

Supporting Information

Rational design of Spiro[fluorene-9,9'-xanthene] based molecule for aggregation induced emission (AIE) and mechanochromism (MC): Synthesis and theoretical investigation

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SI1. Materials and instrumentation

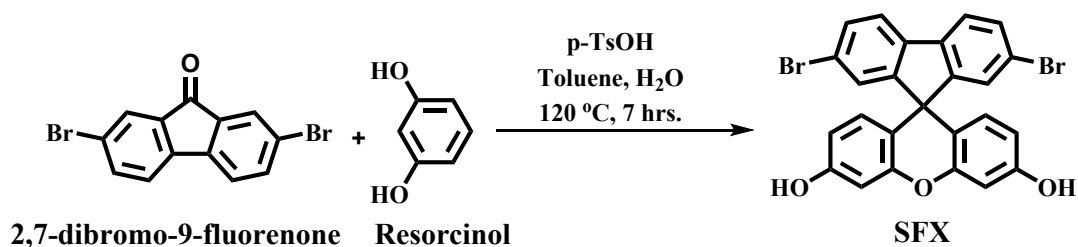
All the reagents used in the present study were purchased from commercial sources (TCI, Alfa Aesar, and Sigma Aldrich) and utilized without further purification. The solvents were carefully dried and distilled by standard procedure using a suitable drying agent before use. The silica gel used for column chromatography was procured from Merck. All the reactions were carried out in an inert environment. The NMR (^1H and ^{13}C NMR) spectra were recorded

using Bruker spectrometers, TMS was used as an internal standard, and the Mass (MALDI-TOF) spectra of the synthesized materials were characterized by Bruker ultraflex TOF. The UV-Vis absorption analysis was performed on a Shimadzu UV-1800 model spectrophotometer. The PL spectra of the materials were carried out using a Fluorolog-3 spectrophotometer. The lifetime analysis of fluorescent materials was measured using a time-correlated single-photon counting (TCSPC) setup on a Fluorolog-3 Triple Illuminator, IBH Horiba Jobin Yvon. The electrochemical analysis was recorded on a BAS100 electrochemical analyzer by using a conventional three electrode system viz, a Pt rod as the working electrode, a platinum wire as the counter electrode, Ag/AgCl as the reference electrode, and 0.1 M tetrabutylammonium hexafluorophosphate in freshly distilled CH_2Cl_2 as the supporting electrolyte. Theoretical calculations of newly synthesized materials were determined with the help of density functional theory (DFT) using the hybrid B3LYP functional and 6-311G (d, p) basis set. The singlet and lowest triplet energies were evaluated via the Δ self-consistent field (Δ SCF) method based on optimized geometries. All the DFT and TD-DFT calculations were conducted using the Gaussian 09 software package.

SI2. Intermediate synthesis

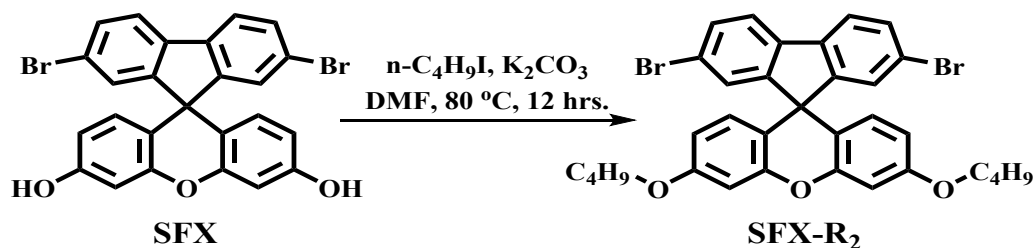
The synthetic procedures for all the intermediates and final product were adopted from previous reports.^{1,2,3}

2,7-dibromospiro[fluorene-9,9'-xanthene]-3',6'-diol (SFX):



Under nitrogen protection, 1,7-dibromo-9-fluorenone (1 g, 2.9 mmol), resorcinol (1.3 g, 11.8 mmol), *p*-TsOH (0.056 g, 0.29 mmol), and toluene (20 mL) were added to a 50 mL two-neck round-bottom flask. After 7 hours of refluxing, the mixture was cooled to room temperature and stirred for 0.5 hours with the addition of 10 mL of water. The crude product was precipitated and separated as a yellow solid by filtration. The organic solution was concentrated and purified using petroleum ether/ethylacetate (3:1) as an eluent using column chromatography on silica gel with a yield of 81%. ¹H NMR (400 MHz, CDCl₃) δ 7.60 (d, *J* = 8.1 Hz, 2H), 7.48 (dd, *J* = 8.1, 1.8 Hz, 2H), 7.23 (d, *J* = 1.7 Hz, 2H), 6.69 (d, *J* = 2.5 Hz, 2H), 6.33 (dd, *J* = 8.5, 2.6 Hz, 2H), 6.22 (d, *J* = 8.5 Hz, 2H), 5.08 (s, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 156.93, 155.85, 151.87, 137.47, 131.22, 130.40, 128.97, 122.40, 121.35, 115.32, 111.64, 107.88, 60.64; HRMS : *m/z* calculated for C₂₅H₁₄Br₂O₃, 519.931, found 519.136 [M]⁺.

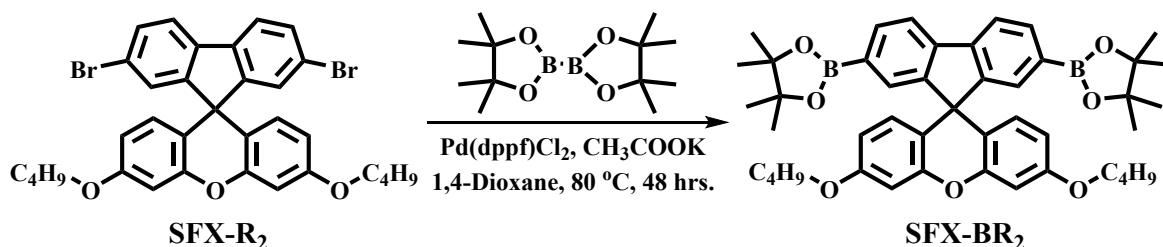
2,7-dibromo-3',6'-dibutoxyspiro [fluorene-9,9'-xanthene] (SFX-R₂):



2,7-dibromospiro[fluorene-9,9'-xanthene]-3',6'-diol(SFX)(1 g, 19.1 mmol), n-iodobutane (1.76 g, 95 mmol), K₂CO₃(1.32 g, 95 mmol), and DMF (20 ml) were stirred together and refluxed at 80 °C for 12 hours under the atmosphere of nitrogen. The resultant mixture was added to 200 mL of water, and then it was extracted with ethylacetate (3 x 100 mL). The resulting extracts were dried over MgSO₄, and the solvent was evaporated in vacuo. Column chromatography (ethylacetate/petroleum ether, 1:200) was employed to purify the crude product to give SFX-R₂ with a yield of 67%. ¹H NMR (500 MHz, CDCl₃) δ 7.59 (d, *J* = 8.1 Hz, 2H), 7.47 (dd, *J* = 8.1, 1.7 Hz, 2H), 7.22 (s, 1H), 6.72 (d, *J* = 2.1 Hz, 2H), 6.40 (dd, *J* = 8.7, 2.4 Hz, 2H), 6.24 (d, *J* = 8.7 Hz, 2H), 3.95 (t, *J* = 6.4 Hz, 4H), 1.80 – 1.72 (m, 4H), 1.52 – 1.44

