# Supplementary Information

## Reducing intersystem crossing rate of the boron-emitters to achieve

# high-efficient and long-lifetime deep-blue OLEDs

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## **Experimental section**

### **Materials and Instrumentation**

All commercially available chemicals were used as received. <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy study was conducted with Oxford AS400 400 MHz spectrometers using tetramethylsilane (TMS;  $\delta$  = 0 ppm) as internal standard. HRMS (ESI) spectra were measured on a Agilent Q-TOF LC/MS spectrometer. UV-visible spectra were obtained using a Purkinje Tu1810. The fluorescence and phosphorescent spectra taken at liquid nitrogen temperature (77 K) were recorded by Fluoromax-4 spectrofluorometer with a 365 nm Ocean Optics LLS excitation source. Electrochemical cyclic voltammetry was performed with a Wuhan corrtest CS300 with a three-electrode cell system using glassy carbon as working electrode, platinum wire as counter electrode, SCE as reference electrode. The ferrocene/ferrocenium redox couple was used for potential calibration. Photoluminescence quantum yields of the emitters in solutions or films were measured with Edinburgh FS5 Spectrofluorometer measurement system. In the range of 25 to 800 °C, SHIMADZU TGA-50 thermogravimeter was selected to perform the thermogravimetric analysis (TGA) of target molecules under nitrogen atmosphere at a heating rate of 10 K min<sup>-1</sup>. SHIMADZU DSC-60 Differential Scanning calorimeter was used to get the melting poing. Transient EL Decays were measured with dual channel arbitrary/function generator (AFG3152C, Tektronix0 and fluorescence phosphorescence spectrometer (FLS980, Edinburgh Instrument). For photophysical measurements, organic thin films with 200 nm thickness were deposited on glass substrates via vacuum deposition under high vacuum (1.0 × 10<sup>-5</sup> Pa) using an ALS vacuum deposition system.

Synthesis



Scheme S1. The synthetic routes of B-N-S-1, B-N-S-2 and B-N-S-3

**Synthesis of compound 3**. 1-bromo-2,3-dichlorobenzene (10.36 g, 45.87 mmol), phenothiazine (10.05 g, 50.46 mmol), tris(dibenzylideneacetone)dipalladium (Pd<sub>2</sub>(dba)<sub>3</sub>) (1.26 g, 1.38 mmol), dicyclohexyl-[2-[2,4,6-tri(propan-2-yl)phenyl]phenyl]phosphane (X-Phos) (1.31 g, 2.75 mmol), t-BuONa (8.82 g, 91.74 mmol) and dry toluene (200 mL) were added to a three-necked flask (1 L) under nitrogen atmosphere. The mixture was heated at 80 °C for 16 h. Then the reaction mixture was diluted with dichloromethane (200 mL) and filtered. After the solvent was removed under

reduced pressure, the residue was purified by chromatography on silica gel (eluent: dichloromethane/hexane=1/50) to afford white solids (16.0 g, 66%). <sup>1</sup> H NMR (400 MHz, Chloroform-*d*) :  $\delta$  7.632 (t, *J* = 5.6 Hz, 1H), 7.444 (d, *J* = 4.4 Hz, 2H), 6.991 (d, *J* = 6.8 Hz, 2H), 6.786–6.862 (m, 4H), 6.009 (d, *J* = 7.6 Hz, 2H). ESI-MS *m/z*: 344 [M]<sup>+</sup>.

Synthesis of compound 5. Compound 3 (12.75 g, 37.04 mmol), 1,2,3.4-tetra-hydroquinoline (6.41 g, 48.15 mmol),  $Pd_2(dba)_3$  (1.02 g, 1.11 mmol), X-Phos (1.06 g, 2.22 mmol), t-BuONa (7.12 g, 74.07 mmol) and dry toluene (250 mL) were added to a three-necked flask (500 mL) under nitrogen atmosphere. The mixture was heated at 110 °C for 19 h. Then the reaction mixture was diluted with dichloromethane (200 mL) and filtered. After the solvent was removed under reduced pressure, the residue was purified by chromatography on silica gel (eluent: dichloromethane/hexane=1/10) to afford white solids (8.5 g, 51%). <sup>1</sup> H NMR (400 MHz, Chloroform-*d*) :  $\delta$  7.503 (s, 1H), 7.421 (t, *J* = 4.8 Hz, 1H), 7.061 (d, *J* = 6.8 Hz, 1H), 6.992 (d, *J* = 7.2 Hz, 2H), 6.941 (d, *J* = 8.0 Hz, 1H), 6.871 (t, *J* = 7.2 Hz, 2H), 6.804 (t, *J* = 7.2 Hz, 2H), 6.685 (t, *J* = 7.6 Hz, 1H), 6.261 (d, *J* = 8.4 Hz, 1H), 6.097 (d, *J* = 8.0 Hz, 1H), 3.615 (s, 2H), 2.911 (t, *J* = 6.4 Hz, 2H), 2.084–2.141 (m, 2H). ESI-MS m/z: 440. [M]<sup>+</sup>,463. [M+Na]<sup>+</sup>.

