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Electronic Supplementary Information (ESI)

Bright white electroluminescence from a single polymer containing thermally activated delayed fluorescence unit and solution-processed orange OLED of approaching 20% external quantum efficiency

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1. Experimental Details

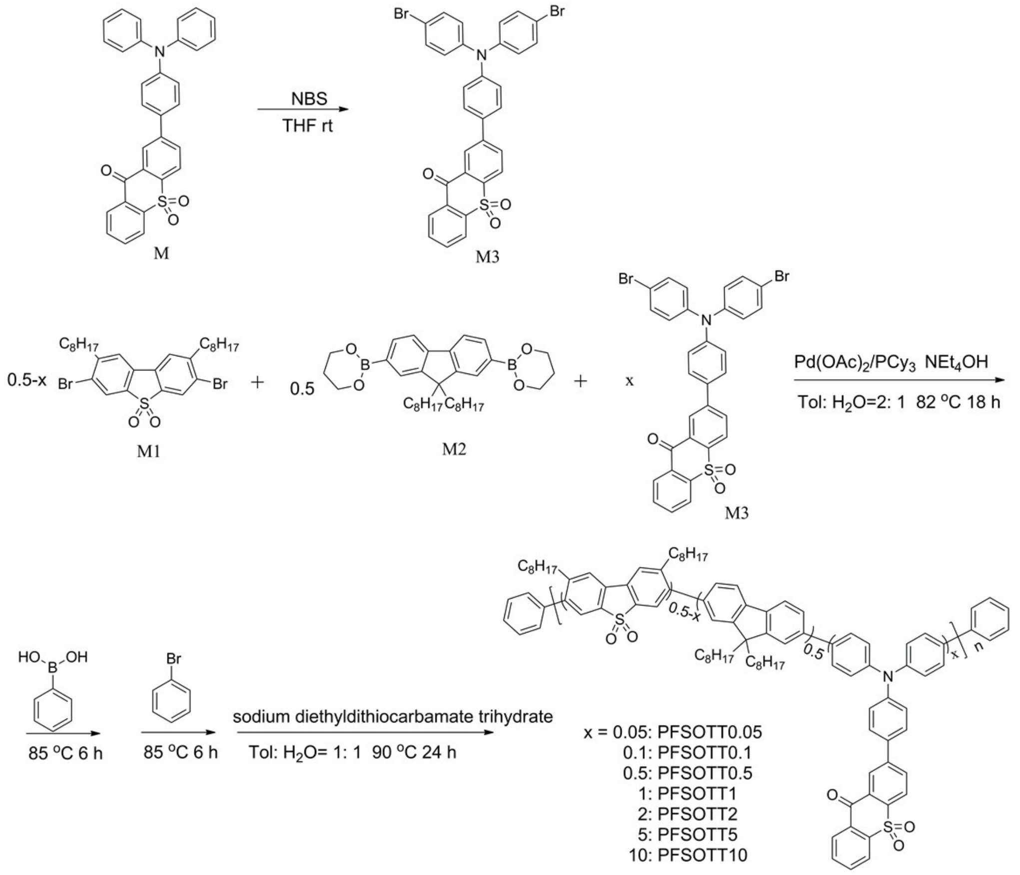
General information: All chemicals and reagents were used as received from commercial sources without further purification. Solvents for chemical synthesis were purified according to the standard procedures. 2-(4-(Diphenylamino)phenyl)-9*H*-thioxanthen-9-one-10,10-dioxide (TXO-TPA),[1] 3,7-dibromo-2,8-dioctyldibenzothiophene-*S,S*-dioxide (**M1**),[2] 9,9-dioctylfluorene-2,7-bis(trimethyleneboronates) (**M2**)[3] were prepared according to procedures described in the literature. ^{1}H NMR and ^{13}C NMR spectra were recorded with Bruker Avance 400 NMR spectrometers. MALDI-TOF mass spectra were performed on an AXIMA CFR MS apparatus (COMPACT). Weight-average and number-average molecular weights (*M*w and *M*n) and polydispersity index (PDI) of the polymers were determined by gel permeation chromatography (GPC) on a PL-GPC220 instrument with polystyrene as a standard and 1,2,4-trichlorobenzene as eluent. Thermogravimetric analysis (TGA) was performed with a Perkin-Elmer TGA-7 instrument. The thermal stability of the samples under a nitrogen atmosphere was determined by measuring their weight loss while heating at a rate of 10 °C min^{-1} from 25 to 800 °C.

Optical measurements: The concentration of the solution samples is 10^{-5} M in toluene. Thin film samples were deposited on quartz glass substrates by spin-coating. UV-visible (UV-vis) absorption and steady state photoluminescence spectra were measured with a Perkin-Elmer Lambda 35 UV-vis spectrometer and a Perkin-Elmer LS 50B spectrofluorometer, respectively. Absolute quantum efficiencies were measured by HAMAMATSU C9920 with an integration sphere. Fluorescence lifetimes were carried out with Edinburgh fluorescence spectrometer (FLS920) and measured using picosecond pulsed diode laser under the excitation at 375 nm.

Electrochemical measurements: Cyclic voltammetry experiments were performed on an EG&G 283 (Princeton Applied Research) potentiostat/galvanostat system. The films of PFSOTTx were tested in acetonitrile using ferrocene as an internal reference and $n\text{-}Bu_4NPF_6$ as the supporting electrolyte. The HOMO energy levels were calculated according to the equation: $E_{HOMO} = -[E(\text{onset, ox vs Fc/Fc}^{+}) + 4.8]$ (eV).

Device fabrication and Characterization: The ITO coated substrate was firstly cleaned respectively with acetone and ethanol in an ultrasonic bath. After treated with UV-ozone for 20 min, the substrate was coated with a layer of PEDOT:PSS for hole injection which was annealed at 120 °C for 10 min. The hole transporting layer (TFB) was spin-coated from p-xylene solution and baked at 120 °C for 10 min. The emitting layer dissolved in chlorobenzene was then spin-coated. After backing the emitting layer at 50 °C for 10 min, the sample was loaded into a vacuum chamber. The electron transporting layer (TmPyPB), the electron injecting layer (Liq) and Al cathode were consecutively evaporated in the vacuum chamber. The device was sealed with curable UV resin in N_2-filled glove-box. The EL properties of the devices were measured in ambient air after encapsulation. A PR735 SpectraScan Spectroradiometer (Photo Research) combined with a Keithley 2400 SourceMeter unit was controlled with a customized software to simultaneously record the current-voltage-luminance characteristics and the EL spectra.

Synthesis



Scheme S1 Synthesis routes for PFSOTTx.

