Electronic Supplementary Information

Mechanical stimuli-induced multiple photophysical responsive AIEgens with high contrast property

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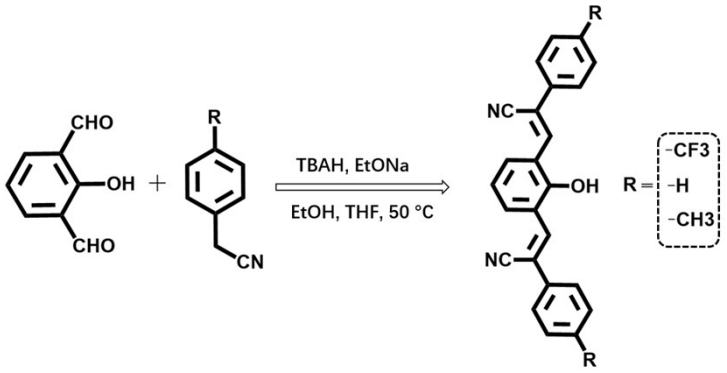
1. General Experimental Details

General. ^{1}H NMR and ^{13}C NMR spectra were measured on a Bruker 400L spectrometer. The UV-vis absorption spectra were recorded on a Cary 5000 spectrophotometer. The emission spectra were recorded on FLS 1000 (Edinburgh Instruments). Transmission electron microscopy (TEM) was performed on a Jeol JEM 2100 with an accelerating voltage of 200 kV. High-resolution mass spectrometry data was measured on a TripleTOF 4600 and high-resolution time-of-flight mass spectrometer. Fourier transform infrared spectroscopy (FT-IR) was performed on Bruker VERTEX 70. Dynamic Light Scattering (DLS) experiments were carried out with Nano-Zeta Potential Analyzer ZS-90. Powder X-Ray diffraction (PXRD) patterns were obtained by using CuKα radiation (Bruker, D8-ADVANCE).

Materials. 2-Hydroxyisophthalaldehyde**,** 2-Methoxyisophthaldehyde, 4-(Trifluoromethyl)phenylacetonitrile, Benzyl cyanide, 4-Methylbenzyl cyanide, Sodium Ethoxide (EtONa) were commercially available from Beijing Hwrkchemical. Tetrabutylammonium Hydroxide (TBAOH) (25% w/w in methanol), N,N-Dimethylformamide (DMF), Acetic Acid, Petroleum ether, Ethanol, Tetrahydrofuran (THF), were commercially available from Adamas. All reagents were of analytical or reagent grades and used without further purification. Deionized water (18.2 MΩ·cm) was obtained from a F'DEER water purification system.

Synthetic Details



Scheme S1 Synthetic route for compound in the work

Synthesis of compound $CNCF_3DSB$-OH: 2-Hydroxyisophthalaldehyde (0.15 g, 1 mmol, 1.00 eq.) and 4-(Trifluoromethyl)phenylacetonitrile (0.37 g, 2 mmol, 2.0 eq.) were added into a round bottom flask capped with a septum under nitrogen atmosphere. Dry ethanol (20 mL) and THF (2 mL) was injected via a syringe and the mixture was stirred at 50 °C for 1 h. Tetrabutylammonium Hydroxide (1 mL), Sodium Ethoxide (0.34 g, 5 mmol, 5.00 eq.) in 5ml ethanol was added into the flask and stirred at 50 °C for 4 h. After cooling to room temperature, acetic acid in ethanol was added to adjust the solution to weak acidity. After collecting the solid by filtration, it was rinsed with ethanol (10 mL), diethyl ether (20 mL), and then dried under high vacuum. The crude product was purified by recrystallization in ethanol to afford white compound **$CNCF_3DSB$-OH** (Yield, 46.8%). ^{1}H NMR (400 MHz, DMSO, 298 K): δ = 9.33 (s, 1H), 8.08-8.10 (d, 4H), 8.06-8.07 (d, 2H), 7.98-9.00 (d, 4H), 7.52 (s, 2H), 6.68-6.70 (t, 1H).^{13}C NMR (100 MHz, DMSO, 298 K): δ = 103.75, 116.08, 118.11, 120.03, 125.69, 127.12,

129.05, 131.20, 134.54, 141.76, 149.35, 156.33. MS(TOF-MS, m/z): MS(ESI^+, m/z):483$[M-H]^-$, 519$[M+Cl]^-$, 529$[M+HCOO]^-$.

Synthesis of compound CNDSB-OH: The synthesis of CNDSB-OH was achieved according to the protocol of the synthesis of $CNCF_3$DSB-OH. Yellow solid was acquired in 39% yield. ^{1}H NMR (400 MHz, DMSO, 298 K): δ = 8.06-8.08 (d, 4H), 7.90 (t, 4H), 7.87-7.88 (t, 2H), 7.85-7.86 (d, 2H), 7.55 (s, 2H), 6.71-6.75 (t, 1H), 5.71 (s, 1H).^{13}C NMR (100 MHz, DMSO, 298 K): δ = 101.91, 117.99, 120.76, 123.38, 129.52, 130.02, 130.71, 131.49, 138.88, 145.82, 153.64. MS(ESI^+, m/z):347$[M-H]^-$, 383$[M+Cl]^-$, 393$[M+HCOO]^-$.

Synthesis of compound $CNCH_3$DSB-OH: The synthesis of $CNCH_3$DSB-OH was achieved according to the protocol of the synthesis of CNCF3DSB-OH. Yellow solid was acquired in 36% yield. ^{1}H NMR (400 MHz, DMSO, 298 K): 8.12-8.14 (d, 4H), 8.09 (d, 4H), 7.99-8.02 (d, 2H), 7.56 (s, 2H), 6.72-6.75 (t, 1H), 5.70 (s, 1H), 2.18 (s, 6H), ^{13}C NMR (100 MHz, DMSO, 298 K): δ = 25.36, 101.60, 117.67, 120.43, 123.15, 130.51, 134.26, 137.49, 138.61, 142.85, 145.63, 153.53. MS(ESI^+, m/z):375$[M-H]^-$, 411$[M+Cl]^-$, 421$[M+HCOO]^-$.

