Electronic Supplementary Information

Boosting Photoluminescence Quantum Yields of Triarylboron/Phenoxazine Hybrids *via* Incorporation of Cyano Groups and Their Applications as TADF Emitters for High-Performance Solution-Processed OLEDs

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General information

All the reagents and solvents used for the synthesis or measurements were commercially available and used as received unless otherwise stated. The ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AVANCE III 400 MHz spectrometer with $CDCl_3$ as the solvent and tetramethylsilane as an internal reference. EI mass spectra were determined by a ZAB 3F-HF mass spectrophotometer. Cyclic voltammetry (CV) was carried out in nitrogen-purged dichloromethane (oxidation scan) at room temperature with a CHI voltammetric analyzer. n-Bu_4PF_6 (0.1 M) was used as the supporting electrolyte. The conventional three-electrode configuration consists of a platinum working electrode, a platinum wire auxiliary electrode, and an Ag wire pseudo-reference electrode with ferrocene (Fc/Fc^+) as the internal standard. The HOMO energy levels (eV) of the compounds were calculated according to the formula: $-[4.8+(E_{\mathrm{onset}}-E_{1/2(\mathrm{Fc/Fc}^+)})]$ eV. Thermogravimetric Analysis (TGA) was performed on a NETZSCH STA 449C unit at a heating rate of 10 °C min^{-1} from 25 to 650 °C under argon. Differential scanning calorimetry (DSC) was performed with a METTLER TOLEDO DSC 3 unit at a heating rate of 20 °C min^{-1} from 25 to 220 °C under argon. The glass transition temperature (T_g) was determined from the second heating scan at a heating rate of 10 °C min^{-1}. UV-vis absorption spectra were recorded on a Shimadzu UV-2700 recording spectrophotometer. Photoluminescence (PL) spectra were recorded on a Hitachi F-4600 fluorescence spectrophotometer. The PL lifetimes were measured by a single photon counting spectrometer from Edinburgh Instruments (FLS920) with a Picosecond Pulsed UV-LASTER (LASTER377) as the excitation source. The photoluminescence quantum efficiencies were measured using an absolute photoluminescence quantum yield measurement system (C9920-02, Hamamatsu Photonics).

Device fabrication and characterization

The ITO substrates were degreased in acetone and ethanol consecutively in an ultrasonic bath before UV-ozone treatment for 10 minutes. A layer of 30 nm thick PEDOT:PSS was spin-coated onto the ITO substrate and then baked at 120 °C for 10 minutes. Another baking at 100 °C for 10 minutes was conducted after spin-coating of the emitting layer. A layer of TmPyPB, served as the electron transporting layer, was thermally deposited onto the emitting layer. After the evaporation of the composite Liq/Al cathode, the devices were encapsulated with UV-curable resin. The current-voltage-luminance characteristics and the EL spectra were measured simultaneously by a customized software controlling a PR735 spectrometer and a Keithley 2400 source measurement unit. The power efficiency and the external quantum efficiency were calculated by assuming a Lambertion emission profile.

Computation details

Quantum chemical calculations were performed with the hybrid DFT functional Becke and Hartree-Fock exchange and Lee Yang and Parr correlation (B3LYP) using the Gaussian 09 program packages. The ground state molecular structures were optimized at the B3LYP/6-31g(d) level of theory.

Table S1. Values from DFT calculation.

Compound	α[a] (°)	HOMO (eV)	LUMO (eV)	S_1 (eV)	T_1 (eV)	ΔE_{ST} (eV)
TP-1PXZ2CN	83.6	-4.54	-1.58	2.92	2.91	0.005
TP-2PXZ1CN	86.5	-4.61	-1.78	2.78	2.78	0.004

[a] Dihedral angles of phenyl plane and adjacent phenoxazine plane.

