Electronic Supporting Information

A Dually Responsive Cyanostilbene Derivative for Paper Fluorescence Anti-Counterfeiting and Informational Encryption

Junxiao Wang[a], Pengyu Li[a], Chendong Ji,[a] Junhong Wu[a], Mingyu Fan[a], Jun Guan*[b], and Meizhen Yin*[a]

[a]*State Key Laboratory of Chemical Resource Engineering, Beijing Laboratory of Biomedical Materials, Beijing University of Chemical Technology, Beijing 100029 (China)*
*E-mail: yinmz@mail.buct.edu.cn**

[b]*Key Lab of Organic Optoelectronics & Molecular Engineering, Department of Chemistry, Tsinghua University. Beijing 100084 (China)*
*E-mail: junguan@mail.tsinghua.edu.cn**

Materials

All solvents were purchased from commercial suppliers and were directly used as received.
4-Pyridylacetonitrile hydrochloride (98%), 4-Hydroxybenzaldehyde (98%), 4-Methoxyphenylacetonitrile (98%), Benzaldehyde (98%), Benzyl cyanide (98%), all purchased from HEOWNS and used without further purification.

Characterization

^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker 400 (400 MHz) spectrometer at room temperature with DMSO-d6 as the solvent and tetramethylsilane (TMS) as the internal standard reference respectively. UV-Vis spectra were obtained on a spectrometer (UV-2600, Shimudzu, Japan). Fluorescence (FL) spectroscopic studies were performed on a fluorescence spectrophotometer (Horiba Jobin Yvon FluoroMax-4 NIR, NJ, USA). ESI-MS were determined by a Waters LCT premier XE spectrometer.

Test Fluorescence Quantum Yield

The solution of **ACN** derivatives is obtained upon dissolving the powder in DMSO (4×10^{-6} M). The powder and test paper is directly placed on the solid sample stand. The absolute quantum yields were measured using integrating sphere on an Edinburgh Instuments FS5 Fluorspectrophotometer Spetrometer.

Theoretical calculations

The TD-DFT simulations of the absorbance spectra were carried out with the Gaussian 09 package. The cam-B3LYP functional and the 6-31G*(d,p) basis set was applied, since it represents a good balance between quality of the results and computational cost.

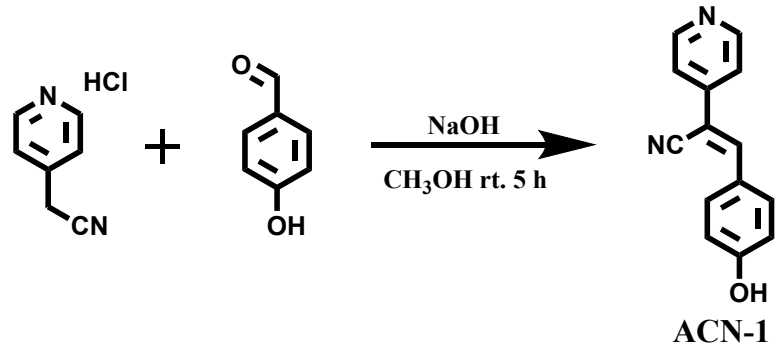
Preparation of fluorescent paper (FP)

The filter paper is dipping into the THF solution of **ACN1** and dries it in the oven forming **FP1**. The content of **ACN**s on the filter paper is controlled by modulating the concentration of THF solutions (4×10^{-4} M and 2×10^{-3} M) forming **FP1** and **FP1H** respectively. The **FP2**, **FP3** and **FP4** is obtained by dipping into the **ACN2**, **ACN3** and **ACN4** THF solutions with 2×10^{-3} M.

Preparation of the PBS solution

The solutions of pH 1.0-14.0 are prepared by adding small amounts of hydrochloric acid (0.5 M) or sodium hydroxide (0.5 M) to sodium phosphate buffer solution (0.1 M).

Synthesis



Scheme S1. Structure and synthesis route to **ACN1.**

Synthesis of (*Z*)-3-(4-hydroxyphenyl)-2-(pyridin-4-yl)acrylonitrile (ACN1): 4-Pyridylacetonitrile hydrochloride (0.3 g, 2 mmol), 4-Hydroxybenzaldehyde (0.29 g, 2 mmol) and NaOH (0.16 g, 4 mmol) were dissolved in 80 ml methanol under stirring at room temperature for 10 hours. Slow neutralization of the mixture with conc. HCl to pH=7 afforded a yellowish precipitate. The mixture is filtrated, washing the filter residue with water 2 times and collect the filter residue. The residue is collected to give **ACN1** (0.16 g, 0.2 mmol) yield 30%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.46 (s, 1H), 8.66 (d, J = 6.2 Hz, 2H), 8.20 (s, 1H), 7.94 (d, J = 8.7 Hz, 2H), 7.70 (d, J = 6.2 Hz, 2H), 6.96 (d, J = 8.7 Hz, 2H). ^{13}C NMR (101 MHz, DMSO) δ 161.21 (s), 150.59 (s), 146.15 (s), 141.95 (s), 132.45 (s), 124.37 (s), 119.66 (s), 117.97 (s), 116.30 (s), 103.33 (s). ESI-MS: Calculated mass: 222.0791; measured: 223.0934.

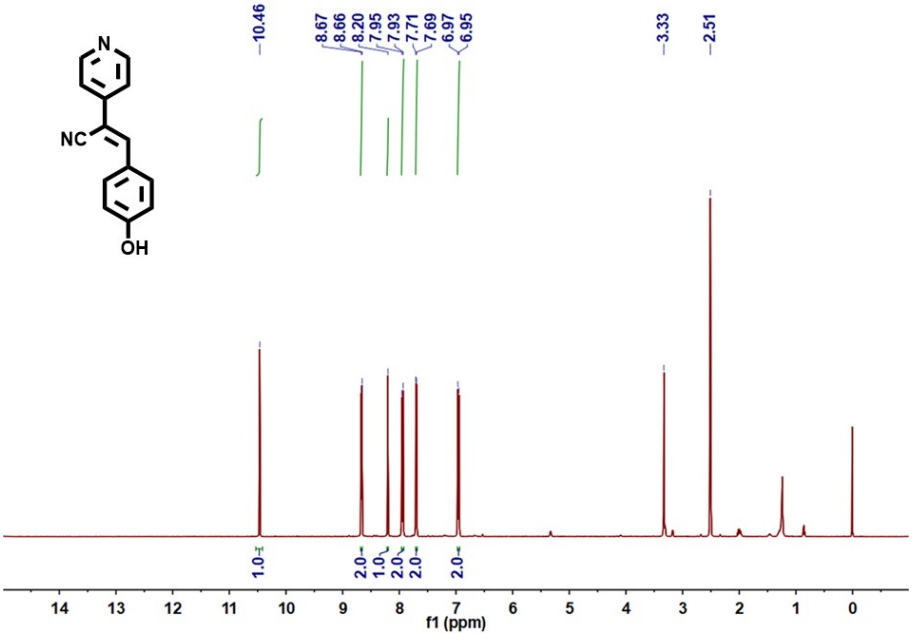


Figure S1. ^{1}H NMR spectrum of **ACN1** in DMSO-d_6.

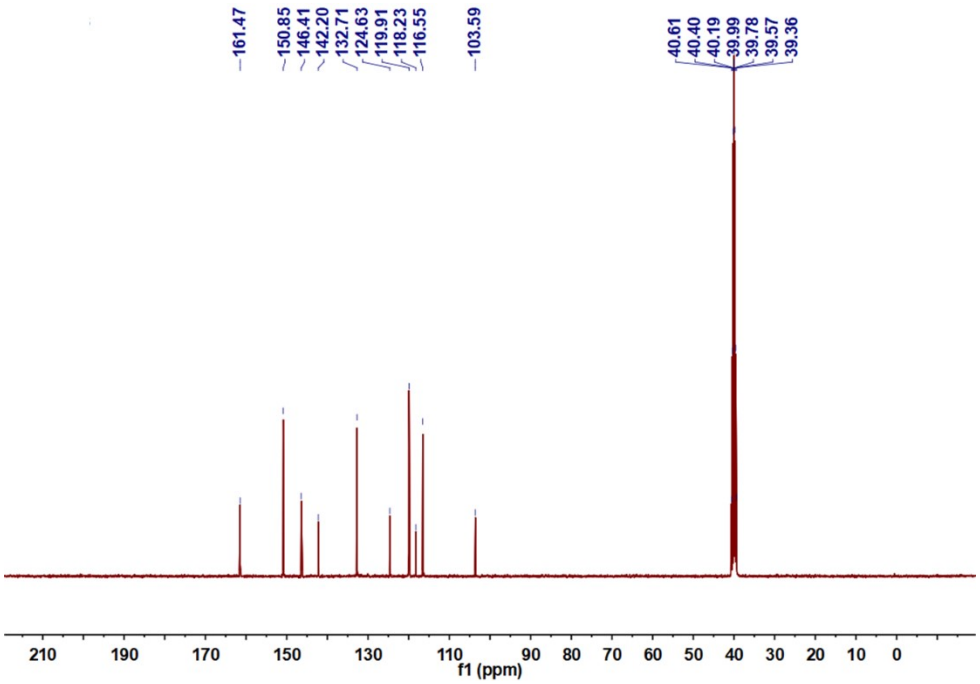


Figure S2. ^{13}C NMR spectrum of **ACN1** in DMSO-d_6.

