

Supporting Information

Synthesis and Properties of Dithiafulvenyl Functionalized Spiro[fluorene-9,9'-xanthene] Molecules

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1. Materials and Characterization

All solvents and reagents, unless otherwise stated, were of high purity quality and used as received. Tetraethylammonium bromide (Et_4NBr), iodomethane, *tert*-butyllithium and triethyl phosphate ($\text{P}(\text{OEt})_3$) were purchased from Energy Chemical.

Reactions were monitored by TLC silica plate (GF-254). NMR spectra measurements were carried out at Bruker 600 MHz for ^1H NMR and 150 MHz for ^{13}C NMR, using chloroform-*d* as solvent. Chemical shifts were reported in parts per million (ppm) relative to internal TMS (0 ppm). Splitting patterns were described as singlet (s), doublet (d), triplet (t), quartet (q), or multiplet (m). Mass spectra measured on Microflex MALDI-TOFMS. UV-Vis spectra were recorded in a HITIACH U-3900 spectrometer. Cyclic voltammetry (CV) was carried out on a CHI600 voltammetric analyzer at room temperature with ferrocenium-ferrocene (Fc^+/Fc) as the internal standard. Differential scanning calorimetry (DSC) was performed on a TA DSC 2010 unit at a heating rate of $10\text{ }^\circ\text{C min}^{-1}$ under nitrogen atmosphere. Thermogravimetric analysis (TGA) was performed on a TA SDT 2960 instrument at a heating rate of $10\text{ }^\circ\text{C min}^{-1}$ under nitrogen atmosphere. Temperature at 5% weight loss was used as the decomposition temperature (T_d).

J–V characteristics of the PVSCs were measured by using a Keithley 2400 source meter under the illumination of a AM 1.5 solar simulator with the light intensity of 100 mW/cm^2 (AM 1.5G, SAN-EIELECTRIC XES-40S2-CE solar simulator), as calibrated by a NREL-traceable KG5 filtered silicon reference cell. The active areas of all solar cells were defined by a 9 mm^2 metal mask. All devices scanned under standard test procedure at a scan rate of 30 mV/s . Incident photon-to-current conversion efficiency (IPCE) spectra of the PVSCs were measured at varying wavelengths (350–850 nm) by a Q Test Station 500TI system (Crowntech, Inc., USA).

2. Synthesis procedures

4,5-bis(methylthio)-1,3-dithiole-2-thione (**MDT**), **SFX1** and **SFX2** were synthesized as depicted in the previous literatures.^[1, 2]

2,2',7,7'-tetracarbaldehyde-spiro[fluorene-9,9'-xanthene](**SFX-A1**)

2,2',7,7'-tetrabromo-spiro[fluorene-9,9'-xanthene] (**SFX1**) (2.0 g, 3.1 mmol) was dissolved in anhydrous THF (70 mL), after the solid was completely dissolved, *tert*-butyllithium (24.6 g, 46.4 mmol, 1.6 M in pentane) was added dropwise under -78°C with the protection of nitrogen. The mixture was stirred for 7 h. After that, DMF (4.5 g, 62.0 mmol) was added dropwise and continue to stir for 2 h. After this period, 2 M HCl (30 mL) was added to the mixture, and warmed up to room temperature. The organic phase was extracted with dichloromethane and dried over anhydrous Na₂SO₄. The filtrate was concentrated by rotary evaporation and purified by column chromatography (CH₂Cl₂: hexane=1:1). A light yellow solid (**SFX-A1**) was obtained (0.73 g, yield 53%). ¹H NMR (600 MHz, CDCl₃, ppm): δ= 9.94 (s, 2H); 9.63 (s, 2H); 8.12 (d, 2H, *J*=7.8Hz); 8.02 (d, 2H, *J*=7.8Hz); 7.82 (d, 2H, *J*=8.4Hz); 7.67 (s, 2H); 7.48 (d, 2H, *J*=8.4Hz); 6.88 (s, 2H). ¹³C NMR (150 MHz, CDCl₃, ppm): δ= 193.91; 192.81; 159.07; 157.65; 146.82; 140.80; 135.97; 134.66; 133.71; 133.07; 128.98; 126.25; 125.21; 121.48. MALDI-TOF: *m/z* [M]⁺ calcd. C₂₉H₁₆O₅, 444.0998; found: 444.0995.

