

Electronic Supplementary Information

Asymmetric thiazolo-thiazole derivative as solvatochromic, reversible and self-color recovery acid-base molecular switch

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EXPERIMENTAL DETAILS

Materials and Methods

All experiments were carried out at room temperature (25 ± 1 °C) unless otherwise mentioned. NMR spectra were measured on a 400 MHz Bruker Avance II 400 spectrometer. NMR spectra were internally referenced to the residual solvent signal at δ 7.26 ppm for CDCl_3 . Absorption spectra were recorded on a Shimadzu UV-Vis spectrophotometer in 3 mL quartz cuvettes having a path length of 1 cm. Fluorescence spectra were recorded on Fluorolog 3-221 fluorimeter equipped with 450 W Xenon lamp. Field effect scanning electron microscopy (FESEM) analysis was carried out in a JEOL JSM-IT 300 Scanning Electron Microscope. A high resolution mass spectrum (HRMS) was measured using Waters Q-TOF Micromass Spectrometer. UV-Vis diffuse reflectance measurements were carried out in the range of 200-800 nm using a Shimadzu UV-2600 spectrophotometer, and BaSO_4 was used as reference. Crystals were observed with an optical microscope (Olympus BX53F).

Aniline, picolyl chloride, potassium oxychloride, triethylamine, trifluoroacetic acid, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) and 2-ethynylpyridine were purchased from TCI Chemicals. Dithiooxamide, hydrochloric acid (35%), sulphuric acid (98%) nitric acid (69%), dimethyl sulfoxide, Polyvinylalcohol (A_v Mw = 60,000) and ammonia was purchased from Sigma-Aldrich. Silica gel (60-120 mesh), methanol, dichloromethane, hexane, acetone and ethyl acetate were purchased locally. Solvents were distilled and dried before use.

Crystallography

Crystals were mounted on Hampton cryoloops. All geometric and intensity data for the crystals were collected using a Super-Nova (Mo) X-ray diffractometer equipped with a microfocus sealed X-ray tube Mo- $K\alpha$ ($\lambda = 0.71073$ Å) X-ray source, and HyPix3000 detector with increasing ω (width of 0.3 per frame)^b at a scan speed of either 5 or 10 s/frame. The CrysAlisPro software was used for data acquisition and data extraction. Using Olex, the structure was solved with the SIR2004 structure solution program using Direct Methods and refined with the ShelXL refinement package using Least Squares minimization. Detailed crystallographic data and structural refinement parameters are summarized in Tables S1-S2 and data can be obtained free of charge from the Cambridge Crystallographic Data Centre.

DFT calculations

DFT calculations were done at the B3LYP level using a triple zeta basis set with new polarization functions. Frequency calculations were also performed and ground state was ensured by the absence of negative frequency. All calculations were performed using ORCA 5.0 an ab-initio, DFT and semi empirical SCF-MO package, which is available as free for the scientific community.

Preparation of PVA-1 film

A clear solution of PVA in DMSO (8 wt%) was prepared by dissolving PVA in DMSO with simultaneous stirring and heating at 80 °C. 1 mg of compound **1** was loaded in a solution of PVA-DMSO (1 mL) and stirred until complete mixing. After complete dissolution, the film was cast in a petridish and left overnight under ambient conditions for drying. The film was then peeled off the glass substrate for further experiments.

Limit of detection with 1

Different concentrations of the acid vapours (HCl) were exposed to the solution of **1** in DMSO, and the limit of detection was calculated by using the Antoine equation, which is derived from the Clausius–Clapeyron equation and gives an interrelationship between vapour pressure and temperature of the pure substances. So, by employing the equation, vapour pressure (P) at different temperatures is calculated for HCl vapours, and the respective concentrations were determined in ppm.

Detection of HCl vapours with PVA-1 film

A simple setup was prepared for detection of HCl vapours with **PVA-1** film by placing the film (1 mm x 1 mm) inside a 15 mL glass vial stoppered with a septum. An amount of 10 mL of HCl (35%) was separately kept in a stoppered conical flask for equilibration after which 0.5 mL of acid vapours in a gas-tight syringe were exposed to the glass vial containing the film. After 5 minutes, the film was taken out, and the emission spectrum was recorded. The same experiment was repeated for multiple cycles.

Synthesis Procedures.

A and **B** were synthesized by following reported procedures.¹

Synthesis of A

To a solution of aniline (0.903 mL, 10 mmol) and potassium hydrogen phosphate (5.22 g, 30 mmol) in acetonitrile (10 mL), 2-(chloromethyl)pyridine hydrochloride (4.57 g, 27.8 mmol) was added portion wise at 0 °C for 30 minutes. The mixture was stirred vigorously and then refluxed at 80 °C for 12 hours. The reaction mixture was quenched with water and extracted with dichloromethane. After evaporation of the solvent, the desired product was obtained as a beige solid after column chromatography on silica with a 1:1 v/v mixture of ethyl acetate and hexane. Yield 0.679 g, 65%. ¹H NMR (400 MHz, CDCl₃), δ (ppm): 4.83 (s, 4H), 6.72-6.71 (m, 3H), 7.17-7.15 (m, 4H), 7.28-7.30 (d, J=8 Hz, 2H), 7.63- 7.61 (t, J=8 Hz, 2H), 8.59-8.60 (d, J=4 Hz, 2H).

Synthesis of B

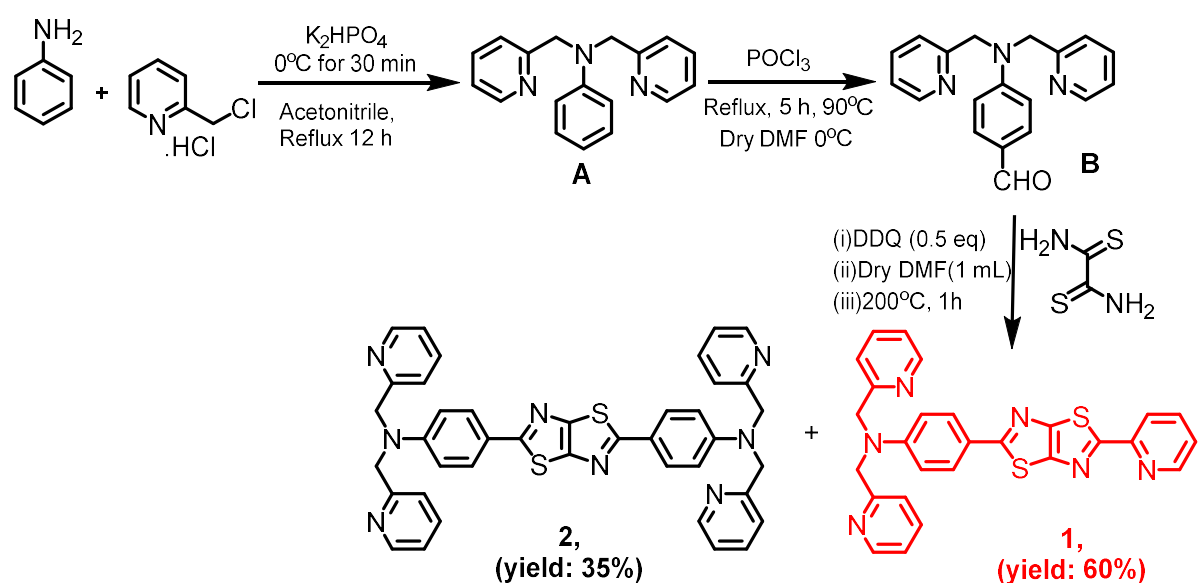
Phosphorus oxychloride (0.163 mL, 1.75 mmol) was mixed with N,N-dimethylformamide (0.550 mL) under N₂ atmosphere and the reaction mixture was stirred for 30 minutes at 0 °C. Compound **A** (0.1 g, 0.36 mmol) was added in portion and refluxed for 12 hours at 90°C. The reaction mixture was quenched by adding ice and further maintained at pH 7 by adding sodium acetate followed by washing with water and extraction with chloroform. The desired product, upon drying, was purified by column chromatography on silica by using hexane:acetone, 5:3 v/v and obtained as a yellow oil. Yield, 0.073 g, 67%. ¹H NMR (400 MHz, CDCl₃), δ (ppm): 4.92 (s, 4H), 6.79-6.77 (d, 2H, J=8Hz), 7.24-7.21 (m, 4H), 7.65-7.69 (m, 4H), 8.62-8.61 (d, 2H, J=4 Hz), 9.73 (s, 1H).

