Electronic Supplementary Material (ESI) for Analytical Methods.

Electronic Supplementary Information

A 'chromogenic' and 'fluorogenic' bis-Schiff base sensor for rapid detection of hydrazine both in solution and vapour phase

Anupam Ghorai, Jahangir Mondal, Sumantra Bhattacharya and Goutam Kumar Patra*

Table of contents.

1. Synthesis and characterisation of **L**
2. Spectroscopic studies
3. Calculation of detection limit
4. Selectivity study of the probe **L** to hydrazine and other species
5. DFT Study on H-bonding interaction
6. Determination of fluorescence quantum yield

1. Synthesis and characterisation of **L**

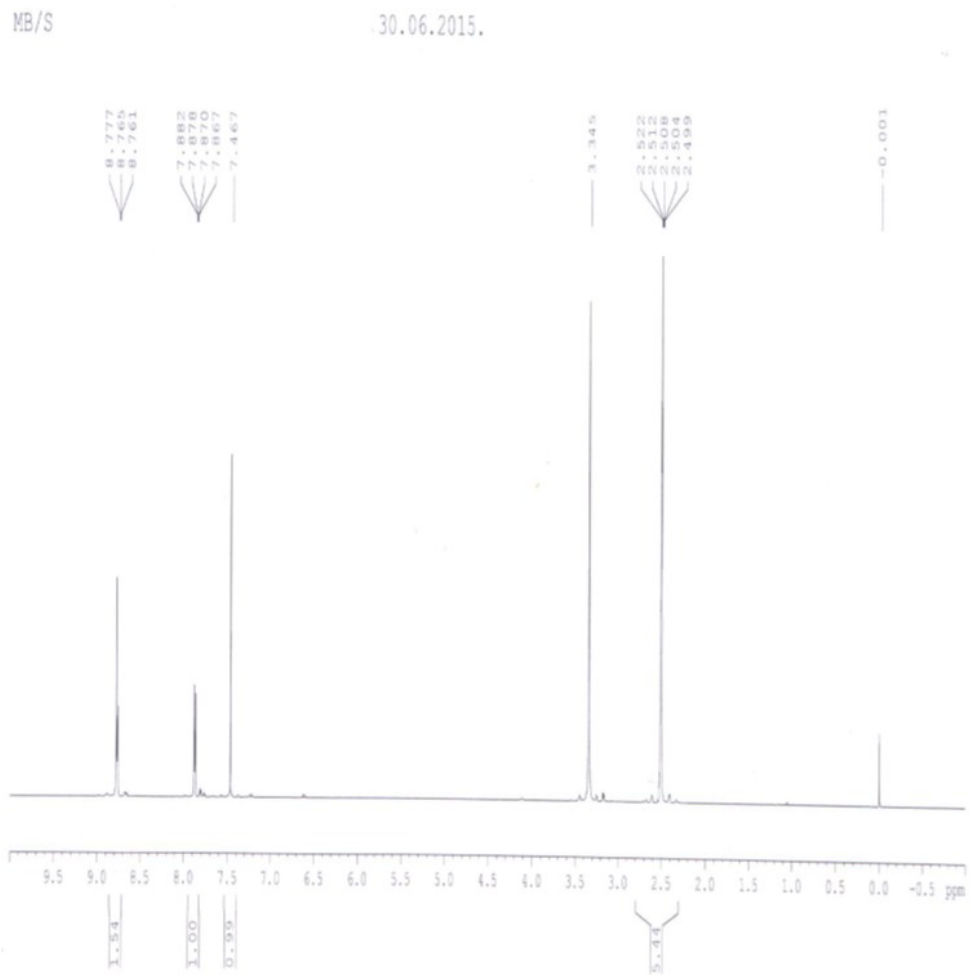


Fig. S1 ^{1}H NMR spectra of **L** in d_6-DMSO.