2,3',6',7'-tetracarbaldehyde-spiro[fluorene-9,9'-xanthene](**SFX-A2**)

The procedure is similar to that for the synthesis of compound **SFX-A1** but using compound 2,3',6',7-tetrabromo-spiro[fluorene-9,9'-xanthene] (**SFX2**) instead of compound **SFX1**. Compound **SFX-A2** was obtained as a light yellow solid (0.84 g, yield 41%). ¹H NMR (600 MHz, CDCl₃, ppm): δ= 9.98 (s, 2H); 9.95 (s, 2H); 8.11 (d, 2H, *J*=7.8Hz); 8.04 (d, 2H, *J*=8.4Hz); 7.83 (s, 2H); 7.70 (s, 2H); 7.36 (d, 2H, *J*=7.8Hz); 6.52 (d, 2H, *J*=8.4Hz). ¹³C NMR (150 MHz, CDCl₃, ppm): δ= 193.71; 193.43; 159.61; 154.39; 146.75; 140.81; 140.30; 134.13; 134.07; 131.41; 129.51; 127.29; 124.93; 121.82. MALDI-TOF: *m/z* [M]⁺ calcd. C₂₉H₁₆O₅, 444.0998; found: 444.0996.

2,2',7,7'-tetrakis((4,5-bis(methylthio)-1,3-dithiol-2-ylidene)methyl)-spiro[fluorene-9,9'-xanthene](SFX-DTF1)

SFX-A1 (100 mg, 0.22 mmol) and **MDT** (408 mg, 1.8 mmol) were dissolved in dry toluene (30 ml) at room temperature, then $\text{P}(\text{OEt})_3$ (9.6 g, 57.8 mmol) was added under a nitrogen atmosphere. The resulting mixture was refluxed for overnight. After the reaction mixture was cooled to room temperature, anhydrous ethanol (30 ml) was added to precipitate a yellow solid. Then the crude product was obtained by filtration. The crude product was washed with absolute ethanol (50 ml) and purified by silicon gel column chromatography (petroleum ether: CH_2Cl_2 =1:2) to afford **SFX-DTF1** as yellow powder (200 mg, yield 76.7%). ^1H NMR (600 MHz, CDCl_3 , ppm): δ =7.75 (d, 2H, J = 8.1 Hz); 7.24 (dd, 2H, J = 8.1, 1.7 Hz); 7.22 (d, 2H, J = 8.5 Hz); 7.05 – 7.02 (m, 4H); 6.41 (s, 2H); 6.34 (d, 2H, J = 2.3 Hz); 6.19 (s, 2H); 2.38 (s, 6H); 2.37 (s, 6H); 2.33 (s, 6H); 2.31 (s, 6H). ^{13}C NMR (150 MHz, CDCl_3 , ppm): δ = 157.57; 152.52; 140.07; 139.33; 135.21; 134.91; 133.76; 129.84; 129.42; 129.26; 128.85; 128.71; 128.06; 127.62; 127.27; 122.95; 119.86; 118.01; 117.18; 70.86; 57.29; 28.51; 21.76; 2.88. MALDI-TOF: $m/z[\text{M}]^+$ calcd. $\text{C}_{49}\text{H}_{40}\text{OS}_{16}$, 1157.8813; found: 1157.8815.

2,3',6',7-tetrakis((4,5-bis(methylthio)-1,3-dithiol-2-ylidene)methyl)-spiro[fluorene-9,9'-xanthene](SFX-DTF2)

The procedure is similar to that for the synthesis of compound **SFX-DTF1** but using compound **SFX-A2** (100 mg, 0.22 mmol) instead of compound **SFX-A1**. Compound **SFX-DTF2** was obtained as a yellow powder (196 mg, yield 75.1%). ^1H NMR (600 MHz, CDCl_3 , ppm): δ =7.72 (d, 2H, J = 8.0 Hz); 7.22 (dd, 2H, J = 8.1, 1.5 Hz); 7.11 (d, 2H, J = 1.8 Hz); 6.96 (d, 2H, J = 1.2 Hz); 6.64 (dd, 2H, J = 8.2, 1.8 Hz); 6.41 (d, 2H, J = 8.2 Hz); 6.39 (s, 4H); 2.43 (d, 12H, J = 2.2 Hz); 2.38 (s, 6H); 2.36 (s, 6H). ^{13}C NMR (150 MHz, CDCl_3 , ppm): δ =157.94; 154.53; 140.06; 139.34; 135.99; 135.28; 130.75; 130.31; 129.21; 127.67; 127.35; 127.19; 125.32; 122.86; 117.94; 117.24; 116.65; 70.84; 56.98; 32.58; 28.51; 21.95; 21.93 – 21.64; 3.89; 2.87. MALDI-TOF: $m/z[\text{M}]^+$ calcd. $\text{C}_{49}\text{H}_{40}\text{OS}_{16}$, 1157.8813; found: 1157.8811.

