Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information

Non-invasive fluorescence switch in polymer films based on spiropyran-photoacid modified TPE

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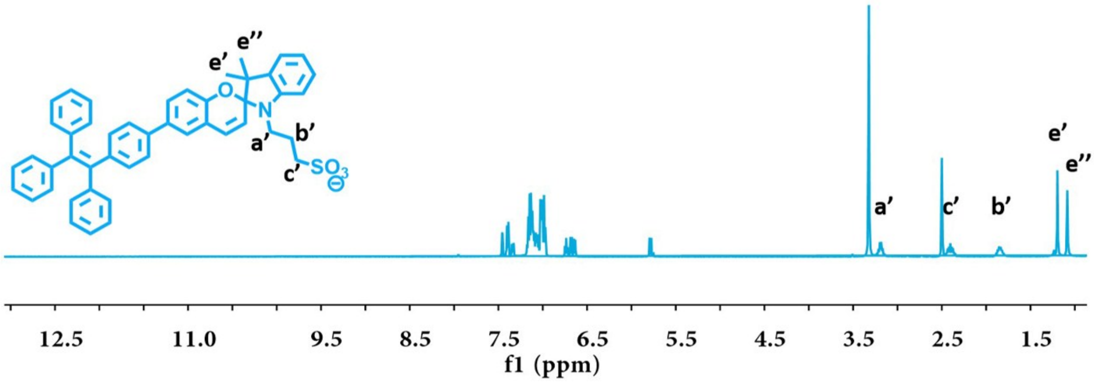


Figure S1. ^{1}H NMR spectrum of RCF SPPATPE in DMSO-d6. After treated with sufficient base, most of the proton signals especially the aliphatic proton peaks a, b and c are shifted to the high field as indicated in ^{1}H-NMR spectrum. It is clearly shown that peak e from the indole part is split into two groups, due to the breakage of the symmetry of ROF structure. At the same time, the disappearance of the characteristic peak d of ROF molecule also indicates the formation of the RCF molecule.

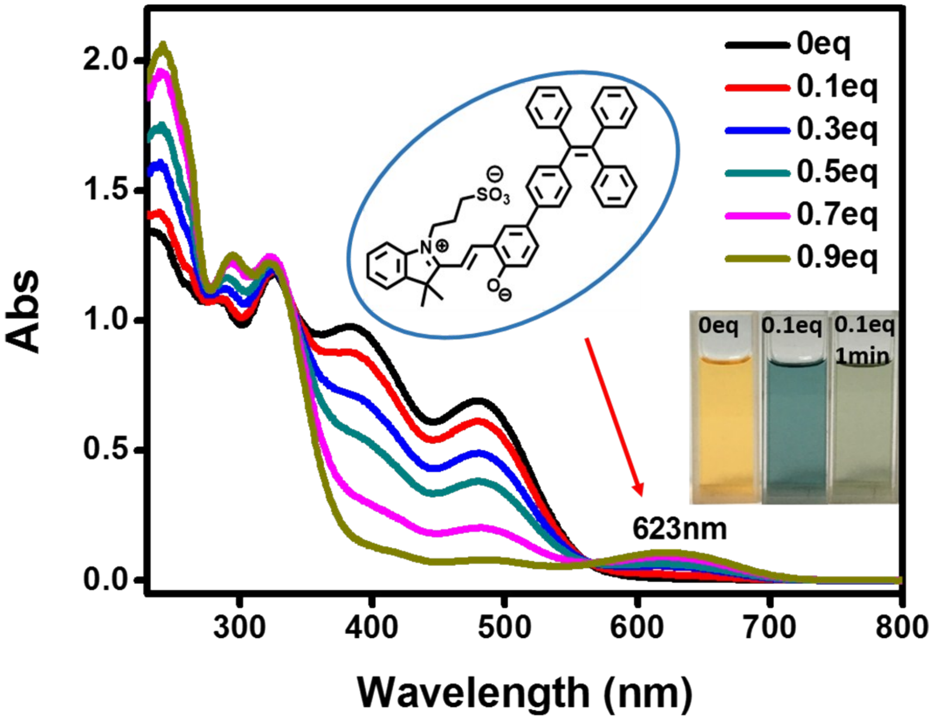


Figure S2. UV-Vis absorption spectra of SPPATPE in ethanol solution (5×10^{-5} M) right after addition of different equivalents of NaOH. Inset: images of SPPATPE solution without (left), with addition of 0.1eq NaOH immediately (middle) and equilibrium for 1 min under ambient light (right).

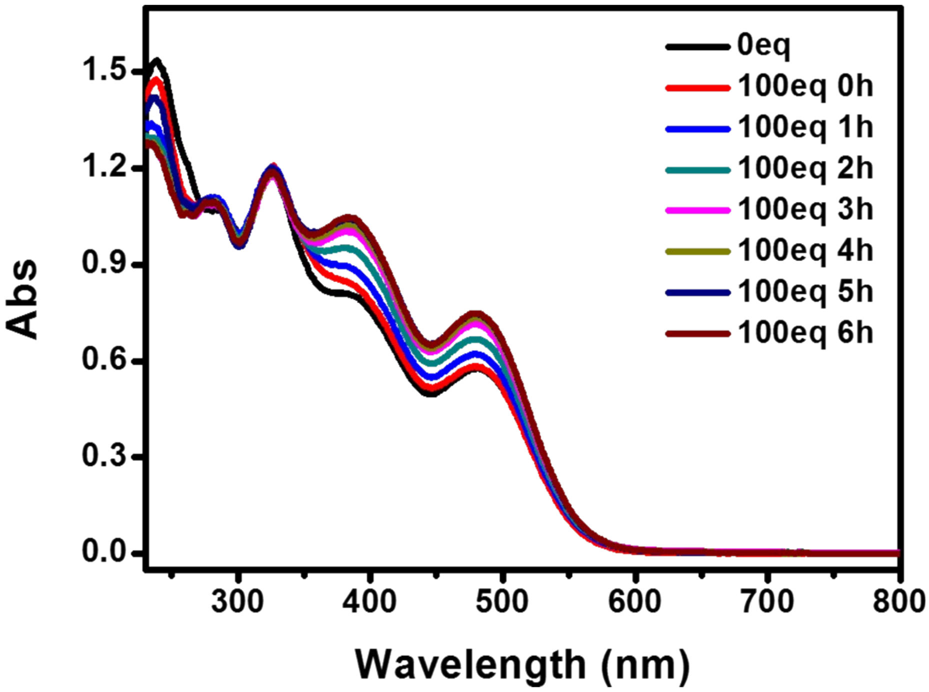


Figure S3. UV-Vis absorption spectra of SPPATPE in ethanol solution (5×10^{-5} M) with addition of 100 equivalent of HCl and kept for different time.

