Supporting Information

Molecular Conformational Transition of Chiral Conjugated Enantiomer Dominated by the Wallach's Rule

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Keywords: chirality, molecular conformation, conjugated enantiomer, Wallach's rule, photophysical property

Supplementary Materials

- Fig. S1 ^{1}H NMR spectra of *rac*-, (*R,R*)- and (*S,S*)-2O8-DPFOH-SFX in $CDCl_3$.
- Fig. S2 ^{13}C NMR spectra of *rac*-2O8-DPFOH-SFX in $CDCl_3$.
- Fig. S3 ^{13}C NMR spectra of (*R,R*)-2O8-DPFOH-SFX in $CDCl_3$.
- Fig. S4 ^{13}C NMR spectra of (*S,S*)-2O8-DPFOH-SFX in $CDCl_3$.
- Fig. S5 Chiral chromatography report of *rac*-2O8-DPFOH-SFX.
- Fig. S6 HPLC of (*R,R*)-2O8-DPFOH-SFX.
- Fig. S7 HPLC of (*S,S*)-2O8-DPFOH-SFX.
- Fig. S8 Simulated circular dichroism spectra of (*R,R*)- and (*S,S*)-2O8-DPFOH-SFX by TD-DFT at the B3LYP/6-31G(d) level.
- Fig. S9 UV-vis absorption and PL spectra of 2O8-DPFOH-SFX films drop-cast from toluene solution in each form.
- Fig. S10 TG curves of 2O8-DPFOH-SFX in each form.

● EXPERIMENTAL SECTION

Chemicals

All the solvents and reagents were purchased from commercial suppliers and used without further purification unless otherwise noted. When required products were purified by flash column chromatography using Kanto Silica Gel (Kanto Chemical Co., Inc., Xuhui District, Shanghai, China) 60N (40-63 μm). Spectrochemical-grade solvents were used for optical measurements. The model spiroterfluorene, 2O8-DPFOH-SFX was obtained according to previously published protocols. The two pure enantiomers, (*R,R*)- and (*S,S*)-2O8-DPFOH-SFX, were obtained by chiral high-performance liquid chromatography (HPLC) with hexane/dichloromethane (1:1) as eluent.

Characterization

The ^{1}H- and ^{13}C-NMR spectra were recorded in $CDCl_3$ with tetramethylsilane (TMS) as the interval standard, using a Bruker 400 MHz spectrometer. Circular dichroism spectra were measured using BRIGHTTIME Chirascan, JASCO810, Jasco-815. The chiral HPLC measurements were conducted using Chiralpak IB N-5 column. The absorption spectra of the solutions and pristine films before and after annealing were measured using a Shimadzu UV-3600 spectrometer (Shimadzu Corporation, Nanjing, Jiangsu, China) at room temperature, and the emission spectra were recorded using a Shimadzu RF-530XPC luminescence spectrometer (Shimadzu Corporation, Nanjing, Jiangsu, China) after excitation at 360 nm. The quartz cells of 10 mm thickness were used to measure the spectra of the dilute solutions, and the solutions were added into a tube and dipped into a quartz container filled with liquid nitrogen. Thermogravimetric analysis (TGA) was conducted by a Shimadzu thermogravimetry and differential thermal analysis DTG-60H at a heating rate of 10 ^{o}C/min and a nitrogen flow rate of 50 cm^3/min. Differential scanning calorimetry (DSC) measurements were performed under a N_2 atmosphere at both the heating and cooling rates of 10 ^{o}C/min using Shimadzu DSC-60A. The AFM images were obtained using a Dimension

3100 (Veeco, CA) in tapping model with a Si tip (resonance frequency: 320 kHz; spring constant: 42 N m^{-1}) at a scanning rate of 1 Hz. XRD spectra were recorded on a Rigaku X-ray diffractometer with Cu Kα radiation (λ = 1.54178 Å), and the operating 2θ angle ranged from 3° to 30°, with the step length of 0.025. The PLQY was measured using an Edinburgh FLSP920 fluorescence spectrophotometer equipped with a xenonarc lamp (Xe900). Nanosecond time-resolved studies were performed with an Edinburgh FLS 980 time-correlated single photon-counting (TCSPC). The thin films were prepared by spin-coating on a quartz plate at a rate of 1500 rpm from 10 mg/mL in toluene solution.

