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Supplementary information

Star-Shaped Thermally Activated Delayed Fluorescence Emitters with a Tri-armed Arylsulfonic Acceptor for Efficient Solution Processed Organic Light Emitting Diodes

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Table of Contents

General Information

All reagents and starting materials employed in this work were purchased from commercial sources, and used without further purification. The ^1H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AVANCE Ⅲ 500 MHZ superconducting-magnet high-field NMR spectrometer at room temperature. High-resolution electrospray (ESI) mass spectra (HR-ESI-MS) were measured using a SCIEX TripleTOF6600 nano-LCMS mass spectrometer. Thermogravimetric analysis (TGA) was carried out with a TA instrument TGA Q50 under nitrogen flow (20 mL min^{-1}), and a heating rate of 10 °C min^{-1} was applied. Differential scanning calorimetry (DSC) was performed with a TA DSC Q200 at a heating rate of 10 °C min^{-1} from 40 to 350 °C under nitrogen. The glass transition temperature (T_g) was determined from the second heating scan at a heating rate of 10 °C min^{-1}.

Cyclic voltammetry (CV) was carried out in nitrogen-purged dichloromethane at room temperature with a CHI voltammetric analyzer. Tetrabutylammonium hexafluorophosphate (0.1 M) was used as the supporting electrolyte. The conventional three-electrode configuration consisted of a platinum working electrode, a platinum wire auxiliary electrode and an Ag/Ag^+ reference electrode with ferroceniumferrocene (Fc^+ /Fc) as the internal standard. Cyclic voltammograms were obtained at scan rate of 100 mV/s. Formal potentials were calculated as the average of cyclic voltammetric anodic and cathodic peaks. The HOMO energy levels of the compounds were calculated according to the formula: $-[4.8 + (E_{1/2(ox/red)} - E_{1/2(Fc/Fc+)})]$ eV. The LUMO energy levels of the compounds were calculated according to the absorption on-set of the longer wavelength.

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. Phosphorescence spectra of doped thin films were conducted at 77K. The transient photoluminescence decay curves 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 Measurement

The ITO coated substrates were consecutively cleaned with acetone and ethanol and dried with N_2 flow. After 20 min ultraviolet light-ozone (UVO) treatment in a UV-ozone surface processor (PL16 series, Sen Lights Corporation), m-PEDOT:PSS was spin-coated onto the ITO surface at 4000 rpm. Afterwards, the substrates were transferred into a N_2 filled glovebox and then baked at 120 °C for 10 min. Subsequently, the corresponding emitting layer was spin-coated at 1000 rpm, followed by baking at 50 °C for 10 min. The electron transporting layer (TmPyPB), the electron injecting layer (Liq), and aluminum cathode were consecutively deposited in a vacuum chamber under 2×10^{-5} mbar. The as-fabricated devices were sealed with curable UV resin and then measured in ambient enviroment. Current density-voltage-luminance characteristics and the EL spectra were recorded with a Keithley 2400 source meter unit and a Photoresearch SpectraScan PR735 spectrometer. The EQE was calculated from the current density, luminance and EL spectrum, assuming a Lambertian distribution.

The poly(4-styrenesulfonic acid) (PSSA) solution (18 wt % in H_2O, d = 1.11 g mL^{-1} at 25 °C, M_w ~75,000 g mol^{-1}) was purchased from Sigma-Aldrich (CAS: 28210-41-5). The PEDOT:PSS (Heraeus Clevios P VP AI 4083) solution was purchased from Xi'an Polymer Light Technology, and m-PEDOT:PSS was prepared according to the reported method.[1]

