Electronic Supplementary Material (ESI) for RSC Advances.

Electronic Supplementary Information (ESI)

A fluorescence molecular switch with high contrast multi-emissions and ON/OFF states

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General information for synthesis and characterizations

Materials

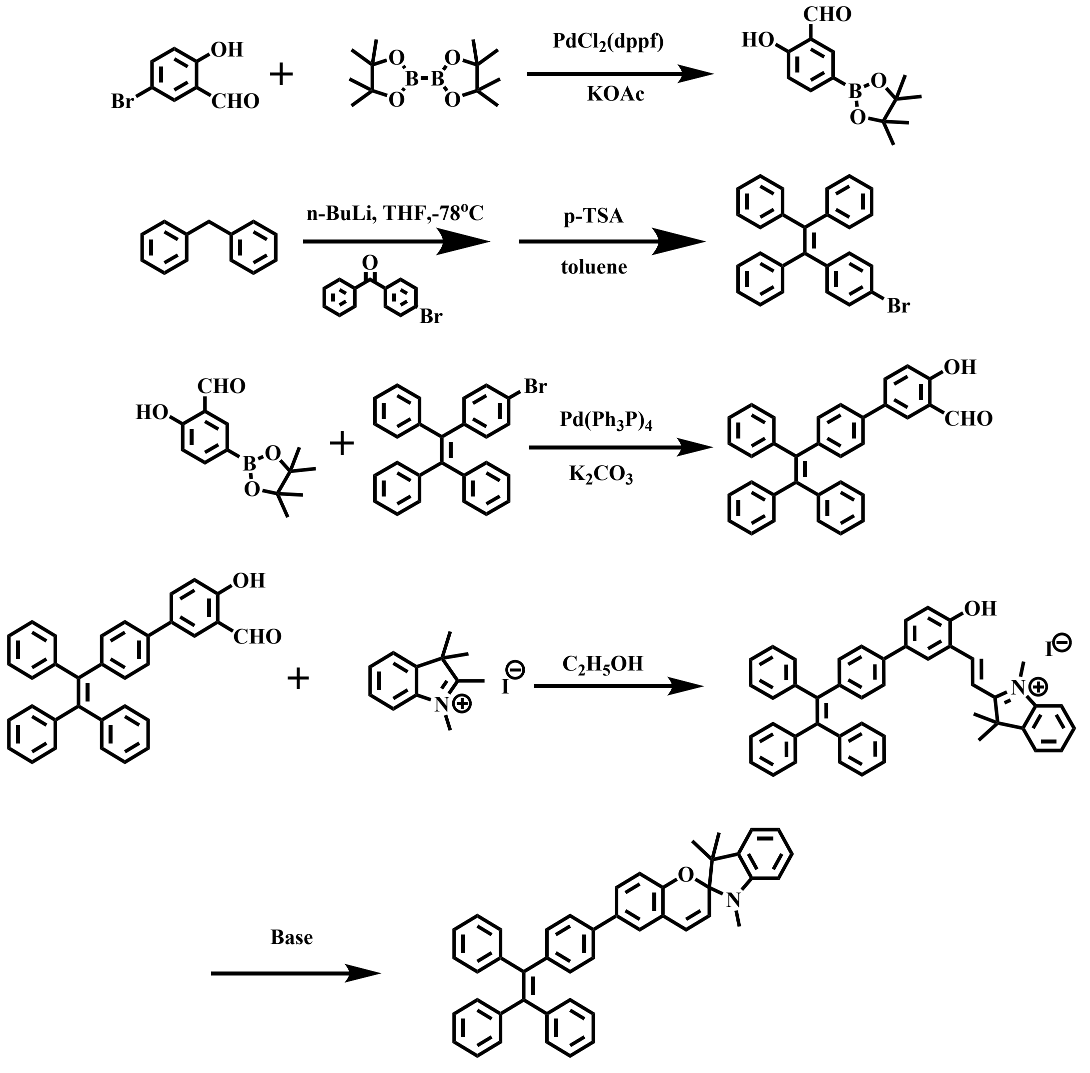
THF, 1,4-dioxane, toluene were treated with calcium hydride and sodium and distilled before use. Zinc powder was activated with dilute hydrochloric acid, and dried and stored under nitrogen. n-butyllithium, bis(pinacolato)diboron, $PdCl_2$(dppf), Pd(Ph_3P)$_4$, 5-bromosalicylaldehyde, diphenylmethane, 4-bomo-benzophenone, tosilate were purchased from Energy Chemical. All these chemicals were used without any further purification.

Instruments

^{1}H NMR spectra and ^{13}C NMR spectra were recorded on a 500MHz BrukerAvance. The deuterated solvent used including $CDCl_3$, DMSO-d_6 with tetramethylsilane (TMS) as an internal standard (δ = 0.00 ppm). Fluorescence spectra of all samples (solid and solution) were measured with a RF-5301PC spectrofluorometer. UV-Vis spectra were measured on a Shimadzu UV-2550 spectrophotometer. Powder XRD patterns were obtained from a PANalytical B.V.Empyrean X-ray diffractomer with Cu-Kα radiation (λ = 1.5418 Å) at 25 ºC (scan range: 4-50°). DSC data were obtained from a NETZSCH DSC 204 instrument at a scanning rate of 5 K min^{-1}. The time of flight mass spectra was recorded using a Kratos MALDI-TOF mass system. The fluorescence quantum yields (Φ_f) and lifetime were measured on FLS 920 lifetime and steady state spectrometer. Thermogravimetric analysis (TGA) was performed on a Q500 at heating rate of 10℃ min^{-1} under nitrogen flow from 35 to 695℃. Photos were taken by a Canon camera.

Synthesis and characterizations:

Compound 1-(4-bromophenyl)-1,2,2-triphenylethene was synthesized according to the method in literatures[1].



Scheme S1. Synthetic route of SPTPE.

2-hydroxy-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzaldehyde:

A 1,4-dioxane solution of 4-bomo-benzophenone, bis(pinacolato)diboron, KOAc were vacuumized and put into flask which full of nitrogen. Then freezed the solution with liquid nitrogen and added $PdCl_2$(dppf) under the nitrogen. Evaporated the flask for 1 min and inlet the nitrogen. After the solution recovered back to room temperature, heat the reaction liquid to reflux over night. Added the water into flask and extracted the solution with dichloromethane. The organic layer was dried with anhydrous sodium sulfate. The solvent was evaporated to dryness and the crude the product was purified by column chromatography(hexane:ethyl acetate=10:1). Yield: 41% . ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.21 (s, 1H), 9.92 (s, 1H), 8.04 (d, *J* = 1 Hz, 1H), 7.95 – 7.93 (dd, *J* = 8.5 Hz, 1 Hz, 1H), 6.97 (d, *J* = 8.5 Hz, 1H), 1.35 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.03, 164.16, 143.34, 141.54, 120.58, 117.21, 84.21, 25.01.

