Supporting Information

Thermally Activated Delayed Fluorescence Exciplexes with Phosphor Component Realizing Deep-Red to Near-Infrared Electroluminescence

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Experimental Section

General Information: Except that the TRZ-1SO_2, TRZ-2SO_2 and TRZ-3SO_2 were synthesized by our group, other compounds were purchased from commercial sources and used as received without further purification. Absorption and PL spectra were measured using a Hitachi UV–vis spectrophotometer U-3010 and a Hitachi fluorescence spectrometer F-4600, respectively. Half-and-half mixed constituting molecules in dichloromethane were coated in quartz tubes and treated at 40 °C under vacuum overnight to form films. Their fluorescence and phosphorescence spectra were measured at 77 K using a Hitachi F-4600 fluorescence spectrometer. The measurement of the phosphorescence spectra was delayed by a chopper with the chopping speed of 40 Hz, corresponding to a delayed time of ≈6.25 ms. The fluorescence quantum yields were measured with 100 nm thick films in N_2 atmosphere with an Edinburgh Instruments FLS920 spectrometer. The temperature-dependent transient PL decay characterizations were conducted by the Collaborative Innovation Center of Suzhou Nano Science & Technology. Cyclic voltammetry was performed on a CHI660E electrochemical analyzer with 0.1 MBu_4NPF_6 as a supporting electrolyte, a saturated calomel electrode (SCE) as the reference electrode, an Ag/AgCl electrode (3.0 M KCl) as the reference electrode with standardized against ferrocene/ferrocenium, and a scan rate of 10 mV s^{-1}. The energy levels of HOMO (E_{HOMO}) and LUMO (E_{LUMO}) of the compounds are determined from half-wave potentials of their oxidation and reduction curves in DMF solution relative to that of Fc+/Fc by using the equations E_{HOMO} [eV] = -(Eox- $E_{1/2,Fc}$ + 5.1) eV and E_{HOMO} [eV] = -(E_{re}- $E_{1/2,}$

$_{Fc}$ + 5.1) eV.

OLEDs Fabrication: Before device fabrication, ITO-coated glasses with a sheet resistance of 15 Ω square^{-1} were first cleaned with isopropyl alcohol and deionized water, then dried in an oven at 120 °C, treated with UV-ozone, and finally transferred to a deposition system with a base pressure of about 4 × 10^{-4} Pa. Organic materials were deposited at a rate of 1–2 Å s^{-1} and the rates were 0.1 and 10 Å s^{-1} for LiF and Al, respectively. The current–voltage characteristics were measured with a computer-controlled Keitheley 2400 source meter. Electroluminescence spectra were measured with a PHOTO RESEARCH SpectraScan PR 745 PHOTOMETER, which can detect in the spectral region 380-1080 nm. All the measurements were carried out under ambient atmosphere at room temperature. The EQE of the NIR emission was obtained by measuring the light intensity in the forward direction and assuming the external emission profile to be Lambertian.

