Electronic Supplementary Information

Charge-transfer transition regulation of thermally activated delayed fluorescence emitters by changing the valence of sulfur atoms

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General information. All reagents are purchased from commercial sources and used without further purification. And the final products Trz-S-DMAc and Trz-SO_2-DMAc are first purified by column chromatography on silica (silica gel, 200-300 mesh) and further improving the purity by vacuum sublimating before using to study their photoluminescence and electroluminescence properties. ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra are recorded on Bruker 400 and 600 spectrometers. Mass spectra are recorded on a Trace-ISQ mass spectrometer. Single-crystal X-ray structure analysis was obtained using an Bruker D8 Venture X-ray single crystal diffractometer. Cyclic voltammetry is performed on a CHI660E instrument. TGA and DSC measurements are tested in TAQ 500 thermogravimeter and DSC1 differential scanning calorimeter, respectively. Steady-state and time-resolved emission spectra are recorded by using an Edinburgh FLS980 spectrophotometer. Photoluminescence quantum yield (PLQY) are evaluated under oxygen-free condition with an integrating sphere. Calculations are performed using the Gaussian 09 package, and the ground state geometries in vacuum are simulated at the level of B3LYP/6-31G(d,p).

Fabrication and Characterization of OLEDs: Indium Tin Oxide (ITO) substrate was cleaned with detergents and deionized water, dried in an oven at 100 °C for 1 h, then treated with ultraviolet-ozone system treatment for 10 min, and finally transferred to a deposition chamber. At a base pressure of about 2×10^{-4} Pa, evaporated each layer onto ITO substrate sequentially to fabricate devices. The deposition rates of all organic layers were 1 - 2 Å s^{-1}. LiF was deposited at the rate of 0.1 Å s^{-1}, and Al was deposited at the rate of 6-7 Å s^{-1}. The Electroluminescence (EL) spectra were measured with a PR655 spectra colorimeter and a Keithley 2400 source meter. EQEs were calculated based on current density, brightness and EL Spectra.

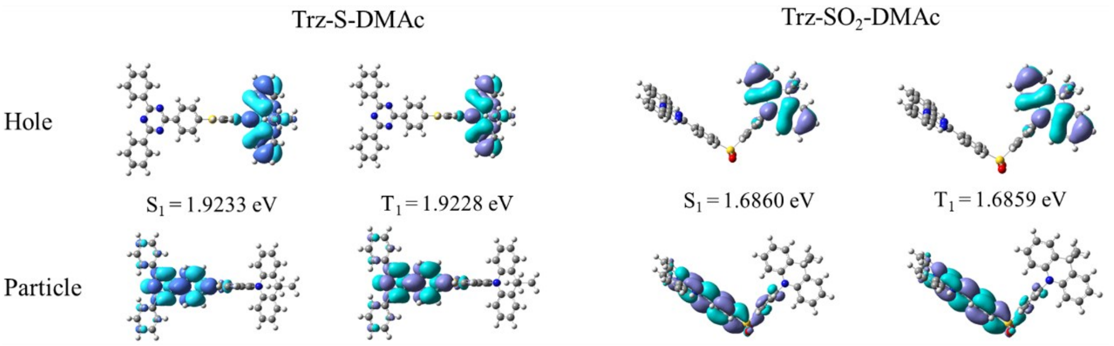

Fig. S1 Natural transition orbitals (NTOs) of S_1 and T_1 states for (a) Trz-S-DMAc and (b) Trz-SO_2-DMAc, and their corresponding energy levels.