Supplementary Materials

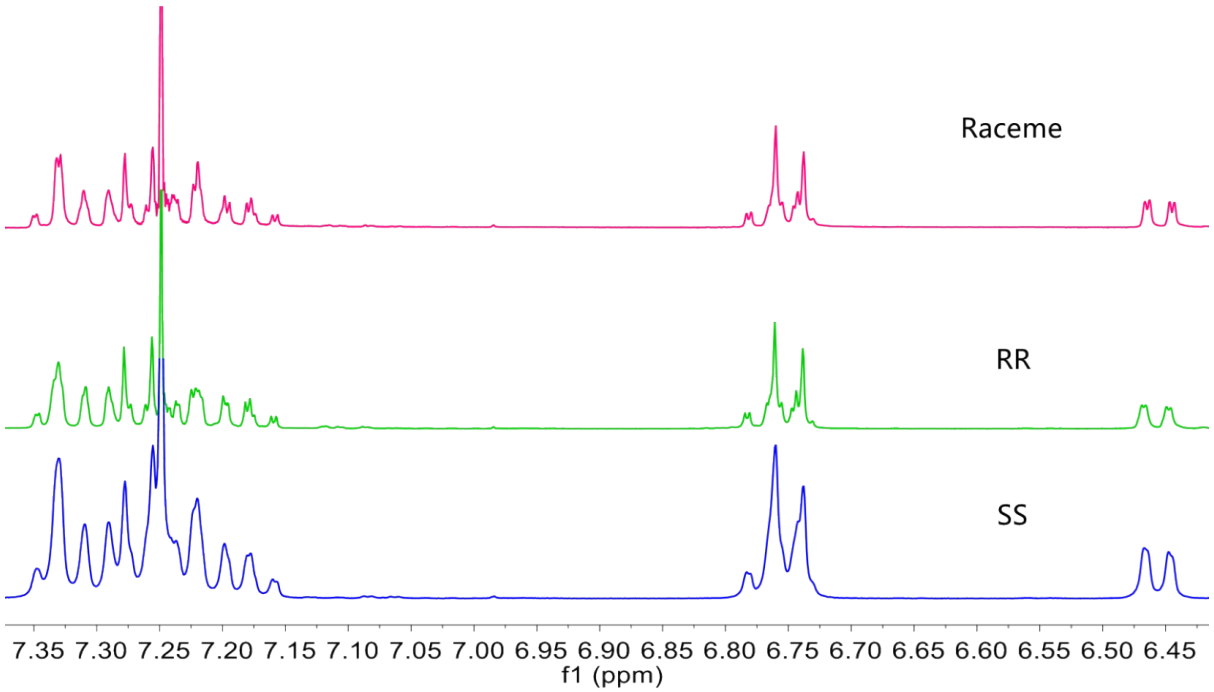


Fig. S1 ^{1}H NMR spectra of *rac*-, (*R,R*)- and (*S,S*)-2O8-DPFOH-SFX in $CDCl_3$.

