Supporting Information

for

Organoboron Emitters with Narrowband Thermally Activated Delayed Fluorescence for Doped Organic Light Emitting Diodes

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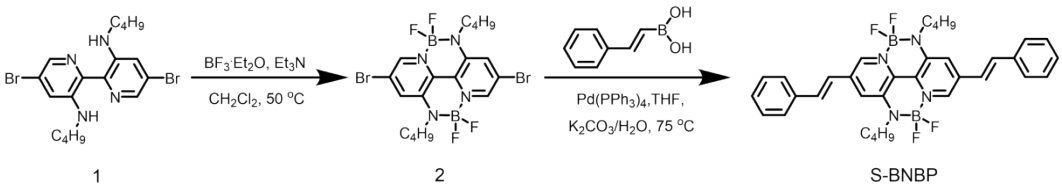
1. Materials and Characterization

Materials and reagents: All reactions were performed under an N_2 atmosphere unless otherwise specified. All reagents and solvents were used as received from commercial resources without further purification, unless otherwise specified. Dichloromethane (DCM) and tetrahydrofuran (THF) used in the reactions were freshly distilled using appropriate drying reagents. Material 1 was prepared according to the methods described in a previous article. The materials investigated in this paper were synthesized according to the procedures described below.



Scheme 1. Synthetic route of S-BNBP.

Synthesis of Dibromo-substituted BNBP (Compound 2): Under nitrogen atmosphere, a solution of $BF_3{\cdot}Et_2O$ (1.3 mL, 20 eq) and Et_3N (0.7 mL, 10 eq) were alternately added to the solution of compound 1 (200 mg, 1 eq) in dry CH_2Cl_2 (15 mL). The reaction mixture was stirred at 50 °C for 2 h with the color changing from yellow to orange. After the reaction, the mixture was extracted and dried. The resulting orange solid was purified by column chromatography on silica gel (DCM/PE = 2/1) as the eluent. The intermediate compound 2 was obtained as an orange-red solid in 91% yield (143 mg, 0.26 mmol).

Synthesis of S-BNBP: The materials of 2 (100 mg, 1 eq), styrylboronic acid (67.3 mg, 2.5 eq) and $Pd(PPh_3)_4$ (30 mg, 0.15 eq) were added to a 100 ml two-necked flask under nitrogen, then anhydrous and oxygen-free THF was added and stirred at 75 °C. K_2CO_3 aqueous solution (0.5 mol/L, 1.1 ml, 3 eq) was added and stirred at 75 °C for 24 h. After extraction with water and DCM, the mixture was dried with anhydrous $MgSO_4$ and purified by column chromatography on silica gel (CH_2Cl_2/PE =2/1). S-BNBP was obtained as a red solid in 78% yield (81 mg, 0.14 mmol). Elemental analysis: C, 68.26; H, 6.07; B, 3.61; F, 12.70; N, 9.36.

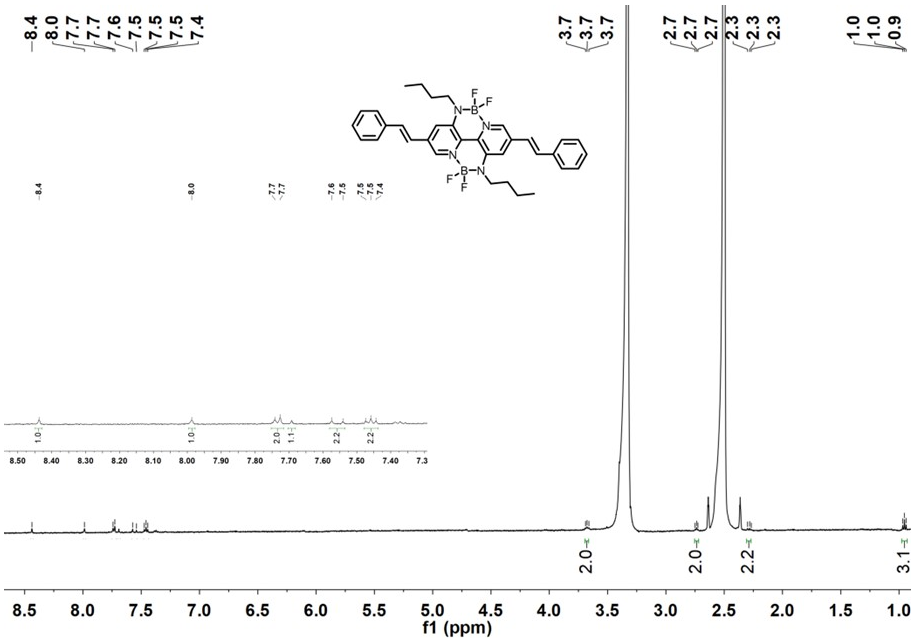


Fig. S1 ^{1}H NMR spectrum of S-BNBP.