Theoretical Calculation

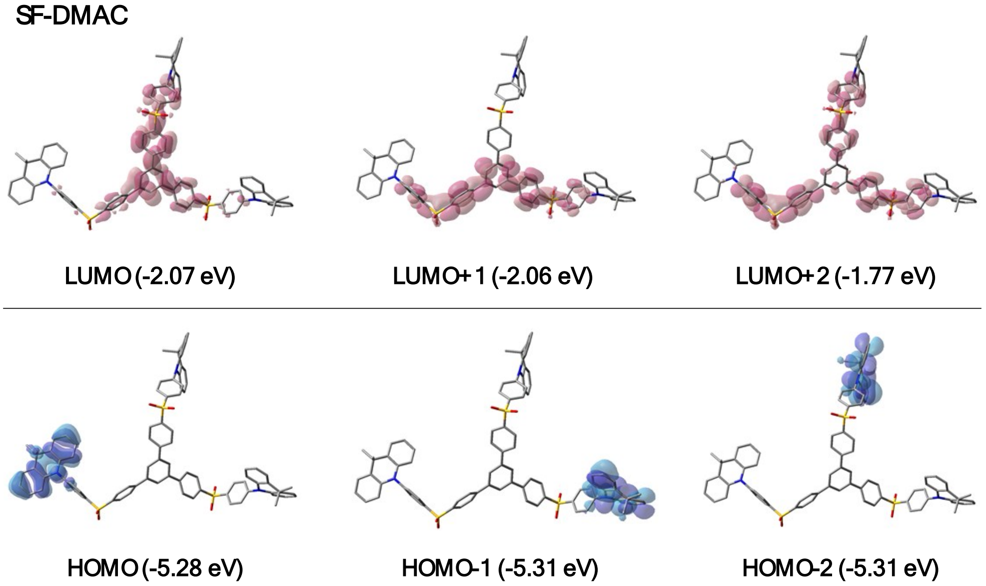


Figure S1. Molecular orbitals HOMO-2, HOMO-1, HOMO, LUMO, LUMO+1, LUMO+2 of SF-DMAC.

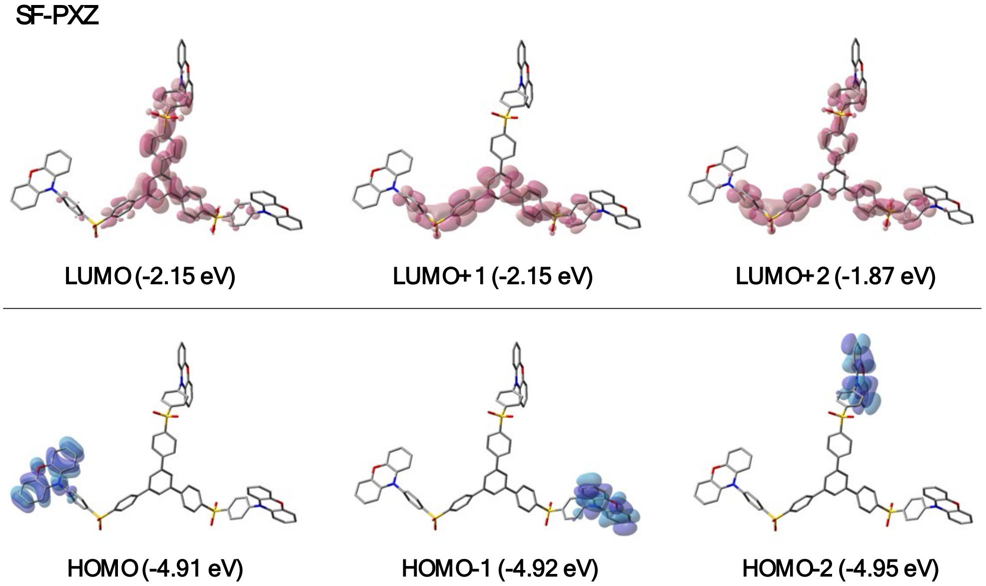


Figure S2. Molecular orbitals HOMO-2, HOMO-1, HOMO, LUMO, LUMO+1, LUMO+2 of SF-PXZ.