M3: 2-(4-(bis(4-bromophenyl)amino)phenyl)-9*H*-thioxanthen-9-one-10,10-dioxide

2-(4-(diphenylamino)phenyl)-9*H*-thioxanthen-9-one-10,10-dioxide (0.97 g, 2 mmol), NBS (0.73 g, 4.1 mmol) and THF (50 mL) were added into a 100 mL flask. The mixture was stirred at room temperature. After 15 h, the solvent was removed using a rotary evaporator. The crude product was purified by flash chromatography using PE/DCM (1:1) as eluent and re-crystallized from DCM/ethanol to give orange cotton-like solid. Yield: 1.26 g, 97%. ^{1}H

NMR (400 MHz, $CDCl_3$) δ 8.51 (d, *J* = 1.9 Hz, 1H), 8.37 (dd, *J* = 7.8, 1.2 Hz, 1H), 8.25-8.18 (m, 2H), 8.03 (dd, *J* = 8.2, 1.9 Hz, 1H), 7.90 (td, *J* = 7.6, 1.3 Hz, 1H), 7.81 (td, *J* = 7.7, 1.2 Hz, 1H), 7.60-7.54 (m, 2H), 7.45-7.38 (m, 4H), 7.20-7.13 (m, 2H), 7.04-6.98 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.54, 148.05, 145.92, 145.46, 141.15, 138.71, 134.73, 133.21, 132.67, 132.27, 132.14, 131.15, 130.80, 129.24, 128.36, 126.83, 126.24, 124.35, 123.63, 123.55, 116.60. MALDI-TOF $[M]^+$ calcd. for $C_{31}H_{19}Br_2NO_3S$: 642.95; found, 642.9. HRMS $[M]^+$ calcd. for $C_{31}H_{19}Br_2NO_3S$: 642.9452; found, 642.9466.

General procedures for Suzuki Polycondensation[2]

Under argon atmosphere, a solution of M1 and M3 (0.5 mmol in total, with the feed molar ratios 40:10, 45:5, 48:2, 49:1, 49.5:0.5, 49.9:0.1 and 49.95:0.05), M2 (279 mg, 0.500 mmol), $Pd(OAc)_2$ (3 mg), and PCy_3 (6 mg) in toluene (10 mL), was stirred and heated at 82 °C, After the mixture became clear, deoxygenized mixture of Et_4NOH (2 mL) and deionized water (2 mL) were added. The solution was kept in the range of 80-85 °C with vigorous stirring under argon for 18 h. Phenylboronic acid in 1 mL of THF was subsequently added and the mixture was refluxed for 6 h. Finally, bromobenzene was added, and the mixture was refluxed for 6 h. After cooling, the resulting polymer was precipitated into methanol (200 mL) and filtered off. The product was dissolved in toluene (20 mL) again and then sodium diethyldithiocarbamate trihydrate (1.50 g) and deionized water (20 mL) were added into the mixture. The solution was kept at 90 °C with vigorous stirring for 24 h. After cooled, the resulting mixture was extracted with chloroform, and then washed three times with deionized water. After concentration, the resulting polymer was received by precipitation in methanol (200 mL). The final purification was carried out by soxhlet extraction with acetone for about 24 h. After drying, the product was resolved and then precipitated into methanol (200 mL). After filtration, the resulted polymers dried under vacuo to give the long filament-like polymers with yields of 80-85%.

PFSOTT0.05: M1 (299 mg, 0.4999 mmol), M3 (0.3 mg, 0.0005 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89-7.70 (br, Ar H), 7.33 (br, Ar H), 2.77 (br, CH_2), 2.04 (br, CH_2), 1.51 (br, CH_2), 1.33-1.00 (br, CH_2), 0.92-0.55 (m, CH_3).

PFSOTT0.1: M1 (298 mg, 0.499 mmol), M3 (0.7 mg, 0.001 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89-7.70 (br, Ar H), 7.33 (br, Ar H), 2.77 (br, CH_2), 2.04 (br, CH_2), 1.51 (br, CH_2), 1.33-1.00 (br, CH_2), 0.92-0.55 (m, CH_3).

PFSOTT0.5: M1 (296 mg, 0.495 mmol), M3 (3.2 mg, 0.005 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89-7.70 (br, Ar H), 7.33 (br, Ar H), 2.77 (br, CH_2), 2.04 (br, CH_2), 1.51 (br, CH_2), 1.33-1.00 (br, CH_2), 0.92-0.55 (m, CH_3).

PFSOTT1: M1 (293 mg, 0.490 mmol), M3 (6.5 mg, 0.010 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94-7.55 (br, Ar H), 7.33 (br, Ar H), 2.77 (br, CH_2), 2.04 (br, CH_2), 1.54 (br, CH_2), 1.42-0.94 (br, CH_2), 0.94-0.53 (m, CH_3).

PFSOTT2: M1 (287 mg, 0.480 mmol), M3 (12.9 mg, 0.020 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94-7.55 (br, Ar H), 7.33 (br, Ar H), 2.77 (br, CH_2), 2.04 (br, CH_2), 1.54 (br, CH_2), 1.42-0.94 (br, CH_2), 0.94-0.53 (m, CH_3).

PFSOTT5: M1 (269 mg, 0.450 mmol), M3 (32.3 mg, 0.050 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (s, Ar H), 8.38 (d, Ar H), 8.22 (t, Ar H), 8.10 (s, Ar H), 7.97-7.56 (br, Ar H), 7.30 (br, Ar H), 2.77 (br, CH_2), 2.10 (br, CH_2), 1.55 (br, CH_2), 1.37-0.92 (br, CH_2), 0.94-0.46 (m, CH_2).

PFSOTT10: M1 (239 mg, 0.400 mmol), M3 (64.5 mg, 0.100 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (d, Ar H), 8.39 (d, Ar H), 8.23 (t, Ar H), 8.13-8.04 (m, Ar H), 7.94-7.55 (m, Ar H), 7.30 (d, Ar H), 7.15 (d, Ar H), 2.77 (br, CH_2), 2.05 (br, CH_2), 1.54 (br, CH_2), 1.35-0.94 (br, CH_2), 0.93-0.47 (m, CH_2).

Table S1 M_w, M_n and PDI values of PFSOTTx evaluated by GPC.