Characterization. UV-vis absorption spectra were measured using Shimadzu UV-3600 and UV-9000s spectrometer. Fluorescence spectra were measured using a Hitachi F-7000 spectrometer. Fluorescence quantum yields and fluorescence lifetimes were determined with an Edinburgh FLS1000 steady state fluorimeter equipped with an integrating sphere. CV was performed with a CHI660C electrochemistry station using Bu_4NPF_6 (0.1 M) as electrolyte, and using Pt as working electrode, platinum wire as auxiliary electrode, and a porous glass wick Ag/AgCl as reference electrode. Single crystal data was obtained by using a Rigaku XtaLAB Synergy. TEM images and the SAED patterns were obtained by JEOL JEM-2100. Powder X-ray diffraction (PXRD) were measured by a D/max 2400 X-ray diffractometer with Cu Kα radiation (λ = 1.54050 Å) operated in the 2θ range from 5° to 50°. Using a homemade micro-PL system for micro-area PL spectral analysis of S-BNBP, i.e. laser confocal scanning microscope (Leica, TCS-SP5) equipped with a UV4 laser (420nm).

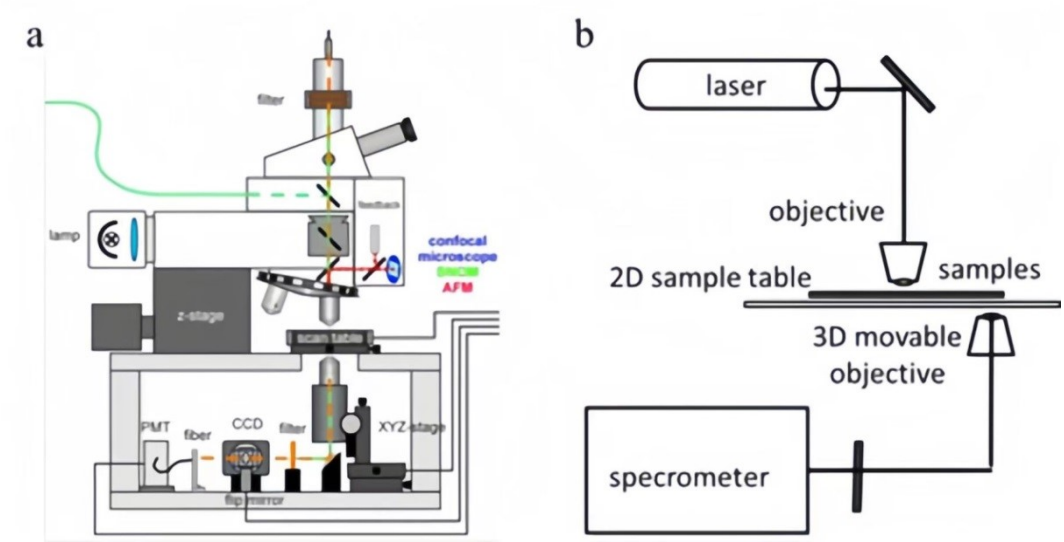


Fig. S2 Schematic illustration of (a) the near-field scanning optical microscopy and (b) the transmittance optical path for the waveguide measurements.

2. X-ray crystal data

Single crystal of $C_{34}H_{36}B_2F_4N_4$ was collected. A suitable crystal was selected and GaKα on a diffractometer. The crystal was kept at 170.00 K during data collection. Using Olex2, the structure was solved with the SHELXT structure solution program using Intrinsic Phasing and refined with the SHELXL refinement package using Least Squares minimisation. CCDC number of 2365183 (S-BNBP) contain the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www. ccdc.cam.ac.uk/structures/.

X-ray crystallographic analysis of S-BNBP. The single crystals all suitable for XRD analysis were grown by recrystallization in toluene at high temperature. Crystal Data for S-BNBP are shown in Table S1.

Table S1. Crystal data for S-BNBP crystal.

