Supporting Information

Naked eye detection of Arsenite, Arsenate, and H_2S using a single paper strip, based on deprotonation mechanism by a Schiff base naphthaldehyde conjugate

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Table of Contents

1. Performance comparison of existing methods and present method for detection of AsO_2^-, AsO_4^{3-} and H_2S.

Table S1. Performance comparison of existing methods and present method for detection of AsO_2^- and AsO_4^{3-}.

Sensors	Analytes	Detection method	Detection medium	Sensitivity	Detection limits	Estimation	Reference
(2-hydroxy napthaldehyde conjugated 2,4-DNP)	**AsO_2^-, AsO_4^{3-} and H_2S**	**colorimetric**	**DMSO:H_2O (4:1 v/v, pH 7.0, 10 mM Tris-HCl buffer).**	**High**	**0.15 µM and 0.17 µM**	**Yes**	**Present work**
RhB molecules	H_2AsO^{4-} and $HAsO_4^{2-}$	fluorometric	Aqueous medium	High	10 g/L	Yes	*Sensors and Actuators B.,* 2017, **241**,1014–1023
benzothiazole Schiff base	As^{3+}/As^{5+}	colorimetric	(DMSO:H_2O ; 1:1, v/v)	High	<7.0 ppb	No	*Anal. Methods*, 2017, **9**, 1779-1785
2-((2-hydroxynaphthalen-1-yl)methylene) hydrazine	AsO_2^- and CN^-	Colorimetric and fluorometric	DMF:H_2O (HEPES buffer of 7.2 pH) (9:1, v/v solution)	High	66 nM	Yes	*RSC Adv.,* 2016, **6**, 100136-100144
2,6-diformyl-p-cresol with 4-aminoantipyrine	AsO_3^{3-}	fluorometric	HEPES buffer (1 mM, pH 7.4) (DMSO-Water 1:9)	High	4.12 ppb	No	*Anal. Chem.,* 2014, **86**, 11357–11361
5-methyl isatin	AsO_2^- and Hg^{2+}	colorimetric	in DMSO	Modarate	10.42 µM for AsO_2^-	No	*Sensors and Actuators B: Chemical*, 2019, **284**, 271-280
hydrazine-based thiocarbamide	PO_4^{3-} and AsO_3^{3-}	Colorimetric and fluorometric	9:1 v/v Acetonitrile: H_2O (pH = 7.2)	Modarate	34 nM	Yes	*New J. Chem.*, 2018, **42**, 6236-6246

Table S2. Performance comparison of existing methods and present method for detection of H_2S.

Sensors	Analytes	Detection method	Detection medium	Sensitivity	Detection limits	Estimation	Reference
(2-hydroxy napthaldehyde conjugated 2,4-DNP)	**H_2S/S^{2-} and AsO_2^-/AsO_4^{3-}**	**colorimetric**	**DMSO:H_2O (4:1 v/v, pH 7.0, 10 mM Tris-HCl buffer).**	**High**	**0.17 µM and 0.15 µM**	**Yes**	**Present work**
2,3-dihydroxybenzaldehyde and sulfanilamide	H_2S	colorimetric	DMSO: Bis–Tris buffer (4:6, 10 mM, pH 7.0)	High	30 µM	Yes	*Anal. Methods*, 2021, **13**, 1332
Naminophthalimide and 8-hydroxyjulolidine-9-carboxaldehyde	Cu^{2+}, PO_4^{3-} and S^{2-}	colorimetric and fluorometric	buffer/DMF solution (3/2, v/v, 10 mM bis-tris, pH = 7.0)	Low	——	No	*Ind. Eng. Chem. Res.*, 2017, **56**, 8399–8407
5-(azo-benzene)-Salicylidene-aniline	H_2S	colorimetric and fluorometric	DMSO DMSO–phosphate-buffered saline (PBS) (4:1, v/v, pH 7.4).	High	——	No	*Luminescence.*, 2017, **32**, 765-771
azo-dye based bis-Schiff base	S^{2-}	colorimetric and fluorometric	HEPES buffer (10 mL, pH 7.00).	High	16 µM	Yes	*Anal. Methods***,** 2018, **10**, 2317-2326
2-aminoethyl piperazine and 4-chloro-7-nitrobenz-2-oxa-1,3-diazole	H_2S, Hg^{2+}	colorimetric	bis-tris buffer solution (10 mM, pH 7.0) to	Modarate	——	No	*Dalton Trans.*, 2016, **45**, 5700-5712
Dabsyl based	H_2S, Hg^{2+}	colorimetric	HEPES-CH_3CN buffer.	colorimetric	28 mM	No	ChemistrySelect, 2016, **1**,1533-1540
4-(piperidin-1-yl) naphthalene-1,2-dione	H_2S	colorimetric and fluorometric	CH3CN: HEPES buffer (50:50, v:v, pH-7.4)	High	0.77 µM	No	*Org. Biomol. Chem.*, 2016, **14**, 570-576
2- hydroxy-1-napthylaldehyde	H_2S/HS^-	colorimetric and fluorometric	CH_3CN:HEPES buffer solution	High	1.67 µM	No	*New J. Chem.*, 2015, **39**, 5669-5675