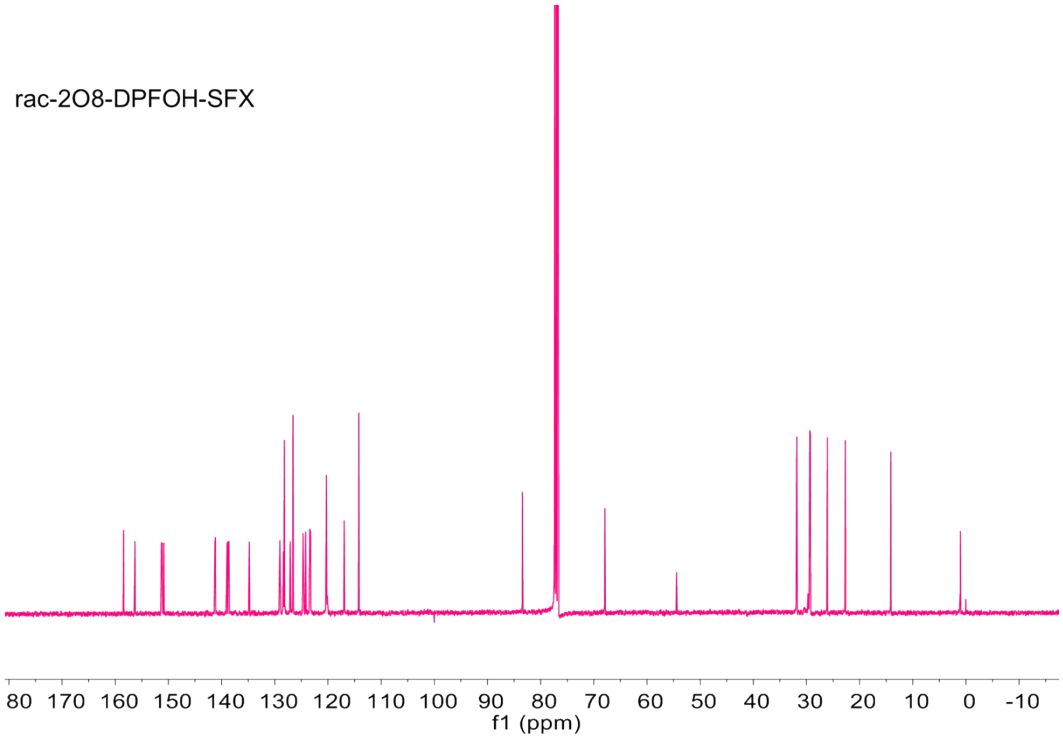


Fig. S2 ^{13}C NMR spectra of *rac*-2O8-DPFOH-SFX in $CDCl_3$.

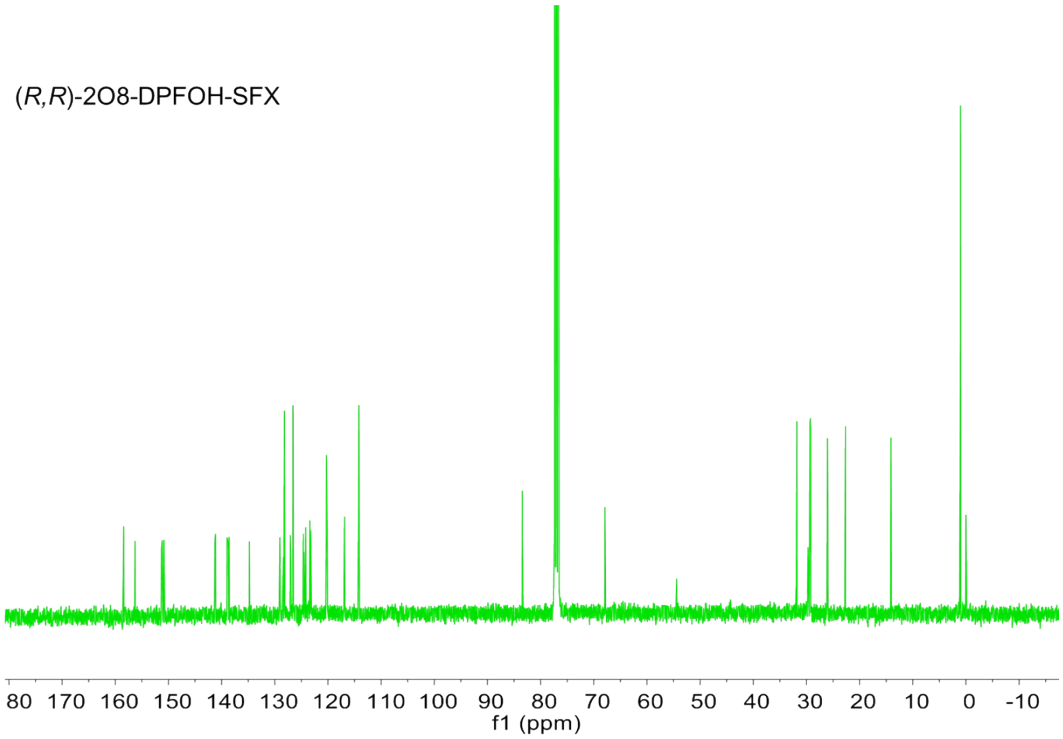


Fig. S3 ^{13}C NMR spectra of (*R,R*)-2O8-DPFOH-SFX in $CDCl_3$.

