

Electronic Supplementary Information

Asymmetric thermally activated delayed fluorescence (TADF) emitters with 5,9-dioxa-13*b*-boranaphtho[3,2,1-*de*]anthracene (OBA) as acceptor and highly efficient blue-emitting OLEDs

Dongdong Song,^a Yue Yu,^b Ling Yue,^a Daokun Zhong,^a Yindi Zhang,^a Xiaolong Yang,^a Yuanhui Sun,^a Guijiang Zhou,^{*a} Zhaoxin Wu^{*b}

^a MOE Key Laboratory for Nonequilibrium Synthesis and Modulation of Condensed Matter, Department of Chemistry, School of Science, State Key Laboratory for Mechanical Behavior of Materials, Xi'an Jiaotong University, Xi'an 710049, P. R. China.

^b Key Laboratory of Photonics Technology for Information, School of Electronic and Information Engineering, Xi'an Jiaotong University, Xi'an 710049, P. R. China.

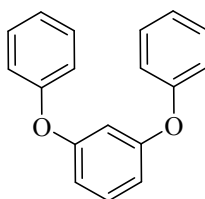
*Guijiang Zhou: E-mail, zhougj@mail.xjtu.edu.cn

*Zhaoxin Wu: E-mail, zhaoxinwu@mail.xjtu.edu.cn

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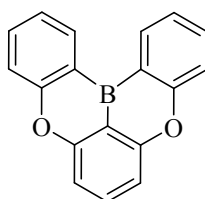
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1,3-Diphenoxybenzene



Under a nitrogen atmosphere, 1,3-dibromobenzene (5.00 g, 0.02 mol), phenol (5.19 g, 0.06 mol), Cs₂CO₃ (20.70 g, 0.06 mol) and CuBr (0.91 g, 0.006 mol) were heated to 160 °C in 35 mL degassed 2-pyrrolidinone for 24 h. After cooling to room temperature, the mixture was extracted with petroleum ether. The organic layer was dried over anhydrous Na₂SO₄ and evaporated under reduced pressure, then purified by column chromatography over silica gel using petroleum ether as the eluent. White solid of the title compound was obtained (4.06 g, 72%). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.32 (t, *J* = 8.0 Hz, 4H), 7.23 (t, *J* = 8 Hz, 1H), 7.10 (t, *J* = 7.6 Hz, 2H), 7.02 (d, *J* = 8.0 Hz, 4H), 6.72–6.69 (m, 3H). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 160.3, 158.3, 132.0, 131.5, 125.3, 120.8, 114.8, 110.9

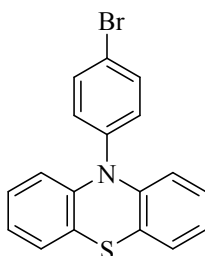
1,4-Benzoxaborino-2,3,4-kl-phenoxaborin



A solution of *n*-butyllithium in hexane (3.66 mL, 2.5 M, 9.16 mmol) was added slowly to a solution of 1,3-diphenoxybenzene (2.00 g, 7.63 mmol) in *o*-xylene (30.0 mL) at 0 °C under a nitrogen atmosphere. After stirring at 70 °C for 4 h, borontribromide (0.87 mL, 9.16 mmol) was added slowly at –40 °C. After the reaction mixture was allowed to warm to room temperature for 1 h, *N,N*-

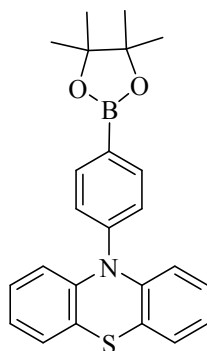
diisopropylethylamine (2.66 mL, 15.26 mmol) was added at 0 °C. After stirring at 120 °C for 5 h, *N,N*-diisopropylethylamine (1.33 mL, 7.64 mmol) was added at 0 °C, the reaction mixture was extracted with CH₂Cl₂. The organic layer was dried over anhydrous Na₂SO₄ and evaporated under reduced pressure, then purified by column chromatography over silica gel using petroleum ether as the eluent. White solid of the title compound was obtained (1.27 g, 62%). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.69 (dd, *J* = 1.6, 7.8 Hz, 1H), 7.79 (t, *J* = 8.0 Hz, 1H), 7.70 (ddd, *J* = 1.6, 7.1, 8.5 Hz, 2H), 7.54 (d, *J* = 8.5 Hz, 2H), 7.38 (d, *J* = 7.1, 7.8 Hz, 2H), 7.22 (d, *J* = 8 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 160.5, 157.4, 134.6, 134.5, 133.6, 122.7, 118.5, 108.4.