Synthesis of compound $CNCF_3$DSB-OCH_3: The synthesis of $CNCF_3$DSB-OCH_3 was achieved according to the protocol of the synthesis of $CNCF_3$DSB-OH. White solid was acquired in 53% yield. ^{1}H NMR (400 MHz, DMSO, 298 K): δ = 8.07-8.09 (d, 2H), 8.03-8.04 (d, 4H), 8.01-8.02 (d, 4H), 7.51 (s, 2H), 7.03-7.04 (t, 1H), 3.05 (s, 3H). ^{13}C NMR (100 MHz, DMSO, 298 K): δ = 63.21, 103.76, 116.50, 118.33, 120.02, 125.68, 127.12, 129.04, 131.19, 134.53, 141.74, 149.34, 156.94. MS(ESI^+,m/z): 499$[M+H]^+$, 521$[M+Na]^+$, 537$[M+K]^+$.

2. Additional Data

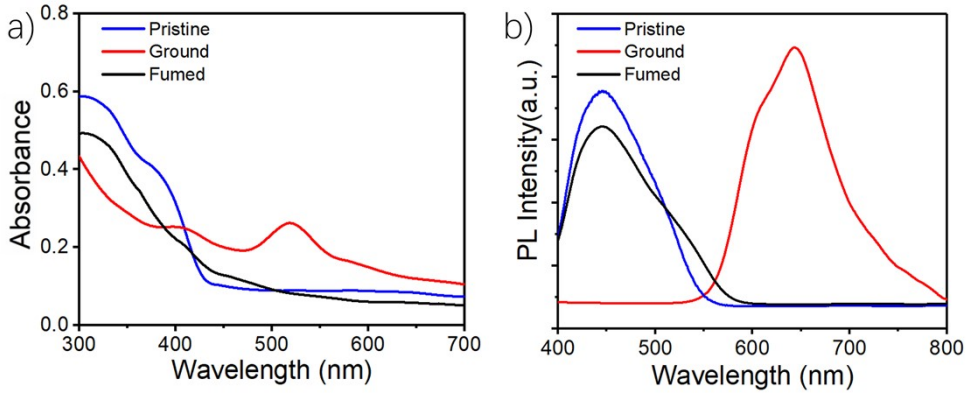


Figure S1 (a) UV-vis absorption and (b) emission spectra of $CNCF_3DSB$-OH in solid state after ground and solvent treatment using $CHCl_3$

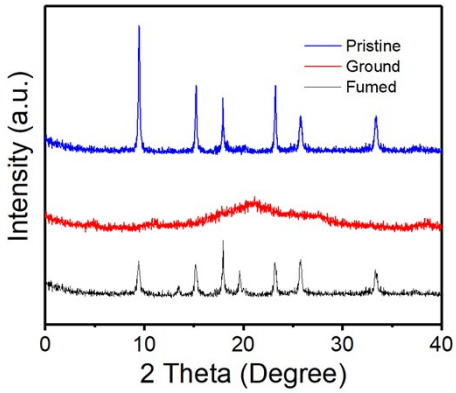


Figure S2 PXRD spectra of $CNCF_3DSB$-OH in solid state before and after ground, followed by solvent treatment using $CHCl_3$

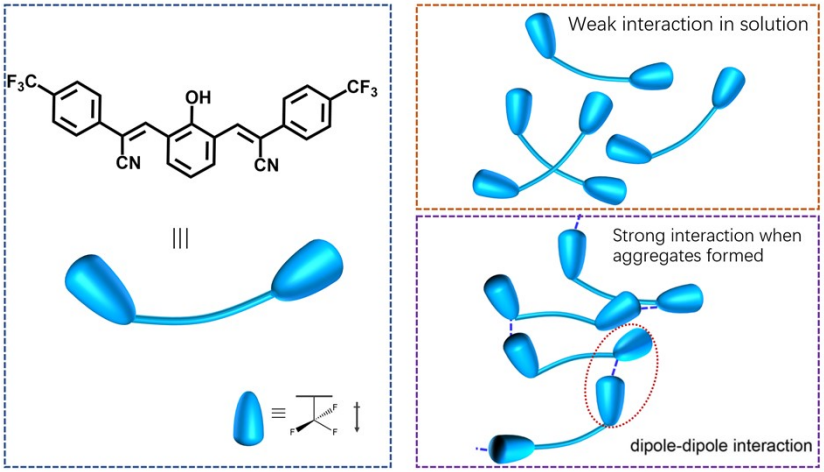


Figure S3 Schematic illustration of the dipole-dipole interaction when aggregates formed.