Synthesis of 1

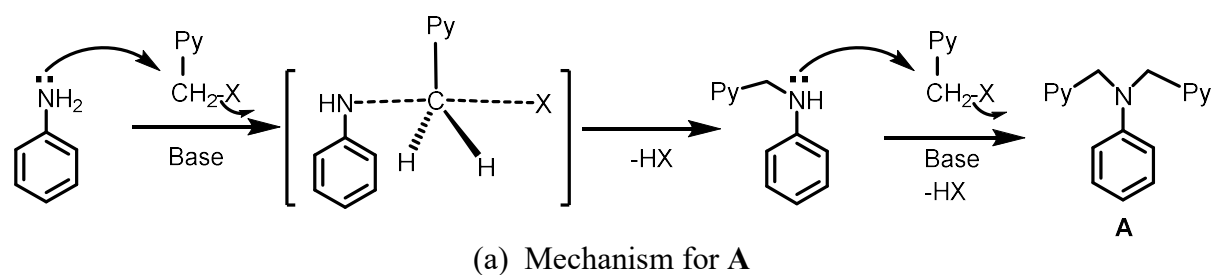
Aldehyde precursor **B** (0.202 g, 0.66 mmol), dithiooxamide (0.020 g, 0.166 mmol) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) were mixed and heated at 200 °C in a sealed tube for one hour. After cooling, the reaction mixture was washed with water and extracted with DCM. After evaporation of the solvent, the desired product (**1**) was obtained as a yellow coloured solid after column chromatography with silica (60-120 mesh) using ethyl acetate: hexane 1:1, v/v. mp: 242°C, Yield 60%. ¹H NMR (CDCl₃), δ (ppm): 4.84 (s, 4H), 6.71-6.73 (d, J=8 Hz, 2H), 7.12-7.15 (m, 4H), 7.23-7.27 (m, 1H), 7.56-7.60 (d, J=16 Hz, 2H), 7.73-7.75 (m, 3H), 8.10-8.12 (d, J=8 Hz, 1H), 8.54-8.55 (m, 3H). ¹³C-NMR (CDCl₃), δ (ppm): 57.24, 112.59, 120.81, 122.32, 123.49, 127.74, 136.99, 149.47, 149.85, 149.91, 157.96, 168.49. HRMS (m/z): expected [M⁺+H], 493.1291, observed, 493.1298.

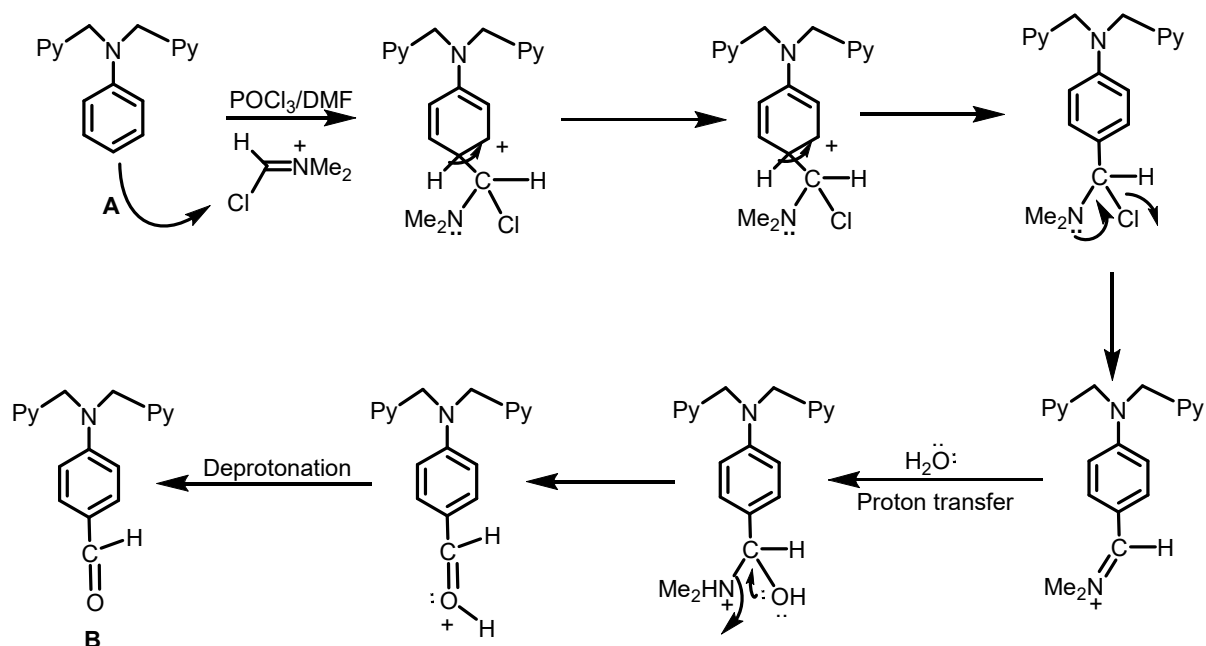
Synthesis of 2

Compound **2** was also obtained using above procedure and purified from the last fraction of column chromatography with 9.7:0.3 v/v dichloromethane: methanol. mp: 221°C, Yield 35%. ¹H NMR (CDCl₃), δ (ppm): 4.82 (s, 8H), 6.68-6.70 (d, J=8 Hz, 4H), 7.11-7.17 (m, 8H), 7.56-7.70 (m, 4H), 7.68-7.70 (d, J=8 Hz, 4H), 8.54-8.55 (d, J=4 Hz, 4H). ¹³C-NMR (CDCl₃), δ (ppm): 52.55, 111.59, 118.36, 119.76, 121.32, 123.56, 127.10, 135.94, 148.74, 148.90, 149.41, 156.84. HRMS (m/z): expected [M⁺], 688.2191, observed, 688.3458.