10-(4-bromophenyl)-10H-phenothiazine (SBr)

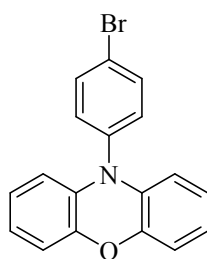


Under a nitrogen atmosphere, phenothiazine (2.00 g, 10.90 mmol), 4-bromoiodobenzene (2.80 g, 10.00 mmol) and Copper powder (3.00 g, 23.40 mmol) were heated to 160 °C in 35 mL *N,N*-dimethylformamide for 48 h. After cooling to room temperature, the mixture was washed with water and extracted with CH₂Cl₂. The organic layer was dried over anhydrous Na₂SO₄ and evaporated under reduced pressure, then purified by column chromatography over silica gel using petroleum ether / CH₂Cl₂ (5:1, v:v) as the eluent. A white solid of the title compound was obtained (2.50 g, 66%). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.70 (d, *J* = 8.6 Hz, 2H), 7.25 (d, *J* = 8.6 Hz, 2H), 7.04 (dd, *J* = 7.3, 1.8 Hz, 2H), 6.86 (m, 4H), 6.24 (dd, *J* = 8.0, 1.4 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 144.2, 143.8, 140.9, 133.8, 131.9, 129.7, 129.5, 122.5, 122.2, 121.2, 117.5, 116.2

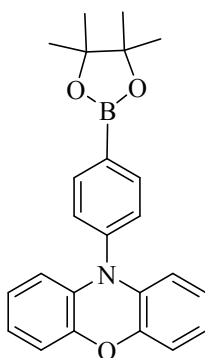
SB



Under a nitrogen atmosphere, bis-(pinacolato)diboro (1.10 g, 4.33 mmol), *N*-(4-bromophenyl)-phenothiazine (1.00 g, 2.833 mmol), KOAc (0.931 g, 9.482 mmol) and Pd(dppf)Cl₂ (0.178 g, 0.632 mmol) were heated to 110 °C in 25 mL degassed 1,4-dioxane for 12 h. After cooling to room temperature, the mixture was extracted with CH₂Cl₂. The organic layer was dried over anhydrous Na₂SO₄ and evaporated under reduced pressure, then purified by column chromatography over silica gel using CH₂Cl₂ / petroleum ether (1:3, v:v) as the eluent. White solid of the title compound was obtained (0.62 g, 53%). ¹H NMR (400 MHz, DMSO-*d*₆): δ (ppm) 7.88 (d, *J* = 8.3 Hz, 2H), 7.35 (d, *J* = 8.3 Hz, 2H), 7.18 (dd, *J* = 7.5, 1.6 Hz, 2H), 7.02 (ddd, *J* = 7.9, 7.7, 1.7 Hz, 2H), 6.95 (ddd, *J* = 7.5, 7.5, 1.3 Hz, 2H), 6.41 (dd, *J* = 8.1, 1.3 Hz, 2H), 1.33 (s, 12H). ¹³C NMR (100 MHz, DMSO-*d*₆): δ (ppm) 144.5, 143.4, 137.3, 127.9, 127.6, 123.9, 122.4, 118.6, 84.3, 25.2.

10-(4-bromophenyl)-10H-phenoxazine (OBr)

Under a nitrogen atmosphere, phenoxazine (2.00 g, 10.00 mmol), 4-bromoiodobenzene (2.80 g, 10.00 mmol) and Copper powder (3.00 g, 23.40 mmol) were heated to 160 °C in 35 mL *N,N*-dimethylformamide for 48 h. After cooling to room temperature, the mixture was washed with water and extracted with CH₂Cl₂. The organic layer was dried over anhydrous Na₂SO₄ and evaporated under reduced pressure, then purified by column chromatography over silica gel using petroleum ether / CH₂Cl₂ (5:1, v:v) as the eluent. White solid of the title compound was obtained (2.30 g, 68%).
¹H NMR (400 MHz, CDCl₃): δ (ppm) 5.91 (dd, *J* = 7.8, 1.4 Hz, 2H), 6.57 – 6.70 (m, 6H), 7.23 (d, *J* = 8.6 Hz, 2H), 7.72 (d, *J* = 8.6 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 113.3, 115.7, 121.7, 122.5, 123.4, 132.9, 134.1, 134.6, 138.2, 144.0.

OB

Under a nitrogen atmosphere, bis-(pinacolato)diboro (1.10 g, 4.33 mmol), N-(4-Bromophenyl)-Phenoxazine (1.00 g, 2.97 mmol), KOAc (0.93 g, 9.48 mmol) and Pd(dppf)Cl₂ (0.18 g, 0.63 mmol) were heated to 110 °C in 25 mL degassed 1,4-dioxane for 12 h. After cooling to room temperature, the mixture was extracted with CH₂Cl₂. The organic layer was dried over anhydrous Na₂SO₄ and evaporated under reduced pressure, then purified by column chromatography over silica gel using CH₂Cl₂ / petroleum ether (1:5, v:v) as the eluent. White solid of the title compound was obtained (0.65 g, 55%). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.02 (d, *J* = 8.0 Hz, 2H), 7.35 (d, *J* = 8.0 Hz,

2H), 6.68 (dd, $J = 7.8$ Hz, 1.4 Hz, 2H), 6.63 (t, $J = 7.6$ Hz, 2H), 6.56 (td, $J = 7.6$ Hz, 1.5 Hz, 2H), 5.91 (d, $J = 7.8$ Hz, 2H), 1.38 (s, 12H). ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 145.9, 139.2, 134.5, 134.3, 125.9, 122.8, 122.7, 139.2, 134.5, 88.1, 24.7.

