Supporting Information

A color-tunable single-component luminescent molecule with multiple emission centers

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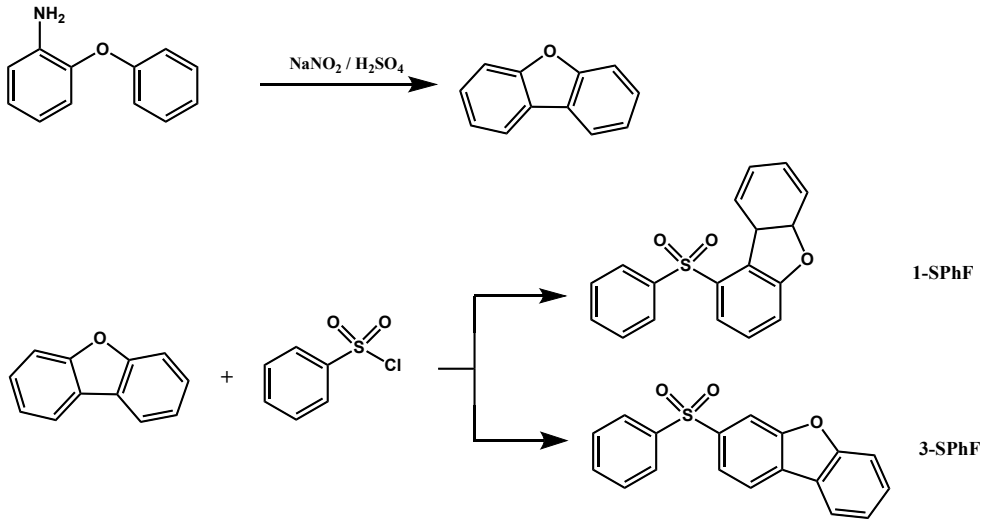
Experimental Procedures

1. Materials and characterization

Materials. 2-Phenoxyaniline, urea, sodium nitrite, benzenesulfonyl chloride, iron chloride were purchased from Aldrich.

Characterizations. Proton and carbon nuclear magnetic resonance (^{1}H NMR and ^{13}C NMR) spectra were attained from a Varian Mercury-Plus 500 Nuclear Magnetic Resonance Spectrometer in $CDCl_3$ and DMSO, using tetramethylsilane as the internal standard. High-resolution EI mass spectra were obtained on a MAT95XP-HRM spectrometer. The photoluminescent (PL) spectra and the UV-visible absorption spectra of the compounds were carried out on Shimadzu RF-5301 PC spectrometer and Hitachi U-3900 spectrophotometer, respectively. The transient photoluminescent spectra were measured with a Shimadzu RF-5301 PC spectrometer or an Ocean Optics Maya Pro2000 with 365 nm Rhinospectrum RhinoLED as the excitation source. Single-crystal analysis of SPh-TP was obtained through an Oxford Diffraction Gemini S Ultra X-ray Single Crystal Diffractometer with a (Cu) X-ray source. The time-dependent density functional theory (TD-DFT) calculations were performed at the rb3lyp/6-31g(d) level with the Gaussian 16 software. Natural transition orbital (NTO) analysis were carried out with TD-DFT simulations and extracted by the Multiwfn and plotted via GaussView with a isovalue of 0.02.[1]

2. Synthetic procedures



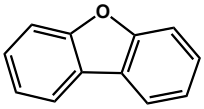
Synthetic details:

Dibenzofuran was synthesized accoding to previous reported.[2]

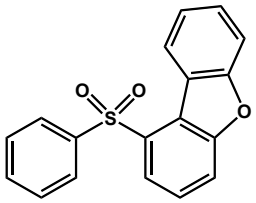
Benzenesulfonyl chloride (3.00 g, 16.97 mmol) and dibenzofuran (4.29 g, 25.48 mmol) were dissoved in dichloromethane solution, ferric chloride (9.32 g, 33.94 mmol) was added in dropwise manner at 40°C under argon atmosphere. After 6 h, the mixture was cooled to room temperature and 1 M HCl (30 mL) was slowly added. The mixture was extracted with dichloromethane, and washed three times with water and dried over sodium sulfate anhydrous. After filtration, the filtrate

was further purified through silica-gel chromatography with n-hexane/CH_2Cl_2 (2/1, v/v) to give 1-SPhF (1.23 g, yield: 23.34 %) and 3-SPhF (0.85 g, yield: 16.13 %).

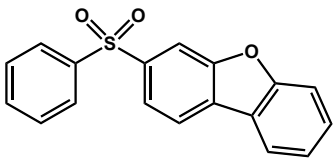
3. Characterization data



Dibenzofuran. Compound dibenzofuran was recrystallized from the n-hexane and obtained as white crystalline solid. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ = 7.96 (d, J=7.5 Hz, 2H), 7.58 (d, J=8.5 Hz, 2H), 7.49-7.44 (m, 2H), 7.38-7.32 (m, 2H). ^{13}C NMR ($CDCl_3$, 298 K): δ 156.19, 127.13, 124.23, 122.69, 120.65, 111.67. High Resolution EI-MS: m/z found: 168.0571 $[M]^+$; calcd for $C_{12}H_8O$: 168.0570



9-(phenylsulfonyl)-4a,9b-dihydrodibenzo[b,d]furan (1-SPhF). Compound 1-SPhF was recrystallized from the mixture of dichloromethane/n-hexane and obtained as white crystalline solid. ^{1}H NMR (500 MHz, DMSO-d_6, 298K): δ = 8.59 (d, J=8 Hz, 1H), 8.15 (d, J=8 Hz, 1H), 8.08 (d, J=7.5 Hz, 1H), 7.95 (d, J=7.5 Hz, 2H), 7.85-7.79 (m, 1H), 7.79-7.74 (m, 1H), 7.68-7.61 (m, 2H), 7.61-7.54 (m, 2H), 7.48-7.43 (m, 1H). ^{13}C NMR (DMSO-d_6, 298K): δ 156.85, 141.15, 134.21, 133.30, 129.20, 128.93, 127.13, 126.64, 125.83, 124.73, 123.55, 121.73, 121.05, 117.17, 111.60. High Resolution EI-MS: m/z found: 308.0504 $[M]^+$; calcd for $C_{18}H_{12}O_3S_1$: 308.0502.



3-(phenylsulfonyl)dibenzo[b,d]furan (3-SPhF). Compound 3-SPhF was recrystallized from the mixture of dichloromethane/n-hexane and obtained as white crystalline solid. ^{1}H NMR (500 MHz, DMSO-d_6, 298K): δ = 8.59 (d, J=7.5 Hz, 1H), 8.15 (d, J=7.0 Hz, 1H), 8.08 (d, J=7.0 Hz, 1H), 7.96 (d, J=7.0 Hz, 2H), 7.85-7.80 (m, 1H), 7.79-7.76 (m, 1H), 7.68-7.61 (m, 2H), 7.61-7.55 (m, 2H), 7.48-7.43 (m, 1H). ^{13}C NMR (DMSO-d_6, 298K): δ 156.59, 140.72, 134.42, 133.98, 130.23, 129.89, 128.31, 127.29, 125.60, 125.28, 124.22, 120.77, 120.58, 118.41, 112.45. High Resolution EI-MS: m/z found: 308.0502 $[M]^+$; calcd for $C_{18}H_{12}O_3S_1$: 308.0502.