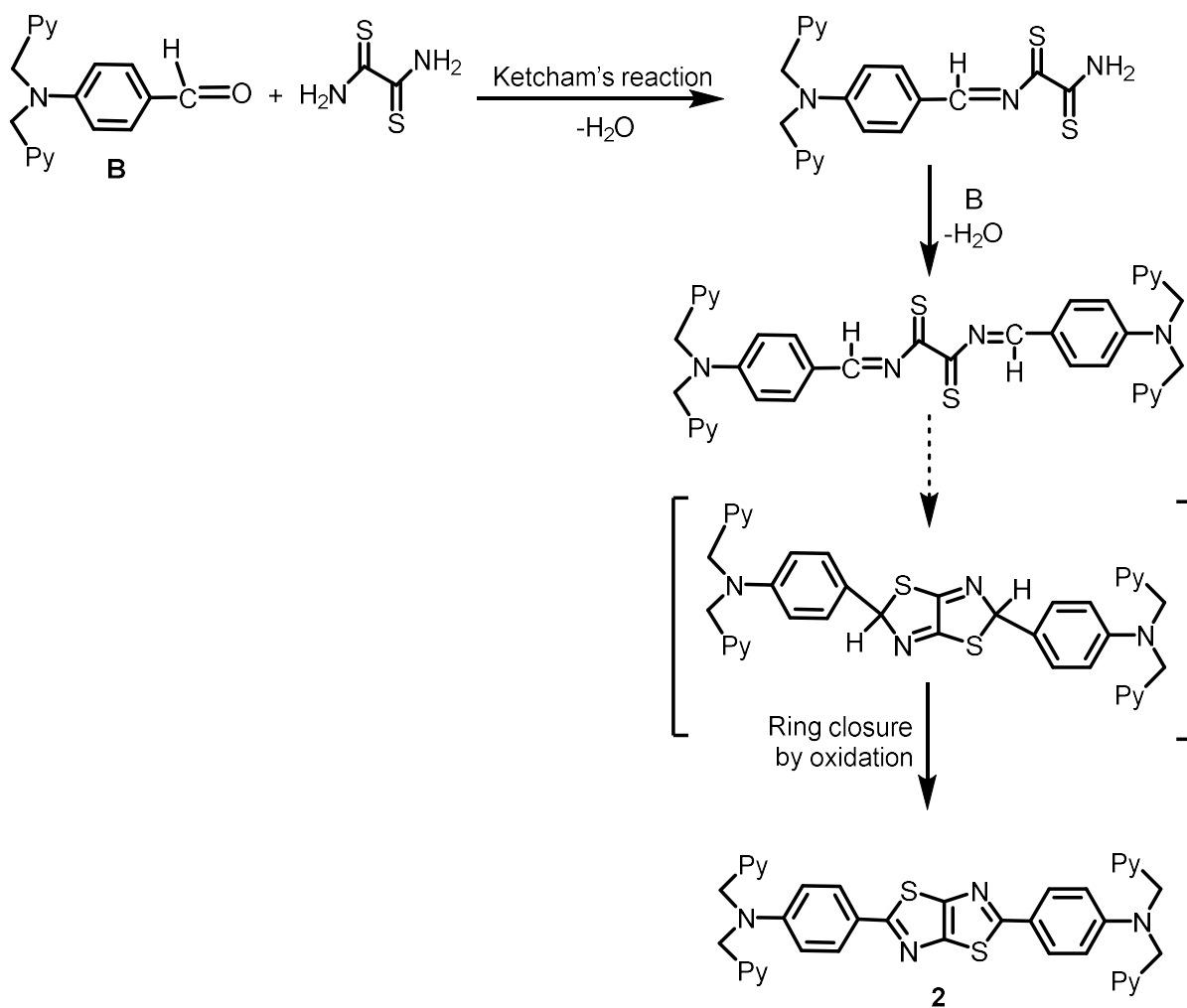
Scheme S1. Synthesis of **A**, **B** and compounds **1**, **2**.



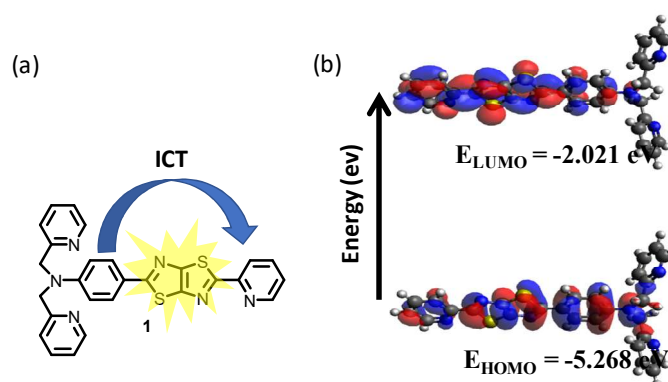


(b) Mechanism for **B**

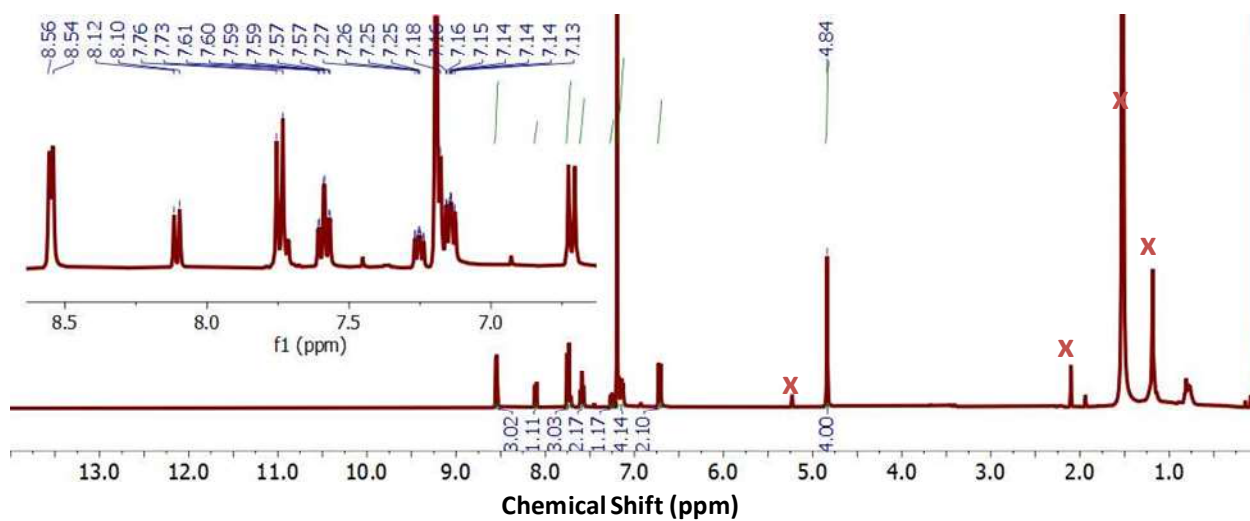
Synthesis of compound **2**, followed by Ketcham reaction, involves the intramolecular two-fold condensation reaction of aldehyde with amine moiety, followed by oxidation to form the thiazolothiazole fused aromatic system.² For **1**, it is hypothesized that a fraction of the *N,N*-bis(pyridine-2-ylmethyl)benzenamine undergoes oxidation to produce pyridine-2-aldehyde (in-situ) which may further involve in Ketcham reaction to yield asymmetric compound **1**.



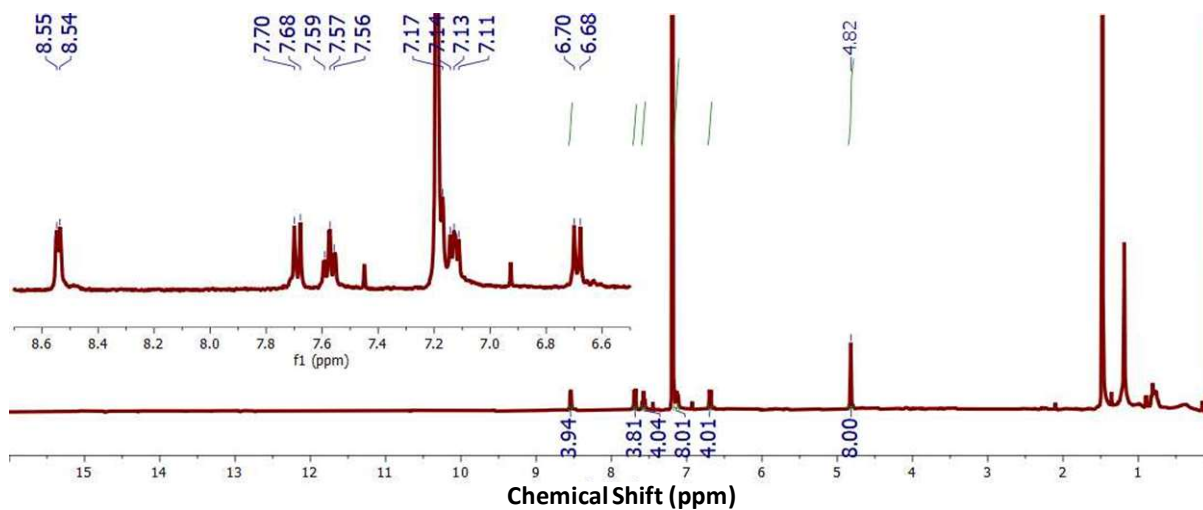
Scheme S2. Mechanistic steps for (a) **A**, (b) **B** and (c) **2**.