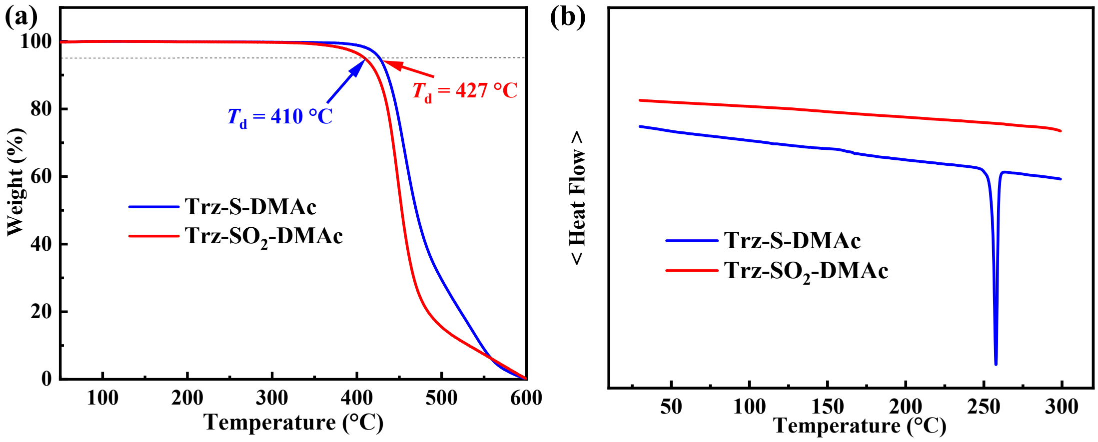

Fig. S2 (a) TGA and (b) DSC curves of Trz-SO_2-DMAc and Trz-S-DMAc.

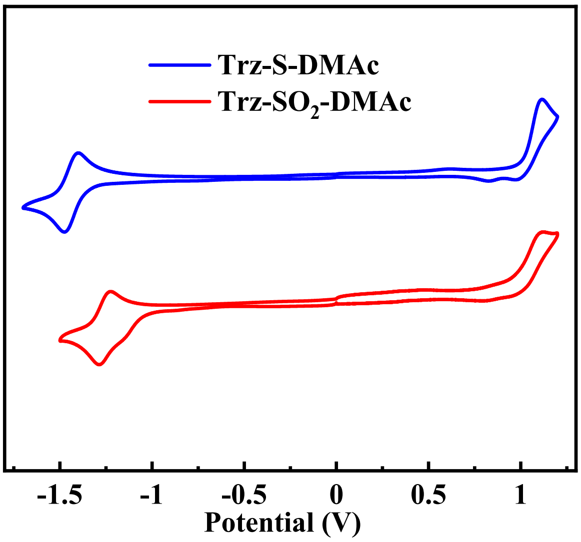

Fig. S3 Cyclic voltammetry (CV) of Trz-S-DMAc and Trz-SO_2-DMAc in DMF.

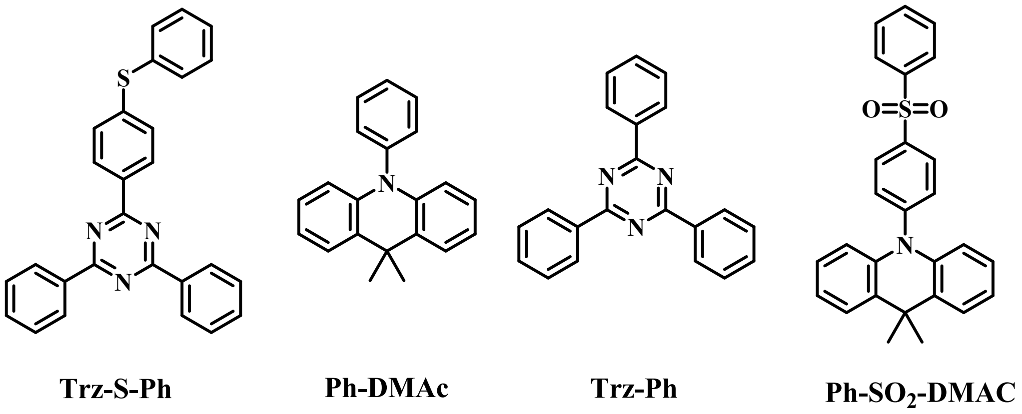

Fig. S4 Detailed structures of the eigen derivatives.