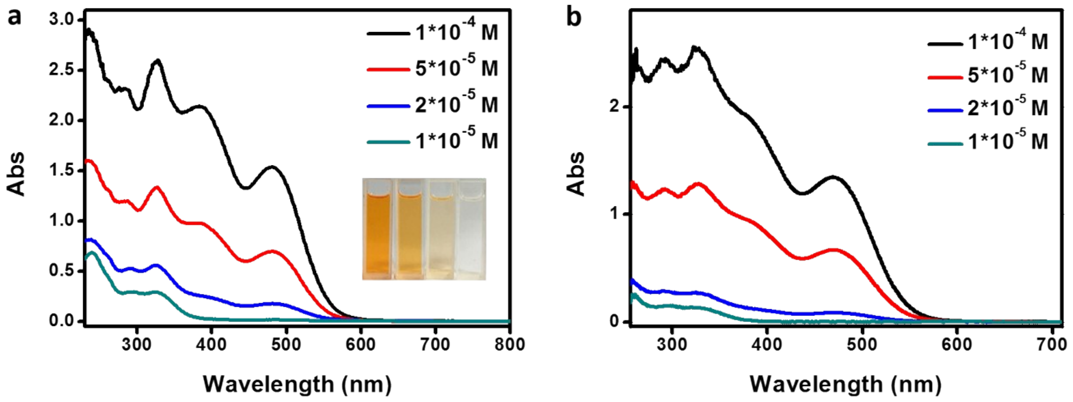


Figure S4. UV-Vis absorption spectra of SPPATPE in ethanol (a) and DMSO (b) solution at different concentrations.

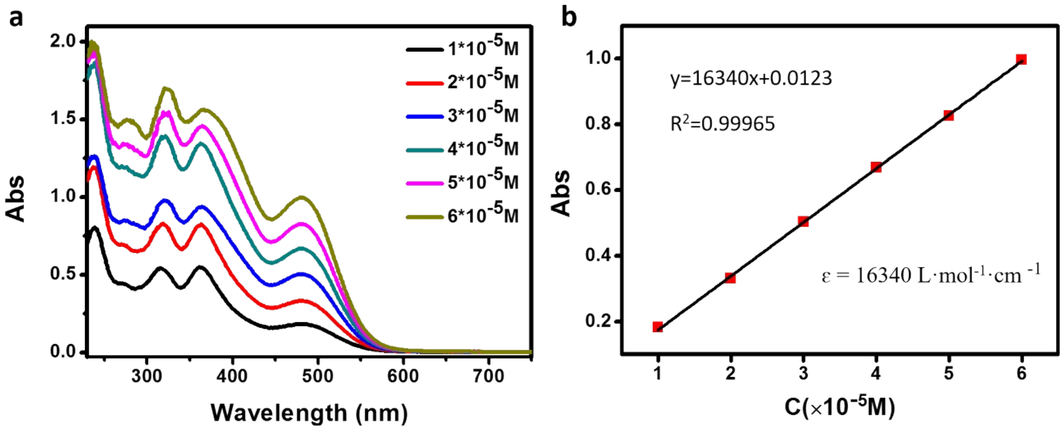
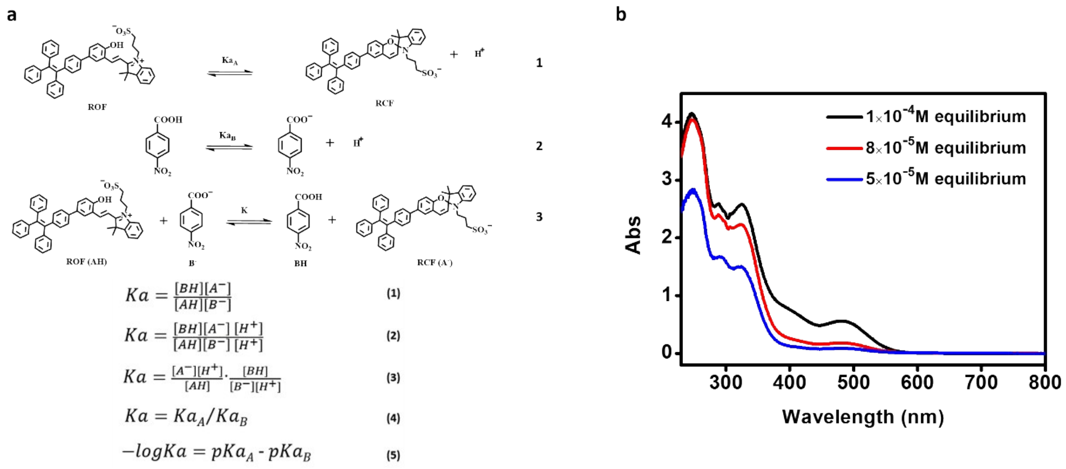


Figure S5. Calculation of the molar absorptivity of SPPATPE in ethanol solutions. Different concentrations of SPPATPE ethanol solutions in presence of 0.05 M HCl (to make sure all the SPPATPE is in the open form) were prepared and their spectra were measured after the solutions were equilibrated for 12 hours (Fig. S5a). According to the equation A=εbc, the molar absorptivity can be obtained and the value is 16340 L/mol·cm (Fig. S5b).