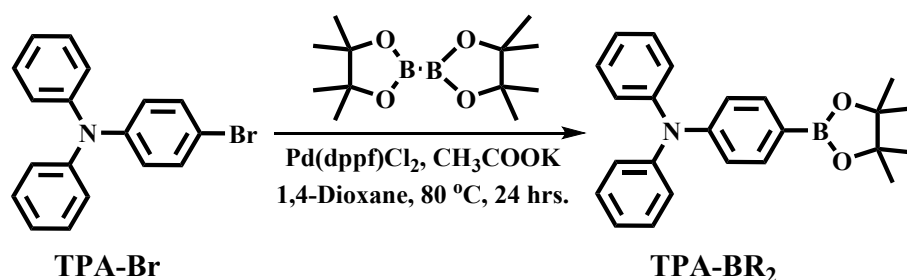
(m, 4H), 0.97 (t, $J = 7.4$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 159.39, 157.13, 151.90, 137.49, 131.15, 129.01, 128.60, 122.39, 121.31, 114.76, 111.37, 101.86, 67.90, 53.53, 31.25, 19.28, 13.87; HRMS : m/z calculated for $\text{C}_{33}\text{H}_{30}\text{Br}_2\text{O}_3$, 635.061, found 635.058 $[\text{M}+\text{H}]^+$.

2,7-dibromo-3',6'-dibutoxyspiro[fluorene-9,9'-xanthene] (SFX-BR₂):



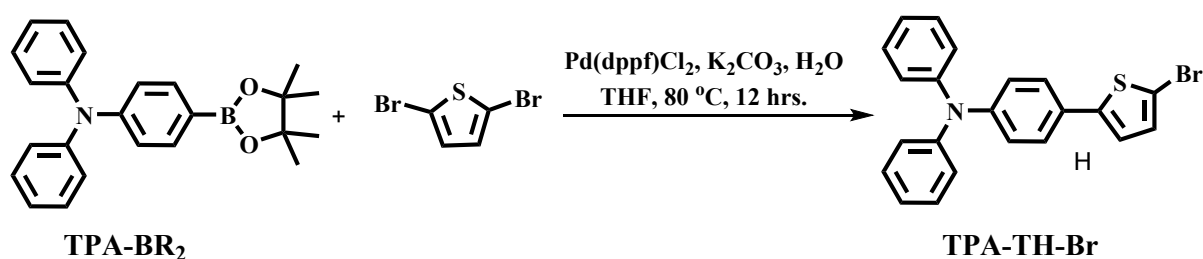
In a mixture of SFX-R₂ (1.0 g, 1.5 mmol), Bis(pinacolato)diboran (1.2 g, 4.7 mmol), and CH₃COOK (0.773 g, 7.8 mmol) was added 1,4-Dioxane (30 ml) and purged it for 20 minutes before addition of [Pd(dppf)Cl₂] (0.01 g) and subsequent purging for 25 minutes. After that, the reaction setup was heated for 48 hours at 80°C in a nitrogen environment. After cooling to room temperature, the resulting mixture was extracted with CH₂Cl₂, and the organic phase was dried over anhydrous sodium sulphate. Then the solvent was drained, and the residue was purified using ethylacetate/petroleum ether (2:100) as an eluent by silica gel column chromatography to give compound SFX-BR₂ as a white solid with a 60% yield. ^1H NMR (500 MHz, CDCl_3) δ 7.73 (qd, $J = 7.7, 0.7$ Hz, 4H), 7.43 (s, 2H), 6.62 (d, $J = 2.5$ Hz, 2H), 6.25 (d, $J = 2.6$ Hz, 1H), 6.23 (d, $J = 2.6$ Hz, 1H), 6.12 (d, $J = 8.7$ Hz, 2H), 3.86 (t, $J = 6.5$ Hz, 4H), 1.70 – 1.64 (m, 4H), 1.40 (m, $J = 15.0, 7.5$ Hz, 4H), 1.20 (s, 24H), 0.89 (t, $J = 7.4$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 158.79, 155.94, 151.90, 142.24, 134.44, 131.95, 129.32, 119.47, 115.92, 111.05, 101.54, 83.76, 67.80, 53.20, 31.30, 29.74, 24.89, 19.28, 13.87; HRMS: m/z calculated for $\text{C}_{45}\text{H}_{54}\text{B}_2\text{O}_7$, 729.548, found 729.524 $[\text{M}+\text{H}]^+$.

4-(Diphenylamino)phenylboronic acid pinacol ester (TPA-BR₂):



A solution of 4-bromotriphenylamine (1.0 g, 3.0 mmol), bis(pinacolato)diboran (1.17 g, 4.6 mmol), Pd(dppf)Cl₂ (0.043 g, 0.02 mmol), and CH₃COOK (890 mg, 9.2 mmol) in 1,4-Dioxane (40 ml) was added, and the reaction mixture was refluxed at 80 °C for 24 hours under N₂ atmosphere. Then the organic mixture was poured into water and the resulting aqueous layer was extracted with CH₂Cl₂. The organic layer dried over anhydrous sodium sulphate. After removal of the solvent, the reaction mixture was purified using 100% petroleum ether as an eluent by silica gel column chromatography to afford TPA-BR₂ with a yield of 81% as a white solid. ¹H NMR (400 MHz, CDCl₃) δ 7.66 (d, *J* = 8.4 Hz, 2H), 7.25 (t, *J* = 7.8 Hz, 4H), 7.10 (d, *J* = 7.9 Hz, 4H), 7.03 (t, *J* = 7.7 Hz, 4H), 1.33 (s, 12H); ¹³C NMR (100 MHz, CDCl₃) δ 150.38, 147.18, 135.67, 129.09, 128.98, 124.76, 123.95, 123.15, 122.45, 121.59, 83.31, 24.66.