Parameters	S-BNBP (CCDC no. 2365183)
Empirical formula	$C_{34}H_{36}B_2F_4N_4$
Formula weight	598.29
Temperature/K	170.00
Crystal system	Triclinic
Space group	P-1
Cell Lengths (Å)	a = 6.2488 (9) Å b =8.9759(12) Å c = 14.662(2) Å
Cell Angles (°)	a = 72.625(5)° b = 79.192(5)° c = 71.413(4)°
Volume	740.04(18) $Å^3$
Z	1
Density (calculated)	1.342 g/cm^3
Absorption coefficient	0.504 mm^{-1}
F(000)	314.0
Crystal size/mm^3	0.19 × 0.04 × 0.02
2θ range for data collection/°	5.524 to 121.598
Index ranges	$-8 \le h \le 8$ $-11 \le k \le 9$ $-18 \le l \le 18$
Reflections collected	10649
Independent reflections	3356 [R_{int} = 0.0563, R_{sigma} = 0.0699]
Data/restraints/ parameters	356/0/200
Goodness-of-fit on F^2	1.092
Final R indexes [I>=2σ (I)]	R_1 = 0.0695, wR_2 = 0.1878
Final R indexes [all data]	R_1 = 0.0865, wR_2 = 0.2013
Largest diff. peak and hole	0.60/-0.34 $Å^{-3}$

3. Absorption and PL spectra

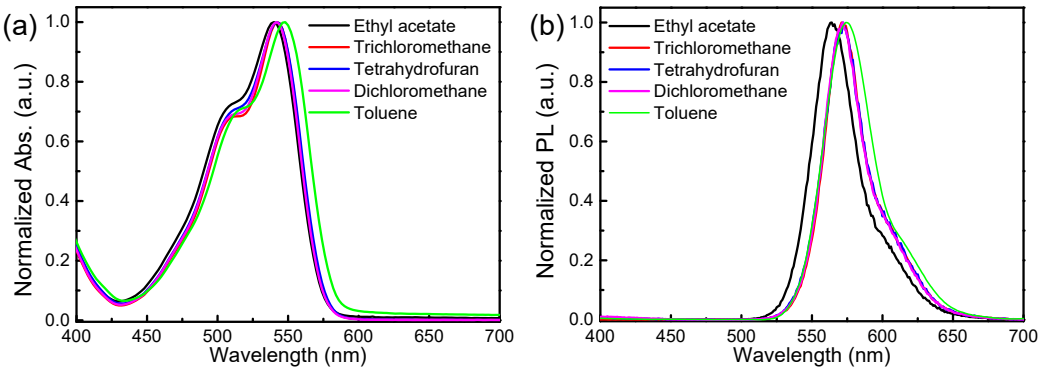


Fig. S3 (a) The absorption and (b) PL spectra of S-BNBP in the different solvents.

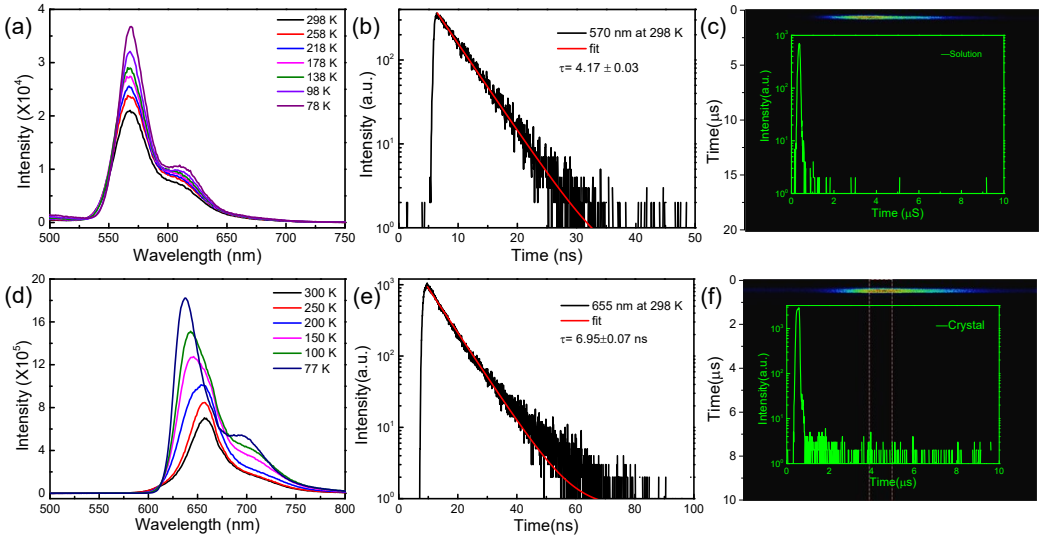


Fig. S4 (a, d) PL spectra at different temperatures, (b, e) fluorescence lifetimes and (c, f) Streak camera images for S-BNBP (a, b, c) in solution and (d, e, f) microsheets.