Electronic Supplementary Information

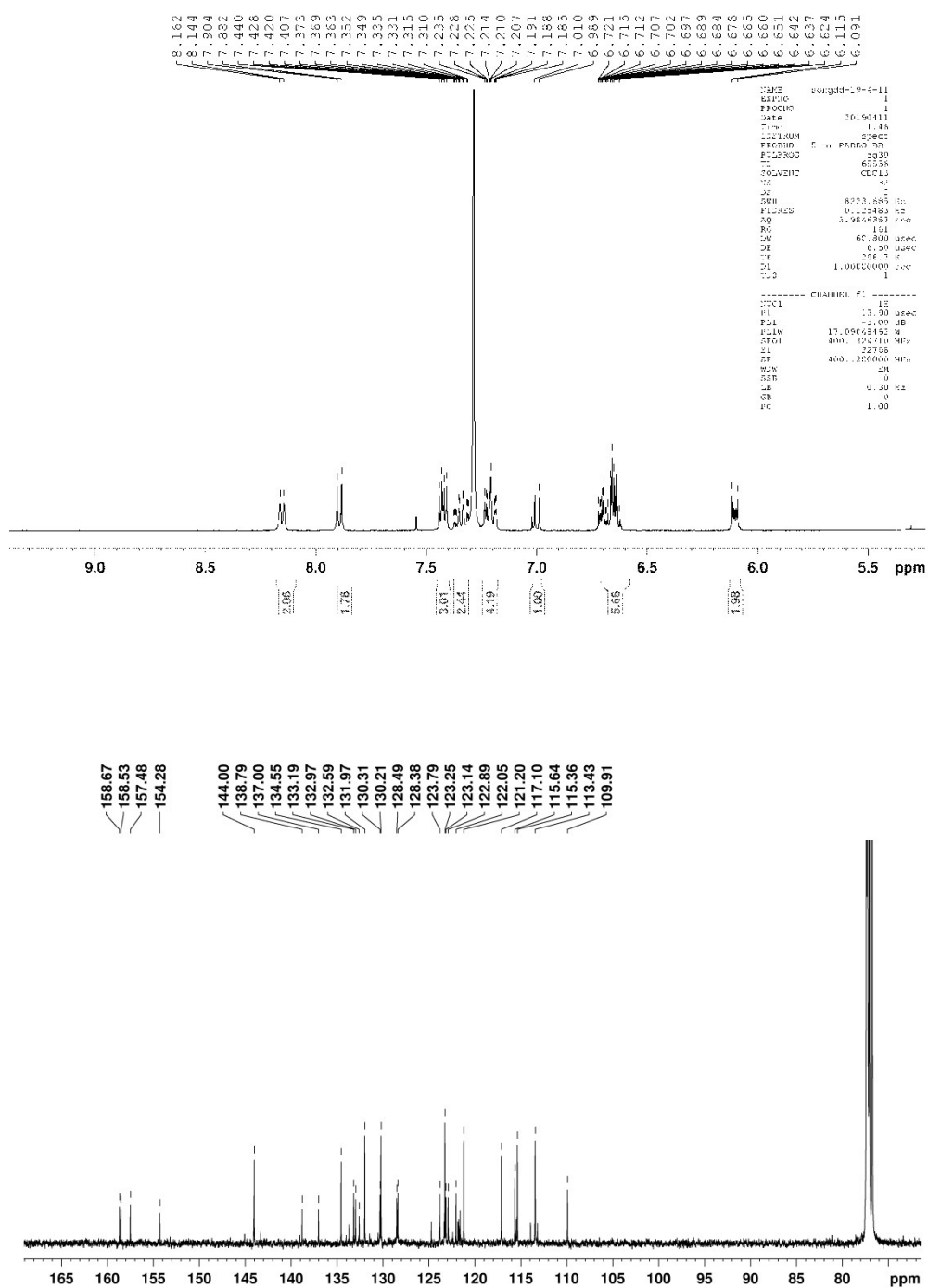


Figure S1. ¹H- and ¹³C-NMR spectra for OBA-O.