Polymers	M_n (*k*Da)	M_w (*k*Da)	PDI
PFSOTT0.05	48.2	102.2	2.12
PFSOTT0.1	50.2	104.0	2.07
PFSOTT0.5	50.8	109.3	2.15
PFSOTT1	51.6	107.9	2.09
PFSOTT2	55.3	117.7	2.13
PFSOTT5	57.3	122.7	2.14
PFSOTT10	58.3	126.0	2.16

2. Additional data

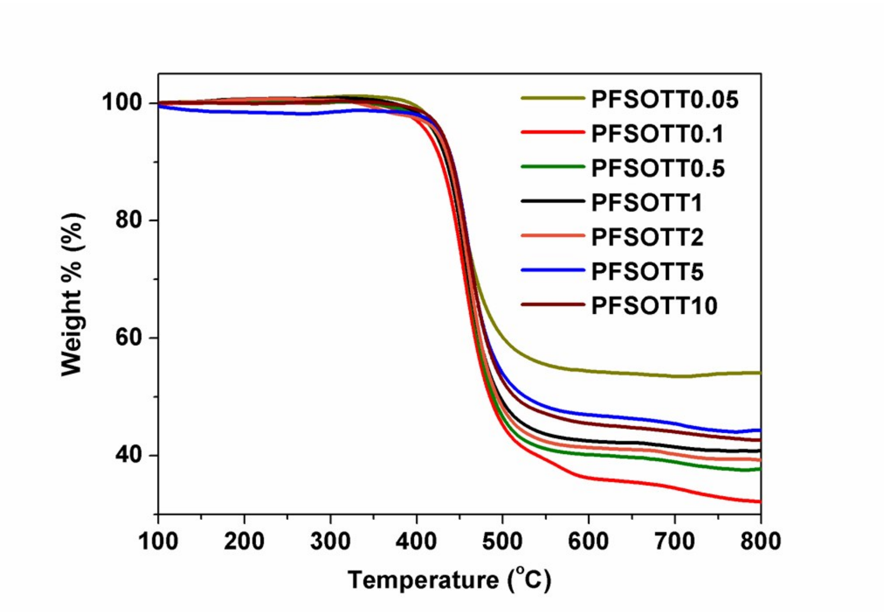


Fig. S1 TGA curves of PFSOTTx at a heating rate of 10 °C min^{-1} under N_2.

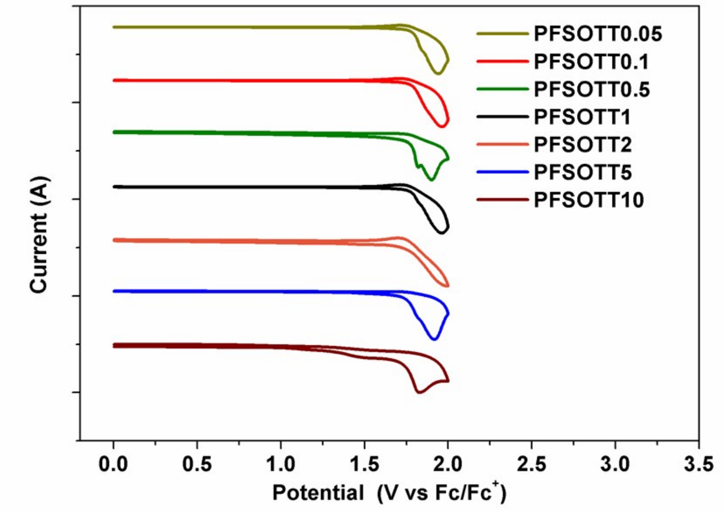


Fig. S2 Cyclic Voltammogram of PFSOTTx for oxidation.

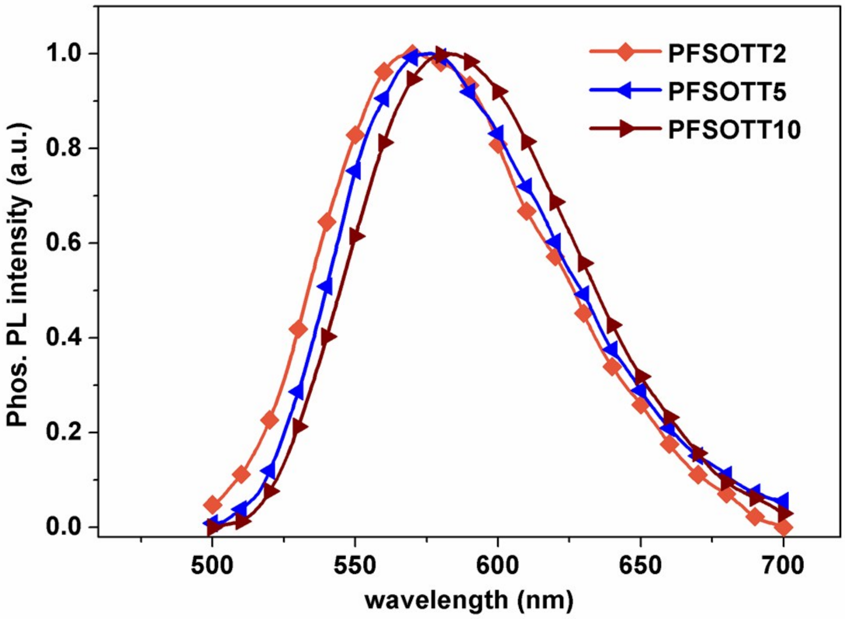


Fig. S3 Phosphorescent spectra of PFSOTT2, PFSOTT5 and PFSOTT10 in toluene at 77 K.

Table S2 E_S, E_T and ΔE_{ST} of PFSOTT2, PFSOTT5 and PFSOTT10.

Polymers	E_S [eV][a]	E_T [eV][b]	ΔE_{ST} [eV][c]
PFSOTT2	2.44	2.18	0.26
PFSOTT5	2.44	2.16	0.28
PFSOTT10	2.44	2.13	0.31

[a] The singlet (E_S) excited energies estimated from the onset wavelength of the spectra at 300 K in toluene. [b] The triplet (E_T) excited energies estimated from the peak wavelength of the spectra at 77 K in toluene. [c] $\Delta E_{ST} = E_S - E_T$.

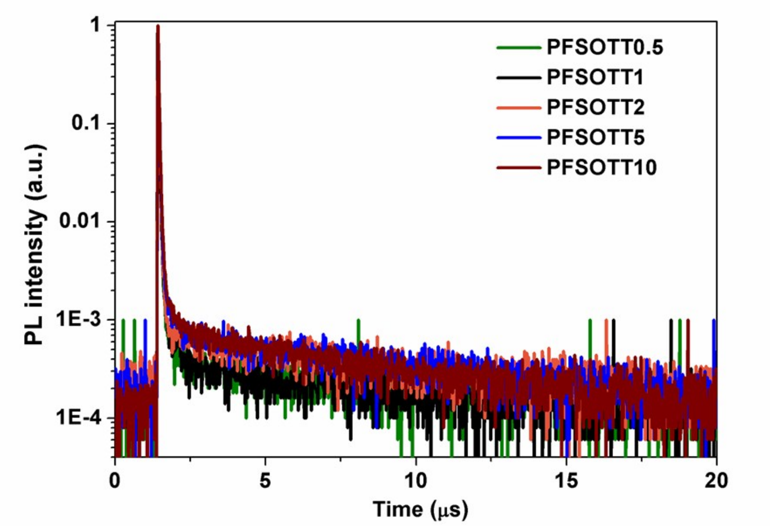


Fig. S4 The transient PL decay spectra of mCP:PFSOTTx (60:40) in film (argon condition, excitation wavelength: 375 nm, and detection wavelength: 546, 554, 567, 581 and 592 nm, respectively) at 300 K.