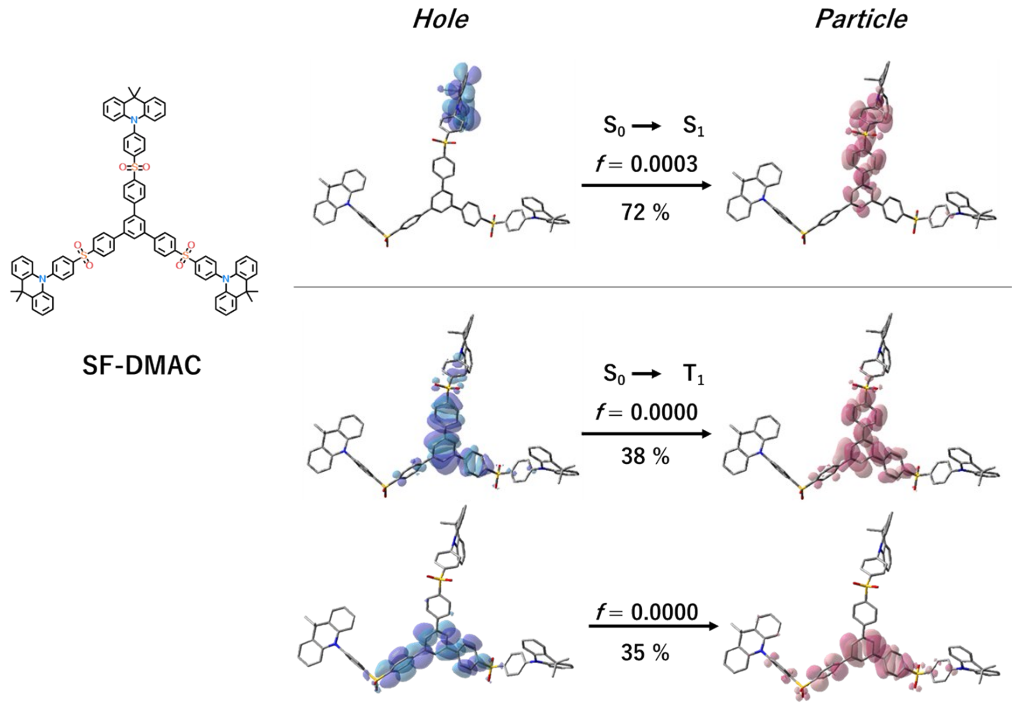


Figure S3. Natural transition orbitals (NTO) of SF-DMAC in the S_1 and T_1 excited states.

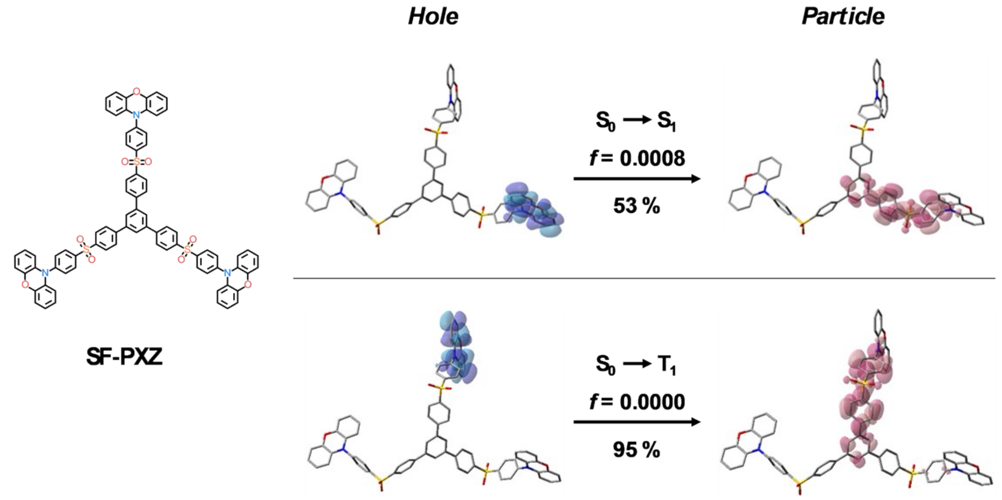


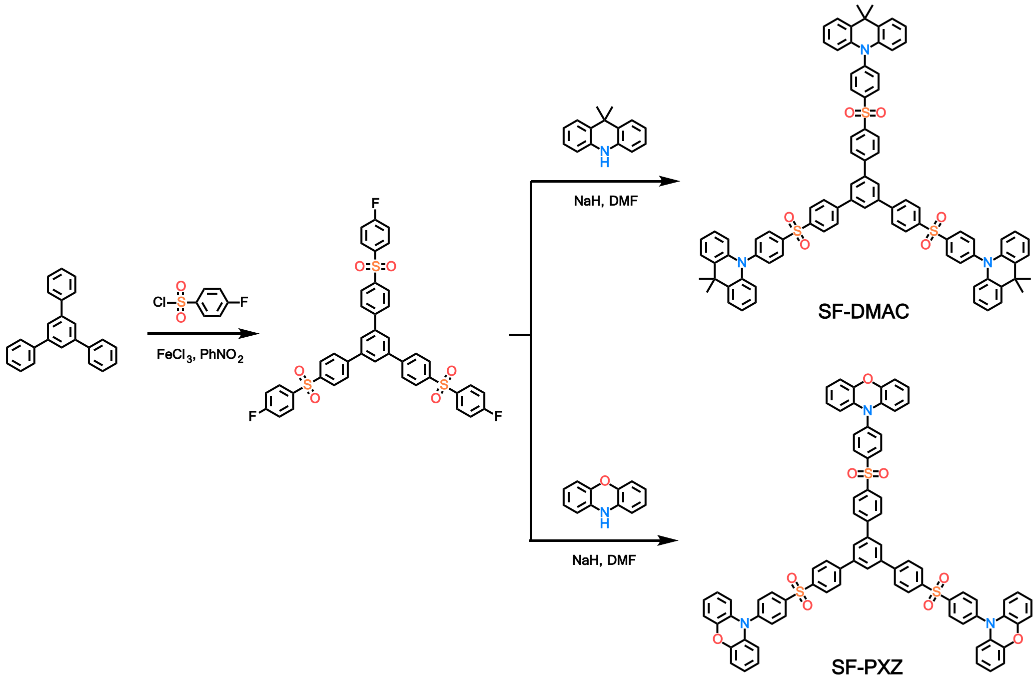
Figure S4. NTO of SF-PXZ in the S_1 and T_1 excited states.