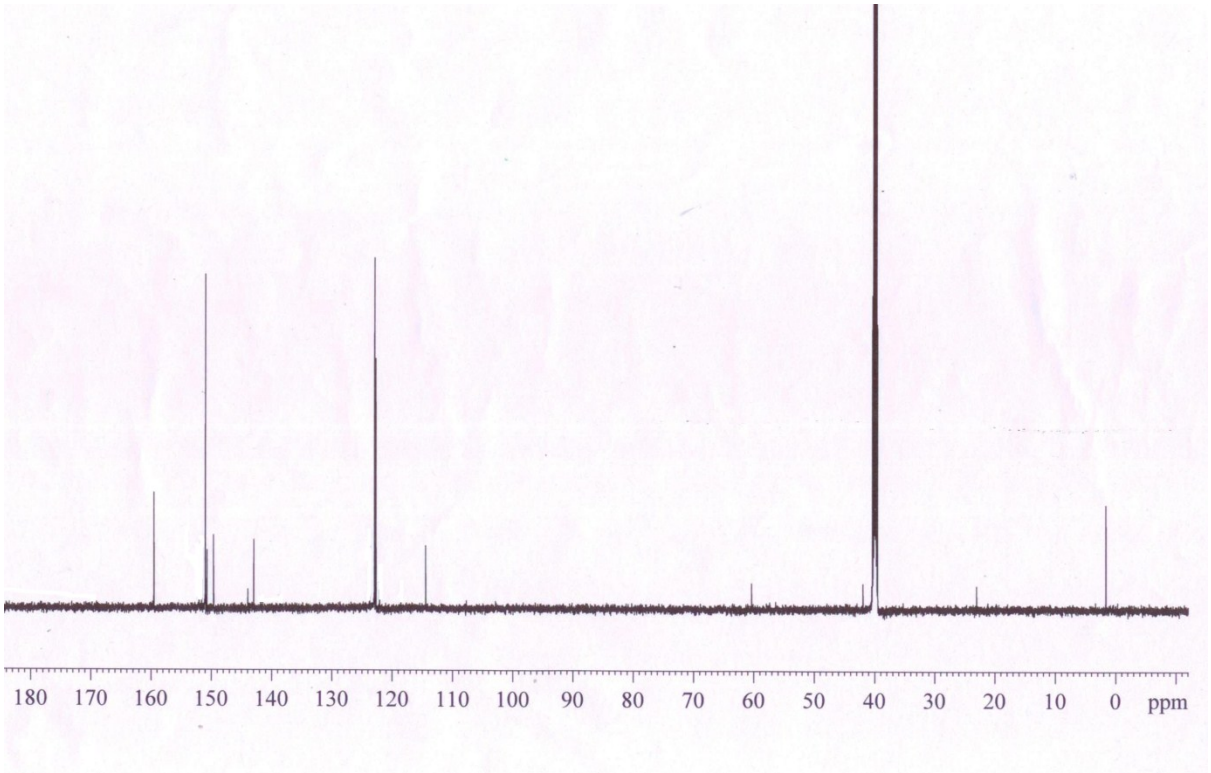


Fig. S2 ^{13}C NMR Spectra of **L** in d_6-DMSO.