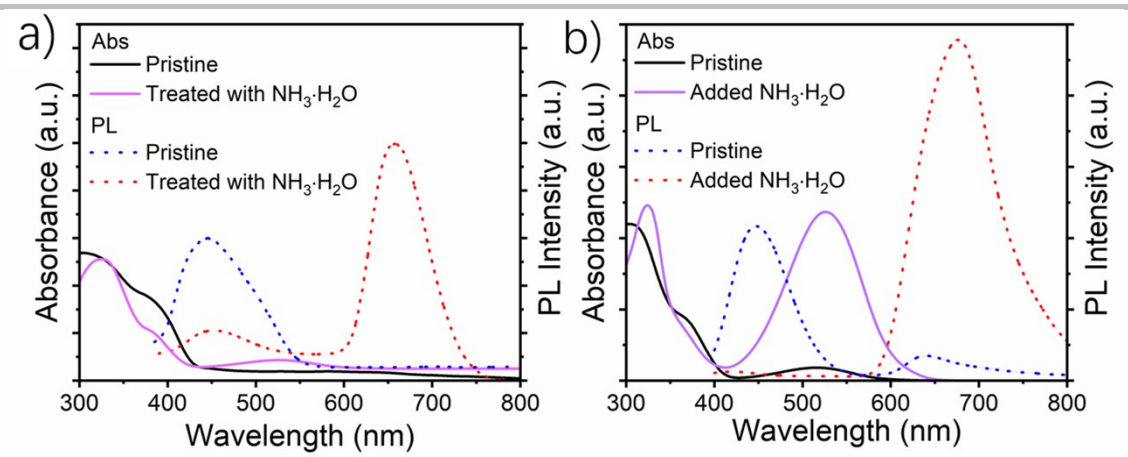


Figure S4 (a) The absorption and emission spectra of $CNCF_3DSB$-OH in solid state before and after being treated with $NH_3·H_2O$ vapor. (b) Absorption and emission spectra of $CNCF_3DSB$-OH in C_2H_5OH before and after the addition of $NH_3·H_2O$.

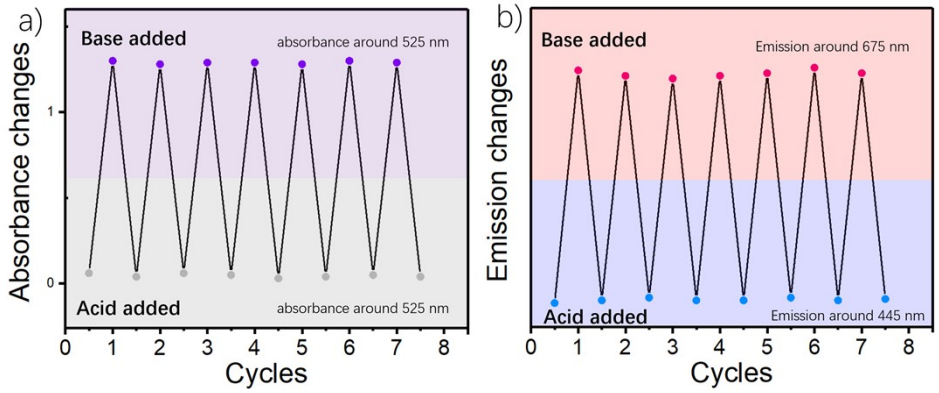


Figure S5 (a) Absorption and (b) emission stimulation cycles with addition of base/acid in in C_2H_5OH.

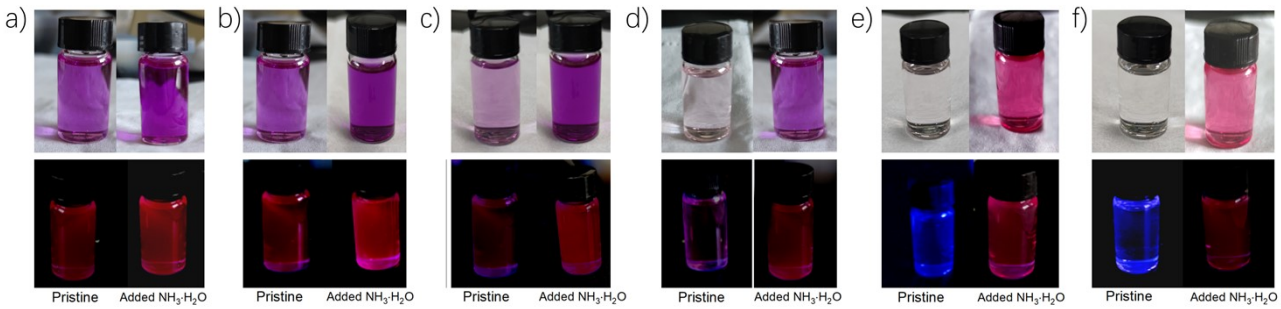


Figure S6. Images of color (top) and luminescence (bottom) in different solvents before and after added $NH_3·H_2O$. (a) DMF, (b) DMSO, (c) CH_3CN, (d) THF, (e) CH_2Cl_2, (f) Toluene

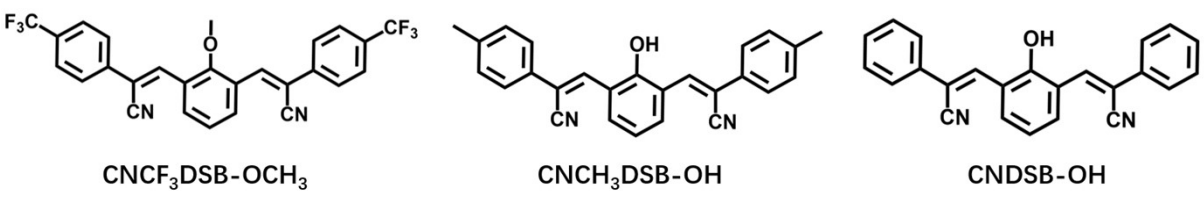


Figure S7. Illustration molecular structure of reference compounds.

