Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

for

Colorimetric and Ratiometric Fluorescent Chemosensor for Fluoride Ion Based on Phenanthroline-Imidazole (PI): Spectroscopic, NMR and density functional studies

Ajit Kumar Mahapatra*[a], Parthasarathi Karmakar [a], Jagannath Roy [a], Srimanta Manna[a], Kalipada Maiti [a], Prithidipa Sahoo [b] and Debasish Mandal[c]

[a] Department of Chemistry, Indian Institute of Engineering Science & Technology

(Formerly Bengal Engineering and Science University), Shibpur, Howrah – 711103, India.

[b]Department of Chemistry, Visva-Bharati University, Santiniketan, Birbhum, West Bengal, India -731235 India.

[c]Department of Chemistry and the Lise Meitner-Minerva Center for Computational Quantum Chemistry, The Hebrew University of Jerusalem, Jerusalem (Israel).

*Corresponding author: Tel.: +91 33 2668 4561; fax: +91 33 26684564;

E-mail: mahapatra574@gmail.com

Content

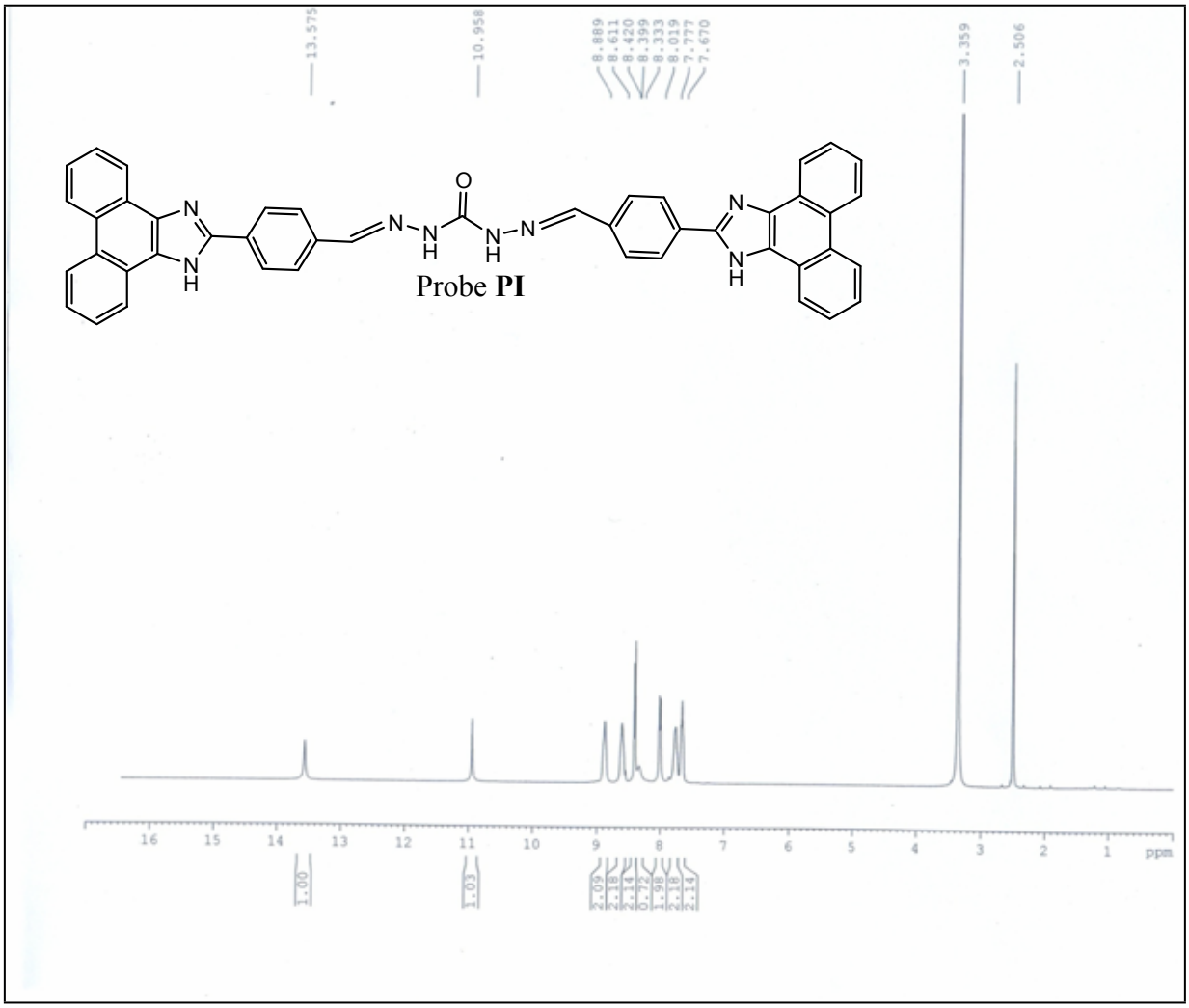

Fig. S1: ^{1}H NMR of probe **PI.**

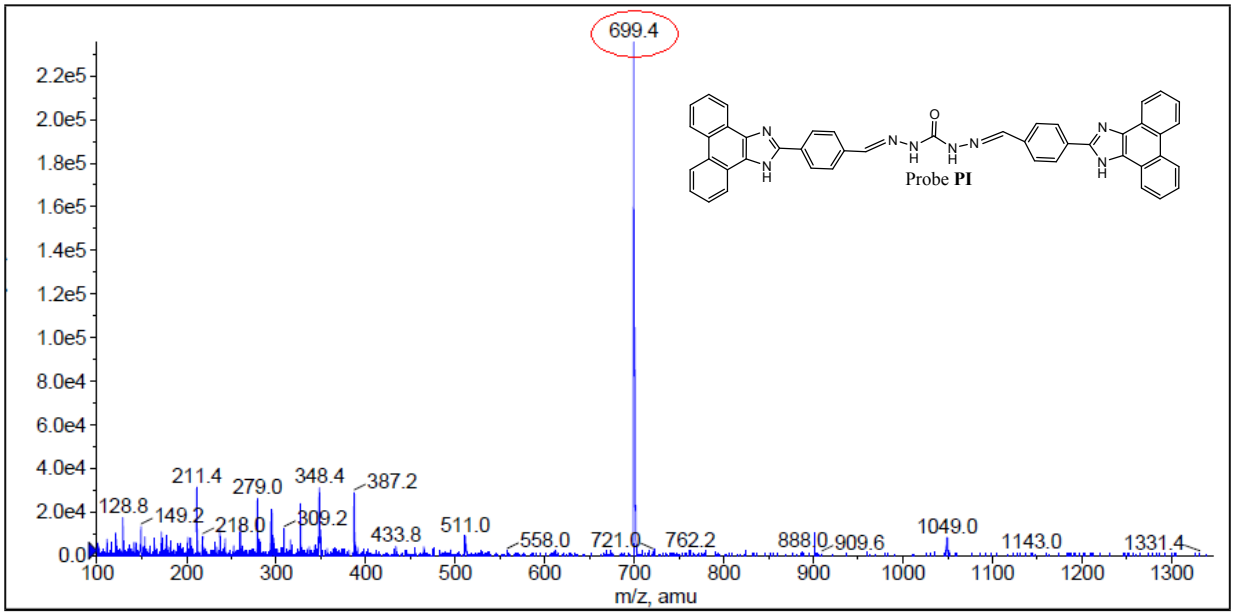

Fig. S2: ESI-MS $[M]^+$ spectrum of probe **PI**

