Electronic Supplementary Information (ESI)

Thermally Activated Delayed Fluorescence with Dual-Emission and Pressure-Induced Bidirectional Shifting: Cooperative Effects of Intramolecular and Intermolecular Energy Transfer

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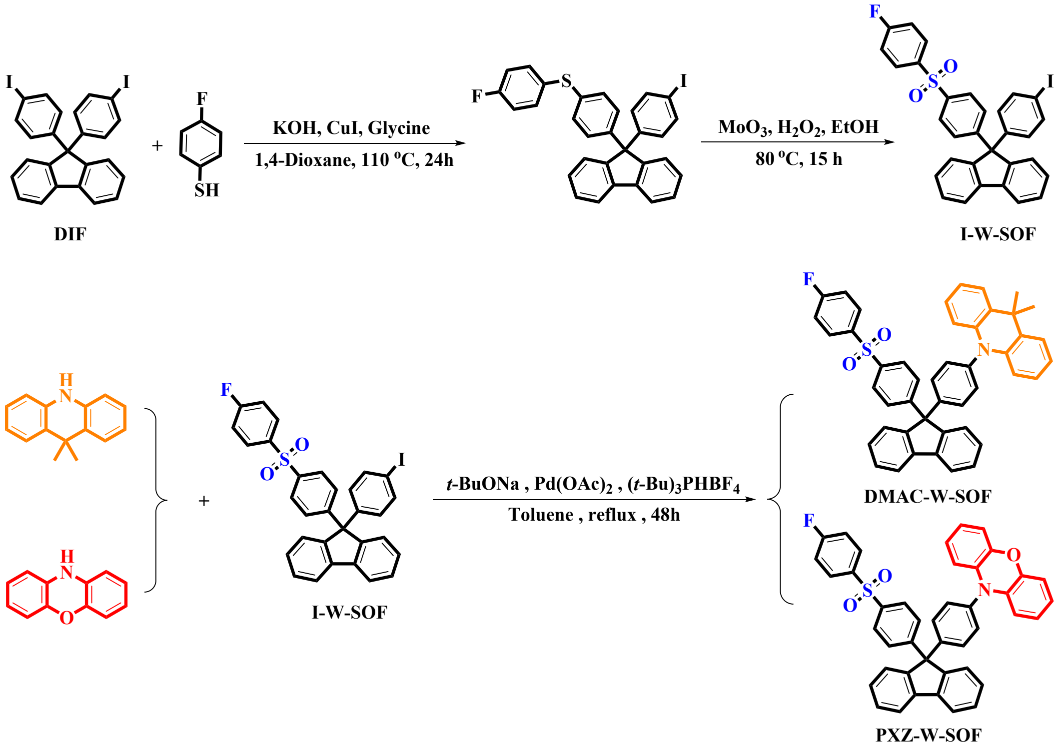
General Information

The ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Advance III (500 MHz) spectrometer with DMSO and $CDCl_3$ as the solvent, respectively. The fluorescence titration experiments were conducted on a HITACHI F-7000 spectrofluorophotometer. Mass spectra were recorded on a Micromass Quattro II triplequadrupole mass spectrometer using electrospray ionization and analyzed with the MassLynx software suite or an Agilent Technologies 6530 Q-TOF mass spectrometer with an ESI resource. UV-Vis absorption spectra were recorded on a TU-1810 UV-Vis spectrophotometer. Photoluminescence (PL) spectra were recorded on a Hitachi F-4700 fluorescence spectrophotometer. For the steady state PL spectra of DMAC-W-SOF and PXZ-W-SOF in toluene and powder state, their excitation wavelengths were 308 nm and 325 nm, respectively. Cyclic voltammetry (CV) was carried out in nitrogen-purged dichloromethane (oxidation scan) at room temperature with a CHI voltammetric analyzer. N-Bu_4PF_6 (0.1 M) was used as the supporting electrolyte. The conventional three-electrode configuration consists of a platinum working electrode, a platinum wire auxiliary electrode, and an Ag wire pseudoreference electrode with ferrocenium-ferrocene (Fc^+/Fc) as the internal standard. The PL lifetimes were measured by a single photon counting spectrometer from Edinburgh Instruments (FLS980) with EPLED and VPLED pulsed UV-LASTER (LASTER277 and LASTER375), and 60 W flashing xenon lamp as the excitation source. Among them, LASTER277 laser was used as the excitation light source for the transient spectra test of DMAC-W-SOF in toluene and powder state; For PXZ-W-SOF, LASTER375 laser was used as the excitation light source in toluene solution, and 60 W flashing xenon lamp mode was used for the powder state and the temperature-dependent transient PL decays measurement, and the excitation wavelength was 325 nm. The photoluminescence quantum efficiency was measured using an absolute photoluminescence quantum yield measurement system (Edinburgh Instruments FLS980).