4-(5-bromothiophen-2-yl)-N,N-diphenylaniline (TPA-TH-Br):



To a solution of TPA-BR₂ (0.2 g, 0.538 mmol), 2,5-Dibromothiophene (0.186 g, 0.76 mmol) and K₂CO₃ (2M) in THF (20 ml) and H₂O (1 mL) was added Pd(dppf)Cl₂ (0.011 g, 0.02 mmol) at room temperature under nitrogen atmosphere. The mixture was then refluxed at 80 °C for 12 hours and cooled to room temperature. The crude was poured into water, and the aqueous layer was extracted with ethyl acetate. The solvent was dried over anhydrous sodium sulphate and

filtered. After removal of the solvent, the residue was purified by column chromatography on silica gel (0 to 1% ethylacetate in petroleum ether) to give TPA-TH-Br (yield: 53%) as a white solid. ^1H NMR (400 MHz, CDCl_3) δ 7.38 – 7.33 (m, 2H), 7.30 – 7.24 (m, 4H), 7.11 (d, $J = 8.7$ Hz, 4H), 7.04 (ddd, $J = 7.3, 4.0, 1.6$ Hz, 4H), 6.99 (d, $J = 3.8$ Hz, 1H), 6.94 (d, $J = 3.9$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 147.54, 147.26, 144.31, 129.33, 128.59, 128.01, 126.77, 124.48, 124.04, 123.81, 123.07, 122.27. HRMS: m/z calculated for $\text{C}_{22}\text{H}_{16}\text{BrNS}$, 406.026, found 406.024 $[\text{M}+\text{H}]^+$.

