

Electronic Supplementary Information for

One-shot borylation synthesis of multiple resonance (MR) blue emitters *via* fusing benzofuran fragments within B/N skeletons

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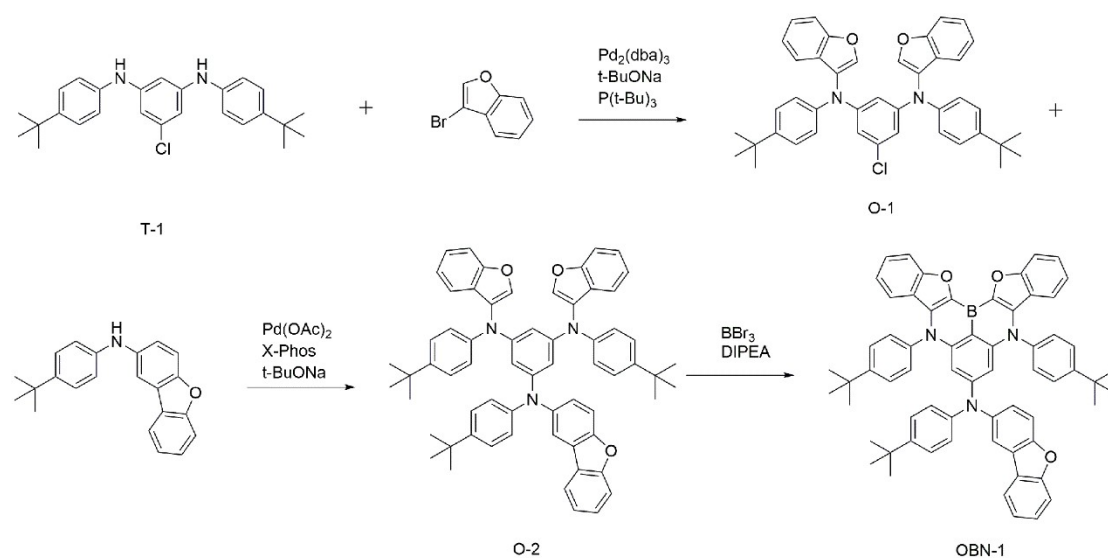
Experimental

General information

All chemical compounds were commercially available without further purification from Energy Chemical Co. and/or J&K Scientific Ltd. Co.. The ¹H nuclear magnetic resonance (NMR) spectra were recorded on Avance-400 (Bruker, 400 MHz) spectrometer, and chloroform-d (CDCl₃) was used as solution. A Hitachi U-3900 spectrophotometer was used to record on ultraviolet-visible (UV-vis) absorption spectra. Fluorescence spectra were determined by a Horiba FluoroMax-4 spectrophotometer. Differential scanning calorimetry (DSC) characteristics were detected by a NETZSCH DSC204 instrument following the heating rate of 10 °C min⁻¹ between 50 and 500 °C under a nitrogen atmosphere, and thermogravimetric analysis (TGA) were determined using a TAQ600 thermogravimeter at a heating rate of 10 °C/min between 50 and 800 °C under nitrogen conditions to monitor weight loss. Cyclic voltammetry (CV) curves of samples were investigated on a cyclic voltammetry (Ivium Tech., Iviumstat) by a BAS 100W Bioanalytical electrochemical work station using platinum disk as working electrode, platinum wire as auxiliary electrode, a porous glass wick Ag/Ag⁺ as pseudo reference electrode and ferrocene/ferrocenium (Fc/Fc⁺) as the internal standard. The redox potential was recorded at a scan rate of 100 mV s⁻¹ in a 0.1 M solution and tetrabutylammonium hexafluorophosphate (TBAPF₆) was as the electrolyte. The mass spectra were performed using a JMS-700 (JEOL) with high resolution fast atom bombardment

(FAB) mode and Advion Expression-L CMS spectrometer in APCI mode. The photoluminescence quantum yields (PLQYs) were tested using the Yokohama C9920-02G assay system.

Single-crystal X-ray diffraction: Single crystal X-ray diffraction data were collected on a Rigaku Synergy-DS diffractometer with Mo KR and Control Software, using the RAPID AUTO at 293 K. The structures were solved with direct methods and refined with a full-matrix least-squares technique, using the Olex2 programs, respectively. The crystallographic data has been deposited with Cambridge Crystallographic Data Centre (CCDC), and signed to CCDC code 2348522 for OBN-1, 2348529 for OBN-2, respectively.



Scheme S1. Synthesis scheme of OBN-1.

N1,N3-bis(benzo[b]thiophen-3-yl)-N1,N3-bis(4-(tert-butyl)phenyl)-5-chlorobenzene-1,3-diamine (O-1):

T-1 (5.00 g, 12.3 mM), 3-bromobenzofuran (4.93 g, 25.00 mM), Pd₂(dppa)₃ (0.23 g, 0.25 mM), t-BuONa (2.25 g, 25.00 mM), P(t-Bu)₃ (0.50 g, 0.25 mM) were degassed and purged with N₂ for three times. Toluene (230 mL) was added into the reaction *via* syringe. After stirring at 100 °C for 12 h, the reaction mixture cool down to room temperature, and 200 mL water were added. Then, collected the organic phase and dried over anhydrous MgSO₄. After evaporation, the crude product was purified by

silica gel column using dichloromethane/petroleum ether (1:4, v/v) mixtures to afford white solid. (6.60 g, yield: 84%). HRMS (EI/MS) m/z $[M]^+$ calcd for $C_{42}H_{39}ClN_2O_2$: 638.27; observed: 639.24.