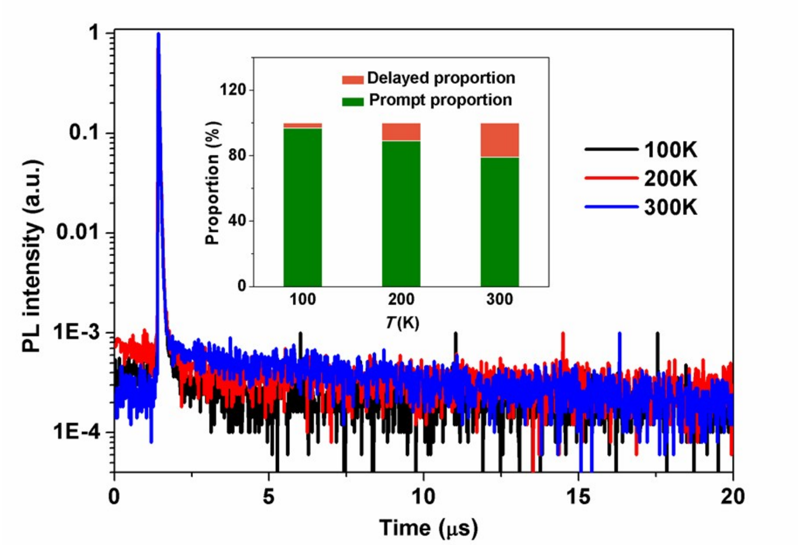


Fig. S5 The transient PL decay spectra of mCP:PFSOTT2 (60:40) in film (argon condition, excitation wavelength: 375 nm, and detection wavelength: 567 nm, respectively) from 100 to 300 K. Inset: the ratios of PLQY (considering the contribution from prompt and delayed fluorescence) of mCP:PFSOTT2 (60:40) from 100 to 300 K.

Table S3 The PLQYs, the prompt and the delayed fluorescence lifetimes and proportions of the doped polymer films in argon condition.

Polymers	PFSOTT0.05	PFSOTT0.1	PFSOTT0.5	PFSOTT1	PFSOTT2	PFSOTT5	PFSOTT10
PLQY[%]	89	93	95	97	99	88	70
τp/proportion [ns]/[%]			24.1/90.6	24.4/87.3	25.3/82.3	26.6/79.7	32.8/81.5
τd/proportion [μs]/[%]			5.4/9.4	6.3/12.7	8.6/17.7	8.1/20.3	6.5/18.5

Table S4 Comparison of the state-of-the art orange/red TADF OLEDs and the polymer based TADF OLEDs

Emitters	small molecule or polymer	EL_{max} (nm)	EQE/PE/CE (%/lm W^{-1}/cd A^{-1})	CIE (x, y)	Ref
HAP-3TPA	small molecule	610	17.5/22.1/25.9	0.60, 0.40	[4]
b1	small molecule	624	12.5/–/–	0.61, 0.39	[5]
DHPZ-2BTZ	small molecule	601	5.0/–/–	–	[6]
FDQPXZ	small molecule	600	9.0/–/–	0.53, 0.46	[7]
4CzTPN-Ph	small molecule	≈590	11.2/–/–	–	[8]
MeODP-DBPHZ	small molecule	≈600	≈10/–/–	–	[9]
POZ-DBPHZ	small molecule	≈610	≈16/–/–	–	[9]
PCZ-CB-TRZ	small molecule	586	11.0/7.6/16.7	–	[10]
2PCZ-CB	small molecule	590	9.2/11.2/19.9	–	[10]
DMAC-Ph-DCPP	small molecule	≈600	16.9/32.8/34.5	0.53,0.46	[11]
DMAC-DCPP	small molecule	≈610	10.1/12.2/12.8	0.60, 0.40	[11]
6AcBIQ	small molecule	≈600	11.2/23.0/–	0.55, 0.44	[12]
LEP	polymer	535	10/–/–	–	[13]
P12	polymer	506	4.3/9.0/24.9	0.24, 0.43	[14]
pCzBP	polymer	508	8.1/9.0/24.9	–	[15]
pAcBP	polymer	540	9.3/20.3/31.8	–	[15]
PAPTC	polymer	510	12.6/37.1/41.8	0.30, 0.59	[16]
Copo1	polymer	533	20.1/40.1/61.3	0.36, 0.55	[17]
Copo2	polymer	535	11.05/–/–	–	[18]
PCzDP-10	polymer	496	16.1/14.3/38.6	0.24, 0.40	[19]
PFSOTT2	polymer	592	19.4/17.9/42.4	0.51, 0.47	Thiswork

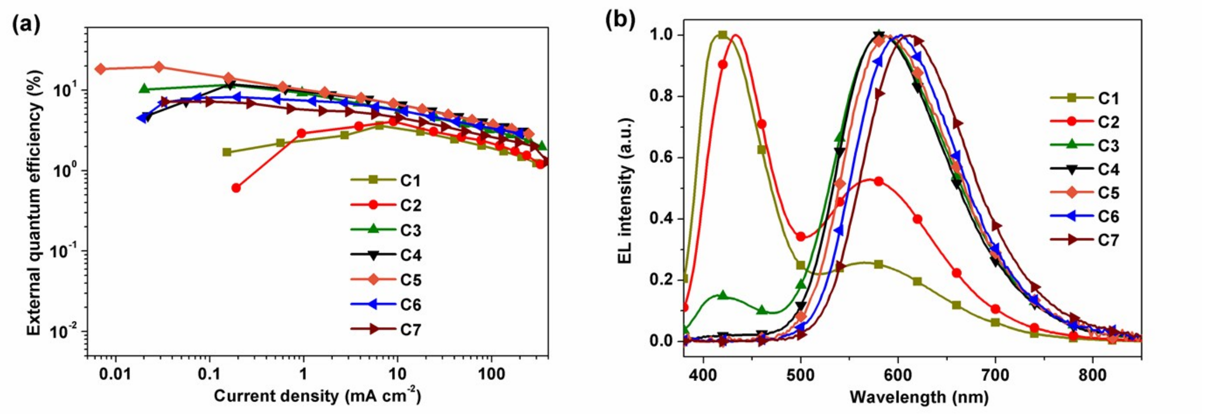


Fig. S6 (a) External quantum efficiency versus current density plots for the devices C1–C7 based on the doped PFSOTTx with the optimized host-guest composition; (b) The EL spectra measured at 10 V.