Synthesis of materials



Scheme S1. Synthetic procedures of **DMAC-W-SOF** and **PXZ-W-SOF**.

9-(4-((4-fluorophenyl)sulfonyl)phenyl)-9-(4-iodophenyl)-9*H*-fluorene (**I-W-SOF**): A mixture of 9,9-bis(4-iodophenyl)fluorene (2.00 g, 3.51 mmol), 4-fluorothiophenol (0.50 g, 3.91 mmol), CuI (0.03 g, 0.16 mmol), Glycine (0.05 g, 0.67 mmol), KOH (0.39 g, 6.96 mmol) and 1,4-dioxane (60 mL) was refluxed under argon for 24 hours. After cooled, the mixture was extracted with brine and CH_2Cl_2, and dried over anhydrous Na_2SO_4. After concentrated under reduced pressure distillation, a yellow liquid was obtained, then MoO_3 (0.10 g, 0.69 mmol) and 30% H_2O_2 (30 mL) were added, and the mixture was refluxed in EtOH (50 mL) for 15 hours. After it was cooled to room temperature, the mixture was extracted with brine and CH_2Cl_2, and dried over anhydrous Na_2SO_4 again. After removal of the solvent, the residue was purified by column chromatography on silica gel using petroleum ether/dichloromethane (1:2 by vol.) as the eluent to give a white powder (0.97 g, yield: 46%). ^{1}H NMR (500 MHz, $CDCl_3$) δ [ppm]: 8.03-8.00 (m, 2H), 7.96 (d, *J* = 5.0 Hz, 2H), 7.87 (d, *J* = 10.0 Hz, 2H), 7.62 (d, *J* = 10.0 Hz, 2H), 7.46-7.42 (m, 6H), 7.35-7.30 (m, 4H), 6.89 (d, *J* = 10.0 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ [ppm]: 165.45, 163.41, 150.52, 148.35, 143.52, 139.08, 138.92, 136.56, 136.49, 136.46, 129.57, 129.49, 128.94, 127.92, 127.20, 127.09, 126.59, 124.83, 119.54, 115.66, 115.48, 91.78, 63.98. MS (ESI) *m/z* for $C_{31}H_{20}FIO_2S$ $(M+Na)^+$ 625.0105, found 625.0115.