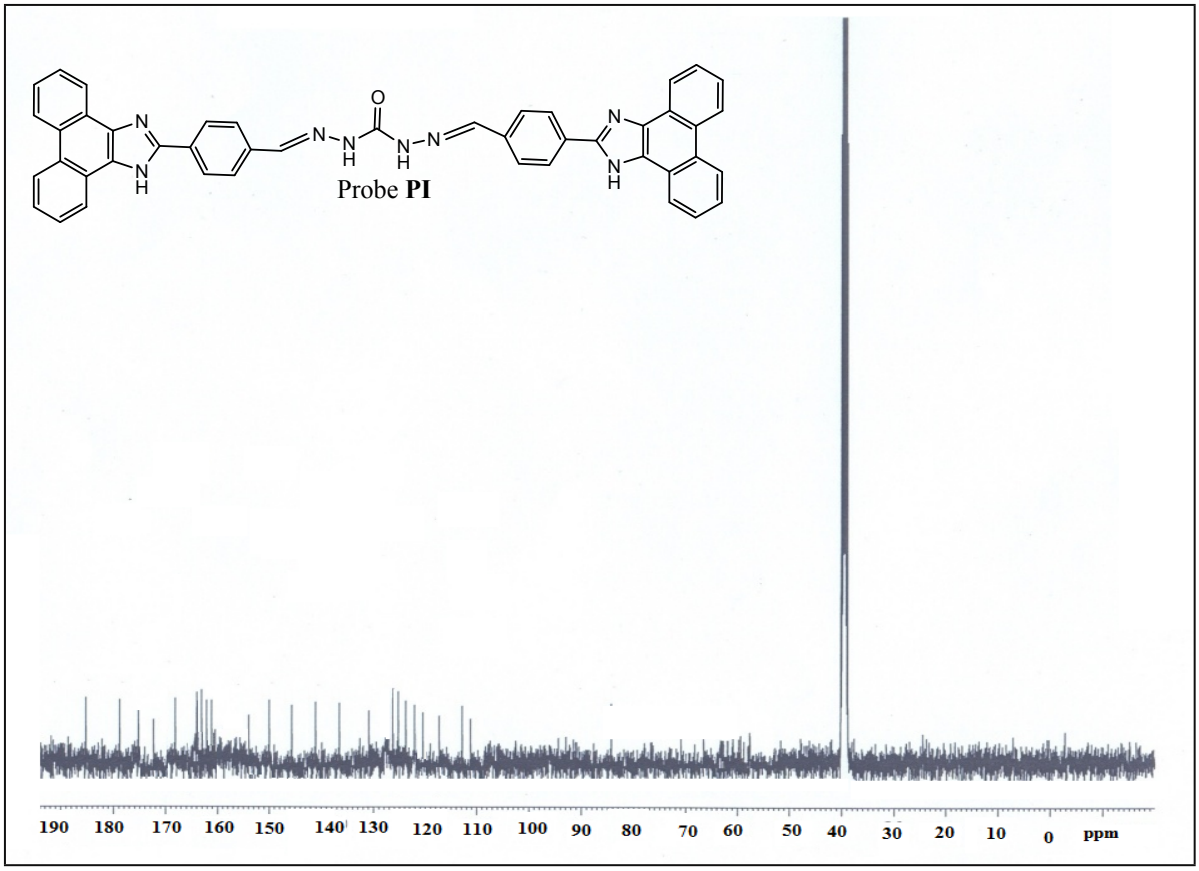

Fig. S3: ^{13}C NMR spectrum of probe **PI.**

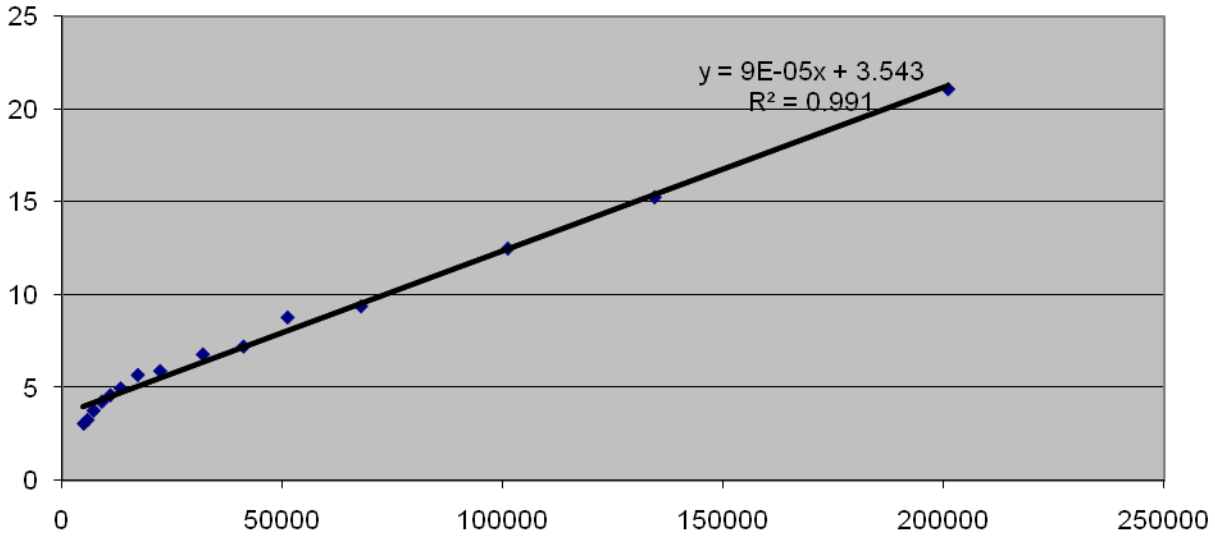

Fig. S4. Binding constant curve of probe **PI** with F^- determined by UV –Vis method.

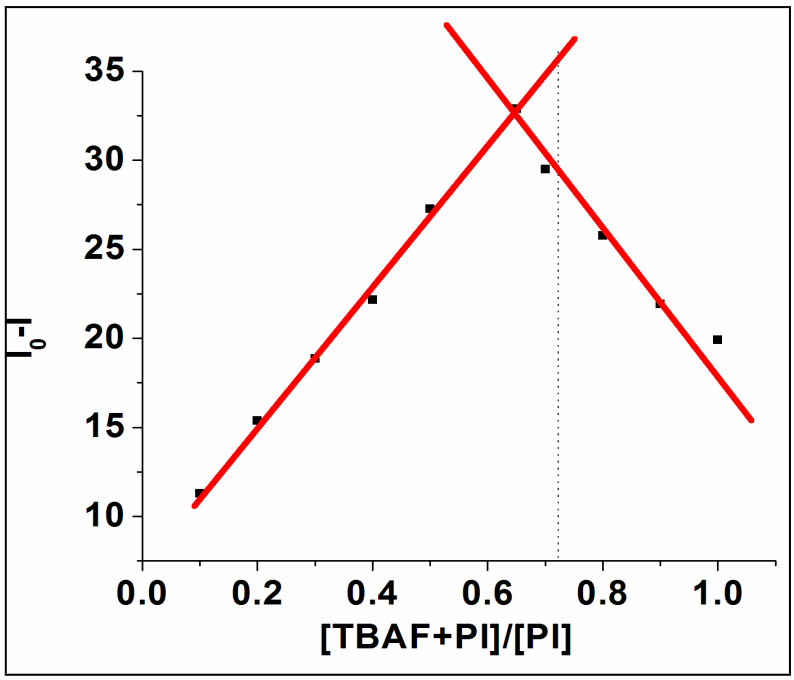

Fig. S5. Job's plot for determining the stoichiometry of probe **PI** and F^- ion by fluorescence method.

