Electronic Supplementary Information (ESI†)

A "turn-on" fluorescent and colorimetric chemodosimeter for selective detection of Au^{3+} ions in solution and in live cells via Au^{3+} -induced hydrolysis of rhodamine-derivative Schiff base

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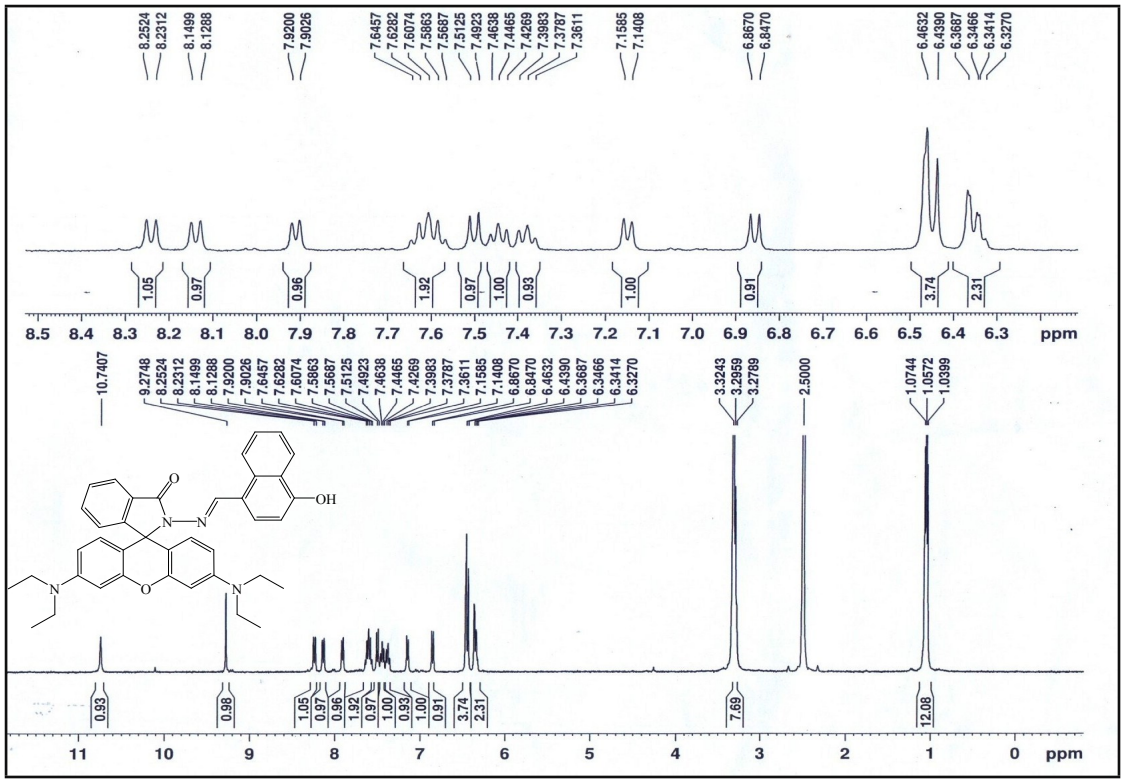


Figure S1: ^{1}H NMR spectrum of compound **2** in DMSO-d_6.

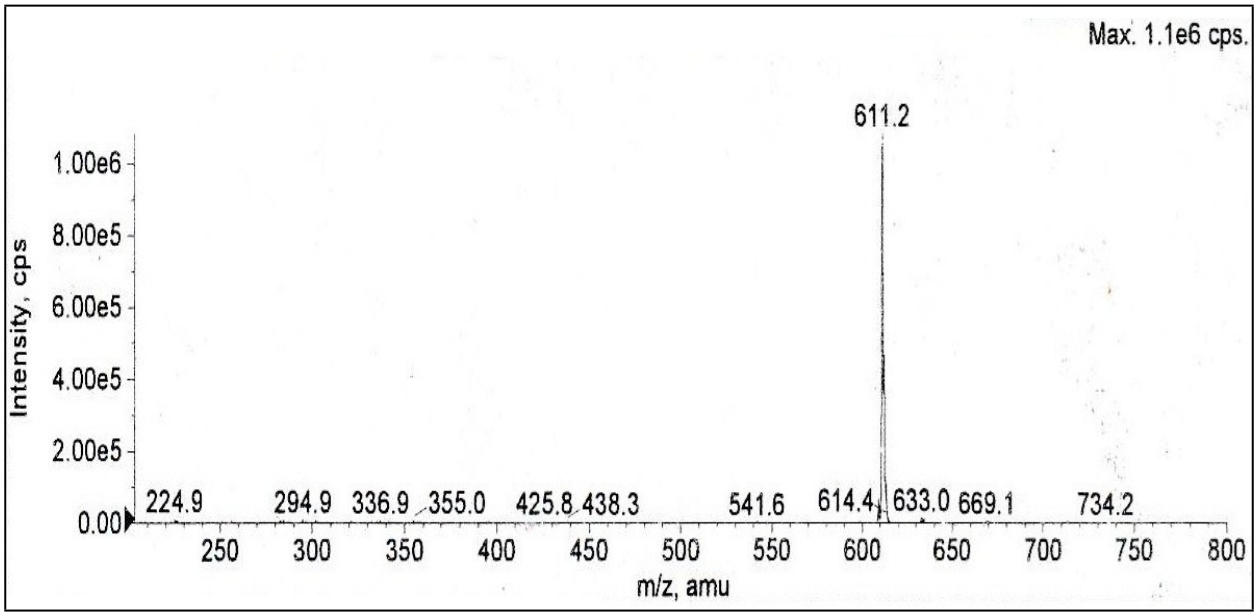


Figure S2: Mass spectrum of compound **2**.