10-(4-(9-(4-((4-fluorophenyl)sulfonyl)phenyl)-9*H*-fluoren-9-yl)phenyl)-9,9-dimethyl-9,10-dihydroacridine (**DMAC-W-SOF**): A mixture of I-W-SOF (1.50 g, 2.49 mmol), 9,9-dimethyl-9,10-dihydroacridine (0.63 g, 3.01 mmol), $Pd(OAc)_2$ (20 mg, 0.09 mmol), $(t\text{-Bu})_3PHBF_4$ (87 mg, 0.30 mmol), *t*-BuONa (0.58 g, 6.04 mmol), and toluene (60 mL) was refluxed under argon for 48 h. After cooled, the mixture was extracted with brine and CH_2Cl_2, and dried over anhydrous Na_2SO_4. After removal of the solvent, the residue was purified by column chromatography on silica gel using dichloromethane/petroleum ether (2:1 by vol.) as the eluent to give a white powder (1.52 g, yield: 89%). ^{1}H NMR (500 MHz, $CDCl_3$) δ [ppm]: 8.03-8.00 (m, 2H), 7.88 (t, *J* = 5.0 Hz, 4H), 7.51-7.45 (m, 10H), 7.40 (t, *J* = 5.0 Hz, 2H), 7.27 (t, *J* = 10.0 Hz, 2H), 7.21 (t, *J* = 5.0 Hz, 2H), 7.03-6.96 (m, 4H), 6.30 (d, *J* = 10.0 Hz, 2H), 1.72 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ [ppm]: 166.54, 164.50, 152.11, 149.78, 144.77, 140.84, 140.29, 140.18, 140.01, 137.61, 131.34, 130.69, 130.61, 130.52, 130.13, 129.07, 128.32, 128.24, 127.75, 126.37, 126.20, 125.24, 120.69, 116.77, 116.59, 114.03, 65.28, 36.00, 31.15. MS (ESI) *m/z* for $C_{46}H_{34}FNO_2S$ $(M+H)^+$ 683.2289, found 683.2259.

10-(4-(9-(4-((4-fluorophenyl)sulfonyl)phenyl)-9H-fluoren-9-yl)phenyl)-10*H*-phenoxazine (**PXZ-W-SOF**): It was prepared by the same procedure with **DMAC-W-SOF** excepting using 10*H*-phenoxazin (0.60 g, 3.28 mmol) to replace 9,9-dimethyl-9,10-dihydroacridine. **PXZ-W-SOF** is a green powder (1.38 g, yield: 84%). ^{1}H NMR (500 MHz, $(CD_3)_2SO$) δ [ppm]: 8.04-8.02 (m, 2H), 7.99 (d, *J* = 5.0 Hz, 2H), 7.91 (d, *J* = 5.0 Hz, 2H), 7.53 (d, *J* = 5.0 Hz, 2H), 7.46-7.34 (m, 10H), 7.29 (d, *J* = 10.0 Hz, 2H), 6.71-6.69 (m, 2H), 6.65-6.59 (m, 4H), 5.82-5.81 (m, 2H). ^{13}C NMR (125 MHz, $(CD_3)_2SO$) δ [ppm]: 166.40, 164.38, 152.14, 149.68, 145.50, 143.57, 140.12, 140.01, 137.78, 137.76, 137.50, 134.18, 131.20, 131.13, 131.00, 130.93, 129.36, 128.81, 128.20, 126.57, 124.14, 121.97, 121.35, 117.64, 117.46, 115.75, 113.58, 65.19. MS (ESI) *m/z* for $C_{43}H_{28}FNO_3S$ $(M+H)^+$ 657.1768, found 657.1771.

X-ray structural analysis:

Table S1. Crystal data and structure refinement for **DMAC-W-SOF** and **PXZ-W-SOF**

Identification code	CCDC：2164967 (DMAC-W-SOF)	CCDC：2164968 (PXZ-W-SOF)
Empirical formula	$C_{46}H_{34}FNO_2S$	$C_{43}H_{28}FNO_3S$
Formula weight	683.80	657.72
Temperature/K	170.0	170.0
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/c$
a/Å	8.1805(3)	11.6223(4)
b/Å	16.2254(5)	22.3952(8)
c/Å	25.9415(10)	13.1540(4)
α/°	90	90
β/°	90.036(2)	101.8440(10)
γ/°	90	90
Volume/Å^3	3443.3(2)	3350.9(2)
Z	4	4
ρ_{calc}g/cm^3	1.319	1.304
μ/mm^{-1}	0.142	0.145
F(000)	1432.0	1368.0
Crystal size/mm^3	0.49 × 0.38 × 0.17	0.42 × 0.236 × 0.19
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.022 to 50.7	4.016 to 54.222
Reflections collected	41959	51990
Independent reflections	6296 [R_{int} = 0.0408, R_{sigma} = 0.0234]	7398 [R_{int} = 0.0516, R_{sigma} = 0.0289]
Data/restraints/parameters	6296/2/462	7398/0/442
Goodness-of-fit on F^2	1.026	1.017
Final R indexes [I>=2σ (I)]	R_1 = 0.0388, wR_2 = 0.0968	R_1 = 0.0464, wR_2 = 0.1226
Final R indexes [all data]	R_1 = 0.0483, wR_2 = 0.1033	R_1 = 0.0646, wR_2 = 0.1356
Largest diff. peak/hole / e Å^{-3}	0.40/-0.41	0.75/-0.38