SI3. NMR (^1H and ^{13}C) spectra

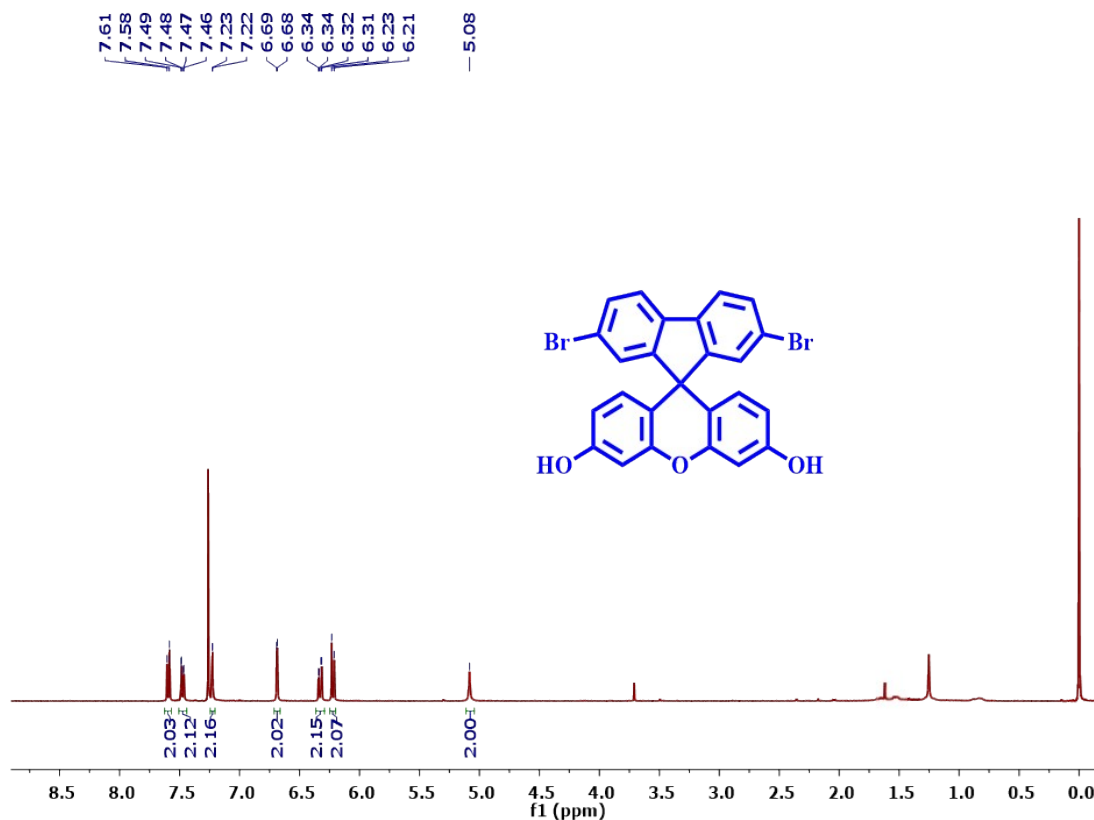


Fig S1. ^1H NMR spectra of SFX

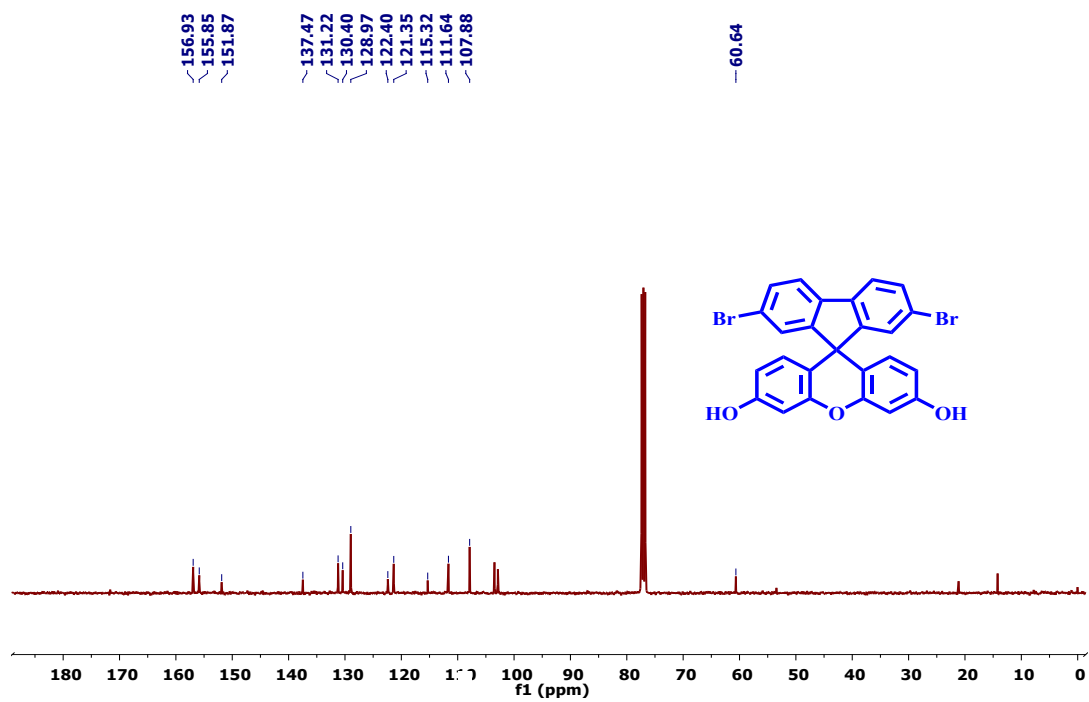


Fig S2. ^{13}C NMR spectra of SFX

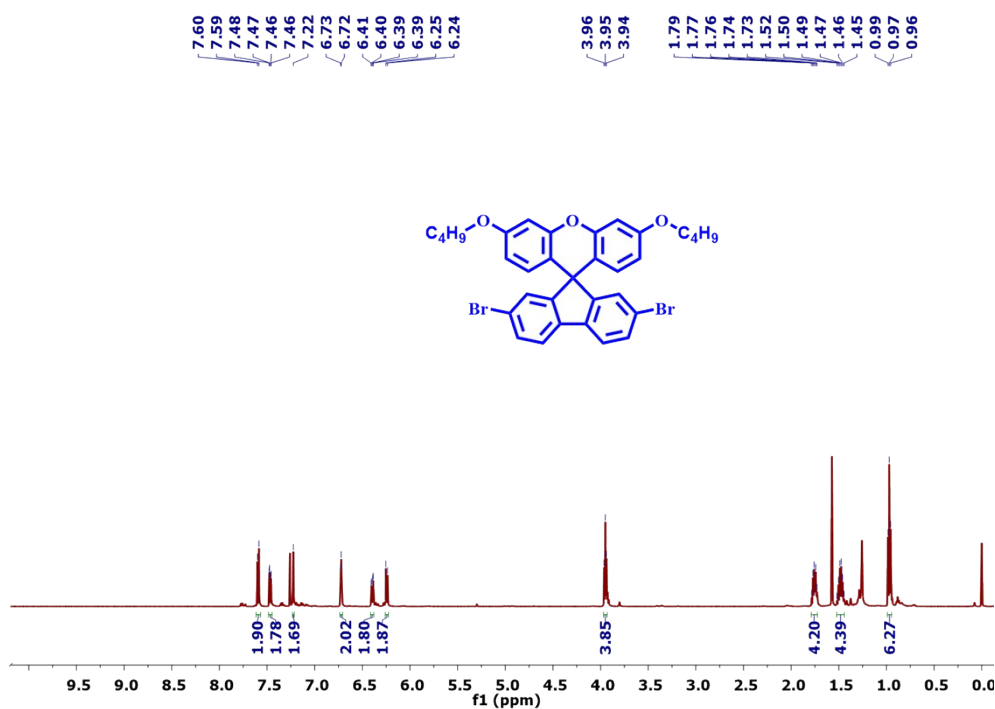