Table S5 The EL data of the devices based on PFSOTTx doped in mCP by 40:60.

Devices	V_{on} (V)[a]	L_{max} (cd m^{-2})[b]	EQE_{max}/CE_{max}/PE_{max} (%)/(cd A^{-1})/(lm W^{-1})[c]	EL (nm)[d]	CIE (x, y)[e]
C1	4	4464	3.6/4.4/2.0	420/566	(0.24, 0.18)
C2	4	6584	4.1/6.8/3.1	432/570	(0.28, 0.25)
C3	6	14780	11.6/25.5/11.7	414/584	(0.47, 0.45)
C4	6	15370	11.9/27.4/10.8	582	(0.49, 0.48)
C5 (B4)	7	15410	19.4/42.4/17.9	592	(0.51, 0.47)
C6	6	11600	8.2/16.5/6.4	602	(0.54, 0.45)
C7	6	8638	7.2/12.3/6.4	612	(0.56, 0.43)

[a]The turn-on voltage (V_{on}). [b]The maximum luminance brightness (L_{max}). [c]The maximum current efficiency (CE_{max}), maximum power efficiency (PE_{max}) and maximum external quantum efficiency (EQE_{max}). [d]The peak wavelength of EL spectra. [e]Commission Internationale de L'Eclairage (CIE) coordinates.

3. **NMR spectra for isolated compounds and polymers.**

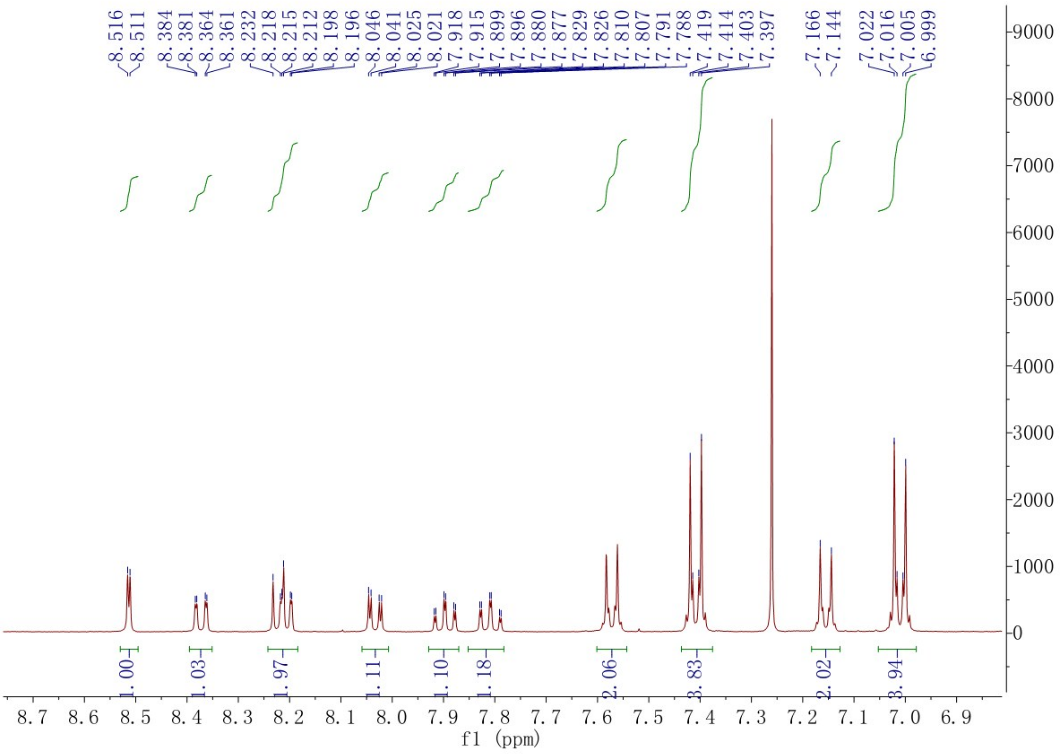


Fig. S7 ^{1}H NMR spectrum of M3 in $CDCl_3$.

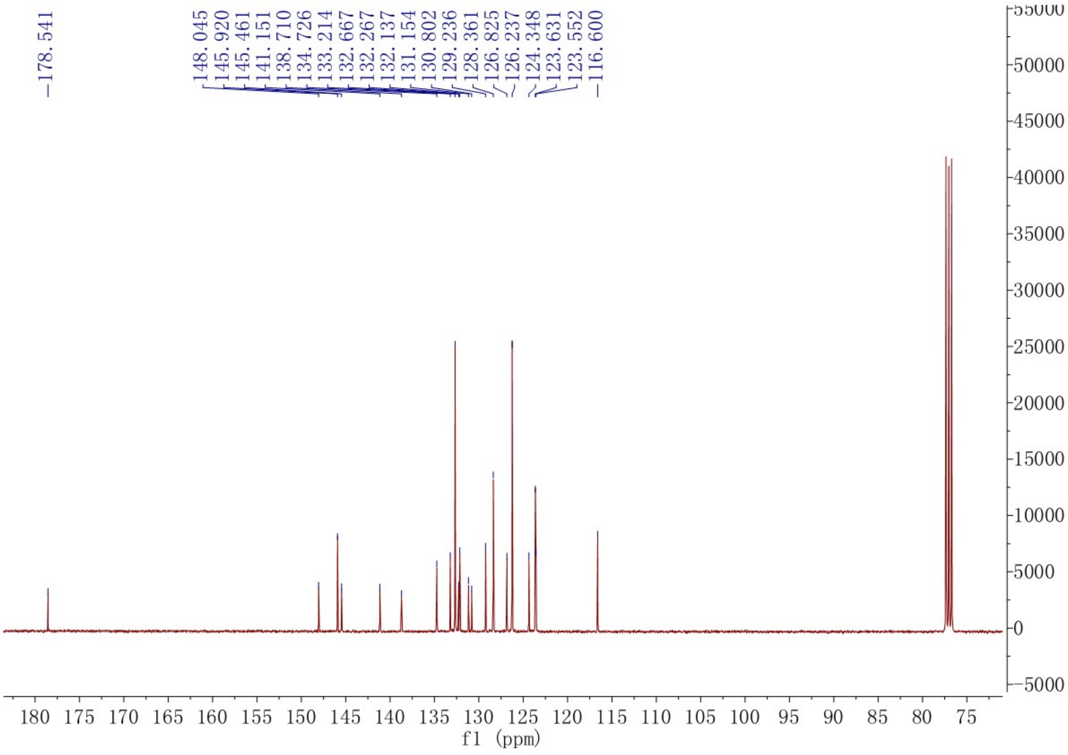


Fig. S8 ^{13}C NMR spectrum of M3 in $CDCl_3$.