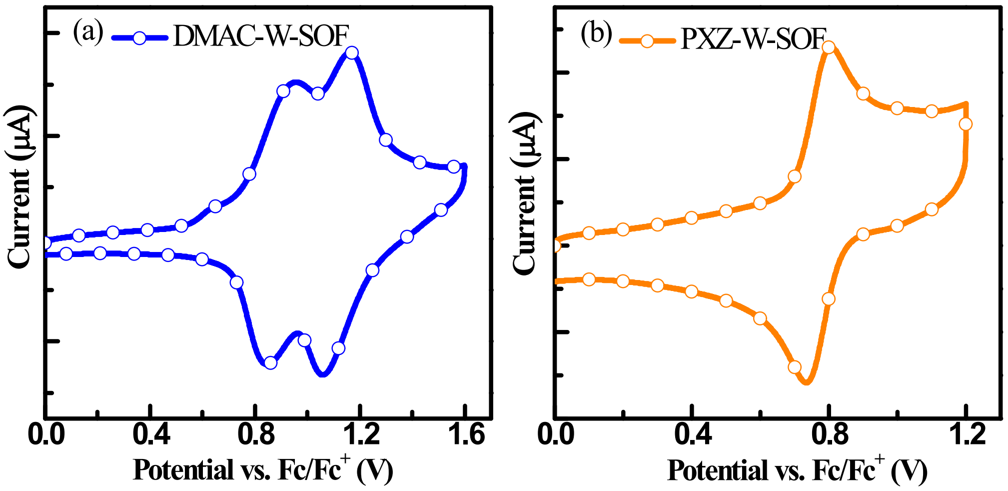


Fig. S1. Cyclic voltammogram of target compounds (a) DMAC-W-SOF and (b) PXZ-W-SOF in CH_2Cl_2 for oxidation scan.