Scheme S3. (a) ICT properties of compound **1**. (b) Representation of HOMO and LUMO of **1**.

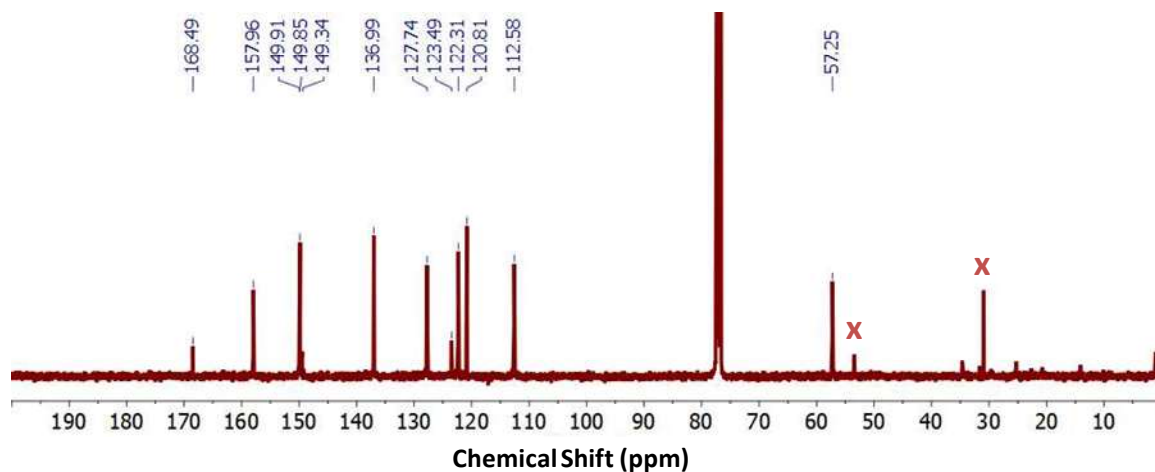


(a)

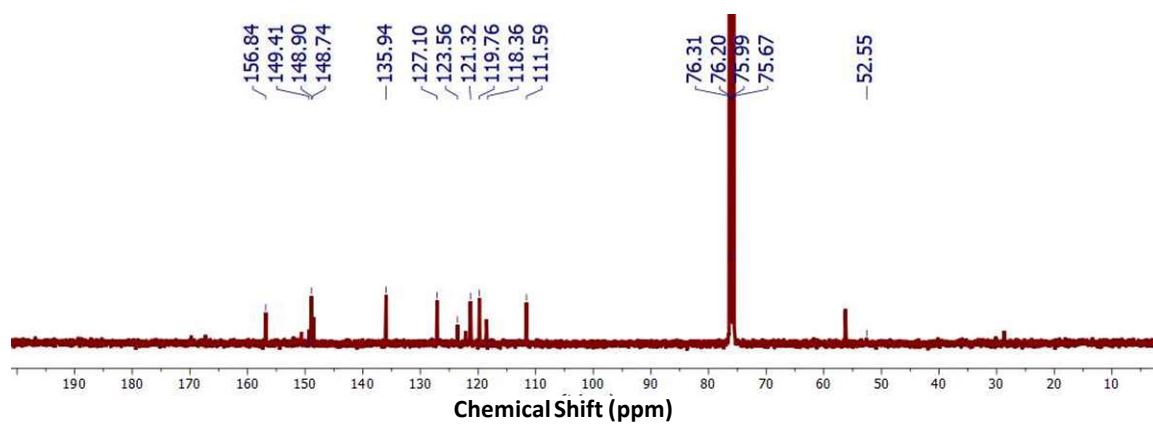


(b)

Fig. S1. ^1H NMR spectra of (a) **1** and (b) **2**, in CDCl_3 at 298K.



(a)



(b)

Fig. S2. ^{13}C NMR spectra of (a) **1** and (b) **2**, in CDCl_3 at 298K.

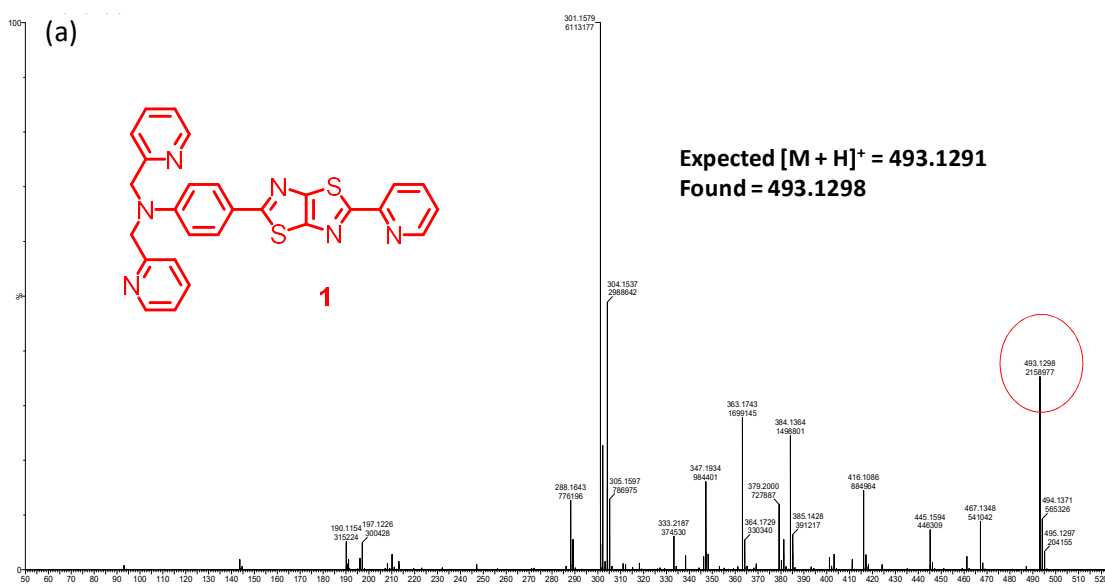




Fig. S3. HRMS spectra of (a) **1**; (b) **2**.

Table S1. Crystallographic data collection and refinement parameters for **1**.

CCDC	2337834
Empirical formula	C ₂₇ H ₂₀ N ₆ S ₂
Formula weight	492.1191
Temperature/K	293(2)
Crystal system	Monoclinic
Space group	P 21/c
a/Å	9.9125(3)
b/Å	6.0776(2)
c/Å	38.9095(12)
α/°	90
β/°	96.144(3)
γ/°	90
Volume/Å ³	2330.61(13)
Z	4
ρ _{calc} /cm ³	1.453
μ/mm ⁻¹	0.258

F(000)	1744
Crystal size/mm ³	0.25 x 0.15 x 0.15
Radiation	MoK α ($\lambda = 0.71073$)
2 Θ range for data collection/ $^{\circ}$	3.393-27.385
Index ranges	-12 \leq h \leq 12, -7 \leq k \leq 7, -48 \leq l \leq 49
Reflections collected	4736
Data/restraints/parameters	2767/0/316
Goodness-of-fit on F ²	1.015
Final R indexes [$I \geq 2\sigma(I)$]	R ₁ = 0.1049, wR ₂ = 0.1112
Final R indexes [all data]	R ₁ = 0.0546, wR ₂ = 0.0.1336

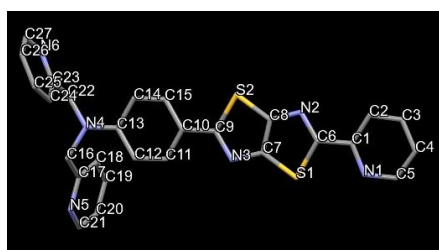


Table S2. Selected bond lengths (\AA) and bond angles ($^{\circ}$) for **1** derived experimentally from single crystal data.

