

Supporting Information

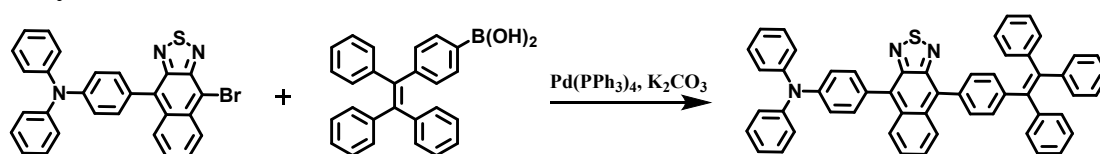
Precise Modulation of Triplet State Distribution for High-Efficiency Non-Doped Standard Saturated Red OLEDs

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1. General information

All the chemical agents were purchased from commercial sources and directly used without further purification. The end-products were further purified by vacuum sublimation for the investigation of photoluminescence (PL) and electroluminescence (EL) properties. ¹H and ¹³C NMR spectra were measured on a Bruker AV 500 spectrometer in CDCl₃ and CD₂Cl₂ at room temperature. UV-vis absorption spectrum was measured on a Shimadzu UV-2600 spectrophotometer. PL spectra were recorded on a Horiba Fluoromax-4 spectrofluorometer. Fluorescence quantum yields were measured using a Hamamatsu absolute PL quantum yield spectrometer C11347 Quantaaurus_QY. Cyclic voltammogram was measured in a solution of tetra-n-butylammonium hexafluorophosphate (Bu₄NPF₆, 0.1 M) in dichloromethane and dimethyl formide containing the sample at a scan rate of 100 mV s⁻¹. Three-electrode system (Ag/Ag⁺, platinum wire and glassy carbon electrode as reference, counter and work electrode respectively) was used in the CV method. HOMO = -[E_{ox} + 4.8] eV, and LUMO = -[E_{re} + 4.8] eV. E_{ox} and E_{red} represent the onset oxidation and reduction potentials relative to Fe/Fe⁺. The optimal ground structure and natural transition orbitals (NTOs) were calculated using the density function theory (DFT) and time-dependent density function theory (TD-DFT) method with M06-2X at the basis set level of 6-31G (d,p). All the calculations were performed using Gaussian 09 package.

2. Synthesis and characterization



Scheme S1 Synthetic route of TNZTPE.

TNZBr (2 mmol, 1.1g), TPEB(OH)₂ (3 mmol, 1.1 g), Pd(PPh₃)₄ (0.05 mmol, 59 mg) were put into two-neck flask. The flask maintains N₂ atmosphere by pumping and filling in with N₂ for three times. Toluene (45 mL) and K₂CO₃ aqueous solution (2 M, 12 mL) were injected into the flask. The reaction carried out at 110 °C for one night. After the mixture was cooled down, the mixture was extracted with DCM for three times. The pure product was received by chromatography using ethyl acetate/petroleum as the eluent to afford a red powder (1.26 g), yield: 83%: ¹H NMR (500 MHz, CD₂Cl₂) δ = 8.04 (d, 1H), 7.80-7.78 (d, 1H), 7.45-7.43 (d, 2H), 7.32-7.24 (m, 33H). ¹³C NMR (126 MHz, CD₂Cl₂), δ = 152.17, 152.03, 148.48, 148.27, 144.47, 144.38, 144.28, 142.35, 141.43, 135.49, 132.98, 132.70, 132.54, 132.02, 131.97, 131.90, 131.72, 131.41, 130.64, 130.28, 130.08, 128.47, 128.41, 128.35, 127.78, 127.57, 127.28, 127.23, 127.16, 126.88, 126.75, 125.66, 124.08, 122.95. HRMS (C₂₈H₁₉N₃S): *m/z* 759.2686 [M⁺, calcd 759.2708].