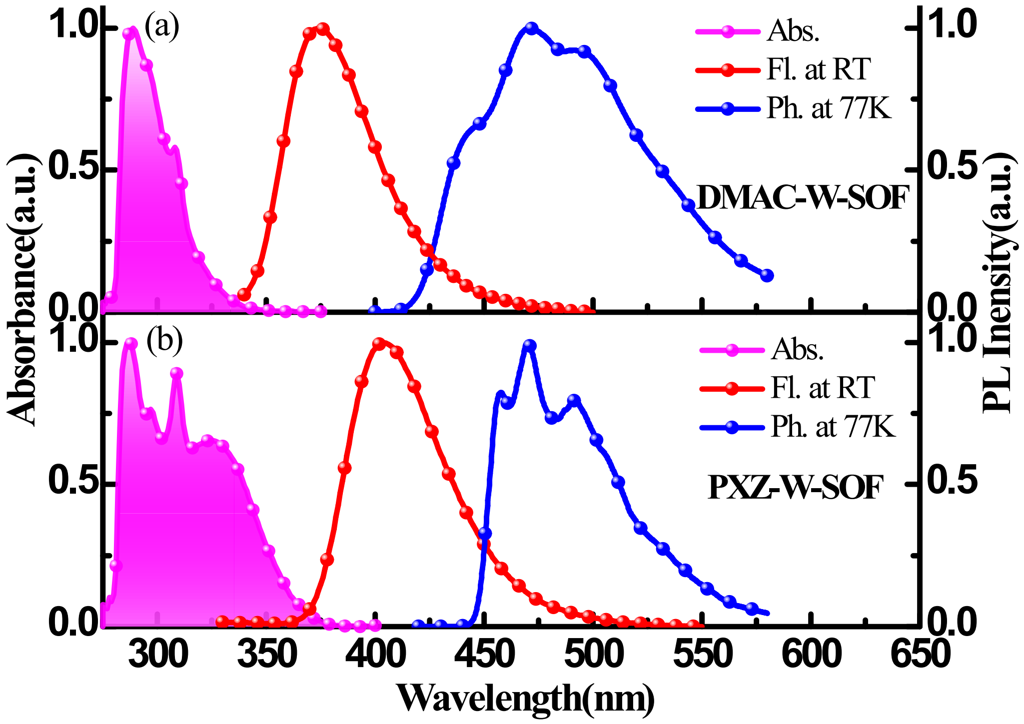


Fig. S2. Normalized UV-Vis absorption of (a) DMAC-W-SOF, and (b) PXZ-W-SOF in toluene. Fluorescence and Phosphorescence spectra of these two compounds were measured in toluene (10^{-4} M) and 2-methyl-tetrahydrofuran, respectively. The pink and the red lines represent UV-Vis and fluorescence spectra, respectively, while the blue lines represent phosphorescence spectra.

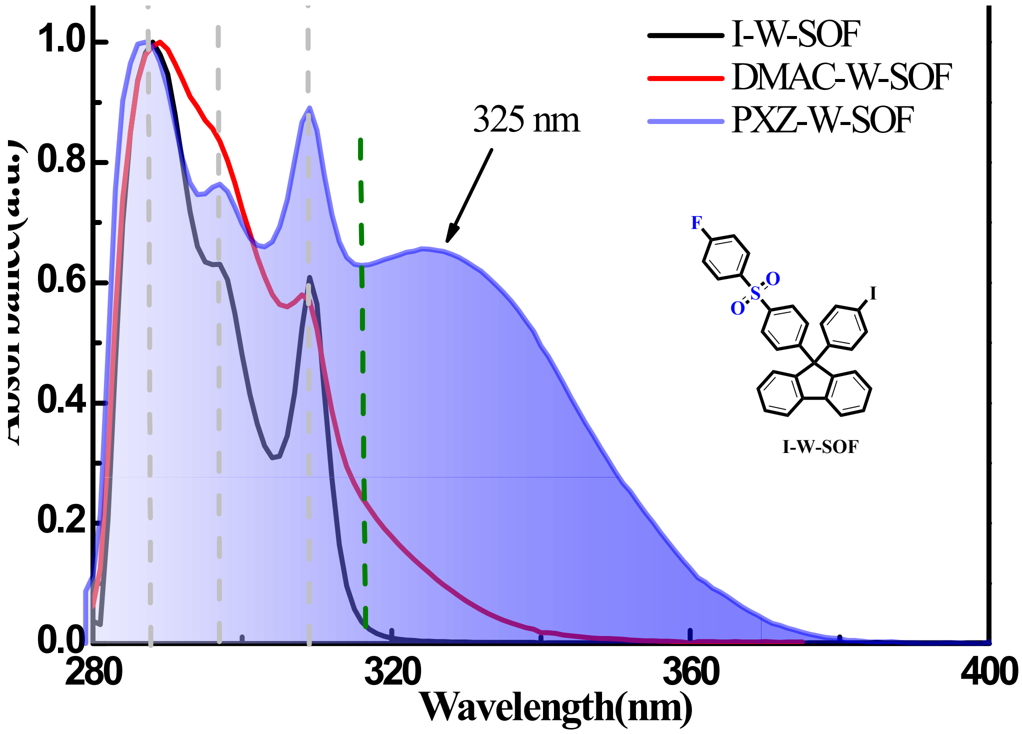


Fig. S3. Normalized UV-Vis absorption of I-W-SOF, DMAC-W-SOF and PXZ-W-SOF in toluene (10^{-4} M) (Insert: molecular structure of I-W-SOF).

