

Electronic supplementary information

Visual detection and efficient capture of hydrogen chloride and ammonia vapours by a sustainable dual emissive metal-organic framework

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Experimental section

Chemicals

Immensely fresh $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, imidazole, dichloromethane, tetrabutylammonium bromide have been acquired from the Sigma-Aldrich Chemical Co. All other reagents and solvents have been bought from commercial sources and used except further clarification. di(1*H*-imidazol-1-yl)methane¹ have been synthesized by a reaction between dichloromethane and imidazole in presence potassium hydroxide and tetrabutylammonium bromide (TBAB) at 40 °C in inert atmosphere condition. Na_2 -dht has been synthesized by the sluggish collation of solid NaOH to the analogous acid (H_2 -dht) in water in a 2:1 ratio and allowed to evaporate until dryness.

Physical measurements

Elemental analyses (C, H, N) have been performed using a PerkinElmer 240C elemental analyzer. FT-IR spectra have been obtained on a PerkinElmer spectrometer (Spectrum II) with the samples. PerkinElmer STA8000 thermal analyzer has been used for thermogravimetric analysis (TGA) with a ramp rate of 10 °C/min from room temperature to 600 °C under nitrogen flow. Powder X-ray diffraction (PXRD) data were collected on a Bruker D8 Discover instrument with Cu-K α radiation ($\lambda = 1.5406 \text{ \AA}$), operating at 40 kV and 40 mA. UV-vis spectra are collected in PerkinElmer Lambda 35 instrument with integrating sphere attachment. Fluorescence measurements were done using HoribaFluoroMax 4 spectrofluorimeter.

Sorption measurements

Quantachrome Autosorb- iQ adsorption instrument have been used to measured adsorption isotherms N_2 (77 K) for the dehydrated frameworks of **1**. Very pure N_2 gas (99.999% purity) has been used for this measurement. The N_2 (at 77 K, liquid nitrogen bath) sorption measurement has been carried out in the pressure range 0–1 bar using dehydrated samples of **1**. Before measurements, all the as-synthesized complexes (40 mg for each) have been dehydrated in the sample tube at 413 K for 3 h under a 1×10^{-1} Pa vacuum. By controlled introducing ultra-pure helium gas (99.999% purity) into the sample tube and allowing it to diffuse into the sample, the dead volume has been measured. The gas adsorption volume for each and every measurement has been calculated from the difference of pressure ($P_{\text{cal}} - P_e$), where P_{cal} signifies the calculated pressure without any gas adsorption and P_e indicates the observed pressure at equilibrium. The pressure change has been monitored by taking the adsorbent in the sample tube, and the degree of adsorption was calculated by observing the decrease in pressure at equilibrium.

Synthesis

Compound 1

After deprotonation of H_2 -dht in aqueous solution by NaOH (2 mmol, 80 mg), the resulting 20 ml solution of Na_2 -fum (1 mmol, 160 mg) was slowly mixed with a methanolic solution (20 mL) of di(1*H*-imidazol-1-yl)methane (1 mmol, 148 mg) and stirred for 20 min to mix well. slowly and carefully, 4ml aqueous solution of Zn(II) from 20 mL aqueous solution of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (1 mmol, 0.297 g) was layered with 6 mL of the aforesaid mixed-ligand solution by using 5 mL of buffer (1:1 water/ MeOH mixture). At the juncture of the solution block-shaped single crystals appropriate for X-ray diffraction analysis were form in the layer tube after 4 days. The crystals were collected, washed with MeOH, and dried under air to separate for experiments. Yield: 96%.

Elemental analysis, calculated for $C_{16}H_{16}N_4O_9Zn$ (473.65): C 40.53; H 3.4; N 11.9; O 30.4; Zn 13.8; Found: C 40.28; H 3.32; N 11.73; O 30.25; Zn 13.68.

Compound 1'

Compound 1' has been prepared by the removing of lattice water and methanol molecules from compound 1 by utilizing the heat at 120 °C for 5 minutes.

