Supporting Information

Achieving Pure Room Temperature Phosphorescence (RTP) in Phenoselenazine-Based Organic Emitters Through Synergism among Heavy Atom Effect, Enhanced $n \rightarrow \pi^*$ Transition and Magnified Electron Coupling by the A-D-A

Molecular Configuration

Daokun Zhong^a, Siqi Liu^a, Ling Yue^a, Zhao Feng^a, Hongyan Wang^a, Peng Yang^a,

Bochao Su^a, Xiaolong Yang^a, Yuanhui Sun^a, Guijiang Zhou^a*

Engineering Research Center of Energy Storage Materials and Devices, State Key Laboratory for Mechanical Behavior of Materials, Xi'an Jiaotong University, Xi'an 710049, P. R. China.

Corresponding author E-mail address: zhougj@mail.xjtu.edu.cn

General Information. Commercial chemicals were used without further purification. All reactions were carried out under nitrogen atmosphere. Prior to use, solvents were carefully dried and distilled from appropriate drying agents All reactions were monitored by thin-layer chromatography (TLC) from Merck & Co., Inc. Column chromatography and preparative TLC was conducted by using silica gel from Shanghai Qingdao (300-400 mesh). ¹H, and ¹³C NMR spectra were recorded in CDCl₃ on a Bruker Avance 400 or 600 MHz spectrometer and Japan Electron Optics Laboratory 400 MHz spectrometer. The chemical shifts were quoted on the solvent residual peak at δ 7.26 ppm for ¹H and 77.0 ppm for ¹³C, respectively. Fast atom bombardment mass spectrometry (FAB-MS) spectra were obtained on a Finnigan MAT SSQ710 system. UV-vis spectra were recorded on a Shimadzu UV-2250 spectrophotometer. The photoluminescent spectra and lifetimes were measured on Edinburgh Instruments FLS920 spectrophotometer. The photoluminescent quantum yields (PLQYs) were determined in CH_2Cl_2 solutions with an integrating sphere. With a scan rate of 100 mV s⁻¹, cyclic voltammetry measurements were carried out on a Princeton Applied Research model 2273A potentiostat through three-electrode configuration with a glassy carbon working electrode, a Pt-sheet counter electrode and a Pt-wire reference electrode in electrolyte of 0.1 M [Bu₄N]PF₆ in degassed CH₃CN.

Synthesis.



Shamed S1. Synthesis of the key intermediate compounds.

The key intermediate compounds PhSe, PhSeBr and PhSeDBr were synthesized according the literature methods^x with the synthetic details and steps (Shamed S1) presented in Supporting Information (SI). The synthetic strategies for the target compounds of PhSeB and PhSeDB were outlined in Scheme 1.

Synthesis of intermediate PhSe. Under nitrogen atmosphere, 4-iodotoluene (2.1 g, 9.8 mmol), the 10H-Phenoselenazine (2.0 g, 8.1 mmol), $Pd(OAc)_2$ (0.11 g, 0.49 mmol), Tri-terbutylphosphine (0.10 g, 0.49 mmol) and Sodium ter-butoxide (3.1 g, 0.03 mmol) were added to a Schlenk tube containing toluene. The resulting mixture was stirred at 110 °C for 18 h. After cooling to room temperature, the mixture was filtered, the organic phase was washed with water and extracted into dichloromethane, then dried with anhydrous Na₂SO₄, evaporated to dryness. The residue was purified by column chromatography on silica gel using petroleum ether. **PhSe:** Yield: 70%. ¹H NMR (400 MHz, CDCl₃) δ 7.35 (d, *J* = 8.4 Hz, 2H), 7.28 – 7.21 (m, 4H), 6.97 – 6.92 (m, 2H), 6.85 (td, *J* = 7.6, 1.2 Hz, 2H), 6.51 (dd, *J* = 8.4, 1.2 Hz, 2H), 2.44 (s, 3H).

General Procedure for Synthesis of PhSeDBr and PhSeBr. A solution of PhSe (1.0

equivalent) in $CH_3Cl/CH_3CN = 1/1$ (V/V) was added dropwise into the solution of NBS and stirred 30 min at 0 °C, then stirred overnight at room temperature. Then the reaction mixture was quenched with sodium thiosulfate solution and extracted with dichloromethane. The organic layer was evaporated. which was further purified from column chromatography with petroleum ether as a white powder.