3. Device fabrication

All the devices were fabricated based on conventional structure (FTO/TiO₂/Perovskite/HTM/Auelectrode). The FTO (SnO₂:F) glass substrates were cleaned sequentially by sonication in acetone, ethanol, followed by a 15 min UV–ozone treatment. A 40 nm thick TiO₂ layer was deposited by putting the FTO glass substrates in a glass container filled with the titanium chloride solution in a 70 °C lab oven for 1 h. The deposited substrates were rinsed by deionized water for 2 min to remove any loosely bound materials, dried in a stream of N₂, and annealed for 30 min at 185 °C on a hot plate. All TiO₂/FTO glasses were treated by UV-ozone treatment for 15 min before deposition of the perovskite layer. The mixed perovskite solution was prepared by dissolving PbI₂ (1 mmol), CH₃NH₃I (1 mmol), DMSO (1 mmol) in an anhydrous solvent DMF (600 mg). Then the mixed solution was spin-coated on top of the TiO₂ at 1000 rpm for 5 s, followed by 4000 rpm for 45 s. Chlorobenzene was dropped on the spinning substrate in the second spinning step. All the samples were annealed at 100 °C for 10 min. The hole-transporting materials was spin-coating on the top of perovskite layer with a spin speed of 4000 rpm for 20 s. Different HTMs (SFX-DTF1, SFX-DTF2 and Spiro-OMeTAD) were dissolved in chlorobenzene with a concentration of 15 mg mL⁻¹, respectively. Finally, 100 nm of Au was deposited as top electrode by thermal evaporation to form an active area of 9 mm².

4. Figures

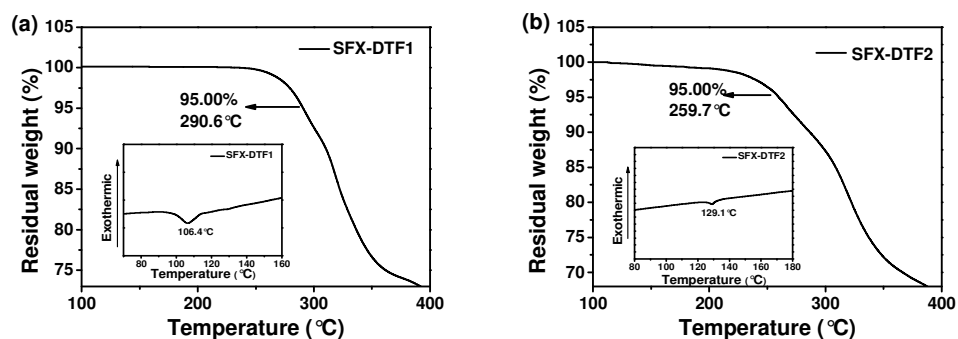


Figure S1. TGA and DSC (inset) curves of (a) **SFX-DTF1** and (b) **SFX-DTF2**.

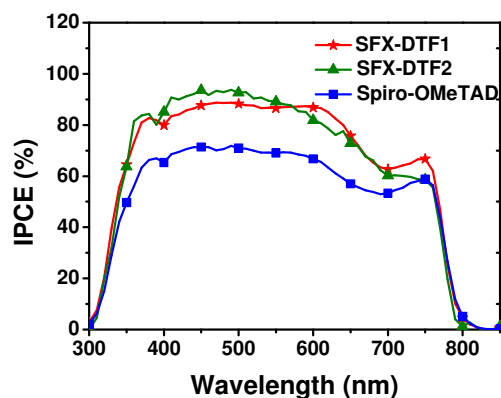


Figure S2. IPCE spectra of the devices using undoped **SFX-DTF1**, **SFX-DTF2** and **Spiro-OMeTAD** as HTMs, respectively.

Table S1. Optical and electrochemical data of **SFX-DTF1**, **SFX-DTF2**.