Table S1. Calculated photophysical parameters of the designed emitters.

Compound	HOMO (eV)	LUMO (eV)	S_1 (eV)	T_1 (eV)	ΔE_{ST} (eV)	f
SF-DMAC	-5.28	-2.07	2.9823	2.8464	0.136	0.0003

SF-PXZ	-4.91	-2.15	2.5443	2.5320	0.012	0.0008

Synthetic Procedures



Scheme S1. Synthesis of **SF-DMAC** and **SF-PXZ**.

Synthesis of 4,4''-bis((4-fluorophenyl)sulfonyl)-5'-(4-((4-fluorophenyl)sulfonyl) phenyl)-1,1':3',1''-terphenyl (SF-F$_3$). The synthesis of SF-F$_3$ has been reported.[2] The crude product was further purified by sublimation under vacuum. Colorless solid was obtained with an overall yield of 62%. The ^{1}H NMR spectrum agreed with the published data. ^{1}H NMR (CDCl$_3$-*d*): δ 8.08-7.97 (m, 12H), 7.79-7.71 (m, 9H), 7.21 (dd, J = 9.2, 7.8 Hz, 6H). ^{19}F NMR (CDCl$_3$-*d*): δ 103.75 (ddd, J = 13.3, 8.4, 5.0 Hz).

General synthetic procedures of the TADF compounds. To a dry Schlenk tube was added 9,9-dimethyl-9,10-dihydroacridine (DMAC) or 10*H*-phenoxazine (PXZ) (3.2 mmol) and sodium hydride (60 wt % suspended in mineral oil, 154 mg, 6.4 mmol) together with a magnetic stirrer. The container was evacuated and back-filled with argon. 5 mL anhydrous *N*,*N*-dimethylformamide (DMF) was then transferred into the tube under argon *via* syringe. The reaction mixture was activated at 50 °C for 30 min. Subsequently, a degassed solution of SF-F_3 (500 mg, 0.64 mmol) in dry DMF (5 mL) was injected into the system, and the mixture was allowed to stir for another 4 hours at 50 °C. After the reaction, the mixture was poured into deionized water, and extracted with dichloromethane (40 mL × 3). The organic layers were combined, dried over anhydrous $MgSO_4$, and purified by flash column.

SF-DMAC. 440mg pale yellow solid with 51% yield. ^1H NMR ($CDCl_3$-*d*): δ 8.18 (dd, J = 16.6, 8.5 Hz, 4H), 7.88 (s, 1H), 7.86 (d, J = 2.1 Hz, 2H), 7.52 (d, J = 8.6 Hz, 2H), 7.47 (dd, J = 6.0, 3.4 Hz, 2H), 6.98 (dd, J = 6.0, 3.4 Hz, 4H), 6.27 (dd, J = 6.0, 3.4 Hz, 2H), 1.66 (s, 6H). ^{13}C NMR ($CDCl_3$-*d*): δ 146.84, 145.47, 141.36, 140.95, 140.37, 140.33, 131.89, 130.92, 130.50, 128.83, 128.53, 126.86, 126.52, 125.56, 121.90, 115.12, 36.37, 30.90. HRMS (ESI, m/z): $[M]^+$ calcd for $C_{87}H_{69}N_3O_6S_3$ 1348.4382, found 1348.4421.