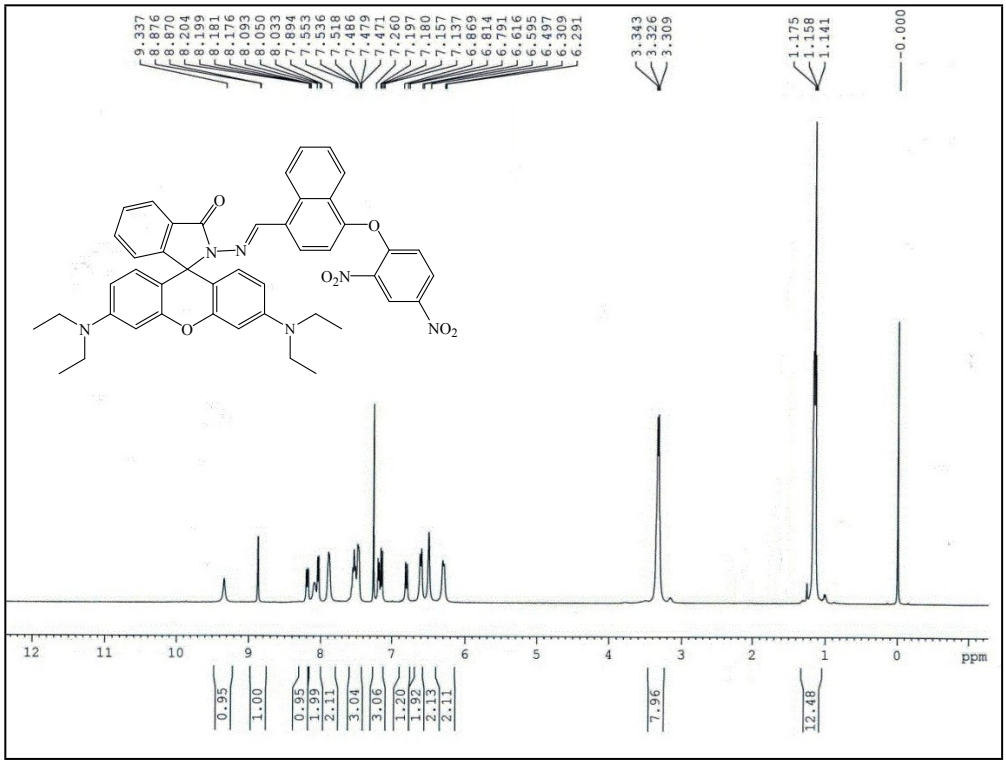


Figure S3: ^{1}H NMR spectrum of probe **L** in $CDCl_3$ solution.

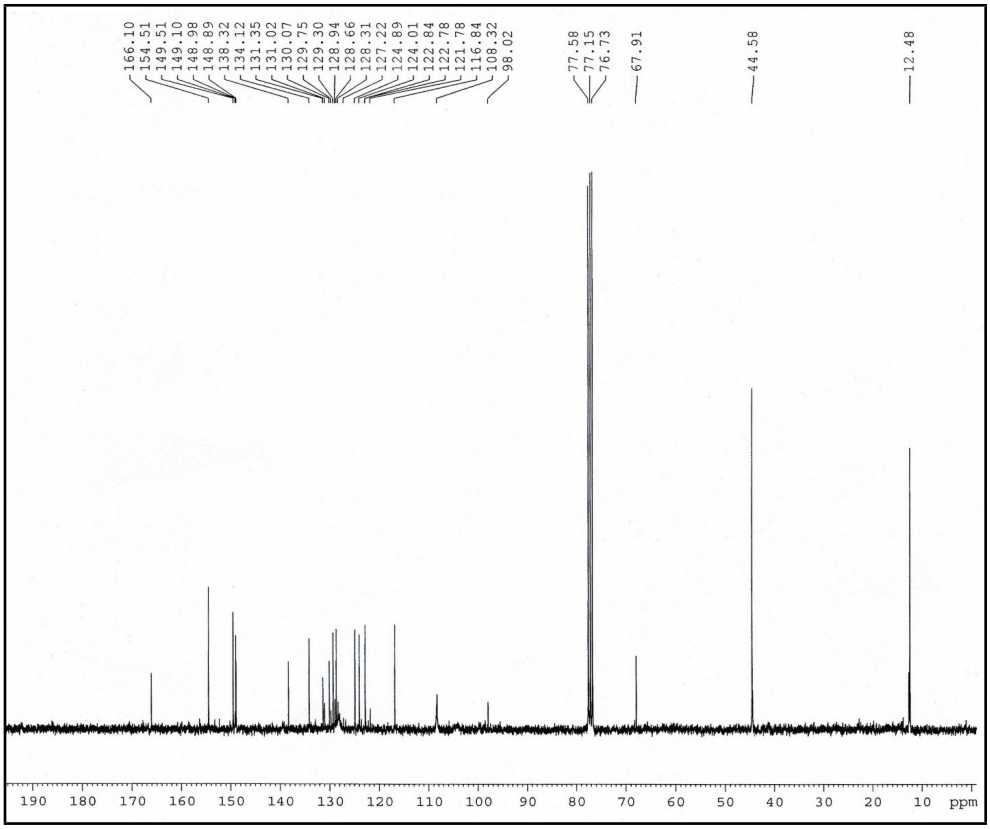


Figure S4: ^{13}C NMR spectrum of probe **L** in $CDCl_3$ solution.