Bond length (\AA) _{Exp}		Bond angle ($^{\circ}$) _{Exp}	
C5-N1	1.341	C1 N1 C5	116.62
N1-C1	1.330	C6 N2 C8	107.41
C1-C2	1.373	C6 S1 C7	87.79
C2-C3	1.375	C7 N3 C9	108.71
C3-C4	1.360	C8 S2 C9	88.33
C4-C5	1.371	C13 N4 C22	119.90
C1-C6	1.468	C13 N4 C16	121.62
C6-S1	1.741	C16 N4 C22	117.52
S1-C7	1.719	C17 N5 C21	116.44
C7-C8	1.361	C23 N6 C27	116.73
N2-C8	1.369	C6 C1 N1	114.78
N2-C6	1.312	C6 C1 C2	121.54
N3-C7	1.364	N4 C22 C23	114.84
N3-C9	1.322	N4 C16 C17	114.42

C9-S2	1.748	S2 C9 C10	121.45
C9-C10	1.458	C15 C10 C9	122.55
C10-C11	1.390	N2 C6 C1	124.08
C11-C12	1.371	S1 C6 C1	118.78
C12-C13	1.399	N2 C6 S1	117.14
C13-C14	1.398	N2 C8 C7	117.91
C14-C15	1.370	S2 C8 C7	109.85
C10-C15	1.385	C8 C7 S1	109.75
C13-N4	1.380		
N4-C22	1.448		
N4-C16	1.452		
N5-C17	1.335		
C17-C18	1.369		
N5-C21	1.339		
C19-C20	1.365		
C20-C21	1.352		
N6-C23	1.334		
N6-C27	1.341		
C22-C23	1.510		

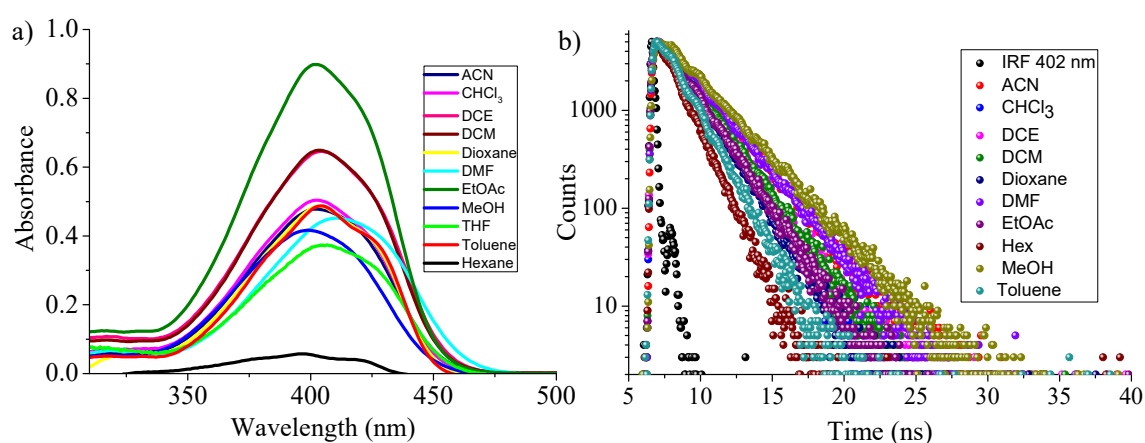


Fig. S4. Absorption spectra of **1** (2×10^{-6} M) in different solvents. (b) Lifetime profiles collected at 530 nm of **1** in different solvents. ($\lambda_{\text{ex}} = 400$ nm)

Table S3. Fluorescence quantum yield **1** in different solvents.

S. No.	Quantum yield
Toluene	0.51
Chloroform	0.89
Dichloromethane	0.88
Dichloroethane	0.83
Ethyl acetate	0.6
Methanol	0.46
Dioxane	0.46
Acetonitrile	0.55
Dimethyl formamide	0.5

Table S4. Lifetime measurements for **1** in different solvents.

Solvent	Life-time (ns)	Relative amplitude	X
Dimethyl formamide	T1 = 0.42 ± 0.08 ns	4.77%	1.350609
	T2 = 2.4 ± 0.01 ns	95.23%	
Methanol	T1 = 0.32 ± 0.01 ns	2.6%	1.787984
	T2 = 2.7 ± 0.02 ns	97.4%	
Acetonitrile	T1 = 2.1 ± 0.33 ns	26.66%	0.863867
	T2 = 2.34 ± 0.09 ns	73.34%	
Tetrahydrofuran	T1 = 0.48 ± 0.07 ns	6.11%	0.695372
	T2 = 1.97 ± 0.01 ns	93.89%	
Dichloroethane	T1 = 0.34 ± 0.02 ns	10.45%	0.806833
	T2 = 2.05 ± 0.011 ns	89.55%	
Dichloromethane	T1 = 0.48 ± 0.07 ns	5.89%	0.983768
	T2 = 2.07 ± 0.01 ns	94.11%	
Chloroform	T1 = 0.44 ± 0.05 ns	6.08%	0.851932
	T2 = 1.92 ± 0.01 ns	93.92%	
2,4-Dioxane	T1 = 0.27 ± 0.03 ns	4.17%	0.736871
	T2 = 1.78 ± 0.01 ns	95.83%	

Ethyl acetate	T1 = 0.47 ± 0.06 ns	7.49%	0.85648
	T2 = 1.91 ± 0.01 ns	92.51%	
Toluene	T1 = 0.48 ± 0.09 ns	9.69%	1.821132
	T2 = 1.54 ± 0.02 ns	90.31%	
Hexane	T1 = 0.49 ± 0.07 ns	10.11%	0.643263
	T2 = 1.3 ± 0.01 ns	89.89%	

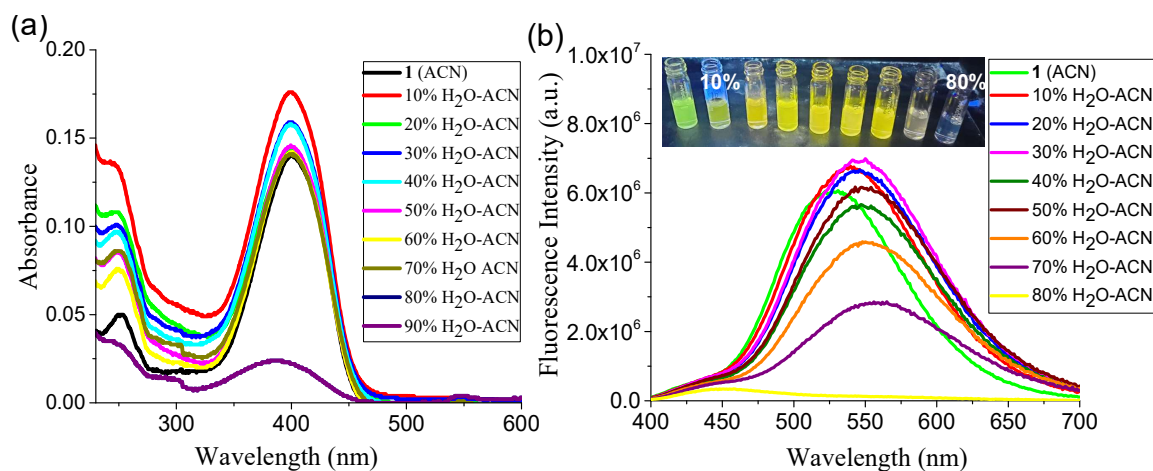


Fig. S5. Changes in the (a) absorption and (b) emission spectrum of **1** (6.6×10^{-6} M) with increasing concentration of water in acetonitrile: water mixtures. (λ_{ex} : 385 nm)