Synthesis of B-N-S-1. To a solution of compound 5 (12.67 g, 28.73 mmol) in *tert*-butylbenzene (500 mL) was added t-BuLi (1.5 M, 78 mL) dropwise under nitrogen atmosphere at -40 °C. After stirring for 1 h, the reaction mixture was heated at 90 °C for 2.5 h. Then the reaction cooled to -30 °C, and boron tribromide (BBr<sub>3</sub>) (9.68 mL, 100.56 mmol) was added, followed by stirring at room temperature for 2 h. The reaction mixture was heated to 120 °C and stirred for 24 h after *N*,*N*-diisopropylethylamine (41 mL) was added at 0 °C. After cooling to room temperature, methanol (20 mL) was added to the reaction mixture. The reaction mixture was diluted with dichloromethane (200 mL),washed with water and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, After the solvent was removed under reduced pressure, the residue was purified by chromatography on silica gel (eluent: dichloromethane/hexane=1/10) to afford yellow solids (1.57 g, 13%). <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) :  $\delta$  8.51 (d, *J* = 7.6 Hz, 1H), 8.38 – 8.30 (m, 1H), 7.64 (td, *J* = 8.2, 2.0 Hz, 1H), 7.51 – 7.36 (m, 4H), 7.33 – 7.24 (m, 2H), 7.21 (dd, *J* = 8.4, 6.4 Hz, 1H), 7.16 – 7.03 (m, 3H), 4.33 – 4.12 (m, 2H), 3.17 – 2.97 (m, 2H), 2.41 (dt, *J* = 13.1, 3.8 Hz, 1H), 2.16 (qt, *J* = 11.8, 5.3 Hz, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  147.08, 145.42, 145.29, 143.73, 143.55, 133.68, 133.38, 132.38, 131.82, 128.93, 128.75, 128.63, 128.02, 127.37, 126.10, 125.41, 124.82, 124.32, 123.64, 122.25, 121.65, 119.87, 109.87, 105.26, 50.88, 32.72, 22.54. HR-MS *m/z*: 415.1466 [M+H]<sup>+</sup>.

Synthesis of compound 6. 1-bromo-2,3-dichlorobenzene (3.31 g, 14.67 mmol), 1,2,3.4-tetra-hydroquinoline (2.15 g, 16.14 mmol), Pd<sub>2</sub>(dba)<sub>3</sub> (0.41 g, 0.44 mmol), t-BuONa (2.82 g, 29.34 mmol), X-Phos (0.42 g, 0.88 mmol) and dry

toluene (200 mL) were added to a three-necked flask (500 MI) under nitrogen atmosphere. The mixture was heated at 80 °C for 16 h. Then the reaction mixture was diluted with dichloromethane (200 mL) and filtered. After the solvent was removed under reduced pressure, the residue was purified by chromatography on silica gel (eluent: dichloromethane/hexane=1/100) to afford white solids (3.03 g, 73%). <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) :  $\delta$  7.398–7.374 (m, 1H), 7.244 (s, 1H), 7.034 (d, *J* = 5.4 Hz, 1H), 6.902 (t, *J* = 7.6 Hz, 1H), 6.673 (t, *J* = 7.2 Hz, 1H), 6.141 (d, *J* = 8.0 Hz, 1H), 3.538 (s, 2H), 2.898 (t, *J* = 6.4 Hz, 2H), 2.089 (t, *J* = 6.0 Hz, 2H). ESI-MS *m/z*: 278 [M]<sup>+</sup>.