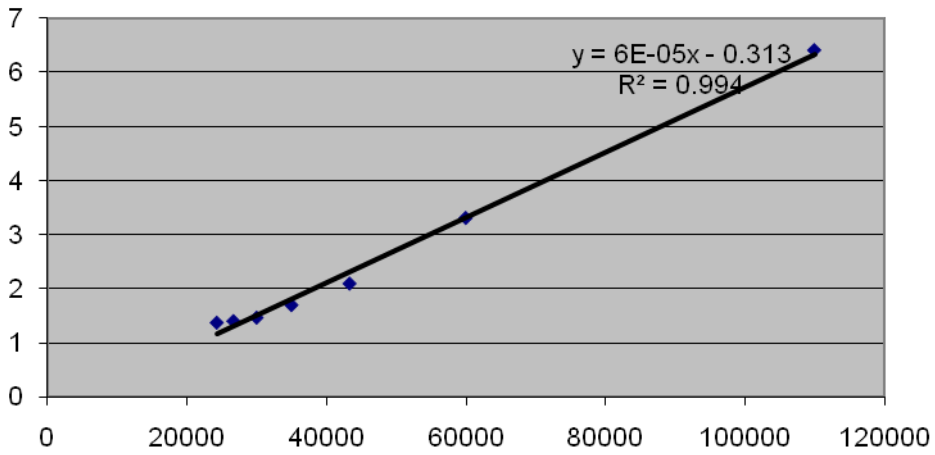

Fig. S6. Binding constant curve of Probe **PI** with F^- determined by fluorescence method.

Calculations for detection limit:

The detection limit (DL) of probe **PI** for F^- were determined from the following equation:

DL = K* Sb1/S

Where K = 2 or 3 (we take 3 in this case); Sb1 is the standard deviation of the blank solution; S is the slope of the calibration curve.

Here, we get Sb1=10383. Hence detection limit =5.2 μM.

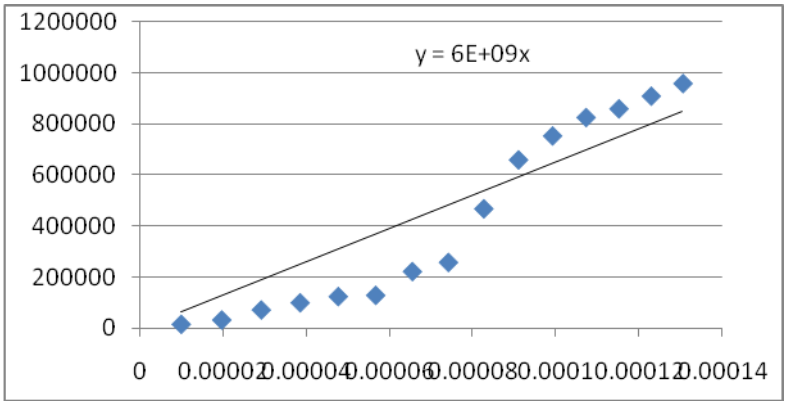

Fig. S7: Calibration curve for fluorescence titration of probe **PI** with F^-.

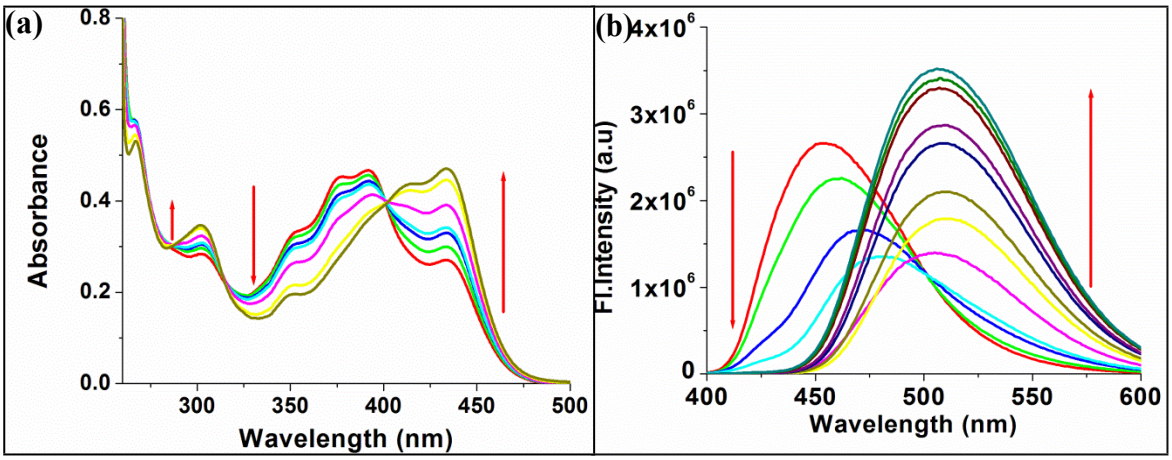

Fig.S8: (a) The changes in UV/Vis spectra of probe **PI** in DMSO (10^{-5}M) after addition of 120 equiv of OH^-. (b) Fluorescence (Excitation=392 nm) titration of probe **PI** with OH^- (as a TBAOH salt from 0 to 100 equiv) in DMSO.