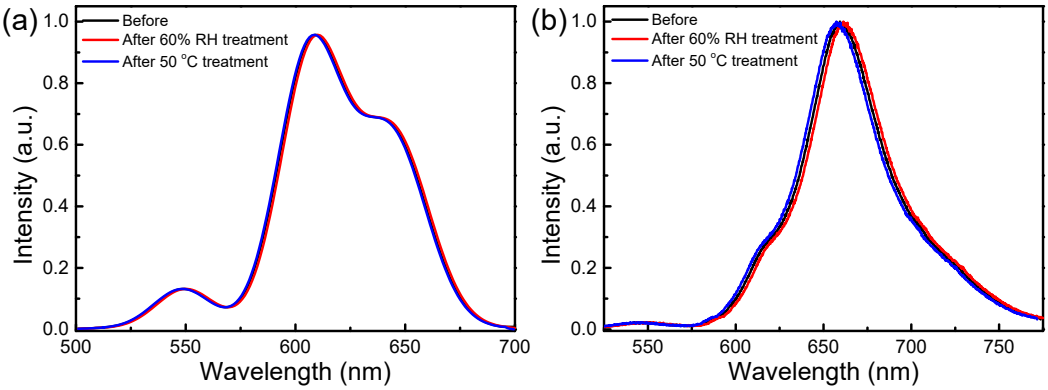


Fig. S5 The PL spectra of (a) thin films and (b) microsheets before and after treatments.

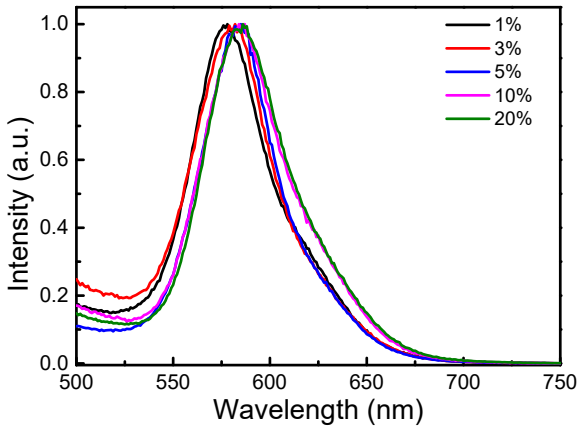


Fig. S6 PL spectra of CBP blend doped with S-BNBP at different doping concentrations.

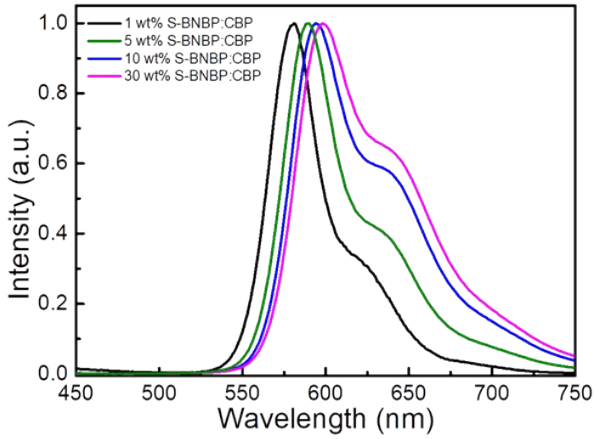


Fig. S7 PL spectra of x wt% S-BNBP:CBP (x=1, 5, 10, 30) doped films.

Note S1. Estimation of the energy difference between the S_1 and T_1 states (ΔE_{ST}) of the 1 wt% S-BNBP/CBP doping film.

The values are determined from PLQY and the lifetimes of the fluorescence and TADF components. Φ_F and Φ_{DF} are calculated by their ratios of the integral areas in the time-resolved spectrum in Fig. S5. Both the prompt and delayed components exhibit biexponential decays, these can be attribute to the coexist of the monomer and dimer in the doping film, so τ_F and τ_{DF} are the average lifetime of the prompt and delayed components, they are calculated by $\tau_{av} = \sum A_i\tau_i^2 / \sum A_i\tau_i$, where A_i is the pre-exponential for lifetime τ_i (A_i is the proportion of τ_i here).