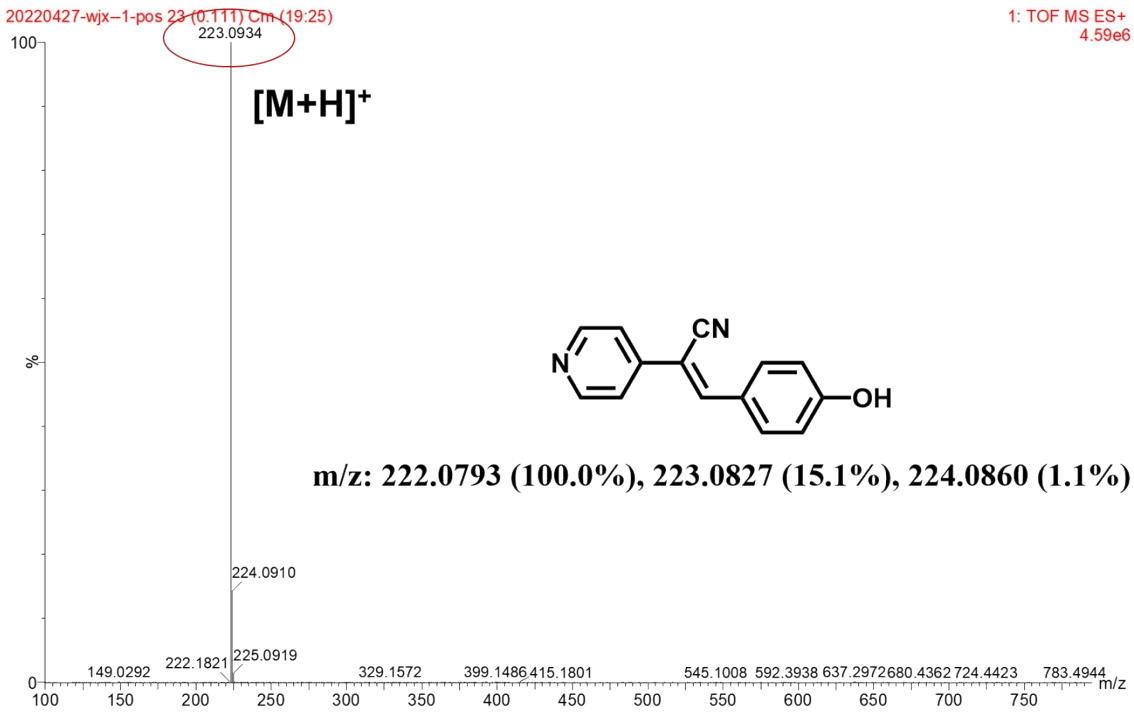
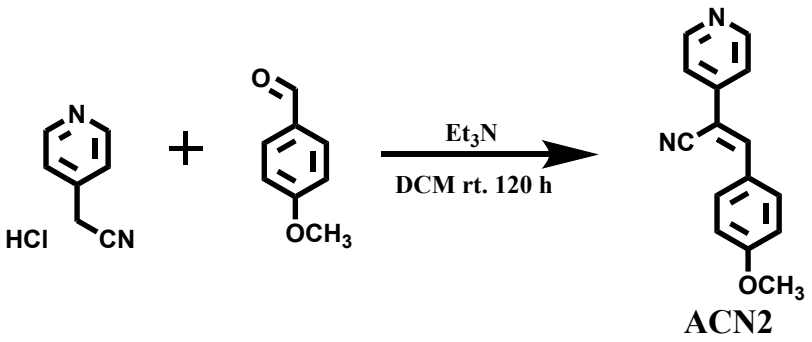


Figure S3. ESI-MS spectrum of **ACN1**.



Scheme S2. Structure and synthesis route to **ACN2.**

Synthesis of (*Z*)-3-(4-methoxyphenyl)-2-(pyridin-4-yl)acrylonitrile (ACN2): 4-Pyridylacetonitrile hydrochloride (0.3 g, 2 mmol), 4-Methoxybenzaldehyde (0.545 g, 4 mmol) and Et_3N (1.5 mL, 10 mmol) were dissolved in 25 ml DCM under stirring at room temperature for 120 hours. After the stated time, the solvent was removed in vacuo and the residue was purified by flash chromatography on silica gel eluting with DCM/MeOH =100/3 mixtures. The yellow product is collected to give **ACN2** (0.32 g, 1.5 mmol) in yield of 40%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.68 (d, J = 6.2 Hz, 2H), 8.27 (s, 1H), 8.03 (d, J = 8.9 Hz, 2H), 7.72 (d, J = 6.2 Hz, 2H), 7.17 (d, J = 1.8 Hz, 2H), 3.87 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ 162.42 (s), 150.89 (s), 146.11 (s), 141.97 (s), 132.36 (s), 126.10 (s), 120.01 (s), 118.02 (s), 115.16 (s), 114.26 (s), 104.95 (s), 56.03 (s). ESI-MS: Calculated mass: 236.0950; measured: 237.1141

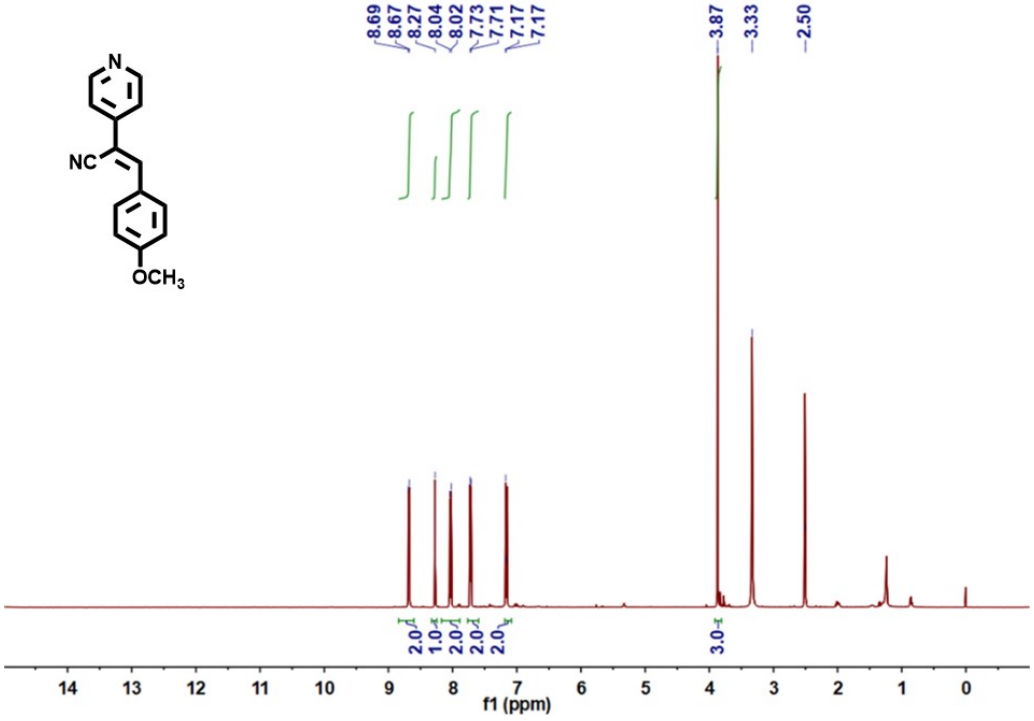


Figure S4. ^{1}H NMR spectrum of **ACN2** in DMSO-d_6.

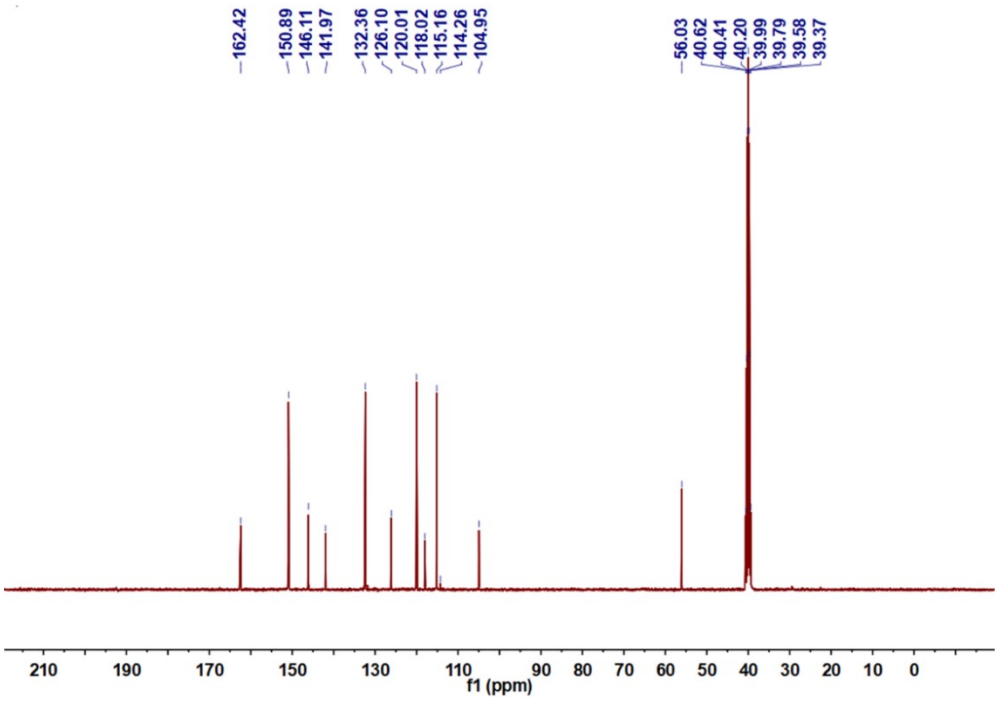


Figure S5. ^{13}C NMR spectrum of **ACN2** in DMSO-d_6.

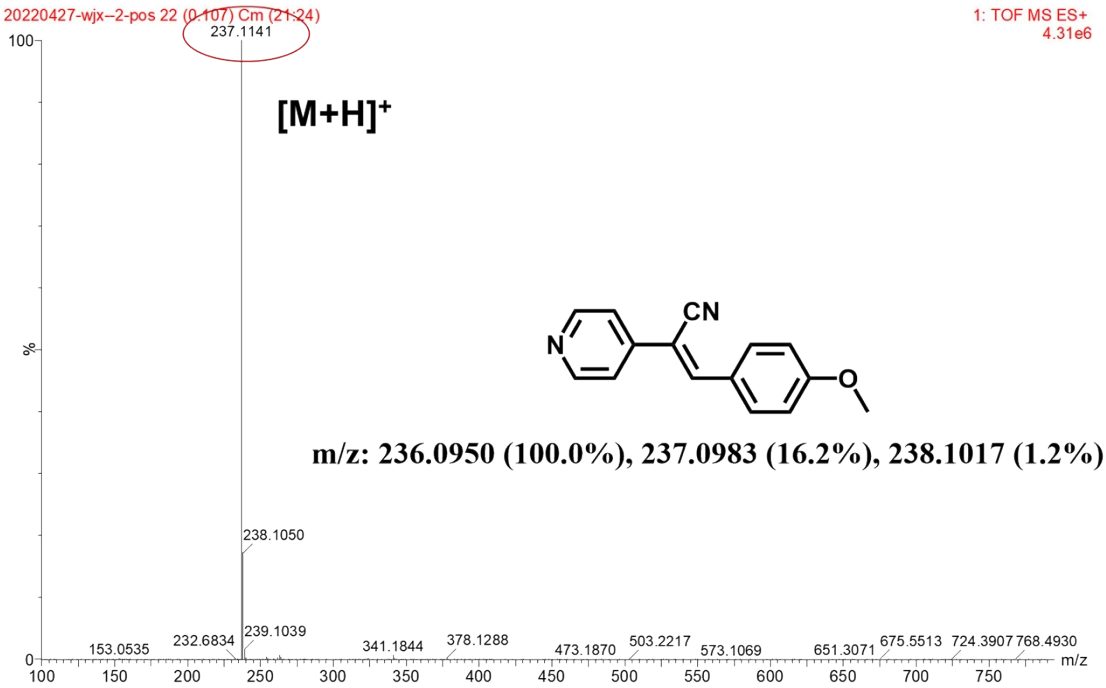
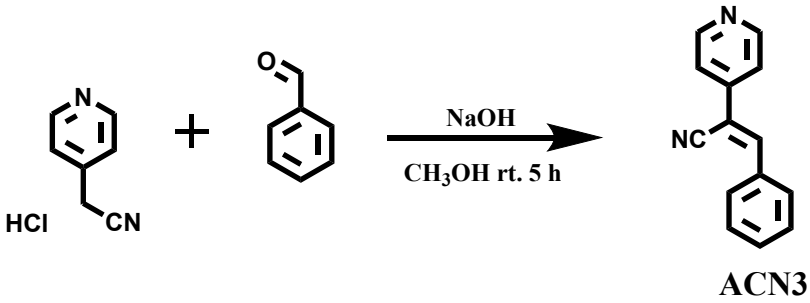


Figure S6. ESI-MS spectrum of **ACN2**.