Crystallographic data collection and refinement

The X-ray single-crystal data for complex 1 has been collected at room temperature in a Bruker made APEX III diffractometer. At first, single crystals of both the compounds have been isolated and then mounted on the glass fiber tip using commercial super glue. Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$) from a sealed tube X-ray source has been used. The raw data have been integrated using the SAINT² program and by utilizing SADABS,³ the absorption corrections were performed. The structures have been solved by SHELXL-2016/6,⁴ and full-matrix least-squares refinements on F^2 for all non-hydrogen atoms were performed by SHELXL-2016/6,⁴ with anisotropic displacement parameters. All the calculations and molecular graphics were done by SHELXL-2016/6,⁴ PLATON v1.15,⁵ WinGX system Ver-1.80,⁶ Diamond v3.2, Mercury,⁷ and TOPOS.^{8,9} All the crystallographic data and structural refinement parameters for the compound 1 has been mentioned in Table S1. CCDC 2351712 contain the supplementary crystallographic data for this paper.

Table S1. Crystallographic data of compound 1

	1
Formula	$C_{16}H_{16}N_4O_9Zn$
Formula weight	473.65
Crystal system	Triclinic
Space group	P-1
$a/\text{\AA}$	8.0263(14)
$b/\text{\AA}$	8.9753(15)
$c/\text{\AA}$	13.924(3)
$\alpha/^\circ$	95.081(5)
$\beta/^\circ$	93.392(5)
$\gamma/^\circ$	92.034(5)
$V/\text{\AA}^3$	996.5(3)
Z	2
$D_c/\text{g cm}^{-3}$	1.552
μ/mm^{-1}	1.288
F_{000}	468
ϑ range/ $^\circ$	2.6, 27.5
Reflections collected	35191
Unique reflections	4576
Reflections $I > 2\sigma(I)$	4083
R_{int}	0.045
Goodness-of-fit (F^2)	1.09
$R_1(I > 2\sigma(I))$ ^[a]	0.0434
$wR_2(I > 2\sigma(I))$ ^[a]	0.1352
$\Delta\rho$ min / max / e \AA^3	-0.47, 1.01

$$^{[a]}R_1 = \frac{\sum |F_o| - |F_c|}{\sum |F_o|}, wR_2 = \left[\frac{\sum (w(F_o^2 - F_c^2)^2)}{\sum w(F_o^2)^2} \right]^{1/2}$$

IR spectroscopy study

IR spectra (KBr pellet, 4000–400 cm^{-1}) (Fig S1): $\nu(\text{O-H})$, 3124 (stretch, H-bonded); 3007 (stretch); $\nu(\text{C-H, imidazole})$, 3007 (stretch); $\nu(\text{C-H, alkane})$, 1416 (bending); $\nu(\text{C-C, imidazole})$, 1539–1487 (stretch); and $\nu(\text{C-O})$, 1235 (stretch).

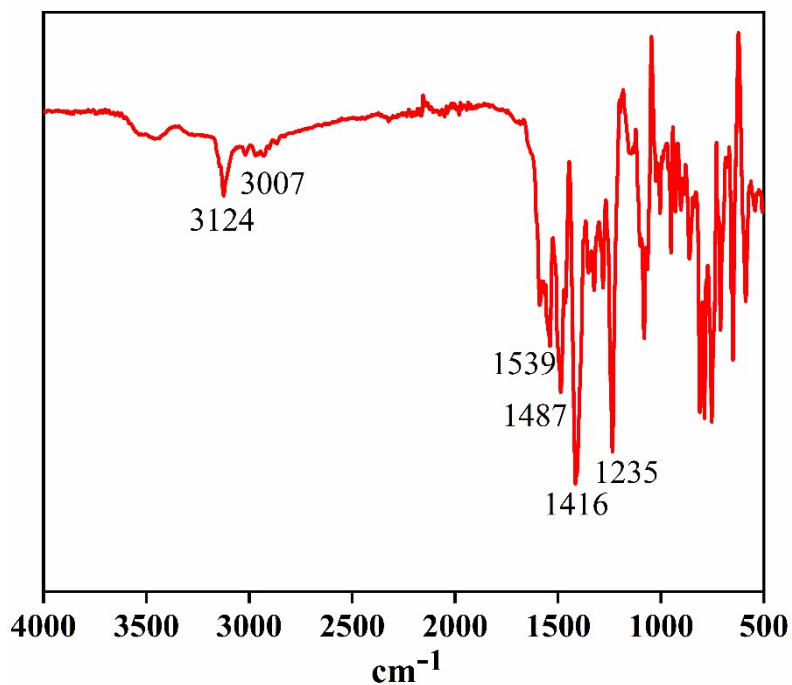


Fig S1. IR spectra of compound 1'