4-hydroxy-4'-(1,2,2-triphenylvinyl)-[1,1'-biphenyl]-3-carbaldehyde: 2-hydroxy-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzaldehyde, 1-(4-bromophenyl)-1,2,2-tri -phenylethene and potassium carbonate were dissolved in 10mL degassed THF and 3mL deionized water. Then freezed the solution with liquid nitrogen and added $Pd(Ph_3P)_4$. Evaporated the flask to remove the oxygen. After the solution recovered back to room temperature, heat the reaction liquid to reflux overnight under stirring. Added 20mL water into the flask and extracted three times with diethyl ether. Concentrated the organic layer and evaporated to remove the solvent. The crude product was purified by fast column chromatography (dichloromethane:hexane=1:1). Yield: 76.5%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.96 (s, 1H), 9.92 (s, 1H), 7.72 – 7.69 (m, 2H), 7.29 (d, J = 8 Hz, 2H), 7.15 – 7.00 (m, 18H). ^{13}C NMR (126 MHz, $CDCl_3$) δ196.62, 160.89, 143.68, 143.64, 143.62, 142.98, 141.37, 140.30, 136.99, 135.49, 132.85, 132.32, 132.24, 131.99, 131.62, 131.53, 131.37, 131.33, 131.31, 128.55, 128.45, 127.80, 127.74, 127.66, 126.55, 126.50, 125.65, 120.70, 118.05.

Open form SPTPE iodate and SPTPE:

Put 1,2,3,3-tetramethyl-3H-indol-1-ium iodide and 4-hydroxy-4'-(1,2,2-triphenylvinyl)-[1,1'-biphenyl] -3-carbaldehyde into flask and add 10mL anhydrous EtOH. Refluxed for 48h and evaporated the solvent to get red crude product. Purified the crude product with dichloromethane/ethyl acetate. Wash the Open form SPTPE iodate dichloromethane solution with Na_2CO_3 aqueous solution to get SPTPE. Yield: 49%. ^{1}H NMR (500 MHz, DMSO) δ 7.46 (d, J = 2 Hz, 1H), 7.38 (d, J = 8 Hz, 2H), 7.34 (dd, J = 8.5 Hz, 2Hz, 1H), 7.16 – 6.96 (m, 20H), 6.77 (t, J = 7 Hz, 14.5Hz, 1H), 6.70 (d, J = 8.5 Hz, 1H), 6.56 (d, J = 7.5 Hz, 1H), 5.79 (d, J = 10.5 Hz, 1H), 2.65 (s, 3H), 1.22 (s, 3H), 1.10 (s, 3H). ^{13}C NMR (126 MHz, DMSO) δ 154.13, 148.28, 143.72, 143.67, 142.05, 141.07, 140.68, 137.94, 136.75, 131.98, 131.69, 131.20, 131.13, 129.85, 128.36, 128.31, 128.26, 128.18, 127.93, 127.07, 127.03, 126.98, 126.97, 125.71, 125.40, 121.92, 120.15, 119.45, 119.43, 115.27, 107.25, 104.63, 51.87, 29.02, 26.18, 20.33.

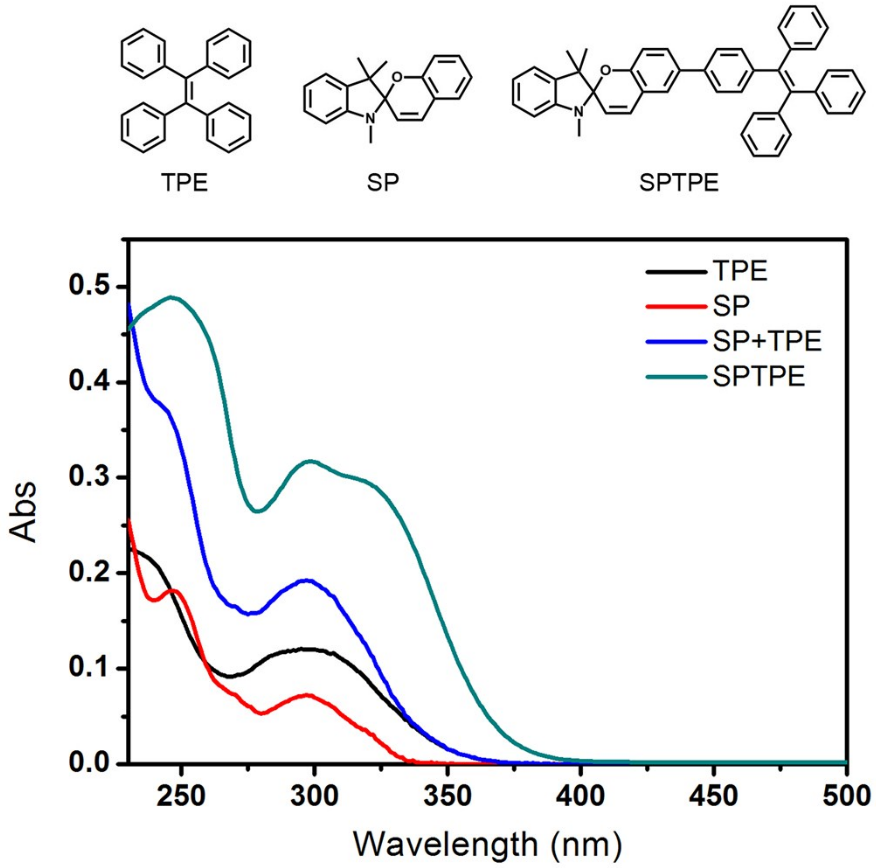


Figure S1 Comparison of the UV-Vis spectra of TPE, SP and SPTPE, the linear addition of UV-Vis absorbance of TPE and SP (SP+TPE) is also presented.

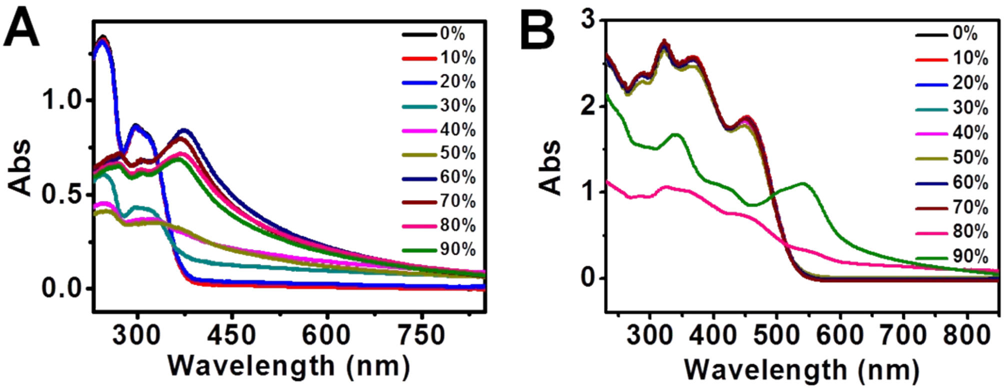


Figure S2 UV-Vis spectra of (A) RCF SPTPE (1×10^{-4} M) and (B) ROF SPTPE (obtained from RCF SPTPE by 50 equiv of HCl treatment for 12h, 1×10^{-4} M) with different water fractions in different acetonitrile/water (v/v) mixtures.