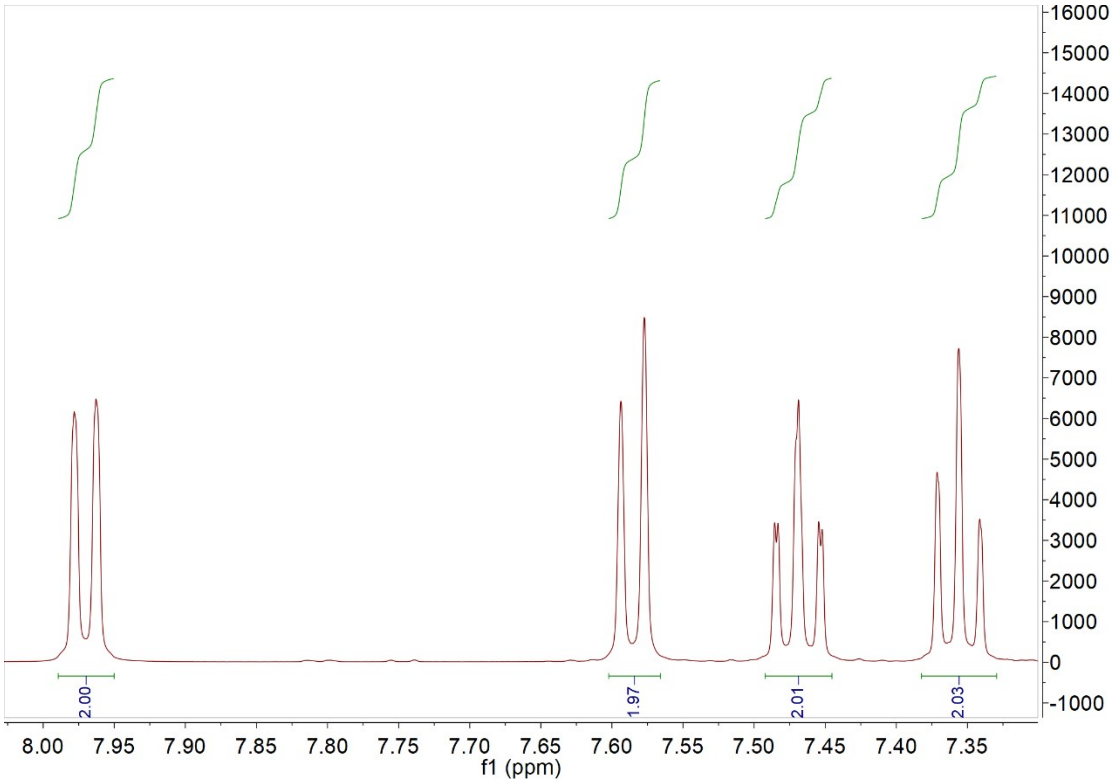


Fig. S1. ^{1}H NMR spectrum of dibenzofuran.

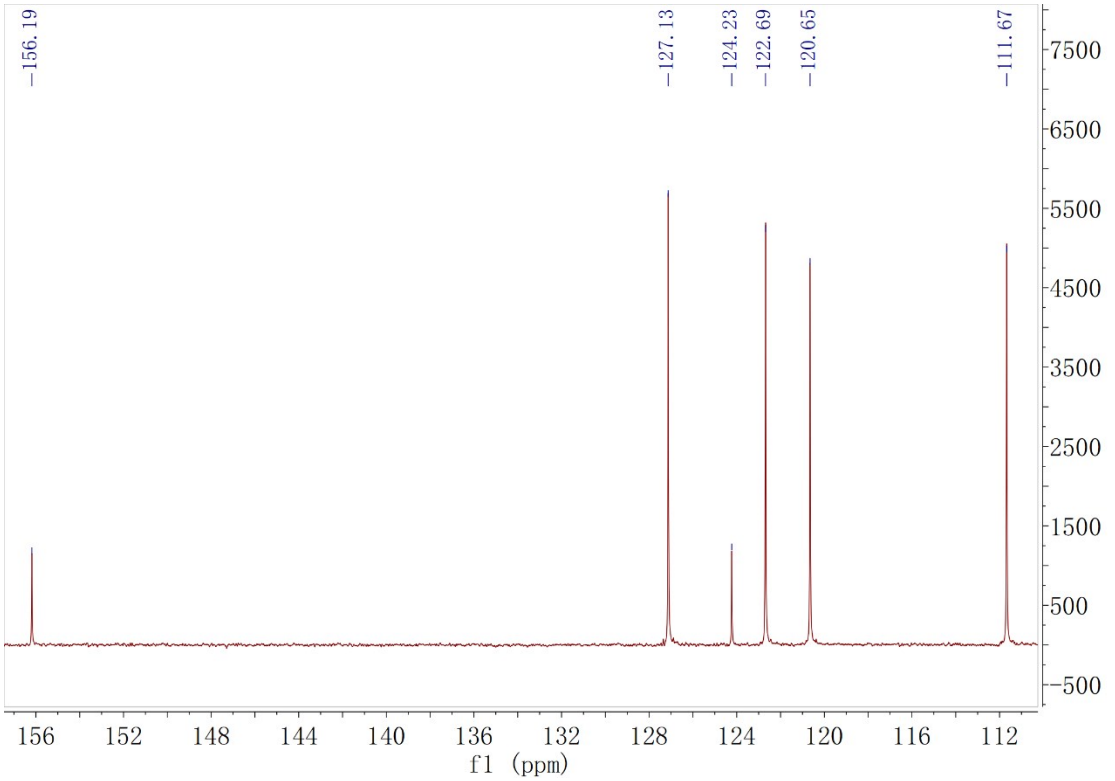


Fig. S2. ^{13}C NMR spectrum of dibenzofuran.

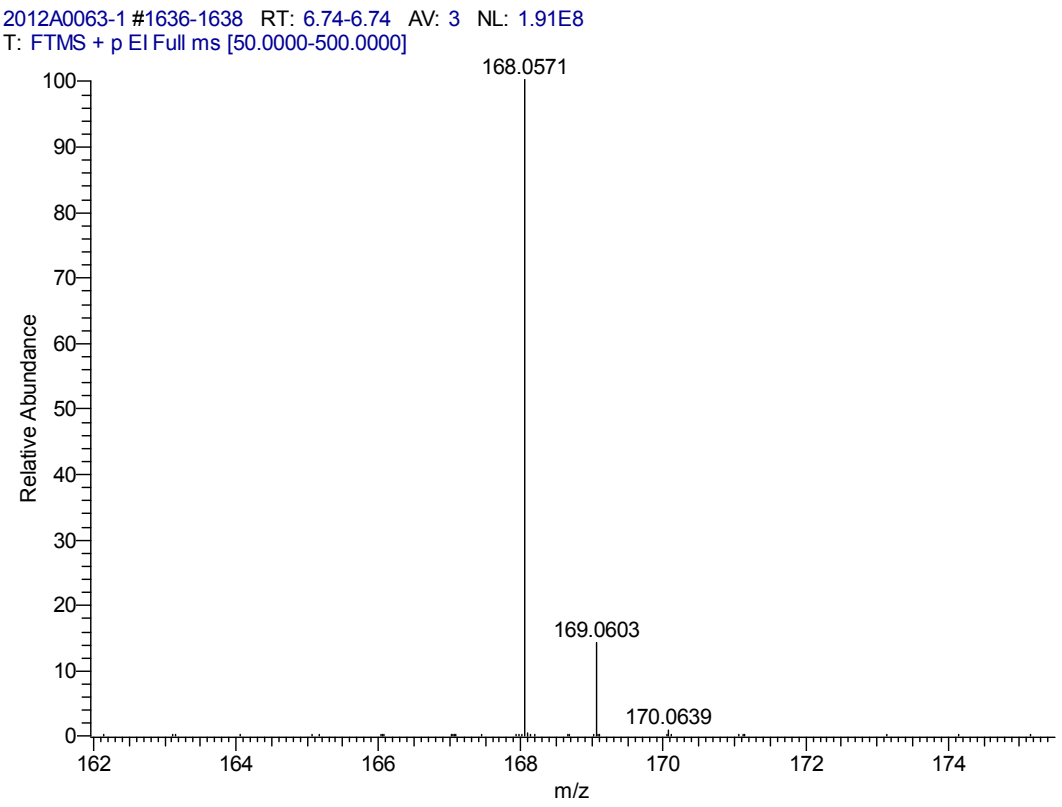


Fig. S3. HRMS spectrum of dibenzofuran.