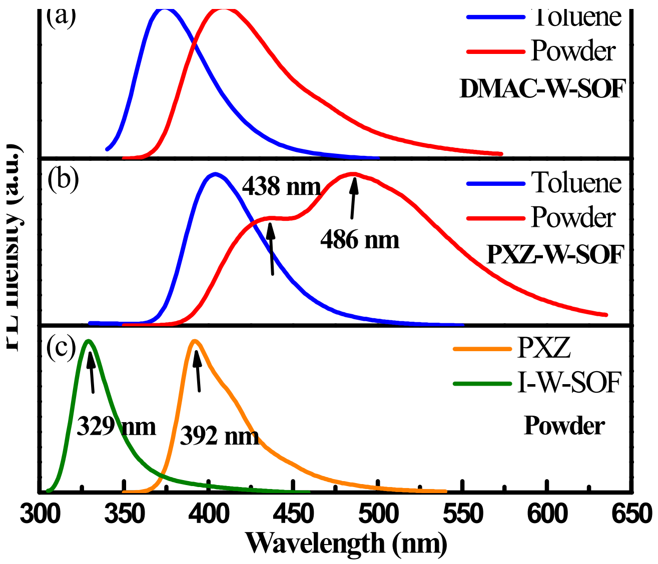


Fig. S4. Normalized fluorescence spectra of (a) DMAC-W-SOF, (b) PXZ-W-SOF and (c) PXZ and I-W-SOF.

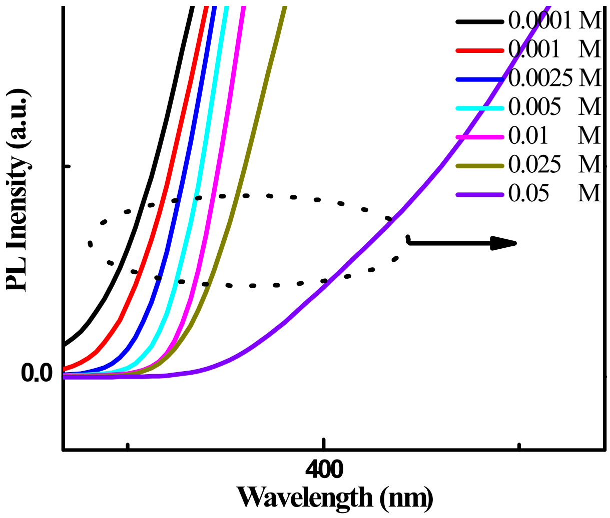


Fig. S5. Zoom-in schematic of the normalized fluorescence spectra of PXZ-W-SOF at different concentrations (0.0001-0.05 M) in toluene solution.