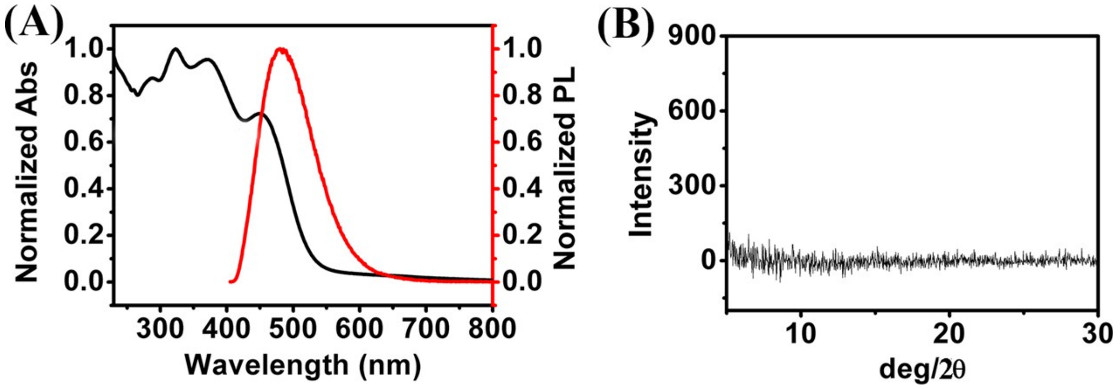


Figure S3 (A) Emission spectrum of the aggregates and UV-vis spectrum of the supernatant of ROF SPTPE at 70% water fraction. (B) Powder XRD of the aggregates.

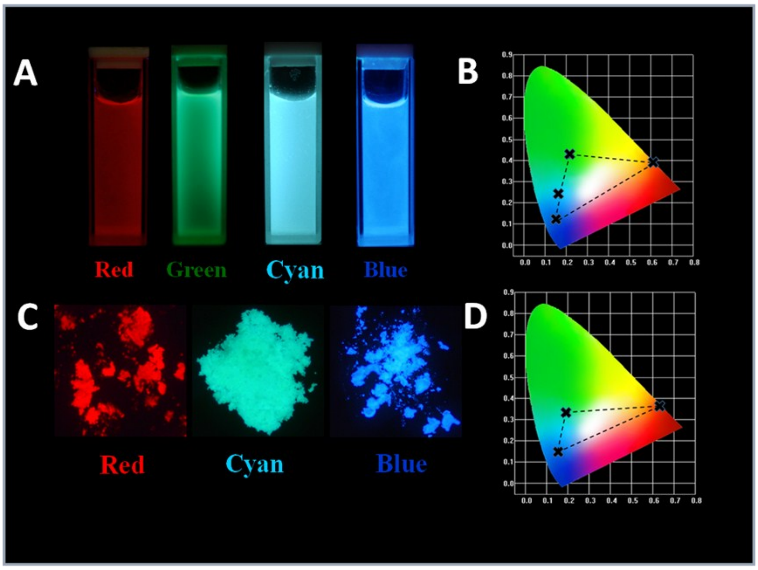


Figure S4 (A) Fluorescent images of aggregates of the SPTPE isomers exhibiting red/green/cyan/blue emissions at different conditions as described in the paper and (B) their corresponding CIE graphs. (C) Fluorescent images of CROF, ARCF and CRCF SPTPE in solid state exhibit red/cyan/blue emissions and (D) their corresponding CIE graphs.

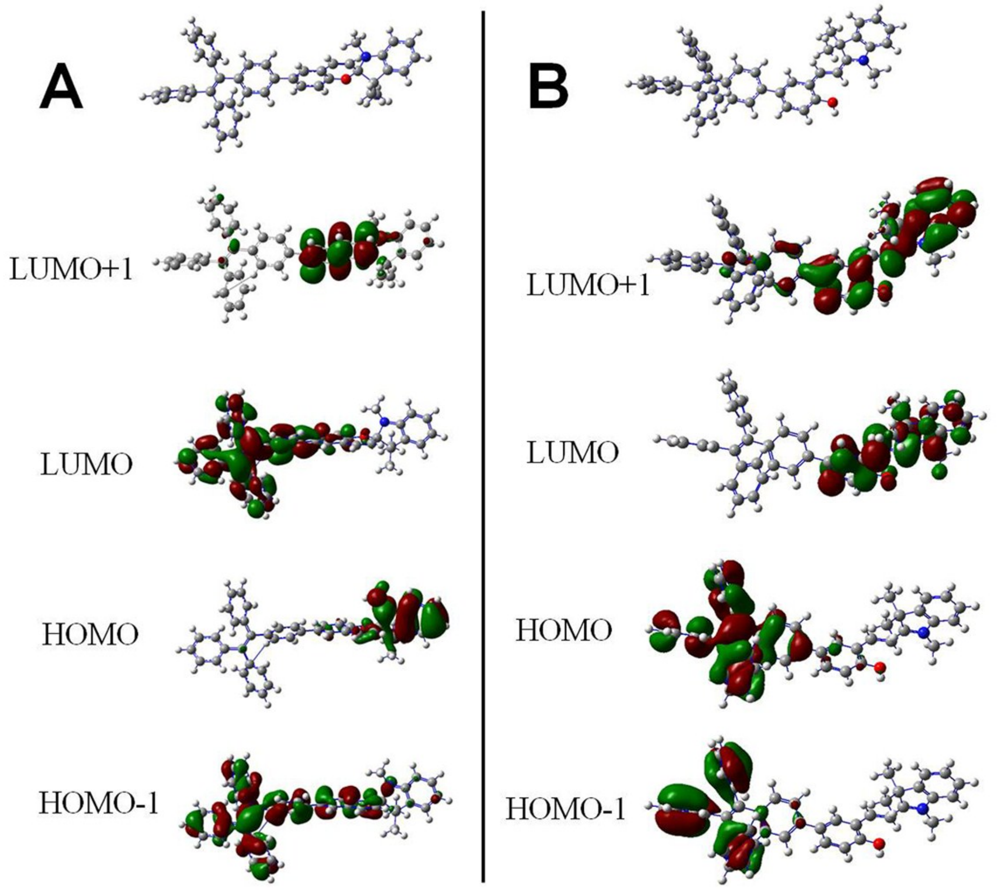


Figure S5 Molecular orbital amplitude plots of HOMO and LUMO energy levels of (A) RCF and (B) ROF SPTPE calculated using B3LYP/6-31G(d) by Gaussian 09.

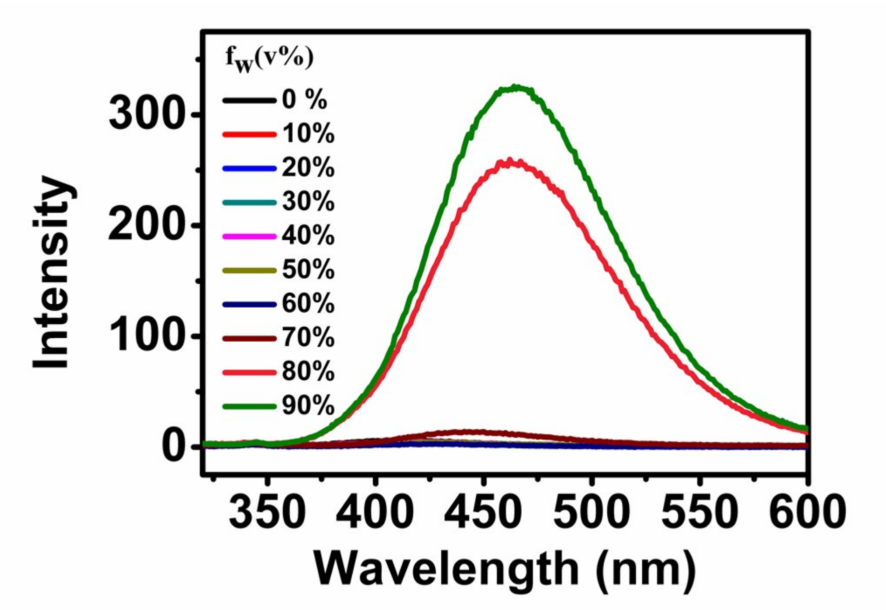


Figure S6 PL spectra of TPE (1×10^{-5} M) in acetonitrile/water (v/v) mixtures with different water fraction.

