Electronic Supplementary Material (ESI) for New Journal of Chemistry.

SUPPORTING INFORMATION

Estimation of hydrogen sulfide from crude petroleum: A unique invention using a simple chemosensor

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1. NMR Studies:

^{1}H NMR of Compound A in DMSO-d_6 :

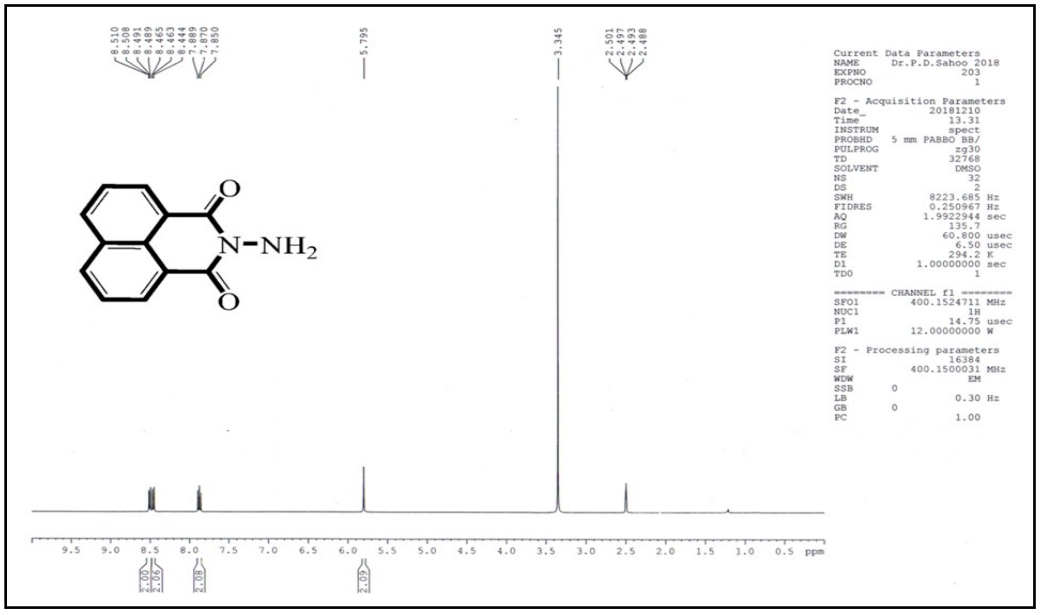

Fig. S1 ^{1}H NMR of Compound **A** in DMSO-d_6 (400 MHz).

^{13}C NMR of Compound A in DMSO-d_6:

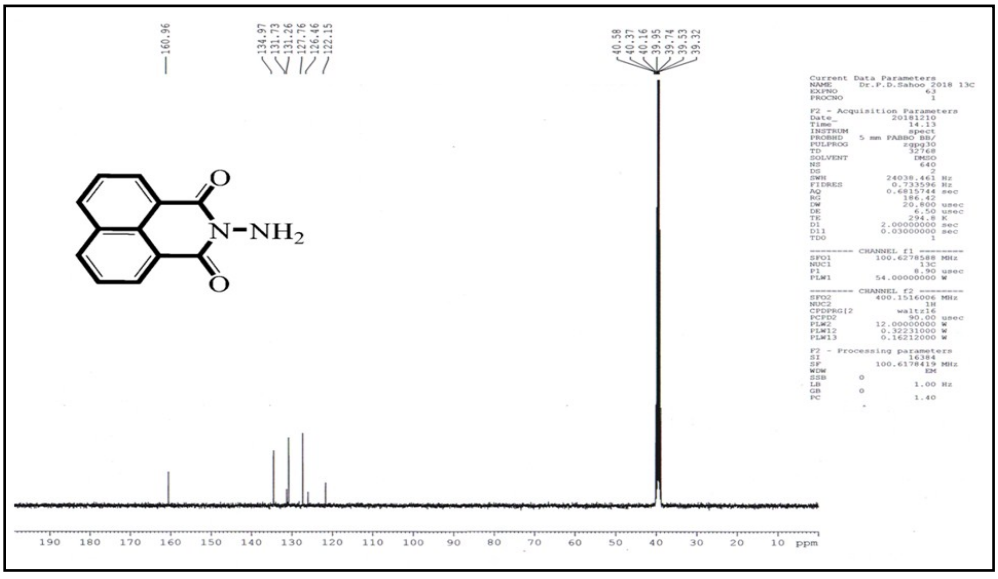

Fig. S2 ^{13}C NMR of Compound **A** in DMSO-d_6 (400 MHz).