Fig S3. ^1H NMR spectra of SFX- R_2

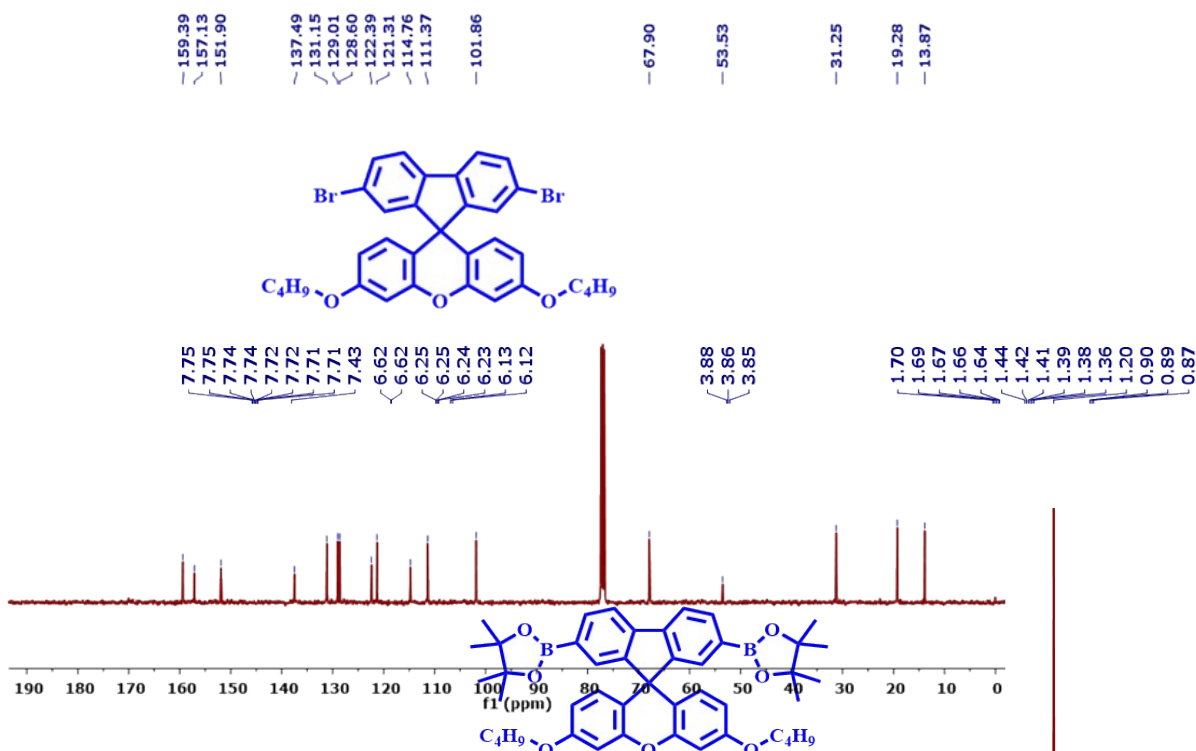


Fig S4. ^{13}C NMR spectra of SFX- R_2

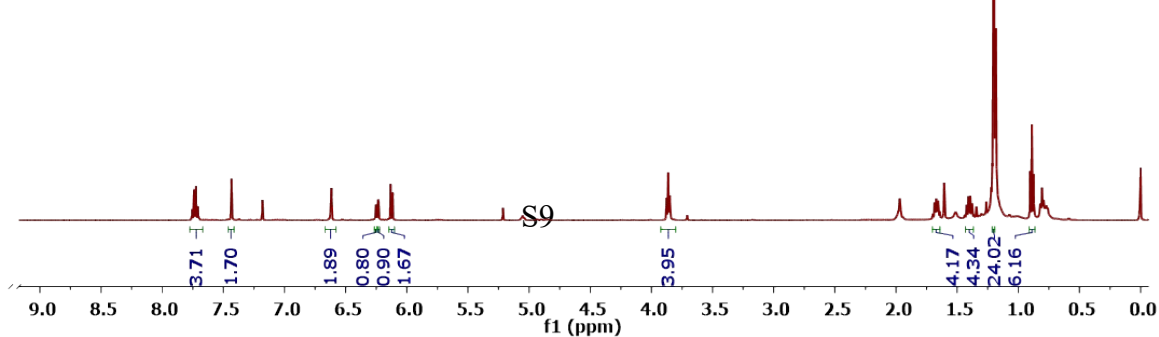


Fig S5. ^1H NMR spectra of SFX-BR₂