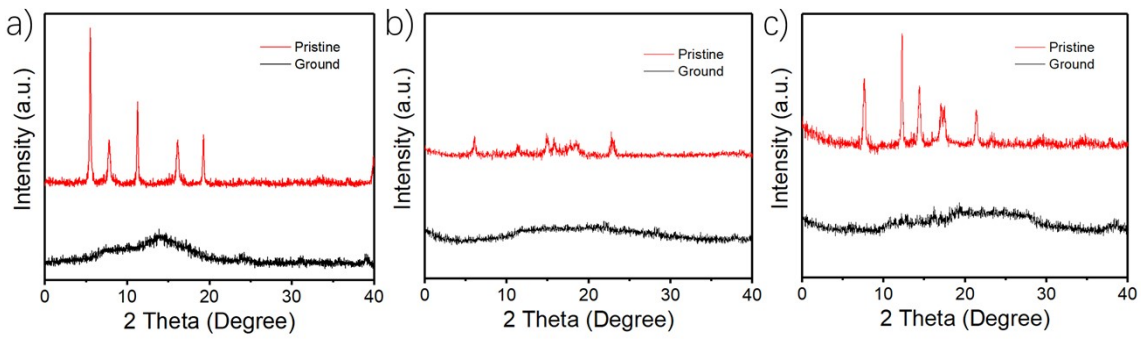


Figure S8. PXRD spectra of reference compounds before and after mechanical force. (a) $CNCF_3DSB\text{-}OCH_3$, (b) $CNCH_3DSB\text{-}OH$, (c) CNDSB-OH

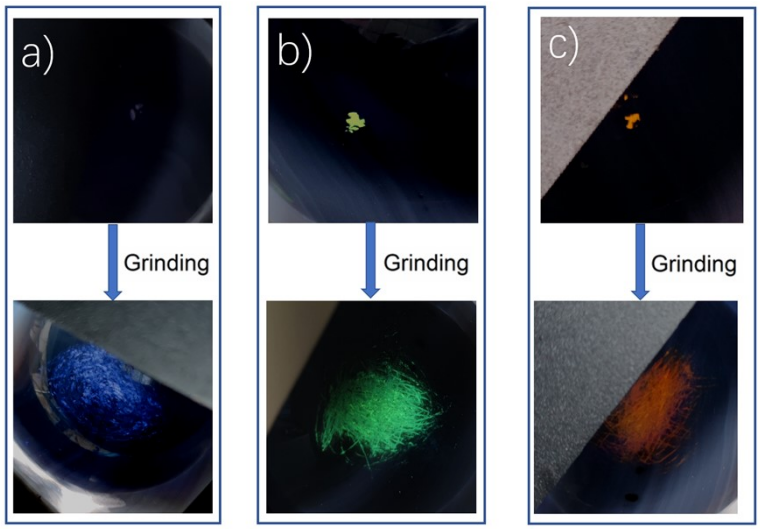


Figure S9 Images of reference compounds before and after mechanical force under 365 nm. (a) $CNCF_3DSB\text{-}OCH_3$, (b) $CNCH_3DSB\text{-}OH$, (c) CNDSB-OH

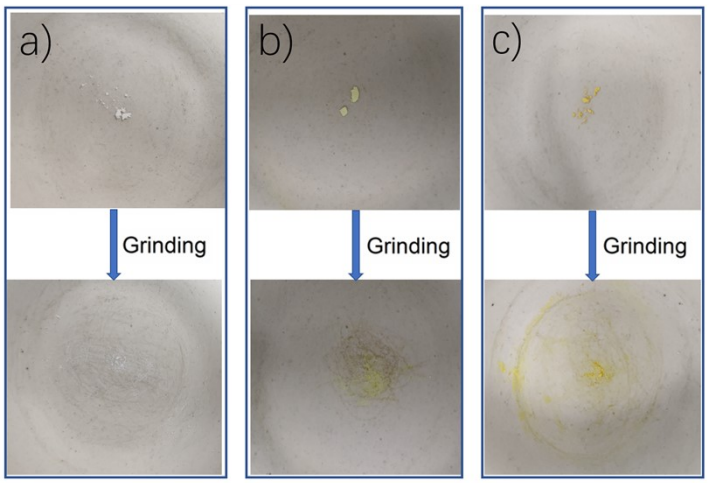


Figure S10 Images of reference compounds before and after mechanical force under daylight. (a) $CNCF_3DSB\text{-}OCH_3$, (b) $CNCH_3DSB\text{-}OH$, (c) CNDSB-OH

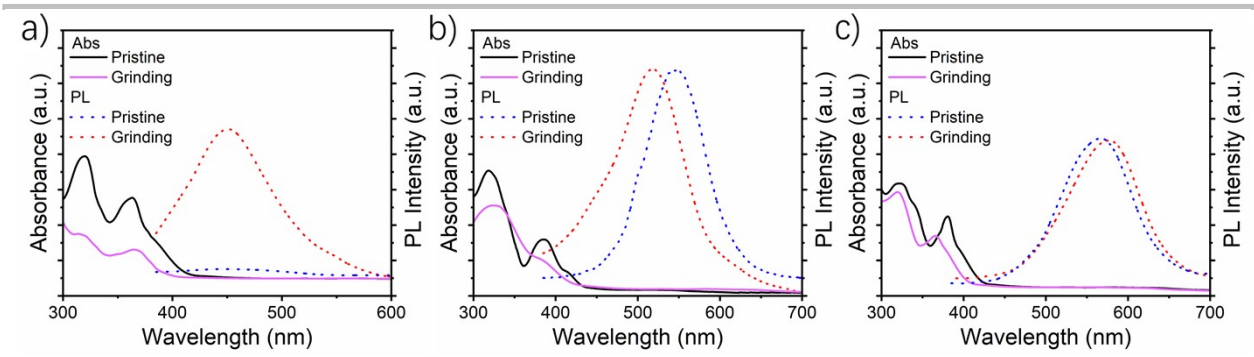


Figure S11 Absorption and emission spectra of reference compounds in solid state before and after grinding. (a) $CNCF_3DSB\text{-}OCH_3$, (b) $CNCH_3DSB\text{-}OH$, (c) CNDSB-OH