Electronic Supplementary Information

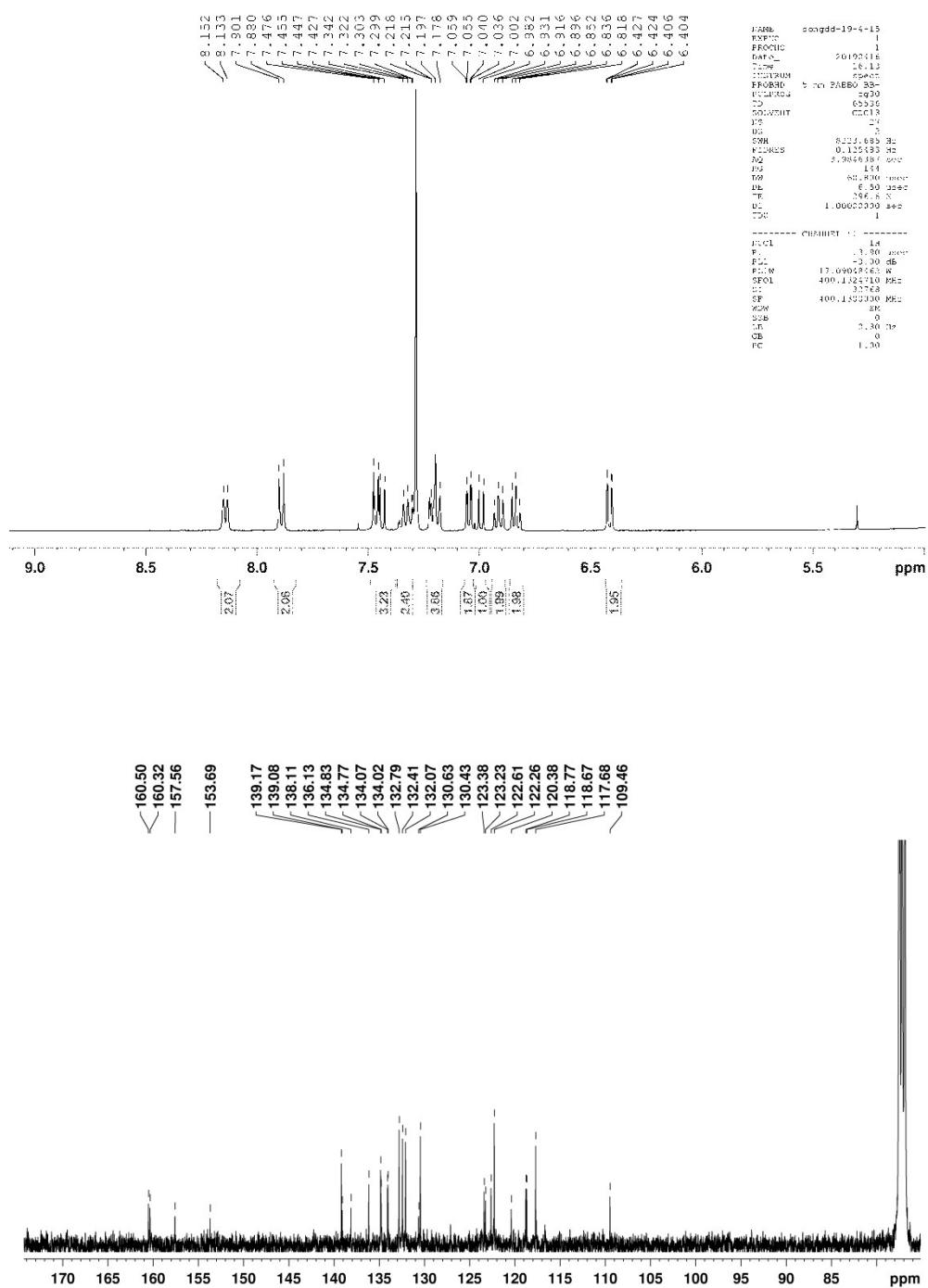


Figure S2. ¹H- and ¹³C-NMR spectra for OBA-S.