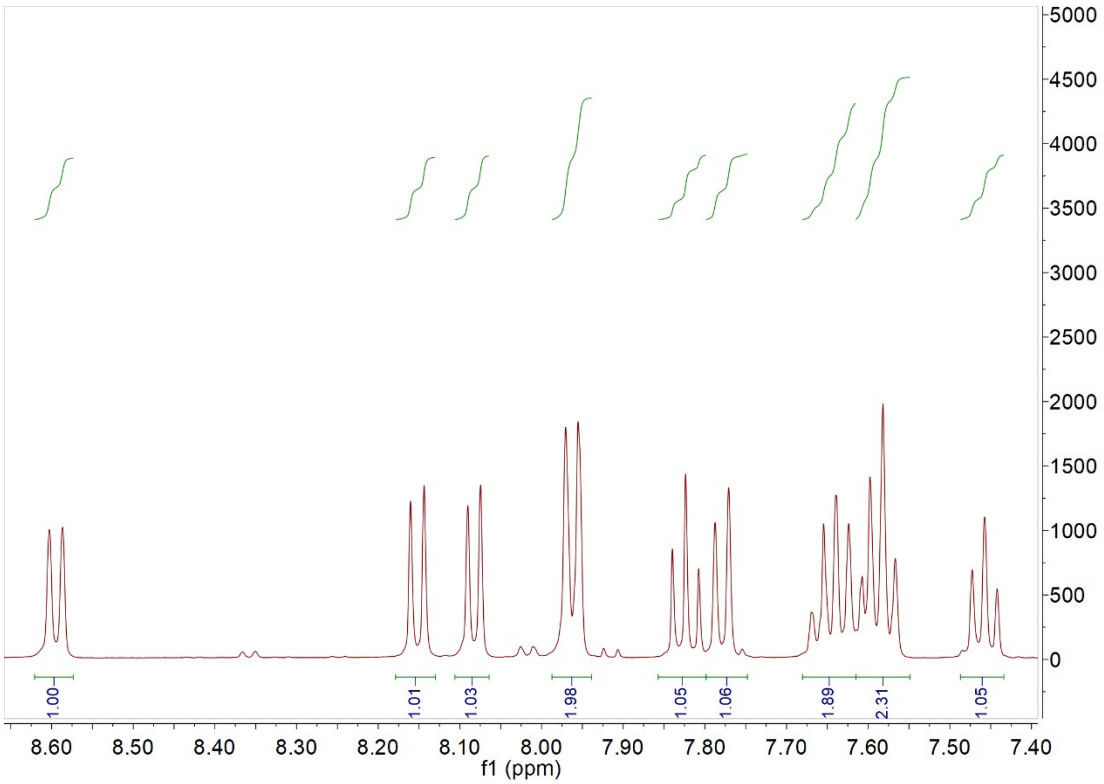


Fig. S4. ^{1}H NMR spectrum of 1-SPhF.

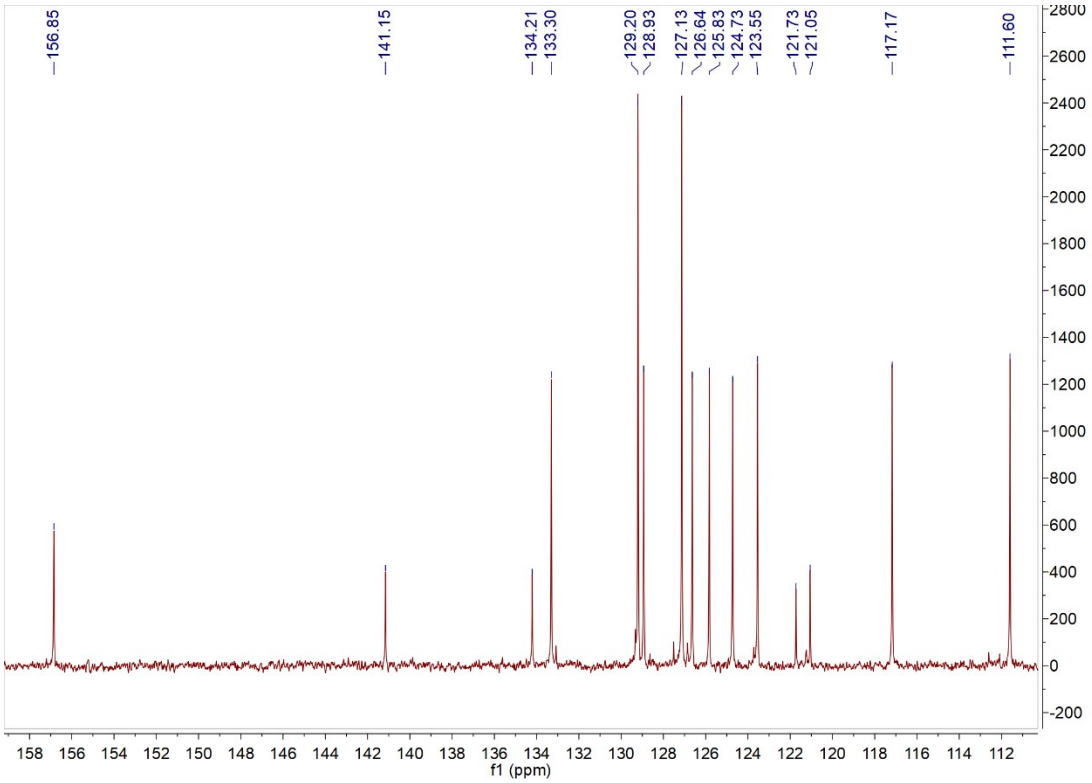


Fig. S5. ^{13}C NMR spectrum of 1-SPhF.