Synthesis of compound 8. Compound 6 (5.00 g, 17.96 mmol), 3,4-dihydro-2H-benzo[b][1,4]thiazine (2.99 g, 19.76 mmol), Pd<sub>2</sub>(dba)<sub>3</sub> (0.49 g, 0.54 mmol), X-Phos (0.51 g, 1.08 mmol), t-BuONa (3.45 g,35.93 mmol) and dry toluene (100 mL) were added to a three-necked flask (500 mL) under nitrogen atmosphere. The mixture was heated at 115 °C for 16 h. Then the reaction mixture was diluted with dichloromethane (200 mL) and filtered. After the solvent was removed under reduced pressure, the residue was purified by chromatography on silica gel (eluent: dichloromethane/hexane=1/10) to afford white solids (4.30 g, 61%). <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) :  $\delta$  7.326 (t, *J* = 7.6 Hz, 1H), 7.273 (d, *J* = 8.0 Hz, 1H), 7.213 (d, *J* = 7.6 Hz, 1H), 7.105 (d, *J* = 7.6 Hz, 1H), 7.047 (d, *J* = 7.2 Hz, 1H), 6.913 (t, *J* = 7.6 Hz, 1H), 6.842 (t, *J* = 7.2 Hz, 1H), 6.641–6.700 (dd, *J* = 7.6 Hz, 16.0 Hz, 2H), 6.280 (d, *J* = 8.4 Hz, 1H), 6.206 (d, *J* = 8.0 Hz, 1H), 3.923 (t, *J* = 4.4 Hz, 2H), 3.576 (s, 1H), 3.171 (s, 2H), 3.169 (s, 2H), 2.901 (t, *J* = 6.0 Hz, 2H). ESI-MS m/z: 393 [M]<sup>+</sup>.

Synthesis of B-N-S-2. To a solution of compound 8 (12.04 g, 30.63 mmol) in *tert*-butylbenzene (500 mL) was added *t*-BuLi (1.5 M, 83 mL) dropwise under nitrogen atmosphere at -40 °C. After stirring for 1 h, the reaction mixture was heated at 90 °C for 2 h. Then the reaction cooled to -30 °C, and BBr<sub>3</sub> (10.32 mL, 107.21 mmol) was added, followed by stirring at room temperature for 2 h. The reaction mixture was heated to 120 °C and stirred for 24 h after *N*,*N*-diisopropylethylamine (43 mL) was added at 0 °C. After cooling to room temperature, methanol (20 mL) was added to the reaction mixture. The reaction mixture was diluted with dichloromethane (200 mL),washed with water and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, After the solvent was removed under reduced pressure, the residue was purified by chromatography on silica gel (eluent: dichloromethane/hexane=1/10) to afford yellow solids (1.26 g, 11%).<sup>1</sup> H NMR (400 MHz, Chloroform-*d*):  $\delta$  8.48 (dd, *J* = 24.7, 7.6 Hz, 2H), 7.73 (t, *J* = 8.2 Hz, 1H), 7.55 (d, *J* = 7.4 Hz, 1H), 7.42 (d, *J* = 7.1 Hz, 1H), 7.24 – 7.11 (m, 2H), 7.04 (d, *J* = 8.3 Hz, 1H), 6.95 (d, *J* = 8.3 Hz, 1H), 4.52 (dd, *J* = 7.2, 3.5 Hz, 2H), 4.17 (t, *J* = 5.9 Hz, 2H), 3.26 (dq, *J* = 5.3, 2.5 Hz, 2H), 3.08 (d, *J* = 6.2 Hz, 2H), 2.28 (m, *J* = 6.0 Hz, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$ 

146.64, 145.12, 143.09, 141.84, 133.81, 133.65, 133.22, 131.08, 130.88, 126.42, 125.83, 124.45, 121.12, 120.01, 119.68, 118.91, 103.16, 102.97, 52.16, 49.03, 29.32, 26.58, 22.62. ESI-MS m/z: 367.1470 [M+H]<sup>+</sup>.

Synthesis of compound 11. 1,3-dibromo-5-(tert-butyl)-2-chlorobenzene (15.00 g, 45.94 mmol), 5-(tert-butyl)-N-(4-(tert-butyl)phenyl)benzo[b]thiophen-3-amine (15.50 g, 45.94 mmol),  $Pd_2(dba)_3$  (1.26 g, 1.38 mmol), t-BuONa (8.83 g, 91.88 mmol), X-Phos (1.60 g, 2.76 mmol) and dry toluene (200 mL) were added to a three-necked flask (500 Ml) under nitrogen atmosphere. The mixture was heated at 110 °C for 3 h. Then the reaction mixture was diluted with dichloromethane (200 mL) and filtered. After the solvent was removed under reduced pressure, the residue was purified by chromatography on silica gel (eluent: dichloromethane/hexane=1/100) to afford white solids (11.3 g, 42%). ESI-MS m/z: 584 [M+H]<sup>+</sup>, 606 [M+Na]<sup>+</sup>