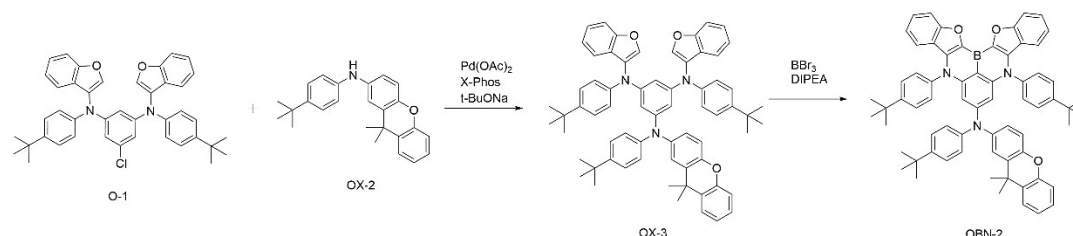
N1,N3-di(benzofuran-3-yl)-N1,N3,N5-tris(4-(tert-butyl)phenyl)-N5-(dibenzo[b,d]furan-2-yl)benzene-1,3,5-triamine (O-2):

O-1 (6.00 g, 9.40 mM), N-(4-(tert-butyl)phenyl)dibenzo[b,d]furan-2-amine (2.96 g, 9.40 mM), Pd(OAc)₂ (0.016 g, 0.094 mM), X-Phos (0.042 g, 0.094 mM), t-BuONa (0.96 g, 10.00 mM) were degassed and purged with N₂ for three times. The mixture was dissolved in xylenes (200 mL) and stirred at 160 °C for 12 h. Then cool down the reaction to room temperature, 200 mL water was added into the mixture. Collected the organic phase and dried over anhydrous MgSO₄. Then the organic solvent was removed with a rotary evaporator, and the resulting precipitate was purified by silica gel column using dichloromethane/petroleum ether (1:4, v/v) as eluant, and then the resulting white solid was obtained (7.09 g, yield: 82%). HRMS (EI/MS) m/z $[M]^+$ calcd for $C_{64}H_{59}N_3O_3$: 917.46; observed: 918.19.

N,5,9-tris(4-(tert-butyl)phenyl)-N-(dibenzo[b,d]furan-2-yl)-5H,9H-14,15-dioxo-5,9-diaza-14b-boradiindeno[2,1-a:1',2'-j]phenalen-7-amine (OBN-1):

O-2 (5.20 g, 5.67 mM) was degassed and purged with N₂ three times and then 150 mL o-DCB was added. BBr₃ (2.89 g, 11.50 mM) was added dropwise into the mixture with stirring at 0 °C in ice-water. After the reaction mixture was stirring at room temperature for 4 h, the reaction mixture was allowed to cool to 0 °C. DIPEA (2.77 g, 21.50 mM) was added into the reaction mixture, and then the reaction mixture was further stirred at 120 °C for 12 h. After cooling to room temperature, the reaction mixture was carefully quenched by addition of water. The product was extracted with dichloromethane, and the combined organic layer was dried over anhydrous MgSO₄. After filtration and evaporation, and the resulting precipitate was purified by silica gel column using dichloromethane/petroleum ether (1:4,v/v) as eluant, and then the resulting yellow-green solid was obtained (2.88 g, yield: 55%). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.78 (ddd, $J = 7.7, 1.3, 0.6$ Hz, 1H), 7.70 (dt, $J = 8.3, 0.9$ Hz, 2H), 7.65 (dd, $J = 2.2, 0.5$ Hz, 1H), 7.55 (dt, $J = 8.3, 0.9$ Hz, 1H), 7.46 (ddd, $J = 8.4, 7.2,$

1.3 Hz, 1H), 7.38 – 7.26 (m, 12H), 7.14 – 7.09 (m, 2H), 7.04 (dd, $J = 8.7, 2.3$ Hz, 1H), 7.00 – 6.95 (m, 2H), 6.86 (ddd, $J = 8.1, 7.2, 1.0$ Hz, 2H), 6.01 (s, 2H), 5.89 (ddd, $J = 8.1, 1.2, 0.6$ Hz, 2H), 1.27 (s, 9H), 1.19 (s, 18H). HRMS (EI/MS) m/z $[M]^+$ calcd for $C_{64}H_{56}BN_3O_3$: 925.44; observed: 925.95.



Scheme S2. Synthesis scheme of **OBN-2**.

N1,N3-di(benzofuran-3-yl)-N1,N3,N5-tris(4-(tert-butyl)phenyl)-N5-(9,9-dimethyl-9H-xanthen-2-yl)benzene-1,3,5-triamine (OX-3)

In a 250 mL round flask, a mixture of O-1 (6.20 g, 9.70 mM), OX-2 (3.47 g, 9.70 mM), Pd(OAc)₂ (0.016 g, 0.097mM), X-Phos (0.043 g, 0.097 mM), t-BuONa (0.93 g, 9.70 mM) and 100 mL xylenes was stirred and refluxed at 160 °C under N₂ atmosphere for 10 h. Then cool down the reaction to room temperature, 200 mL water was added into the mixture and extracted with dichloromethane. The organic solvent was collected and dried by anhydrous MgSO₄. Then the organic solvent was removed with a rotary evaporator, and the resulting precipitate was purified by silica gel column using dichloromethane/petroleum ether (1:4, v/v) as eluant, and then the resulting white solid was obtained (7.26 g, yield: 78%). HRMS (EI/MS) m/z $[M]^+$ calcd for $C_{67}H_{65}N_3O_3$: 959.5; observed: 960.28.