^{1}H NMR of NPSI in DMSO-d_6 :

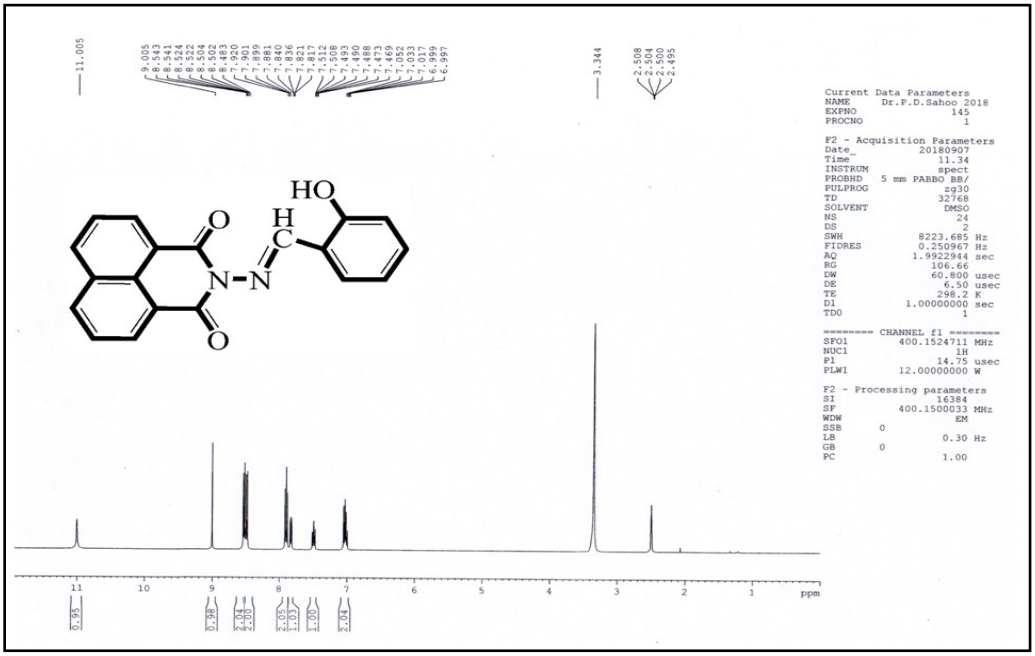

Fig. S3 ^{1}H NMR of **NPSI** in DMSO-d_6 (400 MHz).

^{13}C NMR of NPSI in DMSO-d_6:

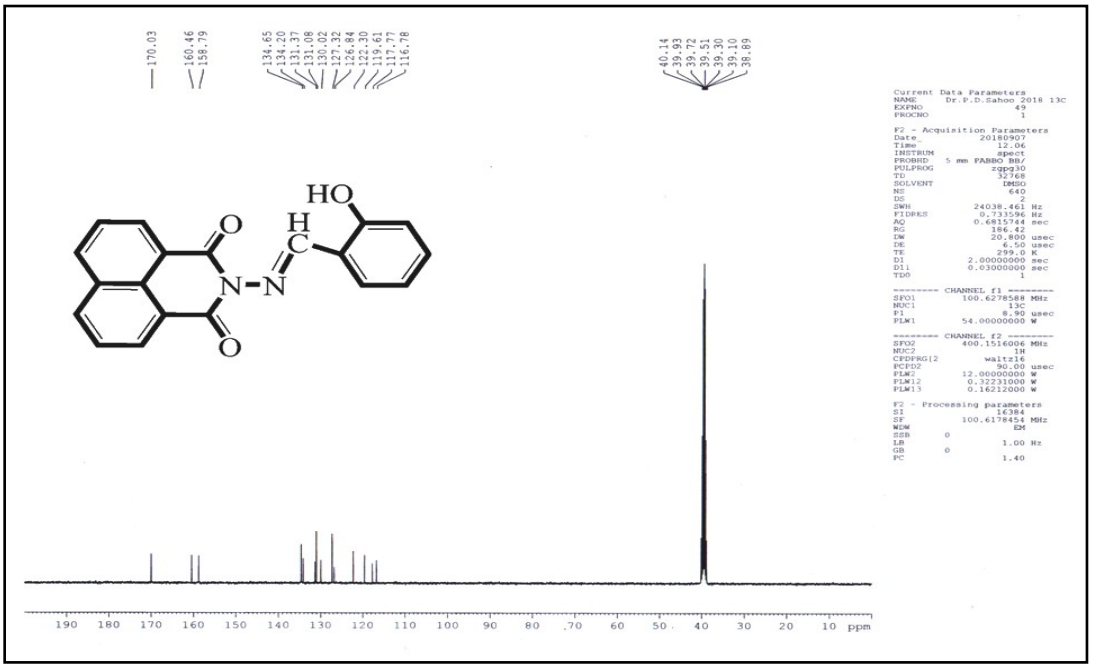

Fig. S4 ^{13}C NMR of **NPSI** in DMSO-d_6 (400 MHz).