$$Ka = \frac{[BH][A^-]}{[AH][B^-]} \qquad (1)$$

$$Ka = \frac{[BH][A^-]\,[H^+]}{[AH][B^-]\,[H^+]} \qquad (2)$$

$$Ka = \frac{[A^-][H^+]}{[AH]} \cdot \frac{[BH]}{[B^-][H^+]} \qquad (3)$$

$$Ka = Ka_A / Ka_B \qquad (4)$$

$$-logKa = pKa_A \text{ - } pKa_B \qquad (5)$$

Figure S6. Calculation of equilibrium constants: because the pH value cannot detected directly in ethanol solutions, sodium paranitrobenzoate was added to the solution as reference. The reaction formula and equations are as Fig. S6a. Therein, ROF SPPATPE was denoted as AH, while paranitrobenzoate was denoted as B^-. AH solutions with different concentrations (1×10^{-4} M, 8×10^{-5} M, 5×10^{-5} M) were prepared and these concentrations were denoted as [AH]i. Then AH and sodium paranitrobenzoate were mixed at a molar ratio of 1:1 (200uL, 160uL and 100uL sodium paranitrobenzoate stock solution were added into 10 mL of the above solutions respectively, the concentration of sodium paranitrobenzoate stock solution in ethanol was 5×10^{-3} M), after the reaction reached to equilibrium, the concentrations of AH which was denoted as [AH]e were obtained based on the absorption spectra with the equation of A=εbc, and the concentrations of BH ([BH]e) and A^- ($[A^-]$e) are the difference between initial concentration and equilibrium concentration ([AH]i-[AH]e). The absorption spectra of SPAPTPE in ethanol at different concentrations after sodium paranitrobenzoate addition were given in Fig. S6b. Therefore, K could be obtained according to equation (1). As pKa_B of p-nitrobenzoic acid in ethanol is known (pKa_B=8.9; Ref: Analytical Chemistry, 1979, 51, 133-140.), Ka_A as well pKa_A of SPPATPE in ethanol solutions could be obtained according to equation (4) and (5). Based on the above testing and calculation, equilibrium constants of SPPATPE in ethanol at different concentrations were obtained, the values are 4.57×10^{-9}, 4.79×10^{-8} and 8.51×10^{-8} when the initial concentrations of SPAPTPE were 1×10^{-4} M, 8×10^{-5} M and 5×10^{-5} M, respectively.

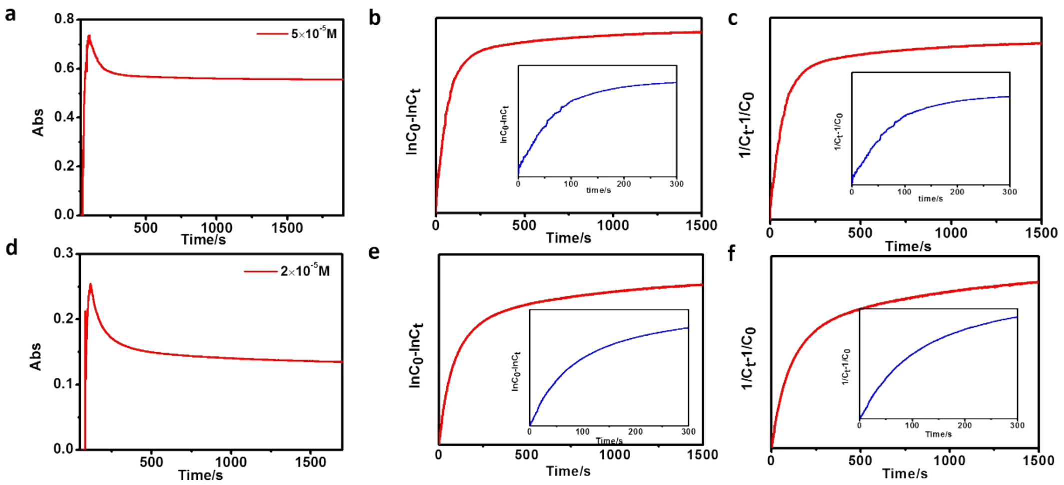


Figure S7. Kinetic data of SPPATPE in ethanol solution at different concentrations (a,b,c: 5×10^{-5} M; d,e,f: 2×10^{-5} M). Inside: enlarged image at initial period. Results indicate that they neither follow first-order kinetics nor second order kinetics.

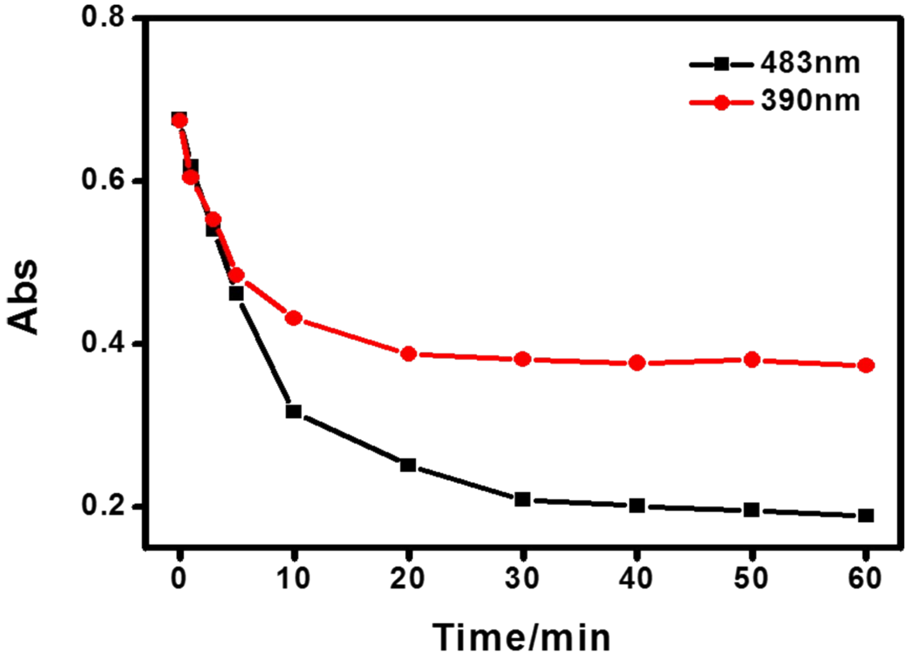


Figure S8. Absorbance decay at 483 nm of the SPPATPE in ethanol solution (5 × 10^{-5} M) with 390 nm and 483 nm light irradiation respectively.