N,5,9-tris(4-(tert-butyl)phenyl)-N-(9,9-dimethyl-9H-xanthen-2-yl)-5H,9H-14,15-dioxa-5,9-diaza-14b-boradiindeno[2,1-a:1',2'-j]phenalen-7-amine (OBN-2)

OX-3 (6.30 g, 6.56 mM) was degassed and purged with N₂ three times and then 120 mL o-DCB was added. BBr₃ (3.28 g, 13.13 mM) was added dropwise into the mixture with stirring at 0 °C in ice-water. After the reaction mixture was stirring at room temperature for 4 h, the reaction mixture was allowed to cool to 0 °C. DIPEA was added into the reaction mixture, and then the reaction mixture was further stirred at 120 °C for 12 h. The reaction mixture was carefully quenched by addition of water

under room temperature. The product was extracted with dichloromethane, and the combined organic solvent was dried by anhydrous MgSO_4 . After evaporation of the solvent, the residue was purified *via* dichloromethane/petroleum ether (1:4, v/v) as eluant, and then the resulting yellow-green solid was obtained (2.47 g, yield: 39%). ^1H NMR (400 MHz, Chloroform- d) δ 7.71 (dt, $J = 8.4, 0.9$ Hz, 2H), 7.53 – 7.45 (m, 4H), 7.39 (dd, $J = 7.9, 1.5$ Hz, 1H), 7.35 – 7.28 (m, 6H), 7.25 (d, $J = 1.6$ Hz, 1H), 7.24 – 7.19 (m, 1H), 7.13 – 7.07 (m, 4H), 7.03 (dd, $J = 8.1, 1.3$ Hz, 1H), 6.97 – 6.83 (m, 5H), 6.83 – 6.76 (m, 2H), 5.88 (d, $J = 8.0$ Hz, 2H), 1.51 (s, 6H), 1.30 (s, 18H), 1.27 (s, 9H). HRMS (EI/MS) m/z $[\text{M}]^+$ calcd for $\text{C}_{67}\text{H}_{62}\text{BN}_3\text{O}_3$: 967.49; observed: 968.06.

Theoretical calculation

The calculations were performed using the Gaussian 16 package based on the density functional theory (DFT) and time-dependent density functional theory (TD-DFT) methods with the b3lyp hybrid functional. All structures were optimized using DFT (S_0 states) or TD-DFT (S_1 states) method with a 6-31G(d,p) basis set. All calculations were performed in the gas phase. The first excited state showed local excitation mainly contributed by the HOMO orbital to the LUMO orbital.

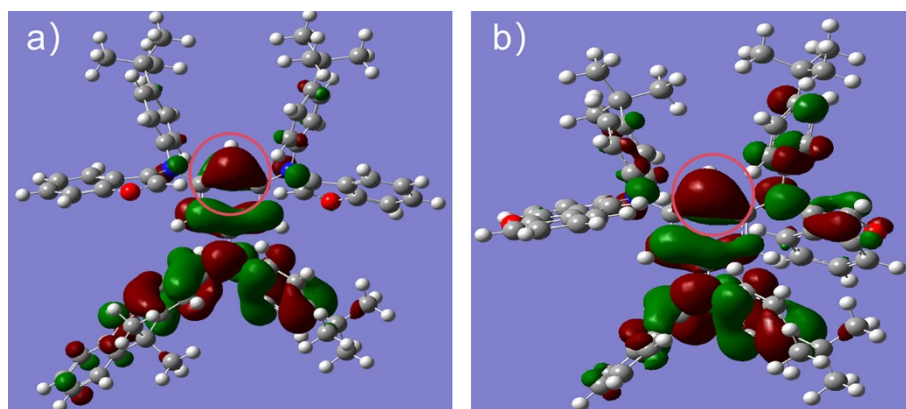


Figure S1. Distributions of highest occupied molecular orbital (HOMO) of (a) O-2, (c) OX-3.

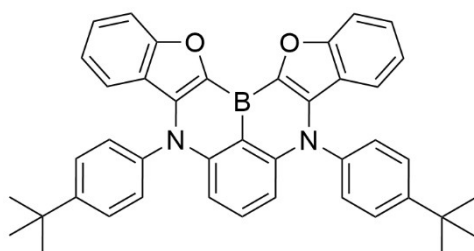


Figure S2. The structure of OBN.