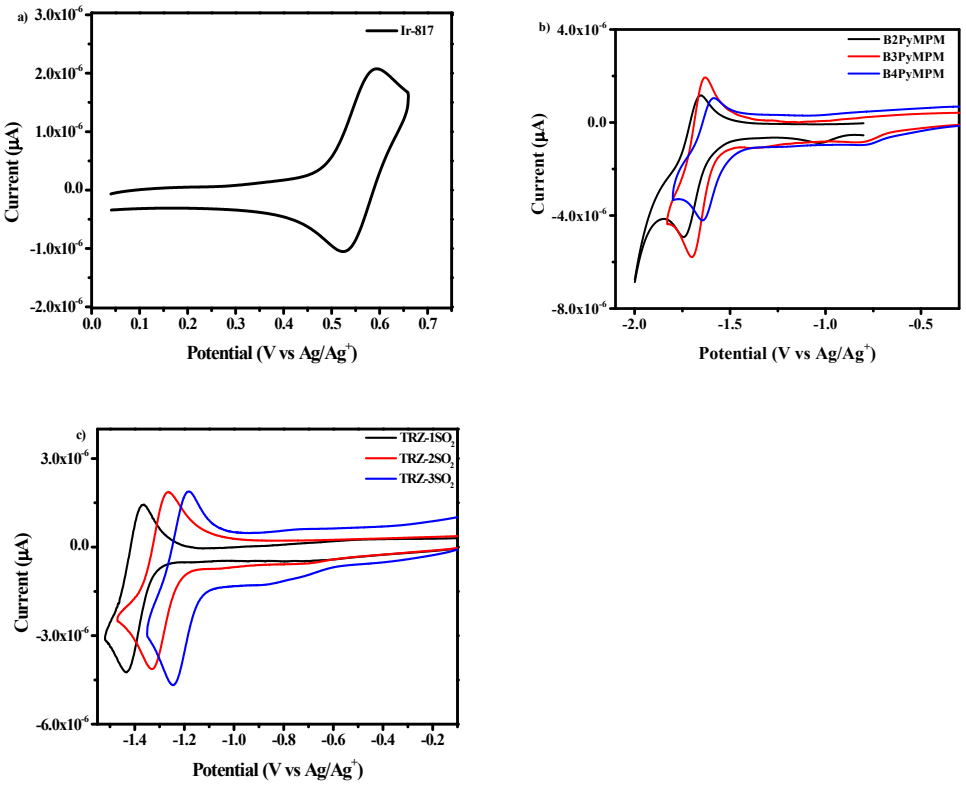

Fig. S1. a) Oxidation curves of Ir-817 in DMF; b) reduction curve of B2PyMPM, B3PyMPM, B4PyMPM in DMF; c) reduction curve of TRZ-1SO_2, TRZ-2SO_2 and TRZ-3SO_2 in DMF.