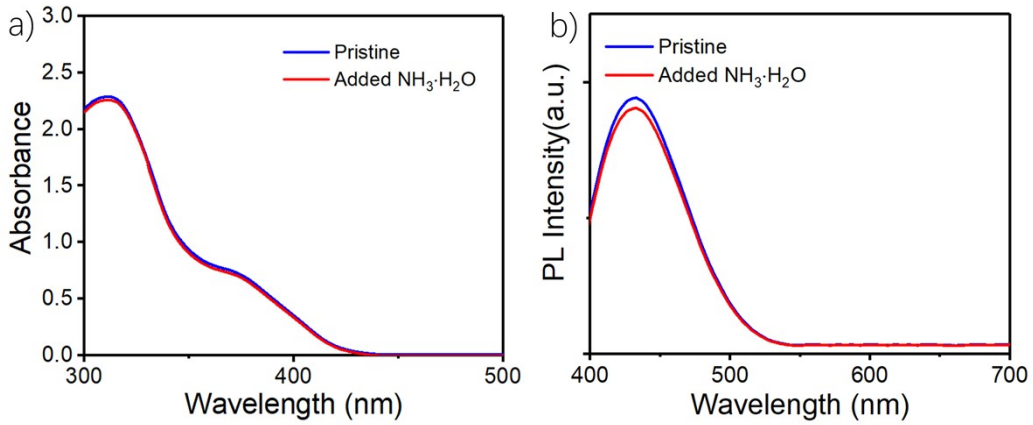


Figure S12 (a) UV-vis absorption and (b) emission spectra of $CNCF_3DSB\text{-}OCH_3$ before and after added $NH_3{\cdot}H_2O$. These measurements were performed at room temperature with the concentration of $CNCF_3DSB\text{-}OCH_3$ 1.0×10^{-4} M.

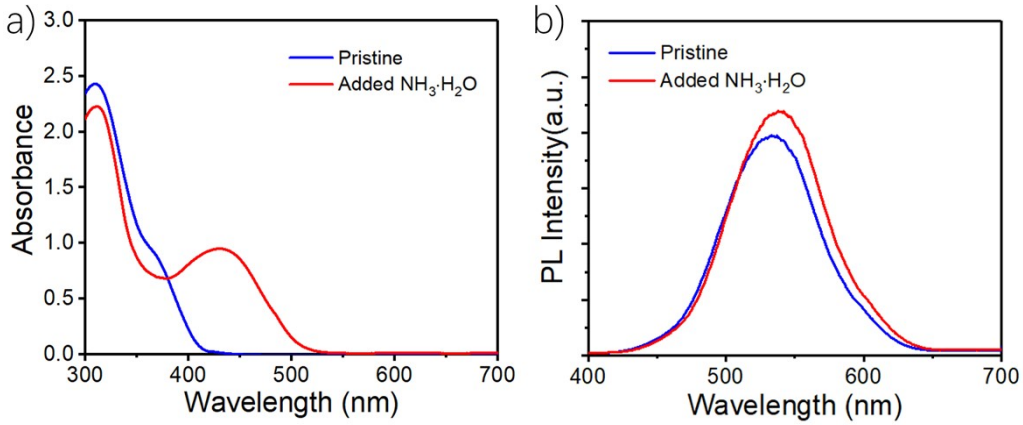


Figure S13 (a) UV-vis absorption and (b) emission spectra of $CNCH_3DSB\text{-}OH$ before and after added $NH_3{\cdot}H_2O$. These measurements were performed at room temperature with the concentration of $CNCH_3DSB\text{-}OH$ 1.0×10^{-4} M.

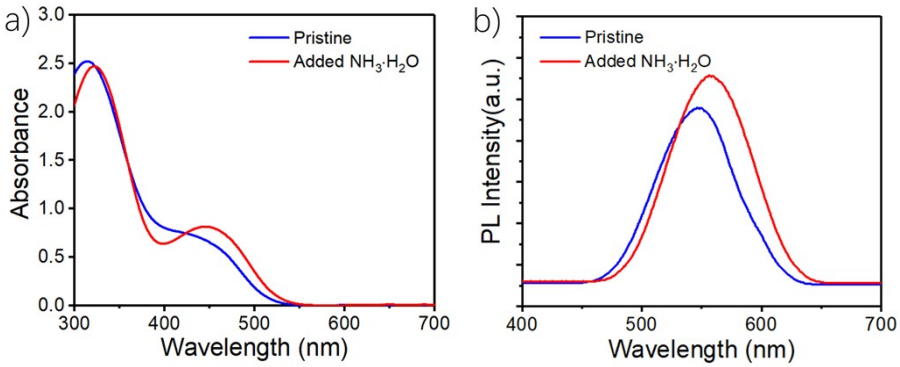


Figure S14 (a) UV-vis absorption and (b) emission spectra of CNDSB-OH before and after added $NH_3 \cdot H_2O$. These measurements were performed at room temperature with the concentration of CNDSB-OH 1.0×10^{-4} M.

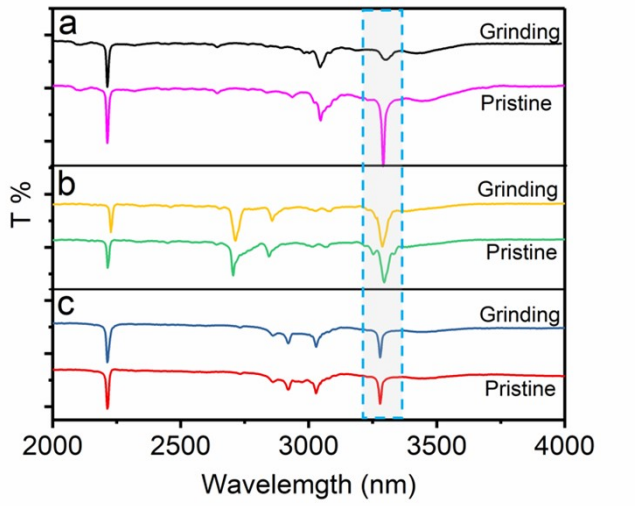


Figure S15 FTIR spectra changes of hydroxyl group before and after grinding. (a) $CNCF_3DSB$-OH, (b) $CNCH_3DSB$-OH, (c) CNDSB-OH