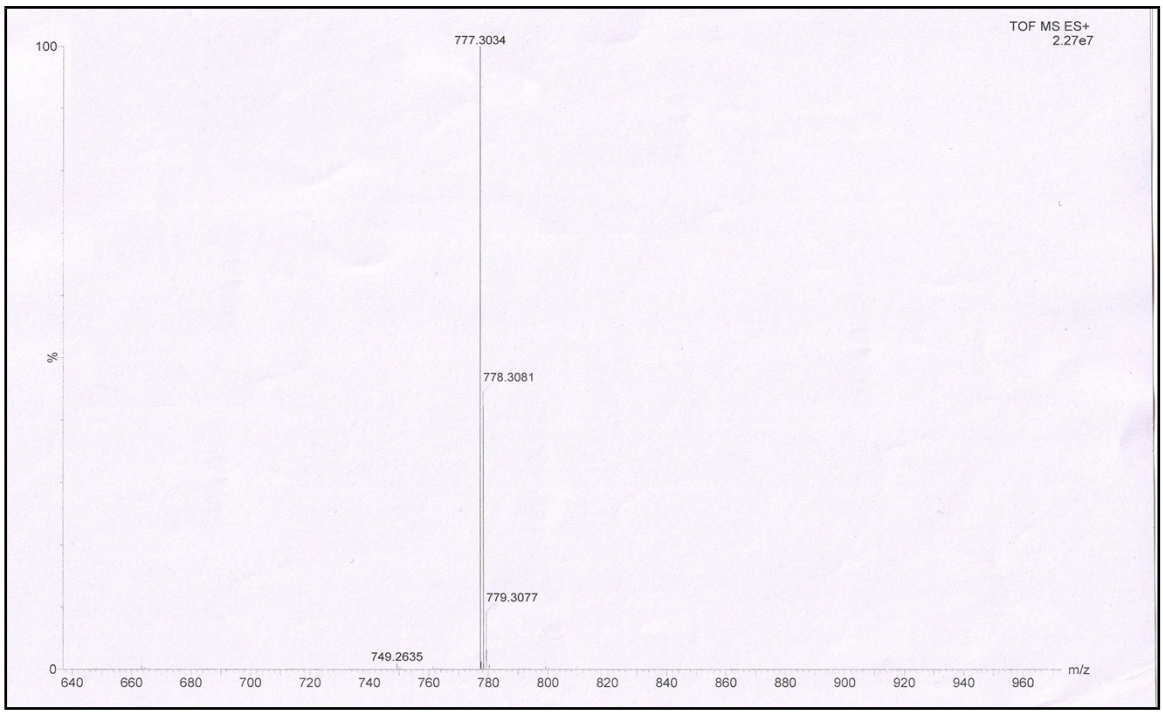


Figure S5: Mass spectrum of probe **L**.

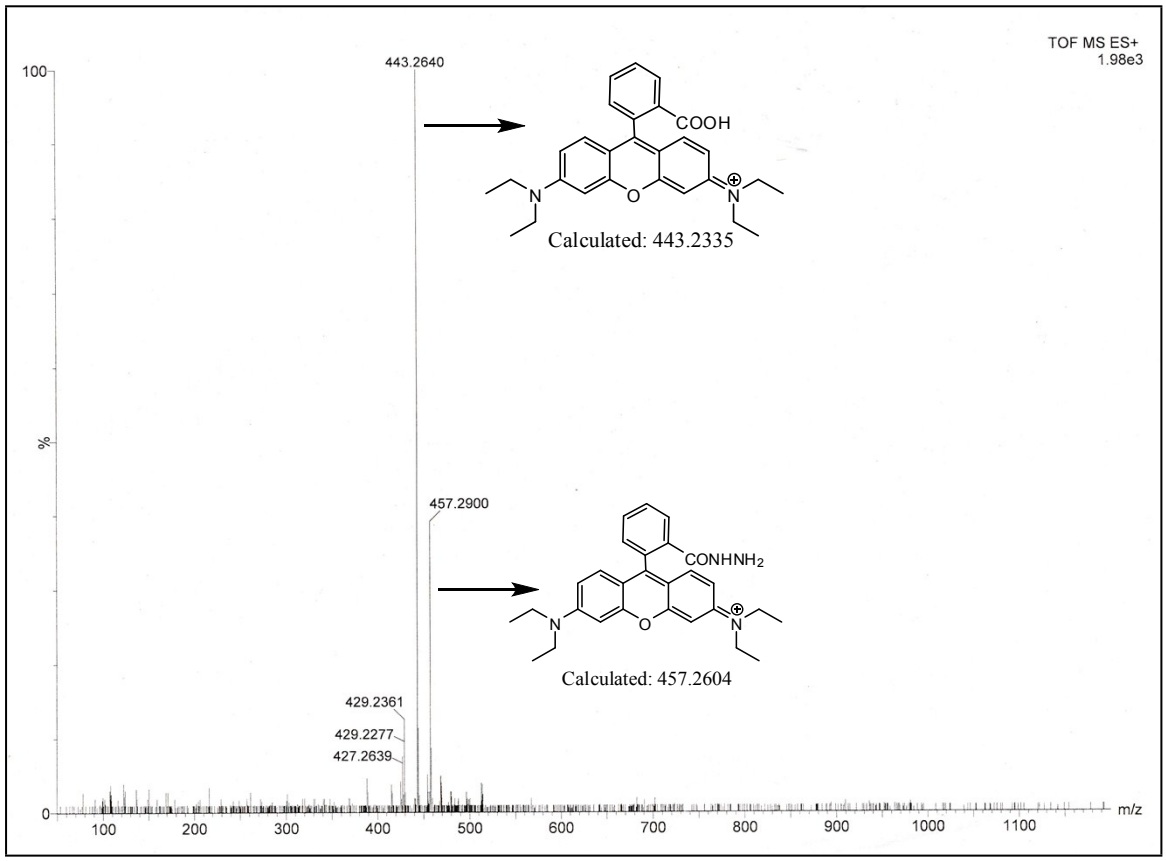


Figure S6: Mass spectrum of hydrolysis products of **L** by Au^{3+} ions.