ACN3

Scheme S3. Structure and synthesis route to **ACN3.**

Synthesis of (*Z*)-3-phenyl-2-(pyridin-4-yl)acrylonitrile (ACN3): 4-Pyridylacetonitrile hydrochloride (0.2 g, 1.3 mmol), Benzaldehyde (0.18 g, 1.7 mmol) and NaOH (0.07 g, 2.0 mmol) in 40 ml of MeOH solution was stirred for 3 h at room temperature. After reaction, 100 ml of deionized water was poured into the reaction mixture. The precipitate was formed and filtered. After dryness, **ACN3** was collected as a red solid in yield of 60%. ^{1}H NMR (400 MHz, DMSO-d6) δ 8.70 (dd, J = 4.7, 1.5 Hz, 2H), 8.35 (s, 1H), 7.99 (dd, J = 7.4, 2.0 Hz, 2H), 7.78-7.72 (m, 2H), 7.61-7.52 (m, 3H). ^{13}C NMR (101 MHz, DMSO) δ 161.21 (s), 150.59 (s), 146.15 (s), 141.95 (s), 132.45 (s), 124.37 (s), 119.66 (s), 117.97 (s), 116.30 (s), 103.33 (s). ESI-MS: Calculated mass: 206.0844; measured: 206.1043

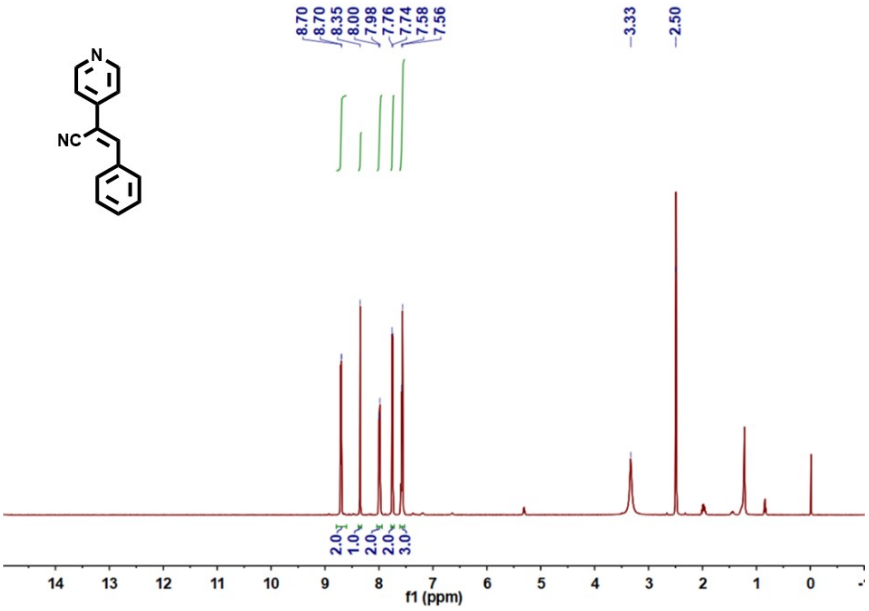


Figure S7. ^{1}H NMR spectrum of **ACN3** in DMSO-d_6.

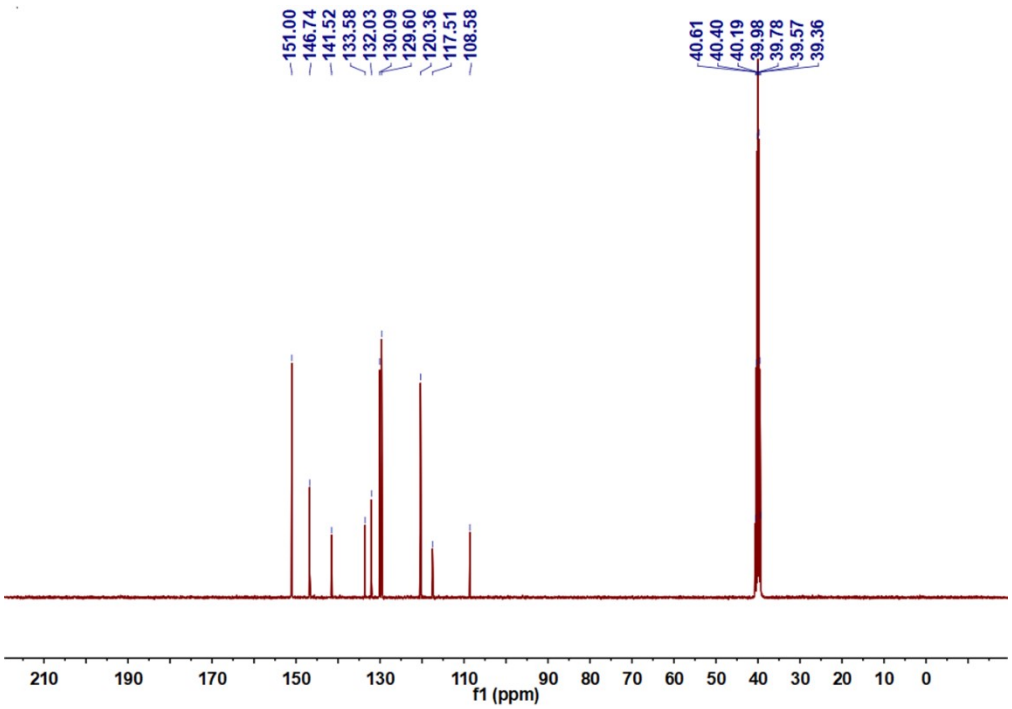


Figure S8. ^{13}C NMR spectrum of **ACN3** in DMSO-d_6.

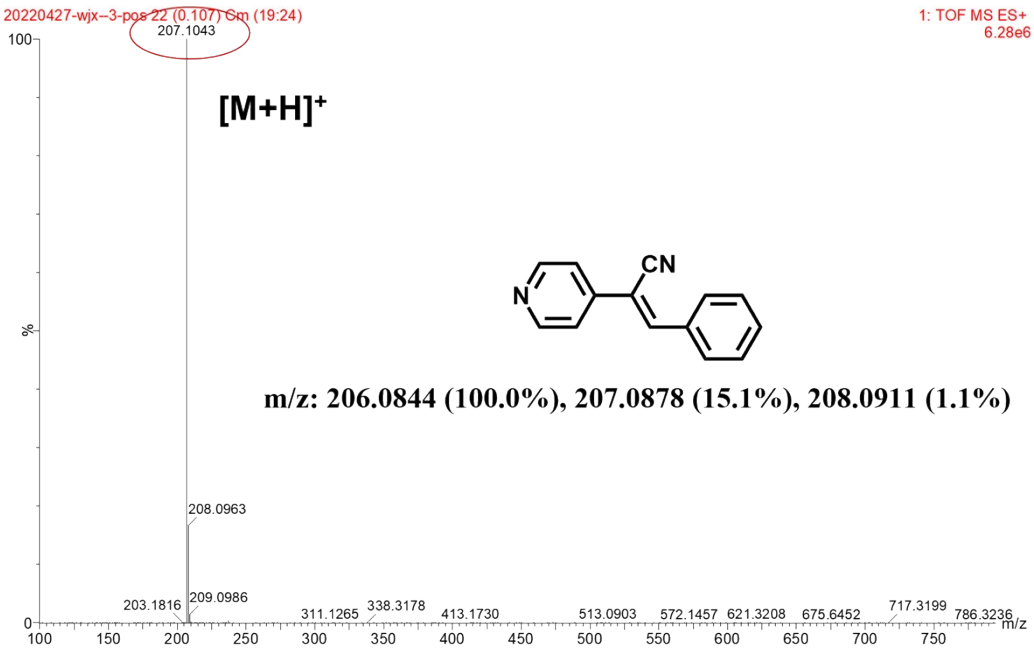
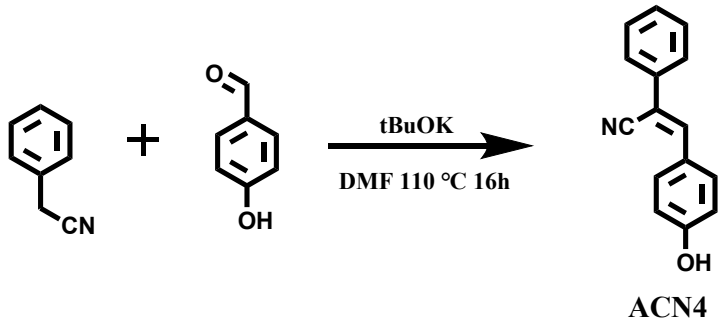


Figure S9. ESI-MS spectrum of **ACN3**.



ACN4

Scheme S4. Structure and synthesis route to **ACN4.**

Synthesis of (*Z*)-3-(4-hydroxyphenyl)-2-phenylacrylonitrile (ACN4): Benzyl cyanide (0.12 g, 1 mmol), 4-Hydroxybenzaldehyde (0.18 mg, 1.5 mmol) DMF (1 ml) and 2 equivalents of tBuOK (0.225 g, 2 mmol) were added in a 10 mL tube equipped with a stirring bar under 110 ℃ for 16 h. When the reaction was completed, the reaction mixture was cooled to room temperature. The reaction was quenched with distilled water and the solution was extracted with ethyl acetate. The crude product was purified by column chromatography (DCM/ ethyl acetate = 50:1) and **ACN4** in yield of 60%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.24 (s, 1H), 7.90 – 7.85 (m, 3H), 7.71 (d, J = 7.3 Hz, 2H), 7.49 (t, J = 7.6 Hz, 2H), 7.40 (t, J = 7.3 Hz, 1H), 6.91 (d, J = 8.7 Hz, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 160.47 (s), 143.37 (s), 134.83 (s), 131.88 (s), 129.59 (s), 129.05 (s), 125.86 (s), 125.23 (s), 119.08 (s), 116.34 (s), 106.26 (s). ESI-MS: Calculated mass: 221.0841; measured: 222.0911.