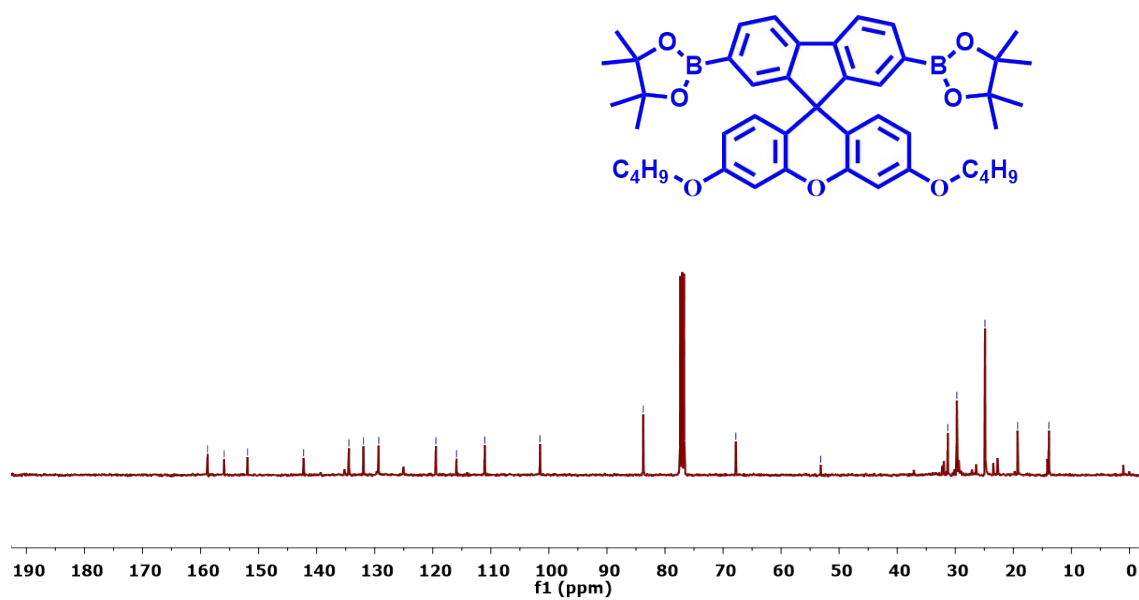


Fig S6. ^{13}C NMR spectra of SFX-BR₂

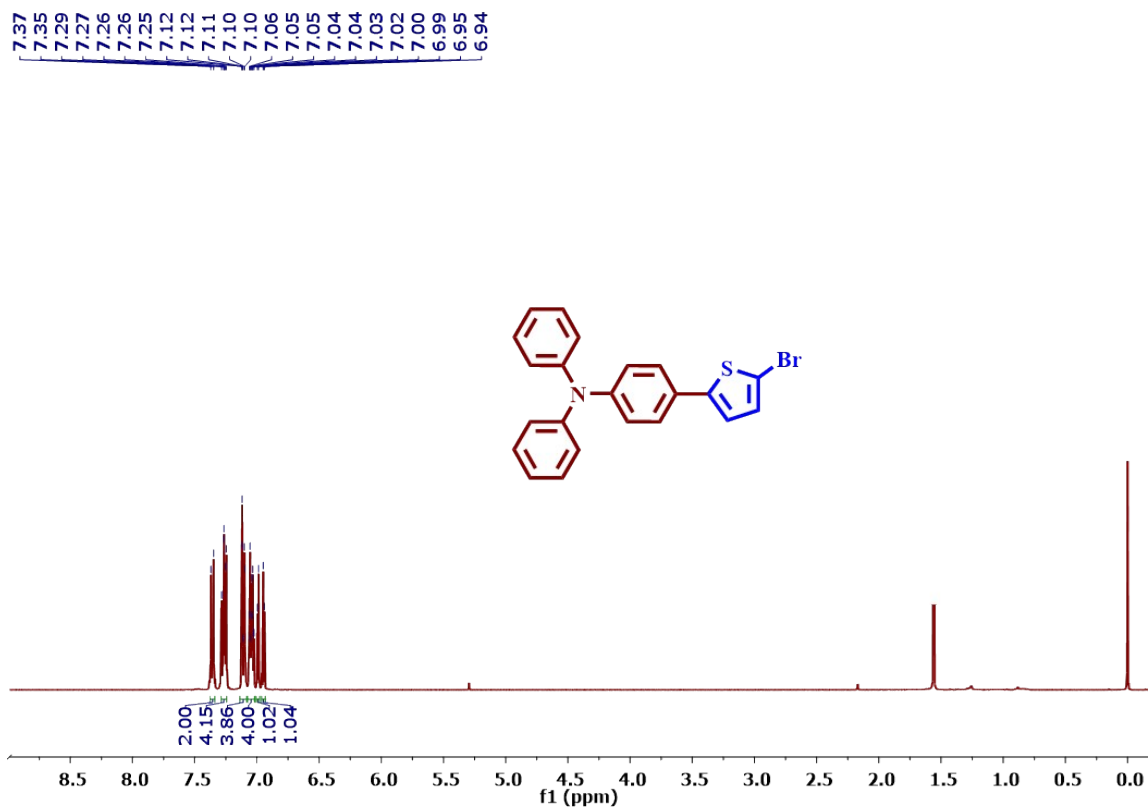


Fig S7. ¹H NMR spectra of TPA-TH-Br

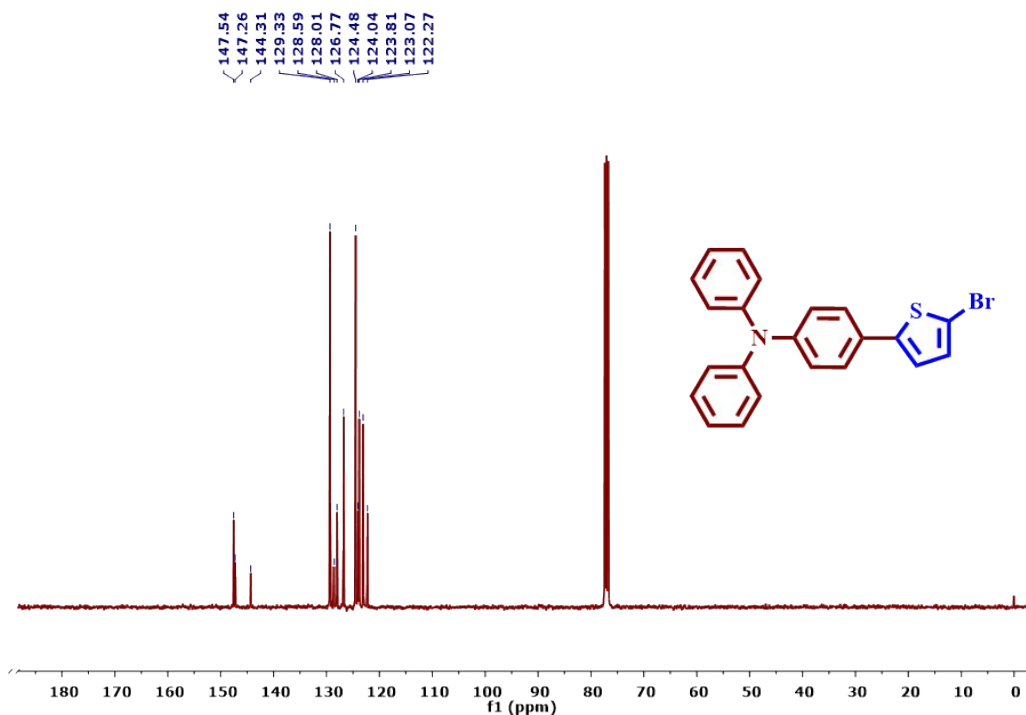
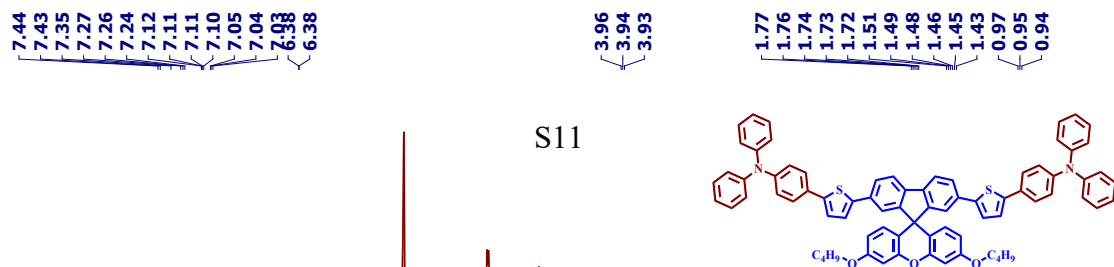