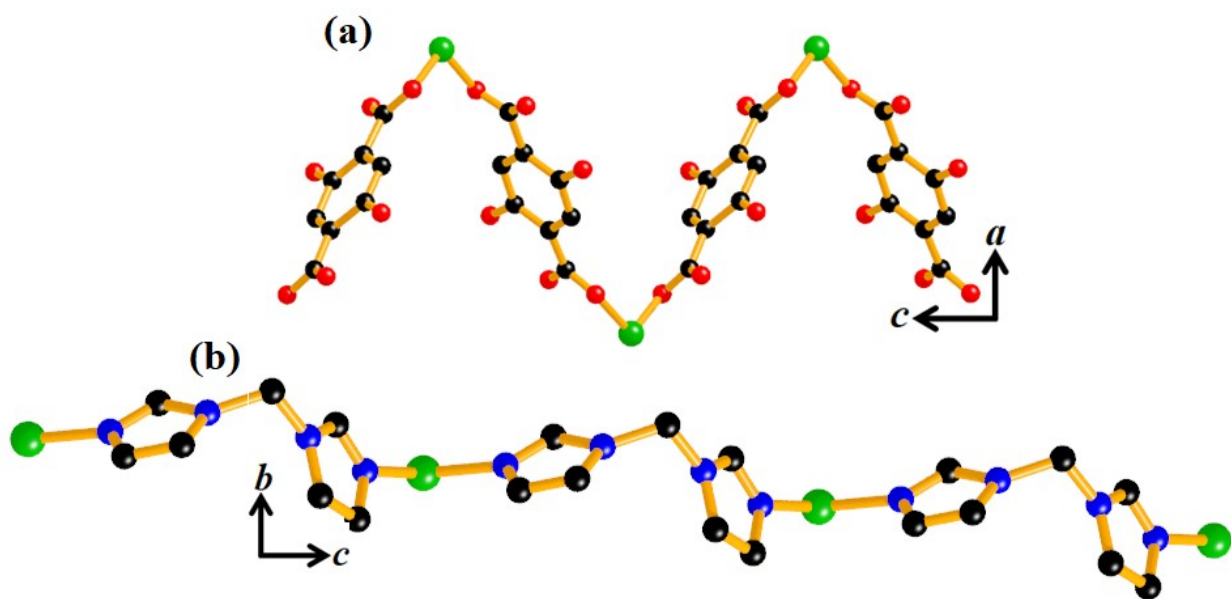


Fig. S2 (a) 1D of compound 1 by acidic linker (b) 1D of compound 1 by neutral linker.

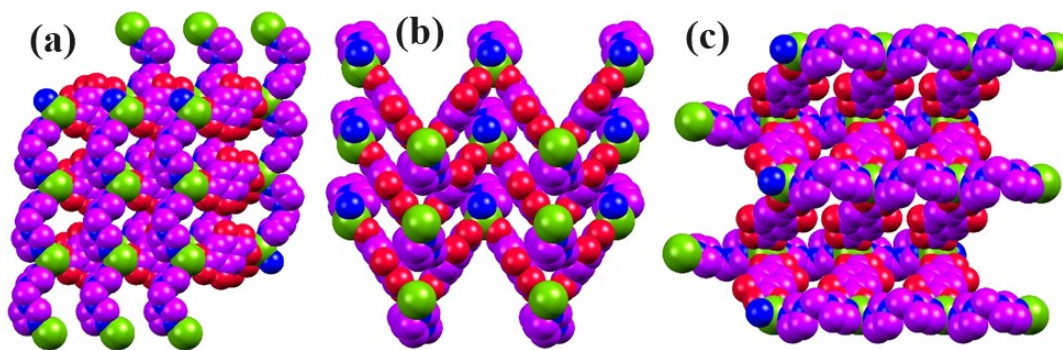


Fig. S3 Space fill model of compound 1' (a) in *a* direction (b) in *b* direction (c) in *c* direction.