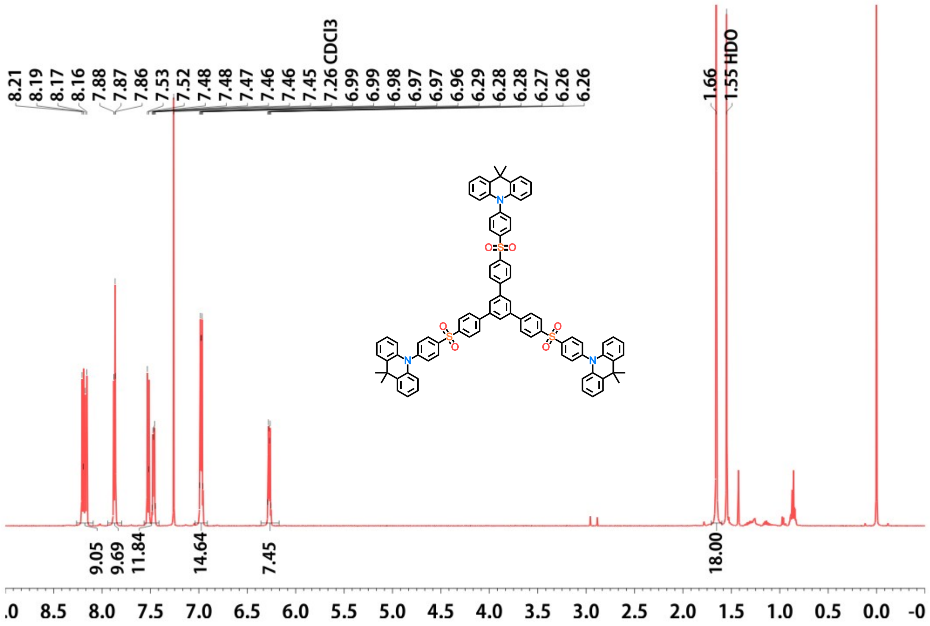


Figure S5. ^1H NMR spectrum of SF-DMAC.

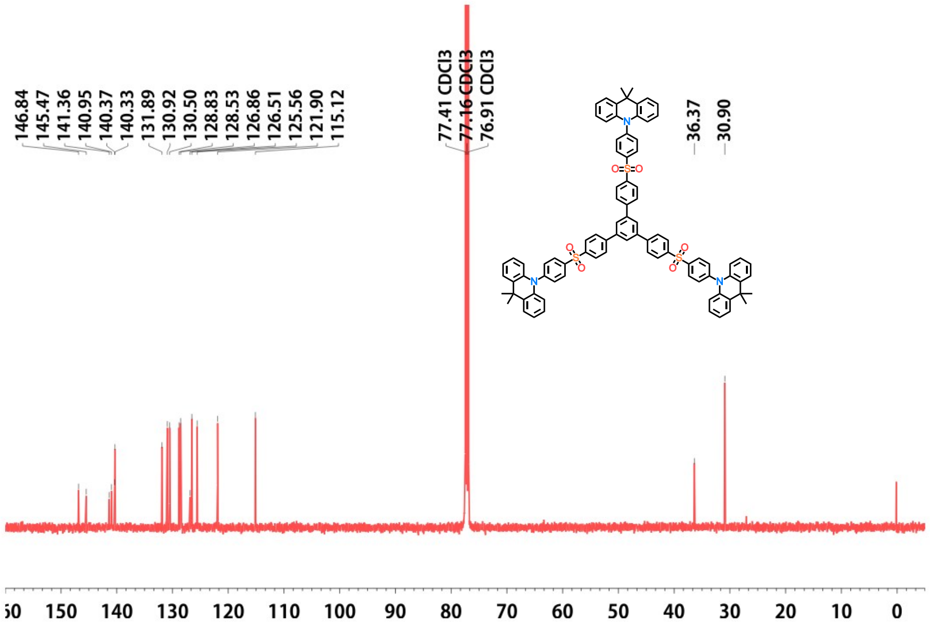


Figure S6. ^{13}C NMR spectrum of SF-DMAC.

SF-PXZ. SF-PXZ was obtained as a bright yellow solid (590 mg, 73 % yield). ^{1}H NMR (CDCl$_3$-*d*): δ 8.19 (d, J = 8.6 Hz, 2H), 8.14 (d, J = 8.5 Hz, 2H), 7.86-7.84 (m, 3H), 7.54 (d, J = 8.6 Hz, 2H), 6.73 (dd, J = 7.9, 1.7 Hz, 2H), 6.69 (t, J = 7.7 Hz, 2H), 6.59 (td, J = 7.7, 1.7 Hz, 2H), 5.91 (dd, J = 8.0, 1.3 Hz, 2H). ^{13}C NMR (CDCl$_3$-*d*): δ 149.82, 144.84, 141.95, 141.32, 140.99, 133.63, 132.99, 129.58, 129.07, 128.20, 127.54, 126.54, 126.48, 126.41, 116.08. HRMS (ESI, m/z): [M]$^+$ calcd for $C_{78}H_{51}N_3O_9S_3$ 1270.2821, found 1270.2860.