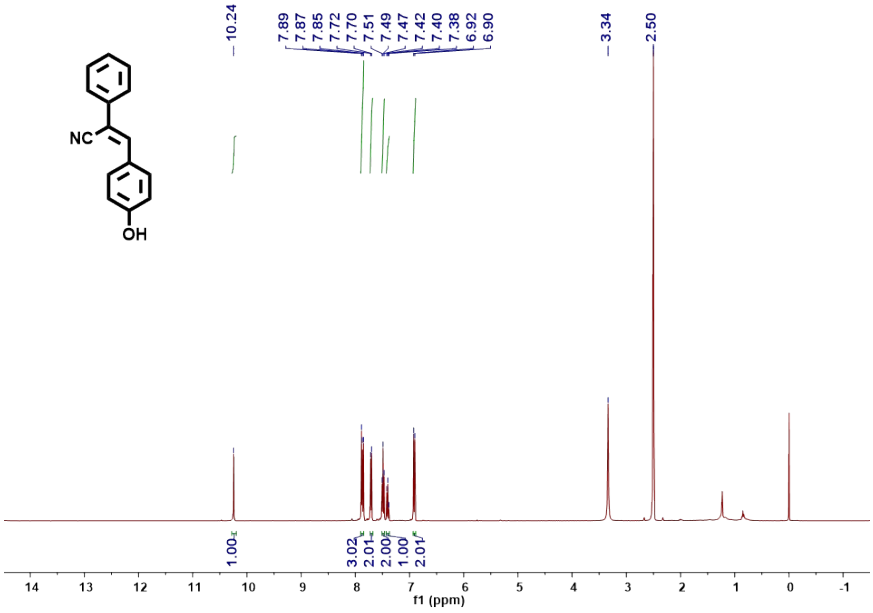


Figure S10. ^{1}H NMR spectrum of **ACN4** in DMSO-d_6.

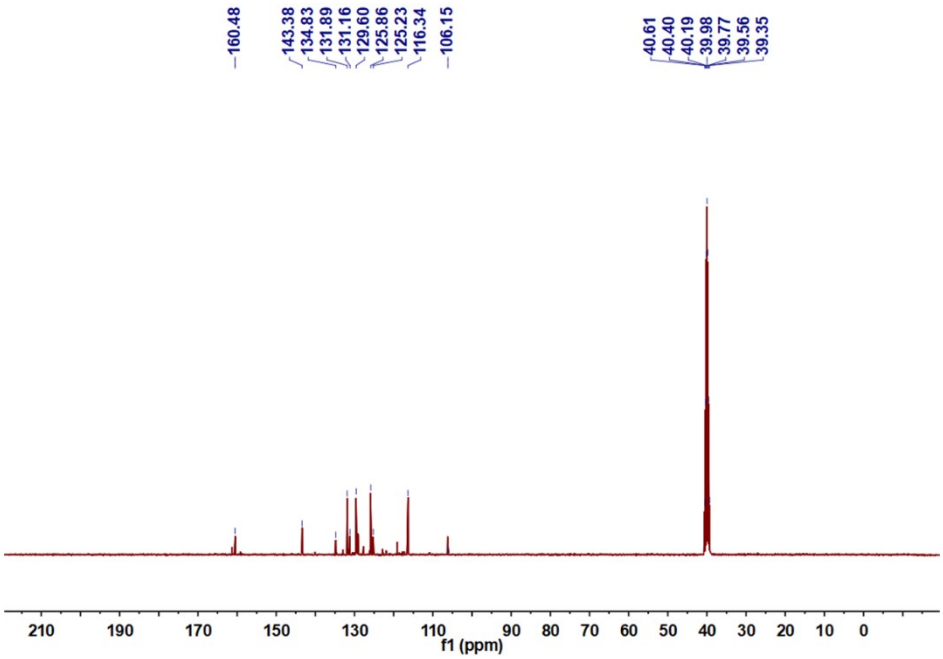


Figure S11. ^{13}C NMR spectrum of **ACN4** in DMSO-d_6.

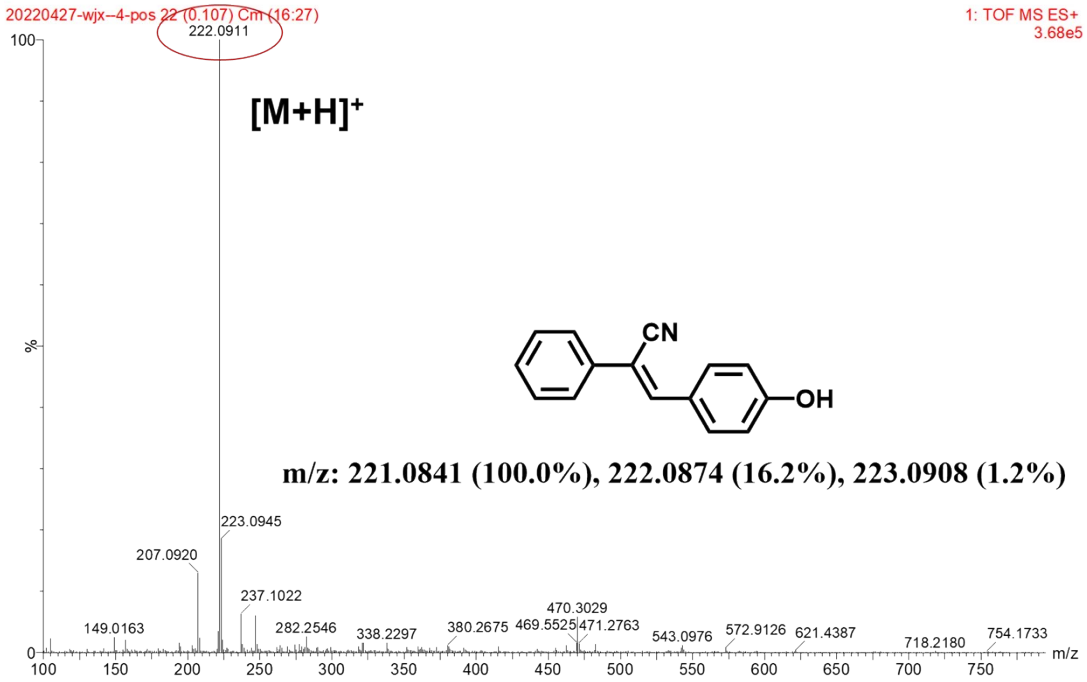


Figure S12. ESI-MS spectrum of **ACN4**.

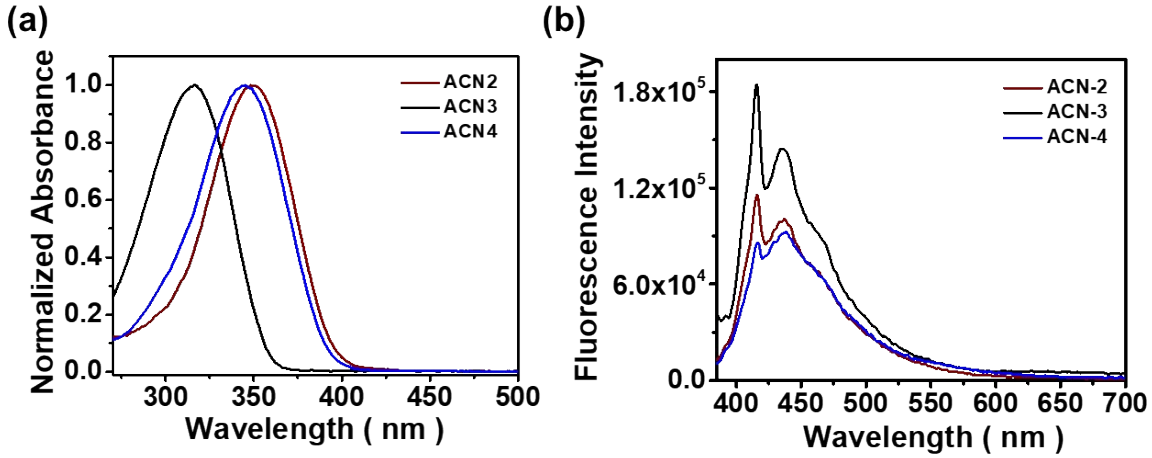


Figure S13. (a) Normalized absorption spectra and (b) fluorescence spectra (λ_{ex} = 370 nm) of **ACN2.3.4.5** in DMSO solution (4×10^{-5} M) at room temperature.

Table S1. Optical data of cyanostilbene derivatives **ACN 1-5**.

	Solution			Solid		
	λ_a (nm)	λ_f (nm)	Φ_f	λ_a (nm)	λ_f (nm)	Φ_f
ACN1	354	430	0.14	435/520	/	/
ACN2	350	436	0.23	400	505	1.52
ACN3	315	436	1.01	380/520	437/550	0.70
ACN4	345	445/560	0.09	420	480	0.85

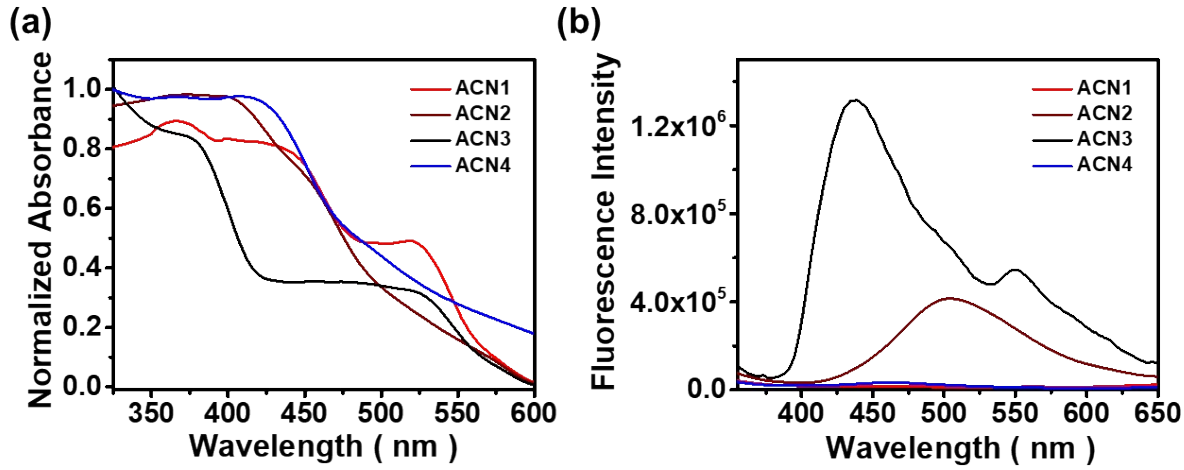


Figure S14. (a) UV-Vis absorption spectra and (b) fluorescence spectra (λ_{ex} = 340 nm) of **ACNs** in the solid states.