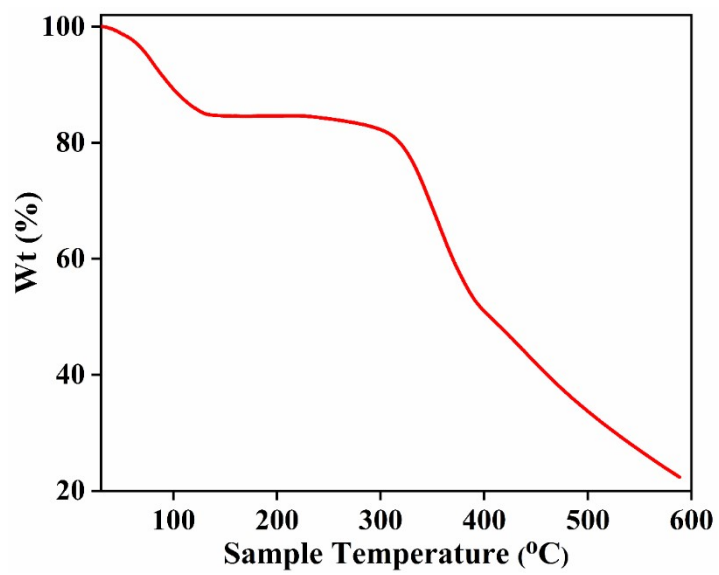


Fig. S4 TGA of compound 1.

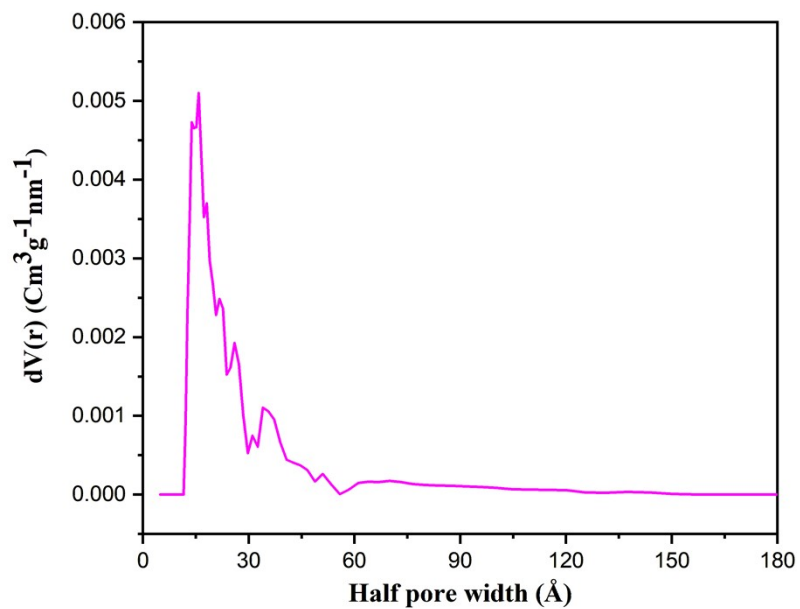


Fig. S5 NL-DFT pore size distribution curve of 1'.

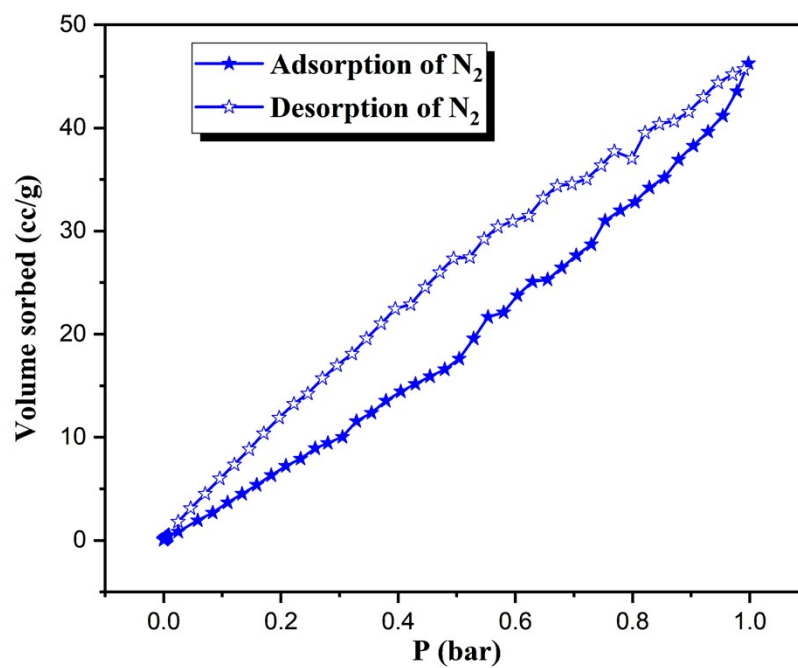


Fig. S6 N₂ adsorption and desorption of compound 1'.