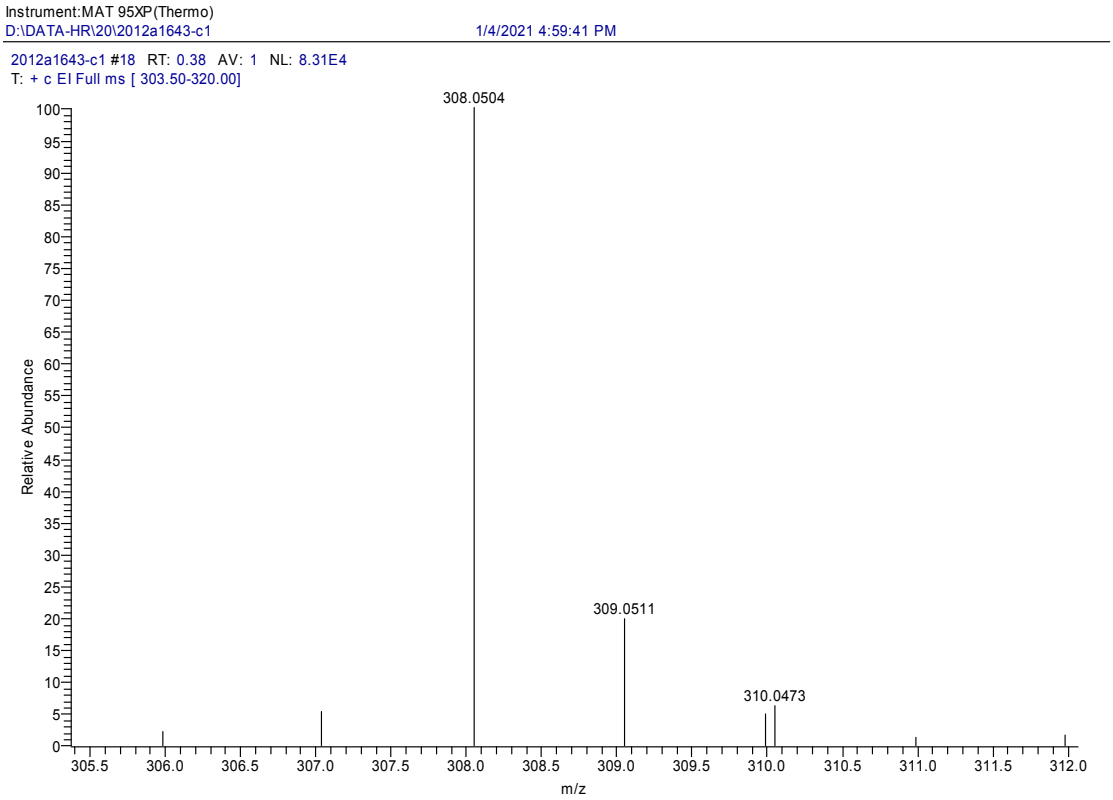


Fig. S6. HRMS spectrum of 1-SPhF.

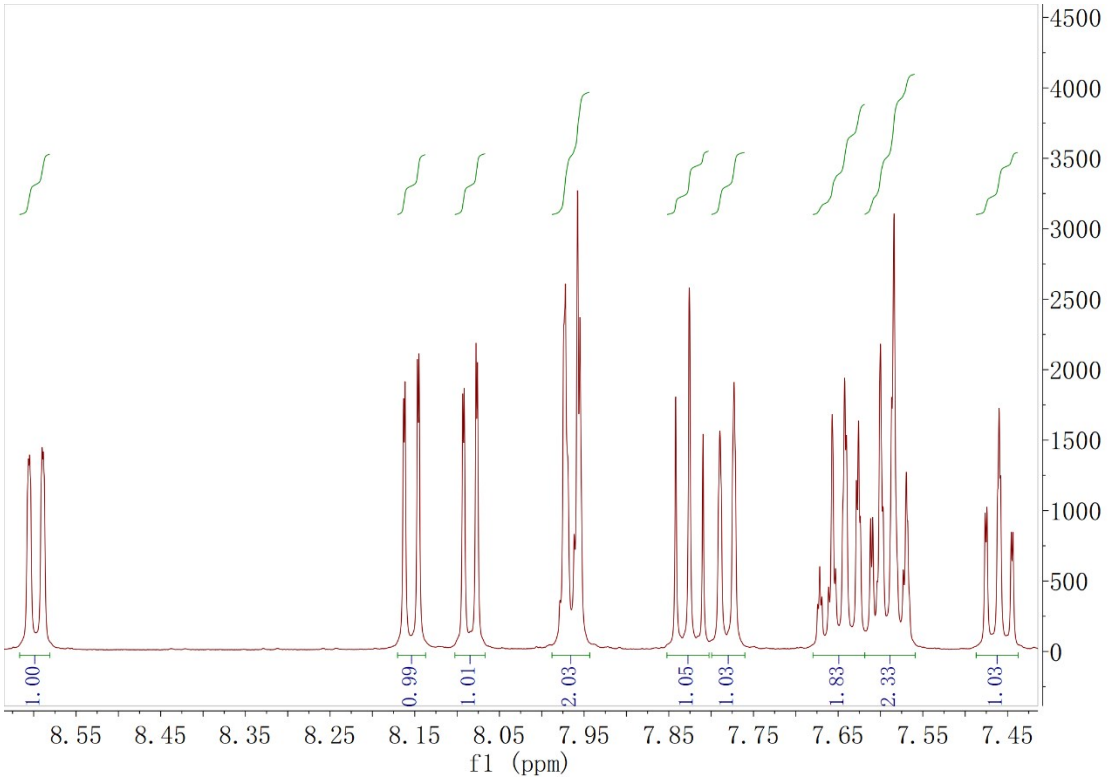


Fig. S7. ^{1}H NMR spectrum of 3-SPhF.

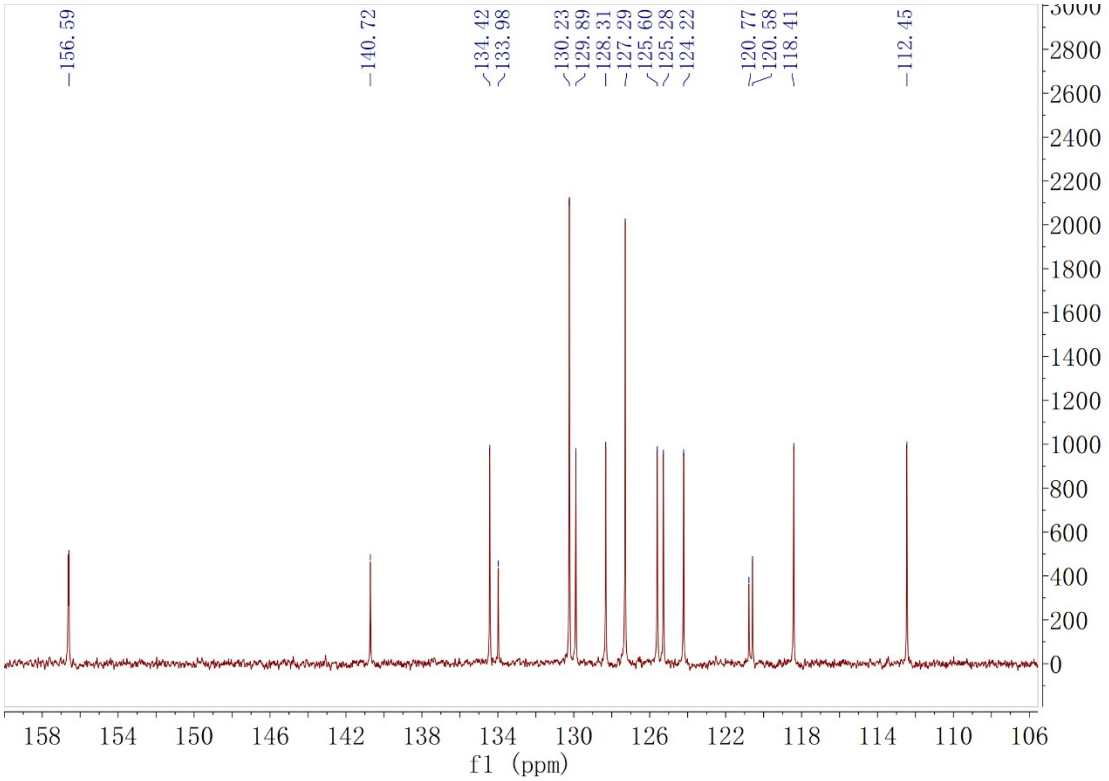


Fig. S8. ^{13}C NMR spectrum of 3-SPhF.