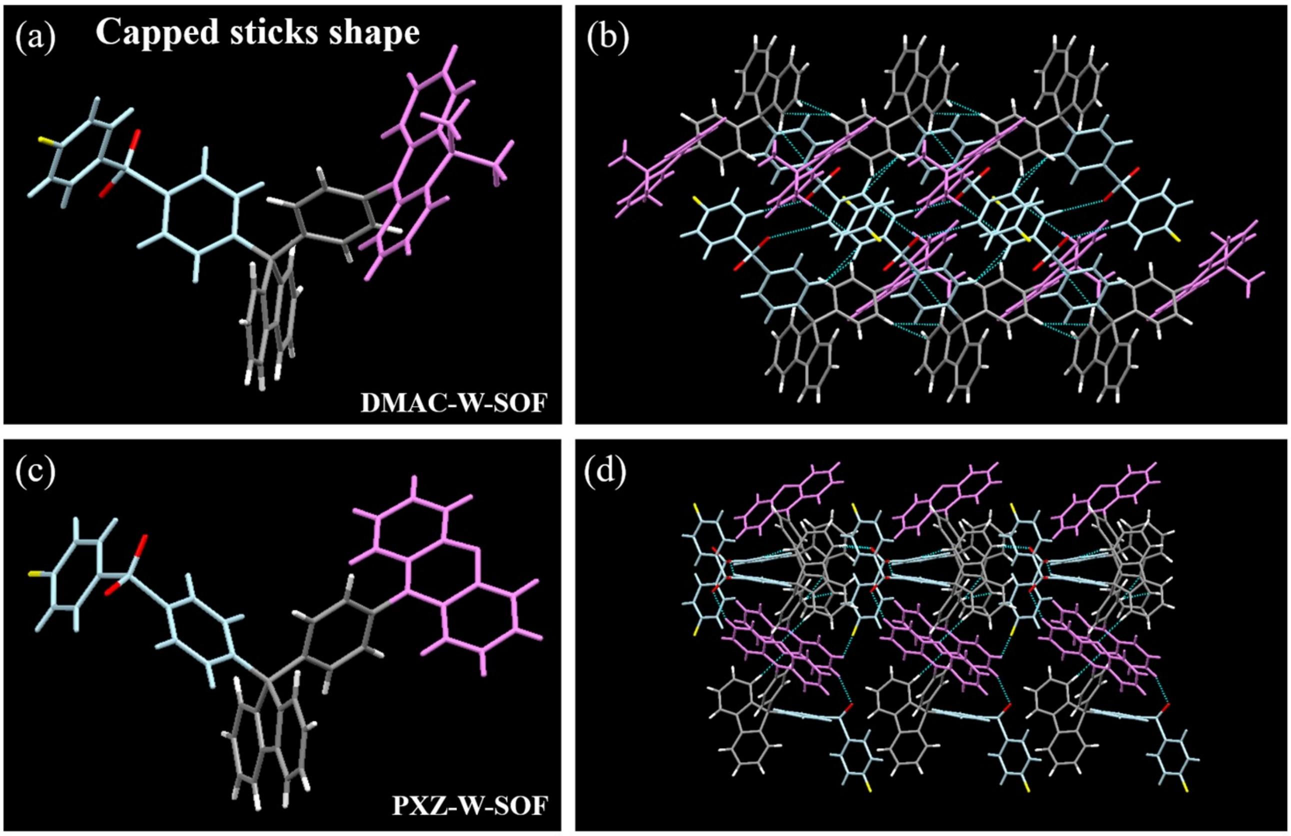


Fig. S6. Single crystal structure of DMAC-W-SOF and PXZ-W-SOF: (a) molecular structure and (b) packing structure of DMAC-W-SOF; (c) molecular structure and (d) packing structure of PXZ-W-SOF.