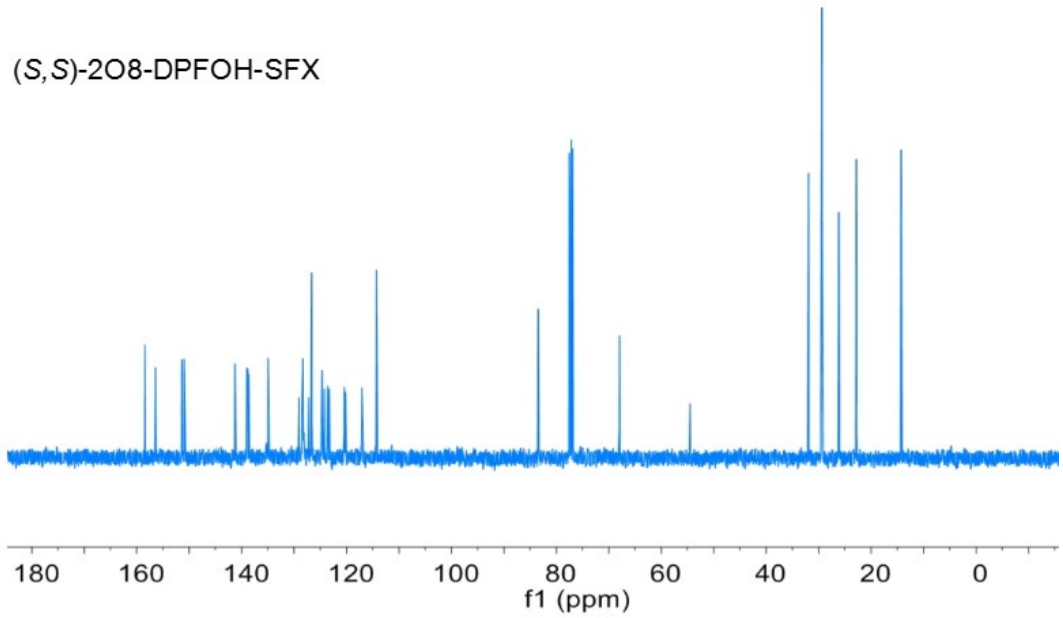
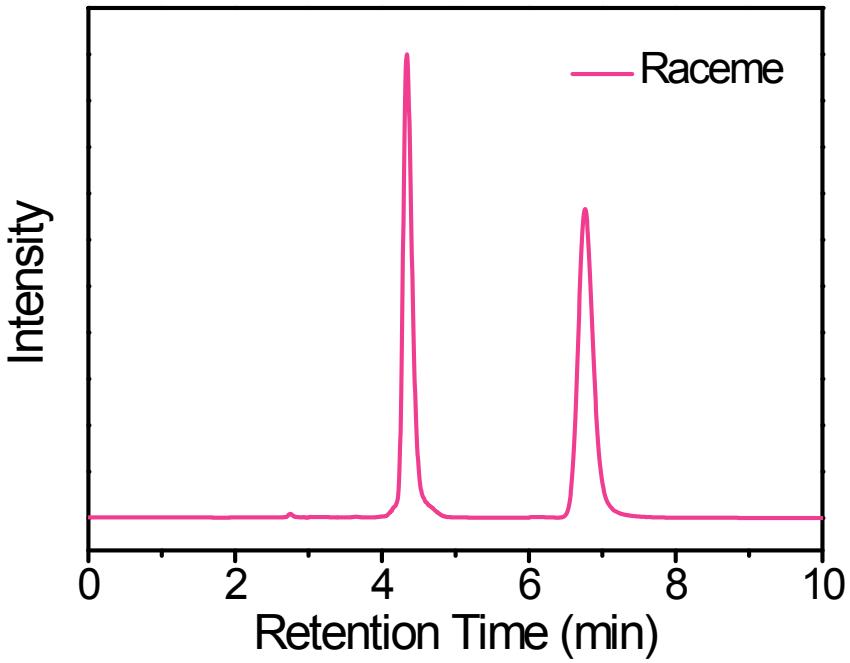


Fig. S4 ^{13}C NMR spectra of (*S,S*)-2O8-DPFOH-SFX in $CDCl_3$.