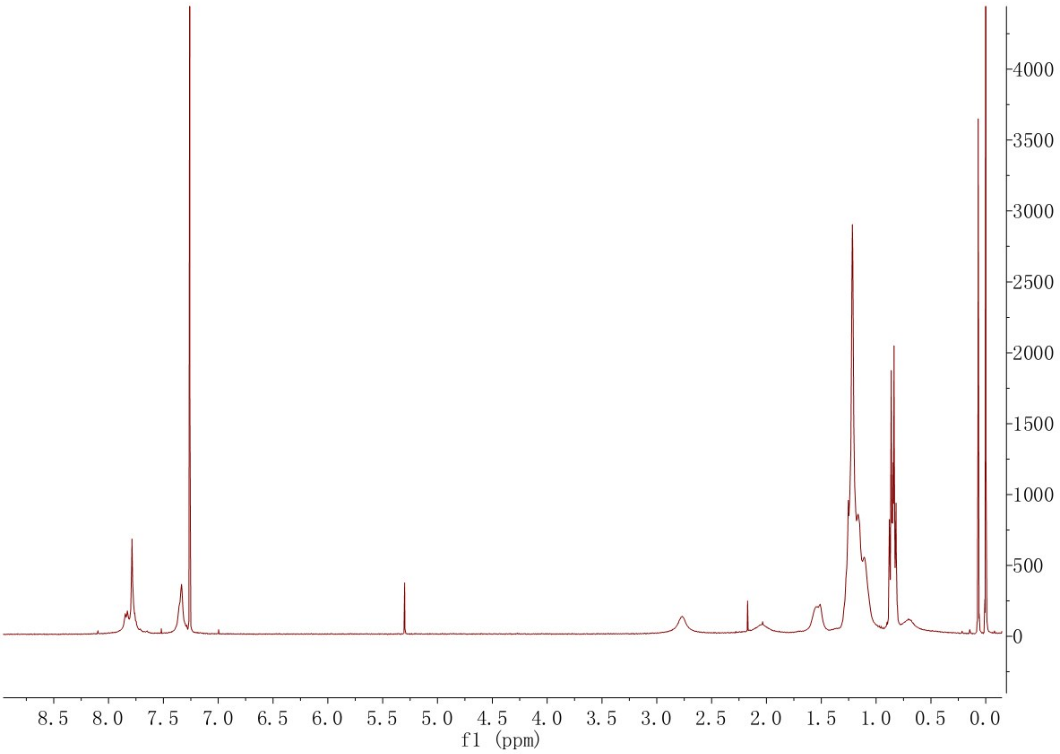


Fig. S9 ^{1}H NMR spectrum of PFSOTT0.05 in $CDCl_3$.

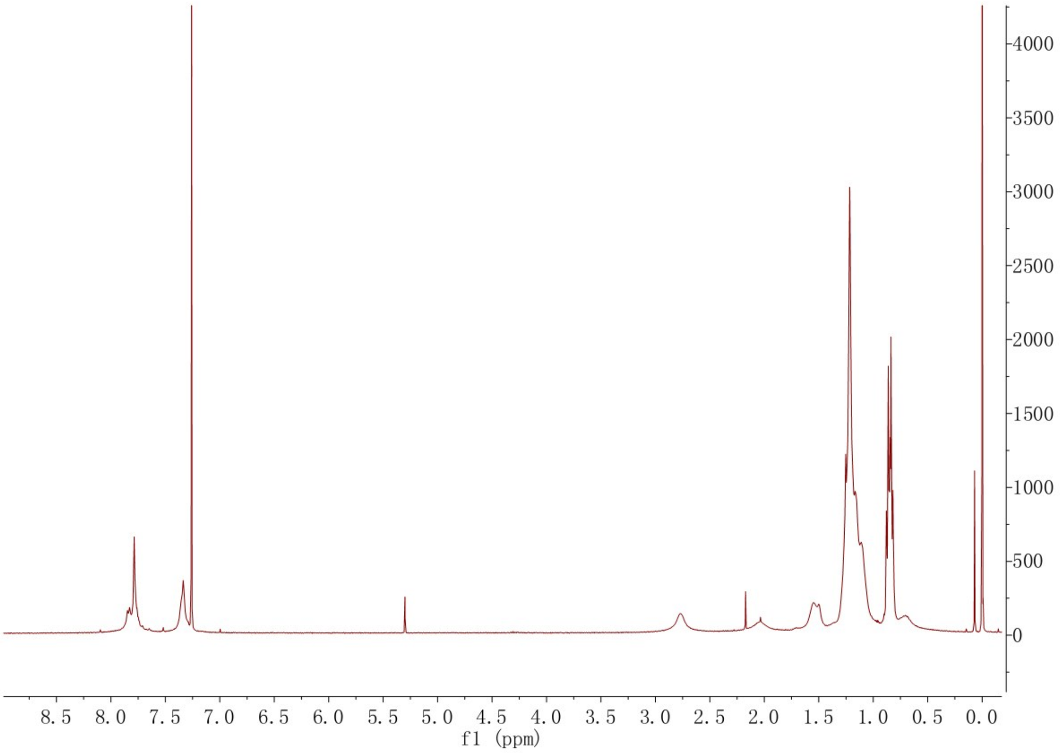


Fig. S10 ^{1}H NMR spectrum of PFSOTT0.1 in $CDCl_3$.