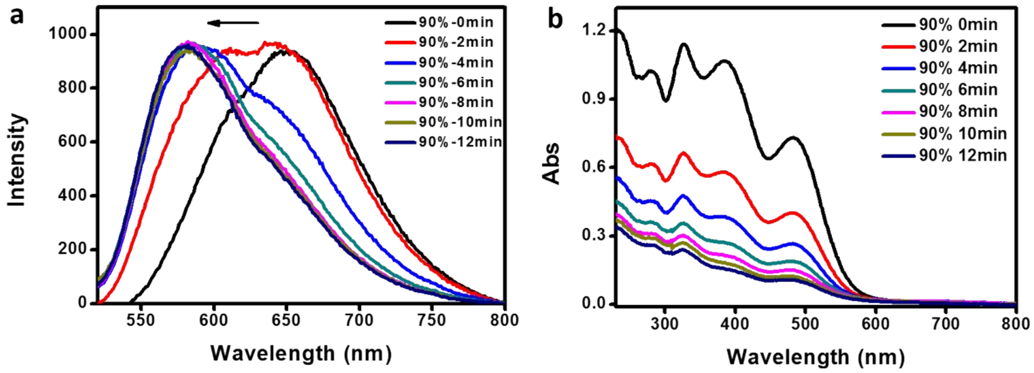


Figure S9. (a) PL and (b) UV-Vis absorption spectra of ROF SPPATPE in 90% ethanol/hexane (v/v) mixtures (5×10^{-5} M) for different time.

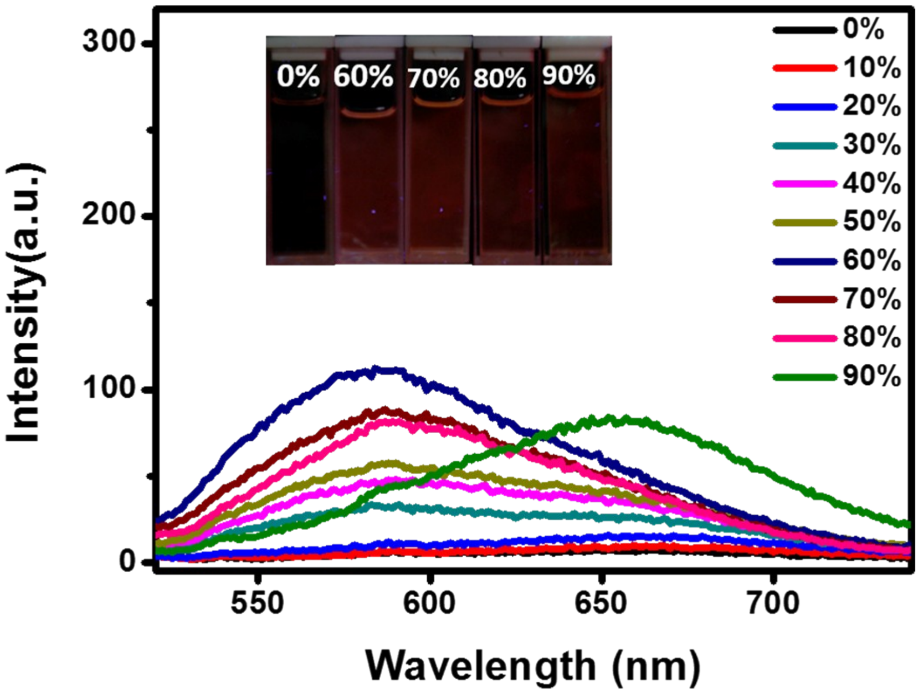


Figure S10. PL spectra of ROF SPPATPE in different hexane/DCM (v/v) mixtures (5×10^{-5} M). Insets: Corresponding fluorescence images.

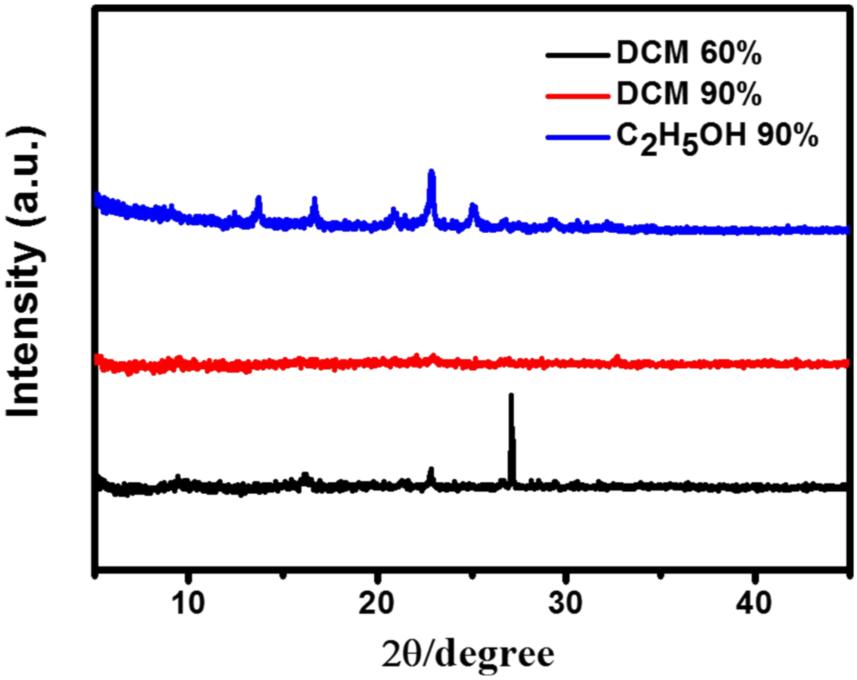


Figure S11. PXRD patterns of ROF SPPATPE precipitated from DCM solution and ethanol (v/v) solution. The volume fractions of the poor solvent of hexane were 60% and 90%, respectively in DCM, and 90% in ethanol.