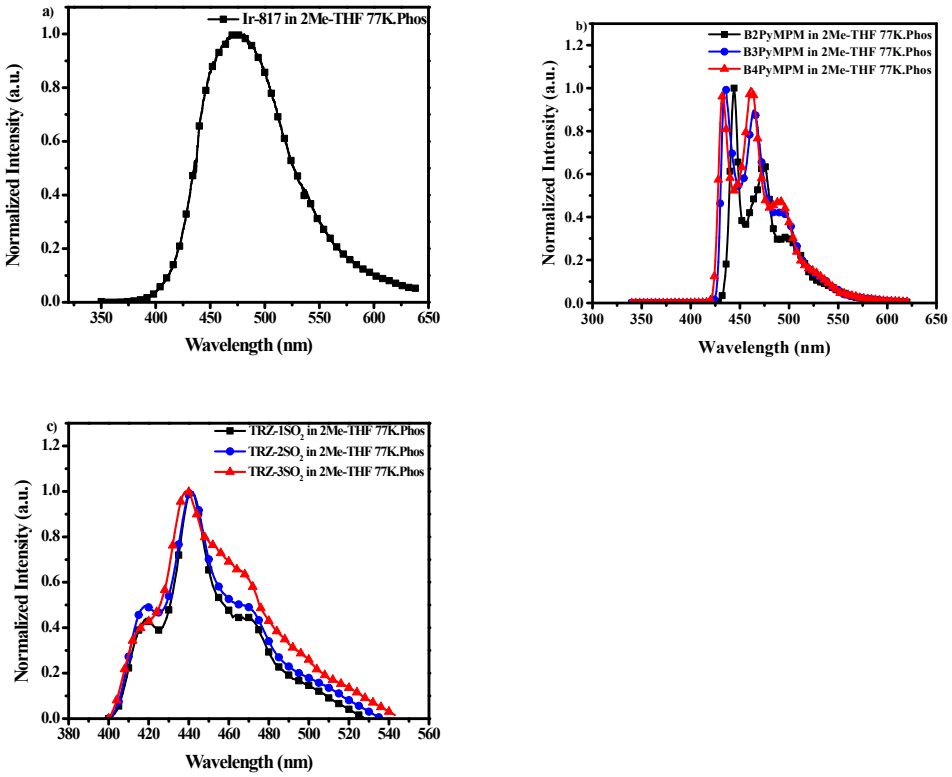

Fig. S2. a) The phosphorescence spectra of Ir-817 in 2Me-THF at 77K; b) The phosphorescence spectra of B2PyMPM, B3PyMPM, B4PyMPM in 2Me-THF at 77K; c) The phosphorescence spectra of TRZ-1SO_2, TRZ-2SO_2, TRZ-3SO_2 in 2Me-THF at 77 K.

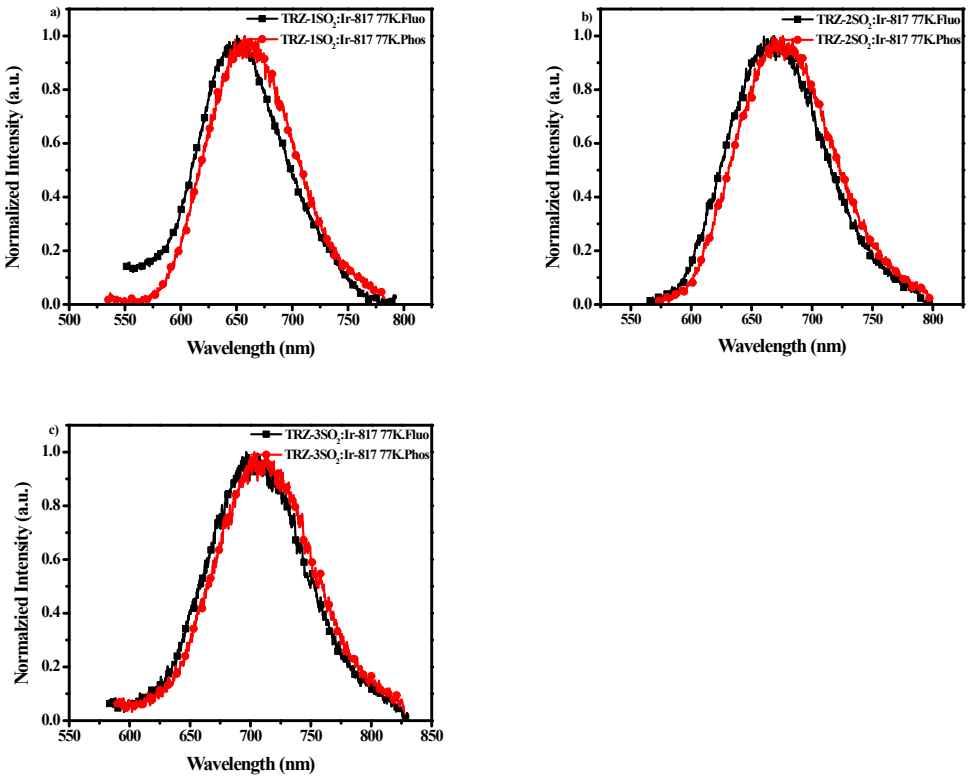

Fig. S3. a) The Fluorescence and phosphorescence spectra of TRZ-1SO_2:Ir-817 mixed films at 77 K; e) The fluorescence and phosphorescence spectra of TRZ-2SO_2:Ir-817 mixed films at 77 K; f) The Fluorescence and phosphorescence spectra of TRZ-3SO_2:Ir-817 mixed films at 77 K.

Table S1. Summary of the key physical properties of these exciplex emitters and their constituting materials.