UV-visible spectroscopy study

Maxima of UV-visible spectroscopy of compound **1'**, after capturing HCl and ammonia vapours by compound **1'** have been observed at 370 nm wavelength respectively. The intensities of absorbance increase due to feasible electronic transition after the capturing of these vapours of the compound **1'** framework.

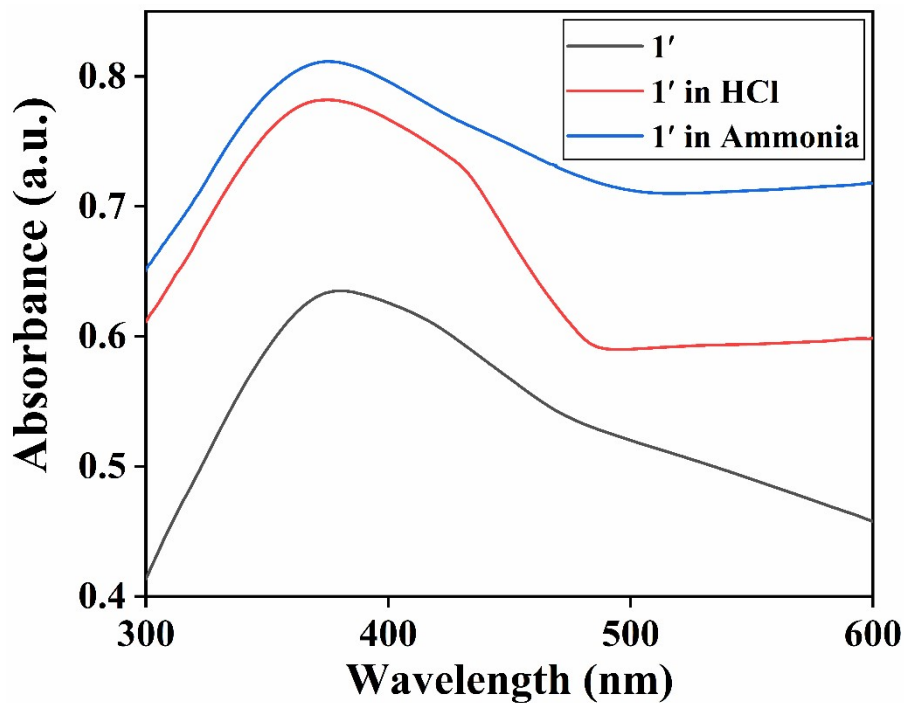


Fig. S7 UV-vis spectra of compound **1'**, compound **1'** in HCl vapour and compound **1'** in NH₃ vapour.

Table S2. Selected bond lengths (Å) and bond angles (°) for complex **1**.

Zn1-O1	1.957(3)
Zn1-O4	1.966(3)
Zn1-N1	2.009(3)
Zn1-N4 ^o	2.013(3)
O1-Zn1-O4	105.06(10)
O1-Zn1-N1	117.94(11)
O1-Zn1-N4 ^o	104.01(11)
O4-Zn1-N1	106.15(11)
O4-Zn1-N4 ^o	123.42(10)
N1-Zn1-N4 ^o	101.27(10)