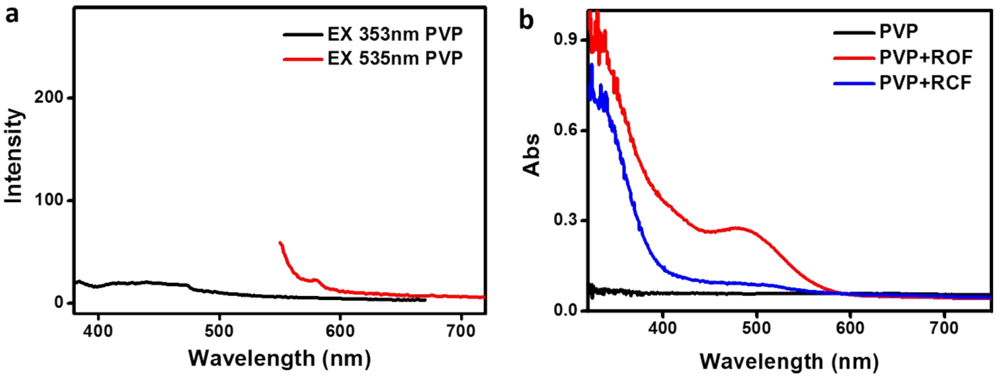


Figure S12. (a) PL spectra of pure PVP film under 353 nm and 535 nm light excitation; (b) UV-Vis absorption spectra of pure PVP film and PVP film doped with ROF and RCF SPPATPE.

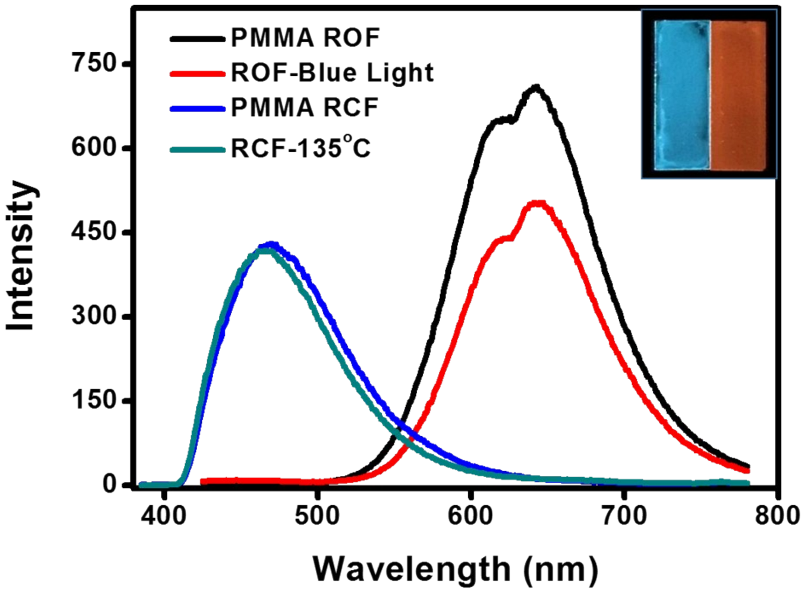


Figure S13. PL spectra of ROF SPPATPE doped PMMA film before and after blue light irradiations, and RCF SPPATPE doped PMMA film before and after 135 ℃ treatment. Inset: fluorescence images of RCF (left) and ROF (right) SPPATPE doped PMMA films.

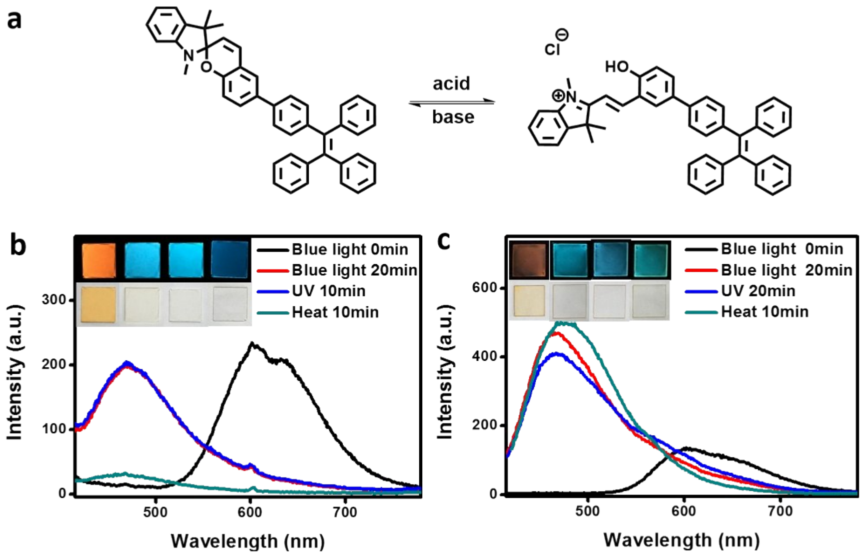


Figure S14. (a) Molecular structure of SPTPE and its acid/base triggered isomerization; (b) PL spectra of ROF SPTPE/PMMA film and (c) ROF SPTPE/PVP film before and after treated with blue light (449 nm), UV light (254 nm) and 135 °C heating, respectively. Inset: corresponding images of the films under 365 nm UV light (up) and ambient light (down).