Compounds	$\lambda_{flou.}$ [a] [nm]	S_1 [b] [eV]	T_1 [c] [eV]	ΔE_{ST} [d] [eV]	HOMO [e] [eV]	LUMO [f] [eV]
Ir-817	474	--	2.617	--	-5.00	-2.25[g]
B2PyMPM	423	--	2.792	--	-6.56[g]	-2.96
B3PyMPM	389	--	2.850	--	-6.71[g]	-3.02
B4PyMPM	403	--	2.867	--	-6.76[g]	-3.14
TRZ-1SO_2	434	--	2.95	--	-6.63[g]	-3.28
TRZ-2SO_2	435	--	2.95	--	-6.68[g]	-3.38
TRZ-3SO_2	435	--	2.95	--	-6.77[g]	-3.49
B2PyMPM:Ir-817	606	2.035	2.023	0.012	--	--
B3PyMPM:Ir-817	632	1.951	1.931	0.020	--	--
B4PyMPM:Ir-817	642	1.922	1.907	0.015	--	--
TRZ-1SO_2:Ir-817	647	1.908	1.888	0.020	---	--
TRZ-2SO_2:Ir-817	666	1.856	1.839	0.017	--	--
TRZ-3SO_2:Ir-817	698	1.783	1.764	0.019	--	--

a) Determined from the emission peak of their film at room temperature; [b] Estimated from the peak of fluorescence spectrum at 77K; [c] Estimated from the peak of phosphorescence spectrum at 77K; [d] ΔE_{ST}= S_1- T_1; [e] Determined from the onset of oxidation potential with respect to that of ferrocene in DMF solution; [f] Determined from the onset of the reduction curve with respect to that of ferrocene in DMF solution; [g] Calculated from the onsets of their absorption spectra.

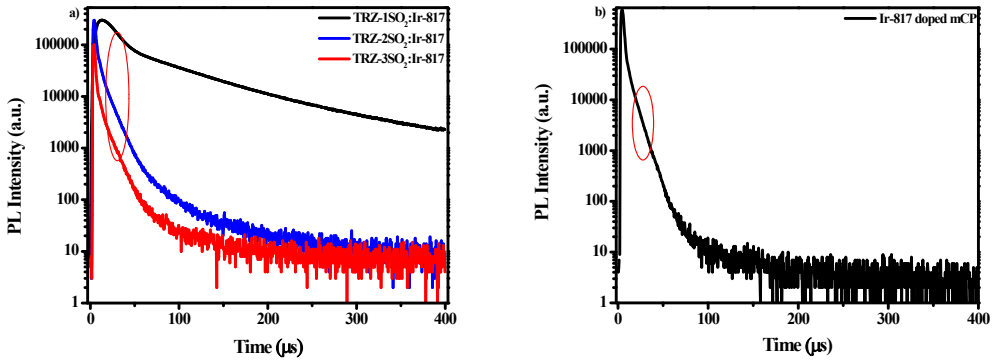

Fig. S4. a) The transient fluorescence decays of TRZ-1SO_2:Ir-817, TRZ-2SO_2:Ir-817 and TRZ-3SO_2:Ir-817 mixed films with 300 nm excitation at room temperature in vacuum; b) The transient fluorescence decays of Ir-817 doped in mCP host film with 300 nm excitation at room temperature in vacuum.

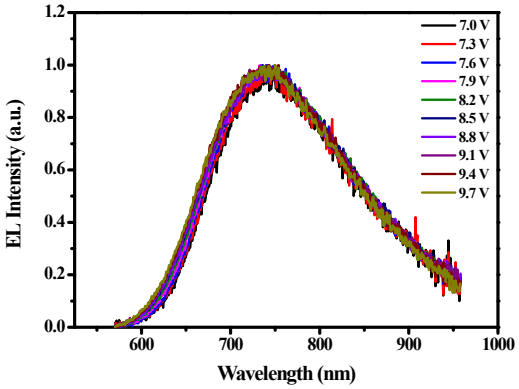

Fig. S5. The EL spectra of TRZ-3SO_2:Ir-817-based OLED under different driving voltage.