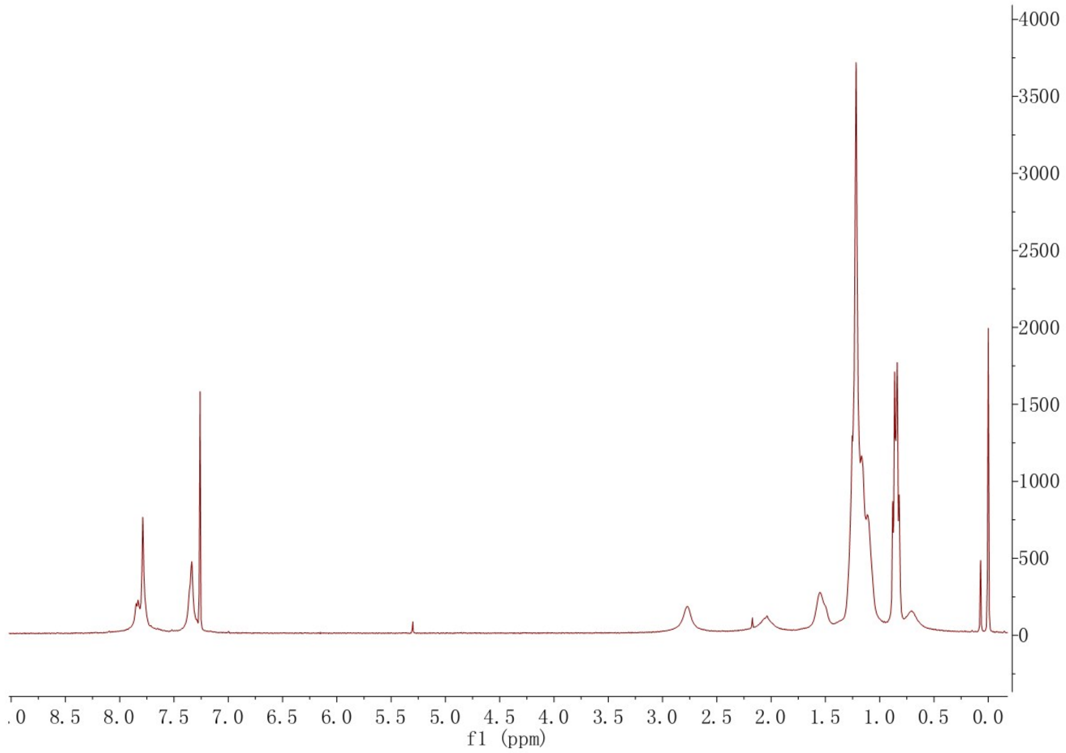


Fig. S11 ^{1}H NMR spectrum of PFSOTT0.5 in $CDCl_3$.

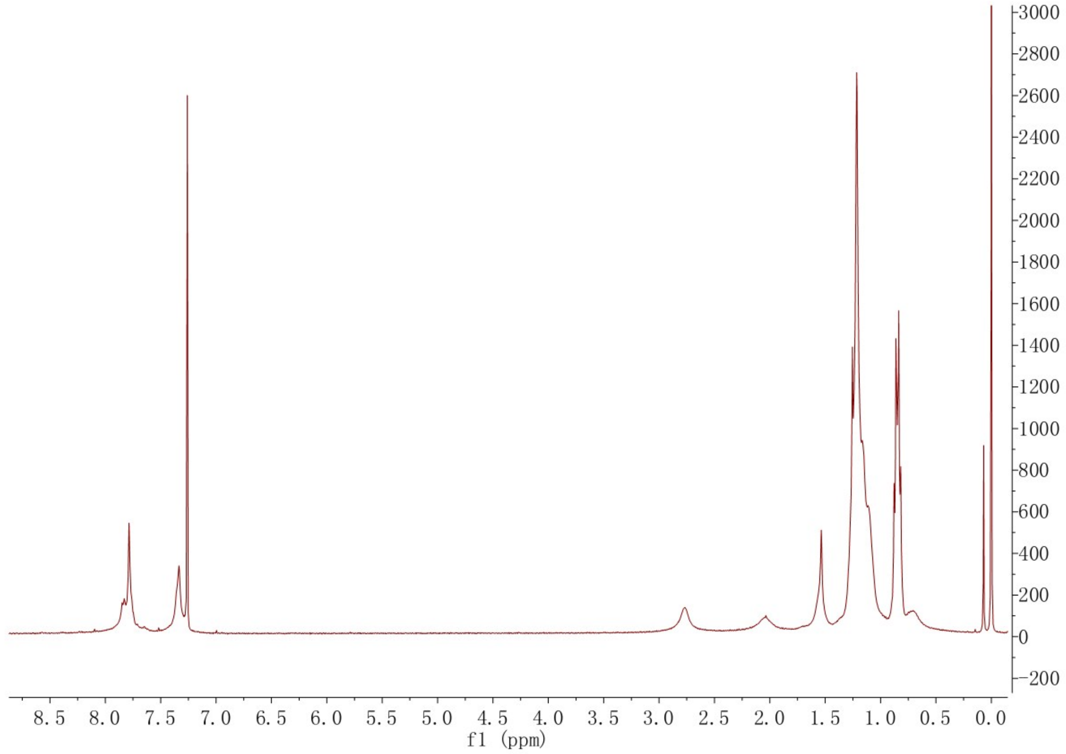


Fig. S12 ^{1}H NMR spectrum of PFSOTT1 in $CDCl_3$.

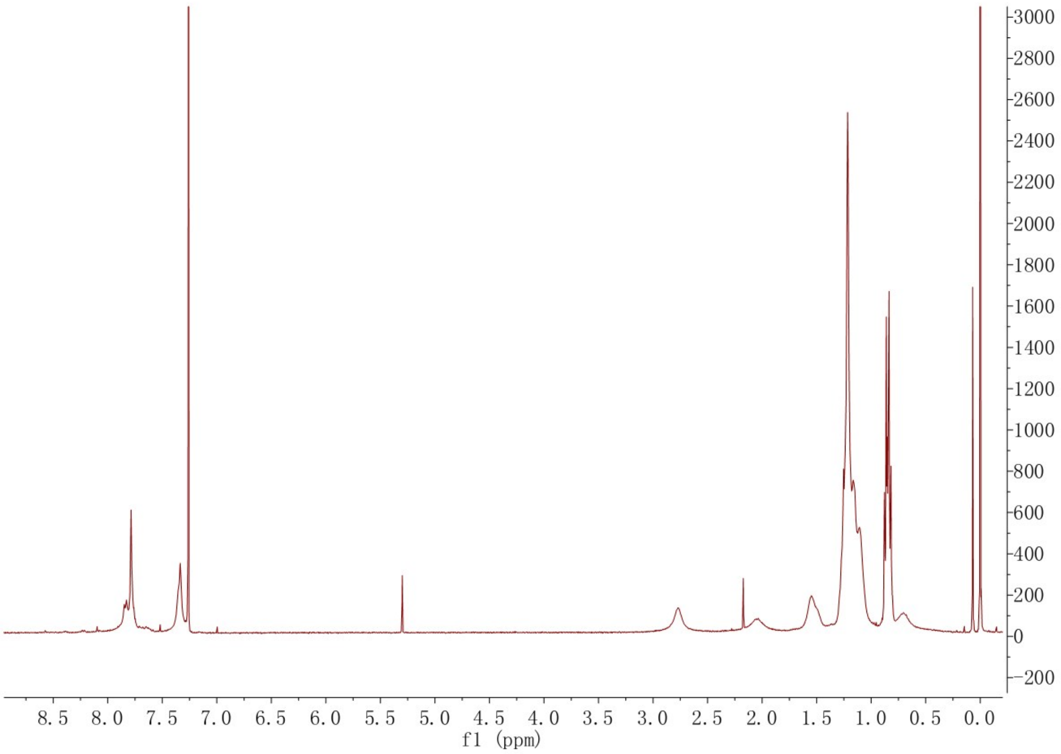


Fig. S13 ^{1}H NMR spectrum of PFSOTT2 in $CDCl_3$.