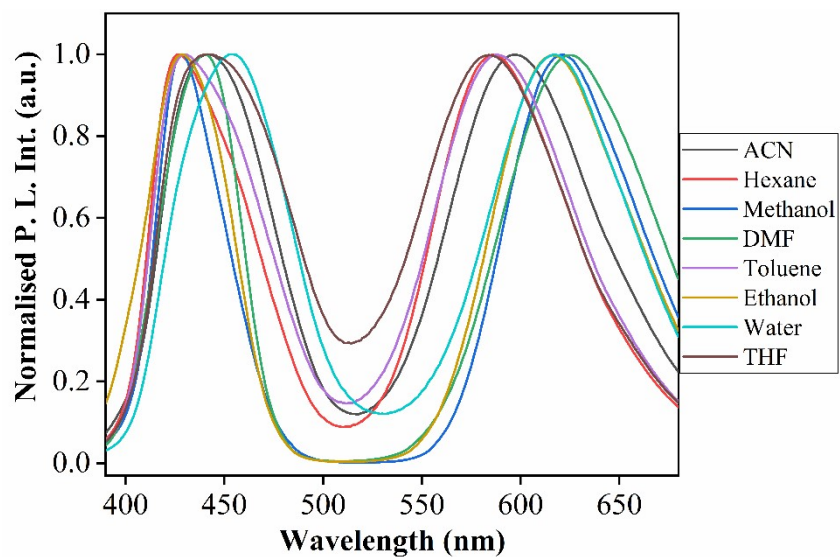


Fig. S8 Emission ($\lambda_{\text{ex}} = 370 \text{ nm}$) spectral changes of **1'** in different solvent. During the experiment concentration of the sample was taken 10^{-5} (M) and the fine suspensions are prepared by taking powder sample of **1'** in each solvent, stirred with micro-magnetic bar in magnetic stirrer for 5 minutes.

Table S3. Emission maxima of compound **1'** in different solvents

1' in different solvent	Maxima of enol form (nm)	Maxima of keto form (nm)
ACN	441	597
Hexane	426	584
Methanol	429	622
DMF	440	624
Toluene	429	588
Ethanol	428	616
Water	454	617
THF	441	584

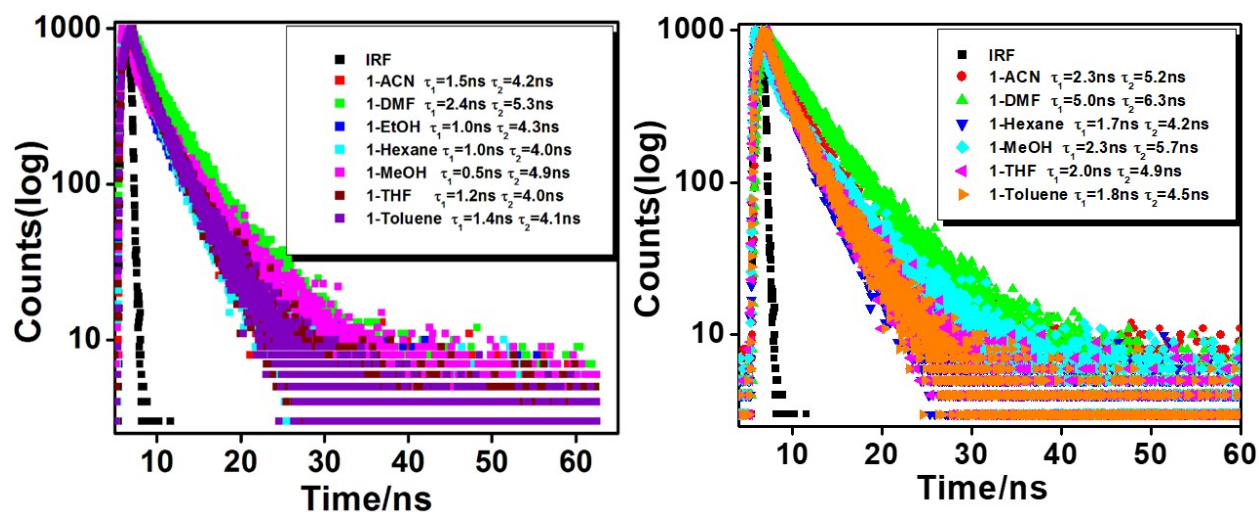


Fig. S9 Excited state decay profile of $1'$ ($\lambda_{\text{ex}} = 370$ nm) in different solvents at room temperature upon monitoring emission in the range of 427- 465nm (enol form). Excited state decay profile of $1'$ ($\lambda_{\text{ex}} = 370$ nm) in different solvents at room temperature upon monitoring emission in the range of 571-617nm (Keto form).