3. Devices fabrication

Glass substrates pre-coated with a 95-nm-thin layer of indium tin oxide (ITO) with a sheet resistance of 20 Ω per square were thoroughly cleaned for 10 minutes in ultrasonic bath of acetone, isopropyl alcohol, detergent, deionized water, and isopropyl alcohol and then treated with O₂ plasma for 5 min in sequence. Organic layers were deposited onto the ITO-coated substrates by high-vacuum (< 5×10⁻⁴ Pa) thermal evaporation. Deposition rates were controlled by independent quartz crystal oscillators, which were 1~2 Å s⁻¹ for organic materials, 0.1 Å s⁻¹ for LiF, and 3-6 Å s⁻¹ for Al, respectively. The emission area of the devices was 3 × 3 mm⁻² as shaped by the overlapping area of the anode and cathode. All the device characterization steps were carried out at room temperature under ambient laboratory conditions without encapsulation except spectrum collection process. EL spectra were taken by an optical analyzer, Photo Research PR745. Current density and luminance versus driving voltage characteristics were measured by Keithley 2420 and Konica Minolta

Table S1 Photophysical results of TNZPy and TNZTPE.

Compounds	$\lambda_{\text{abs}}^{\text{a}}$ (nm)	$\lambda_{\text{em}}^{\text{b}}$ (nm)		$\Phi_{\text{F}}^{\text{c}}$ (%)		τ^{d} (ns)		K_{r}^{e} (10^7 s^{-1})		K_{nr}^{f} (10^7 s^{-1})	
	Soln	Soln	Film	Soln	Film	Soln	Film	Soln	Film	Soln	Film
TNZPy	327/342/507	686	657	2.3	36	10.51	3.48	0.22	10.34	9.29	18.39
TNZTPE	307/507	687	651	1.2	50	1.90	6.01	0.63	8.32	52.0	8.32

a) absorption peaks, concentration: 10 μM ; b) Maximum emission wavelength, Soln: DMF, concentration: 10 μM ; c) Absolute PLQY measured using an integrating sphere, Soln: DMF, concentration 10 μM ; d) fluorescence lifetime; e) $K_{\text{r}} = \Phi_{\text{F}}/\tau$; f) $K_{\text{nr}} = (1-\Phi_{\text{F}})/\tau$.

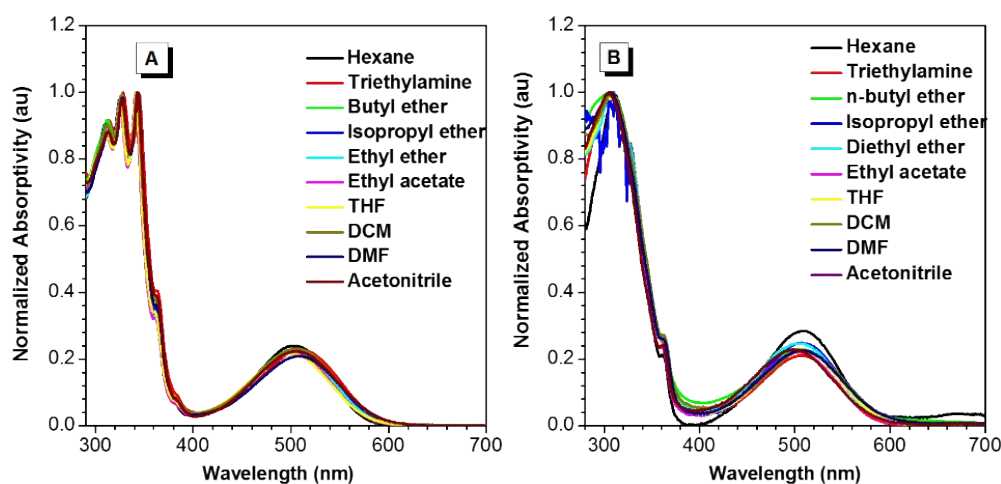


Fig. S4 UV-vis absorption spectra of chromophores in various organic solvents with different polarity: (A) TNZPy, (B) TNZTPE.