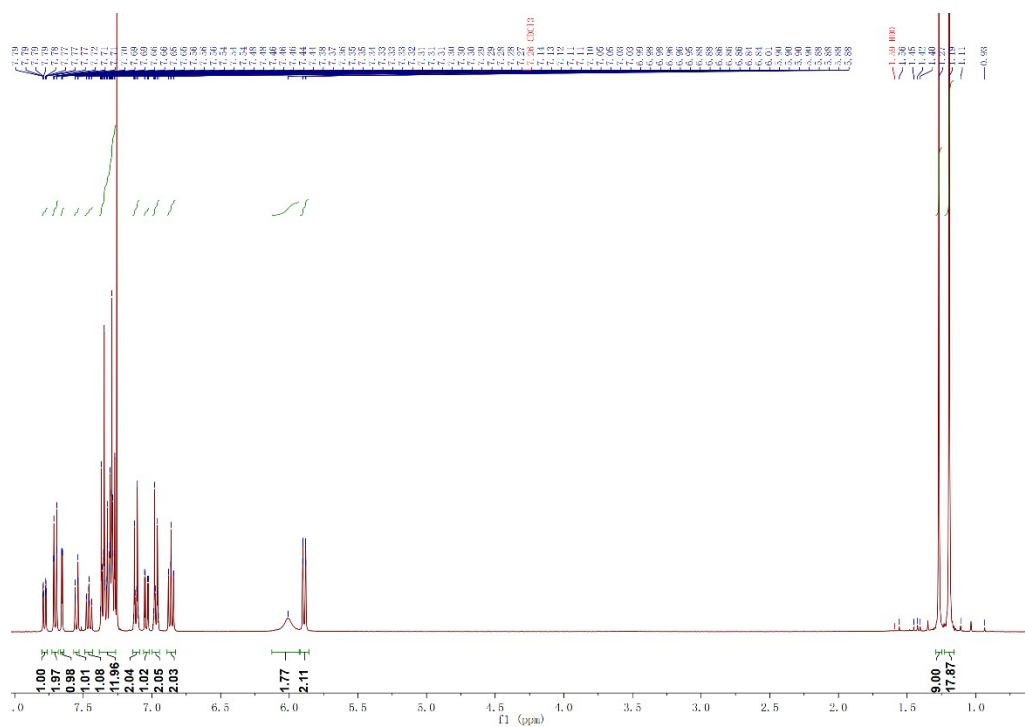


Figure S3. $^1\text{H NMR}$ spectrum of OBN-1 (400 MHz, CDCl_3).

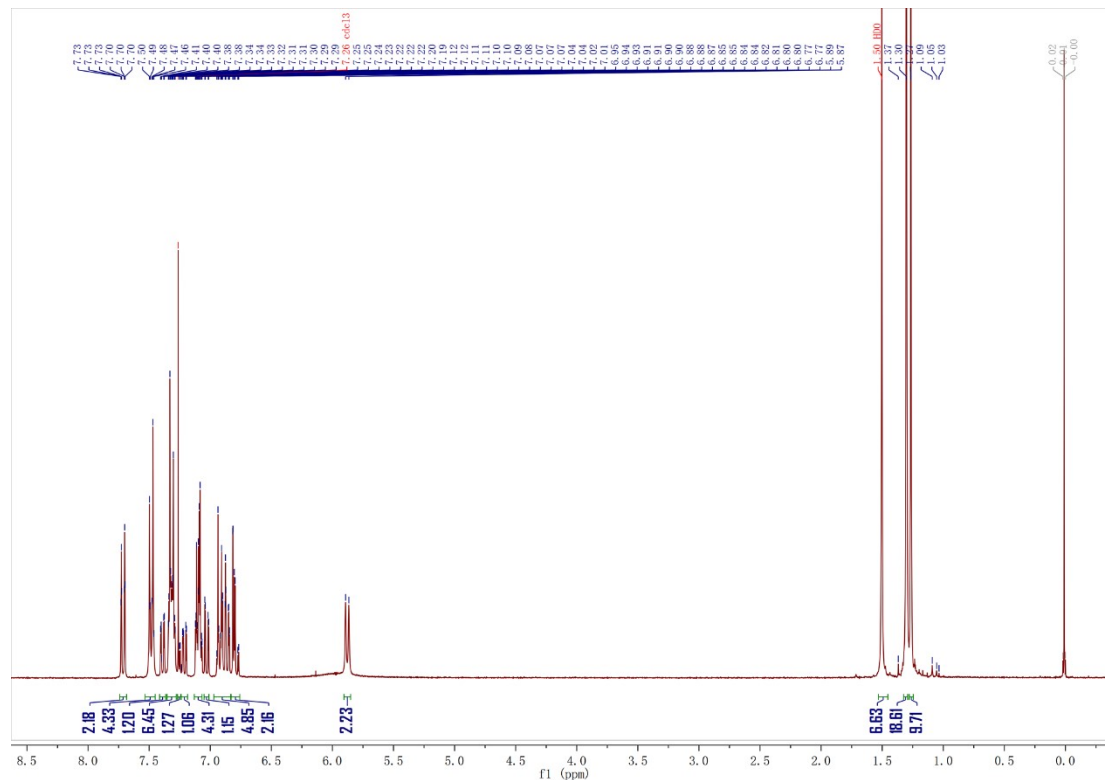


Figure S4. $^1\text{H NMR}$ spectrum of OBN-2 (400 MHz, CDCl_3).

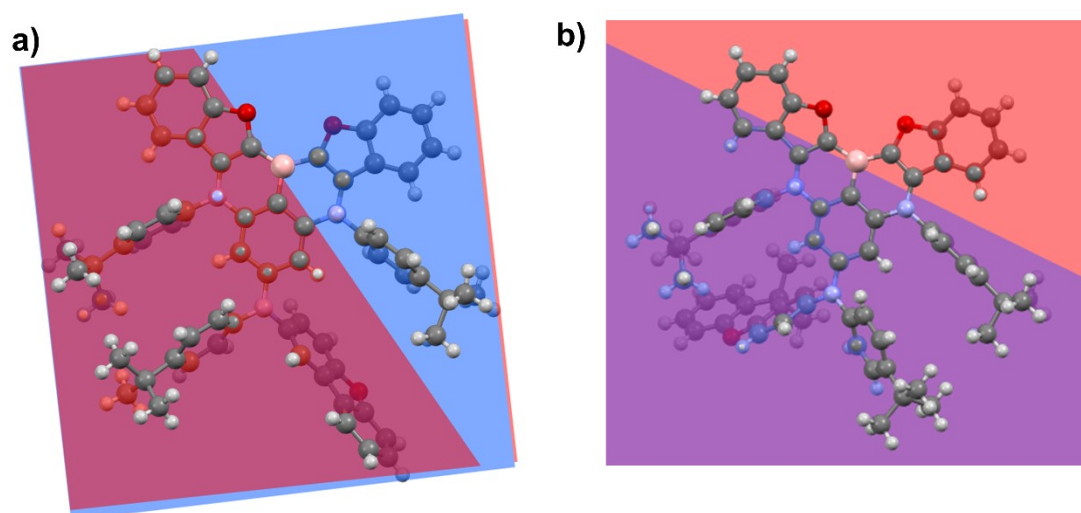


Figure S5. Crystal conformation and their dihedral angles of (a) OBN-1 and (b) OBN-2.