HTM	$\lambda_{\max}^{\text{abs [a]}}$ (nm)	ϵ ($\text{M}^{-1}\text{cm}^{-1}$)	E_{0-0} (eV)	$E_{\text{ox}}^{\text{[b]}}$ (V)	HOMO (eV)	LUMO (eV)	μ ($\text{cm}^2\text{V}^{-1}\text{S}^{-1}$)
SFX-DTF1	379,412,433	5.74×10^4	2.63	0.76	-5.16	-2.53	1.51×10^{-4}
SFX-DTF2	374,410,431	5.95×10^4	2.62	0.79	-5.19	-2.57	3.05×10^{-5}

[a] UV-Vis absorption spectra in THF (1×10^{-5} M) at room temperature. [b] E_{ox} : the first oxidation potentials from CVs associated with the HOMO levels of SFX-DTF.

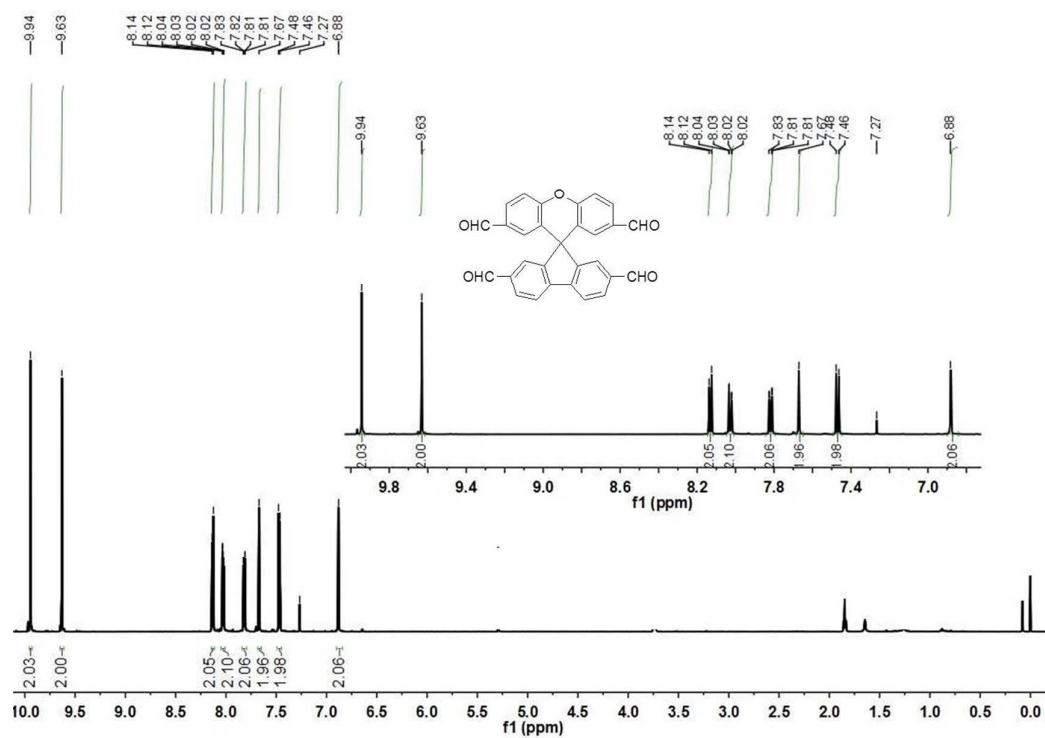


Figure S4. ^1H NMR of SFX-A1.