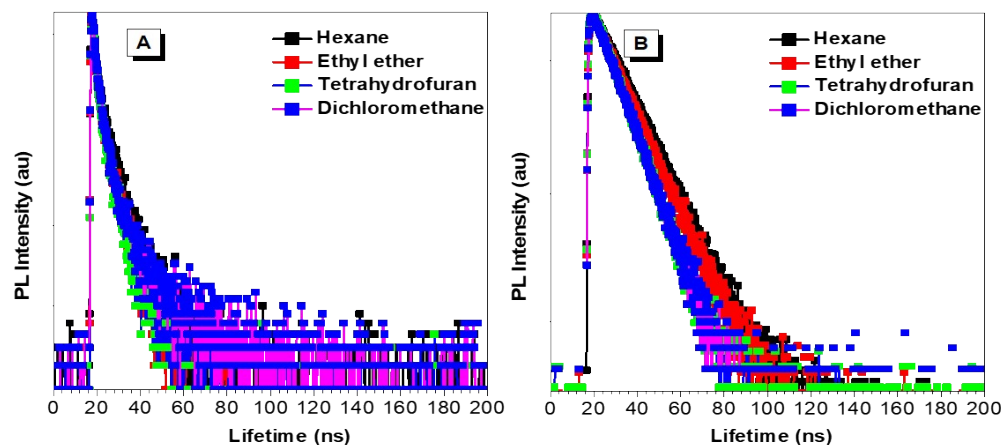


Fig. S5 Logarithmic decay curves in different solvents: (A) TNZPy, (B) TNZTPE.

Table S2 Photophysical data of TNZPy in different solvents.

Solvents	Δf	$\lambda_{\text{abs}}^{\text{a}}$ [nm]	$\lambda_{\text{em}}^{\text{b}}$ [nm]	Stokes shift [cm^{-1}]	$\Phi_{\text{F}}^{\text{c}}$ [%]	Lifetime ^{d)} [ns]
Hexane	0	503	609	3460	57.0	8.45
Triethylamine	0.048	510	633	3810	68.5	9.68
Butyl ether	0.096	505	624	3776	69.3	10.09

Isopropyl ether	0.145	503	628	3957	69.8	10.21
Ethyl ether	0.167	501	635	4212	67.4	11.26
Ethyl Acetate	0.2	501	654	4669	56.1	10.77
Tetrahydrofuran	0.21	506	658	4565	53.9	9.40
Dichloromethane	0.217	508	670	4760	41.2	8.56
Dimethyl Formamide	0.276	506	686	5186	2.3	10.51
Acetonitrile	0.305	497	678	5371	1.0	2.68

^{a)} Absorption peak; ^{b)} Emission peak; ^{c)} Fluorescence quantum yield; ^{d)} fluorescence lifetime.

Table S3 Photophysical data of TNZTPE in different solvents.

Solvents	Δf	$\lambda_{\text{abs}}^{\text{a)}$ [nm]	$\lambda_{\text{em}}^{\text{b)}$ [nm]	Stokes shift [cm^{-1}]	$\Phi_{\text{F}}^{\text{c)}$ [%]	Lifetime ^{d)} [ns]
Hexane	0	509	618	3465	69.3	11.45
Triethylamine	0.048	506	628	3839	74.8	13.24
Butyl ether	0.096	507	639	4074	74.6	11.56
Isopropyl ether	0.145	507	643	4171	38.2	10.59
Ethyl ether	0.167	503	646	4400	37.7	10.53
Ethyl Acetate	0.2	504	658	4644	32.1	9.68
Tetrahydrofuran	0.21	510	662	4502	19.6	8.40
Dichloromethane	0.217	509	670	4720	10.4	8.67
Dimethyl Formamide	0.276	507	687	5167	1.2	1.90
Acetonitrile	0.305	498	682	6417	4.0	1.39

^{a)} Absorption peak; ^{b)} Emission peak; ^{c)} Fluorescence quantum yield; ^{d)} fluorescence lifetime.

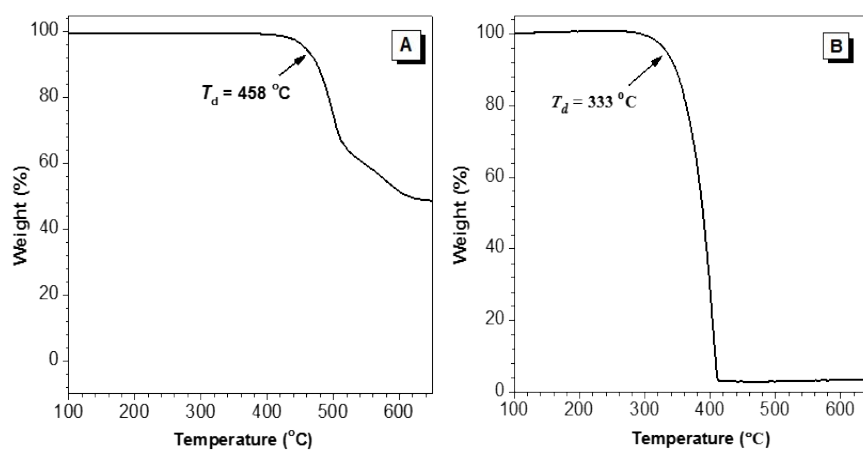


Fig. S6 The spectra of thermal decomposition temperature: (A) TNZPy, (B) TNZTPE.