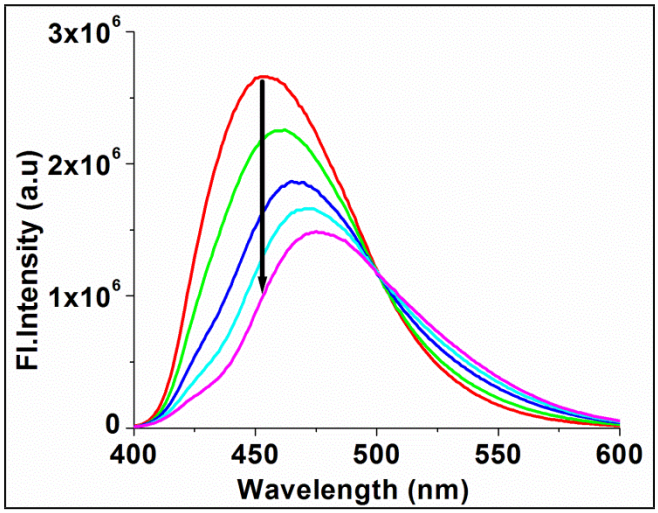

Fig.S9: Fluorescence (Excitation=392 nm) titration of probe **PI** with F^- (as a TBAF salt from 0 to 100 equiv) in DMSO: H_2O (95:5 v/v).

Table S1. Selected electronic excitation energies (eV), oscillator strengths (f), main configurations, and CI Coefficients of the low-lying excited states of CS1 and all the complexes. The data were calculated by TDDFT//B3LYP/6-31+G(*d,p*) based on the optimized ground state geometries.

Molecules	Electronic Transition	Excitation Energy[a]	f[b]	Composition[c]	(composition) %
Probe **PI**					
	$S_0 \rightarrow S_1$	2.8792 eV (430.62 nm)	2.3541	H → L	91.99
	$S_0 \rightarrow S_4$	3.4115 eV eV(363.43 nm)	0.3416	H -1→ L+1	92.07
	$S_0 \rightarrow S_9$	3.7306 eV(332.34 nm)	0.2947	H-2 → L	64.33
Deprotonated Structure of probe **PI-**					
	$S_0 \rightarrow S_1$	2.7012 eV(458.99 nm)	2.5180	H → L	93.81
	$S_0 \rightarrow S_6$	3.3861 eV(366.16 nm)	0.3148	H-1 → L+1	71.11
	$S_0 \rightarrow S_{25}$	4.3384 eV(285.78 nm)	0.3519	H-3 → L+3 H-2 → L+2	33.97
	$S_0 \rightarrow S_{32}$	4.4932 eV(275.94 nm)	0.3895	H-5 → L	57.07
	$S_0 \rightarrow S_{36}$	4.5768 eV(270.90 nm)	0.5110	H-5 → L+1	54.78

[a] Only selected excited states were considered. The numbers in parentheses are the excitation energy in wavelength. [b] Oscillator strength (only the f > 0.25 was considered). [c] H stands for HOMO and L stands for LUMO.

Reference

1. J. Tomasi and M. Persico, *Chem. Rev.*,1994, **94**, 2027−2094.

2. M. Cossi,; V. Barone,; R.Cammi,; J. Tomasi, *Chem. Phys. Lett.* 1996, **255**, 327−335.

3. V. Barone,; M. Cossi and J. J.Tomasi, *Chem. Phys.* 1997, **107**, 3210−3221.

4. V.Barone,; M. Cossi and J. J. Tomasi, *Comput. Chem.* 1998, **19**, 404−417.

5. M. Cossi and V. J. Barone, *Chem. Phys.* 1998, **109**, 6246−6254.