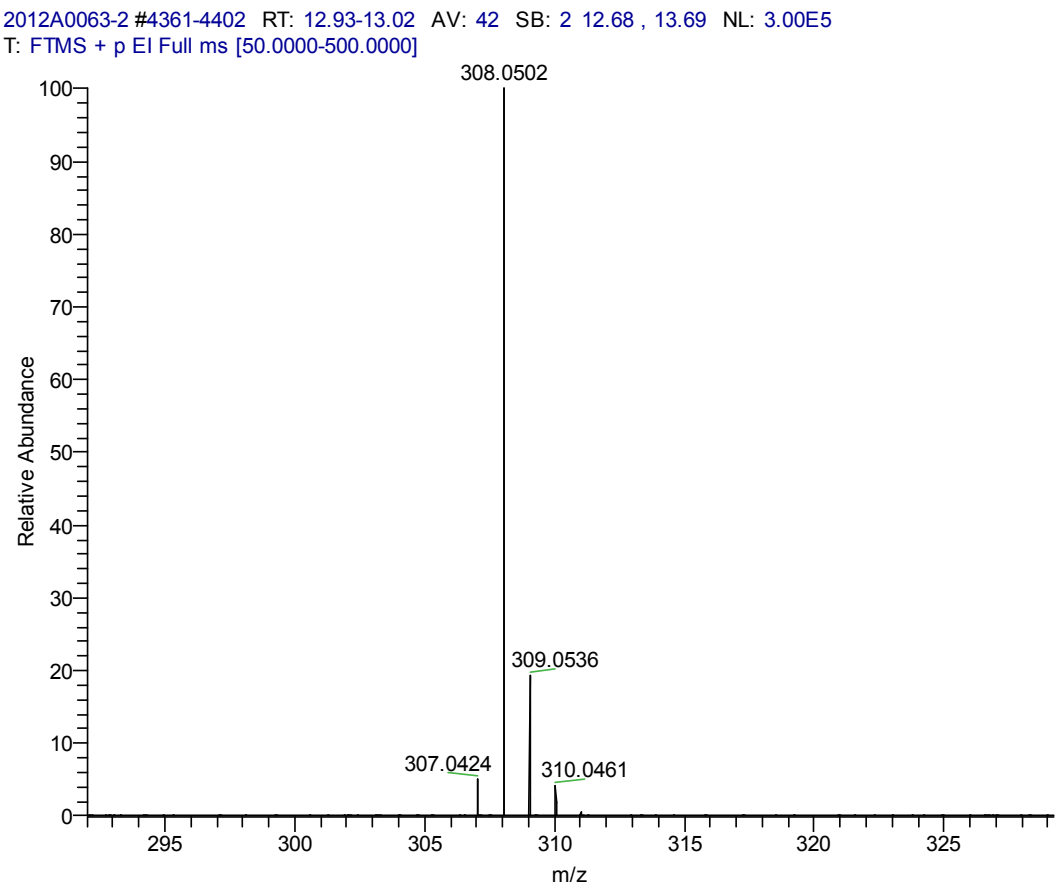


Fig. S9. HRMS spectrum of 3-SPhF.

Results and discussion

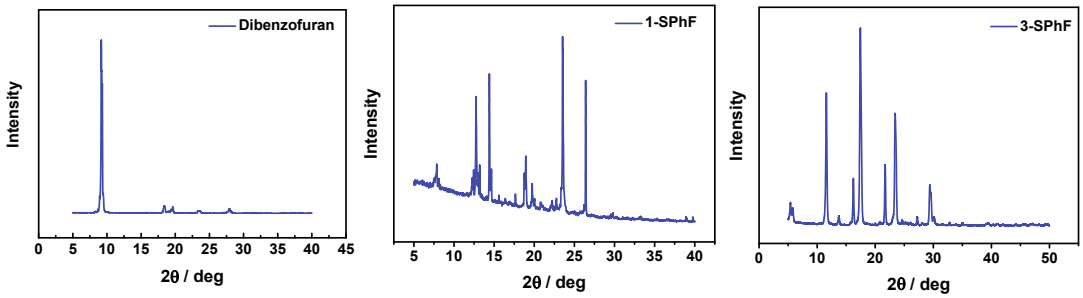


Fig. S10. PXRD of dibenzofuran, 1-SPhF and 3-SPhF crystalline powder.

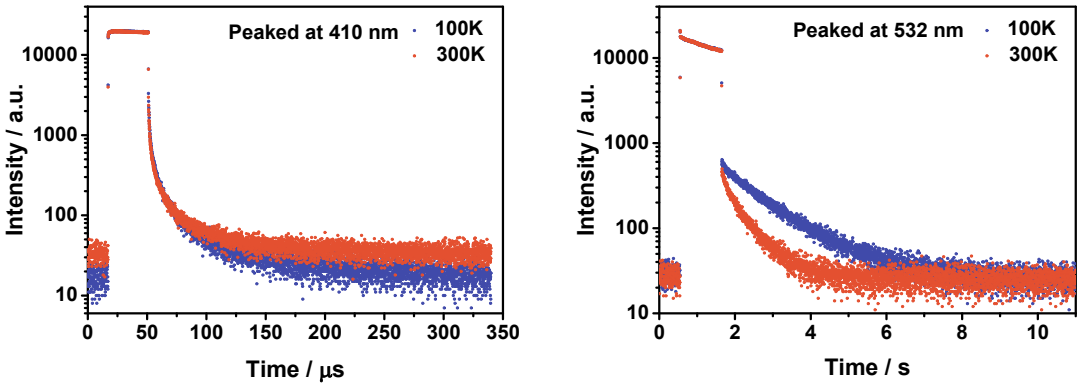


Fig. S11. The emission decay spectra of dibenzofuran recorded at 410 nm and 532 nm.

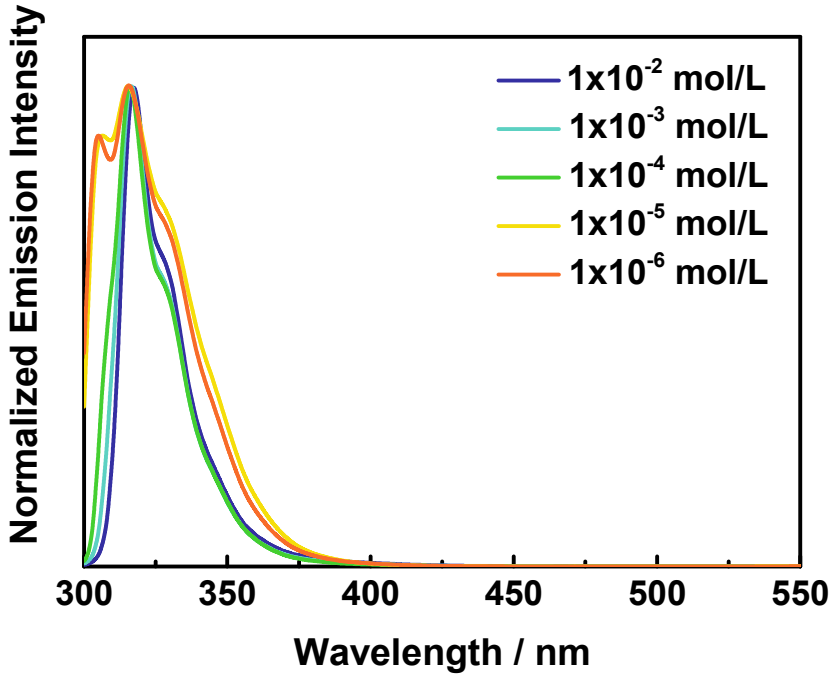


Fig. S12. The concentration-dependent spectra of dibenzofuran in toluene solution.