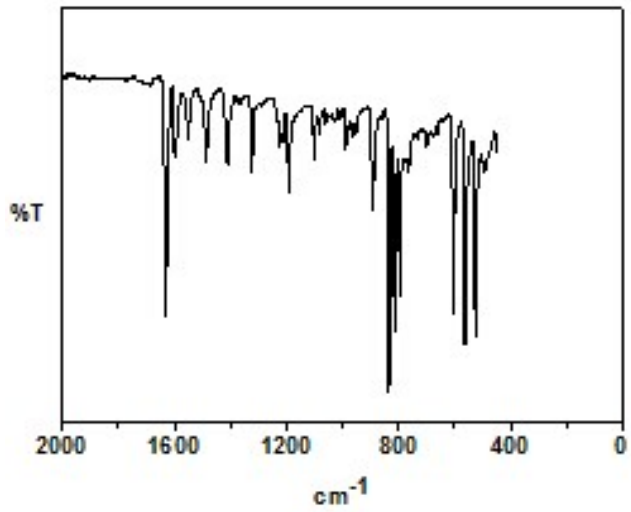


Fig. S3 IR Spectra of **L.**

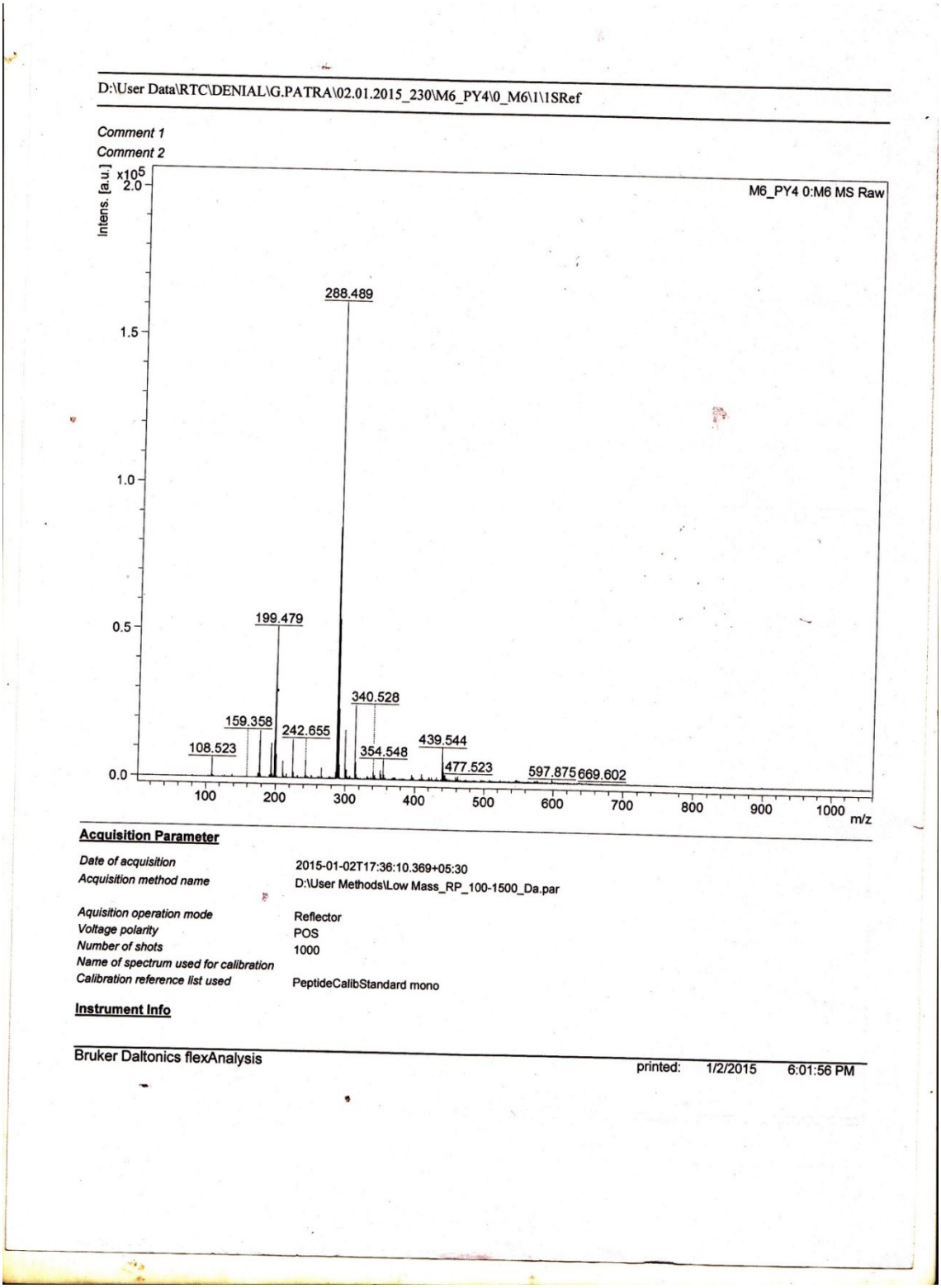