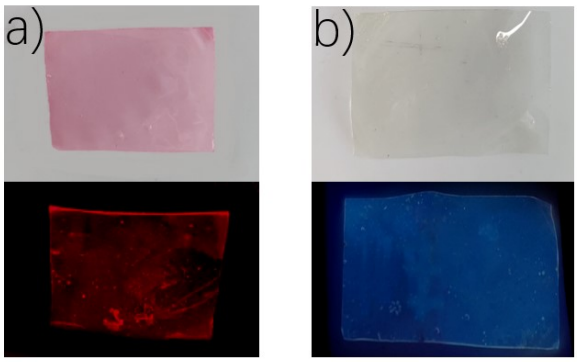


Figure S16 Images of color (top) and luminescence (bottom) in PVA films prepared from (a) DMSO and (b) H_2O solution. $CNCF_3DSB$-OH and PVA can dissolve well in DMSO solution, and the film prepared from their DMSO solution can display light red color and red luminescence, impaling that the molecules are in a dispersed state in PVA. $CNCF_3DSB$-OH can form aggregates in H_2O solution, and the film prepared from the H_2O solution can display colorless and blue luminescence, impaling that the molecules are in aggregated state in PVA.

Appendix

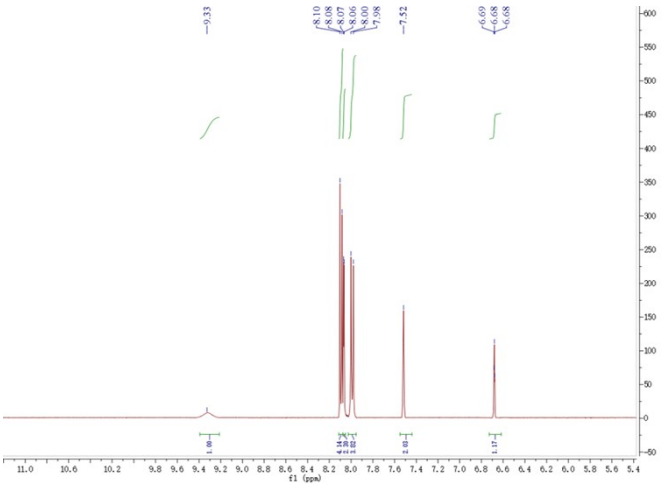