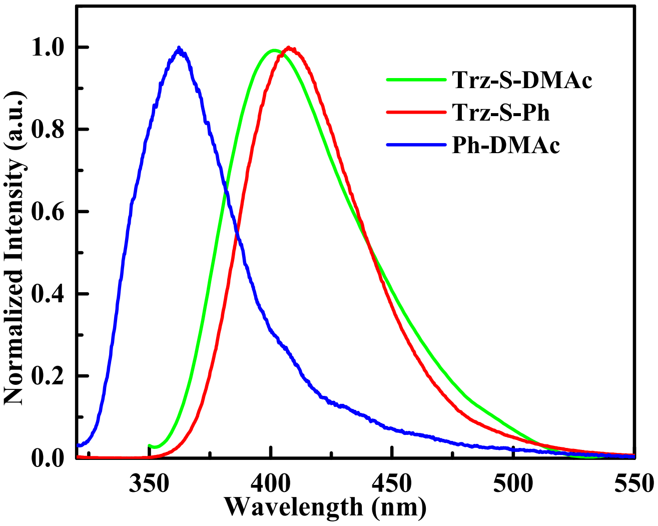

Fig. S5 A PL spectral comparison of the films of Trz-S-DMAc (10^{-5} M), Trz-S-Ph (10^{-3} M), Ph-DMAc (10^{-3} M) diluted in PMMA.

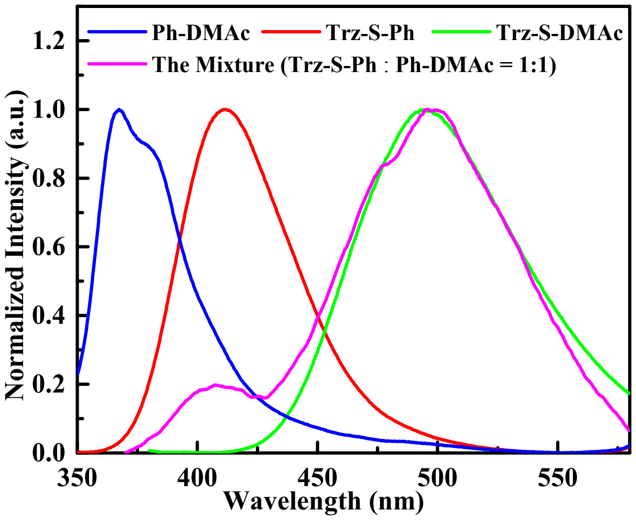

Fig. S6 A PL spectral comparison of the neat films of Trz-S-Ph, Trz-S-DMAc, Ph-DMAc, and the 1:1 mixture of Trz-S-DMAc and Ph-DMAc, in which the components form an exciplex with evidently redshifted emission similar to that of Trz-S-DMAc.

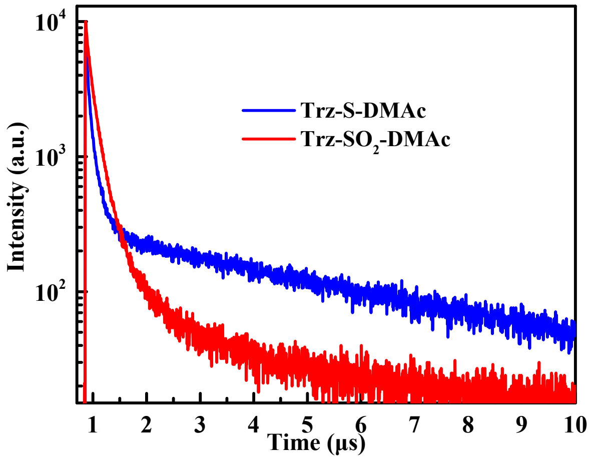

Fig. S7 Transient PL decay curves of Trz-SO$_2$-DMAc and Trz-S-DMAc neat films.