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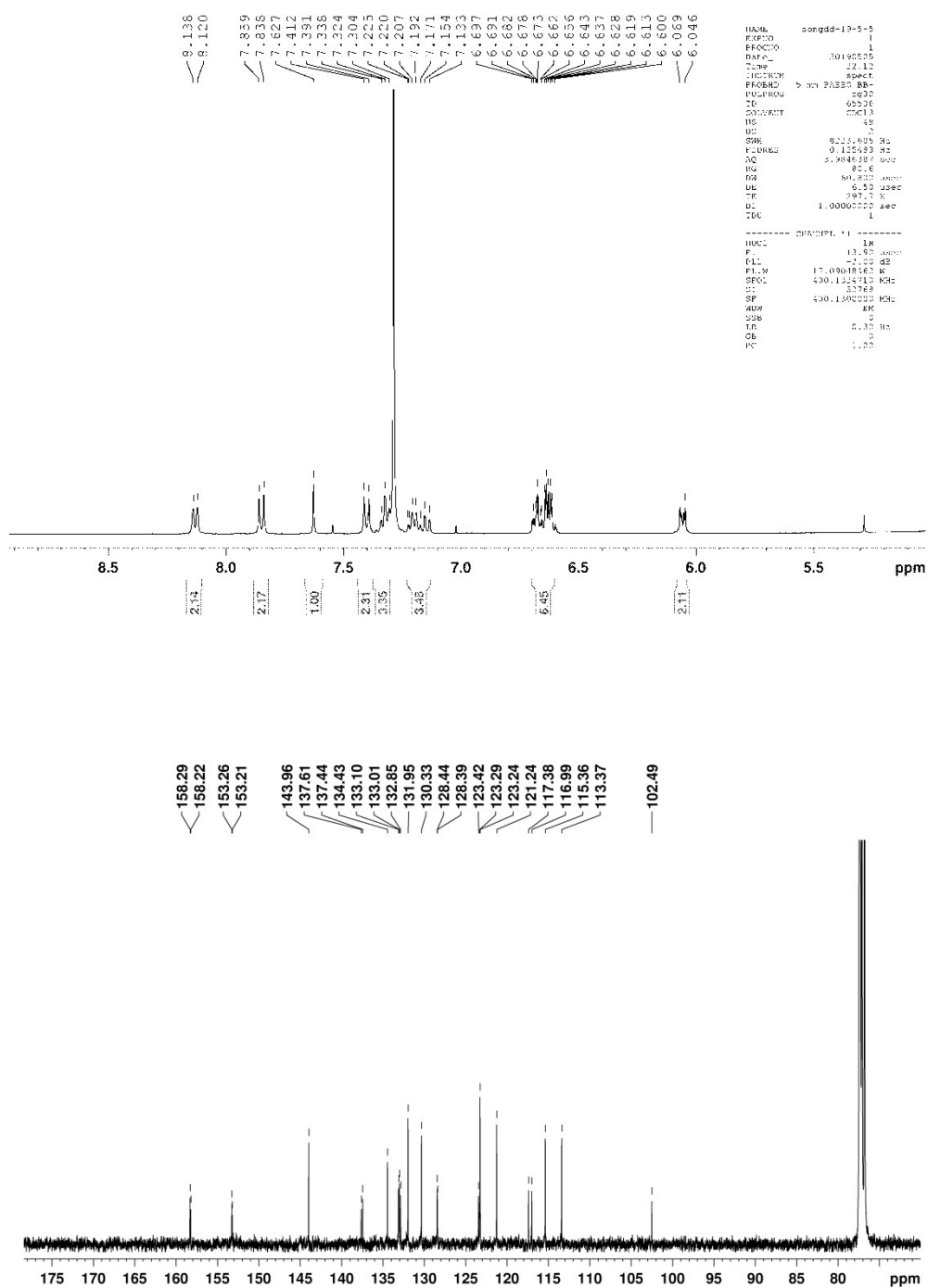


Figure S3. ¹H- and ¹³C-NMR spectra for OBA-BrO.

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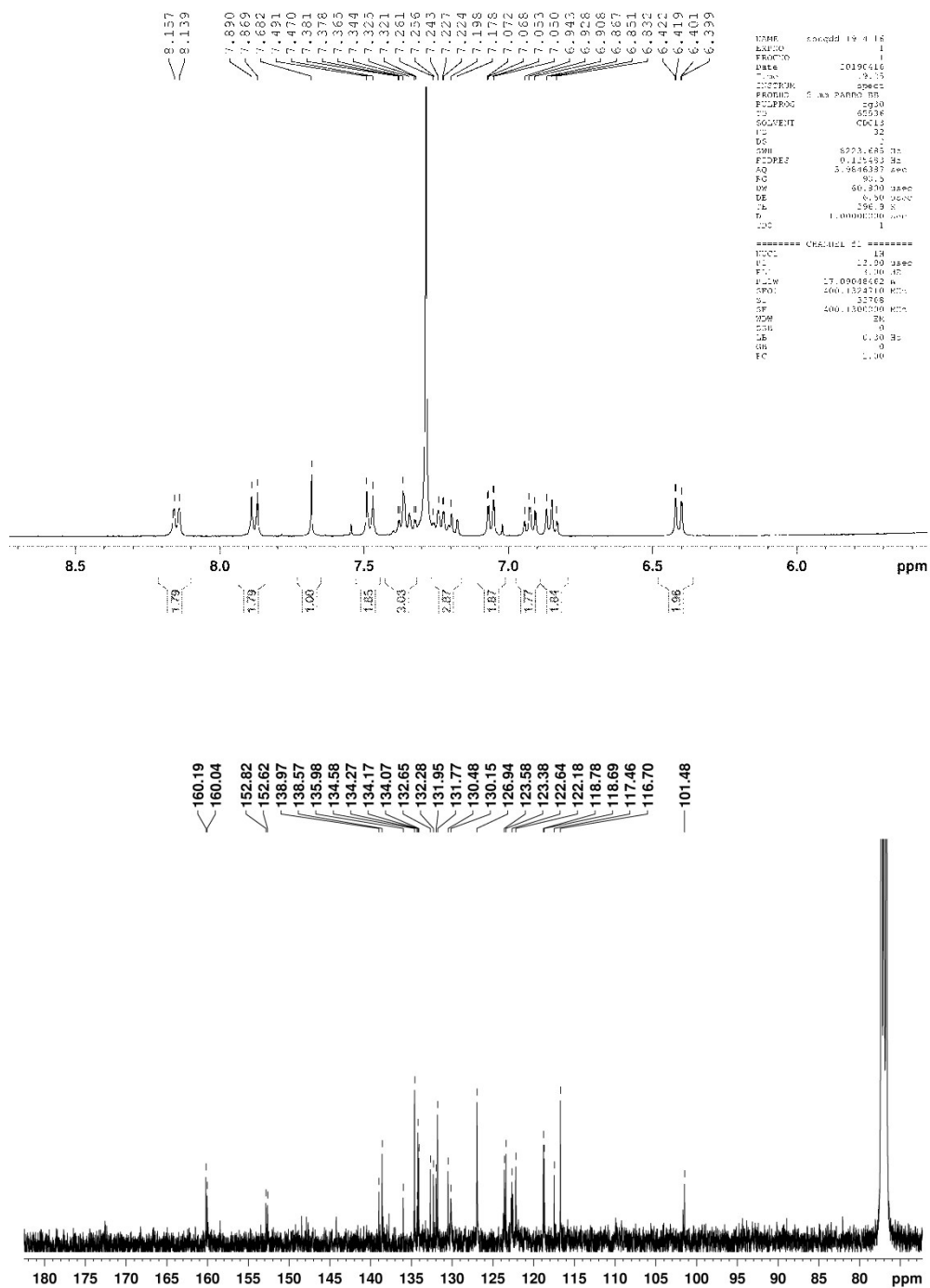