Synthesis of compound 13. Compound 11 (14.0 g, 24.00 mmol), 6-(tert-butyl)-4,4-dimethyl-1,2,3,4-tetrahydroquinoline (5.90 g, 27.14 mmol),  $Pd_2(dba)_3$  (0.66 g, 0.60 mmol), X-Phos (0.69 g, 1.20 mmol), t-BuONa (4.60 g, 35.93 mmol) and dry toluene (300 mL) were added to a three-necked flask (500 mL) under nitrogen atmosphere. The mixture was heated at 115 °C for 14 h. Then the reaction mixture was diluted with dichloromethane (200 mL) and filtered. After the solvent was removed under reduced pressure, the residue was purified by chromatography on silica gel (eluent: ethyl acetate/hexane=1/10) to afford white solids (9.00 g, 53%).<sup>1</sup>H NMR (400 MHz, Chloroform-d)  $\delta$  7.71 (d, J = 8.5 Hz, 1H), 7.37 (dd, J = 8.4, 1.9 Hz, 1H), 7.31 (d, J = 2.0 Hz, 1H), 7.29 – 7.15 (m, 5H), 6.95 – 6.87 (m, 2H), 6.81 (d, J = 8.2 Hz, 2H), 6.10 (d, J = 8.6 Hz, 1H), 3.76 – 3.34 (m, 2H), 1.88 (q, J = 6.3 Hz, 2H), 1.56 (s, 3H), 1.41 (s, 3H), 1.28-1.18 (m, 36H). HR-MS *m/z*: 720 [M+H]<sup>+</sup>.

Synthesis of B-N-S-3. To a solution of compound 13 (9.00 g, 27.73 mmol) in *tert*-butylbenzene (200 mL) was added *t*-BuLi (1.5 M, 34 mL) dropwise under nitrogen atmosphere at -40 °C. After stirring for 1 h, the reaction mixture was heated at 90 °C for 2 h. Then the reaction cooled to -30 °C, and BBr<sub>3</sub> (4.20 mL, 100.56 mmol) was added, followed by stirring at room temperature for 2 h. The reaction mixture was heated to 120 °C and stirred for 12 h after *N*,*N*-diisopropylethylamine (17 mL) was added at 0 °C. After cooling to room temperature, methanol (20 mL) was added to the reaction mixture. The reaction mixture was diluted with dichloromethane (200 mL),washed with water and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, After the solvent was removed under reduced pressure, the residue was purified by chromatography on silica gel (eluent: dichloromethane/hexane=1/10) to afford yellow solids (1.50 g, 17%).<sup>1</sup>H NMR (400 MHz, Chloroform-d)  $\delta$  8.70 (d, *J* = 3.1 Hz, 1H), 7.90 (dd, *J* = 8.5, 2.4 Hz, 1H),

7.78 (d, J = 7.9 Hz, 2H), 7.71 (s, 1H), 7.49 (dd, J = 8.4, 2.2 Hz, 2H), 7.40 (dd, J = 8.5, 2.1 Hz, 1H), 7.05 (s, 1H), 6.64 (s, 1H), 6.40 (s, 1H), 4.19 (s, 2H), 2.12 (t, J = 6.2 Hz, 2H), 1.60 – 1.56 (m, 9H), 1.54 – 1.50 (m, 15H), 1.30 (t, J = 2.0 Hz, 9H), 1.10 (d, J = 2.4 Hz, 9H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  154.40, 152.60, 147.17, 143.16, 141.50, 141.06, 140.17, 133.03, 132.51, 130.44, 129.48, 127.87, 125.22, 123.65, 123.07, 122.19, 120.77, 116.67, 103.23, 100.44, 44.66, 39.03, 36.63, 36.00, 35.29, 34.92, 34.26, 32.32, 32.00, 31.78, 31.63, 30.78.HR-MS *m/z*: 693.4423 [M+H]<sup>+</sup>.

#### Device fabrication and characterization

All devices were fabricated in an ALS vacuum deposition system with a base pressure of  $1.0 \times 10^{-5}$  Pa, and were encapsulated in a glovebox (N<sub>2</sub> < 1 ppm, O<sub>2</sub> < 1 ppm). Prior to deposition, the patterned ITO coated glass substrates were cleaned with detergent, rinsed in deionized water, acetone, and isopropanol, and then dried in an oven for 1 h. Organic layers were deposited in sequence at a rate of 1.0 Å/s. Afterward, Yb (1 nm) and Ag (100 nm) were thermally deposited at rates of  $0.1 \text{ Å s}^{-1}$  and  $1 \text{ Å s}^{-1}$ , respectively. Current density-luminance-voltage characteristics, EL spectra, and EQE of EL device were obtained by using a Keithley 2400 source-meter and an absolute external quantum efficiency measurement system (CS2000, KONICA MINOLTA).