Fig S8. ¹³C NMR spectra of TPA-TH-Br



S11

Fig S9. ¹H NMR spectra of SP-TH

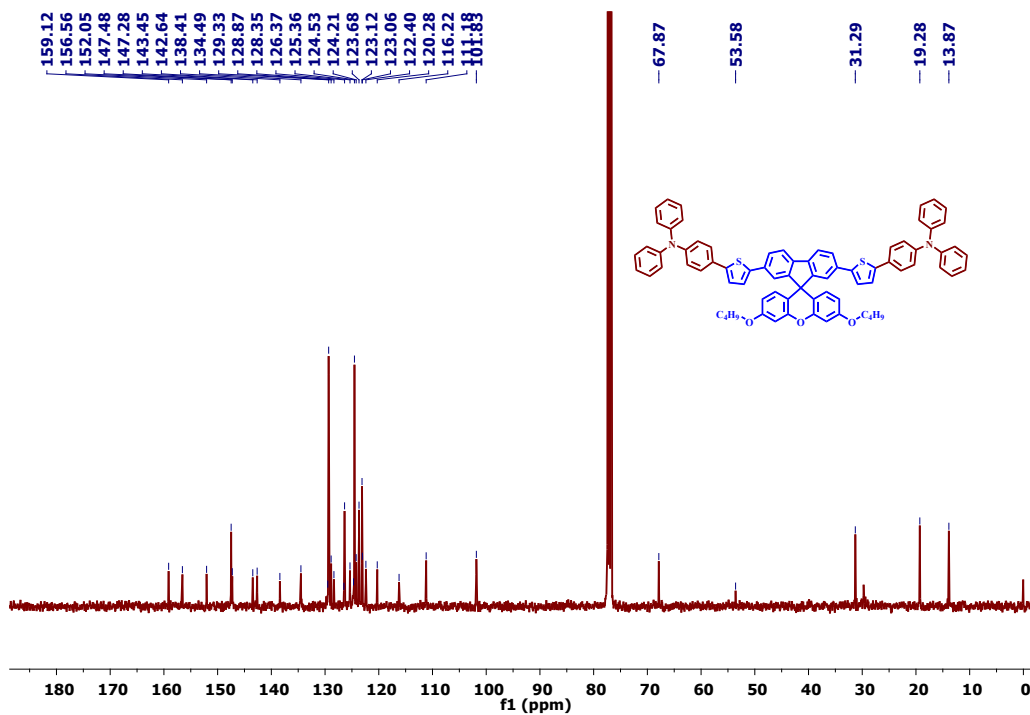


Fig S10. ¹³C NMR spectra of SP-TH

SI4. Mass spectra of SP-TH

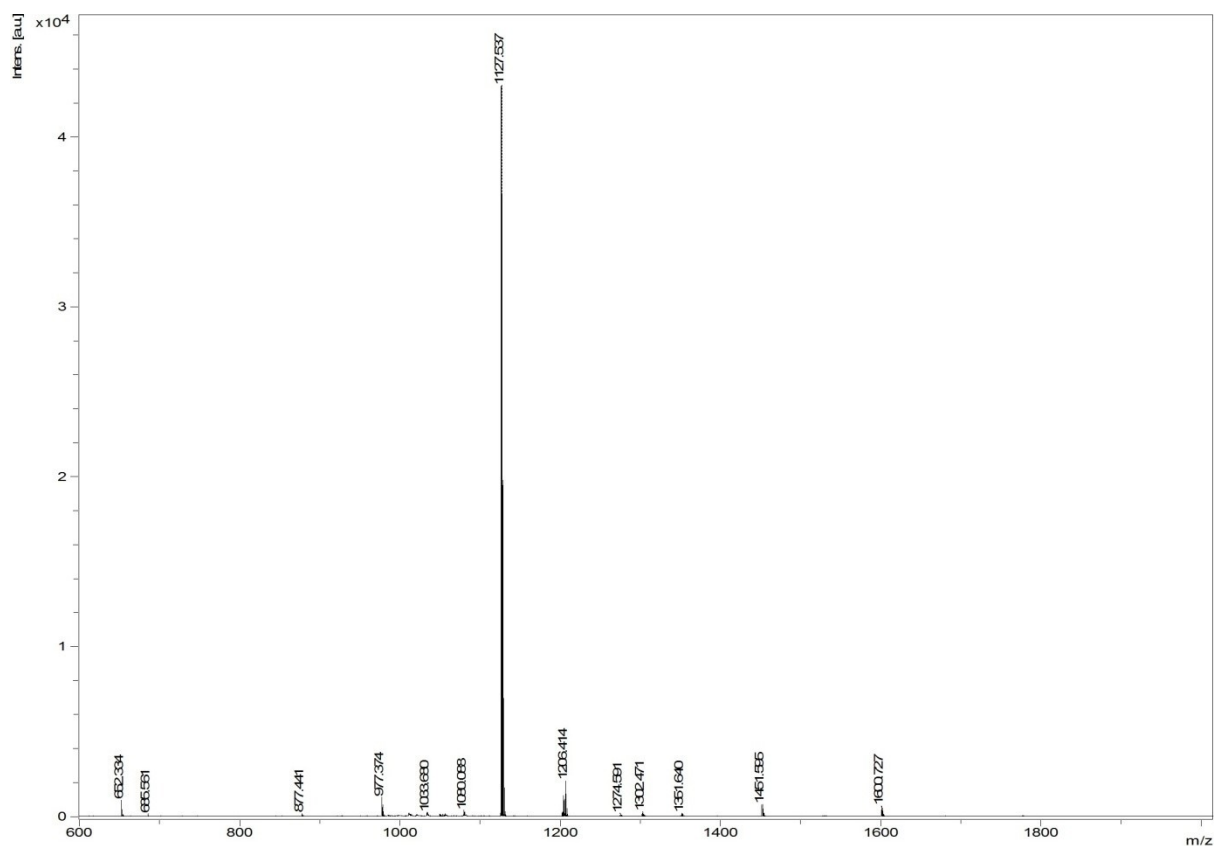


Fig S11. MALDI-TOF spectra of SP-TH

SI5. Theoretical study

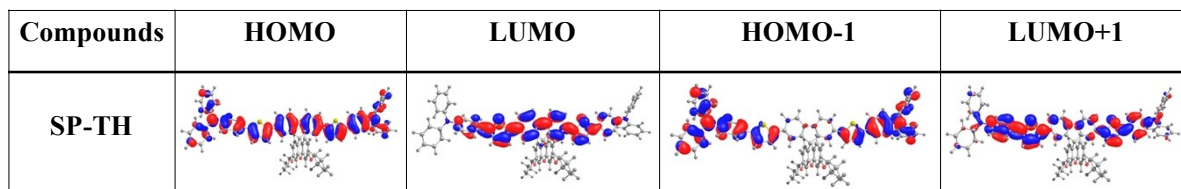


Fig S12. HOMO, LUMO, HOMO-1, LUMO+1 of SP-TH

Table S1: Frontier molecular orbitals energies and excited state energy levels.

Fluorophores	HOMO (eV)	LUMO (eV)	HOMO-1 (eV)	LUMO+1 (eV)	E_g (eV)	S_1 Gas (eV)	T_1 Gas (eV)	f
SP-TH	-4.7054	-1.6158	-4.8670	-1.1099	3.089	2.7178	2.0222	2.448

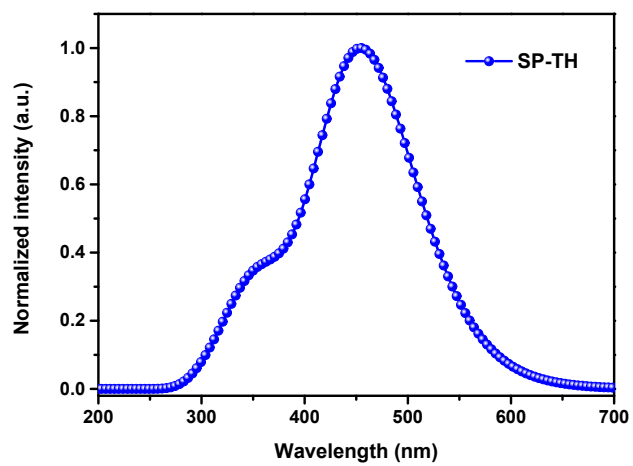


Fig S13. Simulated absorption spectra of SP-TH obtained from the TD-DFT analysis

SI6. Photophysical properties of SP-TH.

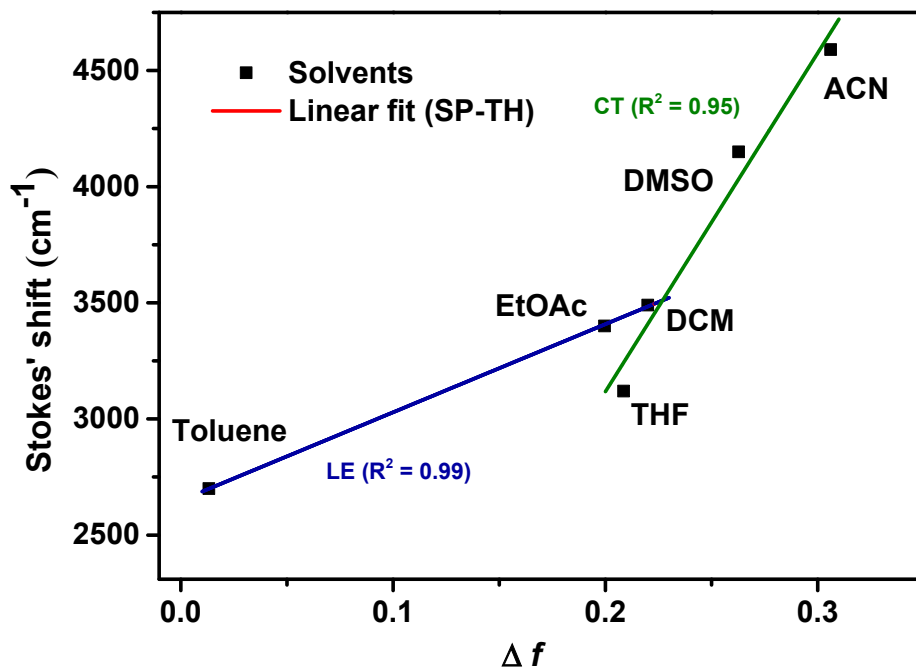




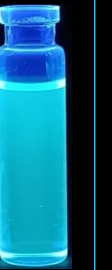
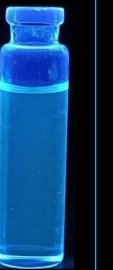





Fig S14. Two segment linear Lippert-Mataga plot of SP-TH in various solvents.

Table S2: Quantum yield (QY) of SP-TH with varying THF-Water ratio and their respective images under UV (365 nm).

Sr. No.	1	2	3	4	5	6	7	8	9
f_w (Vol%)	10	20	30	40	50	60	70	80	90
SP-TH (QY)	0.038	0.069	0.087	0.113	0.163	0.009	0.008	0.011	0.007
Under UV									

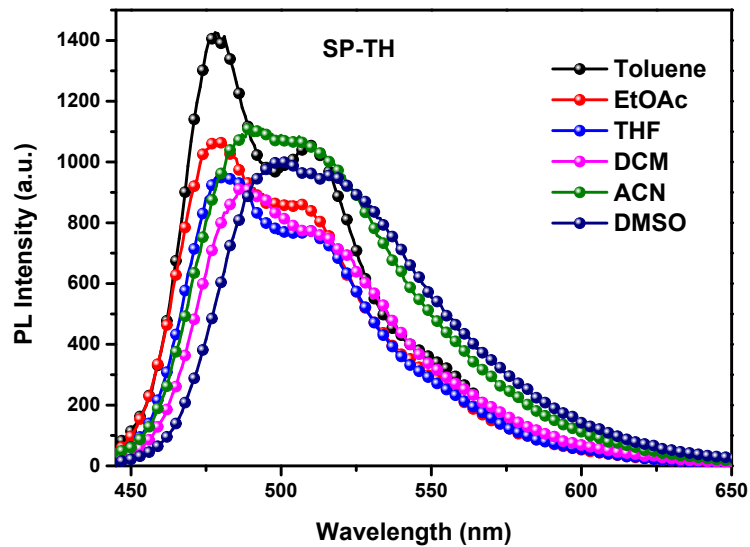


Fig S15. PL emission spectra of SP-TH in different solvents.