Table S1 Chiral chromatography report.

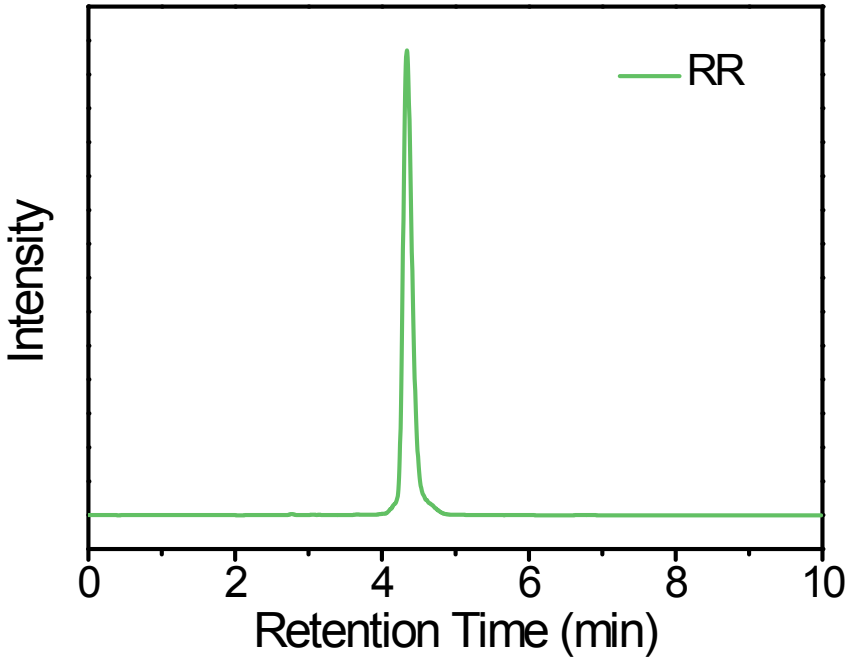
Column	CHIRALPAK IB N-5 (IBN5CD-VD005)
Column size	0.46 cm I.D. × 15 cm L
Injection	2 uL
Mobile phase	Hexane/DCM = 50/50 (V/V)
Flow rate	0.5 mL/min
Wavelength	UV 254 nm
Temperature	25 °C
HPLC equipment	Shimadzu LC-20AD CP-HPLC-05



<Peak Table>

Peak No.	Ret. Time	Area	Area%	T.Plate	Tailing	Resolution
1	4.350	1681845	50.7989	4124.230	1.075	2.830
2	6.760	1628942	49.2011	4114.095	1.092	--

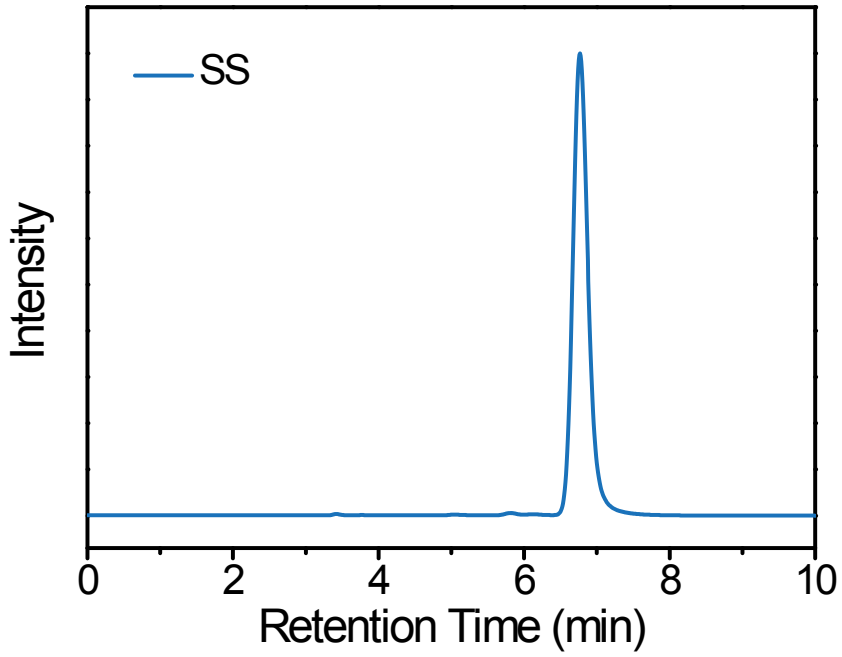
Fig. S5 Chiral chromatography report of *rac*-2O8-DPFOH-SFX.