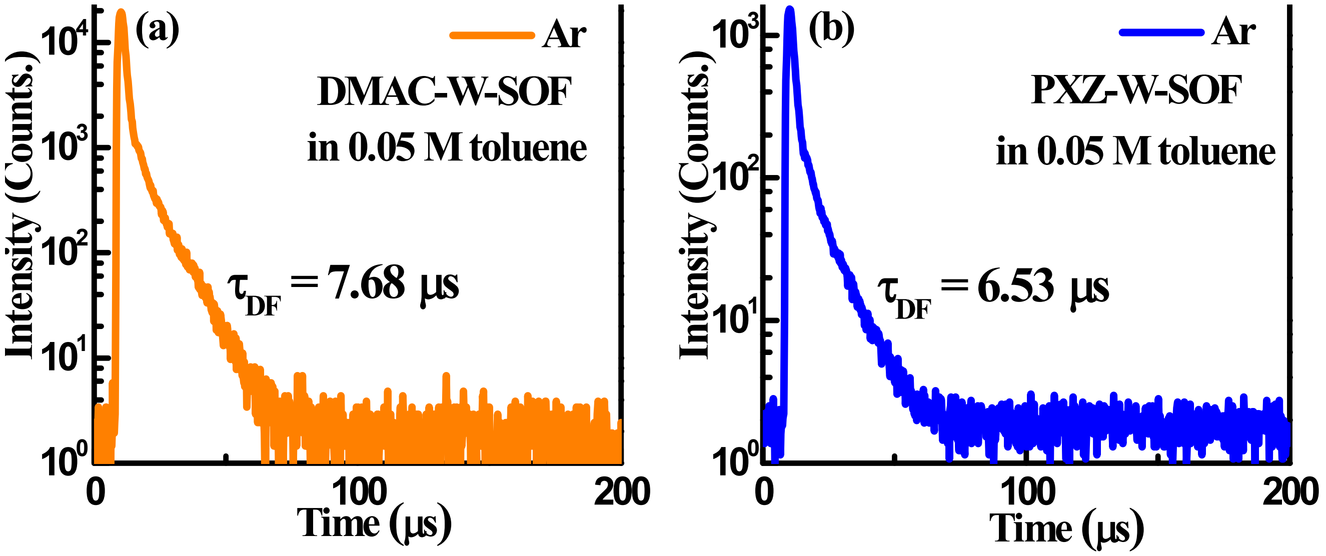


Fig. S7. Transient PL characteristics of (a) DMAC-W-SOF and (b) PXZ-W-SOF in toluene (0.05 M) under argon conditions at room temperature.

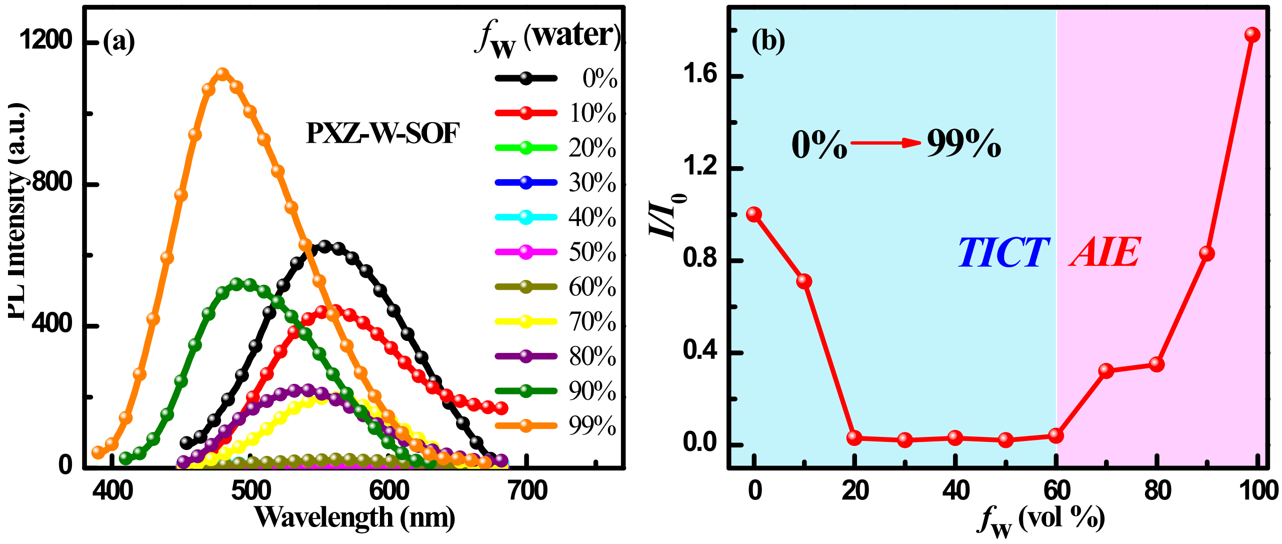


Fig. S8. (a) PL spectra of PXZ-W-SOF in THF/water mixtures (10^{-4} M) with different water fractions (f_w = 0 to 99%) at room temperature, and (b) plots of PL peaks vs f_w of PXZ-W-SOF.