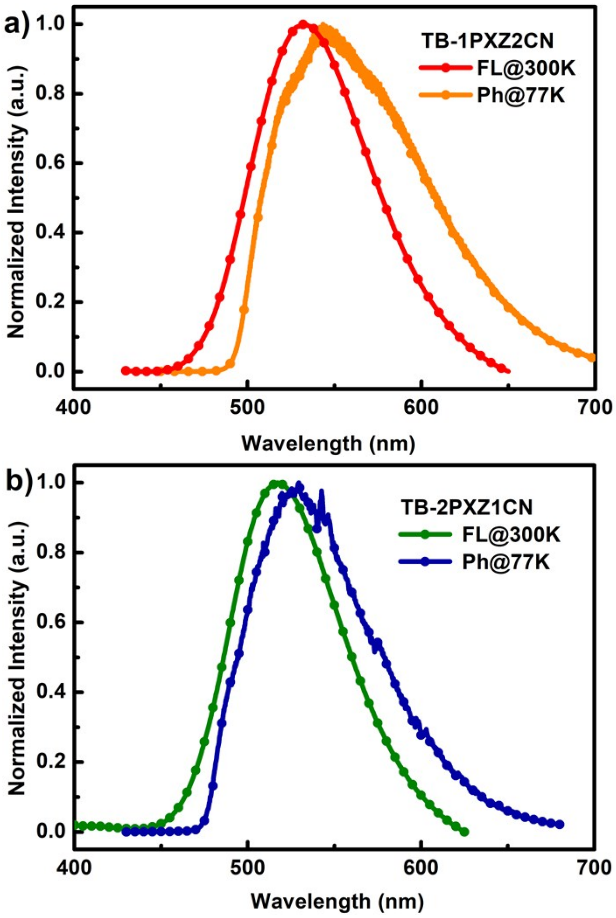


Fig. S1. The fluorescence (300 K) and phosphorescence (77 K) spectra of TB-1PXZ2CN and TB-2PXZ1CN doped in CzSi films (10 wt.%), respectively.

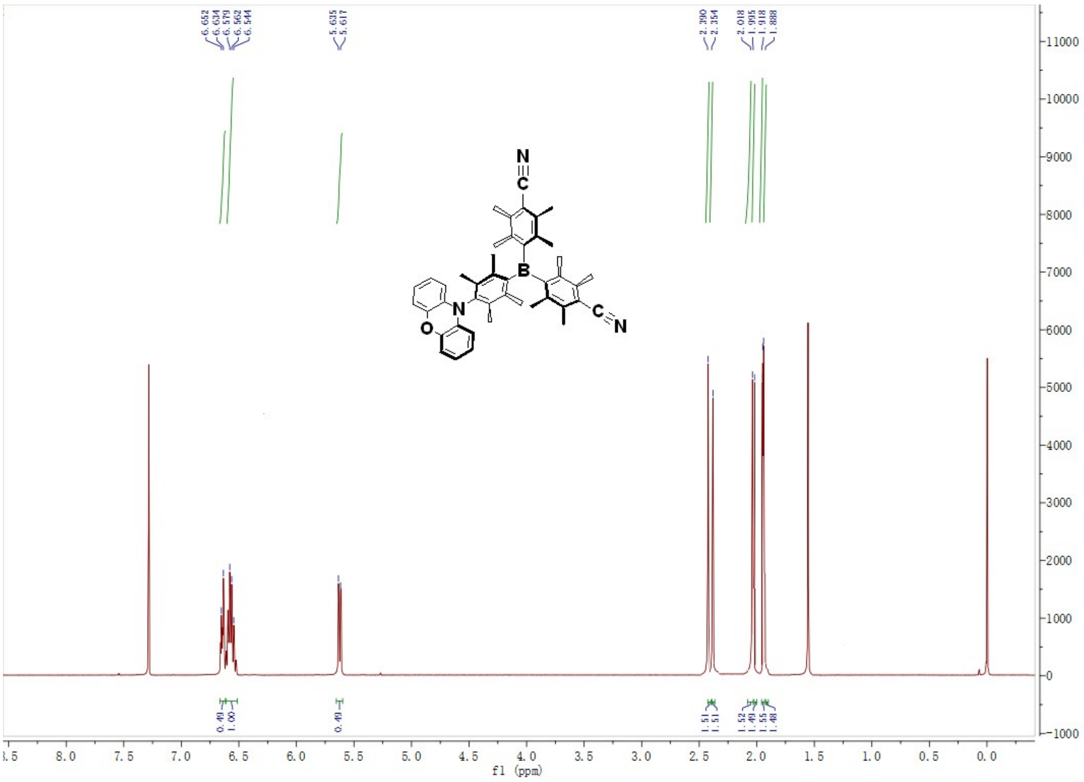


Fig. S2. ^{1}H NMR spectra of TB-1PXZ2CN.

