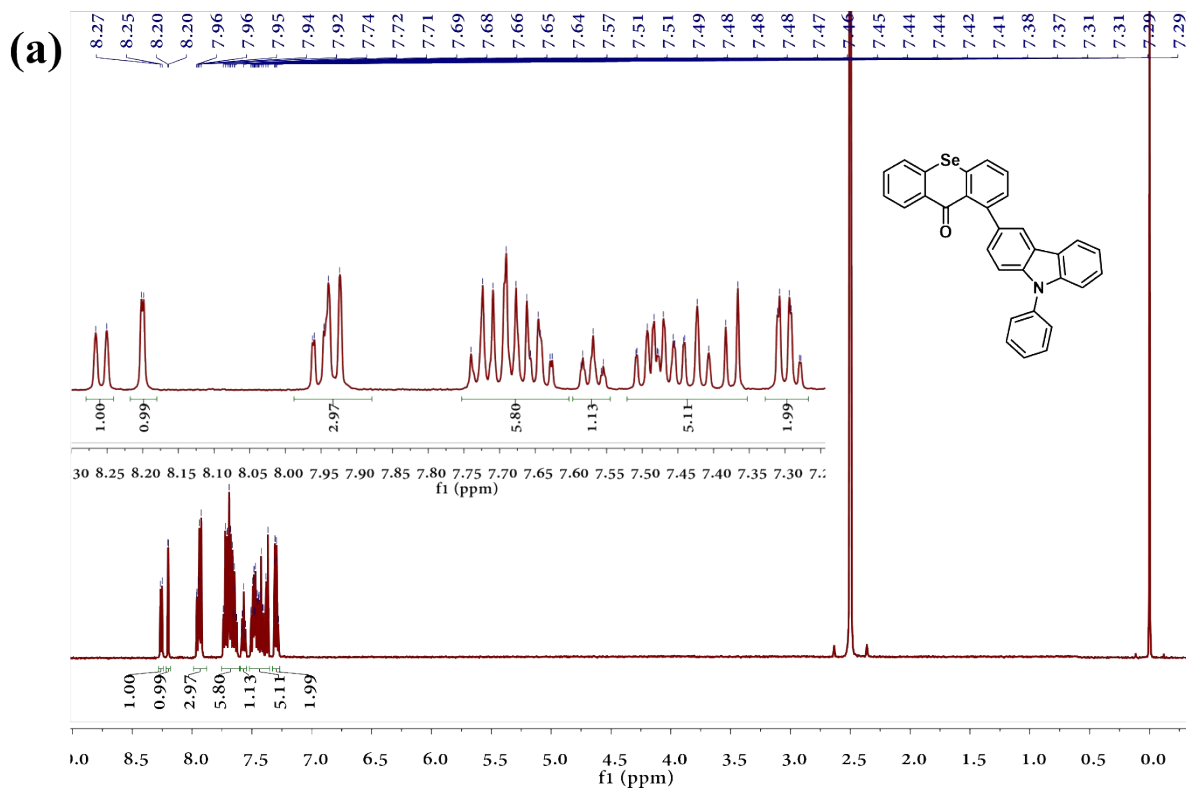


Figure S1.  $^1\text{H}$  NMR (a) and  $^{13}\text{C}$  NMR (b) of Molecule 1.