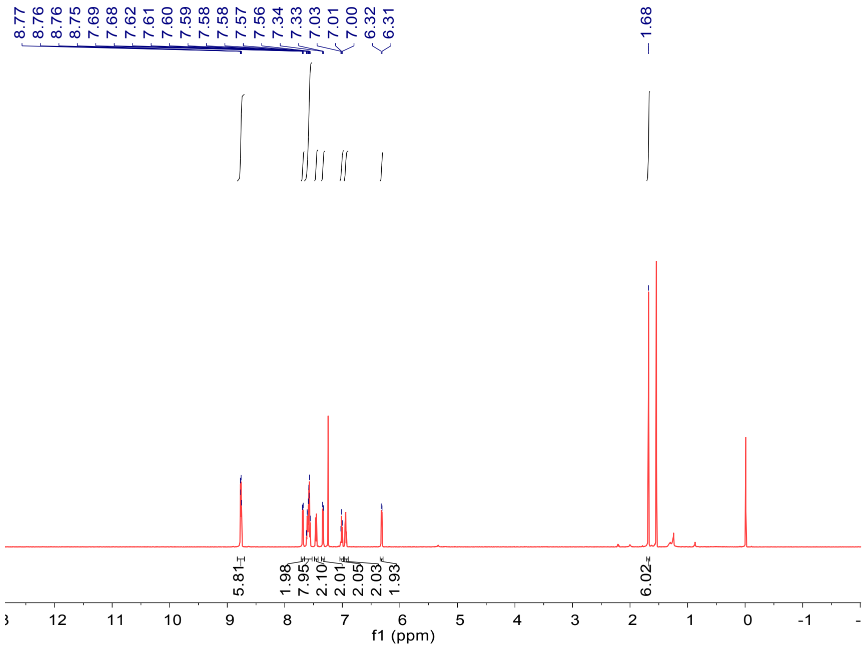

Fig. S8 Copy of ^{1}H NMR spectrum of Trz-S-DMAc.

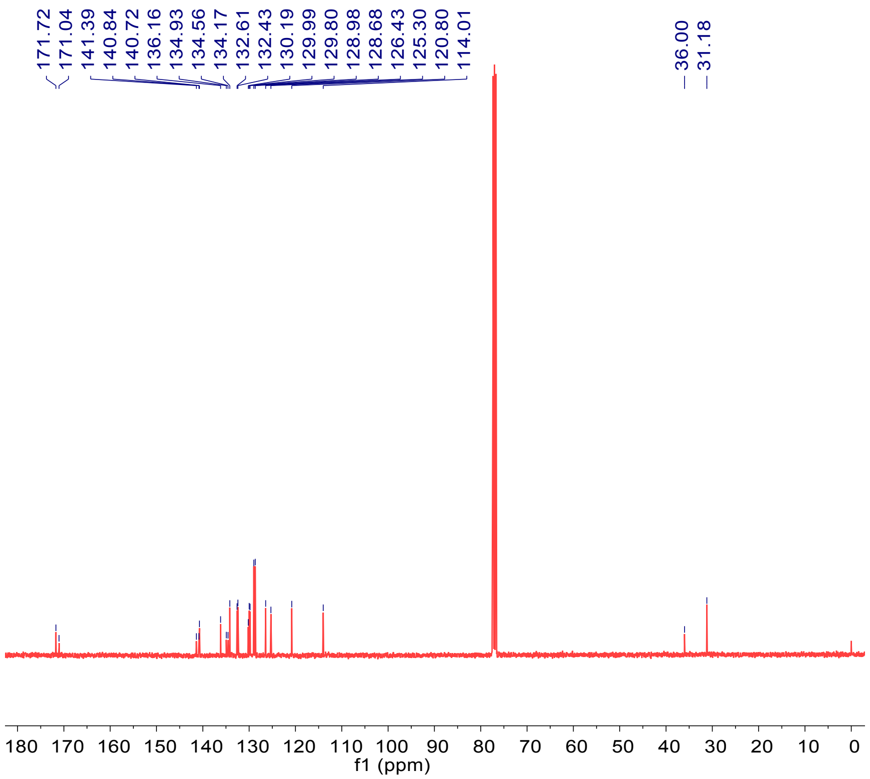

Fig. S9 Copy of ^{13}C NMR spectrum of Trz-S-DMAc.