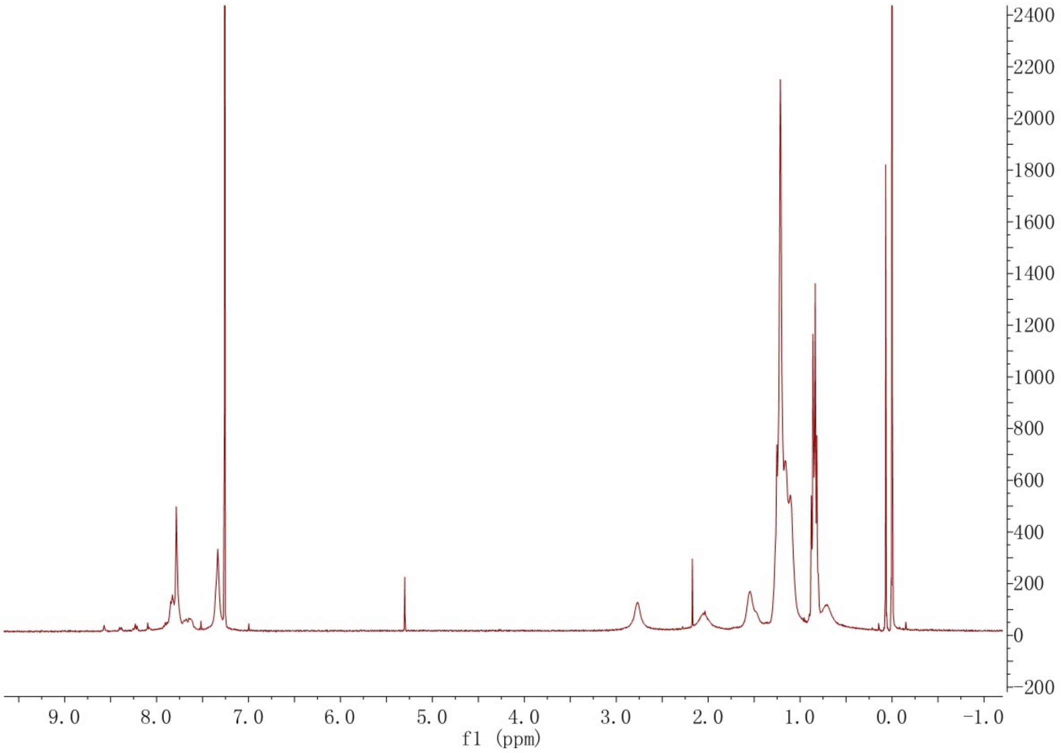


Fig. S14 ^{1}H NMR spectrum of PFSOTT5 in $CDCl_3$.

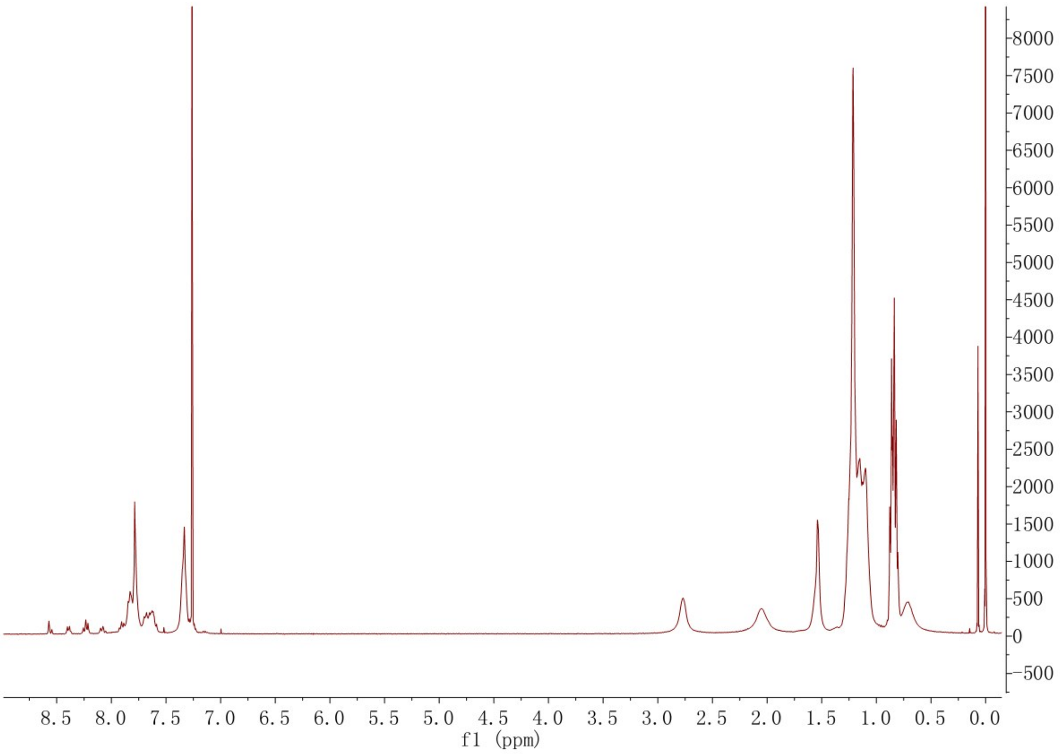


Fig. S15 ^{1}H NMR spectrum of PFSOTT10 in $CDCl_3$.

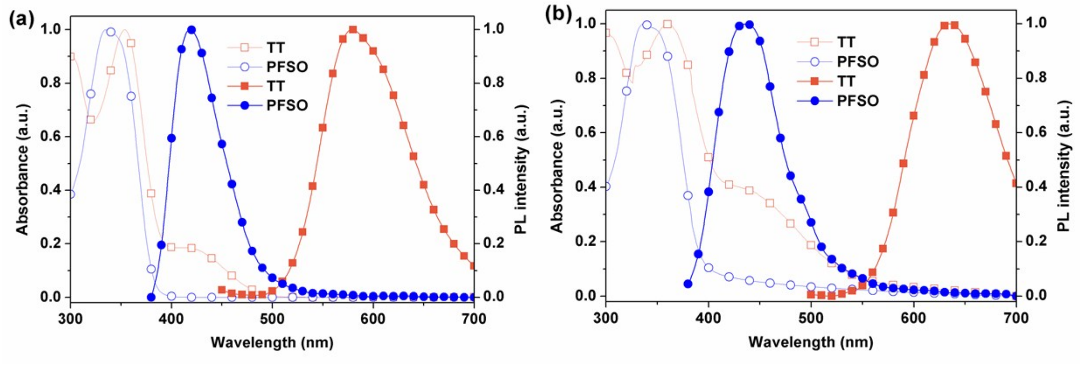


Fig. S16. UV-vis absorption and PL spectra of TT and PFSO (a) in toluene and (b) in neat film.

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