PhSeBr: Yield: 65%. ¹H NMR (400 MHz, CDCl₃) δ 7.50 (d, *J* = 2.4 Hz, 1H), 7.40 (d, *J* = 8.4 Hz, 2H), 7.27 (dd, *J* = 12.0, 4.8 Hz, 3H), 7.14 (dd, *J* = 8.8, 2.4 Hz, 1H), 7.02 – 6.94 (m, 1H), 6.89 (td, *J* = 7.6, 1.2 Hz, 1H), 6.38 (dd, *J* = 8.4, 1.2 Hz, 1H), 6.29 (d, *J* = 8.8 Hz, 1H), 2.38 (s, 3H).

PhSeDBr: Yield: 69%. ¹H NMR (400 MHz, CDCl₃) δ 7.42 (d, *J* = 8.4 Hz, 2H), 7.23 – 7.20 (m, 2H), 6.95 – 6.90 (m, 2H), 6.82 (td, *J* = 7.6, 1.2 Hz, 2H), 6.53 (dd, *J* = 8.4, 1.2 Hz, 2H), 2.45 (s, 3H).

General Procedure for Synthesis of PhSeB and PhSeDB. Under nitrogen atmosphere, A solution of PhSeBr and PhSeDBr (1.0 equivalent) in dry THF was cooled to -78 °C. Then, *n*BuLi (1.1 or 2.2 equivalent) was added dropwise and stirred 1.5 h at this temperature. After that, dimesitylfluoroborane (1.1 equivalent) was added at -78 °C, and stirred 2 h at this temperature. The reactive mixture was warmed to room temperature and stirred overnight. The reaction was quenched with water, extracted into dichloromethane and dried with anhydrous sodium sulfate. After evaporated to dryness, the residue was purified by column chromatography over silica gel using petroleum ether/AcOEt, 8/1, v/v as eluent. The product was obtained as white solid.

PhSeB : Yield: 56%. ¹H NMR (400 MHz, CDCl₃) δ 7.37 (d, *J* = 8.0 Hz, 3H), 7.33 (d, *J* = 1.6 Hz, 2H), 7.28 (d, *J* = 8.4 Hz, 3H), 7.15 (dd, *J* = 7.4, 1.8 Hz, 1H), 7.02 (dd, *J* = 8.4, 1.7 Hz, 1H), 6.78 (s, 3H), 6.33 (dd, *J* = 8.3, 1.4 Hz, 1H), 6.28 (d, *J* = 8.5 Hz, 1H), 2.44 (s, 3H), 2.28 (s, 6H),

2.01 (s, 12H). ¹³C NMR (151 MHz, CDCl₃) δ 147.75, 143.87, 140.71, 138.66, 138.29, 138.19, 138.14, 137.03, 131.22, 130.69, 129.90, 129.42, 128.19, 128.05, 127.13, 123.34, 117.64, 116.41, 115.69, 114.19, 23.51, 21.25, 21.18. FAB-MS (m/z): 585 [M]+; Anal. Calcd for C₃₇H₃₆BNSe: C, 76.04; H, 6.21; N, 2.40; found: C, 76.59; H, 6.33; N, 2.58.



PhSeDB: Yield: 53%. ¹H NMR (400 MHz, CDCl₃) δ 7.34 (d, *J* = 8.1 Hz, 2H), 7.23 (s, 1H), 7.00 - 6.94 (m, 3H), 6.76 (s, 10H), 6.17 (d, *J* = 8.4 Hz, 2H), 2.41 (s, 3H), 2.26 (s, 12H), 2.00 (s, 27H). ¹³C NMR (151 MHz, CDCl₃) δ 146.44, 141.39, 140.66, 139.72, 138.79, 138.24, 137.23, 136.74, 135.07, 131.49, 130.38, 128.07, 118.56, 115.30, 23.50, 21.17. FAB-MS (m/z): 833 [M]+; Anal. Calcd for C₅₅H₅₇B₂NSe: C, 84.07; H, 7.31; N, 1.78; found: C, 83.99; H, 7.53; N, 1.68.