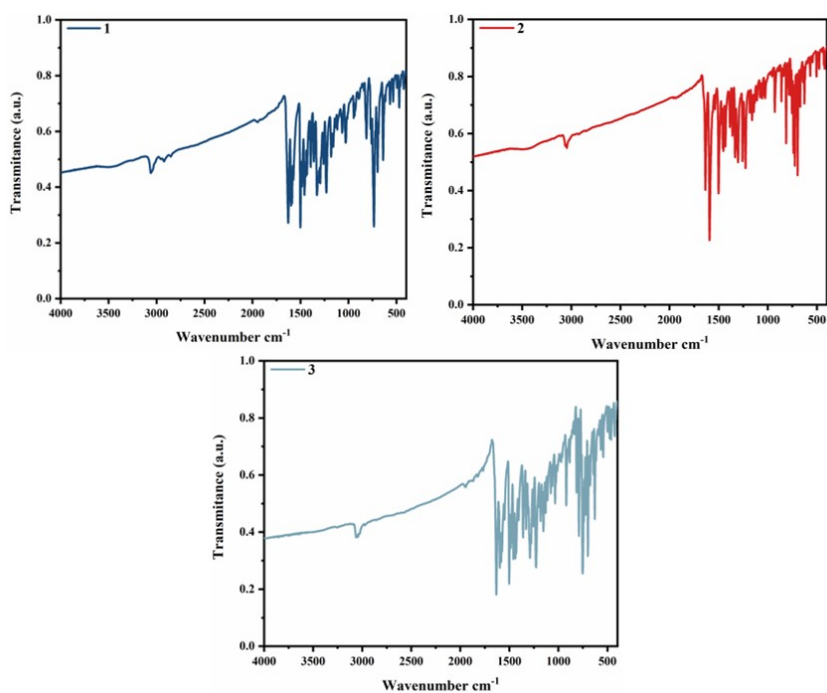




**Figure S2.**  $^1\text{H}$  NMR (a) and  $^{13}\text{C}$  NMR (b) of Molecule 2.

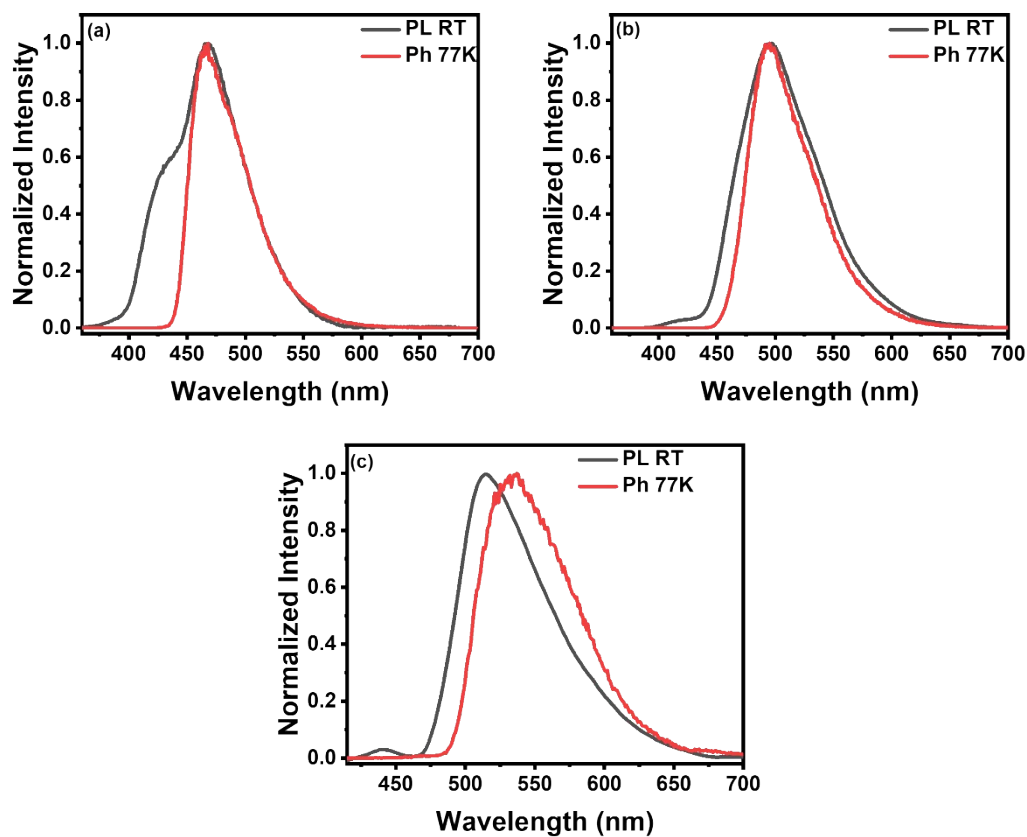


**Figure S3.**  $^1\text{H}$  NMR (a) and  $^{13}\text{C}$  NMR (b) of Molecule 3.