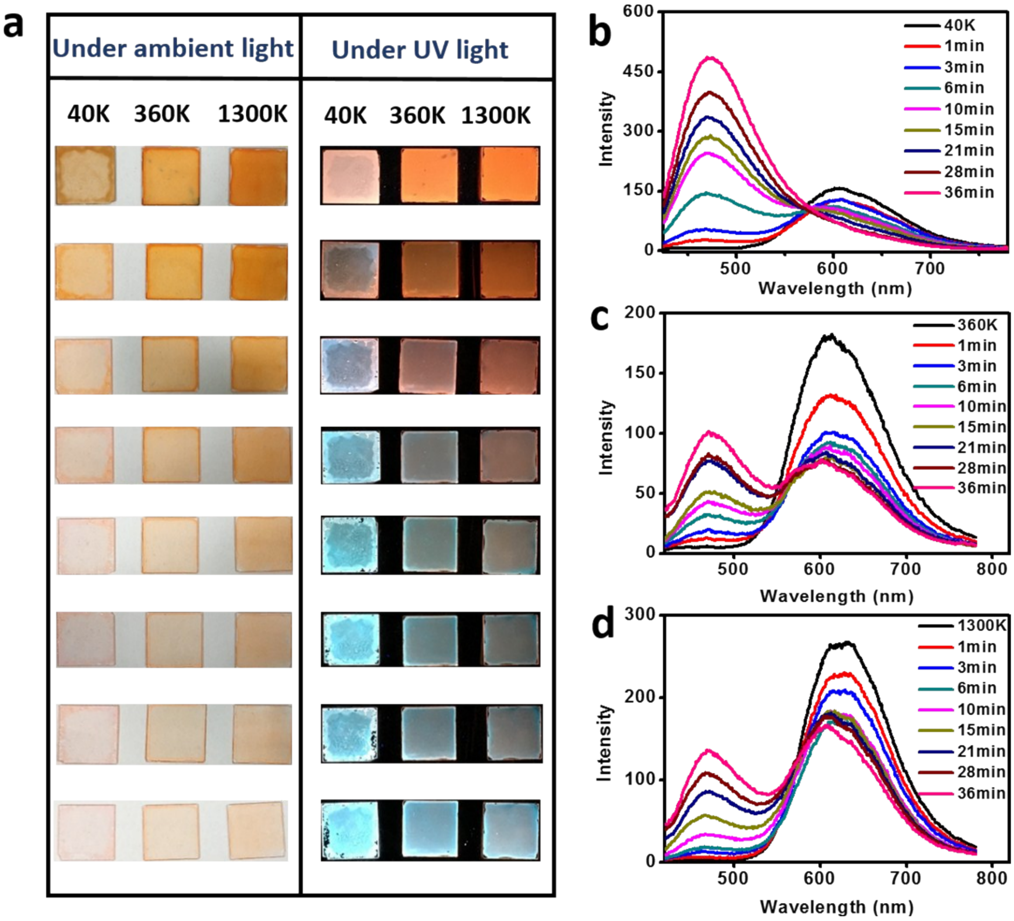


Figure S15. (a) Photos of SPPATPE/PVP films with different molecular weight after irradiated with blue light for different times, (left) under ambient light and (right) under 365 nm UV light; and (b-d) their corresponding PL spectra: (b) SPPATPE/PVP (40K) film (c) SPPATPE/PVP (360K) film and (d) SPPATPE/PVP (1300K) film.

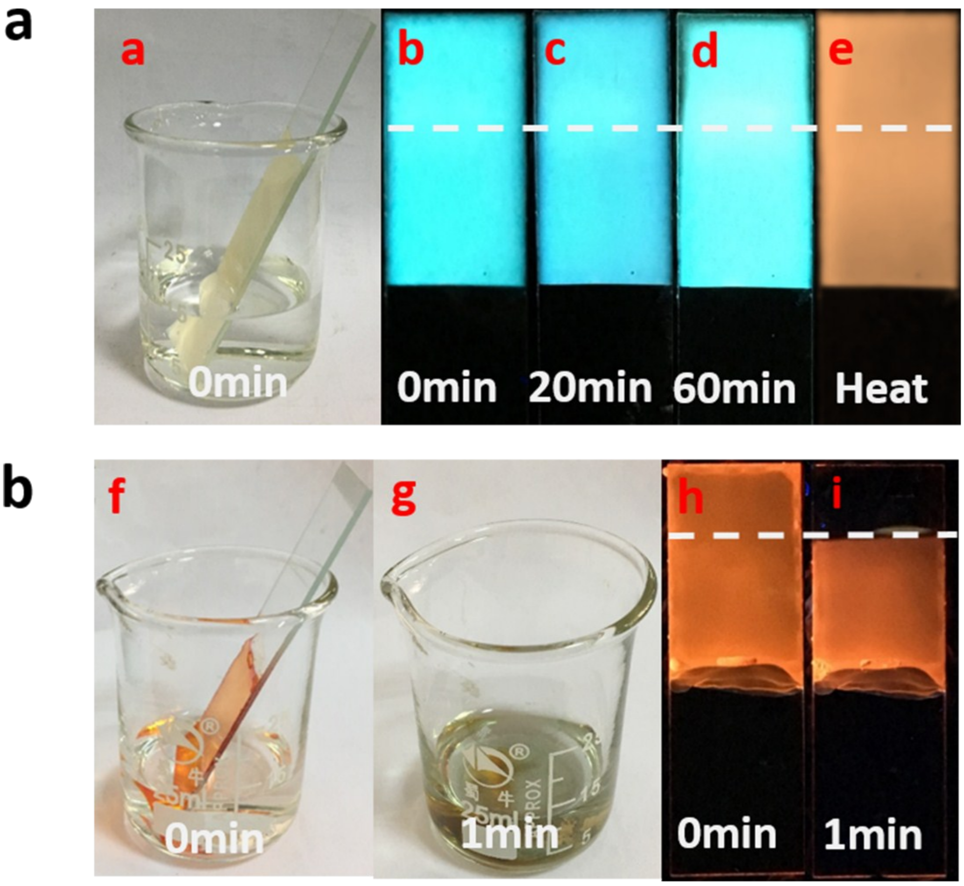


Figure S16. Water proof property test of (a) SPPATPE/PVP/PDMS films and (b) SPPATPE/PVP films. Above the white dotted line is the wetted part. SPPATPE/PVP film dissolved after immersion in water for 1min.