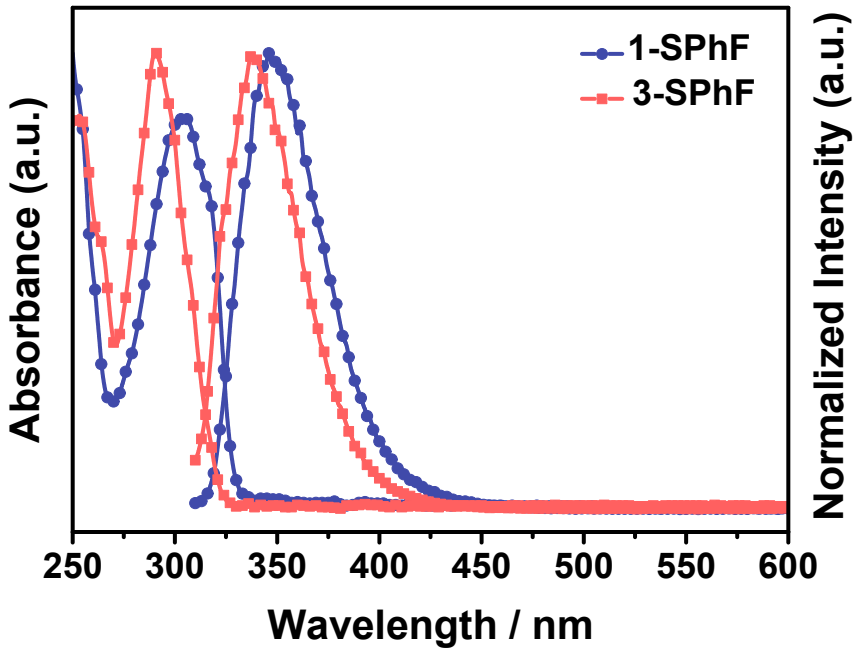


Fig. S13. The normalized PL spectra and UV-vis absorption spectra of 1-SPhF and 3-SPhF in dilute tetrahydrofuran solution (1×10^{-5} mol/L).

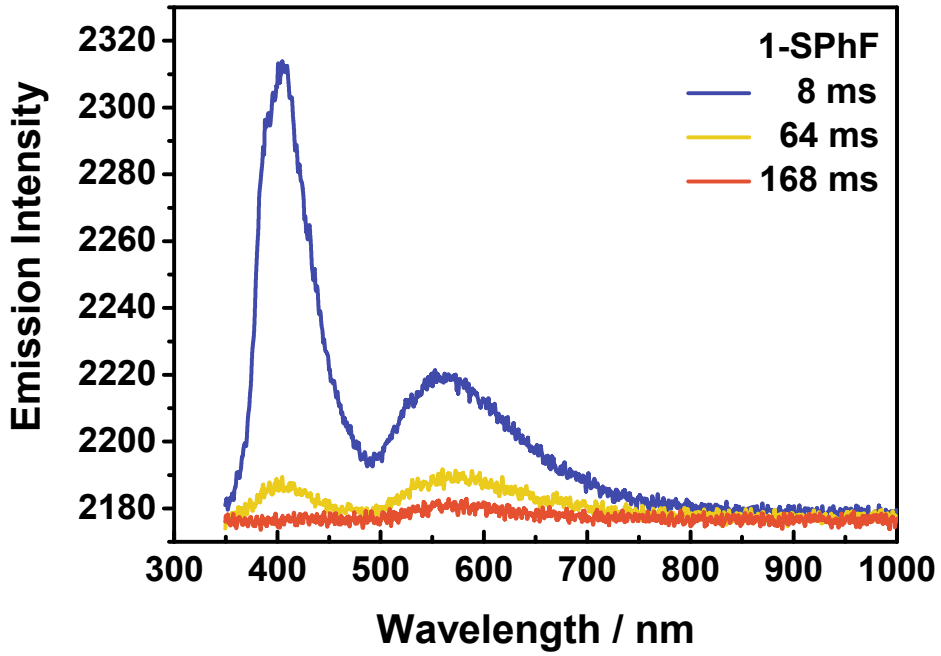


Fig. S14. The time-resolved spectra of 1-SPhF.

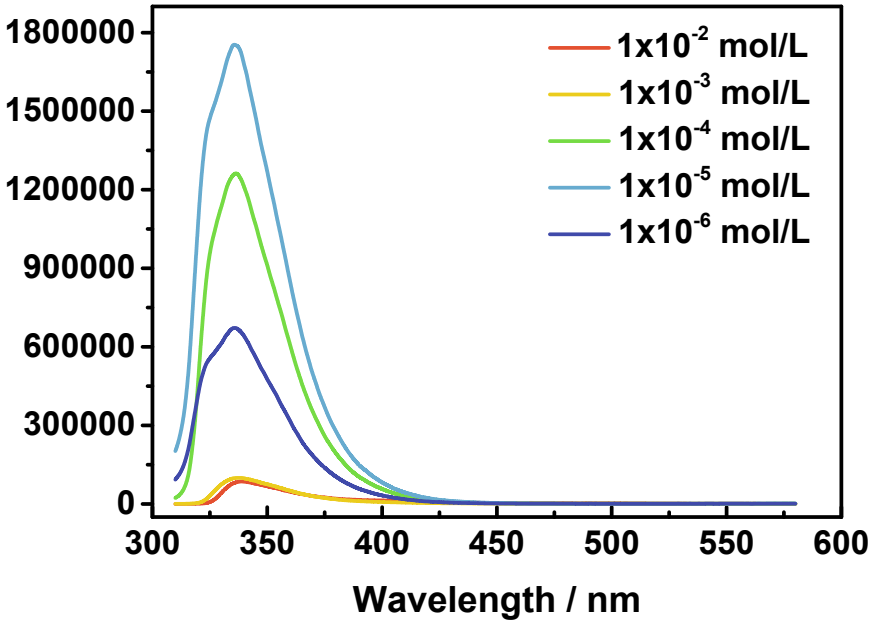


Fig. S15.Concentration-dependent spectrum of 3-SPhF in toluene.

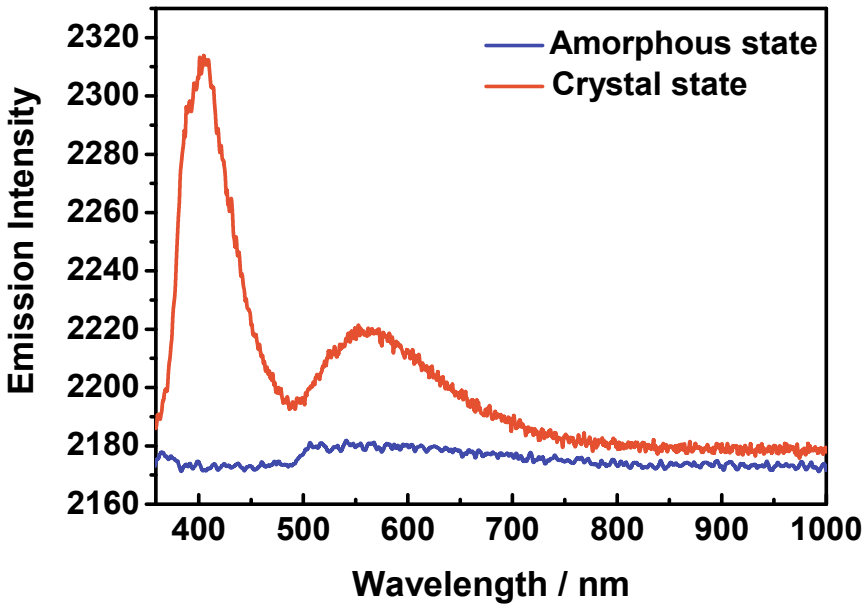


Fig. S16. The phosphorescence spectra of 1-SPhF in amorphous state and crystal state.