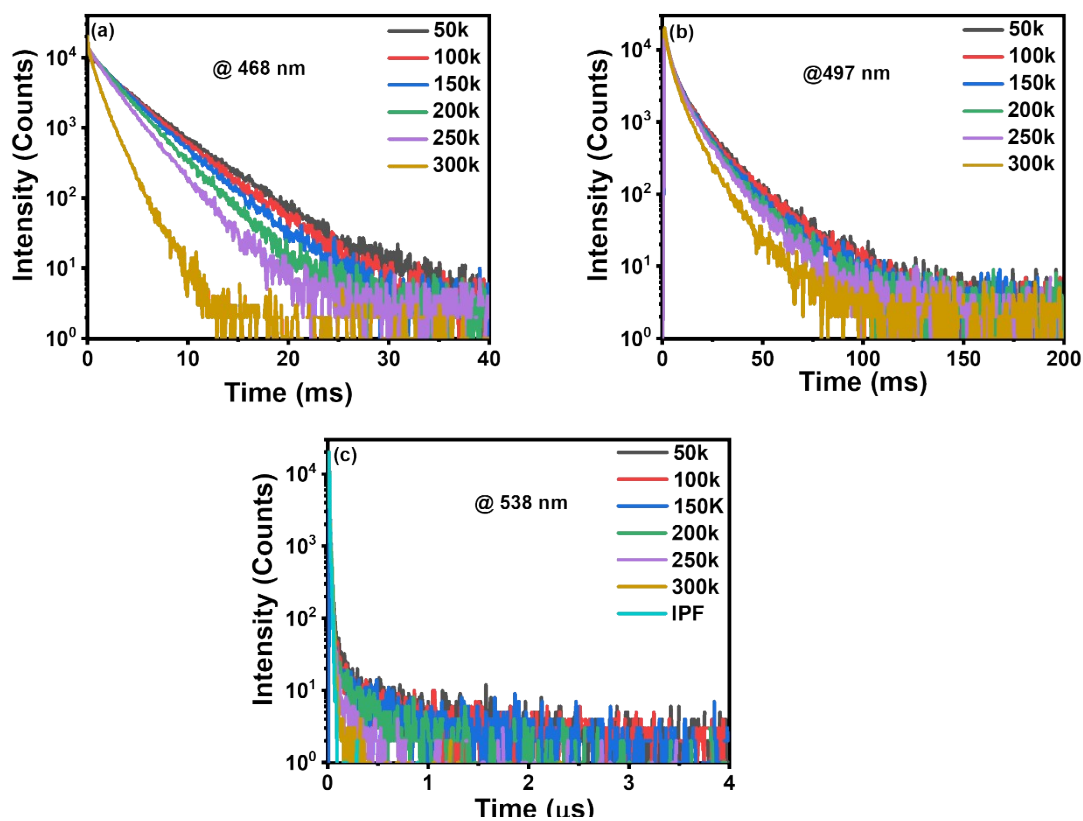


**Figure S4.** The FT-IR spectra of **1**, **2**, and **3**.

## 2. Photophysical measurements



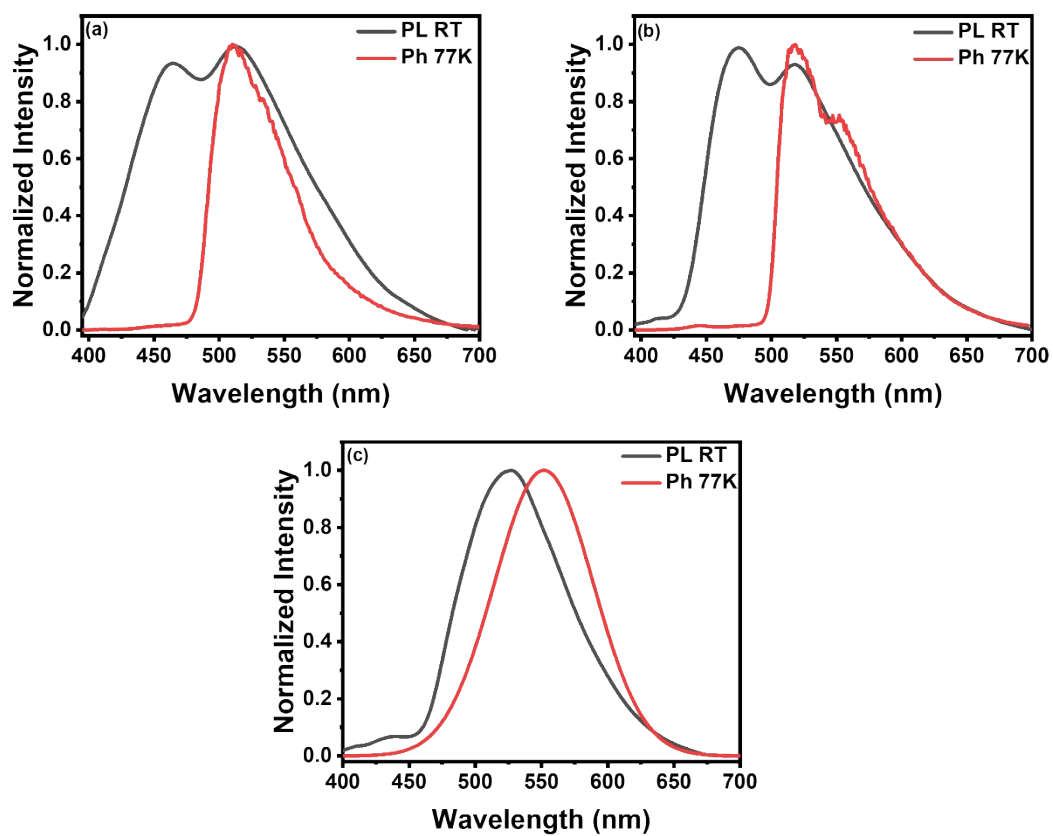
**Figure S5.** Steady-state PL (black) at room temperature and delay spectra (red) at 77 K (delay time: 1 ms) of molecule **1** (a), **2** (b), and **3** (c) doped films.



**Figure S6.** Temperature-dependent time-resolved PL decay spectra of molecule **1** (a), **2** (b), and **3** (c) doped films.