 Table S1. Crystal Parameters of PhSeDB

compound	PhSeDB
CCDC	2295656
Empirical formula	$C_{55}H_{57}B_2NSe$
Formula weight	832.59
Temperature (K)	150(2)
Crystal system	orthorhombic
Space group	P21
a (Å)	11.7688(12)
b (Å)	12.3845(17)
c (Å)	31.339(3)
α (°)	90
β (°)	90
γ (°)	90
Volume (Å ³)	4571.4(9)
Ζ	4
F(000)	1752
Radiation	MoKa ($\lambda = 0.71073$)
Index ranges	$-15 \le h \le 15, -16 \le k \le 16, -41 \le l \le 41$
Reflections collected	10806
Data/restraints/parameters	10804/0/545
R1, wR2 (all data)	0.0424, 0.0822
GOF on $F^{2 a}$	1.003

^{*a*} GOF = $[(\Sigma w | F_0| - | F_c|)^2 / (N_{obs} - N_{param})]^{1/2}$.



Figure S1. TGA curves of PhSeB and PhSeDB.



Figure S2. The transient PL decay data under nitrogen for PhSeB and PhSeDB measured in CH_2Cl_2 solution.



Figure S3. The PLQY of RTPemitters.

RTP	PLQY	τ_{P}		EL		ЪĆ
emitters	(%)	(ms)	CE	PE	EQE	- Ref.
PhSaDR	77.8	0.63	$\frac{(cdA^{-1})}{53.6}$	$\frac{(\text{Im W}^{-1})}{49.6}$	<u>(%)</u> 18.2	This work
	//.0	0.05	55.0	49.0	10.2	
PhSeB	67.0	0.65	29.5	24.1	10.5	This work
27PNDO	13.0	_	_	—	11.0	[1]
PSeB ₂		1.74			5.7	[2]
PhSe	28.8	0.84	24.1	17.3	7.5	[3]
mPhSe	33.9	0.44	27.5	21.6	8.7	[3]
BuPhSe	34.0	0.44	28.4	22.3	9.0	[3]
PSe1	33.0	0.61	-	-	10.7	[4]
PSe2	35.0	0.64	-	-	10.0	[4]
PSe3	27.0	0.93	-	-	8.1	[4]
PSe3Cz	50.2	0.82	45.9	-	13.2	[5]
bTEoCN	37.0	15.2	19.3	21.5	8.7	[6]
BPXSeDRZ	66.3	2.1	53.7	48.2	17.2	[7]
DBPXSeDRZ	66.9	1.7	46.7	40.2	17.9	[7]

Table S2. PL and EL performances of the representative systems for RTP emitters.





Figure S4. The chemical structures of functional materials used to fabricate OLED devices.



Figure S5. Current density-voltage-luminance (J-V-L) curves for the devices except the optimized ones



Figure S6. Relationship between EL efficiencies and luminance for the devices except the optimized ones. (a) Device A1, (b) Device B1.



Figure S7. Relationship between EL efficiencies and luminance for the devices except the optimized ones. (a) Device A3, (b) Device B3.

References

[1] D. R. Lee, S. H. Han and J. Y. Lee, Journal of Materials Chemistry C 2019, 7, 11500-11506.

[2] C. L. Kim, J. Jeong, D. R. Lee, H. J. Jang, S.-T. Kim, M.-H. Baik and J. Y. Lee, *The Journal of Physical Chemistry Letters* **2020**, *11*, 5591-5600.

[3] C. L. Kim, J. Jeong, H. J. Jang, K. H. Lee, S.-T. Kim, M.-H. Baik and J. Y. Lee, *Journal of Materials Chemistry C* 2021, 9, 8233-8238.

[4] D. R. Lee, K. H. Lee, W. Shao, C. L. Kim, J. Kim and J. Y. Lee, Chemistry of Materials 2020, 32,

2583-2592.

[5] C. L. Kim, J.-M. Kim, H. Jang, D. R. Lee and J. Y. Lee, *ACS Applied Energy Materials* 2022, 5, 4985-4990.

[6] M. Li, W. Xie, X. Cai, X. Peng, K. Liu, Q. Gu, J. Zhou, W. Qiu, Z. Chen, Y. Gan and S. J. Su, *Angewandte Chemie International Edition* **2022**, *61*: e202209343.

[7] Z. Chen, Q. Gu, M. Li, W. Qiu, Y. Jiao, X. Peng, W. Xie, D. Liu, K. Liu, Z. Yang and S. J. Su, *Advanced Optical Materials* **2024**, 2302503.