Figure S1. <sup>1</sup>H NMR spectrum of B-N-S-1 (400 MHz, CDCl<sub>3</sub>).



Figure S2. <sup>13</sup>C NMR spectrum of B-N-S-1 (100 MHz, CDCl<sub>3</sub>).



Figure S3. HR-MS spectrum of B-N-S-1 in CDCl<sub>3</sub>.



Figure S4. <sup>1</sup>H NMR spectrum of B-N-S-2 (400 MHz, CDCl<sub>3</sub>).



Figure S5. <sup>13</sup>C NMR spectrum of B-N-S-2 (100 MHz, CDCl<sub>3</sub>).



100 120 140 160 180 200 220 240 260 280 300 320 340 360 380 400 420 440 460 480 500 520 540 560 580 600 620 640 660 680 700 720 740 760 780 800

Counts vs. Mass-to-Charge (m/z)

Figure S6. HR-MS spectrum of B-N-S-2 in CDCl<sub>3</sub>.



Figure S7. <sup>1</sup>H NMR spectrum of B-N-S-3 (400 MHz, CDCl<sub>3</sub>).



Figure S8. <sup>13</sup>C NMR spectrum of B-N-S-3 (100 MHz, CDCl<sub>3</sub>).



Figure S9. HR-MS spectrum of B-N-S-3 in CDCl<sub>3</sub>.



Figure S10. (a) TGA and (b) DSC curves of the emitters.

Table S1	Summary	of thermal	properties
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Emitter	T <sub>s</sub> ª)[1Å∕s, ⁰C]	T <sub>d</sub> <sup>b)</sup> [5%, °C]	ΔT <sup>c)</sup> [ °C]	Tg <sup>d)</sup> [°C]
B-N-1	195	356	161	٨
B-N-S-1	240	411	171	133
B-N-S-2	220	378	158	87
B-N-S-3	270	404	134	162

a)  $T_s$ : Sublimation temperature at 1 Å/s in apophorometer. b)  $T_d$ : Decomposition temperature. c)  $\Delta T$ : The gap between  $T_s$  and  $T_d$ ; d)

T<sub>g</sub>: Glass transition temperature.



Figure S11. CV curves of the emitters.



Figure S12. PL spectra data of the emitters in different polar solvents.

 Table S2. Summary of PL spectra data of the emitters in different polar solvents.

Emitte	n-hexane		toluene		tetrahydrofuran		dichloromethane	
r	$\lambda_{\text{PL}}{}^{a)}[nm]$	FWHM <sup>b)</sup> [nm]	$\lambda_{\text{PL}}{}^{a)}[nm]$	FWHM <sup>b)</sup> [nm]	$\lambda_{\text{PL}}{}^{a)}[nm]$	FWHM <sup>b)</sup> [nm]	$\lambda_{\text{PL}}^{a)}[nm]$	FWHM <sup>b)</sup> [nm]
B-N-1	437	24	451	26	451	30	458	33
B-N-S-1	472	38	483	41	482	44	492	50
B-N-S-2	444	29	458	33	462	37	465	40
B-N-S-3	447	20	457	25	458	30	465	36

a) PL peak wavelength. b) Full width at half maximum.



Figure \$13. a) The energy-level diagrams of the devices. b) Chemical structure of materials used in the devices.



Figure S14. Normalized EL spectra operated at different voltages of the devices



Figure S15. Transient EL decay spectra at 4 V and the fitting results of the delayed component of the devices





Figure S16. TGA (a) and DSC (b) curves of the host material in devices.



**Figure S17.** a) EL spectra at 1000 cd m<sup>-2</sup>, b) luminance-voltage-current density (L–V–J) characteristics, c) CE/EQE-luminance curves, d) device operational lifetimes at an initial luminance of 1000 cd m<sup>-2</sup>.

Emitter	V <sub>on</sub> a) (V)	CE <sub>max</sub> (cd A <sup>-1</sup> )	PE <sub>max</sub> (Im W <sup>-1</sup> )	EQE <sub>max</sub> (%)	CIE <sup>b)</sup> (x, y)	λ <sub>ει</sub> c) (nm)	FWHM <sup>c)</sup> (nm)	LT <sub>95</sub> <sup>d)</sup> (hr)
PtON-TBBI	3.02	0.29	0.27	0.26	0.164, 0.144	450	84	<1
B-N-S-3	3.04	6.5	5.2	6.7	0.128, 0.119	461	35	136

Table S3. Summary of device performance with PtON-TBBI and B-N-S-3 as emitter.