Table S1. Summary of TD-DFT calculation for DABNA-1, OBN-1, and OBN-2 at the S_0 and S_1 geometry at the b3lyp/6-31G(d,p) level.

Optimized structure	HOMO (eV)	LUMO (eV)	wavelength (nm)	Singlet energy (eV)	Triplet energy (eV)	rate constants of fluorescence(K_F)
DABNA-1	4.7538	1.0925	428.60	2.8928	2.6376	5.05×10^7
OBN-1	4.4983	1.0735	453.74	2.7325	2.3189	9.96×10^7
OBN-2	4.5076	1.0857	454.41	2.7285	2.3152	1.01×10^8

Table S2. Correlation between FWHM and variation of ground state and excited state calculated at the b3lyp/6-31G(d,p) level.

Compound	FWHM ^a (nm)	FWHM ^b (nm)	ΔE ^c (eV)	RMSD ^d
DABNA-1	26	28	0.2370	0.098
OBN-1	25	46	0.2592	0.140
OBN-2	24	23	0.2627	0.199

^a Full width at half maximum (nm) of PL spectra in DCM solution at 298 K. ^b Full width at half maximum (nm) of EL spectra. ^c $\Delta E = E(S_1 \leftarrow S_0) - E(S_1 \leftarrow S_1)$ which represents the recombination energy from the excited state S_1 to the ground state S_0 . ^d Root mean square displacement of optimized S_1 and S_0 structures, the formula is shown below.

$$RMSD = \sqrt{\frac{1}{N} \sum_i^{atom} [(x_i - x_i')^2 + (y_i - y_i')^2 + (z_i - z_i')^2]}$$

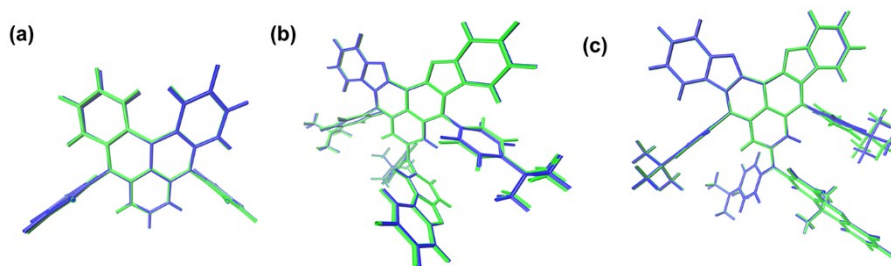


Figure S6. Comparison of the optimized structures of (a) DABNA-1, (b) OBN-1, and (c) OBN-2 in the S_0 (blue) and S_1 (green) states.

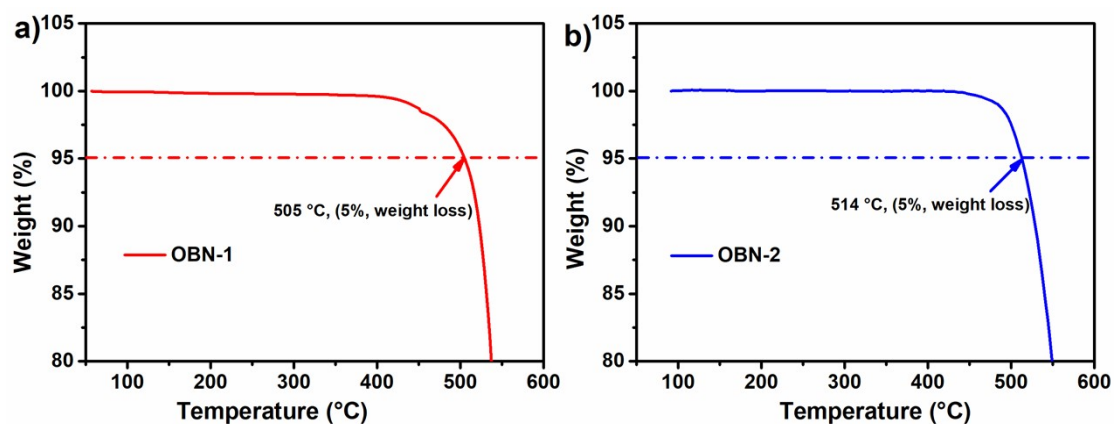


Figure S7. Decomposition temperature (T_d) of (a) OBN-1, and (b) OBN-2.