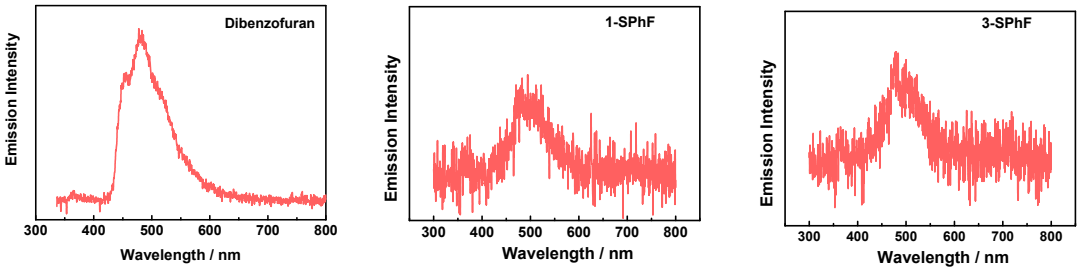


Fig. S17. The phosphorescence spectra of dibenzofuran, 1-SPhF and 3-SPhF in Me-THF (1×10^{-5} mol/L) at 77 K.

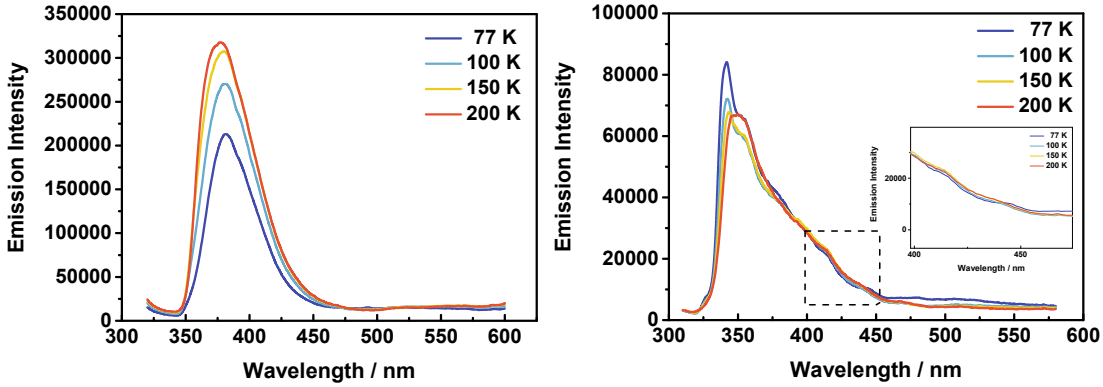


Fig. S18. The PL spectra of 1-SPhF and 3-SPhF at different temperatures.

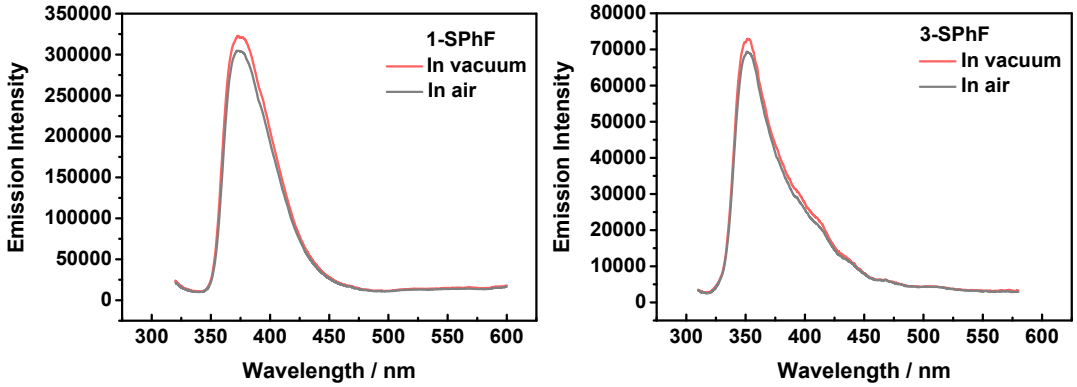


Fig. S19. The PL spectra of 1-SPhF and 3-SPhF in vacuum and in air.

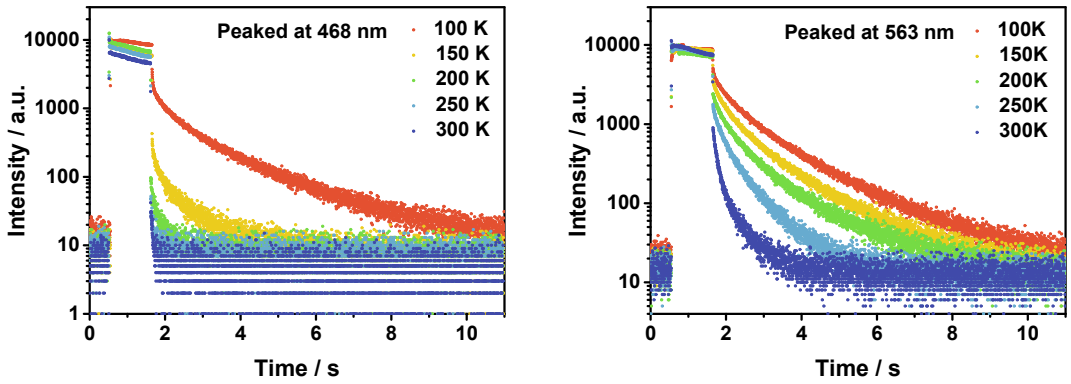


Fig. S20. The emission decay spectra of 1-SPhF recorded at 468 nm and 563 nm under different temperatures.

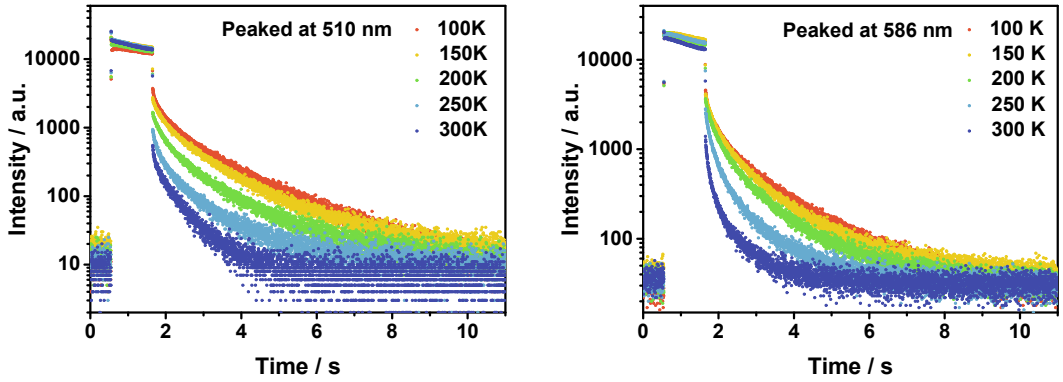


Fig. S21. The emission decay spectra of 3-SPhF recorded at 510 nm and 586 nm under different temperatures.