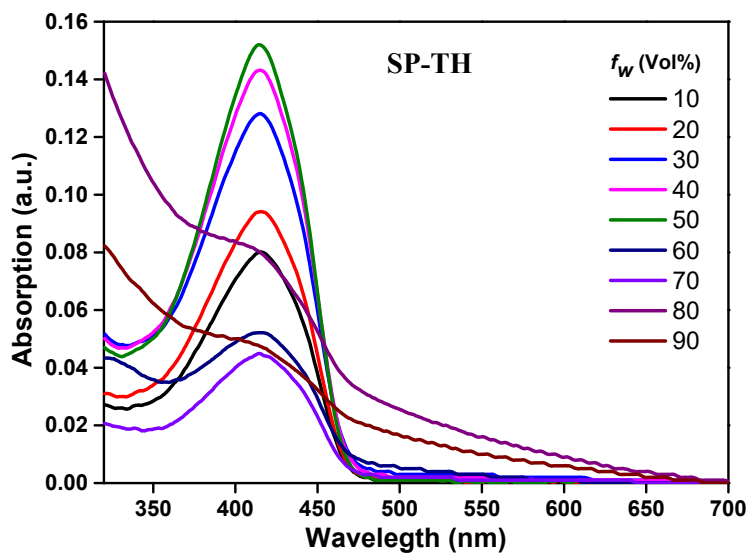


Fig. S16. The investigation of UV-Vis absorption with different water fraction (f_w , vol %) of SP-TH.

SI7. Electrochemical analysis

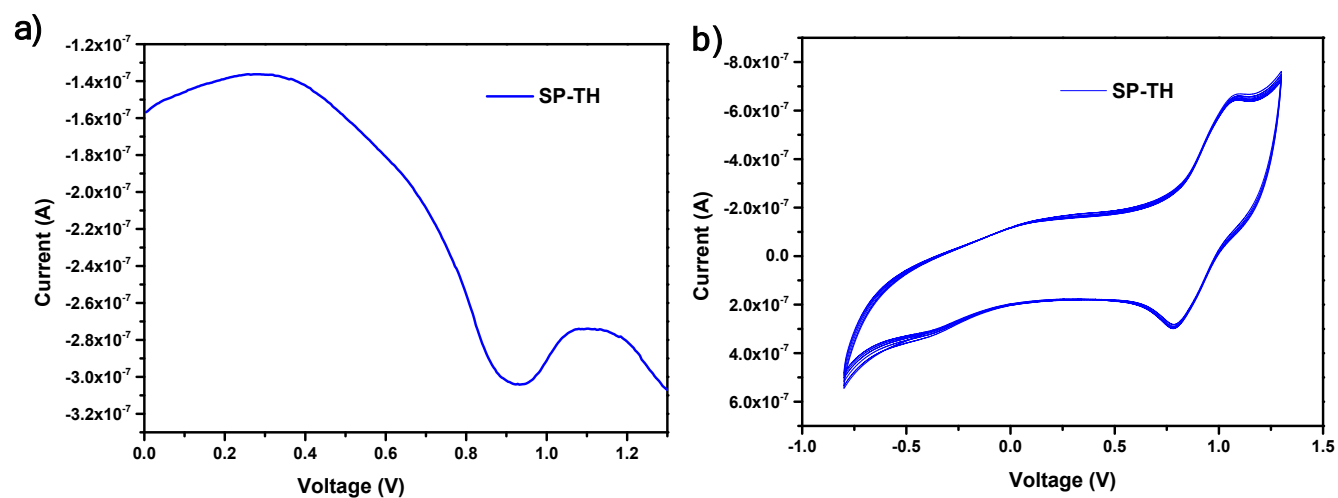


Fig S17. a) Differential pulse voltammetry (DPV) and b) Cyclic voltammogram (15 cycles) of SP-TH.

SI8. Vertical excitation wavelengths, orbital contribution and oscillator strength (f) of SP-TH

Excitation energies and oscillator strengths:

Singlet gas phase

Excited State 1: Singlet-A 2.7178 eV 456.20 nm $f=2.4489$

296 -> 299 0.13656

297 (Homo) -> 298 (LUMO) 0.68940

This state for optimization and/or second-order correction.

Total Energy, $E(\text{TD-HF/TD-DFT}) = -4103.11766582$

Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 2.9803 eV 416.02nm $f=0.0296$

296 -> 298 0.69810

Excited State 3: Singlet-A 3.3035 eV 375.32nm $f=0.0349$

297 -> 299 0.69229

Excited State 4: Singlet-A 3.3926 eV 365.46nm $f=0.3148$

293 -> 298 -0.12898

295 -> 298 0.66283

296 -> 299 -0.12958

Excited State 5: Singlet-A 3.4099 eV 363.60 nm $f=0.0031$

294 -> 298 0.69770

Excited State 6: Singlet-A 3.4829 eV 355.98 nm $f=0.3428$

295 -> 298 0.12968

296 -> 299 0.66615

297 -> 298 -0.12905

Triplet gas phase

Excited State 1: Triplet-A 2.0222 eV 613.12 nm $f=0.0000$

292 -> 299 -0.15687

295 -> 298 -0.24065

296 -> 299 0.22456

297 -> 298 0.57494

Excited State 2: Triplet-A 2.2332 eV 555.18 nm $f=0.0000$

292 -> 298 -0.23375

296 -> 298 0.43236

296 -> 300 0.12300

297 -> 299 0.43729

Excited State 3: Triplet-A 2.7090 eV 457.68 nm $f=0.0000$

290 -> 298 -0.16131

295 -> 298 0.39635

296 -> 299 0.36667

297 -> 300 0.31315

297 -> 303	0.12591		
Excited State 4:	Triplet-A	3.0206 eV	410.46 nm $f=0.0000$
292 -> 298	0.31633		
295 -> 299	0.34829		
296 -> 298	0.32954		
296 -> 300	0.17735		
297 -> 299	-0.10166		
297 -> 307	0.11088		
297 -> 308	0.17797		
Excited State 5:	Triplet-A	3.1018 eV	399.72nm $f=0.0000$
292 -> 298	-0.13409		
296 -> 298	0.42820		
296 -> 300	-0.24078		
297 -> 299	-0.41244		
297 -> 308	-0.12264		
Excited State 6:	Triplet-A	3.1629 eV	391.99nm $f=0.0000$
292 -> 304	-0.11196		
292 -> 305	0.11149		
295 -> 304	0.23360		
296 -> 304	-0.27801		
296 -> 305	0.28862		
297 -> 304	0.34704		
297 -> 305	0.11446		

References

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