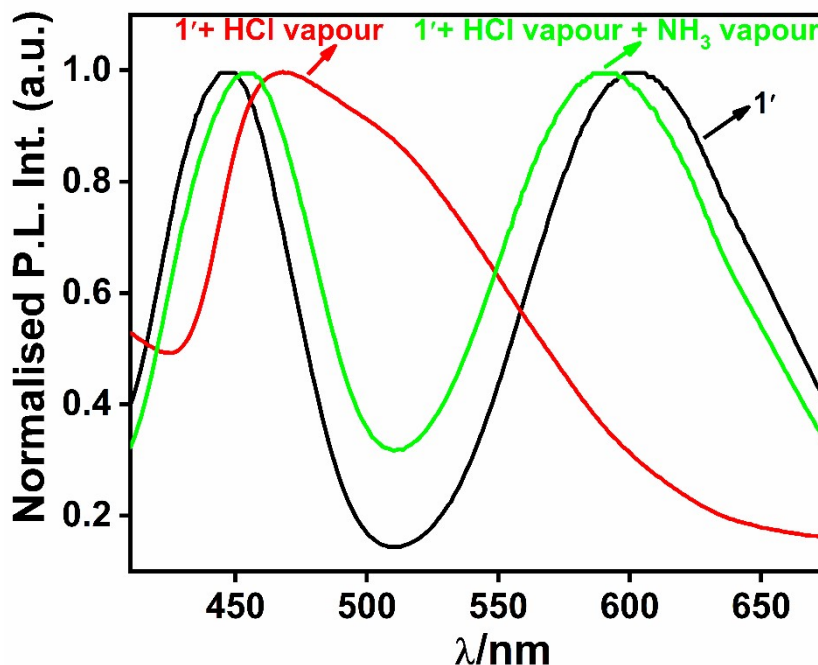


Fig. S10 Emission ($\lambda_{\text{ex}} = 370$ nm) spectral changes of $1'$ in presence of HCl vapour and followed by NH_3 vapour in solid state to check reversibility. The reversibility has been checked for three consecutive cycles and the data collected after the third cycle leaching NH_4Cl each time with distilled water.

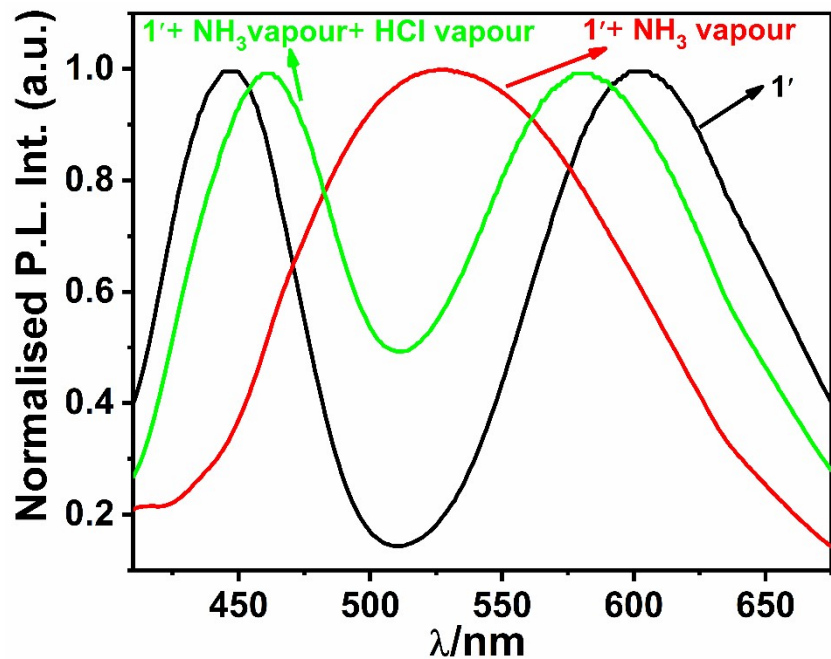


Fig. S11 Emission ($\lambda_{\text{ex}} = 370 \text{ nm}$) spectral changes of **1'** in presence of NH_3 vapour and followed by HCl vapour in solid state to check reversibility. The reversibility has been checked for three consecutive cycles and the data collected after the third cycle leaching NH_4Cl in each cycle with distilled water.