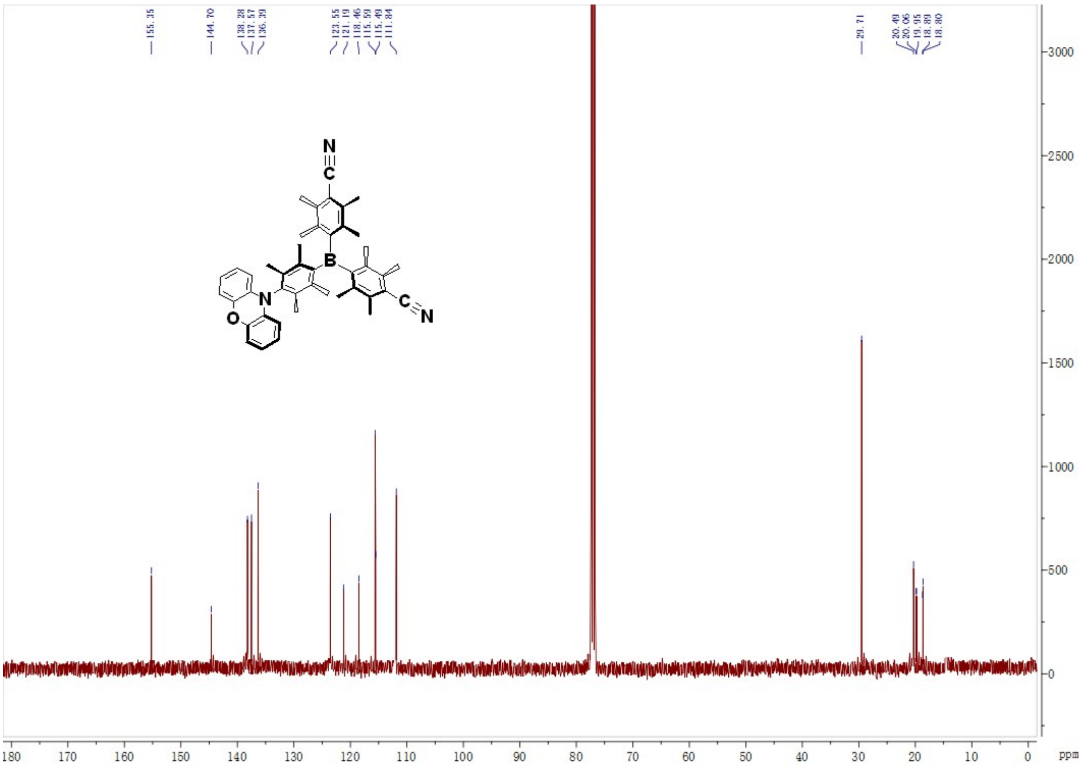


Fig. S3. ^{13}C NMR spectra of TB-1PXZ2CN.

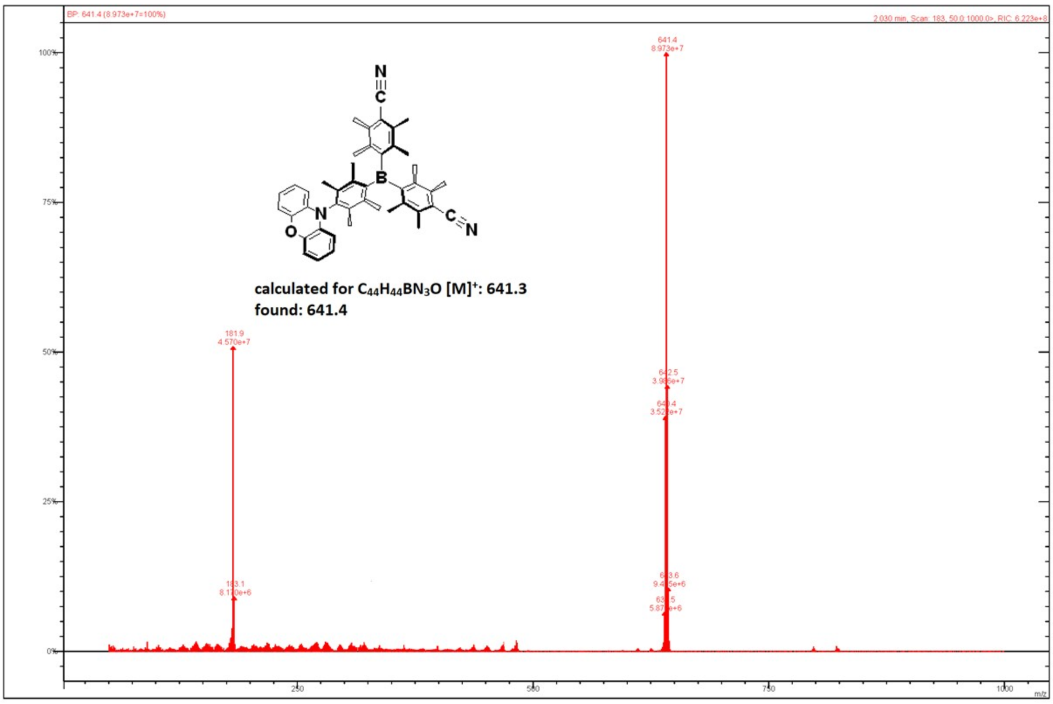


Fig. S4. Mass spectra of TB-1PXZ2CN.