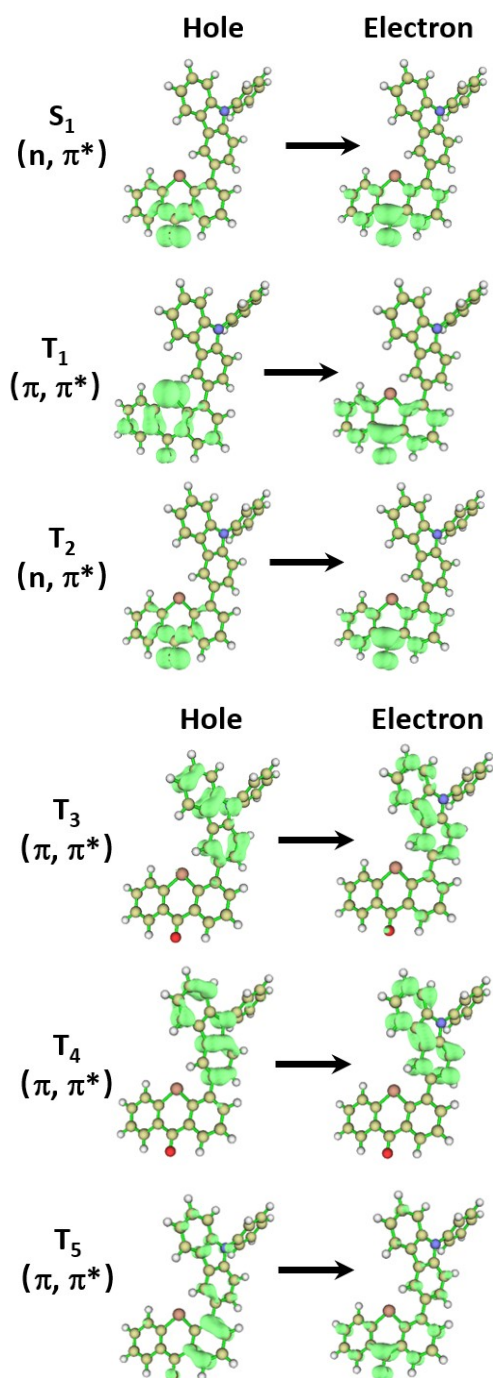
**Table S1.** Summary of the photophysical properties of **1**, **2**, and **3** crystal powder

Compound	$\lambda_{em}$ [nm]	$\Phi_{PL}$ [%]	$\Phi_{FL}$ [%]	$\Phi_{Ph}$ [%]	$\tau_{FL}$ [ns]	$\tau_{Ph}$ [ms]	$k_{ISC}$ [ $10^8 \text{ s}^{-1}$ ]	$k_r^p$ [ $10^2 \text{ s}^{-1}$ ]	$k_{nr}^r + k_q$ [ $10^4 \text{ s}^{-1}$ ]
1	464	3.1	1.3	1.8	0.76	10.11	12.99	17.82	9.21
	513								
2	475	4.1	2.2	1.9	0.83	19.68	12.57	9.64	4.97
	518								
3	526	0.3	0.3	--	1.76	--	--	--	--