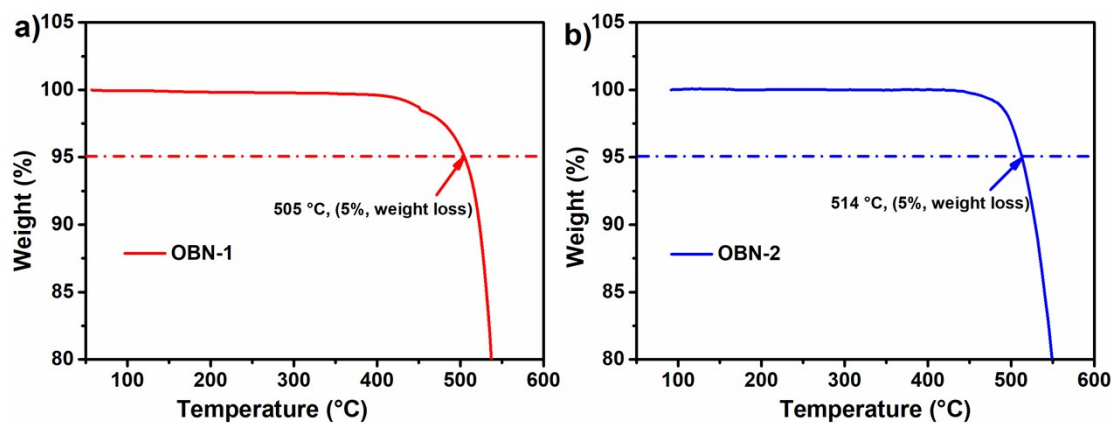


Figure S8. DSC curves of (a) OBN-1, (b) OBN-2.

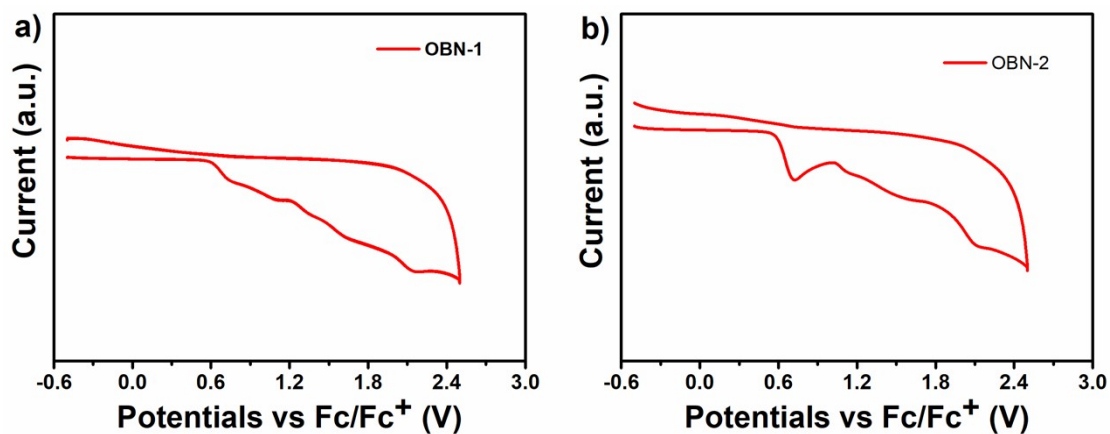


Figure S9. Cyclic voltammety data for the oxidation of (a) OBN-1 and (b) OBN-2.

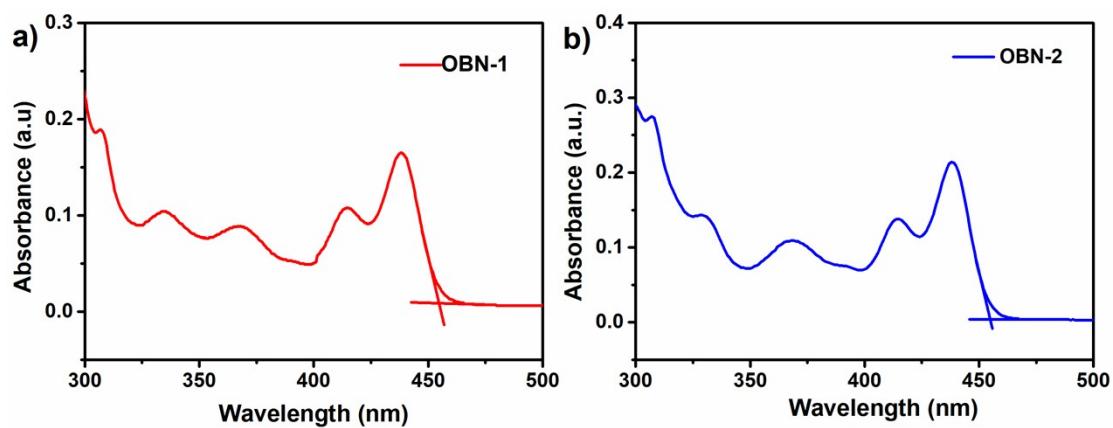


Figure S10. The absorbance (UV) spectra of (a) OBN-1, (b) OBN-2 and their absorption onset in DCM solution.

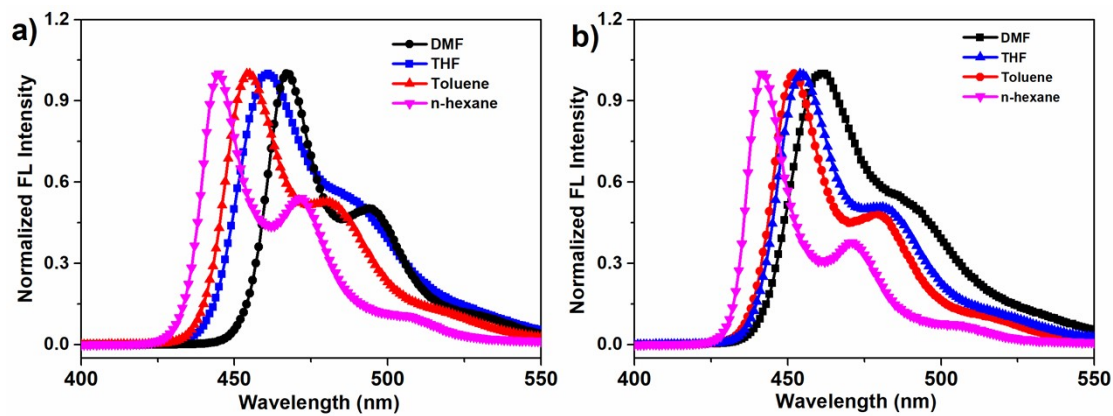


Figure S11. Normalized fluorescence spectra in different solvent (1×10^{-5} M) of (a) OBN-1 and (b) OBN-2.