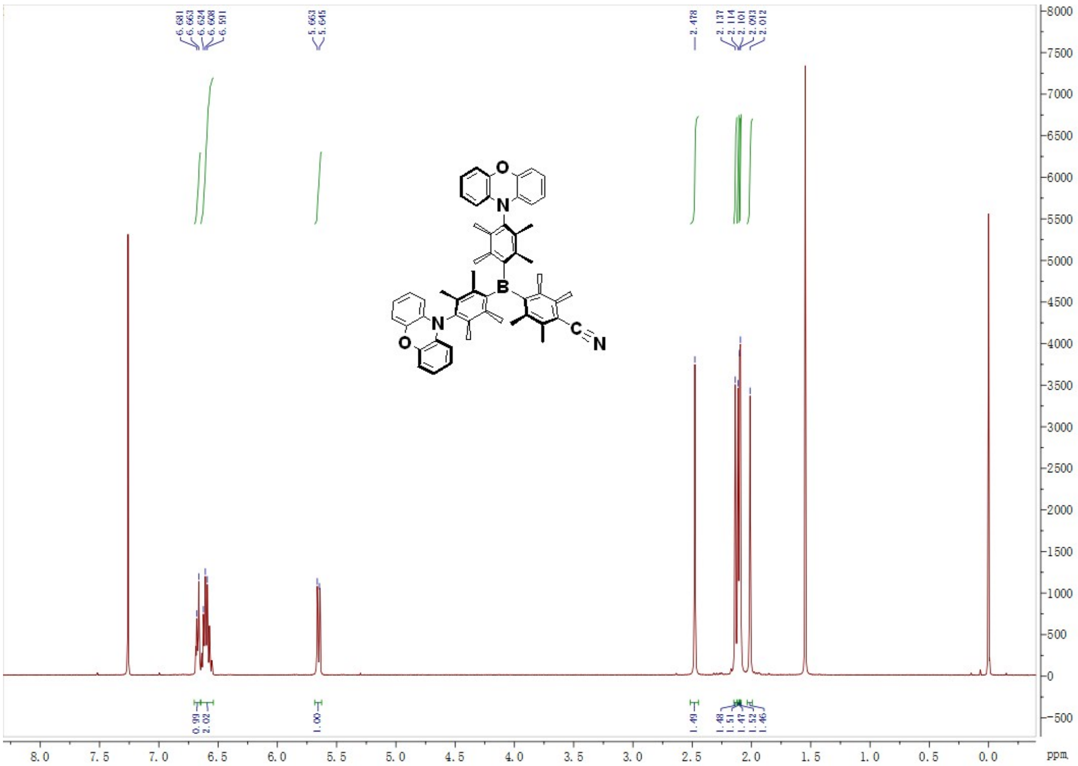


Fig. S5. ^{1}H NMR spectra of TB-2PXZ1CN.