2. Mass spectrum of NPSI :

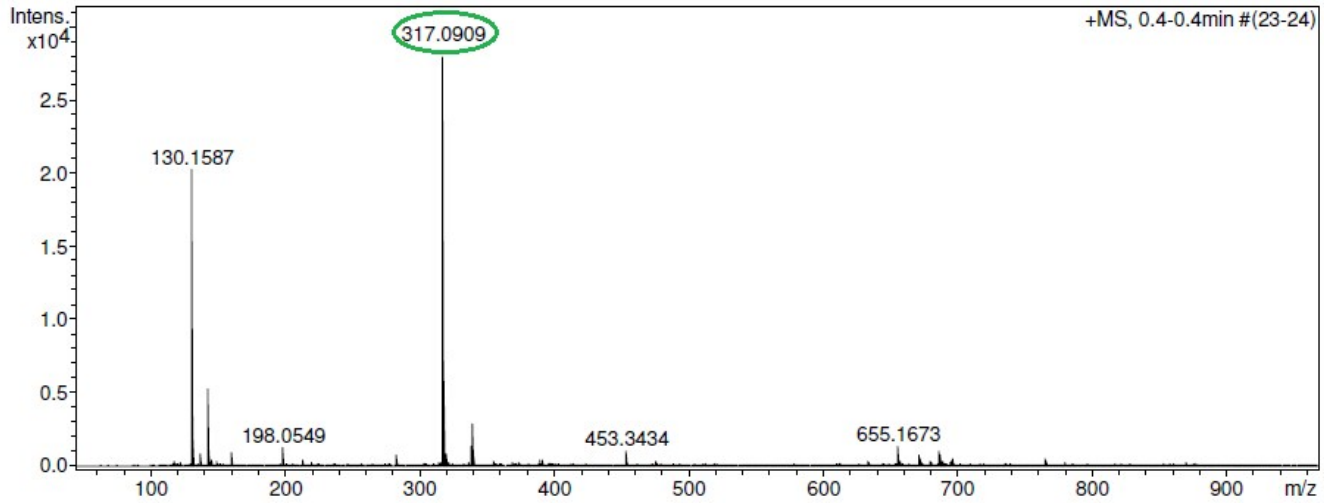

Fig. S5 HRMS of **NPSI.**

3. Job's plot for determining the stoichiometry of interaction by fluorescence method:

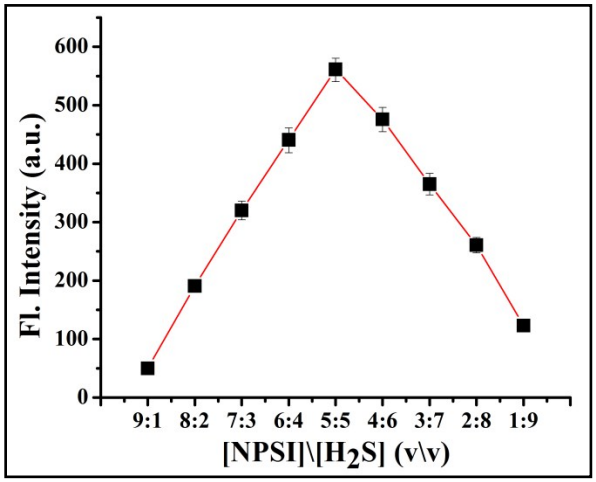

Fig. S6 Job's plot of interaction of **NPSI** with H_2S in acetonitrile-water (1:8, v/v), neutral pH(10 mM phosphate buffer), ([**NPSI**] = [H_2S] = 1 μM) by fluorescence method.

4. Calculation of binding constants of NPSI towards H_2S:

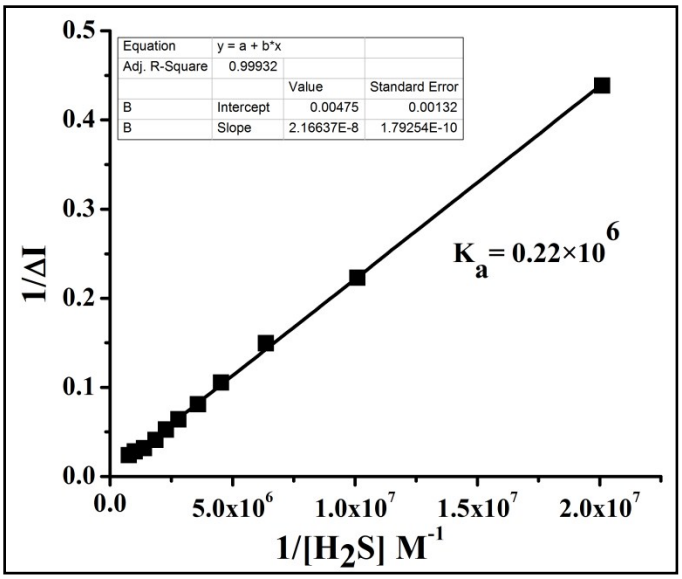

Fig. S7 Linear regression analysis for the calculation of binding constant values of **NPSI** towards H_2S.

The association const. (K_a) of **NPSI** for sensing H_2S was determined from the equation: K_a = intercept/slope. From the linear fit graph we get intercept=0.00475, slope = 2.16637×10^{-8} . Thus we get, $\mathbf{K_a}$ = (0.00475) / (2.16637×10^{-8}) = 0.22×10^6 M^{-1}.

5. Calculation of limit of detection (LOD) of NPSI with H_2S:

The detection limit of the chemosensor **NPSI** for H_2S was calculated on the basis of fluorescence titration. To determine the standard deviation for the fluorescence intensity, the emission intensity of four individual receptors without H_2S was measured by 10 times and the standard deviation of blank measurements was calculated.

The limit of detection (LOD) of **NPSI** for sensing H_2S was determined from the following equation[2].

$$LOD = K \times SD/S$$

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

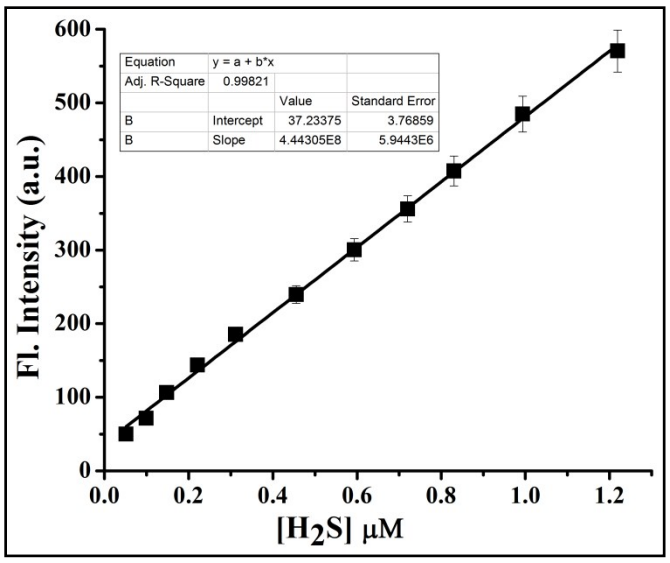

Fig. S8 Linear fit curve of **NPSI** with respect to H_2S concentration. Standard deviation are represented by error bars (n=3).