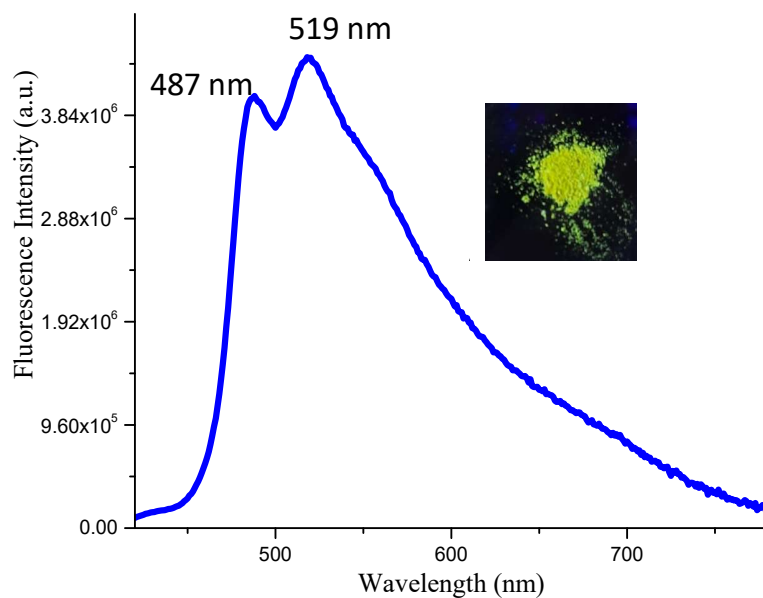


Fig. S6. Solid state emission spectrum of **1** (λ_{ex} : 400 nm). Inset shows the photograph of **1** in UV light.

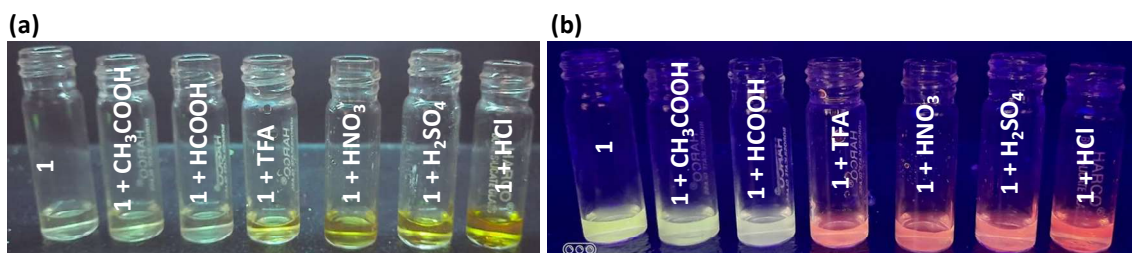


Fig. S7. Photographs of solution of **1** (9:1 H₂O:DMSO) after the addition of equimolar solutions of different acids under (a) normal light and (b) UV light.

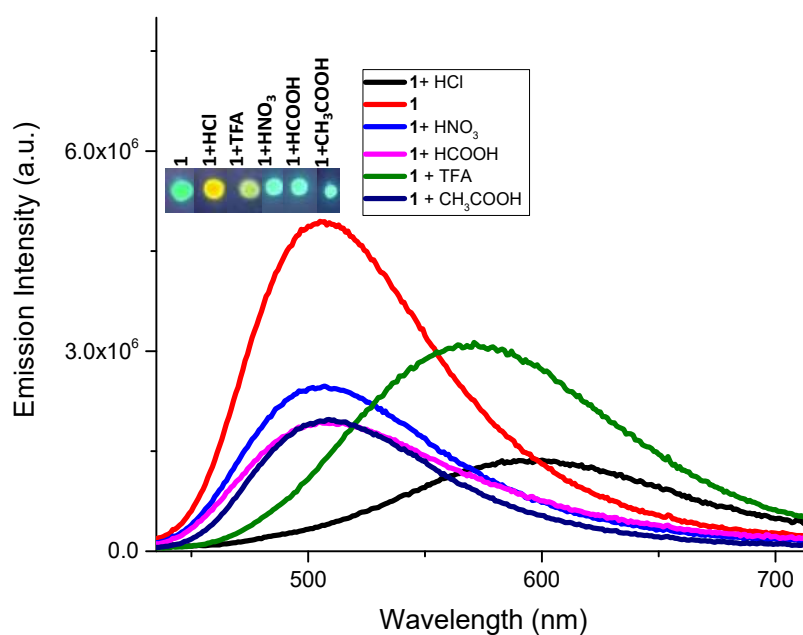


Fig. S8. Emission spectra of compound **1** (50 μM) (adsorbed on silica plate) exposed to vapour of various acid (HCl, HNO₃, TFA, for 5 sec and HCOOH, CH₃COOH for 2 min, respectively). Inset: Photographs of **1** covered on TLC plates before and after fumed with vapour of HCl, TFA, HNO₃, for 5 sec and HCOOH, CH₃COOH for 2 min, under UV illumination (365 nm).

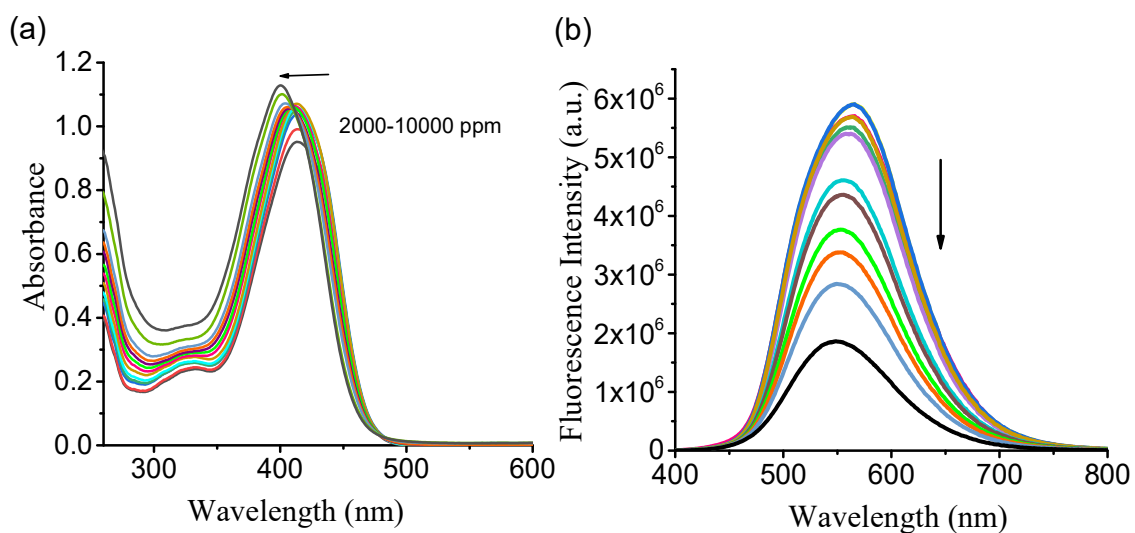


Fig. S9. Change in the absorption and emission spectra of **1** in DMSO (3.8×10^{-6} M) as a function of varying amounts of HCl vapours ranging from 2000-10000 ppm. (λ_{ex} : 385 nm)