Table S2 Changes of the absorption peaks of **ACN1-4**.

compound	pH value of buffer solutions	Wavelength of the maximum absorption peaks (nm)
ACN1	2.0	385
	7.0	354
	13.0	415
ACN2	2.0	345
	7.0	380
ACN3	2.0	310
	7.0	340
ACN4	7.0	335
	13.0	385

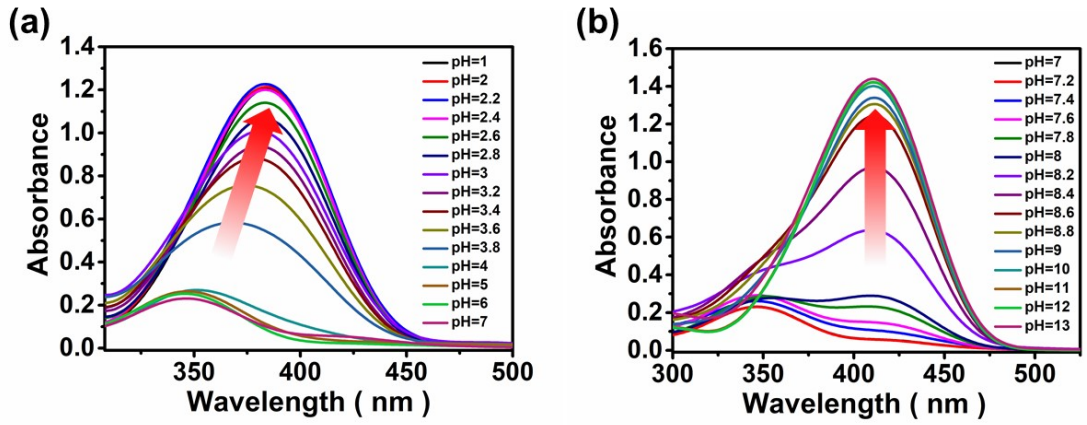


Figure S15. Absorption spectra of **ACN1** (4×10^{-5} M, V_{DMSO}: V_{Buffer}=1:9) in aqueous solutions with different pH values.: (a) pH 1.0-7.0, (b) pH 7.0-13.0.

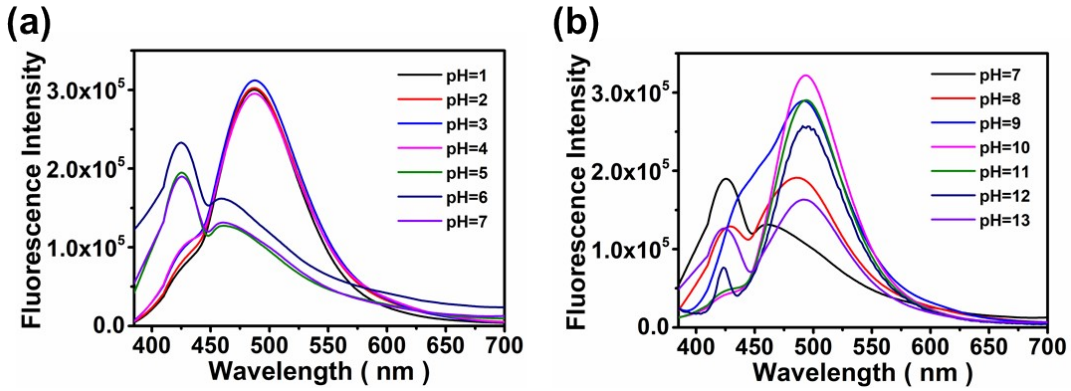


Figure S16. Fluorescence spectra (λ_{ex} = 370 nm) of **ACN1** (4×10^{-5} M, V_{DMSO}: V_{Buffer}=1:9) in buffer aqueous solutions: (a) pH = 1.0-7.0, (b) pH = 7.0-13.0.

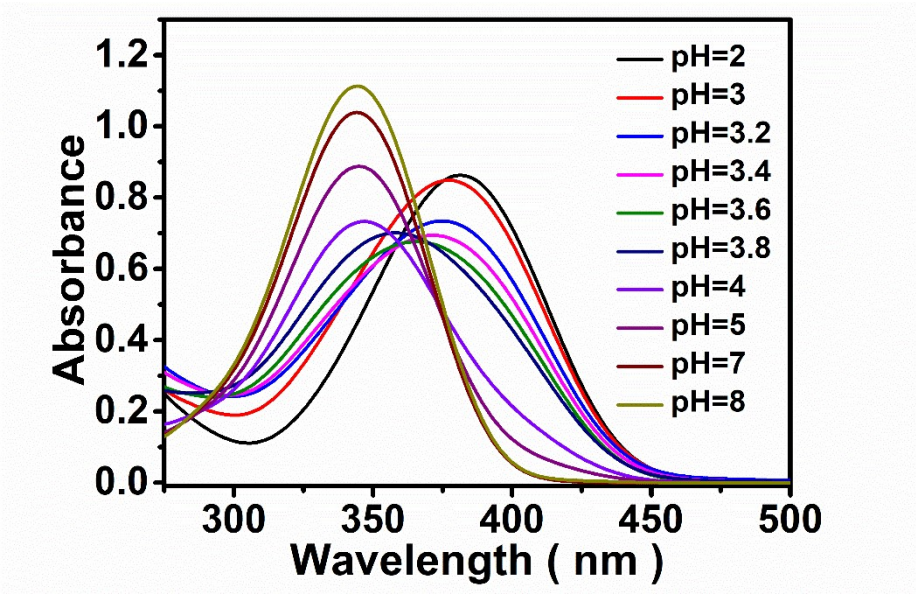


Figure S17. Absorption spectra of **ACN2** (4×10^{-5} M, V_{DMSO}: V_{Buffer}=1:9) in aqueous solutions with different pH values.

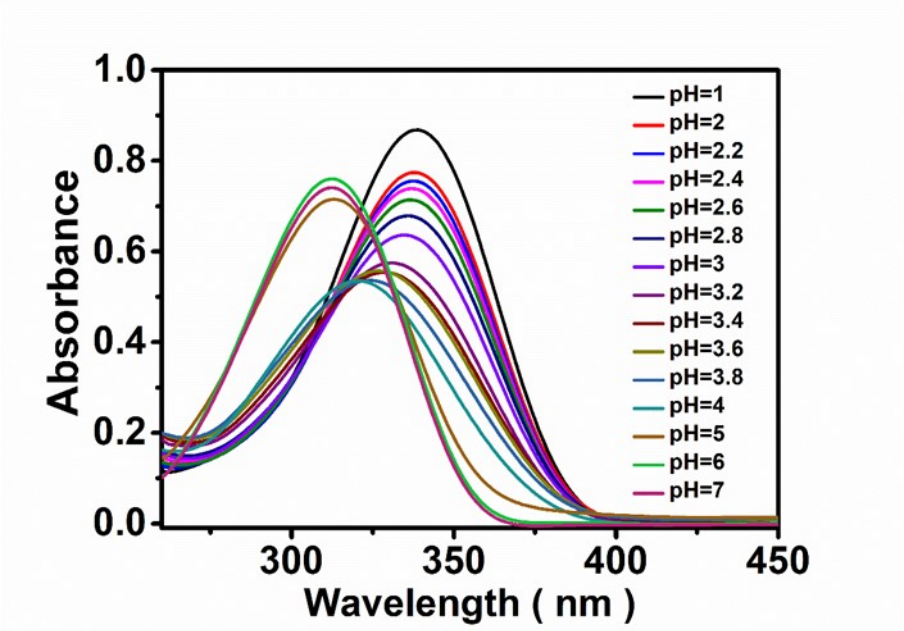


Figure S18. Absorption spectra of **ACN3** (4×10^{-5} M, V_{DMSO}: V_{Buffer}=1:9) in aqueous solutions with different pH values.

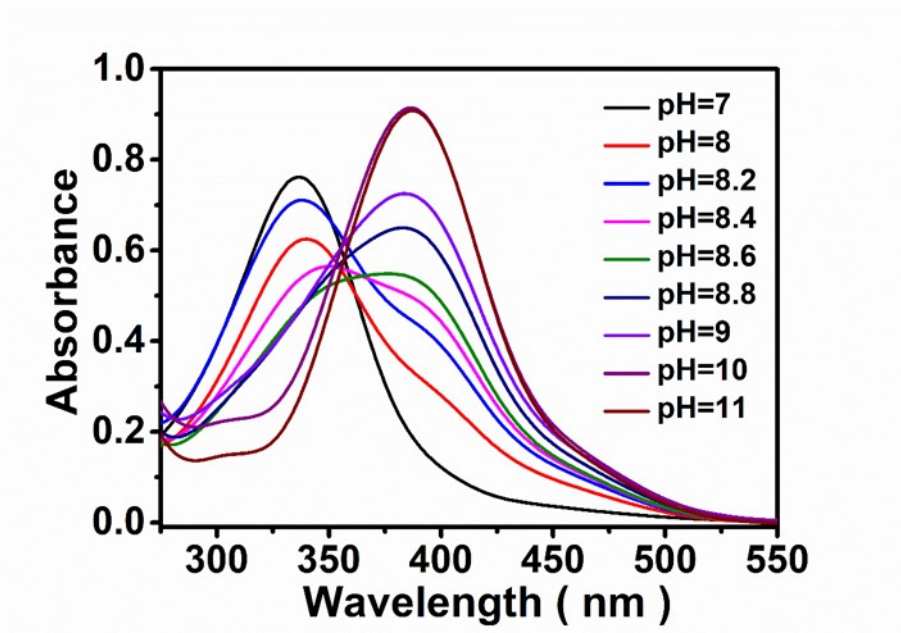


Figure S19. Absorption spectra of **ACN4** (4×10^{-5} M, V_{DMSO}: V_{Buffer}=1:9) in aqueous solutions with different pH values.

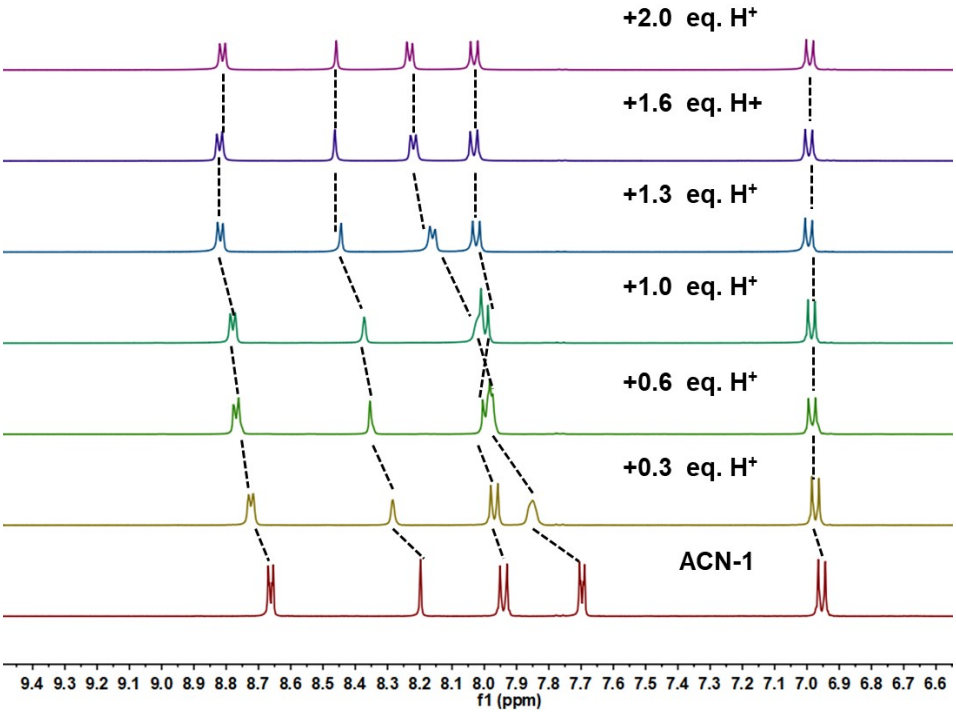


Figure S20. ^{1}H NMR spectra of the titration experiment of ACN1 response to different amounts of DCl (DMSO-d_6, from up to down: 0, 0.3, 0.6, 1.0,1.3 ,1.6 and 2.0 equiv. of DCl).