From the linear fit graph we get slope = 4.44305×10^8, and SD value is 7.344

Thus using the above formula we get the Limit of Detection = 4.96×10^{-8} M, i.e 49.6 nM. Therefore **NPSI** can detect H_2S up to this very lower concentration by fluorescence technique.

6. pH titration curve of NPSI upon gradual addition of H_2S:

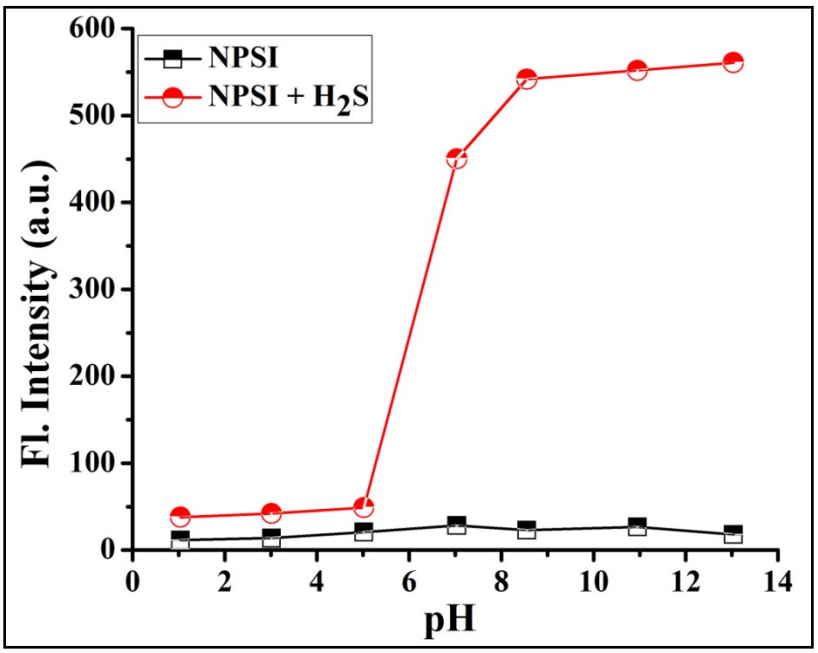

Fig. S9 Fluorescence responses of probe **NPSI** (black) and **NPSI**-H_2S (red) in different pH conditions in CH_3CN/H_2O (1:8, v/v).