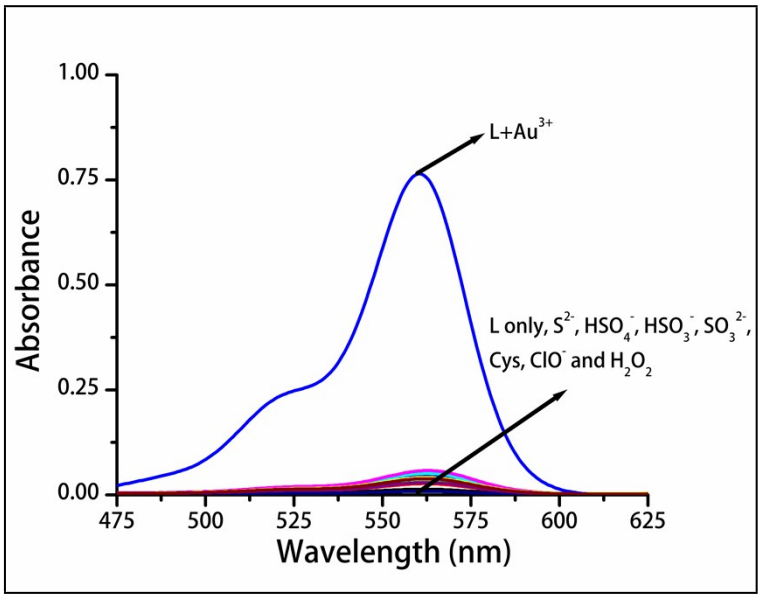


Figure S7: UV−vis absorption spectra of **L** (1.0×10^{-5} M) in the presence of various anions, amino acid and reactive oxygen species (1.0×10^{-4} M) in CH_3CN/H_2O (1: 1, v/v, 10 mM HEPES buffer, pH 7.4) solution.

Calculation for Limit of Detection (LOD):

The LOD of **L** for Au^{3+} was determined using the following equation:

LOD = 3Sbl/S, Sb1 is the standard deviation of the blank solution; S is the slope of the calibration curve.

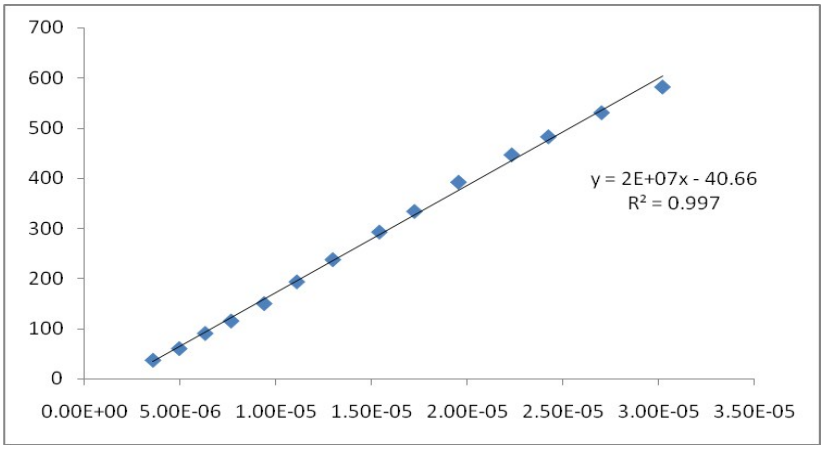


Figure S8: Calibration curve for fluorescence titration of **L** with Au^{3+}.

From the graph we get slope (S) = 2×10^7 Standard deviation (Sb1 = 10.05925)

Thus, using the formula, we get the LOD = 1.508887×10^{-6} M = 1.51 μM.

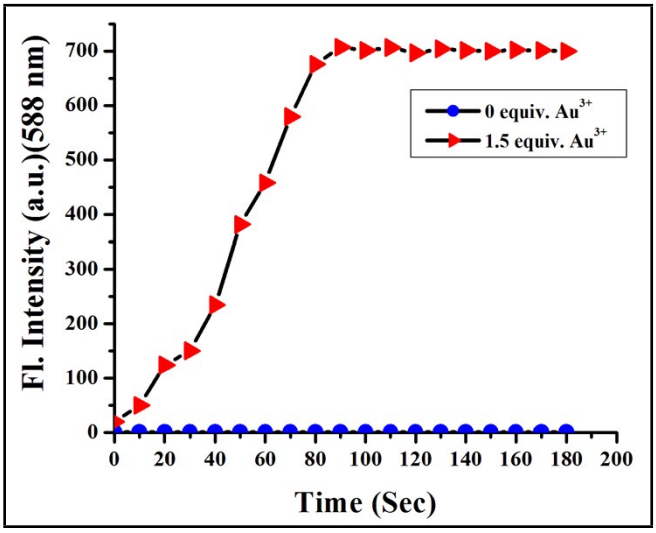


Figure S9: Time dependent change of emission intensity of probe **L** in the absence and presence of 1.5 equivalent Au^{3+} ions) in CH_3CN/H_2O (1 : 1, v/v, 10 mM HEPES buffer, pH 7.4) solution (λ_{ext} = 560 nm).

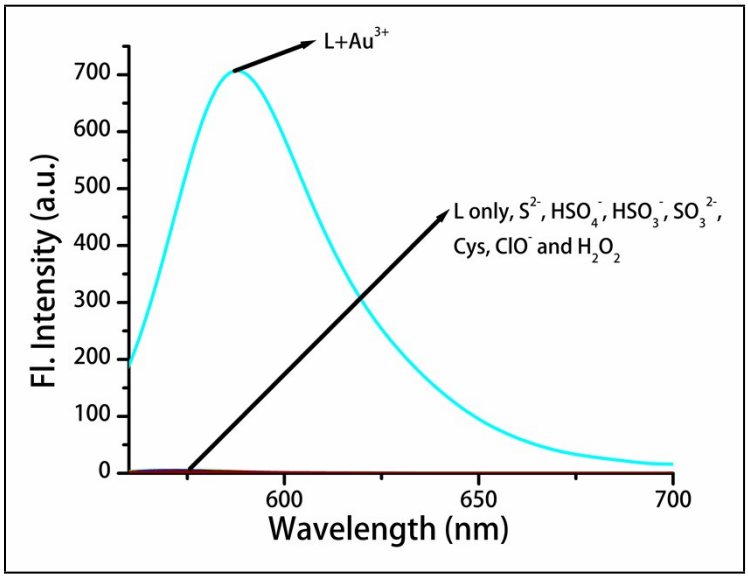


Figure S10: Fluorescence emission spectra of **L** (1.0×10^{-5} M) in the presence of various anions, amino acid and reactive oxygen species (1.0×10^{-4} M) in CH_3CN/H_2O (1: 1, v/v, 10 mM HEPES buffer, pH 7.4) solution. λ_{ext} = 560 nm.