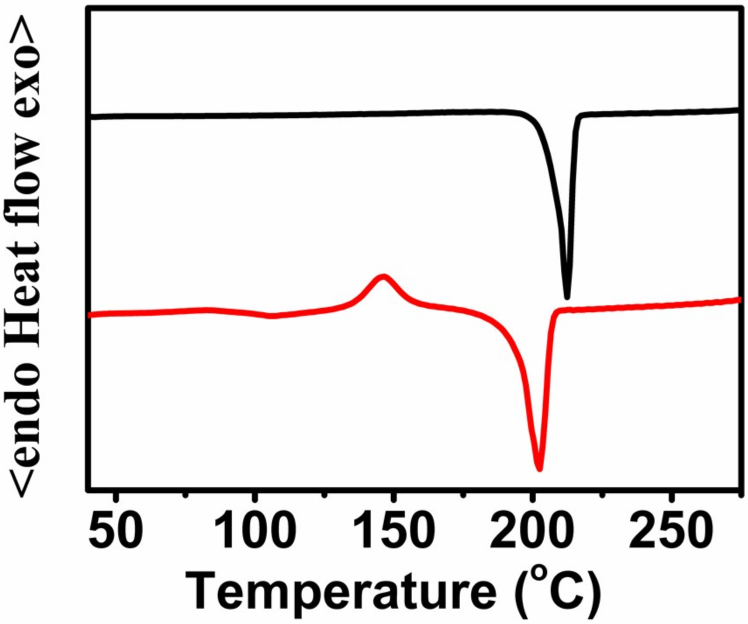


Figure S7 DSC curves of ARCF (red line) and CRCF (black line) SPTPE.

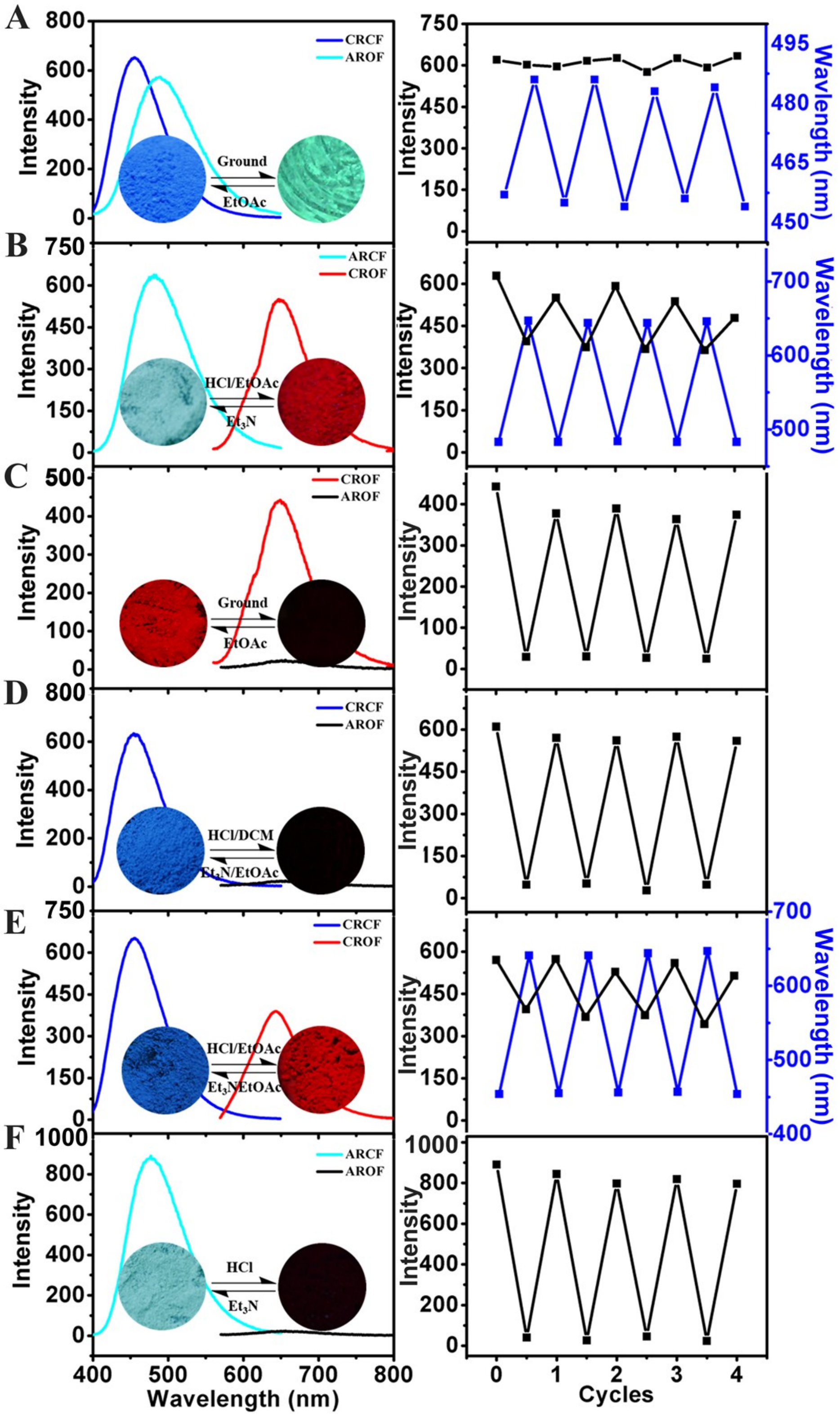


Figure S8 Fluorescent images and corresponding PL spectra of SPTPE converting reversibly between different solid state, as well as the PL intensity and wavelength contrast profile for several repeating cycles.

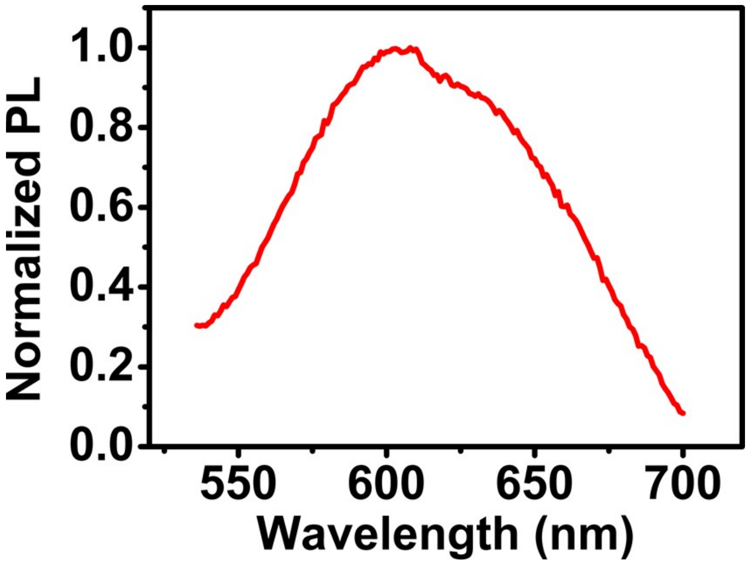


Figure S9 PL spectrum of ROF SPTPE in PEG film with low concentration (wt%=0.1%).