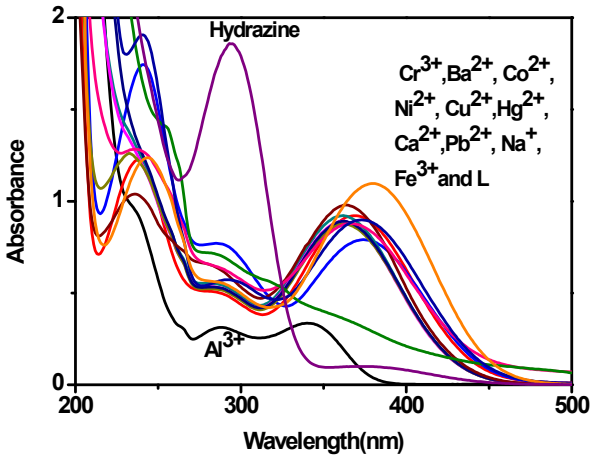
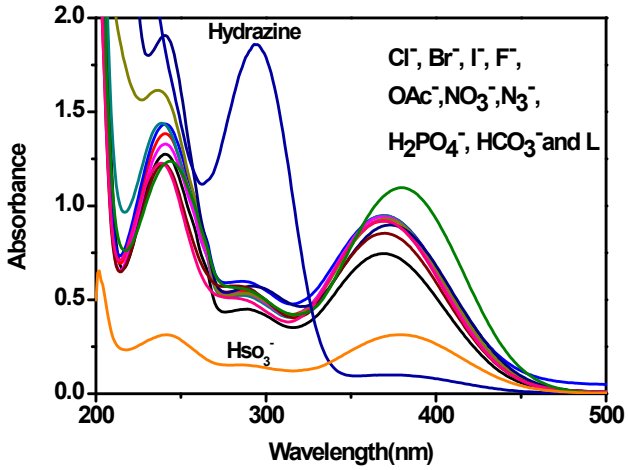