Figure S4. ¹H- and ¹³C-NMR spectra for OBA-BrS.

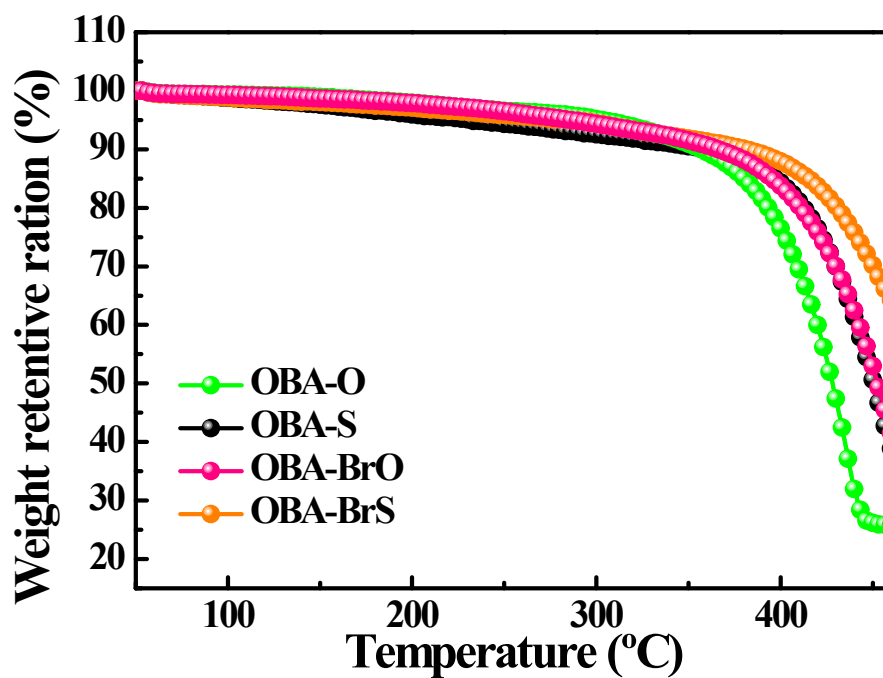


Figure S5. TGA curves of these OBA-based emitters.