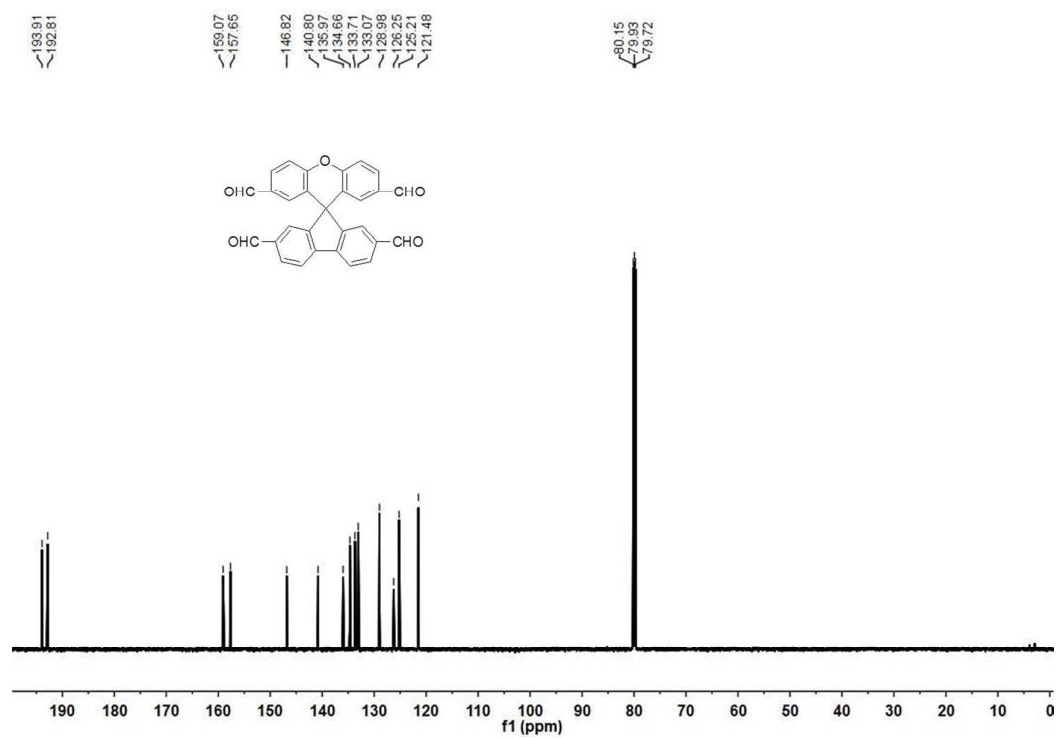


Figure S5. ¹³C NMR of **SFX-A1**.

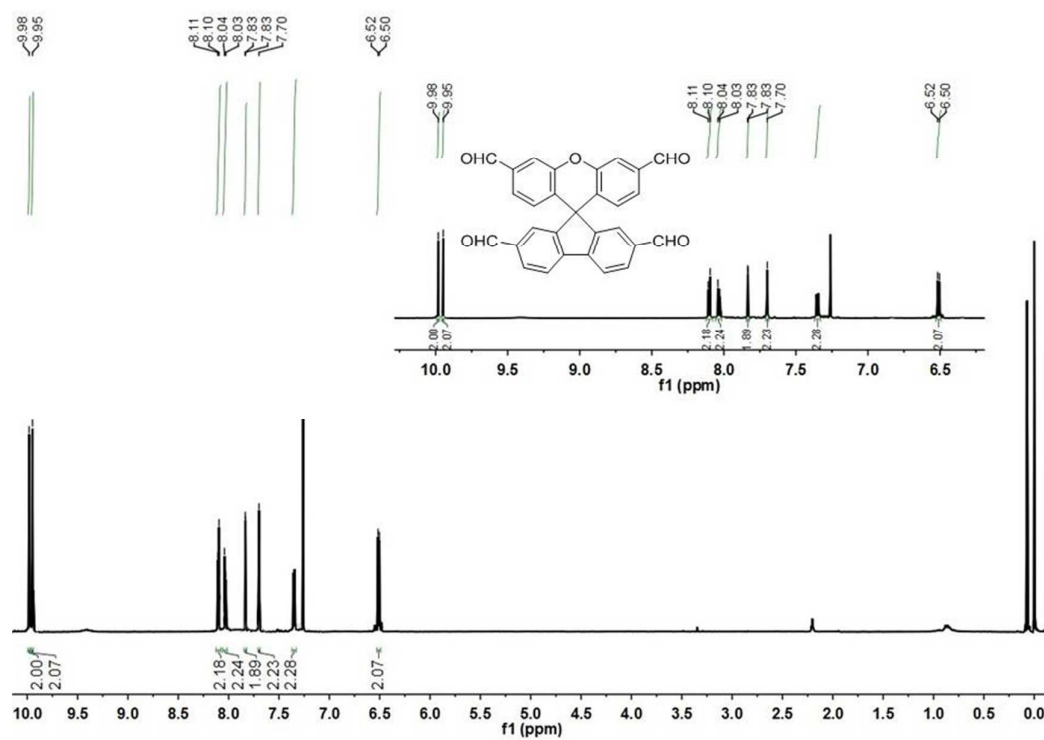


Figure S6. ^1H NMR of SFX-A2.