Fig. S4 Mass spectra of **L.**

2. Spectroscopic studies



(a)



(b)

Fig. S5 Absorbance spectra of **L** (10 μM) before and after addition of various (a) cations (2 equiv.) and (b) anions (2 equiv.).

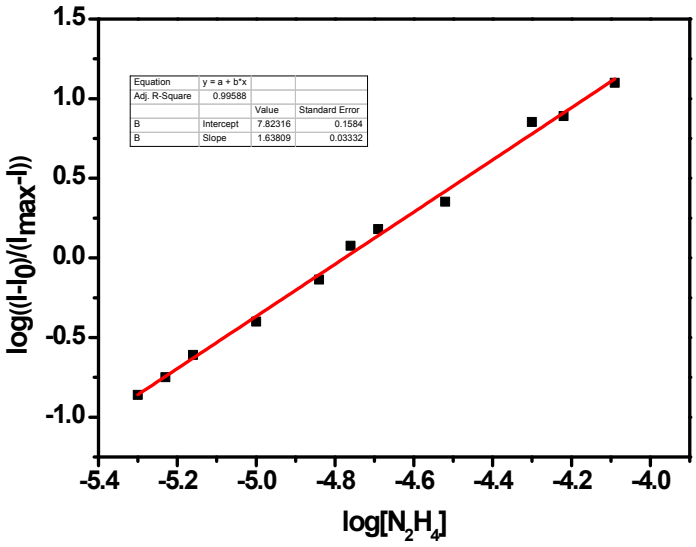


Fig. S6 Hill plot

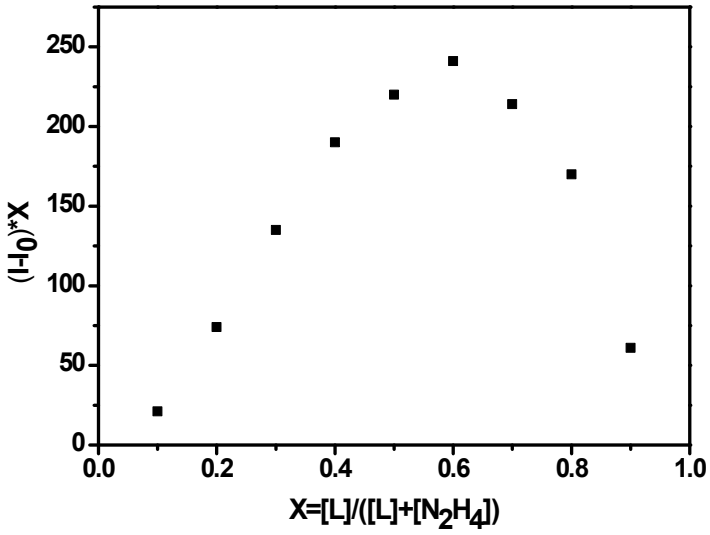


Fig. S7. Job's plot

3. Calculation of detection limit

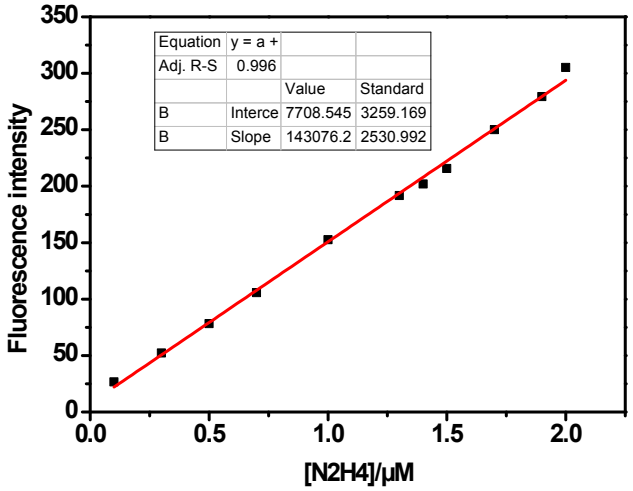


Fig. S8 Detection limit of the probe **L** for hydrazine.

The detection limit DL of the probe for hydrazine was determined from the following equation:

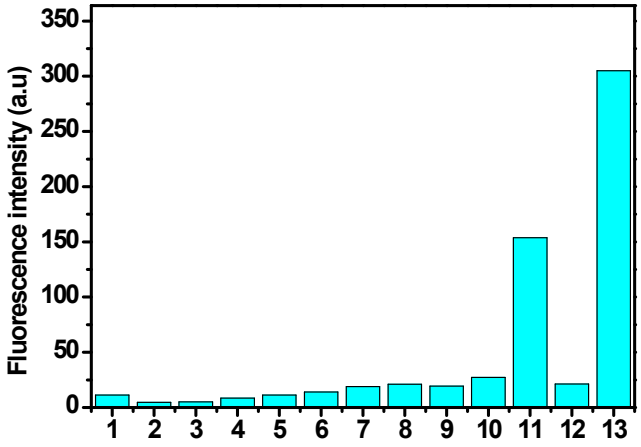
C_{DL} = 3 Sb/m

Here Sb is the standard deviation of the blank solution; m is the slope of the calibration curve.

From the graph we get slope = 143076.29 and Sb value is 5225.02

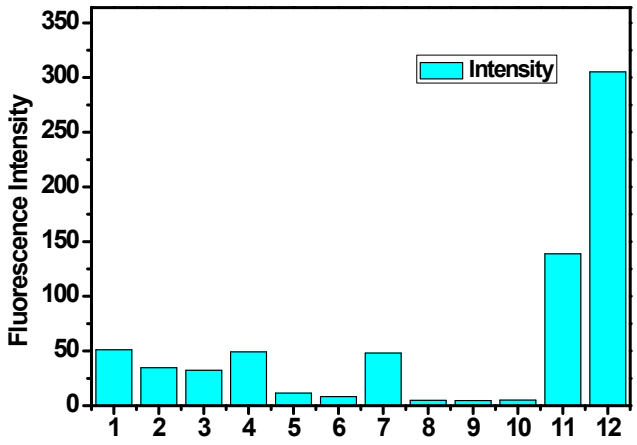
Thus using the formula we get the Detection Limit = 0.1 μM or 3.2 ppb i.e. the probe can detect hydrazine in this minimum concentration.