$\Phi = 0.186$

$\Phi_F = 0.181$

$\Phi_{DF} = 0.005$

$\tau_F = 3.75$ ns

$\tau_{DF} = 0.155$ μs

$k_F = 4.83\times10^7$ s^{-1} $\quad k_F = \Phi_F / \tau_F$ (1)

$k_{IC} = 2.11\times10^8$ s^{-1} $\quad \Phi = k_F / (k_F + k_{IC})$ (2)

$k_{ISC} = 7.70\times10^6$ s^{-1} $\quad \Phi_F = k_F / (k_F + k_{IC} + k_{ISC})$ (3)

$\Phi_{IC} = 0.790$ $\quad \Phi_{IC} = k_{IC} / (k_F + k_{IC} + k_{ISC})$ (4)

$\Phi_{ISC} = 0.029$ $\quad \Phi_{ISC} = 1-\Phi_{IC} - \Phi_F = k_{ISC} / (k_F + k_{IC} + k_{ISC})$ (5)

$k_{DF} = 1.11\times10^6$ s^{-1} $\quad k_{DF} = \Phi_{DF} / \Phi_{ISC}\, \tau_{DF}$ (6)

$\Delta E_{ST} = 0.066$ eV $\quad k_{DF} = 1/3(kFexp\ (-\Delta E_{ST}/RT))$ (7)

$k_{RISC} = 1.32\times10^6$ s^{-1} $\quad k_{RISC} = k_F\, k_{DF} / (k_F - k_{ISC})$ (8)

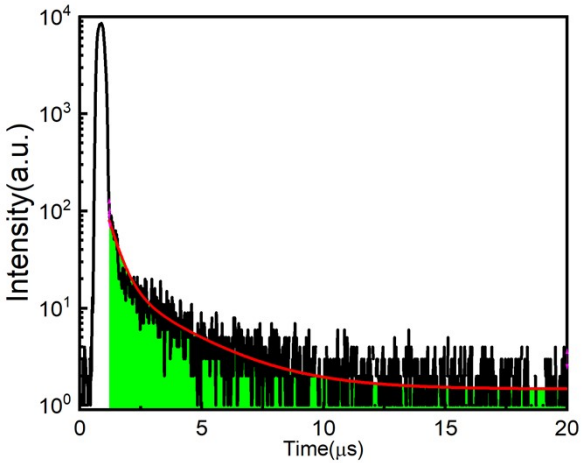


Fig. S8 Transient decay spectra of 1 wt% S-BNBP/CBP thin film at 298 K.

4. Cyclic voltammetry measurement

Cyclic voltammetry (CV) was performed with a CHI660C electrochemistry station using Bu_4NPF_6 (0.1 M) as electrolyte, and using Pt as working electrode, platinum wire as auxiliary electrode, and a porous glass wick Ag/AgCl as reference electrode. The HOMO energy level (E_{HOMO}) and the LUMO energy level (E_{LUMO}) can be calculated by the following formula:

$$E_{HOMO} = -(4.80 + E_{onset}^{ox}),$$

$$E_{LUMO} = -(4.80 + E_{onset}^{red}).$$

Table S2. Performance of boron-based red TADF OLEDs

Device	V_{on} (V)	L_{max}(cd/m^2)	EQE_{max} (%)	λ_{max} (nm)	CIE (x, y)	FWHM (nm)	Reference
Px-CNP	5.5	101860	3	606	(0.53, 0.44)	>100	1
DMAC2oDBA	3.4	10000	10.1	615	(0.59, 0.40)	72	2
$Ir(btp)_2acac$	3.9	1044	3.82	618	(0.67, 0.32)	>100	3
$Ir(btp)_2acac$: tBuPZ	3.2	847.2	4.11	618	(0.63, 0.33)	>100	3
$Ir(btp)_2acac$:PZ	3.0	932.3	3.92	618	(0.63, 0.34)	>100	3
dPhADBA	3.5	-	11.1	613	(0.60, 0.39)	102	4
dmAcDBA	3.2	-	24.9	583	(0.51, 0.48)	98	4
SpAcDBA	3.0	-	30.0	567	(0.46, 0.52)	96	4
NF-R	4.7	586	0.28	632	(0.64, 0.36)	-	5
NF-S	4.6	554	0.25	632	(0.64, 0.36)	-	5
D-R	4.0	1055	2.0	598	(0.57, 0.43)	-	5
D-S	4.0	1008	2.0	600	(0.57, 0.42)	-	5
5 wt% S-BNBP:CBP	3.2	9528	2.81	590	(0.58, 0.41)	42	This work

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