Figure S17 ^{1}H NMR spectum of $CNCF_3DSB$-OH

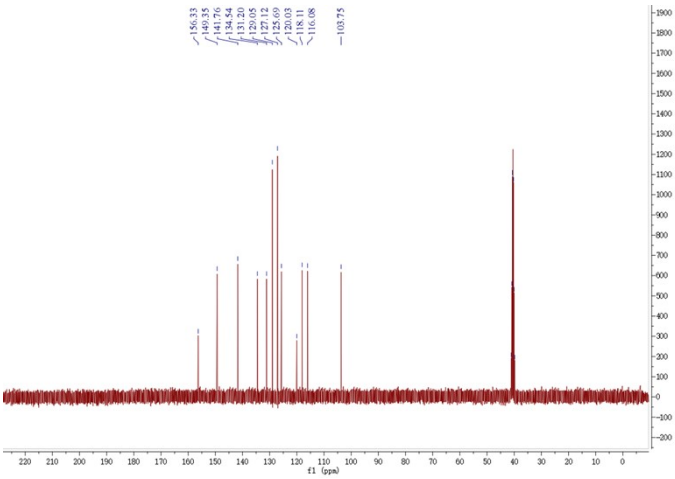


Figure S18 ^{13}C NMR spectum of $CNCF_3DSB$-OH

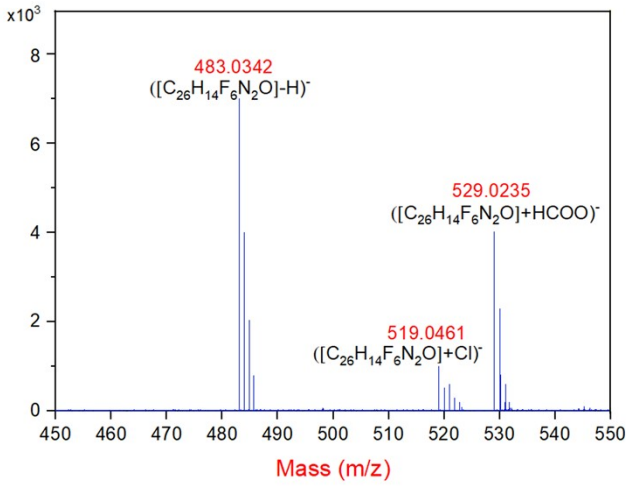


Figure S19 High-resolution mass spectrum spectum of $CNCF_3DSB$-OH in methanol

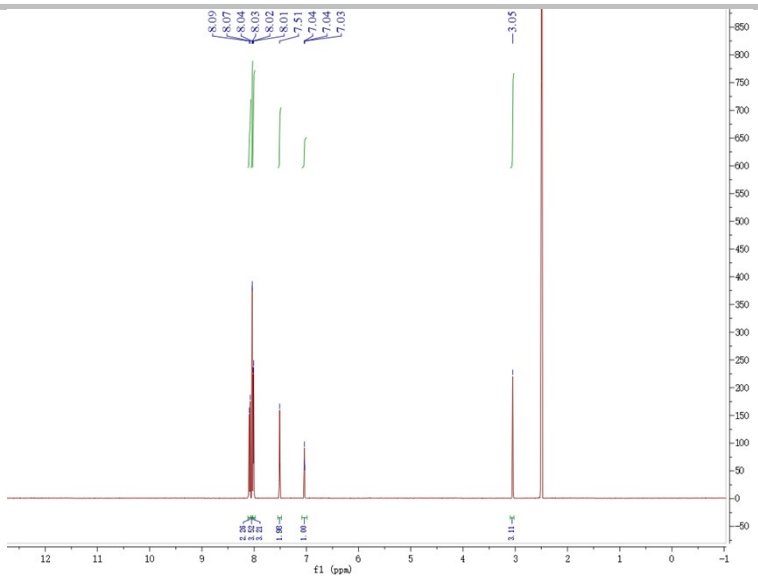


Figure S20 ^{1}H NMR spectum of $CNCF_3DSB\text{-}OCH_3$

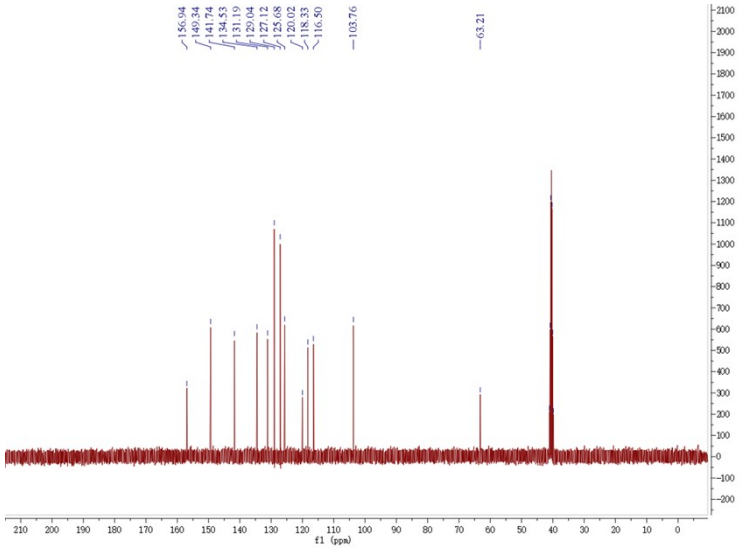


Figure S21 ^{13}C NMR spectum of $CNCF_3DSB\text{-}OCH_3$

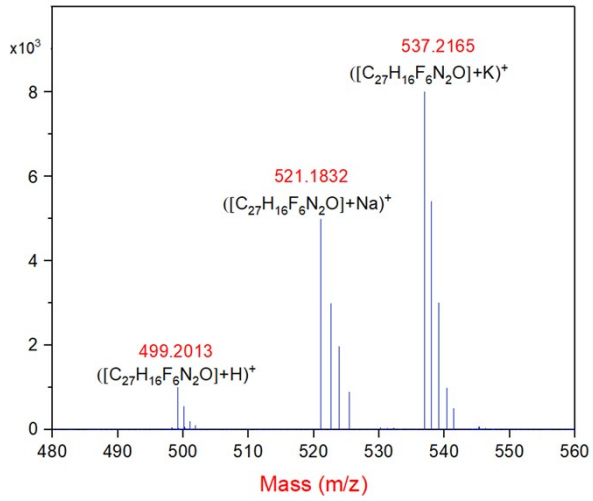


Figure S22 High-resolution mass spectrum spectum of $CNCF_3DSB\text{-}OCH_3$ in methanol