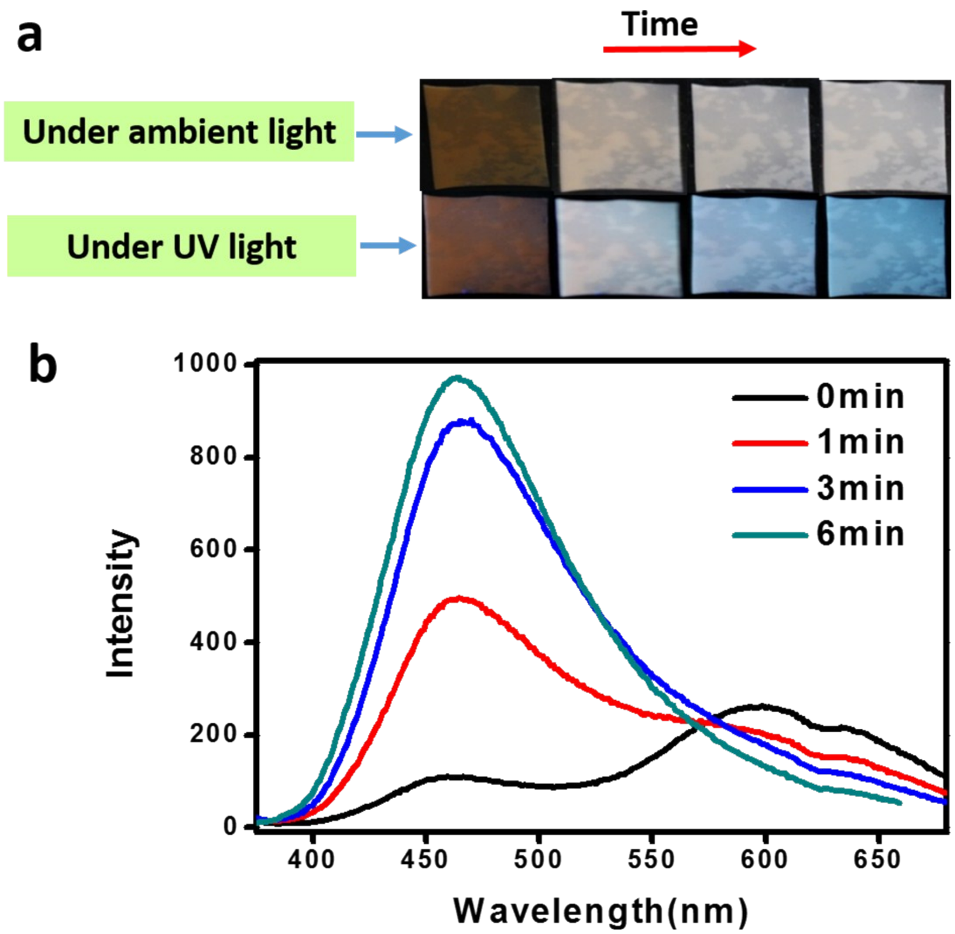


Figure S17. (a) Images of SPPATPE/PVP/PDMS film (0.2 % weight content) with blue light irradiation for different time, (up) under ambient light and (down) under UV light (365 nm); and (b) their corresponding PL spectra.

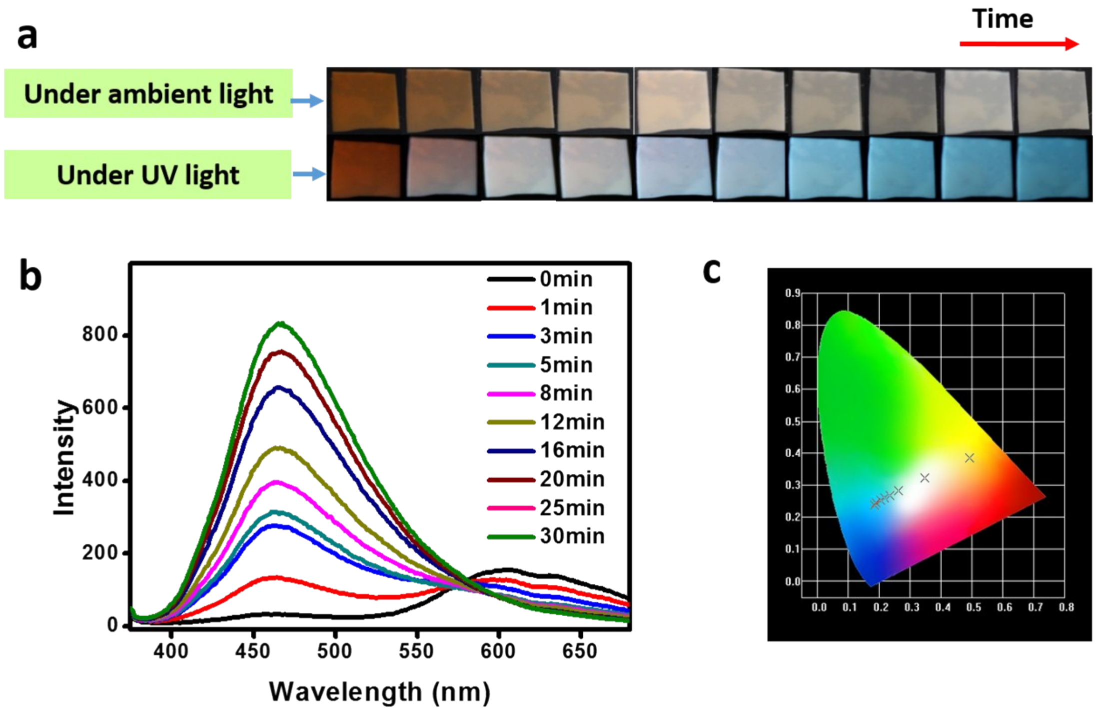


Figure S18. (a) Images of SPPATPE/PVP/PDMS thin film (0.3 % weight content) with blue light irradiation for different time, (up) under ambient light and (down) under UV light (365 nm); and their corresponding (b) PL spectra and (c) CIE graph.

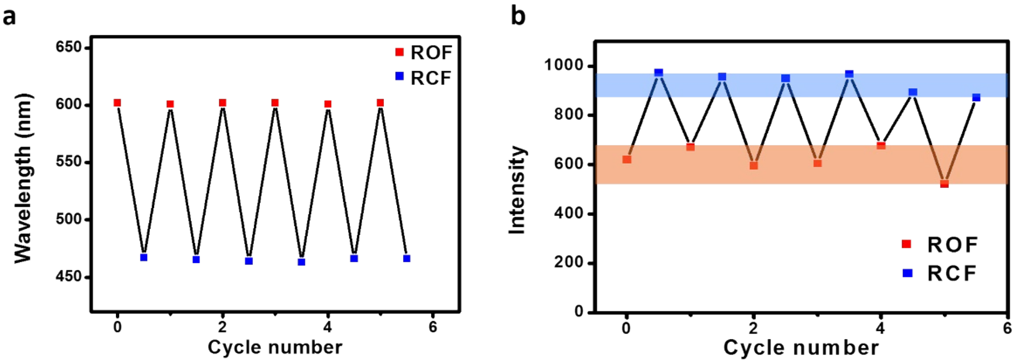


Figure S19. (a) Wavelength and (b) intensity contrast profiles of the SPPATPE/PVP/PDMS hybrid thin film (0.22 % weight content) with switching cycles.