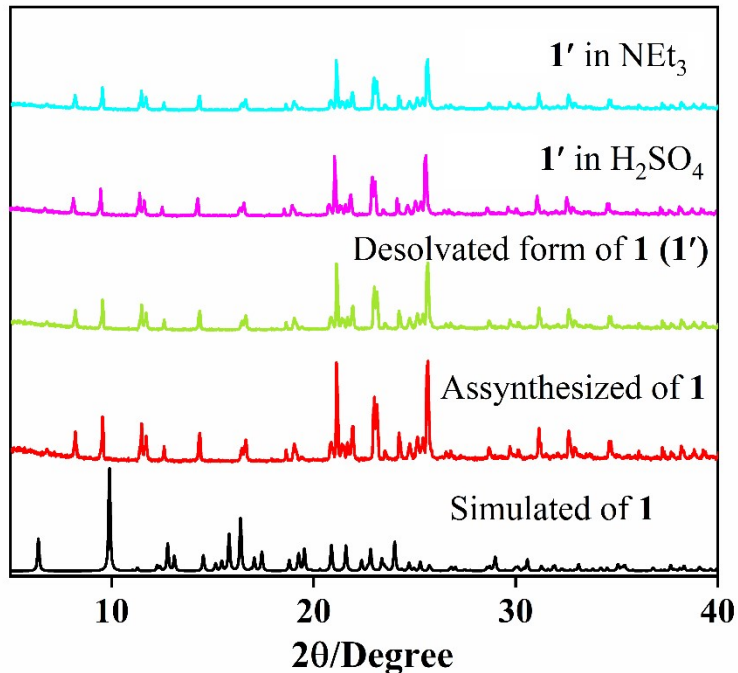


Fig. S12 PXRD pattern of compound **1'** in presence of H_2SO_4 and NEt_3 vapours.

Vapours adsorption/capturing calculation

The gas adsorption test was conducted in a balance with 1/100,000 tolerance at room temperature. As the substrate, the weight of the compound 1' was recorded in advance (m1) in two parts for HCl and NH₃ capturing, 100 mg each. After treating with HCl vapour, the adsorption capacity of HCl (Δm_2) could be obtained by weighing again. Similarly, the adsorption of NH₃ (Δm_3) could be measured by compound 1' the nanofilm in an ammonia atmosphere. Every adsorbing time is 5 min.

HCl vapour capturing

m1=100 mg (Weight of the compound 1' taken)

m2 = 140.625 mg (After treating with HCl vapour weight of compound 1')

$\Delta m_2 = m_2 - m_1$

= 140.625-100 mg

= 40.625 mg

So, amount of HCl capture by compound 1' is $\frac{40.625}{100} = 0.406$ g/g

So, 1000 mg compound 1' adsorbs 40.625×10 mg = 406.25 mg

So, amount of HCl capturing is 406.25mg/g i.e. $0.40625/36.5 = 0.01113$ mol/g = 11.13 mmol/g

NH₃ vapour capturing

m1=100 mg

m3 = 130.693

$\Delta m_3 = 130.693 - 100$

= 30.693 mg

So, amount of NH₃ capture by compound 1' is $\frac{30.693}{100} = 0.307$ g/g

So, 1000 mg compound 1' adsorbs 30.693×10 mg

So, amount of NH₃ capturing is 306.93 mg/g i.e. $0.307\text{g/g} = 0.307/17 = 0.01805$ mol/g = 18.05 mmol/g

Reference

1. E. Diez-barra, A. De la hoz, A. Sanchez-migallon and J. Tejada, *Heterocycles(sendai)*, 1992, **34**, 1365-1373.
2. SMART (V 5.628), SAINT (V 6.45a), XPREP, SHELXTL; Bruker AXS Inc.: Madison, WI, 2004.
3. G. M. Sheldrick, SADABS, Version 2.03; University of Göttingen, Germany, 2002.
4. G. M. Sheldrick, SHELX 2016/6; University of Göttingen, Göttingen, Germany, 2014.
5. A. L. Spek, *Acta Crystallogr. Sect. D*, 2009, **65**, 148–155.
6. L. J. Farrugia, *J. Appl. Crystallogr.*, 1999, **32**, 837–838.
7. C. F. Macrae, P. R. Edgington, P. McCabe, E. Pidcock, G. P. Shields, R. Taylor, M. Towler and J. V. D. Streek, *J. Appl. Cryst.*, 2006, **39**, 453–457.
8. V. A. Blatov, A. P. Shevchenko and V. N. Serezhkin, *J. Appl. Crystallogr.*, 2000, **33**, 1193.
9. V. A. Blatov, L. Carlucci, G. Ciani and D. M. Proserpio, *CrystEngComm*, 2004, **6**, 377–395.