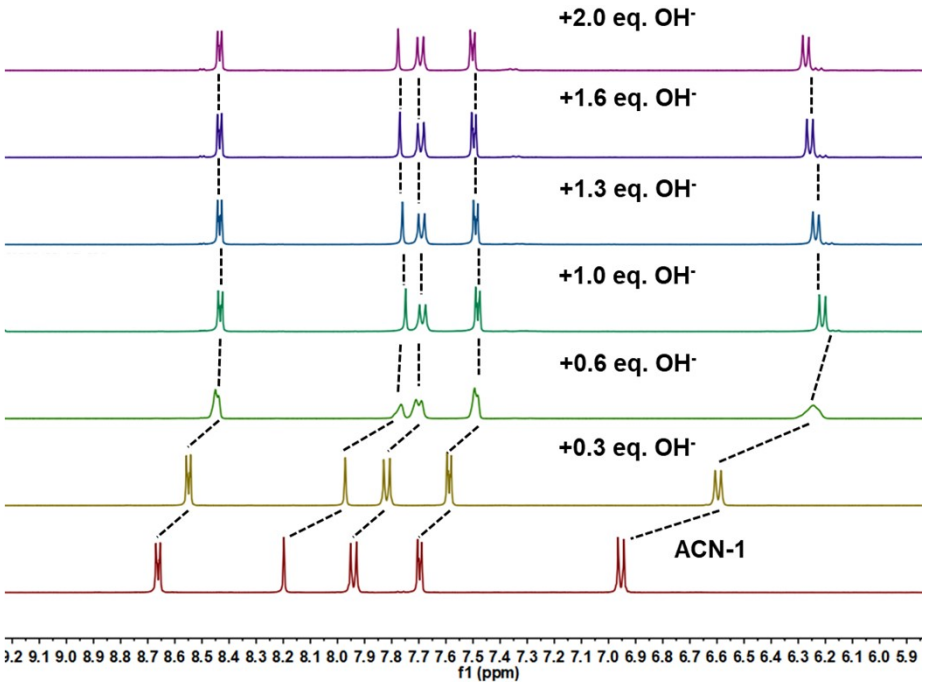


Figure S21. ^{1}H NMR spectra of the titration experiment of **ACN1** response to different amounts of NaOD (DMSO-d_6, from up to down: 0, 0.3, 0.6, 1.0,1.3 ,1.6 and 2.0 equiv. of NaOD).

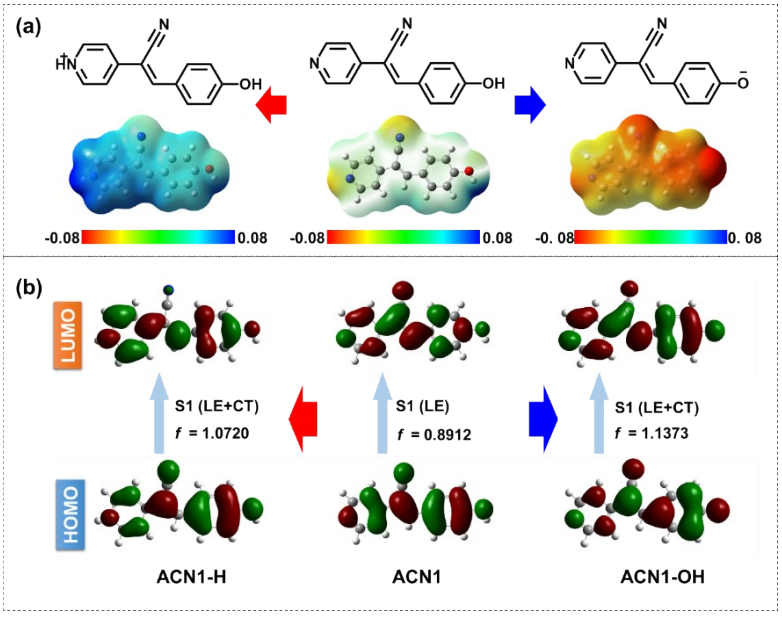


Figure S22. (a) Electrostatic potential surfaces of **ACN1**, **ACN1-H** and **ACN1-OH**. (b) HOMOs and LUMOs of the S_0-S_1 transitions of **ACN1**, **ACN1-H** and **ACN1-OH**.

Table S3. Calculated energy levels and electronic transition characters of the singlet states of **ACN1, ACN1-H** and **ACN1-OH**.

	Excite State	Energy	Wavelength	Oscillator Strengths	Transitions	Excitation Type	Ratio
ACN1	S1	3.85 eV	382 nm	*f*=0.8912	H→L	LE	97.2%
	S4	4.89 eV	253 nm	*f*=0.0251	H-1→L	LE+CT	74.7%
ACN1-H	S1	3.12 eV	397 nm	*f*=1.0720	H→L	LE+CT	96.0%
	S3	4.49 eV	276 nm	*f*=0.0141	H-3→L H-2→L+1 H→L+1	CT	2.5% 6.5% 88.3%
	S4	4.88 eV	254 nm	*f*=0.0426	H-2→L H→L+2	LE+CT	82.2% 8.6%
ACN1-OH	S1	3.09 eV	400 nm	*f*=1.1373	H→L	LE+CT	96.0%
	S4	4.18 eV	297 nm	*f*=0.0740	H-2→L+2 H→L+2	CT	5.5% 88.5%

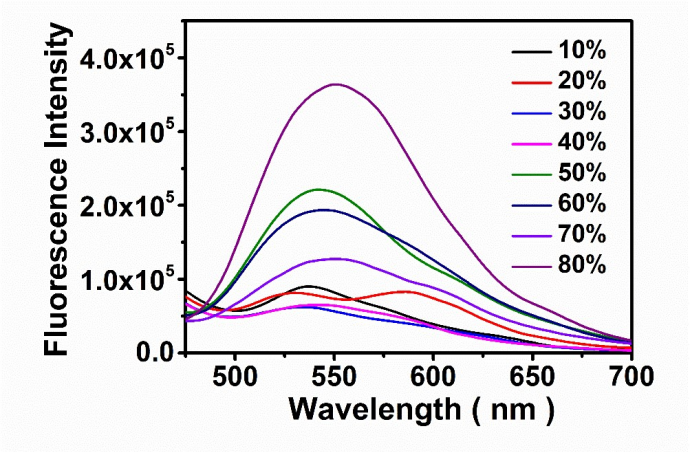


Figure S23. Fluorescence spectra (λ_{ex} = 370 nm) of **ACN1** treated with acid solution in THF/Hexane mixtures with different Hexane fraction(f_{Hex}), concentration: 4×10^{-5} M.

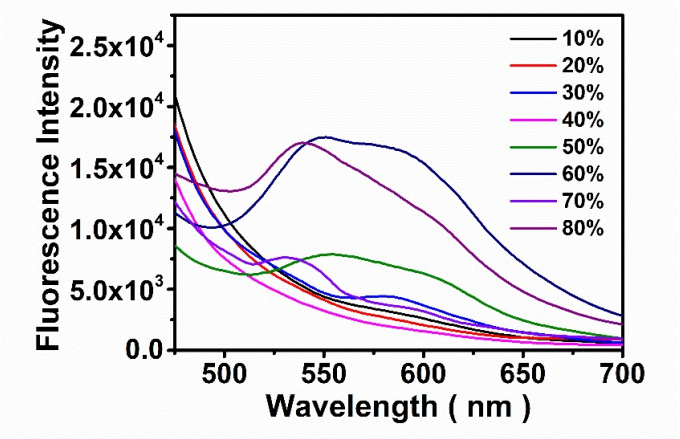


Figure S24. Fluorescence spectra (λ_{ex} = 370 nm) of **ACN1** treated with base solution in THF/Hexane mixtures with different Hexane fraction(f_{Hex}), concentration: 4×10^{-5} M.

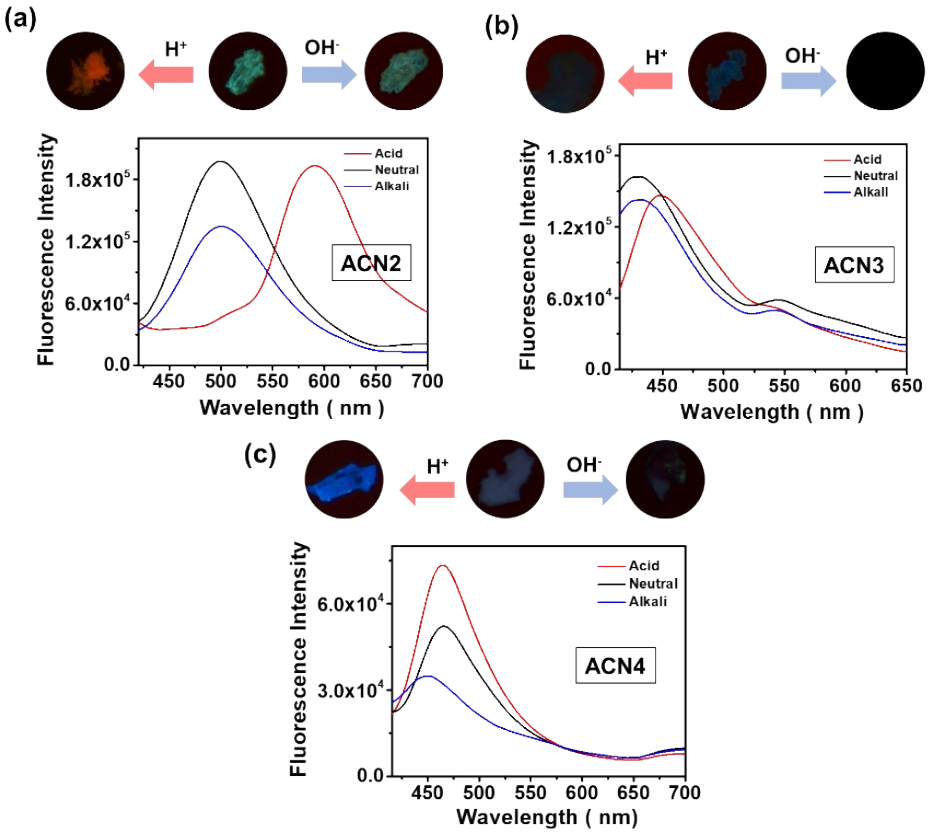


Figure S25. Fluorescence photographs and spectra (λ_{ex} = 370 nm) (a) **ACN2** (b) **ACN3** (c) **ACN4** solid powder after acid/base treatment.