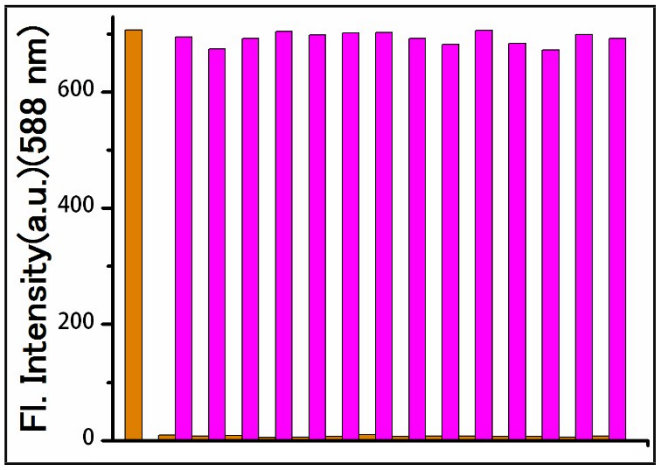


Figure S11: Fluorescence response of **L** (c = 1.0 × 10^{-5} M) to 1.5 equiv. addition of Au^{3+} (the orange bar portion) and to the mixture of 10 equiv. of other metal ions with 1.0 equiv. of Au^{3+} (the magenta bar portion, left to right- Cr^{3+}, Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}, Hg^{2+}, Pt^{2+}, Pd^{2+}, Al^{3+} and Ag^{+}).

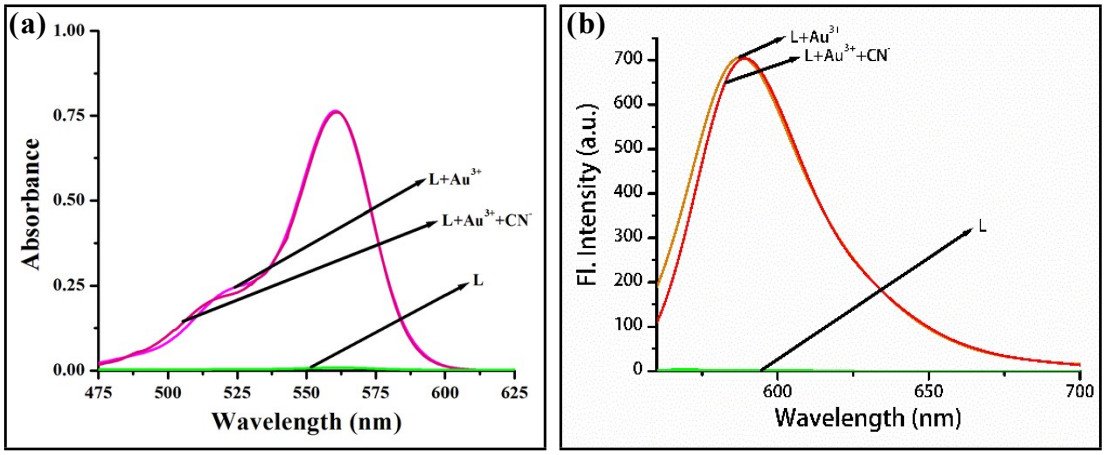


Figure S12: (a) UV−vis absorption spectra of **L** (c = 1.0 × 10-5 M) to 1.5 equiv addition of Au^{3+} (the magenta graph) and to the mixture of 10 equiv. of $^{t}Bu_4NCN$ ions with 1.5 equiv. of Au^{3+} (the pink graph); (b) Fluorescence response of **L** (c = 1.0 × 10^{-5} M) to 1.5 equiv addition of Au^{3+} (the orange graph) and to the mixture of 10 equiv. of $^{t}Bu_4NCN$ ions with 1.5 equiv. of Au^{3+} (the red graph).

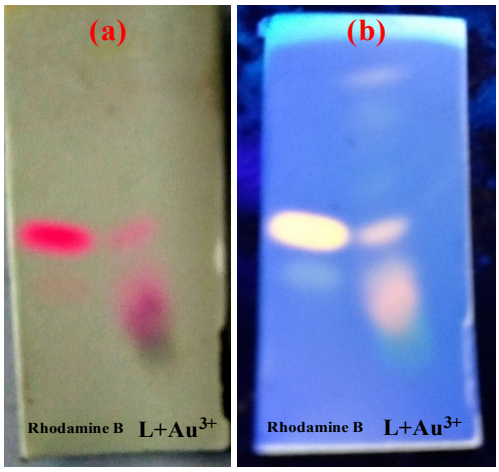


Figure S13: TLC study of pure rhodamine B and **L**+Au^{3+} (a) under visible light and (b) under UV light.