7. Partial HRMS of the mixed assay system:

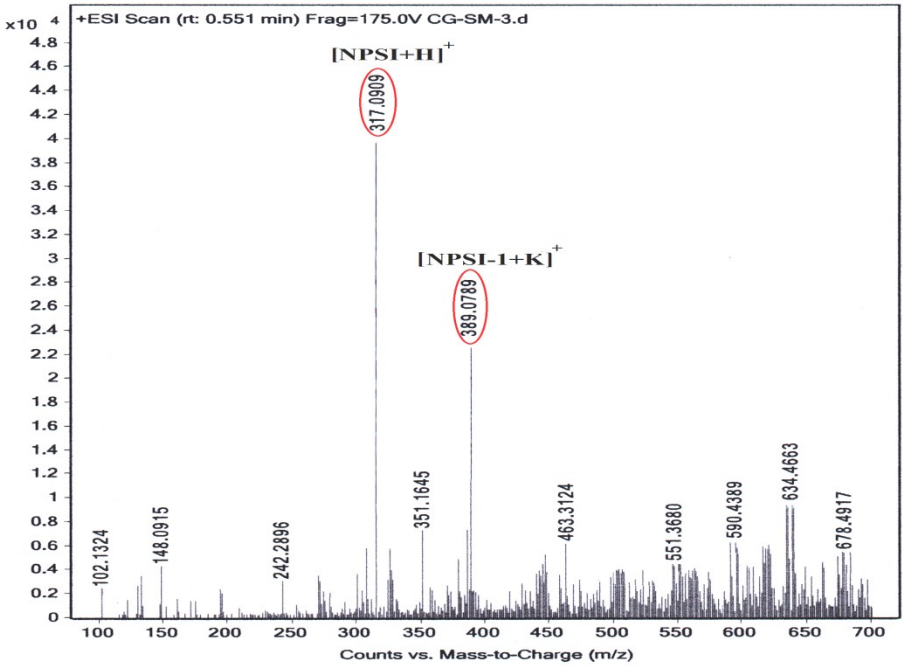

Fig. S10 Partial HRMS spectra of **NPSI-H_2S** mixture in acetonitrile, taken after two hours of mixing.

8. Details of energy calculations using Density Functional Theory (DFT):

Details	NPSI	NPSI-1
Calculation method	B3LYP	B3LYP
Basis set	6-311G**	6-311G**
E(CAM-B3LYP) (a.u.)	-1066.707	-1466.141
Charge, Multiplicity	0, 1	0, 1
Solvent (CPCM)	Water	Water

Table S1. Details of the geometry optimization in Gaussian 09 program.

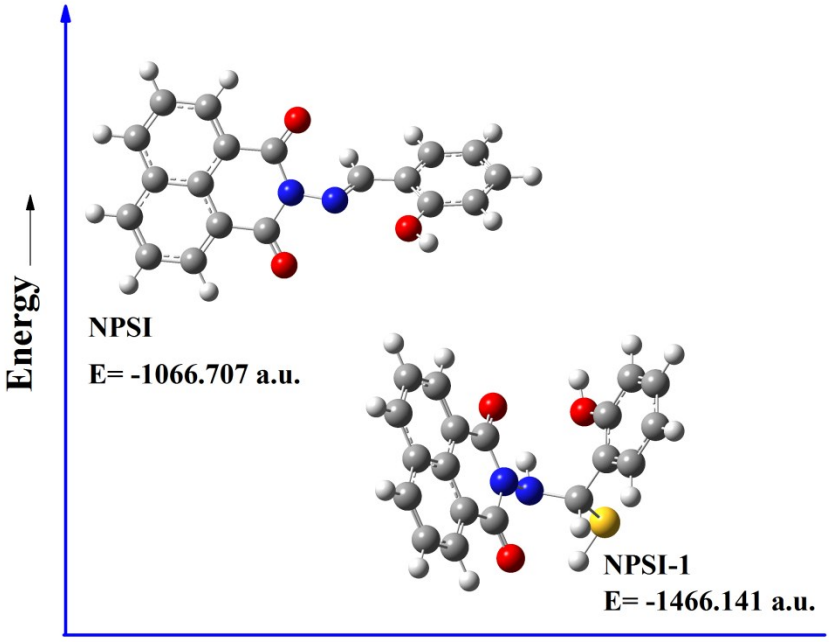

Fig. S11. Energy optimized geometries of **NPSI** and **NPSI-1** obtained at the B3LYP/6-311G** levels of theory with CPCM solvation (H_2O).

Table S2. Selected electronic excitation energies (eV), oscillator strengths (f), main configurations of the low-lying excited states of all the molecules and complexes. The data were calculated by TDDFT//B3LYP/6-311G(d,p) based on the optimized ground state geometries.

Molecules	Electronic Transition	Excitation Energya[a]	f[b]	Composition[c] (%)
NPSI	$S_0 \rightarrow S_2$	3.66 eV 338.66 nm	0.3239	H-1 → L (60%)
	$S_0 \rightarrow S_5$	4.05 eV 305.90 nm	0.2305	H → L+1 (49%)
NPSI-1	$S_0 \rightarrow S_3$	3.44 eV 370.02 nm	0.2591	H -1 → L (68.6%)
	$S_0 \rightarrow S_{20}$	3.4997 eV 225.44 nm	0.1973	H -9 → L (51%)

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

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)**
NPSI	-0.24646	-0.09788	0.14858	4.05	93.39
NPSI-1	-0.24909	-0.1097	0.13939	3.79	87.47