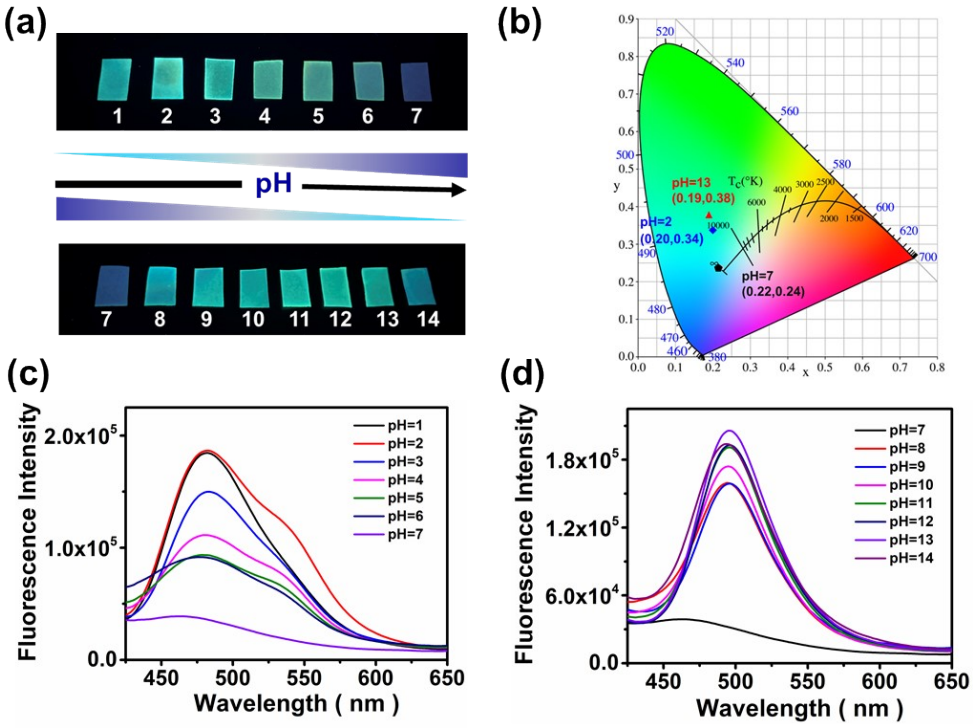


Figure S26. (a) Fluorescence photographs of **FP1** after detecting different pH solutions. (b) CIE coordinate diagram for **FP1** under pH=2.0 and pH=13.0. FL spectra (λ_{ex} = 370 nm) of test paper in (c) acid and (d) base pH conditions.

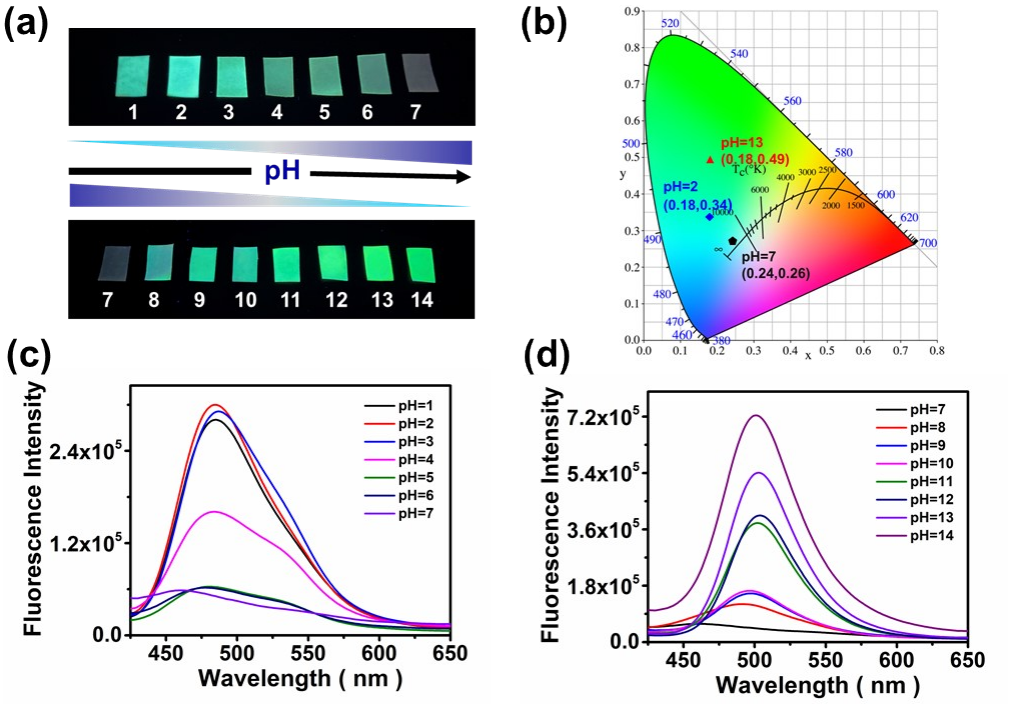


Figure S27. (a) Fluorescence **(FL)** photos of **FP1H** after detecting different pH solutions. (b) CIE coordinate diagram for **FP1H** under pH=2.0 and pH=13.0. Fluorescence spectra (λ_{ex} = 370 nm) of test paper in (c) acid and (d) base conditions.

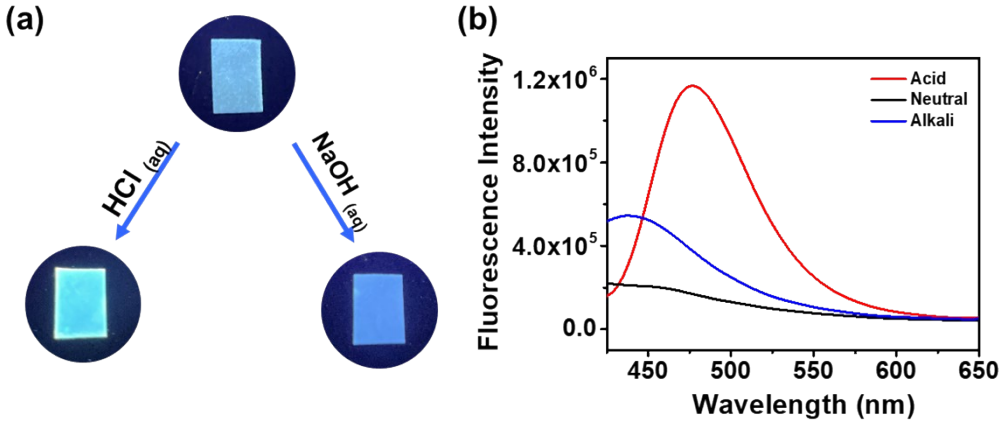


Figure S28. (a) Fluorescence photos and (b) spectra (λ_{ex} = 370 nm) of **FP2** after treated by acid and base solutions.

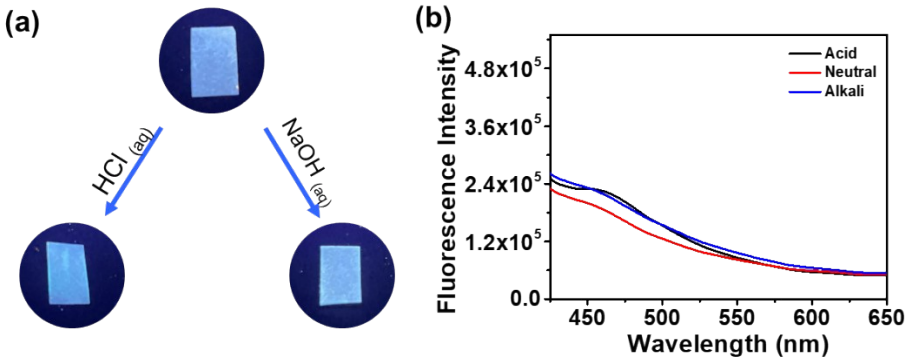


Figure S29. (a) Fluorescence photos and (b) spectra (λ_{ex} = 370 nm) of **FP3** after treated by acid or base solution.

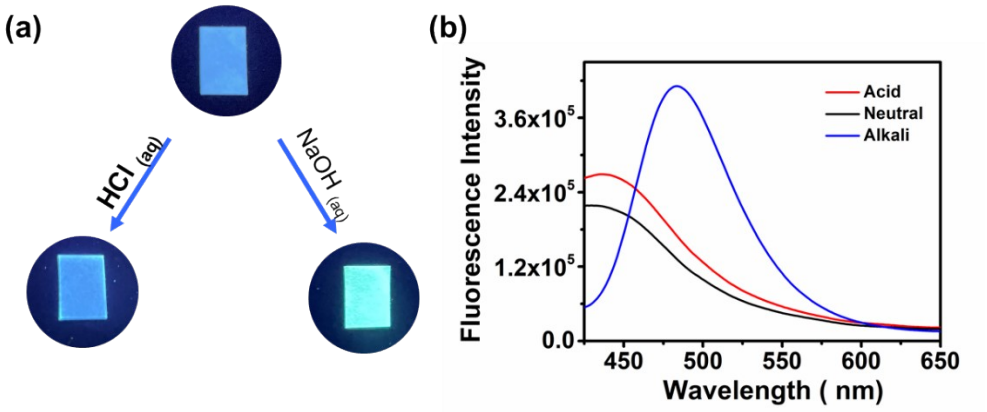


Figure S30. (a) Fluorescence photos and (b) spectra (λ_{ex} = 370 nm) of **FP4** after treated by acid or base solution.

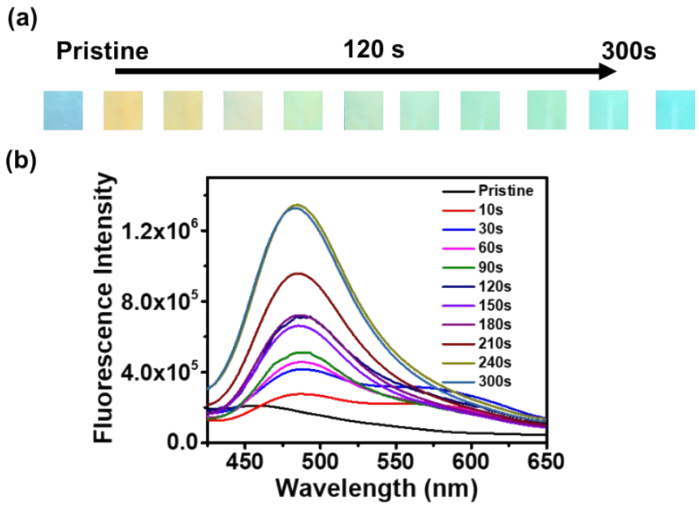


Figure S31. Time-dependent fluorescence photos and fluorescence spectra (λ_{ex} = 370 nm) of **FP1H** under fuming with HCl vapors.