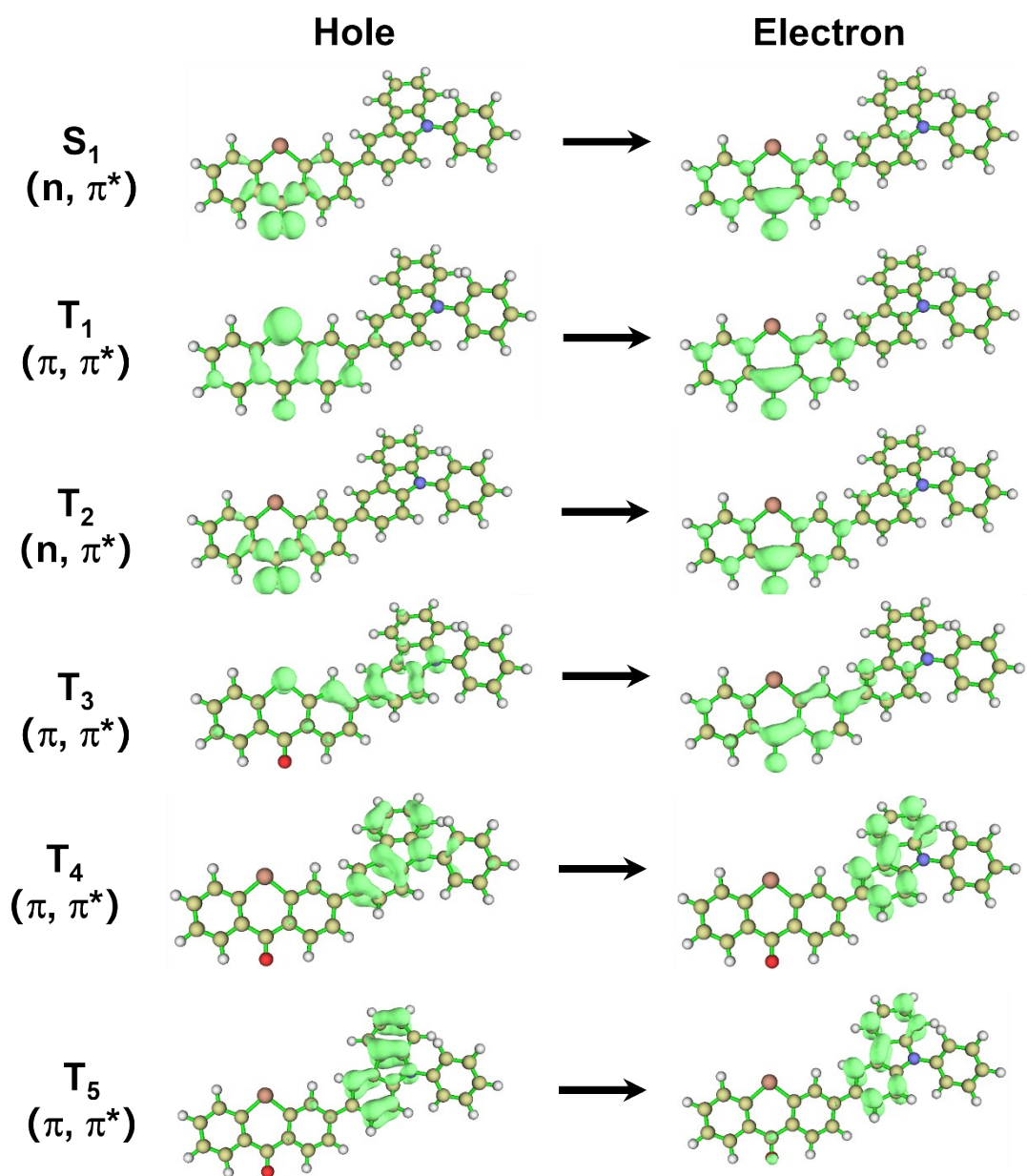


**Figure S7.** Steady-state PL (black) at room temperature and delay spectra (red) at 77 K (delay time: 1 ms) of **1** (a), **2** (b), and **3** (c) crystal powder.