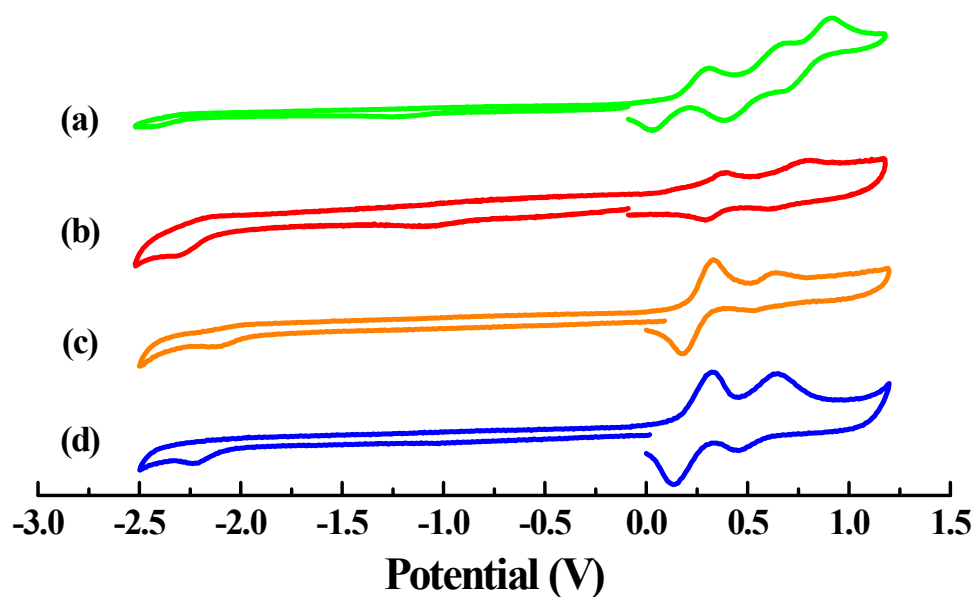


Figure S6. Cyclic curves of these asymmetric OBA-based emitters measured in CH_3CN and ferrocene/ferrocenium (Fc/Fc^+) couple at room temperature. (a) OBA-O, (b) OBA-S, (c) OBA-BrO, (d) OBA-BrS.

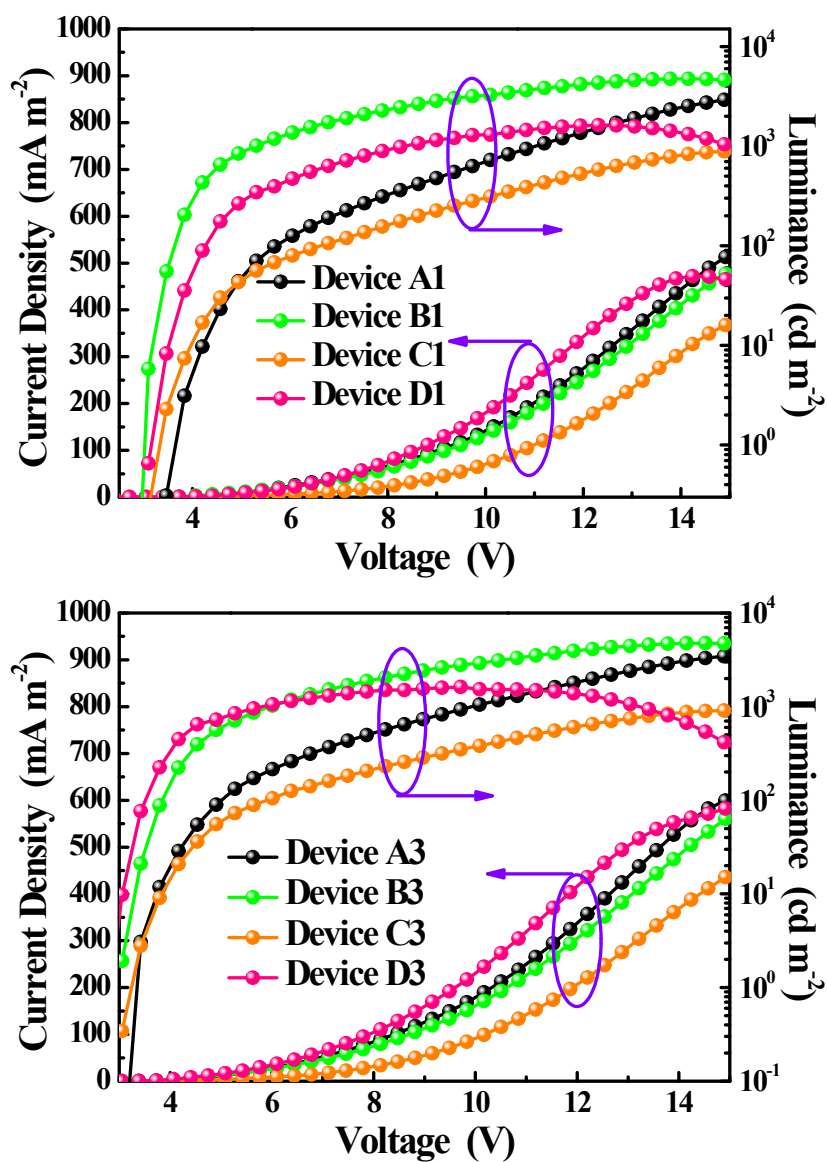


Figure S7. Current density–voltage–luminance (J – V – L) curves for the devices except the optimized ones.