2. NMR Studies

¹H NMR of NADNP in DMSO-d_6:

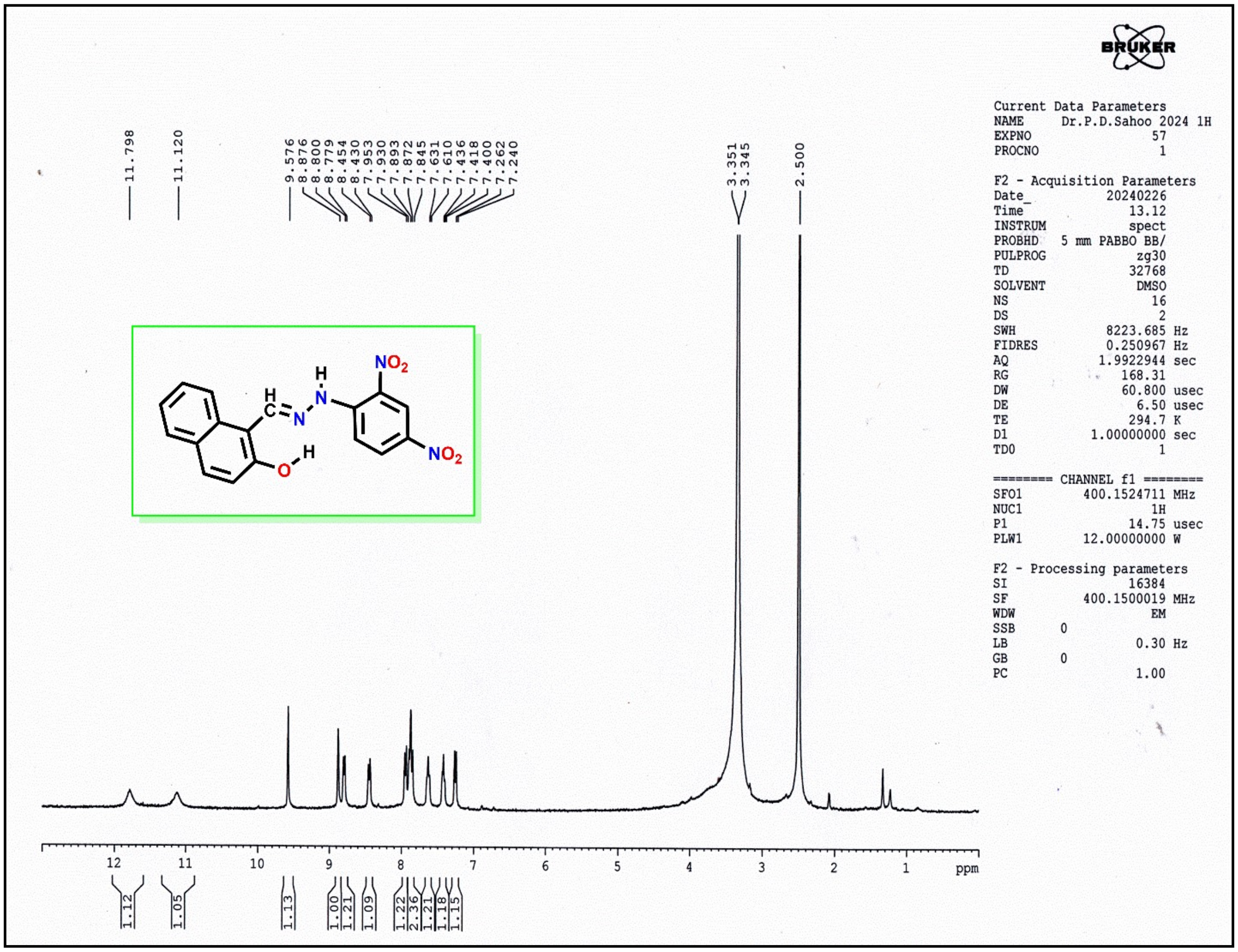


Fig. S1 ¹H NMR of NADNP in DMSO-d_6 (400 MHz).