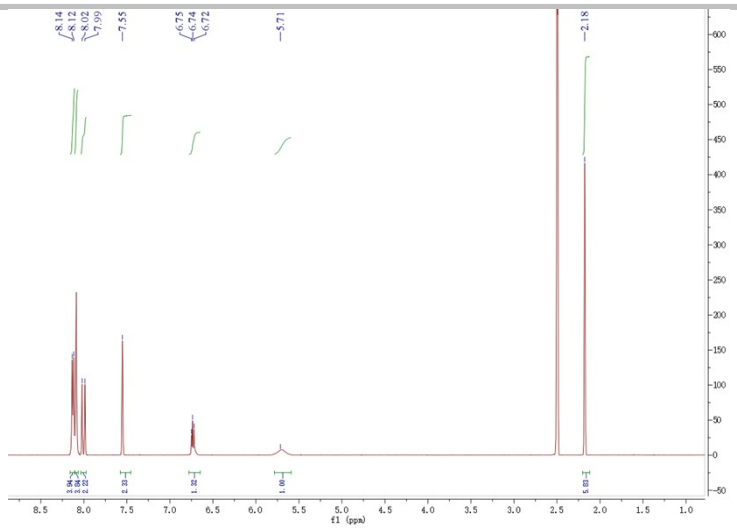


Figure S23 ^{1}H NMR spectum of CNCH$_3$DSB-OH

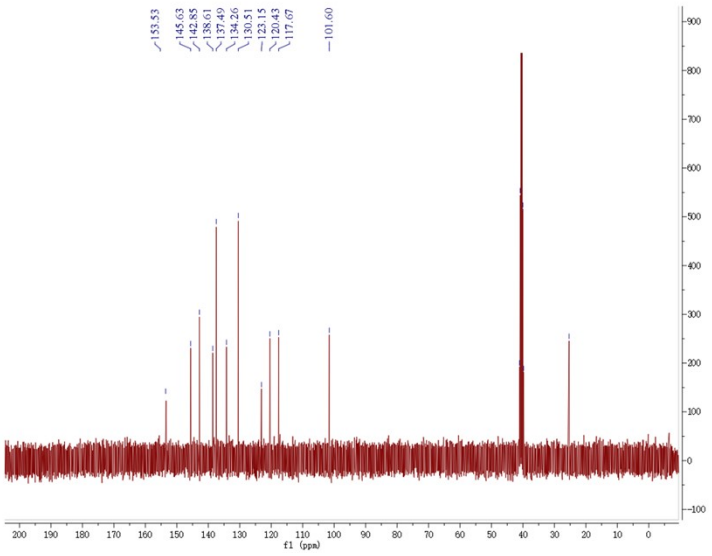


Figure S24 ^{13}C NMR spectum of CNCH$_3$DSB-OH

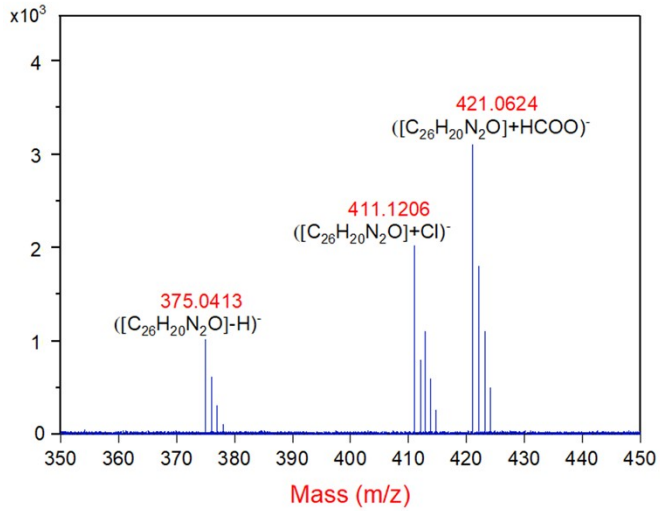


Figure S25 High-resolution mass spectrum spectum of CNCH$_3$DSB-OH in methanol

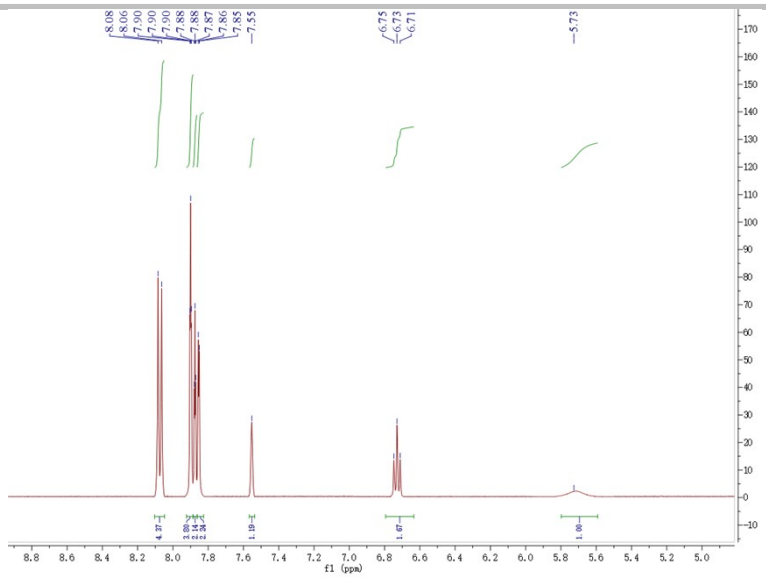


Figure S26 ^{1}H NMR spectum of CNDSB-OH

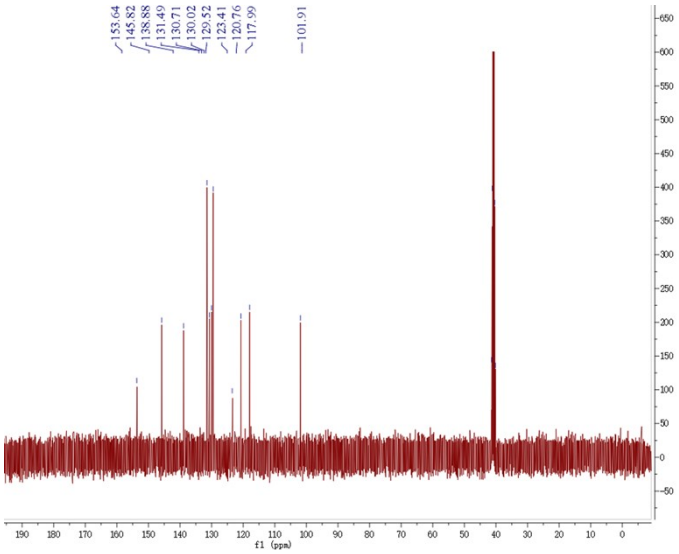


Figure S27 ^{13}C NMR spectum of CNDSB-OH

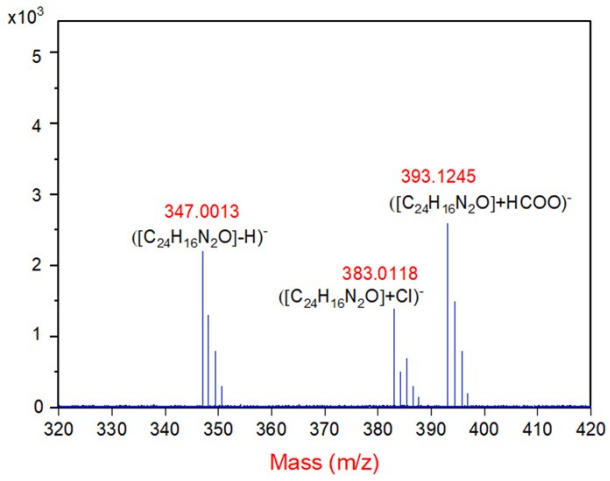


Figure S28 High-resolution mass spectrum spectum of CNDSB-OH in methanol