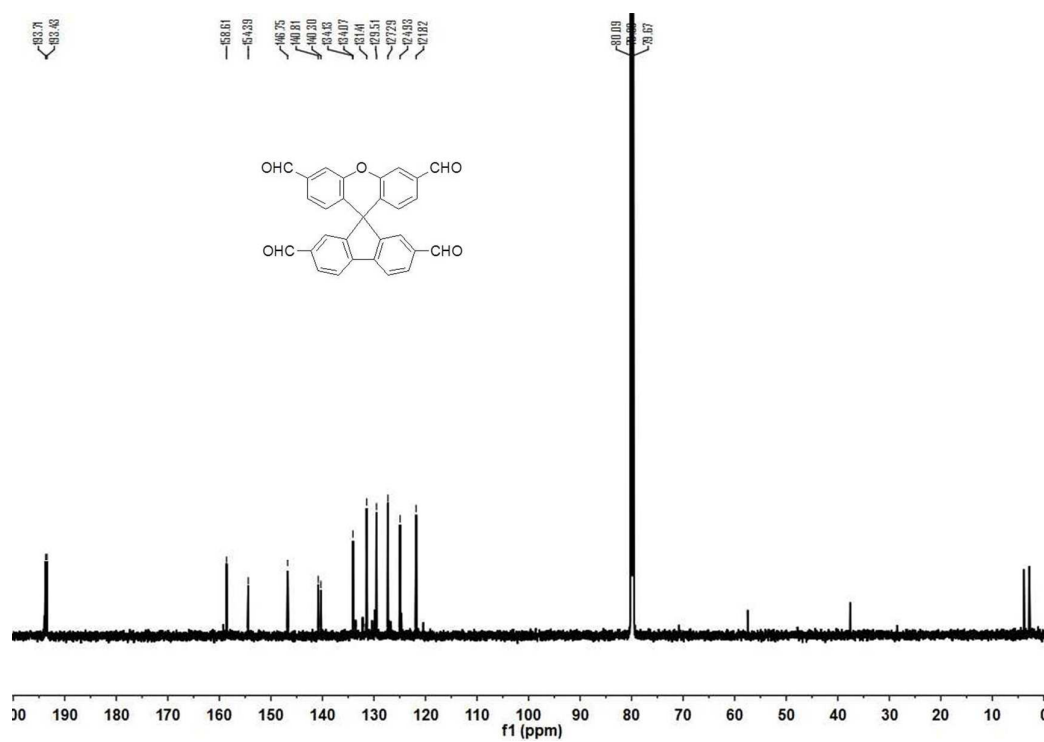


Figure S7. ¹³C NMR of **SFX-A2**.