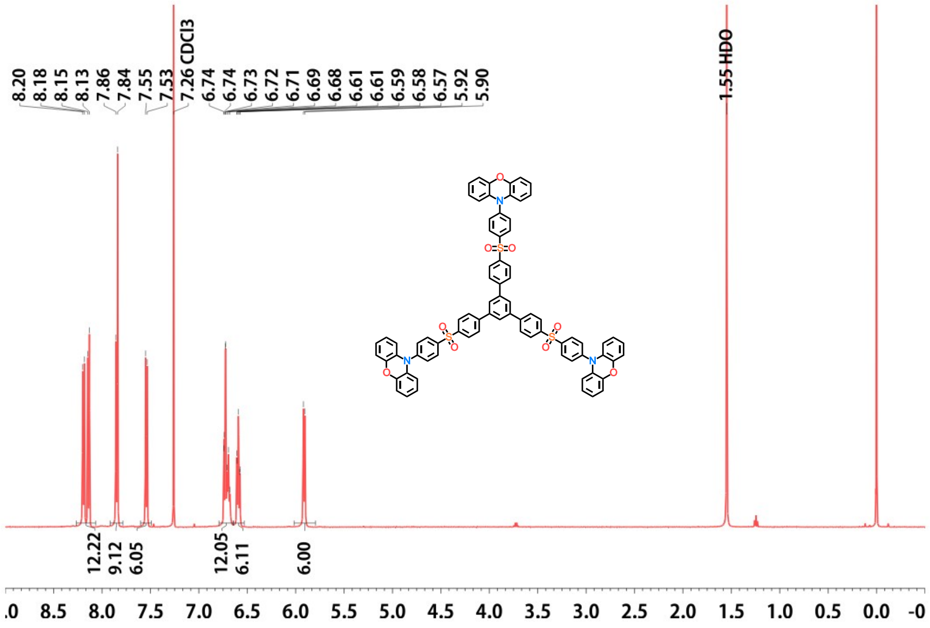


Figure S7. ^{1}H NMR spectrum of SF-PXZ.

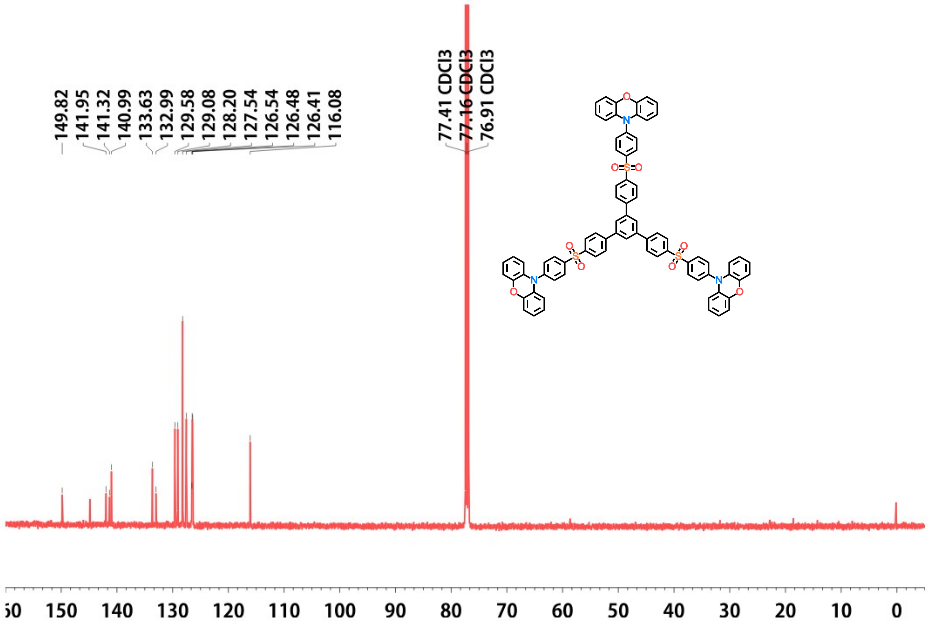
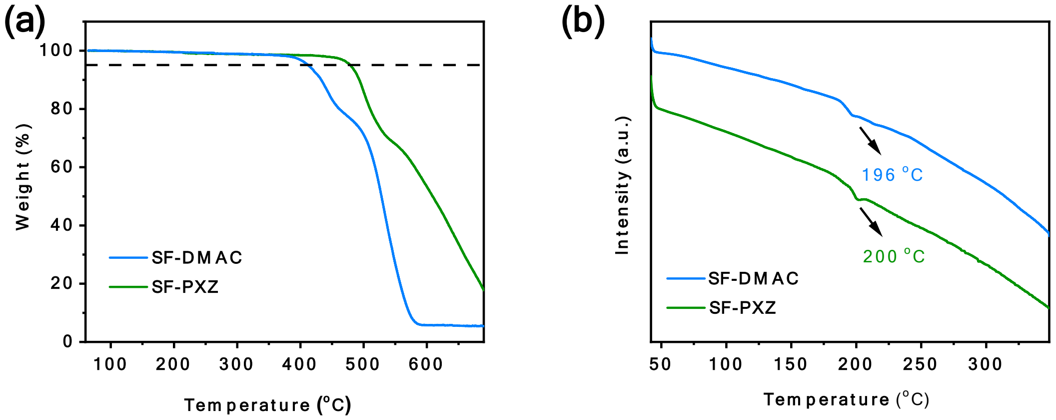