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

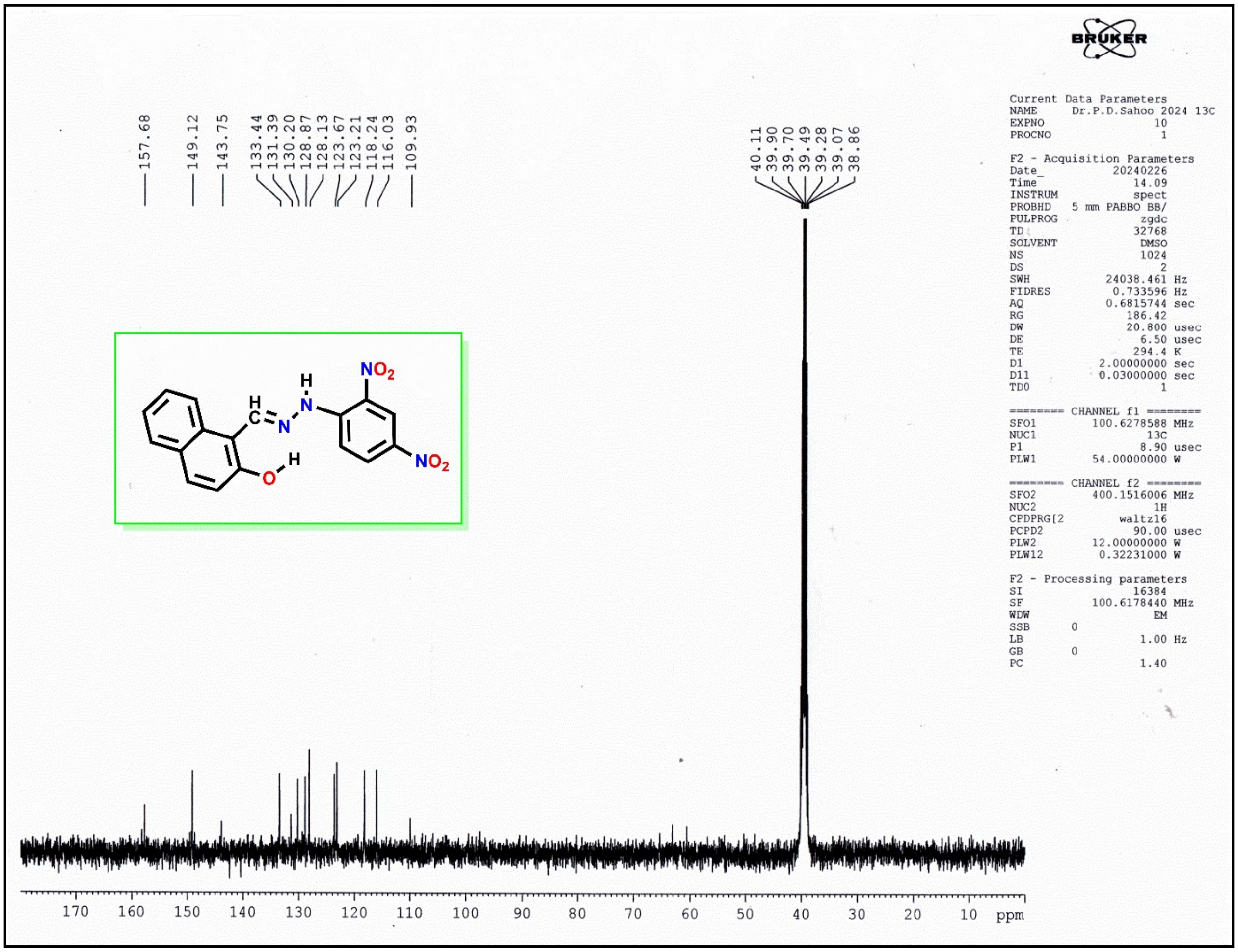


Fig. S2 ^{13}C NMR of NADNP in DMSO-d_6 (100 MHz).