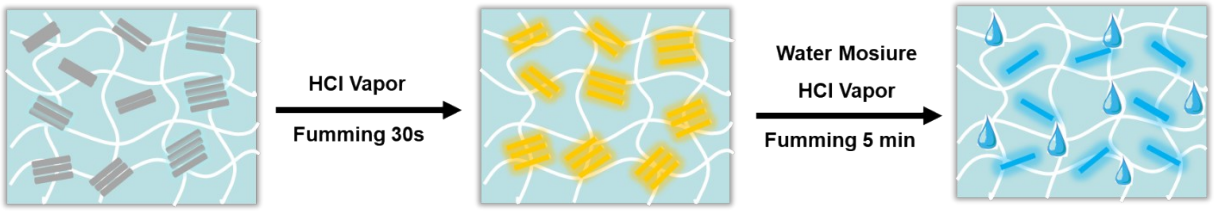


Figure S32. Schematic diagram of fluorescence changes under HCl fuming for different times.

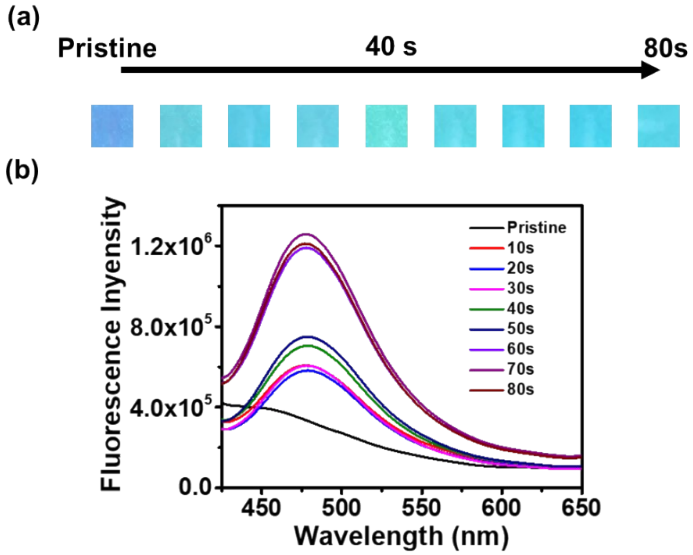


Figure S33. Time-dependent fluorescence photos and fluorescence spectra (λ_{ex} = 370 nm) of **FP1** under fuming with HCl vapors.

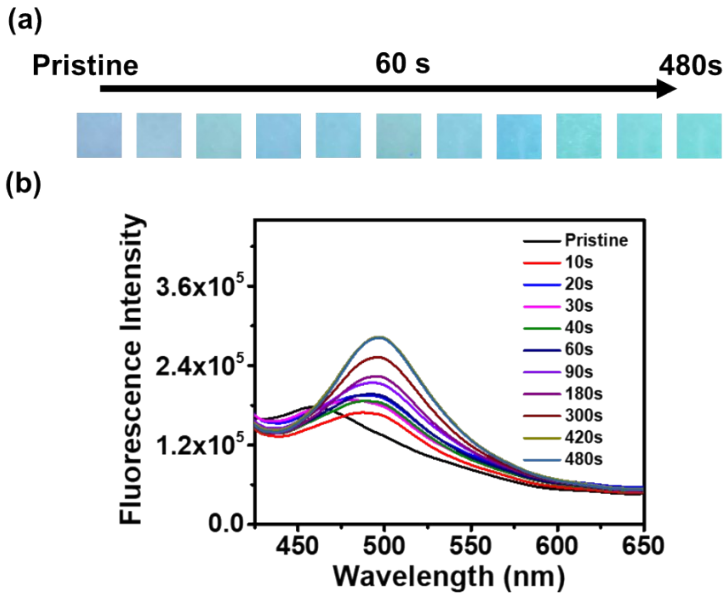


Figure S34. Time-dependent fluorescence photos and fluorescence spectra (λ_{ex} = 370 nm) of **FP1H** under fuming with NH_3 vapors.

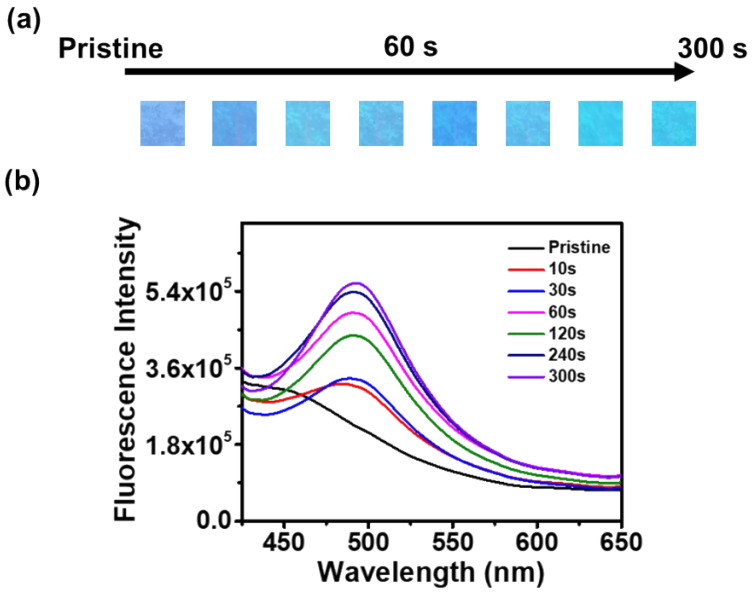


Figure S35. Time-dependent fluorescence photos and fluorescence spectra (λ_{ex} = 370 nm) of **FP1** under fuming with NH_3 vapors.

Figure S36. Paper anti-counterfeiting using (a) acid or (b) base solution as security inks. Fluorescent patterns of "BUCT" are observed on FP1H under UV light and after placing for15 days.

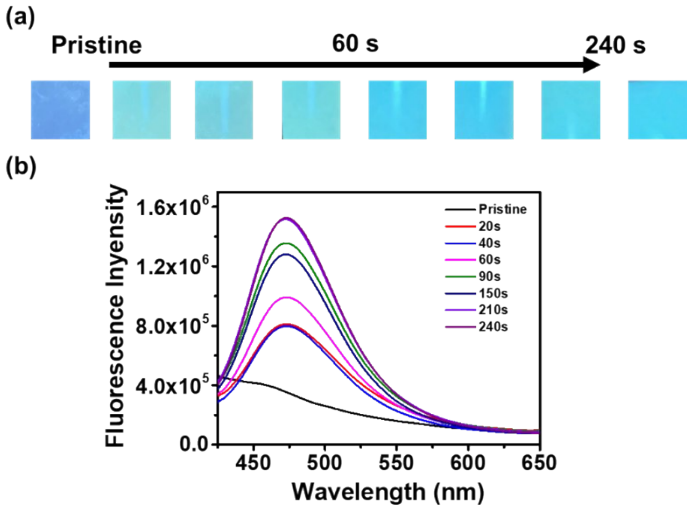


Figure S37. Time-dependent fluorescence photos and fluorescence spectra (λ_{ex} = 370 nm) of **FP2** fuming with HCl vapors.

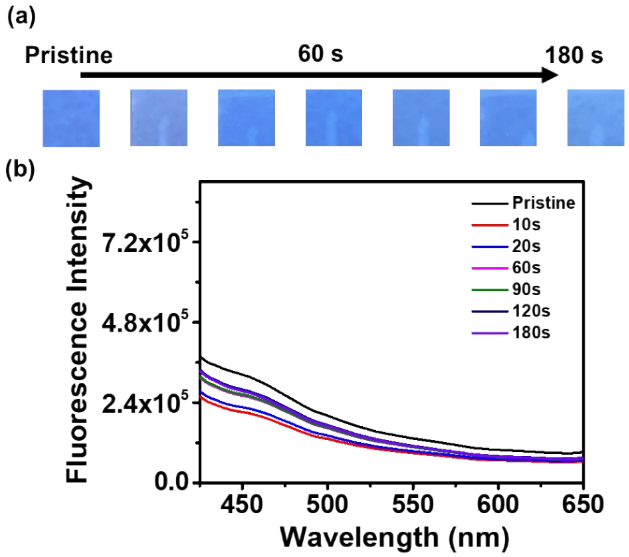


Figure S38. Time-dependent fluorescence photos and fluorescence spectra (λ_{ex} = 370 nm) of **FP3** fuming with HCl vapors.

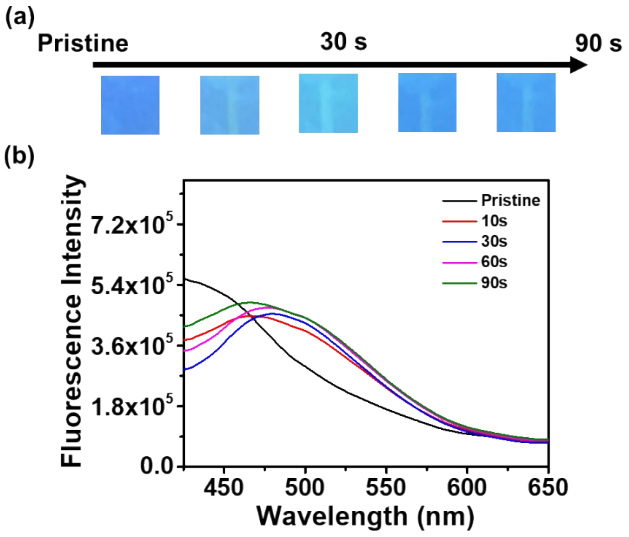


Figure S39. Time-dependent fluorescence photos and fluorescence spectra (λ_{ex} = 370 nm) of **FP4** fuming with NH_3 vapors.

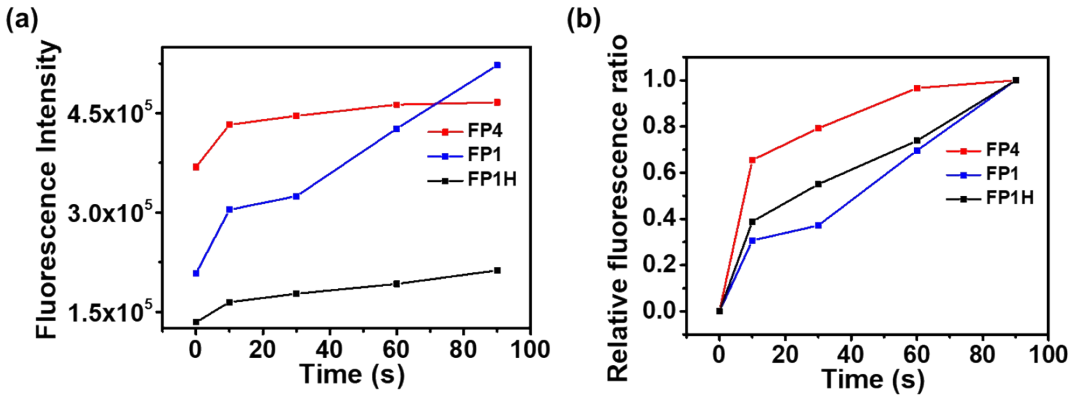


Figure S40. (a) Fluorescence changes and **(b)** changes in fluorescence ratio of **FP4** (red line), **FP1** (blue line) and **FP1H** (black line) under the fumigation of NH_3 vapor.