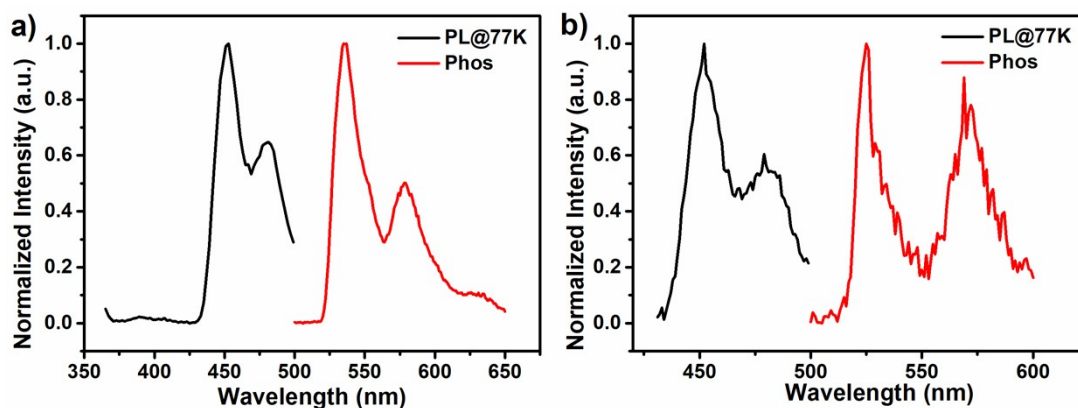


Figure S12. Normalized fluorescence and phosphorescence spectra in toluene solution (1×10^{-5} M, 77 K) of (a) OBN-1 and (b) OBN-2.

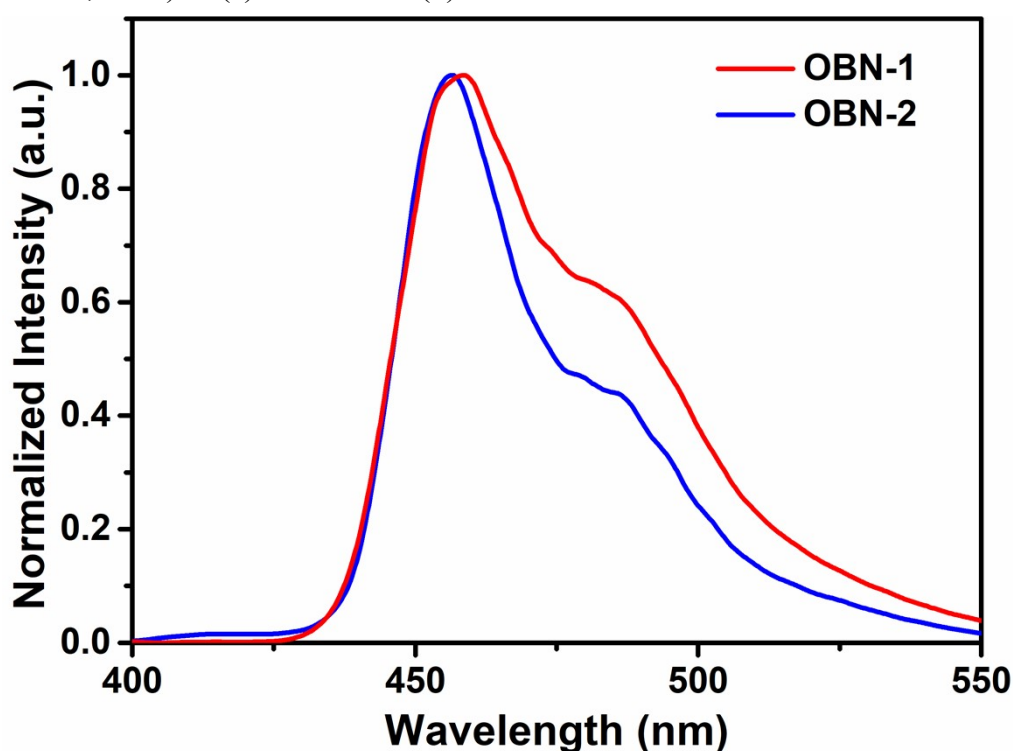


Figure S13. Normalized fluorescence spectra of 3 %wt of DBANA-1, OBN-1, and OBN-2 doped in FBH films.