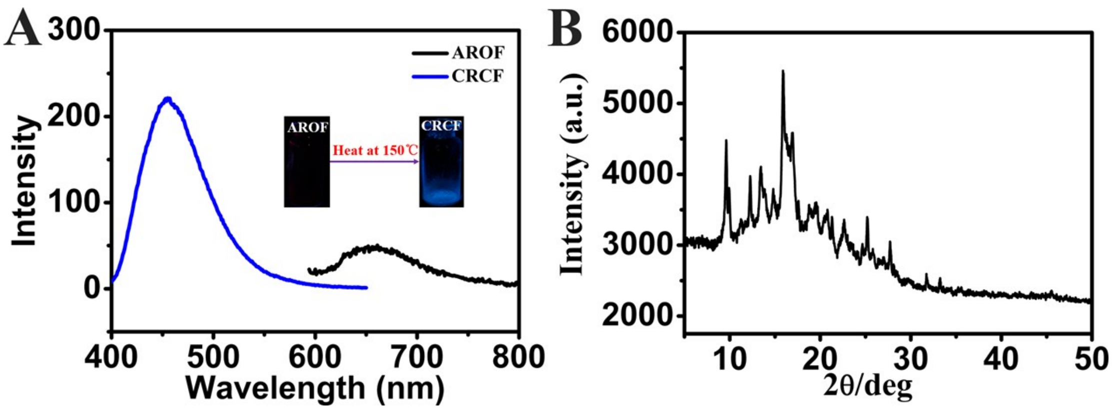


Figure S10 (A) PL spectra and corresponding fluorescent images of AROF and CRCF SPTPE conversion upon heat treatment, and (B) PXRD pattern of CRCF SPTPE from AROF SPTPE after 150^{o}C treatment.

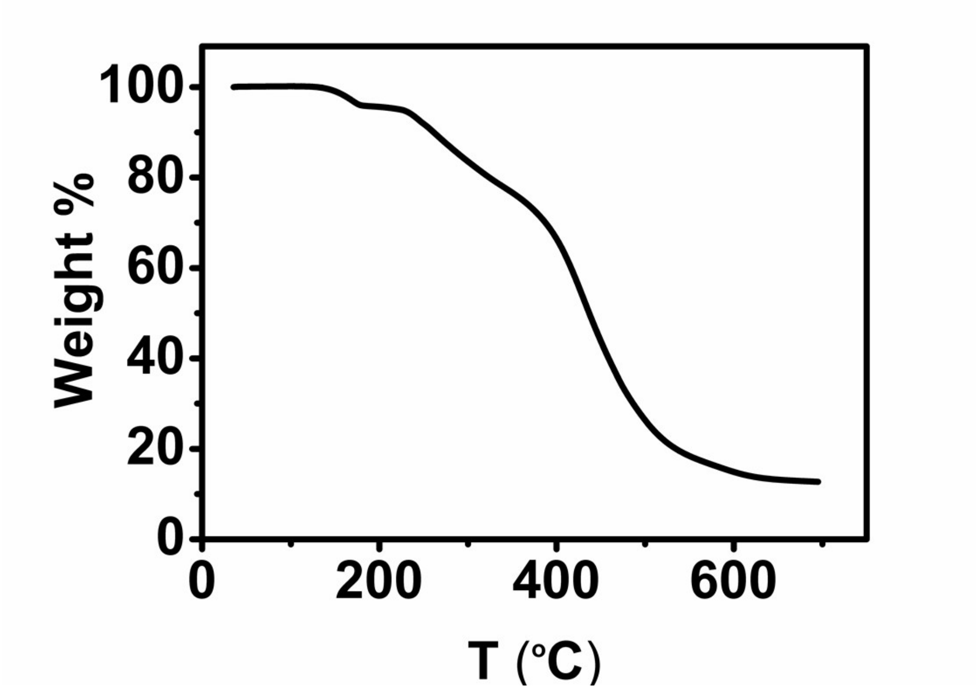


Figure S11 TGA curve of AROF SPTPE.

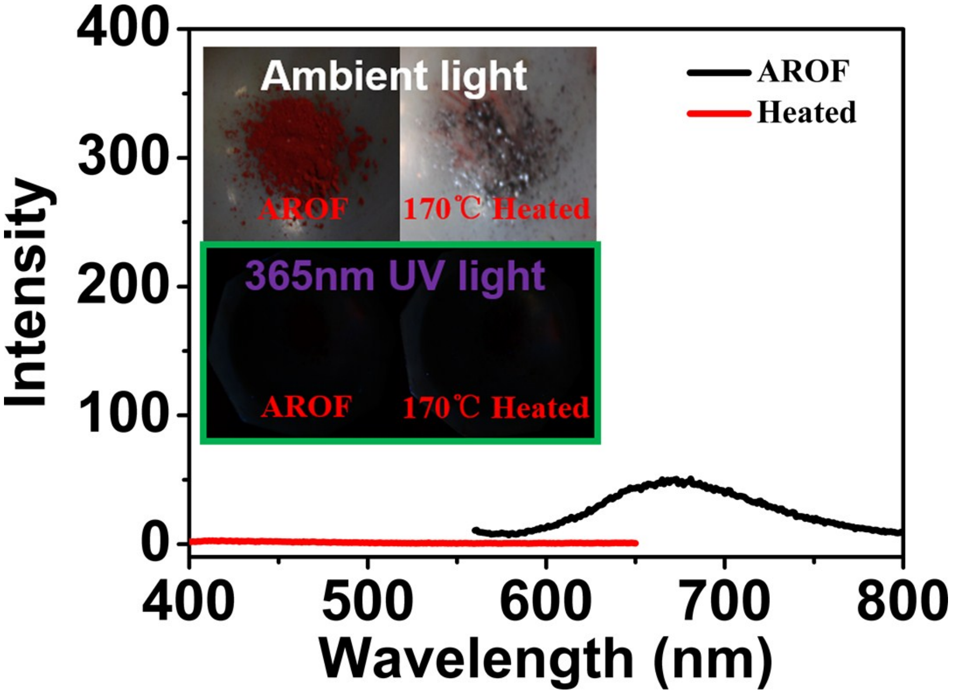


Figure S12 PL spectra and corresponding images of AROF SPTPE (PF_6^- as counterion) before and after heat treatment.

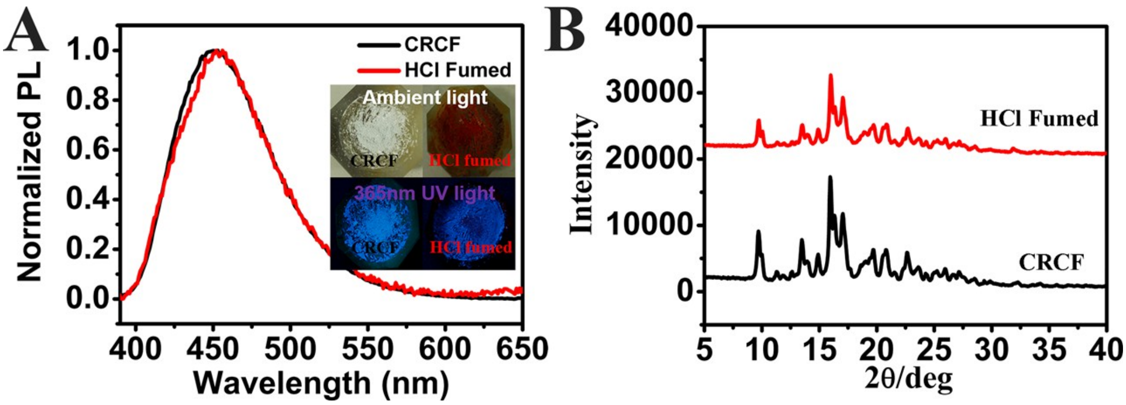


Figure S13 (A) PL spectra and corresponding images, and (B) PXRD patterns of CRCF SPTPE before and after HCl fuming.