<Peak Table>

Peak No.	Ret. Time	Area	Area%	T.Plate	Tailing	Resolution
1	4.339	12507.1	99.921	3647.113	--	--
2	5.902	9.9	0.079	2768.764	--	0.719

Fig. S6 HPLC of (*R,R*)-2O8-DPFOH-SFX.



<Peak Table>

Peak No.	Ret. Time	Area	Area%	T.Plate	Tailing	Resolution
1	5.001	5485	0.175	3484.001	--	--
2	6.760	3128222	99.825	4423.147	1.269	4.720

Fig. S7 HPLC of (*S,S*)-2O8-DPFOH-SFX.

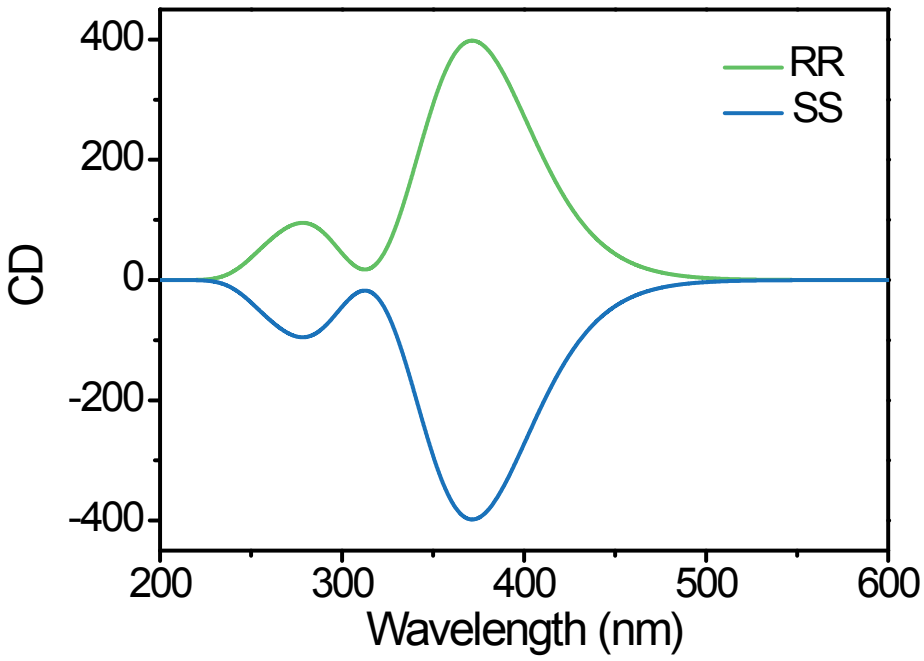


Fig. S8 Simulated circular dichroism spectra of (*R,R*)- and (*S,S*)-2O8-DPFOH-SFX by TD-DFT at the B3LYP/6-31G(d) level.