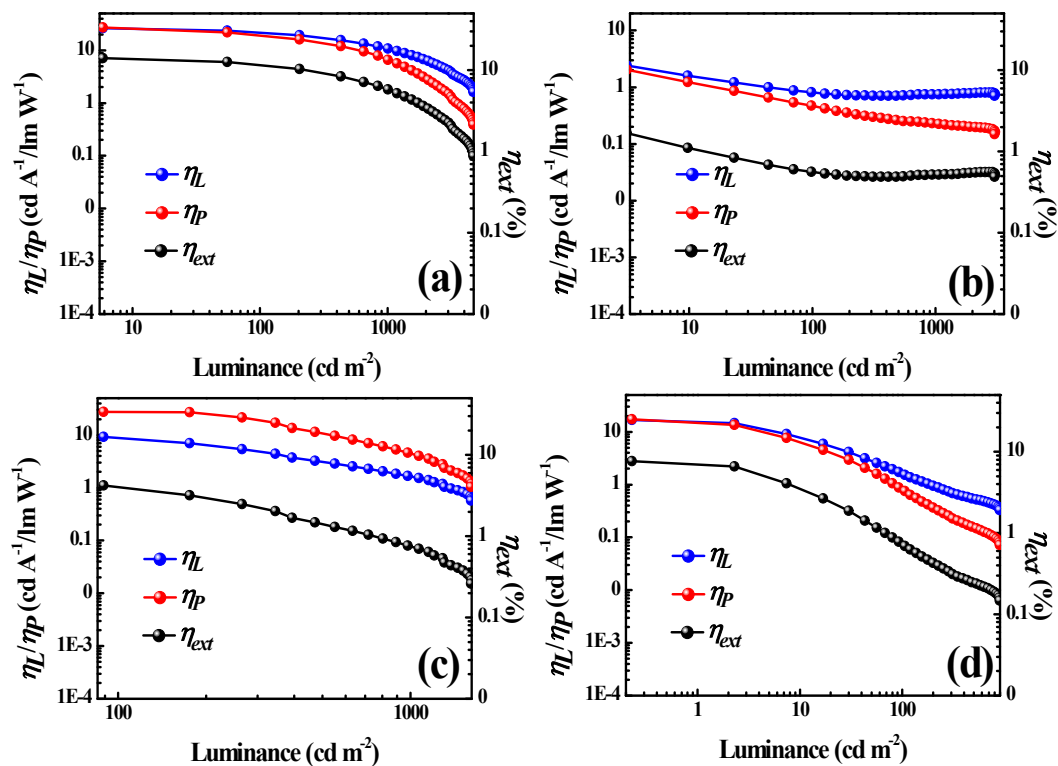


Figure S8. Relationship between EL efficiencies and luminance for the devices except the optimized ones. (a) Device A1, (b) Device B1, (c) Device C1 and (d) Device D1.

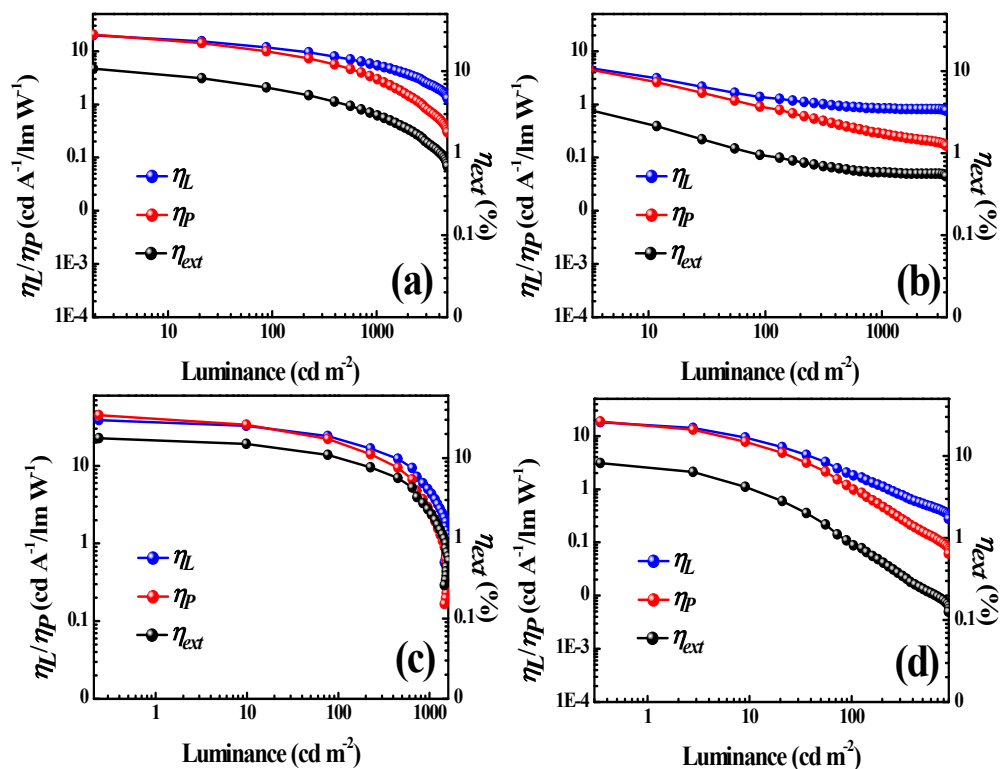


Figure S9. Relationship between EL efficiencies and luminance for the devices except the optimized ones. (a) Device A3, (b) Device B3, (c) Device C3 and (d) Device D3.