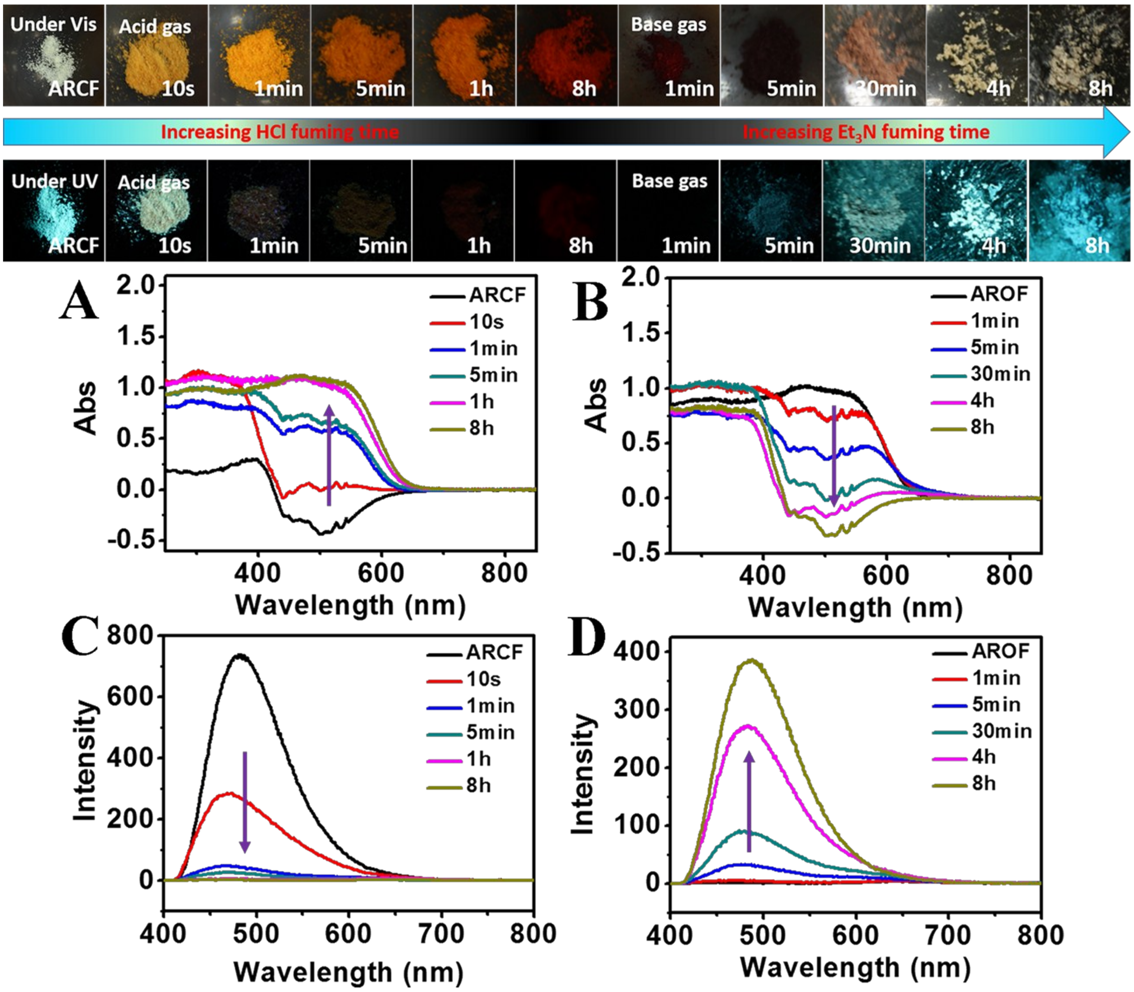
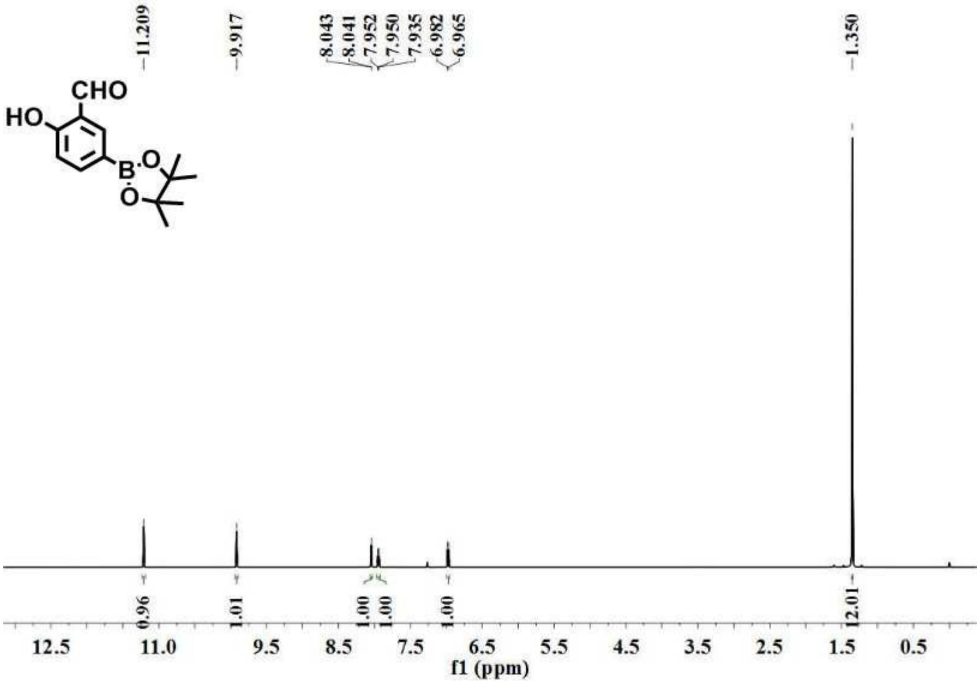
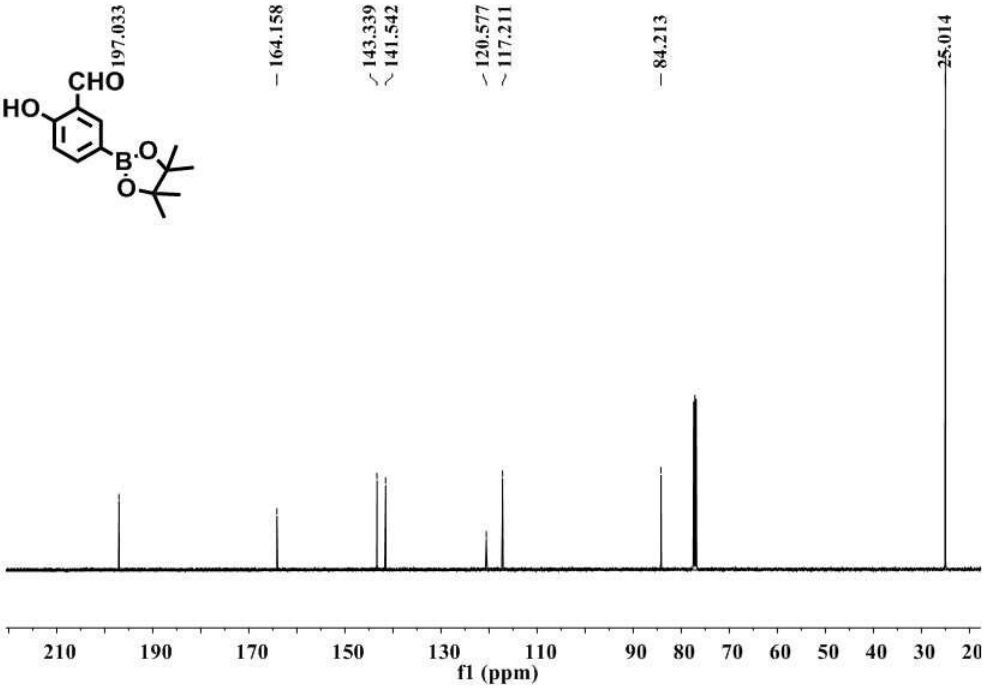