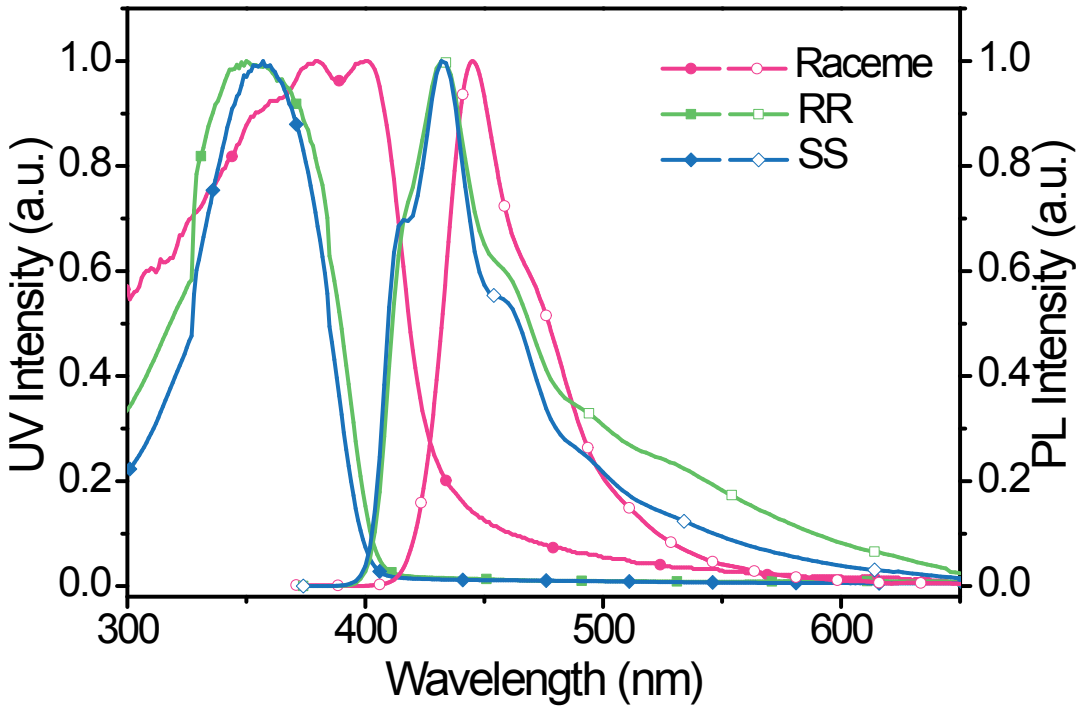


Fig. S9 UV-vis absorption and PL spectra of 2O8-DPFOH-SFX films drop-cast from toluene solution in each form.

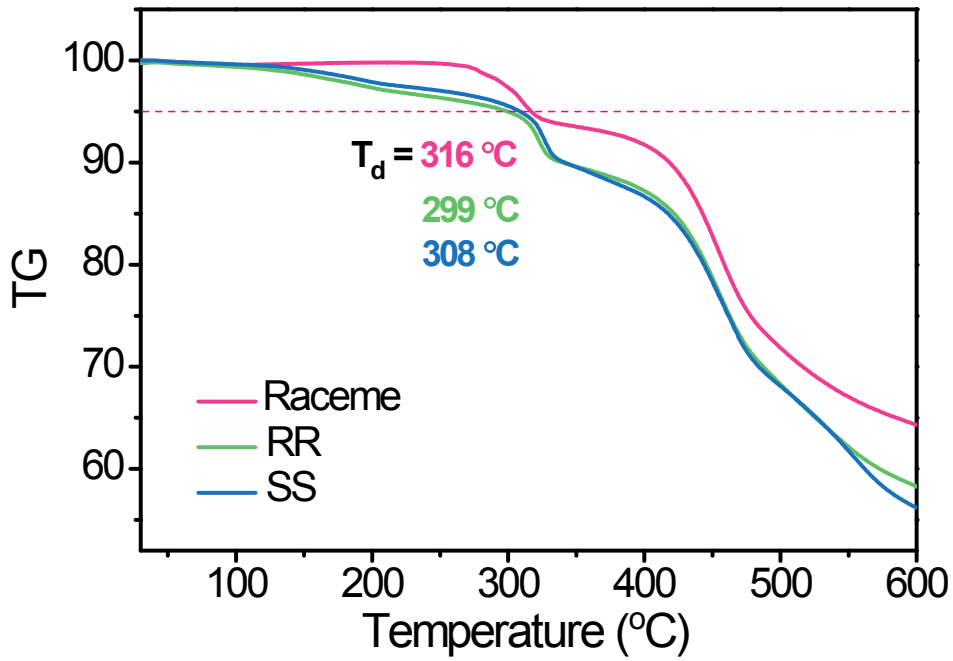


Fig. S10 TG curves of 2O8-DPFOH-SFX in each form.