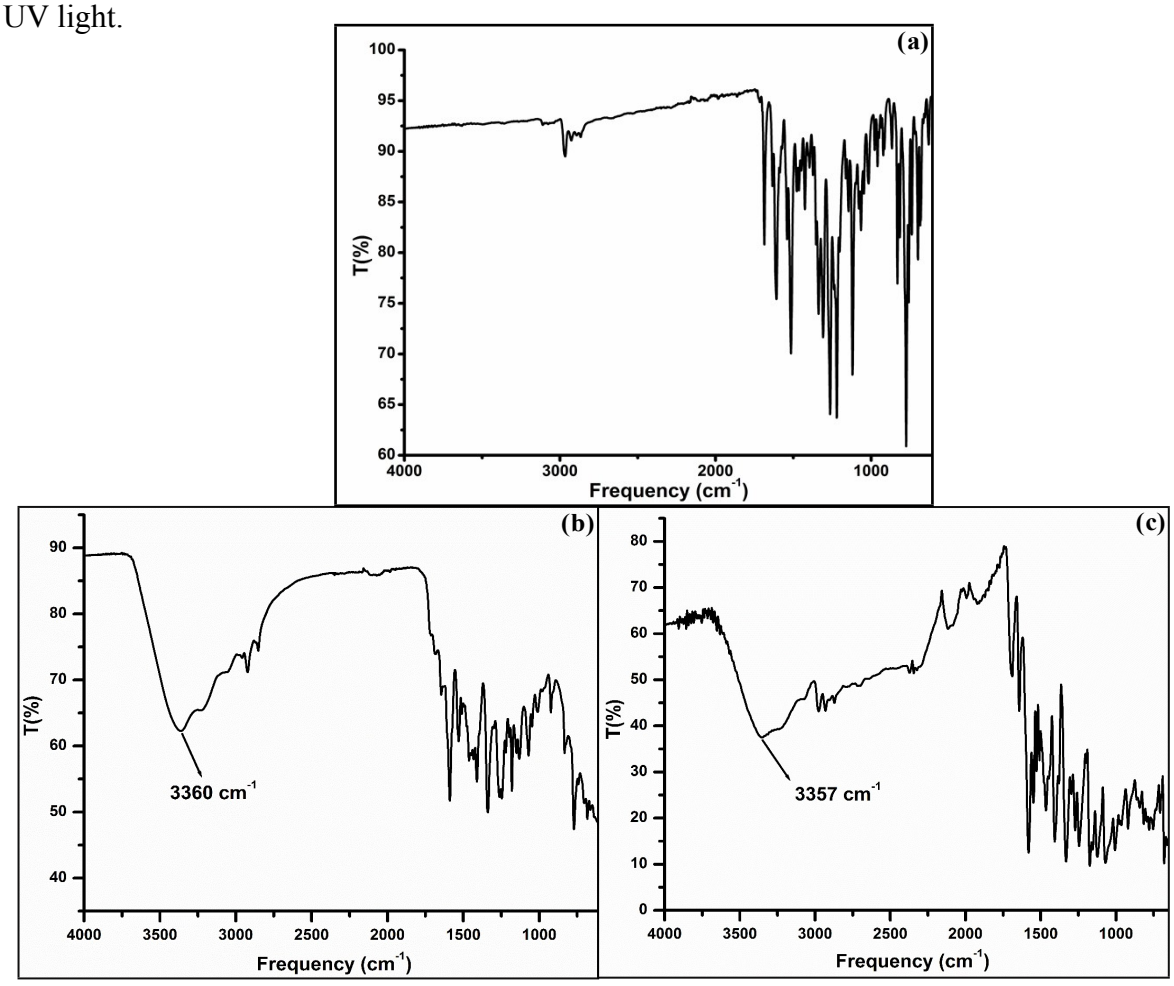
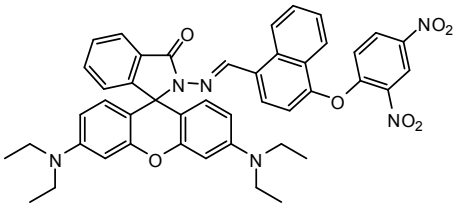
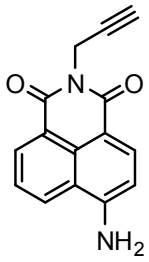
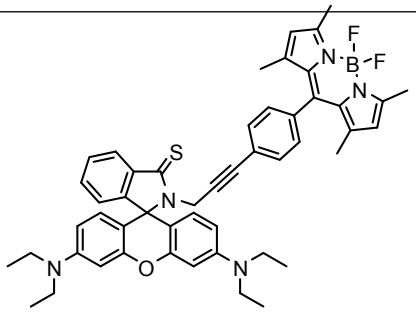
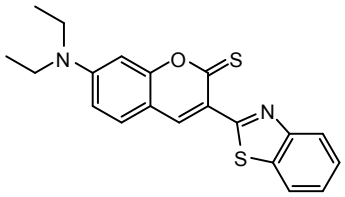
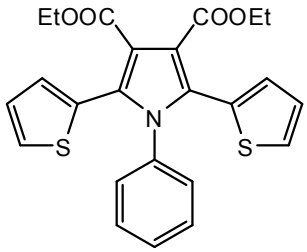
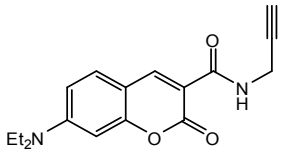
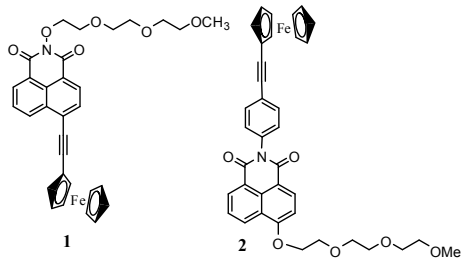
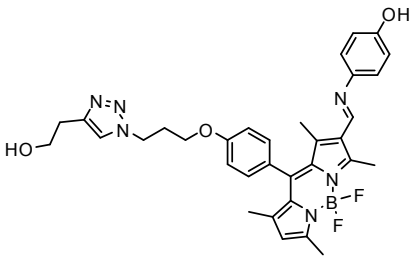
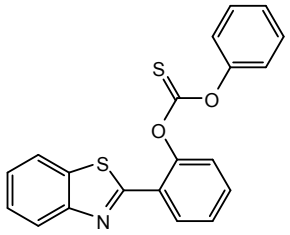


Figure S14: FTIR spectra of (a) **L**; (b) **L**+Au^{3+} and (c) pure rhodamine B.