Figure S14 (A, B) Time dependent UV-vis absorption and (C, D) corresponding PL spectra of ARCF SPTPE with HCl fuming and AROF SPTPE with triethylamine fuming, respectively. The upper rows are real object images of the acid/base treatment process under visible light and UV light.

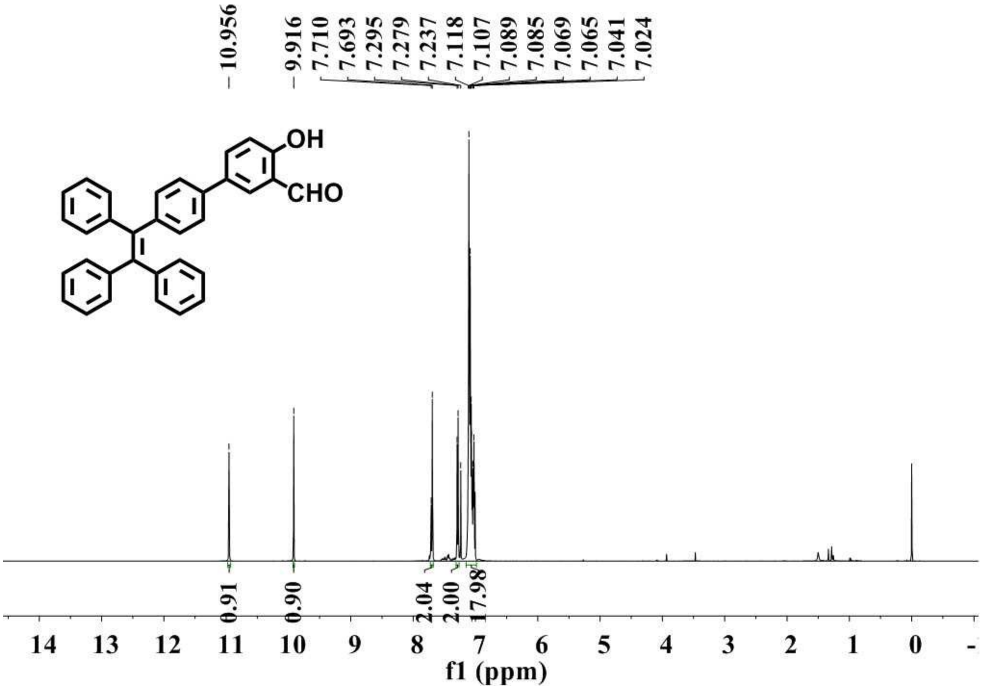
^{1}H NMR and ^{13}C NMR spectra of SPTPE and corresponding pre-products.



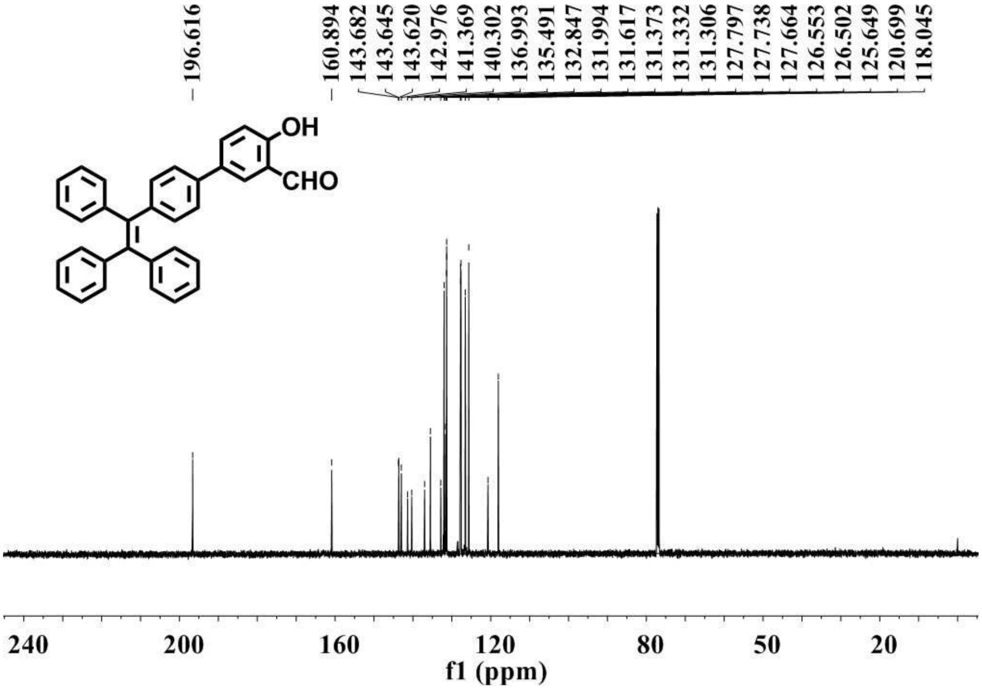
^{1}H NMR spectrum of 2-hydroxy-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzaldehyde in $CDCl_3$