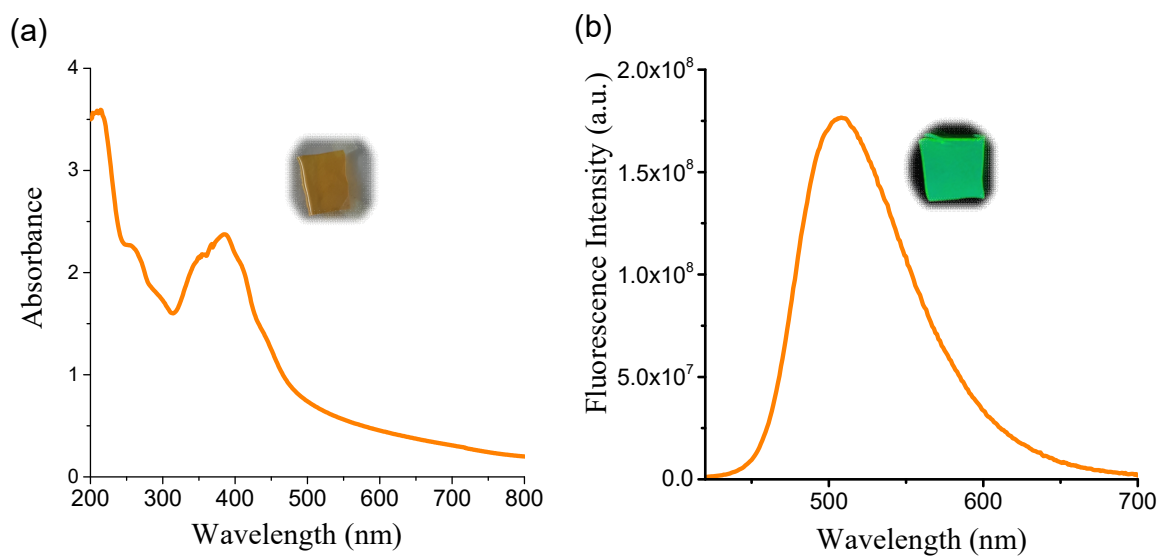


Fig. S10. (a) Solid-state absorption and (b) emission spectra of **PVA-1** film. (λ_{ex} : 380 nm)

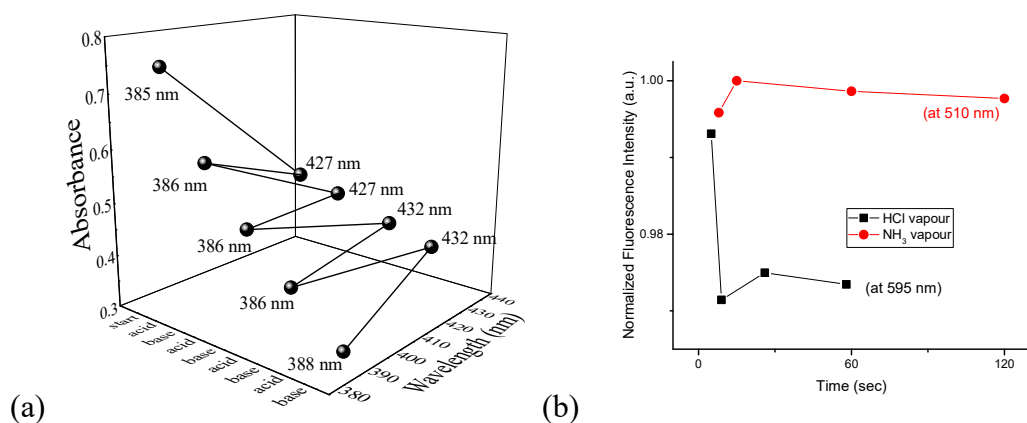


Fig. S11. (a) Change in absorbance of the PVA-1 film during the acid and base vapour exposure cycles. (b) Influence of response time on the fluorescence intensity of PVA-1 in the presence of HCl and NH₃ vapour.

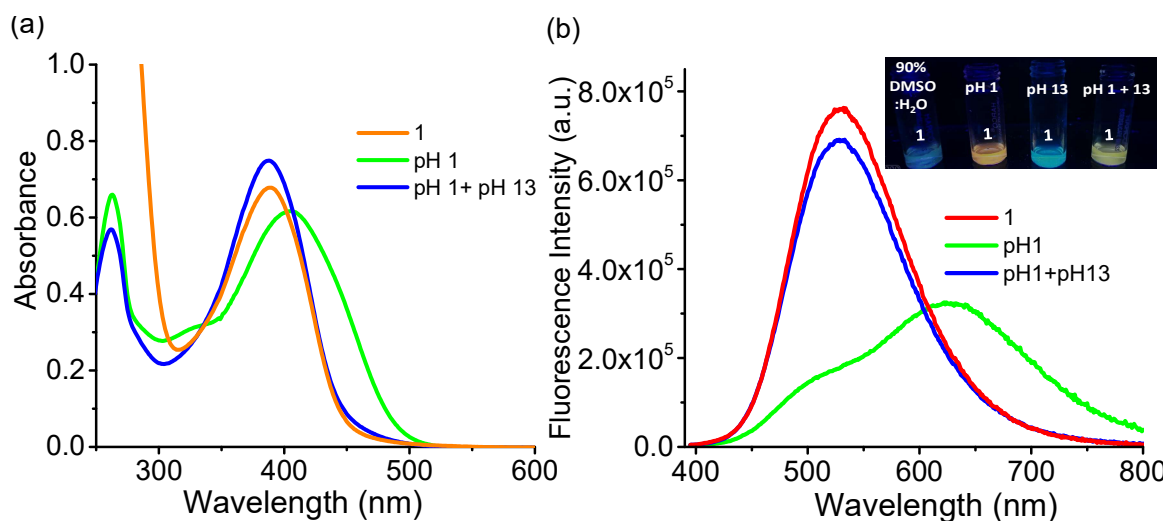


Fig. S12. Change in the absorption and emission spectra of compound 1 (2.9×10^{-5} M) in DMSO-water upon exposure to equivalent amounts of HCl and ammonia vapours. (λ_{ex} : 385 nm)

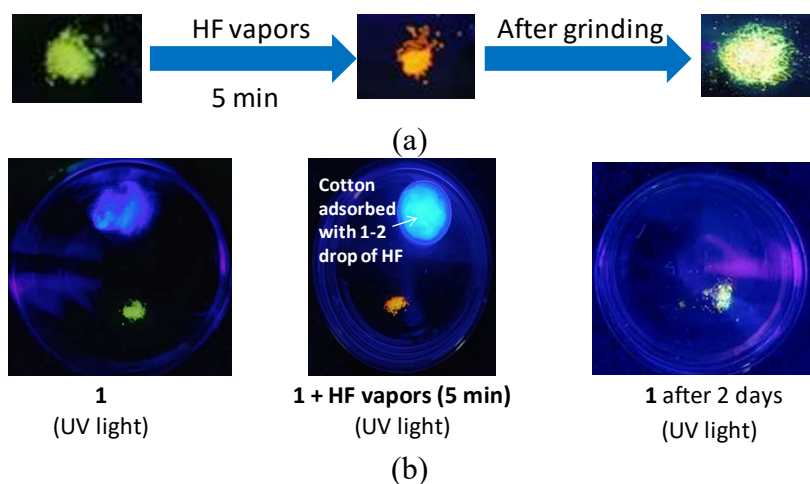


Fig. S13. Investigation of (a) mechanochromic and (b) self-colour recovery of **1** in powder form using HF vapors.