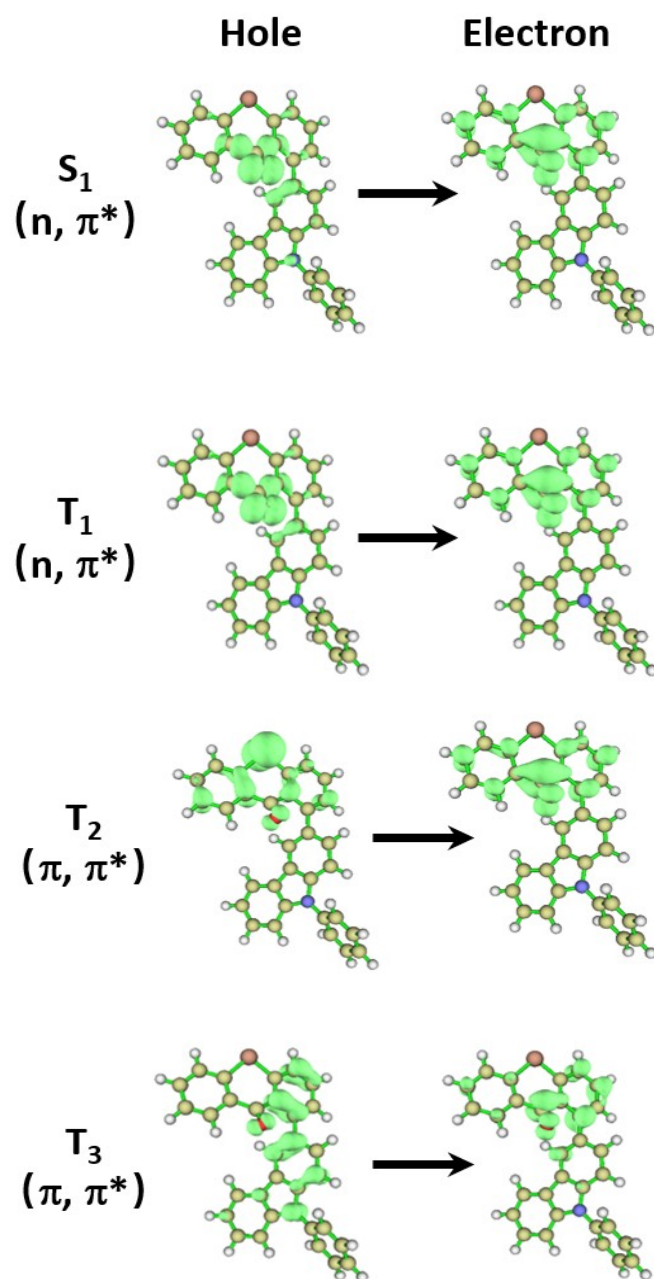
### 3. Theoretical calculation results



**Figure S8.** Hole-Electron analysis of molecule **1** in the lowest single ( $S_1$ ) and triplet manifolds ( $T_n$ ) base on the geometry of  $S_0$  state.

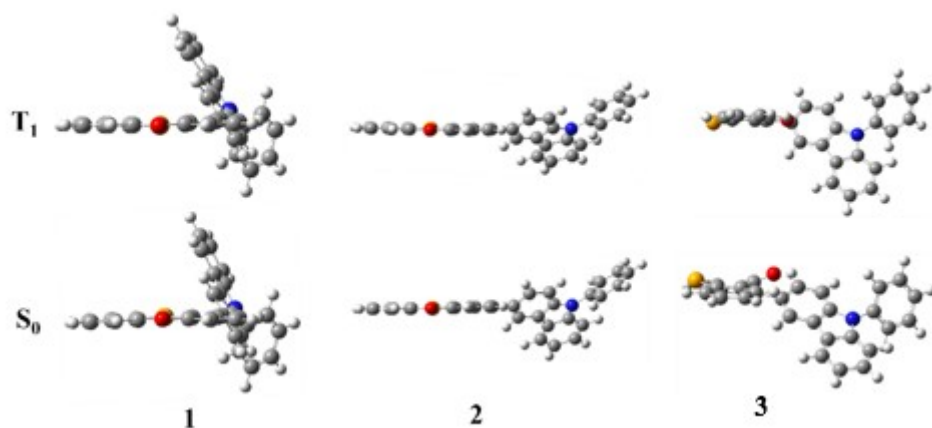


**Figure S9.** Hole-Electron analysis of molecule **2** in the lowest single ( $S_1$ ) and triplet manifolds ( $T_n$ ) base on the geometry of  $S_0$  state.



**Figure S10.** Hole-Electron analysis of molecule **3** in the lowest single ( $S_1$ ) and triplet manifolds ( $T_n$ ) base on the geometry of  $S_0$  state.





**Figure S11.** The geometry of the lowest triplet ( $T_1$ ) and ground state ( $S_0$ ) for molecule **1**, **2**, and **3**.

**Table S2.** The dihedral angle and reorganization energy molecule **1**, **2**, and **3**.

Compound	$\angle O=C-Ph$			$\angle Se-Ph$			1 [eV]
	$S_0$	$T_1$	$D S_0-T_1 $	$S_0$	$T_1$	$D S_0-T_1 $	
1	1.25°	-0.97°	2.22°	1.34°	-4.67°	6.01°	0.39
2	0.58°	0.30°	0.28°	0.65°	0.68°	0.03°	0.34
3	25.01°	-0.78°	25.79°	15.32°	-9.79°	25.11°	1.15