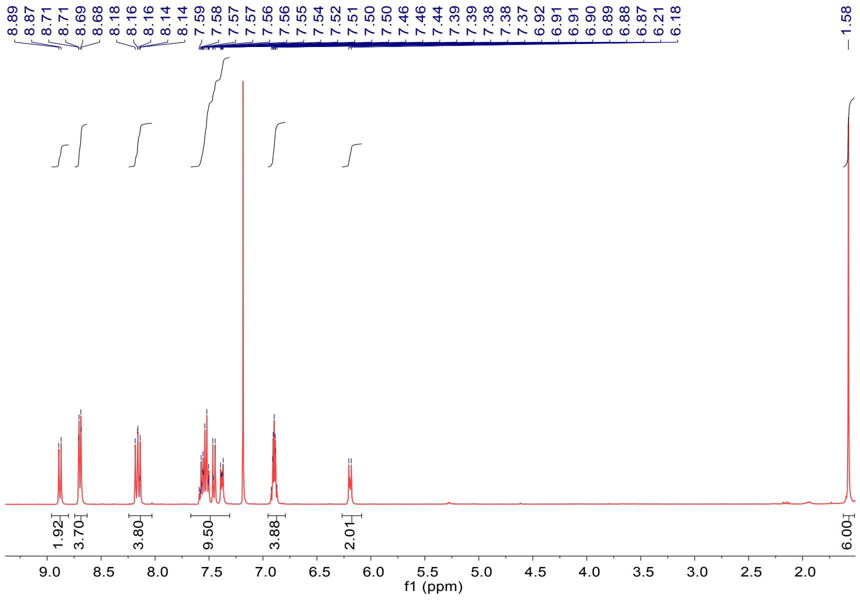

Fig. S10 Copy of ^{1}H NMR spectrum of Trz-SO$_2$-DMAc.

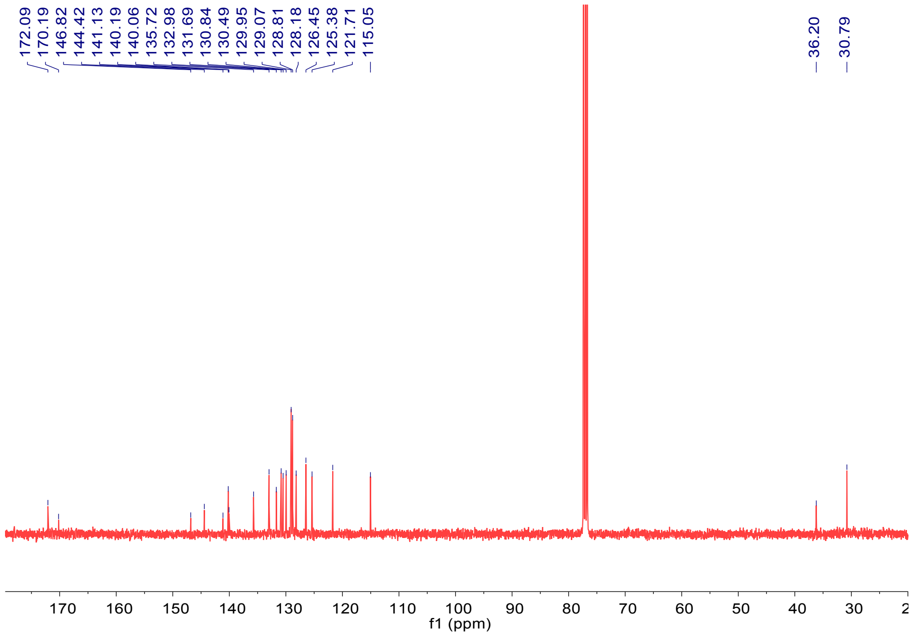

Fig. S11 Copy of ^{13}C NMR spectrum of Trz-SO$_2$-DMAc.