Figure S8. ^{13}C NMR spectrum of SF-PXZ.



Thermal Analysis

Figure S9. The thermogravimetric analysis (TGA) plots and DSC thermograms (second heating cycle) of SF-DMAC, and SF-PXZ under N_2 stream (flow rate: 20 ml min^{-1}; heating rate: 10 °C min^{-1}).

Table S2. Thermal analysis of the three compounds.

Compound	T_d[a] (°C)	T_g (°C)
SF-DMAC	413	196
SF-PXZ	479	200

[a] Temperature at weight loss of 5%.

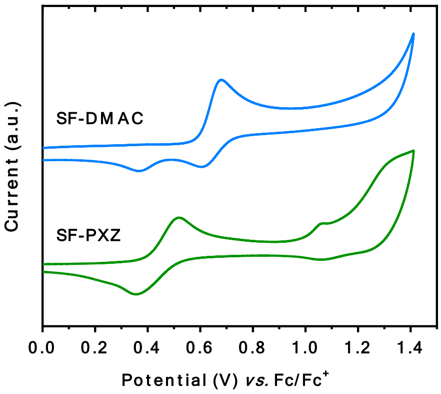


Figure S10. Cyclic voltammograms of SF-DMAC and SF-PXZ in 1×10^{-3} M dichloromethane solution. The electrode potentials were measured versus Ag/Ag$^+$ electrode.

Single Crystal X-ray Crystallographic Data

X-ray single crystal data of SF-PXZ were collected on a Bruker D8 Venture diffractometer using MoK radiation (λ = 0.71073) source. The selected crystal was kept at 150.0 K during data collection. Using Olex2,[3] the structure was solved with the ShelXT[4] structure solution program using Intrinsic Phasing and refined with the ShelXL[5] refinement package using Least Squares minimization. Selected crystal data and experimental details are listed in Table S3. Full crystallographic information in CIF format has been deposited at the Cambridge Crystallographic Data Center (CCDC) under deposition number 1973790 via www.ccdc.cam.ac.uk/data_request/cif.

Table S3. Crystal data and structure refinement for SF-PXZ.

Empirical Formula	$C_{78}H_{52}N_3O_9S_3$	
Formula Weight	1271.40	
Crystal System	triclinic	
Space Group	P-1	
Unit cell dimensions	a = 13.3936(4) Å	α = 74.6620(10) °
	b = 13.7117(4) Å	β =81.9760(10) °
	c = 22.4900(7) Å	γ =60.9520(10) °
V	3481.82(18) Å^3	
Z	2	
Density (calculated)	1.213 g/cm^3	
μ	0.165 mm^{-1}	
F(000)	1322.0	
R_1 [I>2σ(I)]	R_1 = 0.0857, wR_2 = 0.2347	
R_2 (all data)	R_1 = 0.1322, wR_2 = 0.2696	
Crystal size	0.19 × 0.15 × 0.12	
2θ range for data collection	4.508° to 52.874°	
Index ranges	$-16 \leq h \leq 16$, $-17 \leq k \leq 16$, $-28 \leq l \leq 28$	
Goodness-of-fit on F^2	1.025	
Reflections collected/unique	39878	