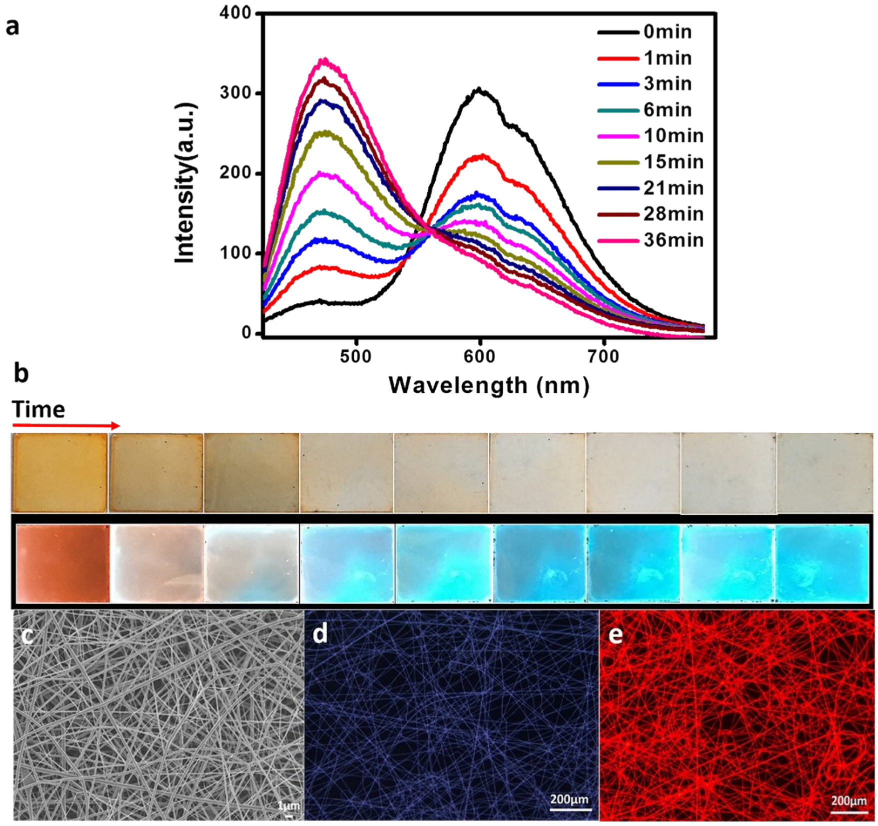


Figure S20. (A) PL spectra of SPPATPE/PVP/PDMS nanofibers irradiated with blue light for different times; and (B) their images under ambient light (up) and under 365 nm UV light (down); (C) SEM image of the nanofibers; and their fluorescence microscope images (D) before and (E) after blue light irradiation.

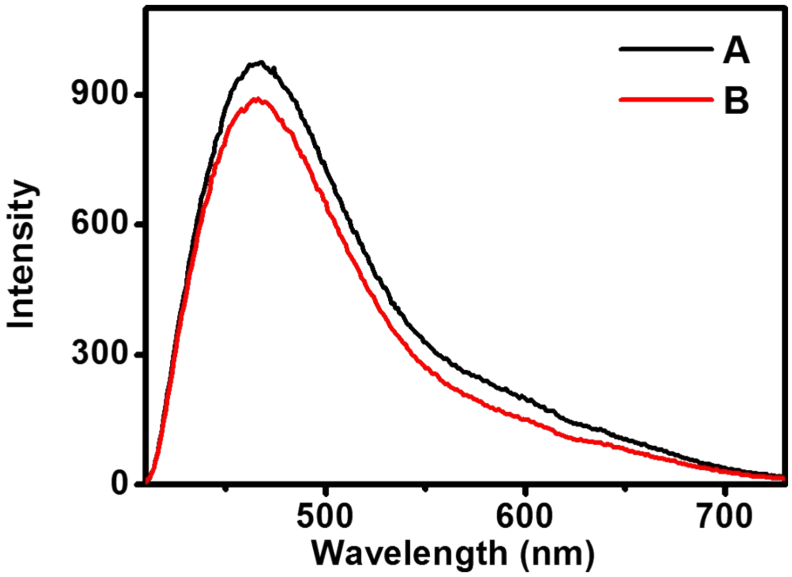


Figure S21. PL spectra of SPPATPE/PVP/PDMS film irradiated with a solar simulator for 30 minutes (A), then stored in dark for 20 days (B).

Calculation of photo-isomerization quantum yields of SPPATPE in ethanol solution for the first 1 min upon 483 nm and 390 nm light irradiation: The photon flux was about 2.26×10^{-2} umol cm^{-2} s^{-1}, which was calculated from optical power density and the energy of photon. The amount of the molecules converted from ROF to RCF were calculated from the difference of the absorption value between 0 min and 1 min. The amount of the photons which were absorbed by the molecules were the difference between the total number of incident photons and the number which transmitted the solution. The total number of incident photons is the photon flux × irradiation area × irradiation time. The number of the photons which transmitted the solution were obtained from the absorption spectra before and after irradiation: transmittance was obtained based on the following equation: $-\log T = A_{average}$. The number of the photons which transmitted the solution is photon flux × irradiation area × T × irradiation time. The transmission varies with irradiation time and it is taken as an average value of the T before and after irradiation. Using the same method, the photon flux was about 6.84×10^{-3} umol cm^{-2} s^{-1} and the quantum yield was calculated to be 0.013 when light resource was 390 nm.