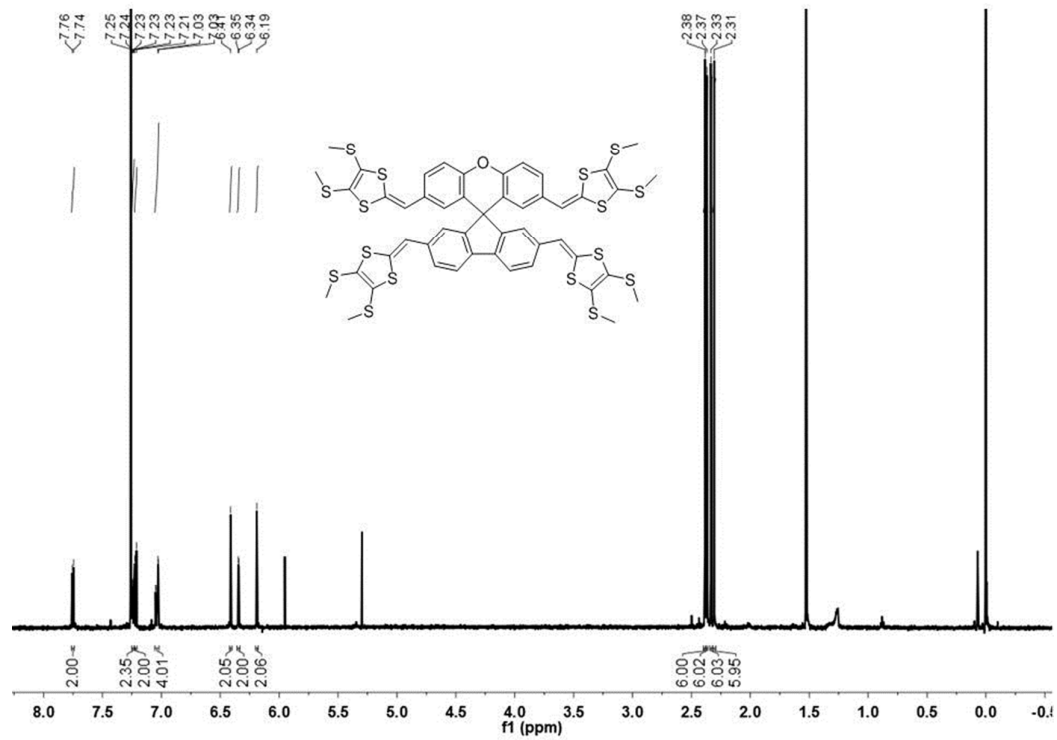


Figure S8. ^1H NMR of SFX-DTF1.

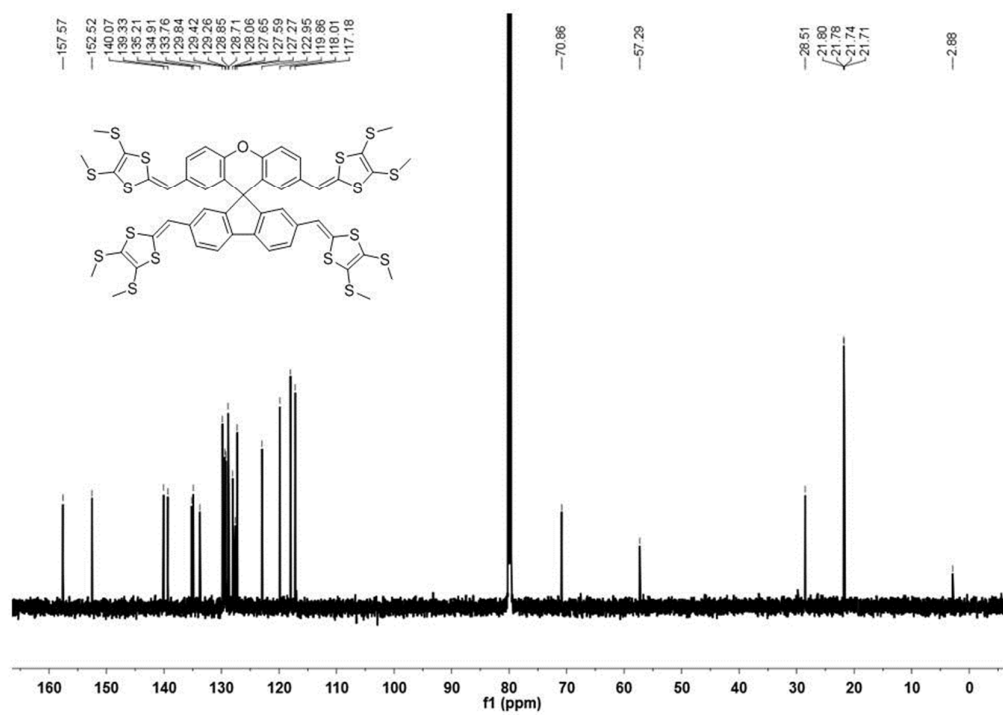


Figure S9. ¹³C NMR of SFX-DTF1.