Photophysical Properties

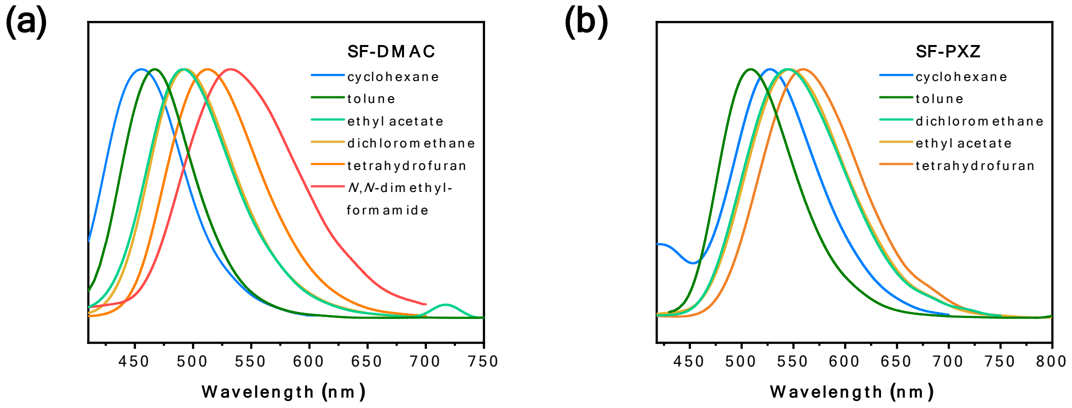


Figure S11. Solvatochromic effect of SF-PXZ.

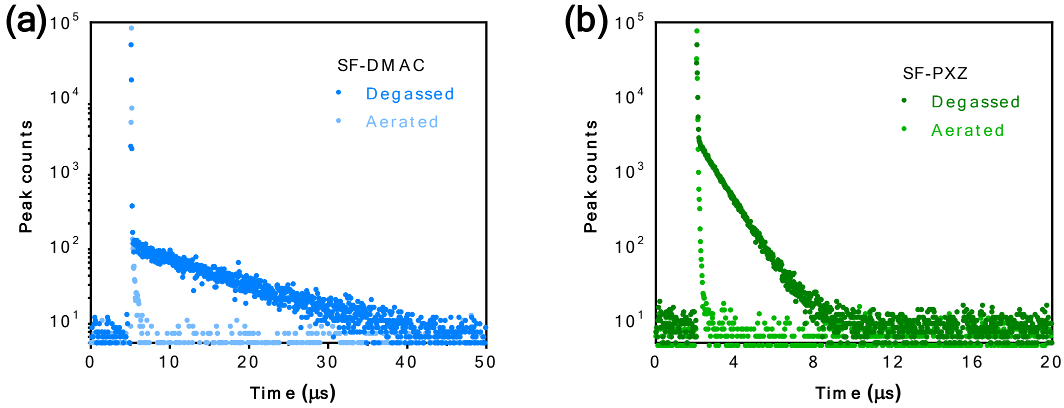


Figure S12. Transient PL decay curves of SF-DMAC and SF-PXZ in 1×10^{-5} M toluene solution.

Table S4. Summary of transient PL decay properties in 1×10^{-5} M toluene solution.

Compound	τ_p[a] (ns)	τ_d[a] (μs)	**ratio$_p$** (%)	**ratio$_d$** (%)
SF-DMAC	22.8	1.2	73.8	26.2
SF-PXZ	21.2	1.0	50.7	49.3

[a] Lifetime of prompt and delayed fluorescence.

Calculation of RISC Process

Assuming that the nonradiative decay from S_1 to S_0 is negligible, the efficiency of RISC (Φ_{RISC}) and ISC (Φ_{ISC}) can be estimated using the following equations.

$\Phi_{ISC} = 1 - \Phi_p$……………………………………………………………Eq.(1)

$\Phi_{RISC} = \Phi_d/(1 - \Phi_p)$…………………………………………………Eq.(2)

Where the Φ_p and Φ_d indicates prompt and delayed fluorescence components and can be distinguished from the total PLQY(Φ) by comparing the integrated intensities of prompt and delayed components in the transient photoluminescence spectra. The Φ_{ISC} of the compound SF-DMAC, SF-PXZ can be calculated to be 58%, 65%; and Φ_{RISC} of 27%, 48%. ΔE_{ST} of these compounds in doped films at room temperature can be reliably estimated using an approximate relationship between ΔE_{ST}, k_d, and k_p as follows,[6]

$k_p = \Phi_p/\tau_p$……………………………………………………………Eq.(3)

$k_d = \Phi_d/\tau_d$……………………………………………………………Eq.(4)

$k_d = 1/3(k_p exp(- \Delta E_{ST}/RT)]$…………………………………………Eq.(5)

where R and T represent the ideal gas constant and absolute temperature, respectively. the rate constants of ISC (k_{ISC}) and RISC (k_{RISC}) can be estimated based on the following equations,[7]

$k_{ISC} = (\Phi_p k_p)/(\Phi_p + \Phi_d)$…………………………………………Eq.(6)

$k_{RISC} = (\Phi_p k_p k_d)/(\Phi_p k_{ISC})$………………………………………Eq.(7)

The k_{ISC} and k_{RISC} values of the emitters were estimated and these are summarized in Table 2.

References

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