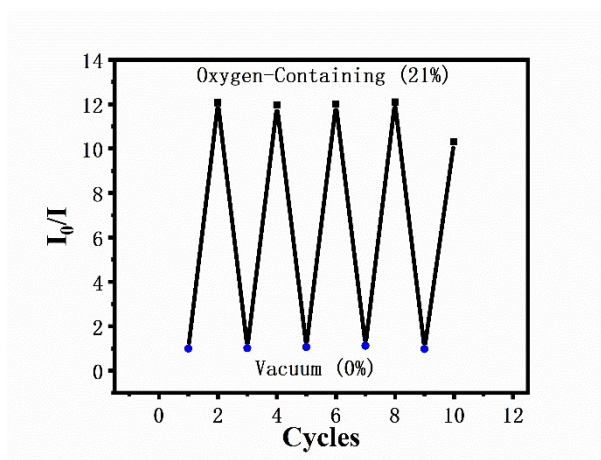
**Table S3.** Energy levels of molecule **1**, **2**, and **3**.

Excited Stated	1 [eV]	2 [eV]	3 [eV]
$S_1$	3.72	3.73	3.47
$T_1$	3.13	3.09	3.01
$T_2$	3.42	3.34	3.31
$T_3$	3.68	3.49	3.47
$T_4$	3.71	3.70	3.51
$T_5$	3.79	3.79	3.70

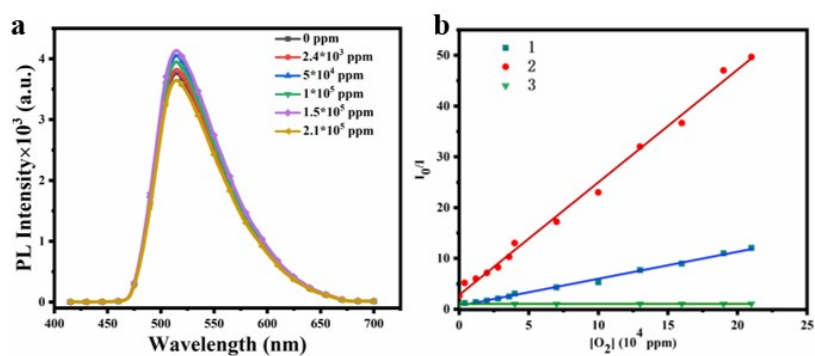
**Table S4.** SOC constant of molecule **1**, **2**, and **3**.

SOC	1 [cm <sup>-1</sup> ]	2 [cm <sup>-1</sup> ]	3 [cm <sup>-1</sup> ]
$Z_{S0-T1}$	8.33	2.31	38.17
$Z_{S1-T1}$	61.45	54.12	8.32
$Z_{S1-T2}$	0.98	3.89	51.61
$Z_{S1-T3}$	0.85	24.64	9.6
$Z_{S1-T4}$	1.07	3.87	3.65
$Z_{S1-T5}$	0.83	1.62	3.10

#### 4. Oxygen Sensing



**Figure S12.** reversible oxygen response of molecule **1** doped film.



**Figure S13.** (a) PL spectra of **3** doped film and (b) Stern-Volmer quenching plots of **1**, **2**, and **3** at different concentrations of oxygen.

**Table S5.** Summary of the oxygen sensing properties of molecule **1**, **2**, and SeX-CzPh.

Compound	$K_{sv} \times 10^{-4}$ [ppm <sup>-1</sup> ]	LOD [ppm]	Linear [10 <sup>4</sup> ppm]	$R^2$
1	0.53	11.4	0-21	0.995
2	2.22	2.8	0-21	0.997
Sex-CzPh	1.27	4.9	0-21	0.997

## Reference

1. X. Liu, L. Yang, X. Li, L. Zhao, S. Wang, Z. H. Lu, J. Ding and L. Wang, *Angew. Chem. Int. Ed.*, 2021, **60**, 2455-2463.