Table S1. The comparison of the present probe **L** with other reported probes for Au^{3+} ions

Sl. No.	Structure of Probe	Media	Detection limit	Theoretical calculation	Biological application
1.	**Our Probe** 	CH_3CN/H_2O (1:1, v/v, 10 mM HEPES buffer, pH 7.4)	1.51 μM	Yes	Our chemodosimeter can detect and image intracellular Au^{3+} ions in MDA- MC3T3 cells.
2.	 (*Organic Letters,* 2010, **12**, 5310-5313) [1]	HEPES buffer (0.01 M, pH)7.4) (0.05% DMSO, v/v)	0.05 μM (10 ppb)	No	No
3.	 *(Chem. Eur. J. 2011,* **17**, 9066 – 9069) [2]	Phosphate buffer (pH¼7.2) (0.15% CH_3CN, v/v)	3.9×10^{-7} M	No	No

4.	 (*Inorg. Chem. 2012, 51,* 2880−2884) [3]	In a mixture of CH_3CN and acetate buffer solution (pH 4.7, 10 mM) (1:1, v/v).	1.1×10^{-7} M	No	No
5.	 (*Tetrahedron* 2013, *69,* 2048-2051)[4]	Phosphate buffer (pH¼7.2) (0.15% CH_3CN, v/v)	No	No	No
6.	 (*Anal. Methods*, **2013**, *5*, 3639–3641) [5]	HEPES buffer	4.4×10^{-7} M	No	No
7.	 (*Dyes and Pigments* 2015, **112**, 236-238) [6]	Mixture of CH_3CN and 10 mM, pH 8.0 PBS buffer solution (1/1, v/v)	95 ppb	No	No

8.	 (*RSC Advances* 2015, **5**, 82887-82893) [7]	THF-H_2O buffered with 10 mM HEPES (2 μM)	10 nM	No	No
9.	 (*Dyes and Pigments* 2019, **164**,14-19) [8]	1:1 (*v/v*) mixture of acetate buffer solution (pH = 4.76, 20 mM) and DMSO	4.8×10^{-8} M (9.5 ppb)	No	No

*[1] Starting materials for the synthesis of our probe **L** are easily available compared to the reported compound.

*[2] The synthetic steps for the probe recorded are more than our probe and a few steps are of low yield.

*[3] Compared to the synthesis of **L** (our work), yield of the reported compound is low.

*[4] The reported compound detects Au^{3+} ions through 'turn-off' mechanism. However, a 'turn-on' chemosensor (fluorescence enhanced) would be more efficient for metal ion detection.

*[5] Yield of the reported compound is low.

*[6] Our probe shows 696-fold fluorescence enhancement in presence of Au^{3+} ions compared to the reported probe (9-fold).

*[7] The synthetic steps for the probe recorded are more than our probe. Our probe **L** selectively detects Au^{3+} ions whereas the reported probe is sensitive not only to Au^{3+} ions, but also to Hg^{2+}, Fe^{3+}.

*[8] Yield of the reported probe is low.

*[1-8] None of the above-mentioned tabulated probes, except ours, reported their biological applications.

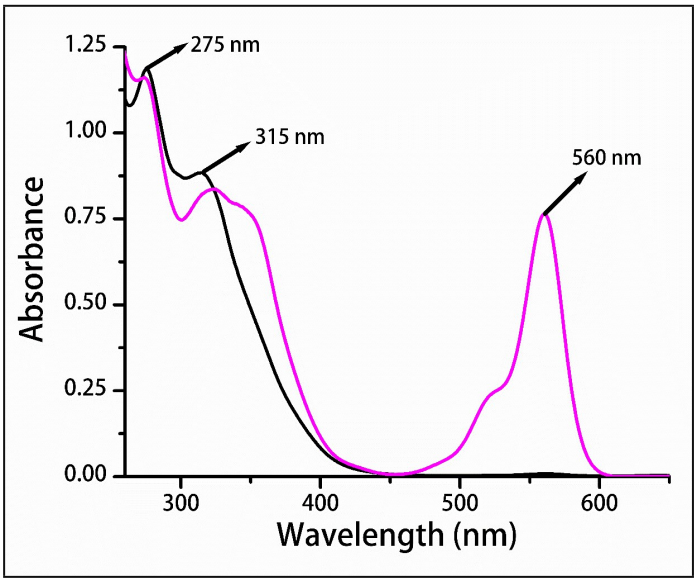


Figure S15: UV-vis spectra of (a) **L** (black); (b) **L** + Au^{3+} (magenta color).

Theoretical study:

Table S2. Calculated excitation energies (eV), oscillator strengths (f), contributions for **L**, **I_2 and P**. The data were calculated by the TDDFT//B3LYP/6-31+G(*d,p*) level of theory based on the optimized ground state geometries.

Species	Electronic Transition	Excitation Energy	f	Contributions[a]
L	$S_0 \rightarrow S_{11}$	3.3025 eV 375.43 nm	0.8188	H-1 → L+2 (93%)
	$S_0 \rightarrow S_{29}$	4.0045 eV 309.61 nm	0.2111	H -10→ L (52%)
I_2	$S_0 \rightarrow S_1$	2.5763 eV 481.24 nm	0.9883	H → L (99%)
	$S_0 \rightarrow S_{17}$	4.9369 eV 251.14 nm	0.4577	H - 1→ L + 2 (80%)
P	$S_0 \rightarrow S_1$	2.5238 eV 491.26 nm	0.9900	H → L (99%)
	$S_0 \rightarrow S_{16}$	4.9031 eV 252.87 nm	0.5616	H → L (99%)

[a] H and L represents HOMO and LUMO respectively.