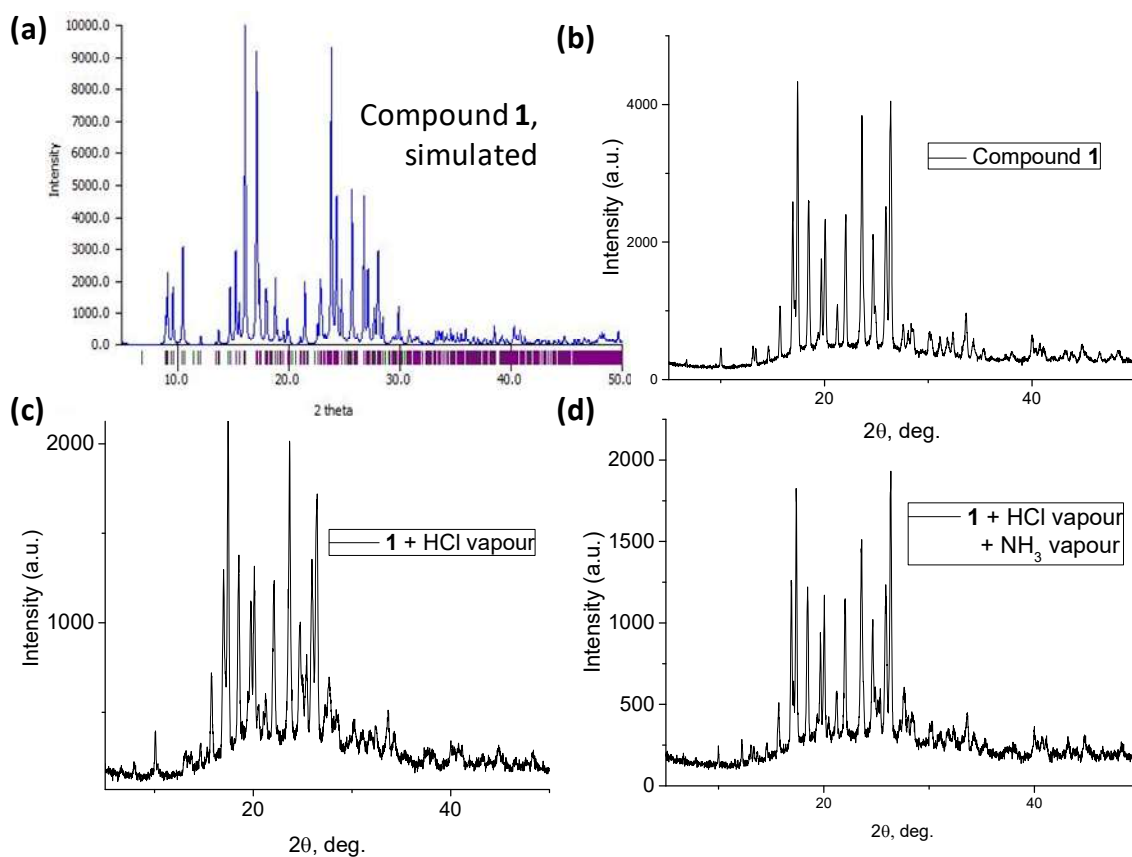


Fig. S14. (a) Simulated and (b) experimental powder X-ray diffraction (PXRD) spectra of **1**. PXRD pattern of **1** in the presence of (c) HCl and (d) NH₃ vapours.

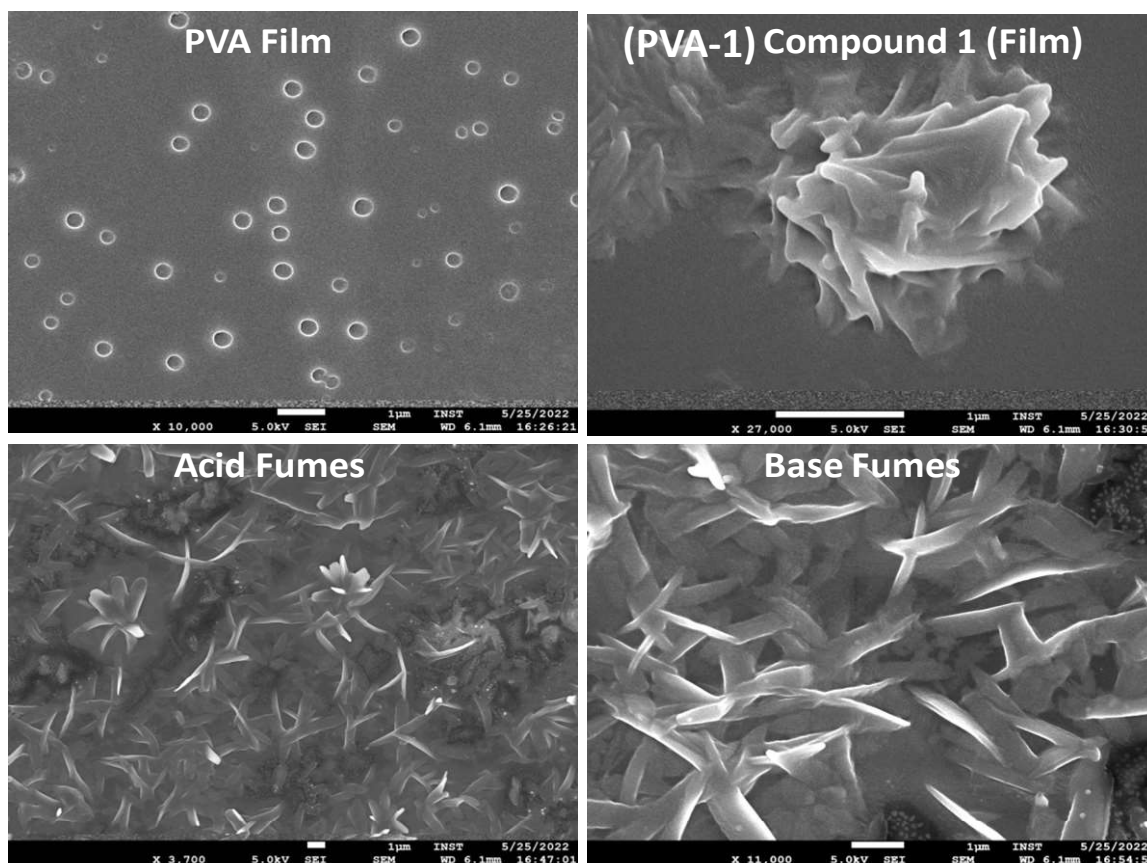


Fig. S15. FESEM images showing the morphology of (a) PVA, (b) PVA-1 film and PVA-1 film after exposure to (c) HCl vapours and (d) followed by exposure to ammonia vapours.

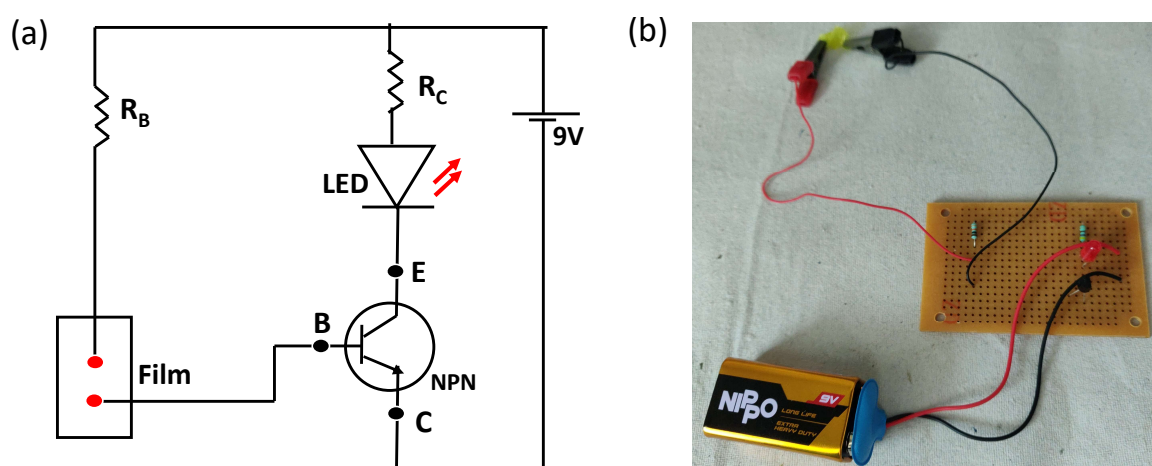


Fig. S16. (a) Schematics and (b) photograph of the electronic prototype for HCl vapour detection (E, emitter terminal; B base terminal; C, collector terminal of the NPN transistor) using PVA-1 film.



Media1.mp4

Video S1. Demonstration of the prototype for detection of HCl vapours using **PVA-1** film.

[Video S2.mp4](#)

Video S2. Control experiment for detection of HCl vapours using **PVA** film (without compound **1**).

References

1. S. Shah, N. Naithani, S. C. Sahoo, P. P. Neelakandan and N. Tyagi, *J. Photochem. Photobiol. B: Biol.*, 2023, **239**, 112631.
2. Z. Tokarova, R. Gasparova, N. Kabanova, M. Gasparova and R. Balogh, *Reactions* **2023**, 4(2), 254-273.