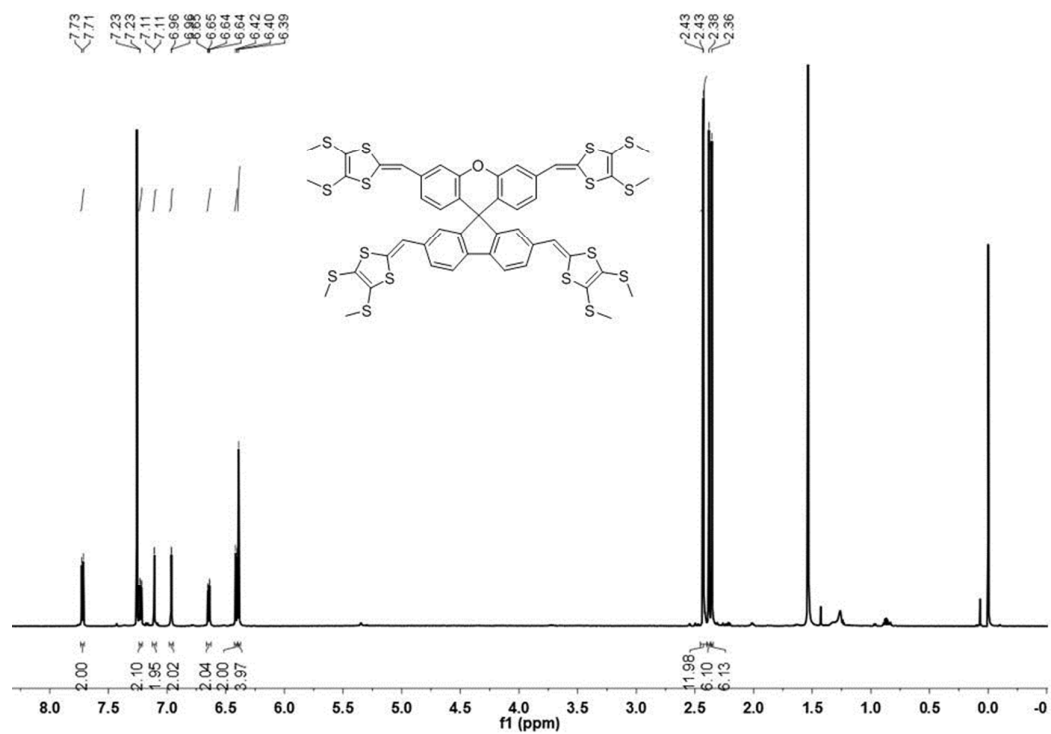


Figure S10. ¹H NMR of SFX-DTF2.

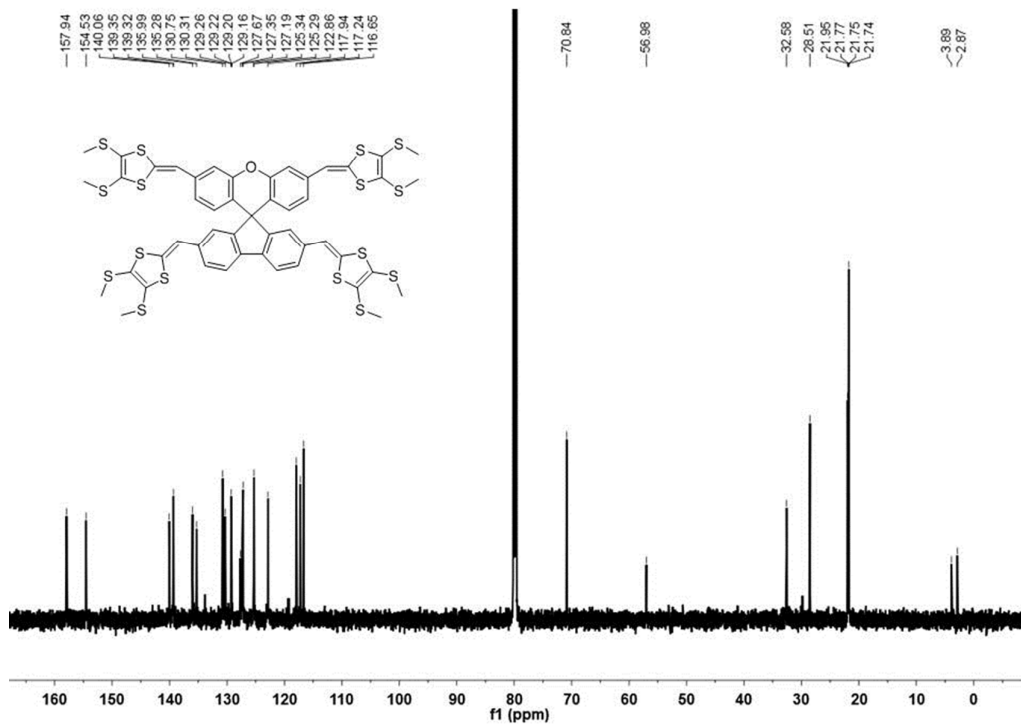


Figure S11. ^{13}C NMR of SFX-DTF2.

Reference

- (1) Svenstrup, N.; Becher, J. *Synthesis*. **1995**, 3, 215.
- (2) Liang, X. Z.; Wang, C.; Wu, M.; Wu, Y. Z.; Zhang, F.; Han, Z. X.; Lu, X. Q.; Guo, K. P.; Zhao, Y.-M. *Tetrahedron*. **2017**, 73, 7115.