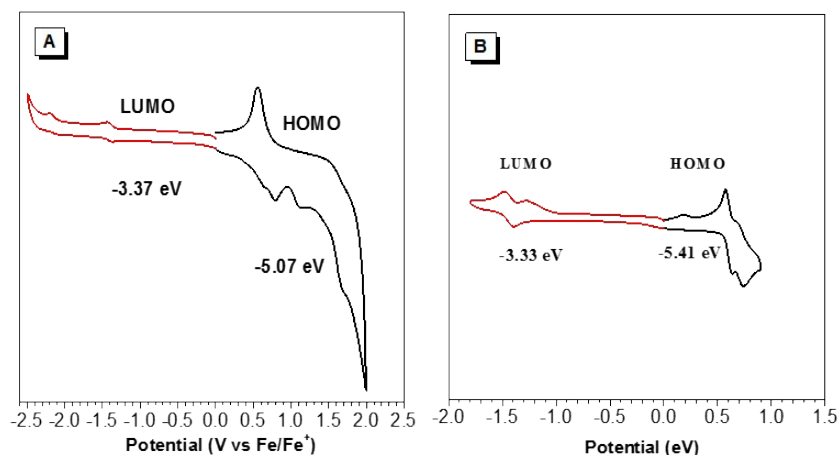


Fig. S7 Electrochemical property: (A) TNZ, (B) TNZPy, (C) TNZTPE.

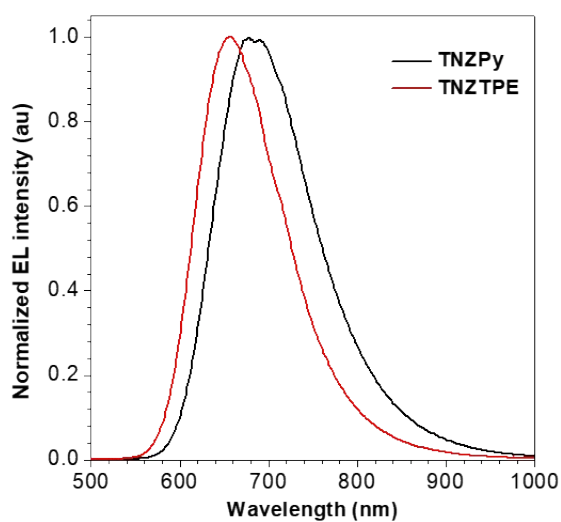


Fig. S8 EL spectra of TNZPy and TNZTPE.

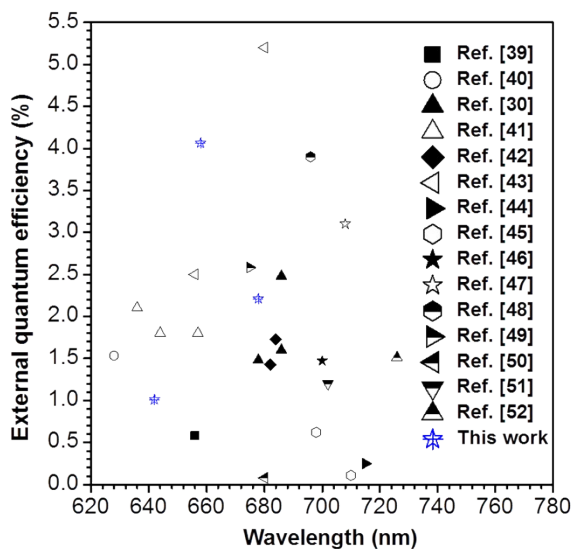


Fig. S9 Maximum EQE summary of the representative non-doped red OLEDs based on pure organic fluorescent materials with emission peak from 620 to 730 nm in recent five years.