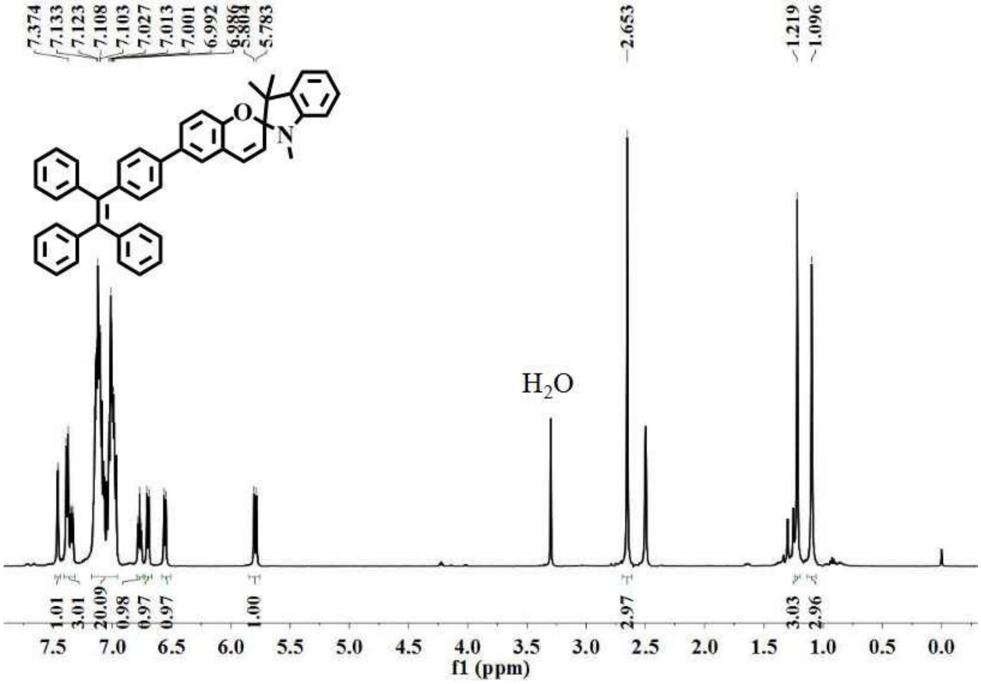
^{13}C NMR spectrum of 2-hydroxy-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzaldehyde in $CDCl_3$



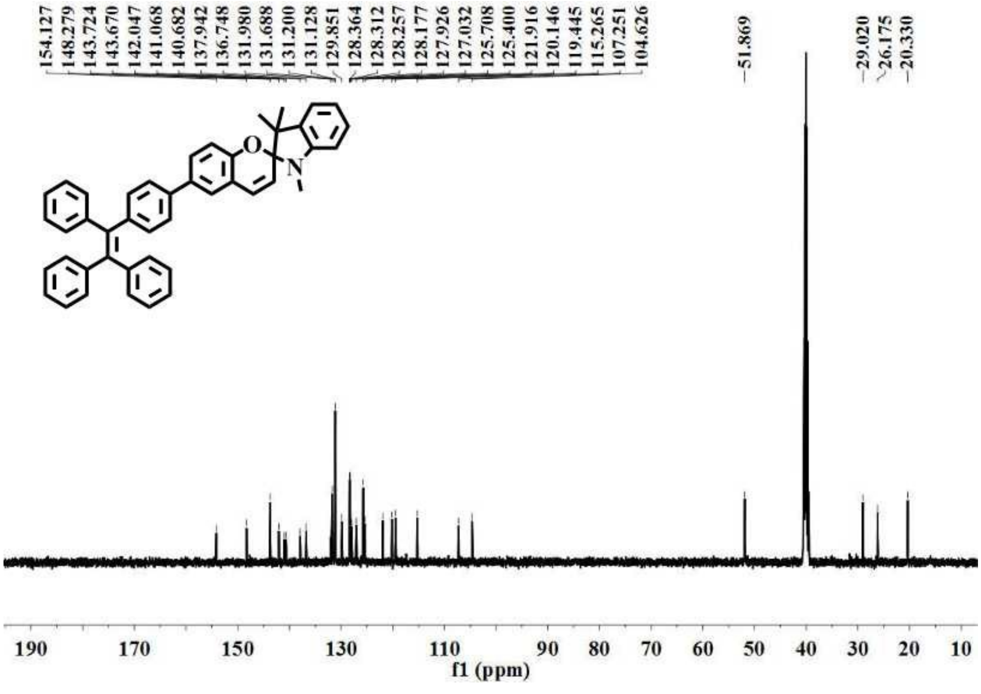
¹H NMR spectrum of 4-hydroxy-4'-(1,2,2-triphenylvinyl)-[1,1'-biphenyl]-3-carbaldehyde in $CDCl_3$



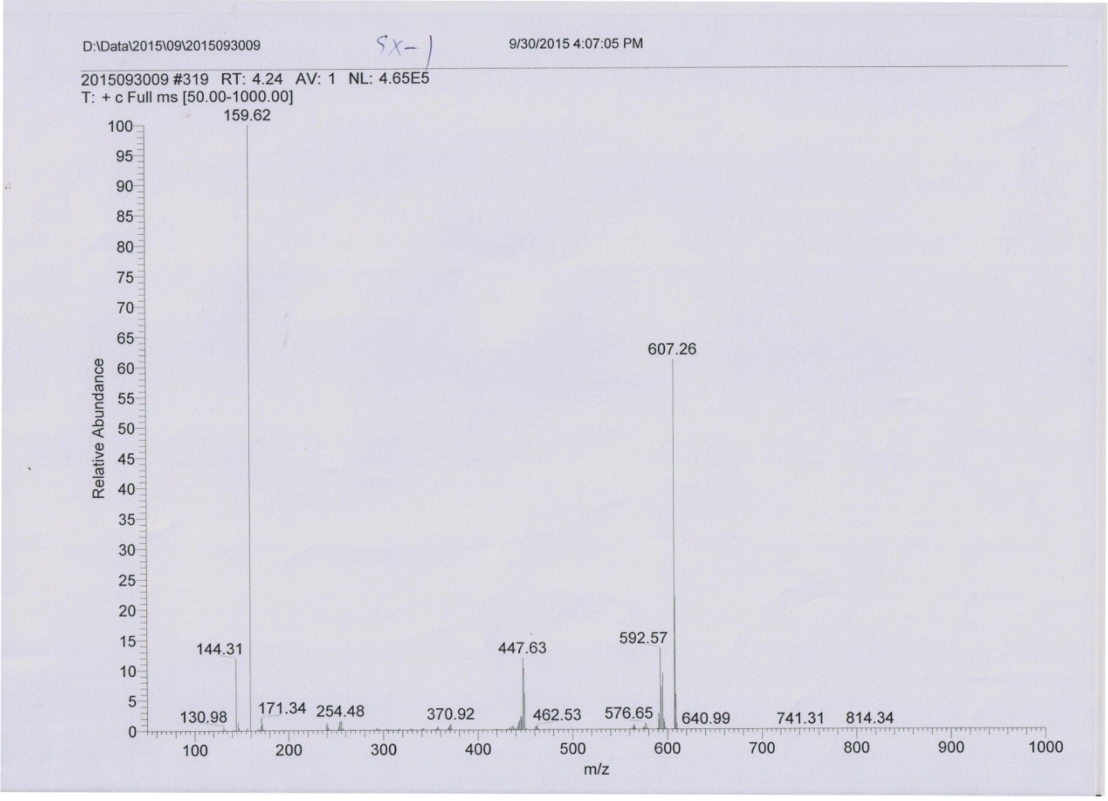
¹³C NMR spectrum of 4-hydroxy-4'-(1,2,2-triphenylvinyl)-[1,1'-biphenyl]-3-carbaldehyde in $CDCl_3$



^{1}H NMR spectrum of SPTPE in DMSO-d$_6$



^{13}C NMR spectrum of SPTPE in DMSO-d$_6$



MS spectrum of SPTPE

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Reference:

S1. Guoxing Liu, Di Wu, Jinhua Liang, Xie Han, Sheng Hua Liu and Jun Yin, Org. Biomol.Chem., 2015, 13, 4090.