4. Selectivity study of the probe L to hydrazine and other species



(a)

(a) Fluorescence responses of probe **L** (10 μM) to hydrazine and metal ions (1. only **L,** 2. Na^{+}, 3. Ca^{2+}, 4. Ba^{2+}, 5. $Cr^{3+,}$ 6. $Co^{2+,}$ 7. Cu^{2+}, 8. Pb^{2+}, 9. Hg^{2+}, 10.Cd^{2+}, 11. Ni^{2+}, 12.Fe^{3+} and 13. Hydrazine). Each spectrum was recorded after 2 minute.

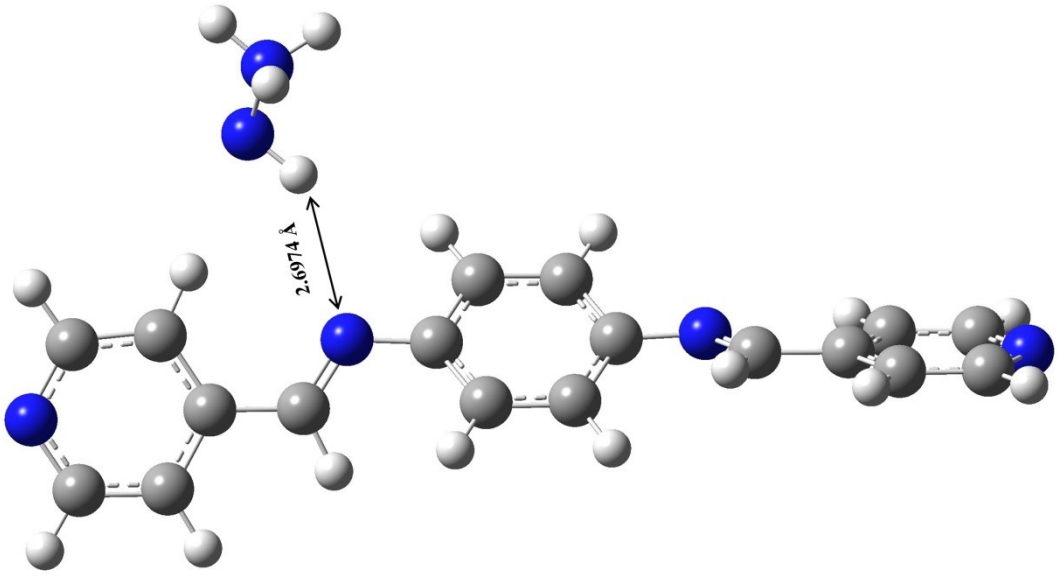


(b)

(b) Fluorescence responses of probe **L** (10 μM) to hydrazine and other anions (1.$H_2PO_4^-$, 2.Cl^-, 3 Br^-, 4. HCO_3^-, 5.I^-, 6.F^-, 7.OAc^-, 8.NO_3^-, 9.N_3^-, 10. only **L** and 11. hydrazine). Each spectrum was recorded after 2 minute.

Fig. S9 Selectivity studies of **L** (10 μM) with various (a) cations and (2 equiv.) (b) anions (2 equiv.)

5. DFT Study on H-bonding interaction



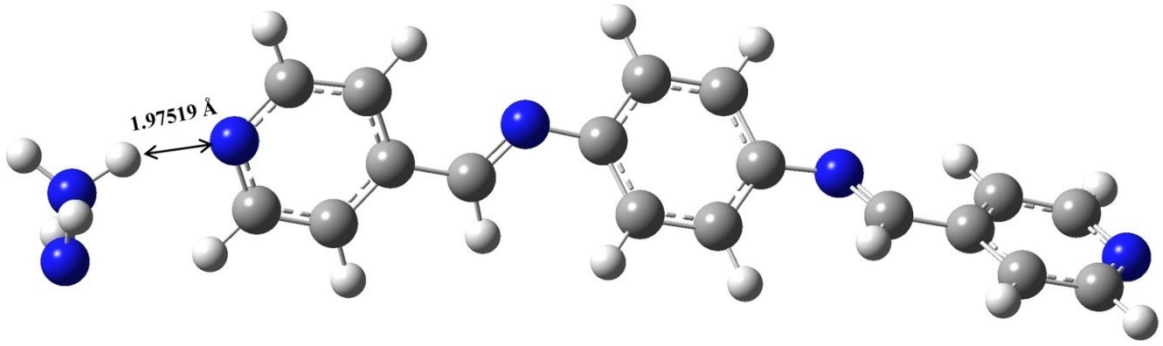


Fig. S10 The optimized structures of hydrazine and the ligand. (a) When $^{-}$NH-NH_3^+ interacts with the N atom of chain, (b) $^{-}$NH-NH_3^+ interacts with terminal N. The value is the distance of the optimum structure.