Table S3. Energies of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO)

Species	E_{HOMO} (a.u)	E_{LUMO} (a.u)	ΔE (a.u)	ΔE (eV)	ΔE (kcal/mol)
L	-0.19977	-0.1200	0.07977	2.170669332	50.1
I_2	-0.21700	-0.1145	0.10250	2.789189000	64.3
P	-0.22087	-0.1212	0.09966	2.711908056	62.5

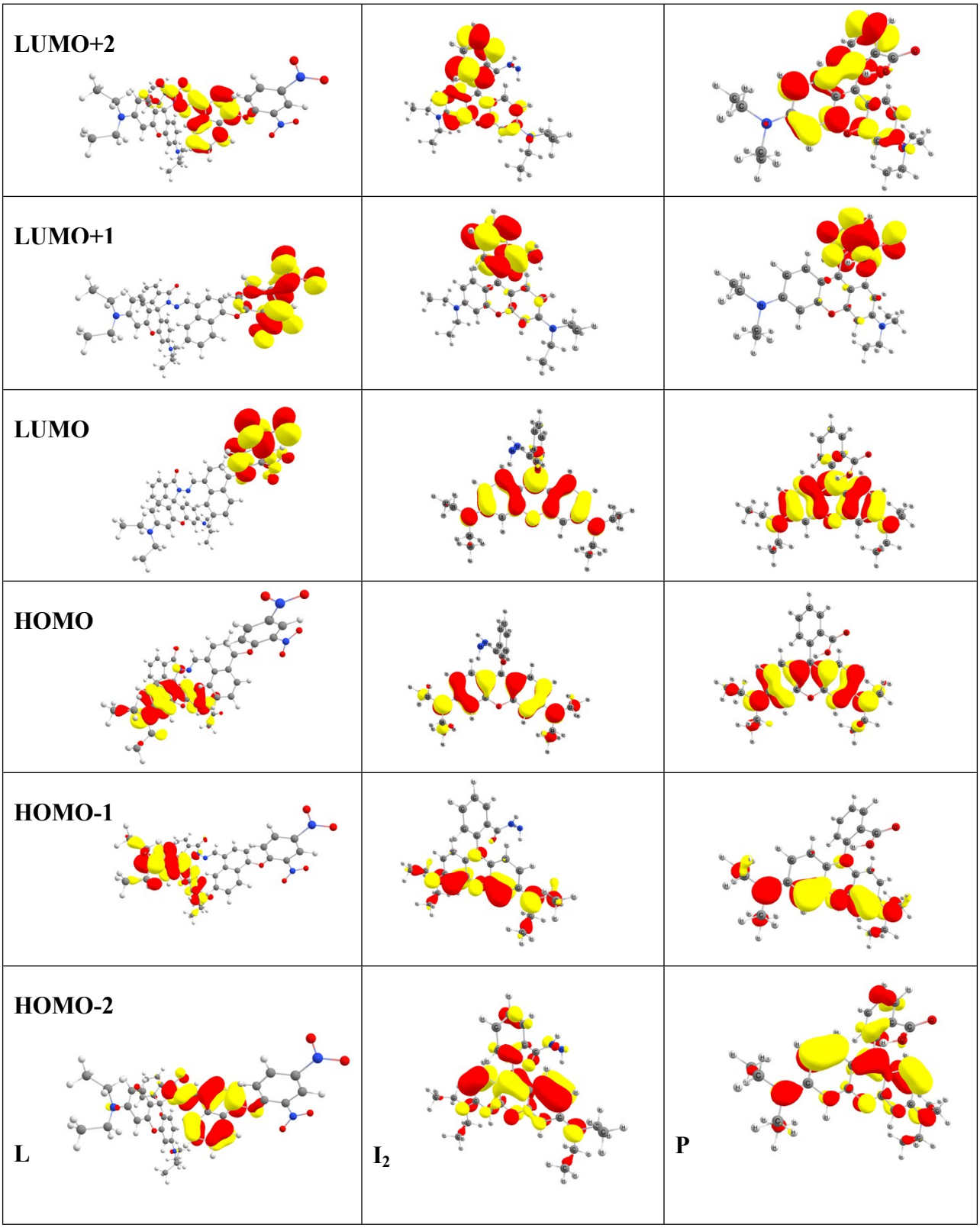


Figure S16: Molecular orbital plots of **L**, $\mathbf{I_2}$ and **P**.

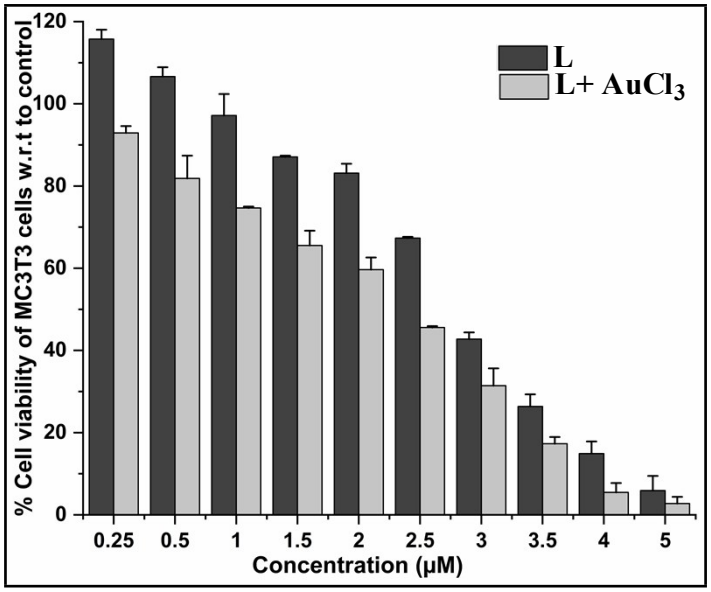


Figure S17: MTT assay studies.

Quantum yield (ϕ) calculation:

Here, the quantum yield ϕ was measured by using the following equation:

$\phi_x = \phi_s (F_x / F_s) (A_s / A_x) (n_x^2 / n_s^2)$

Where,

X & S indicate the unknown and standard solution respectively, ϕ = quantum yield,

F = area under the emission curve, A = absorbance at the excitation wave length,

n = index of refraction of the solvent. Here ϕ measurements were performed using Rhodamine B in ethanol as standard [ϕ = 0.69]

For standard (s) rhodamine B in ethanol the following values were determined:

n_s = 1.3614 (for ethanol); n_x=1.3441 (for acetonitrile); ϕ_s = 0.69.

We calculated the quantum yield of **L** using the above equation and the value was found to be 0.001.

We calculated the quantum yield of **L** in presence of Au^{3+} ions using the above equation and the value was found to be 0.689.