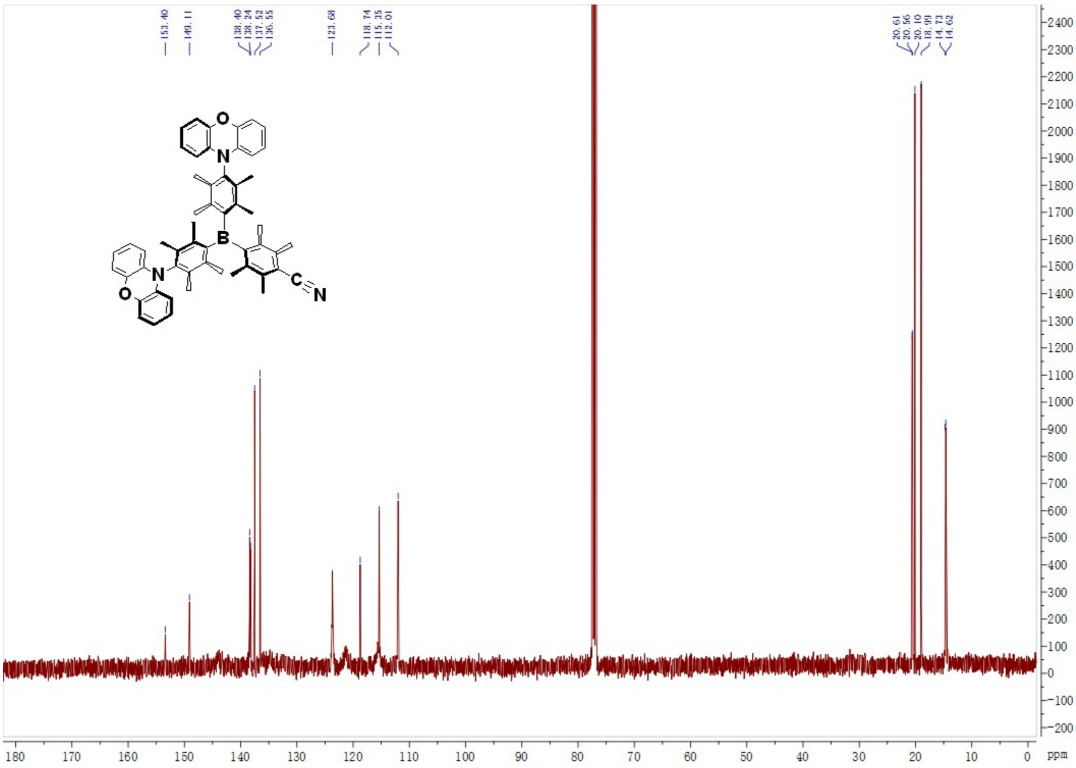
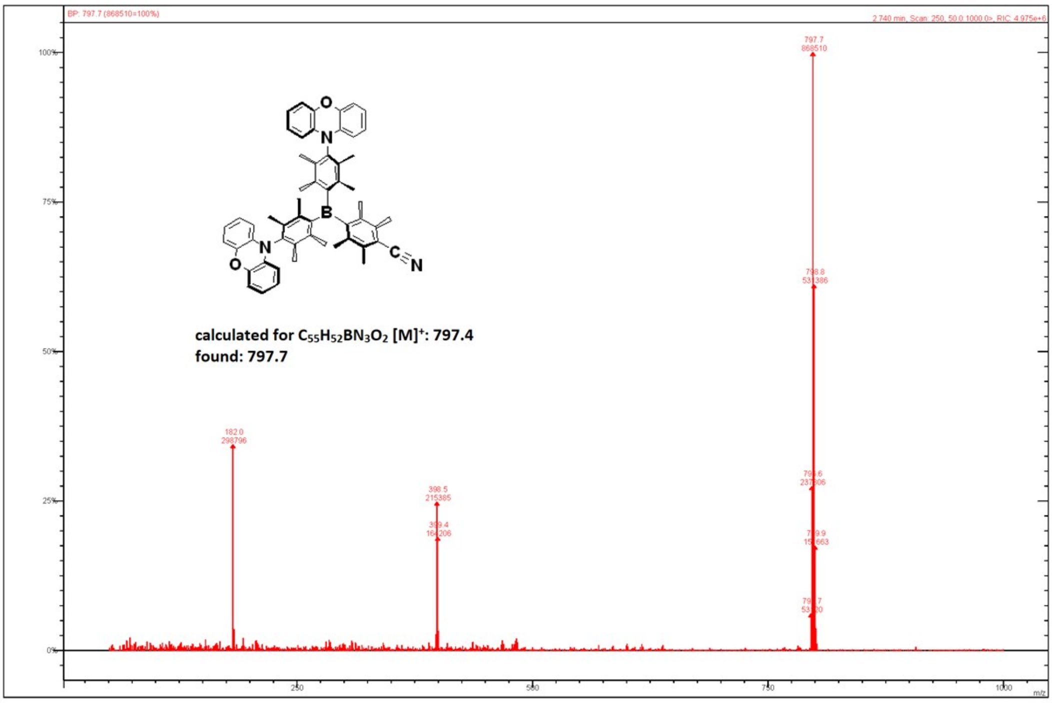


Fig. S6. ^{13}C NMR spectra of TB-2PXZ1CN.



calculated for $C_{55}H_{52}BN_3O_2$ $[M]^+$: 797.4
found: 797.7

Fig. S7. Mass spectra of TB-2PXZ1CN.