Table S1 Excitation of ligand

Most important orbital excitation	**λ [nm]**	***f***	**Experimental λ [nm] (*ε*)**
H->L	406.11	0.9736	370
H-7->L, H-6->L+1, H->L+1	353.09	0.0031	
H-1->L, H->L+1, H->L+4	308.95	0.0020	
H-5->L+1, H-4->L	301.50	0.0023	
H-9->L, H-8->L+1, H-7->L+1, H-3->L, H-1->L+1, H->L	292.26	0.4117	287
H-3->L+1, H-2->L, H->L+3	283.34	0.0357	
H-6->L, H-3->L, H-2->L+1, H->L+2	282.99	0.0565	
H-6->L, H-1->L+1	269.69	0.0306	
H-7->L, H-1->L,H-1->L+5, H->L+4	252.84	0.0835	
H-9->L, H-8->L, H-7->L+1, H-3->L+1, H->L+3	240.69	0.3710	239
H-9->L, H-8->L+1, H-7->L+1, H-1->L+4, H->L+5	230.72	0.0676	

Table S2 Excitation of ligand-hydrazine mixture (Terminal)

Most important orbital excitation	**λ [nm]**	***f***
H->L	406.47	1.0019
H-11->L, H-10->L+1, H-9->L, H-9->L+1, H-8->L, H-8->L+1, H-7->L, H-6->L, H-5->L, H-4->L+1, H->L	290.98	0.4103
H-11->L, H-10->L+1, H-9->L+1, H-8->L+1, H-7->L+1, H->L+5	240.83	0.3661

Table S3 Excitation of ligand-hydrazine mixture (chain)

Most important orbital excitation	**λ [nm]**	***f***
H->L	403.01	0.9498
H-10->L, H-10->L+1,H-9->L,H-8->L,H-8->L+1,H-5->L, H-3->L+1, H-1->L+1,H->L+1	291.32	0.2094
H-11->L, H-10->L+1, H-9->L+1, H-8->L+1,H->L+5	240.21	0.3761

Table S4 Mulliken Charge analysis

System	**Mulliken charge on ligand**
GP_GO6-31GPP3D2PB3LYP_hydrazine_chain	-0.012366
GP_GO6-31GPP3D2PB3LYP_hydrazine_terminal	0.010054
GP_GO6-31GPP3D2PB3LYP_NH-NH3_chain	-0.026694
GP_GO6-31GPP3D2PB3LYP_NH-NH3_terminal	0.009230

6. Determination of fluorescence quantum yield.

The fluorescence quantum yield was obtained by comparing the integrated area of the corrected emission spectrum of the samples with the reference under the same excited wavelength. The concentration of the reference L-tryptophane (Φ=0.14)[1] in aqueous solution was adjusted to match the absorbance of the test sample. The quantum yield of **L**-N_2H_4 was tested by using a colourless solution containing of 1 μM probe **L** and 10 μM hydrazine.

Emission for probe **L** and **L**-N_2H_4 was integrated from 350 to 550 nm with excitation at 310 nm. The quantum yields were calculated with the following equation[2].

$$\Phi_{sample} = \Phi_{reference} \times \frac{\int emission_{sample}}{\int emission_{reference}} \times \frac{A_{reference}}{A_{sample}}$$

Reference:

1. Y. P. Zhang, Y.J. Wei, N. Li and S. J. Qiu, *Chinese Journal of Analytical Chemistry,* 2004, **32**, 779.

2. C. A. Parker and W. T. Rees, *The Analyst*, 1960, **85**, 587.