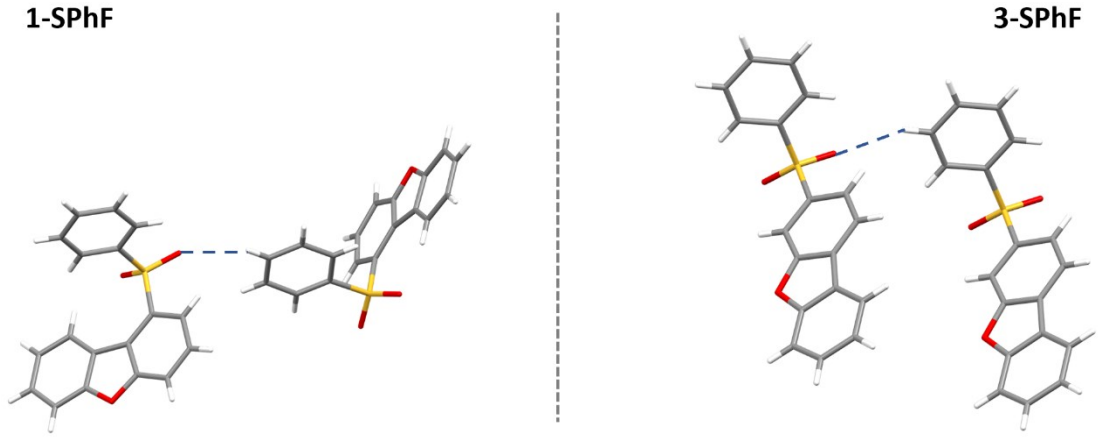


Fig. S22. The common intermolecular interaction in single crystals of 1-SPhF and 3-SPhF.

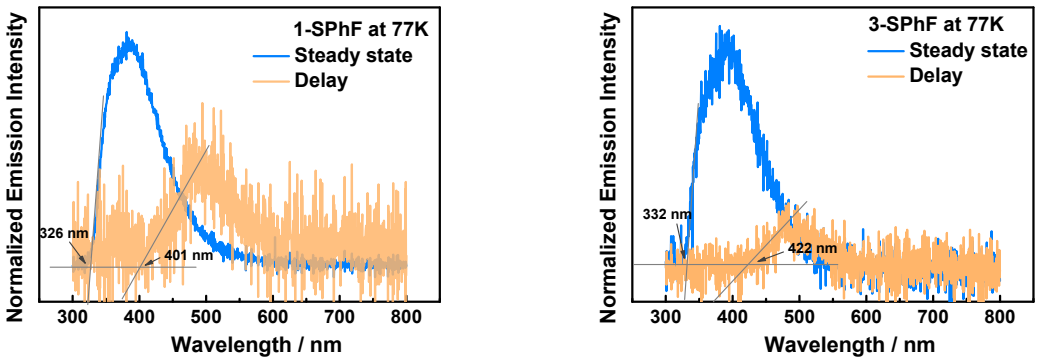


Fig. S23. The PL spectra of 1-SPhF and 3-SPhF in dilute 2-methyltetrahydrofuran at 77 K.

Table S1. The HOMO and LUMO distributions of 1-SPhF and 3-SPhF in coupled molecules.

Compound	Coupled molecule	LUMO	HOMO	ΔE_{ST} / eV
1-SPhF				0.98
				0.83
				0.90
3-SPhF				1.09
				0.86
				0.60

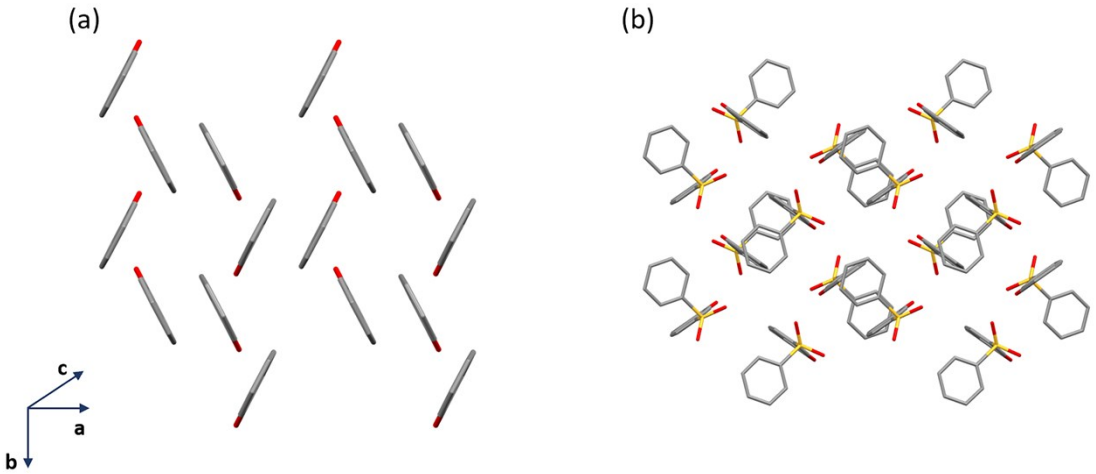


Fig. S24. Herringbone type in single crystal of (a) dibenzofuran and (b) 3-SPhF.

Table S2. The photoluminescence parameters of 1-SPhF and 3-SPhF.

Compound	Wavelength (nm)	Lifetime	QY (%)	
			Total	DF+RTP
1-SPhF	372	5.6 ns	46	15
	403	78.2 μs		
	563	242.1 ms		
3-SPhF	352	4.5 ns	55	26
	423	282.5 μs		
	510	497.7 ms		
	586	230.0 ms		

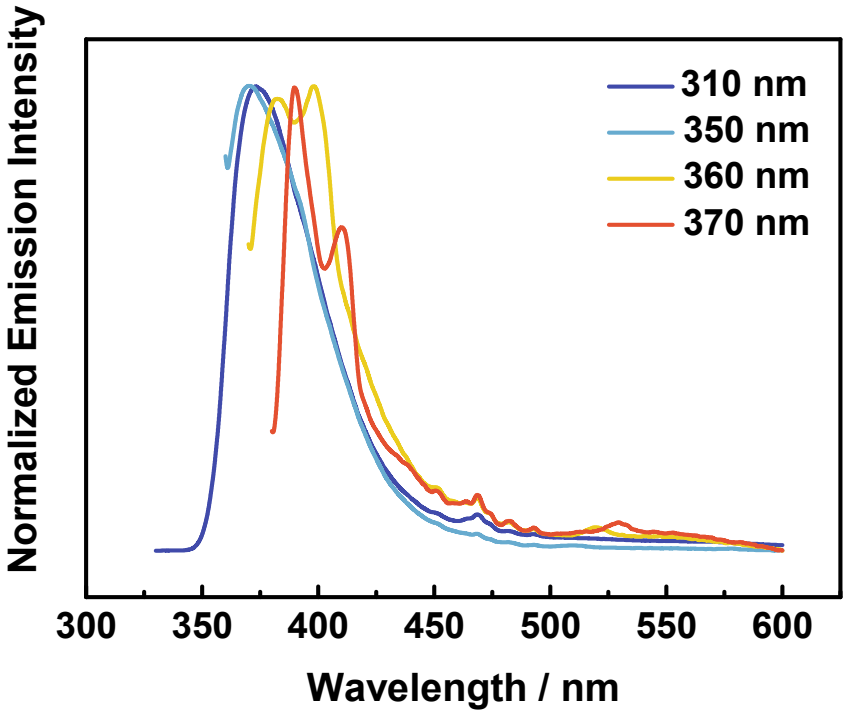


Fig. S25. The normalized emission spectra of 1-SPhF under different excitation wavelengths.

Reference

1. Lu, T. & Chen, F. Multiwfn: A Multifunctional Wavefunction Analyzer. *Journal of Computational Chemistry* **33**, 580-592 (2012).
2. Yue, G. et al. A Facile Synthetic Method of Dibenzofuran and Its Derivatives. *Chinese Journal of Applied Chemistry* **21**, 20-23 (2004).
3. Chen, J. et al. Achieving Dual-Emissive and Time-Dependent Evolutive Organic Afterglow by Bridging Molecules with Weak Intermolecular Hydrogen Bonding. *Advanced Optical Materials* **7**, 1801593 (2019).