Device Fabrication and Measurements

The indium tin oxide (ITO) glass substrates with a sheet resistance of $15 \Omega / \text{sq}$ a thickness of 135 nm were cleaned in ultrasonic baths with optical detergent, deionized water, acetone and isopropanol successively. Then ITO glass substrates were dried in a convection oven at $120 \text{ }^\circ\text{C}$ for 10 min. After treated with plasma for 5 minutes, ITO glass substrates were transferred to a vacuum chamber. Then the organic layers were deposited onto the ITO glass substrates with designed shadow mask at a rate of 1.0 \AA

s⁻¹ under high vacuum ($<8 \times 10^{-5}$ Pa) with O₂ and H₂O at a sparse concentration below 1 ppm. After depositing organic materials, Ag were successively evaporated at a rate of 5.0 Å s⁻¹. The mask make an active layer of 2 × 2 mm². The deposition rates were monitored *via* a quartz crystal monitor. The OLED measurement modules were encapsulated using a capping glass. The getter was attached under the glass cap in the encapsulated device.

The EL spectrum, luminance intensity as well as CIE coordinate of the OLEDs were evaluated through Photo Research PR-670 at room temperature (298 K) in an air atmosphere. And the external quantum efficiency (EQE) was estimated in terms of brightness according to assuming Lambertian distribution. The current-voltage-luminance (J-V-L) characteristics were recorded on a Keithley 2400 semiconductor characterization system calibrated by a silicon photodiode. The lifetime was measured using lifetime tester (Polaronix M6000). All measurements were carried out under argon conditions at room temperature.

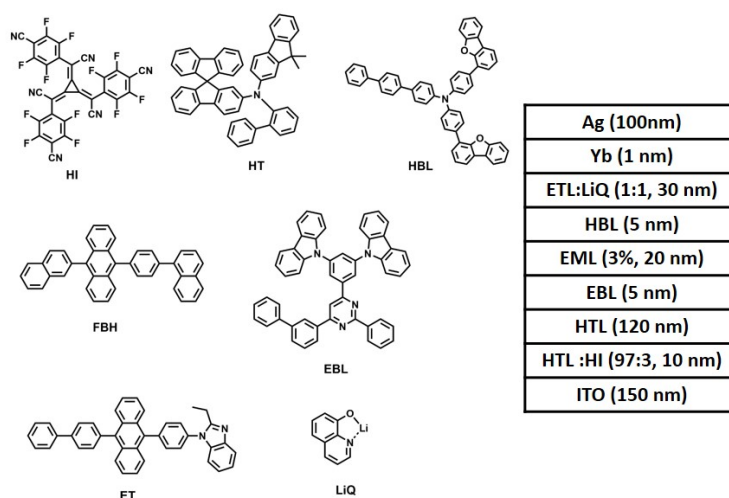


Figure S14. Molecular structures, and device structures and thickness of bottom device.

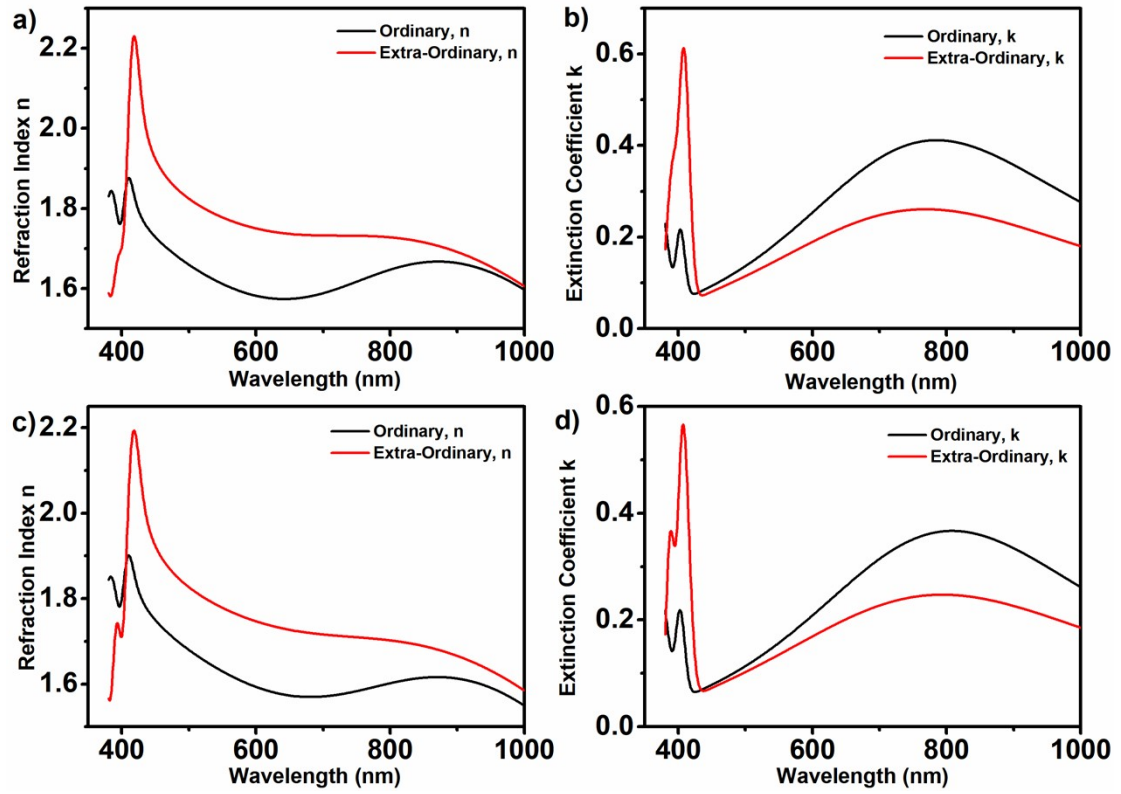


Figure S15. Ordinary (horizontal direction) and extraordinary (vertical direction) (a, c) refractive indices and (b, d) extinction coefficients of OBN-1 (a, b) and OBN-2 (c, d) doped film.