3. Job's plot of NADNP with AsO_2^- and AsO_4^{3-}.

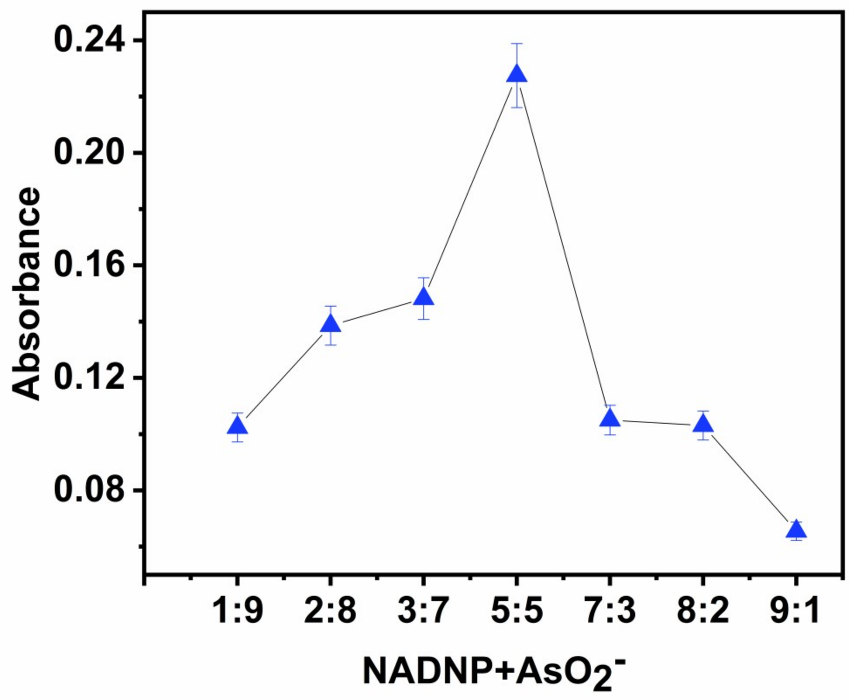


Fig. S3 Job's plot of NADNP (100 μM) with AsO_2^- (100 μM) in DMSO, at neutral pH, by UV-vis method (at 519 nm), which indicate 1:1 stoichiometry for NADNP with AsO_2^-. Standard deviations are represented by error bar (n=3).

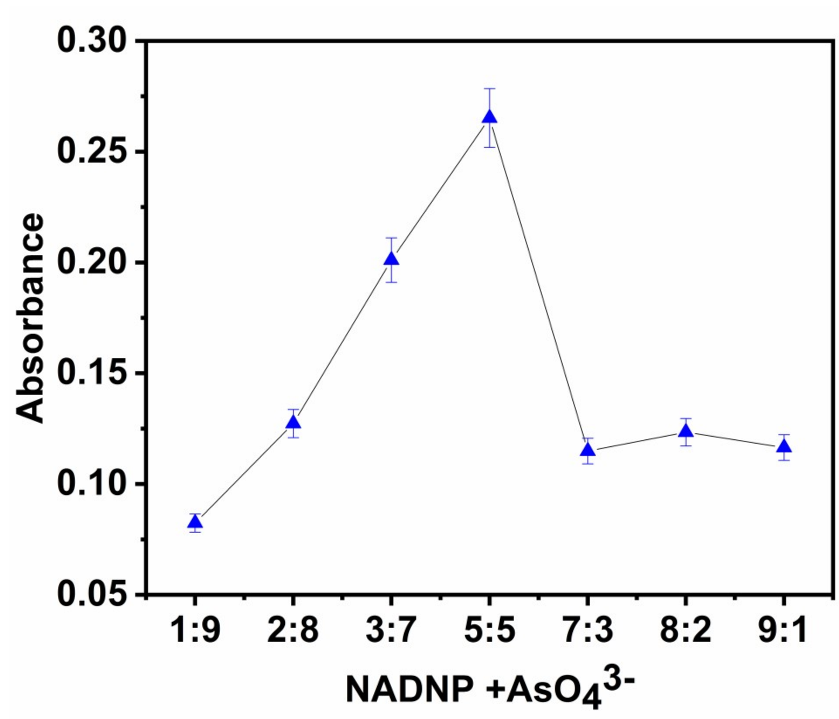


Fig. S4 Job's plot of NADNP (100 μM) with AsO_4^{3-} (100 μM) in DMSO, at neutral pH, by UV-vis method (at 515 nm), which indicate 1:1 stoichiometry for NADNP with AsO_4^{3-}. Standard deviations are represented by error bar (n=3).

4. Evaluation of the association constants by UV-vis method (NADNP-As^{3+}/As^{5+} complex):

a) Determination of the association constants for the formation of NADNP-As^{3+}complex:

Association constant was calculated according to the Benesi-Hildebrand equation. K_a was calculated following the equation stated below.

$$1/(A-A_o) = 1/\{K(A_{max}-A_o)\,[G]^n\} + 1/[A_{max}-A_o]$$

Here, A_o is the absorbance of receptor in the absence of guest, A is the absorbance recorded in the presence of added guest, A_{max} is absorbance in presence of added $[G]_{max}$ and K_a is the association constant, where [G] is [AsO_2^-]. The association constant (Ka) could be determined from the slope of the straight line of the plot of 1/(A-Ao) against 1/[AsO_2^-]and is found to be:

Binding constant calculation graph (UV-vis method):

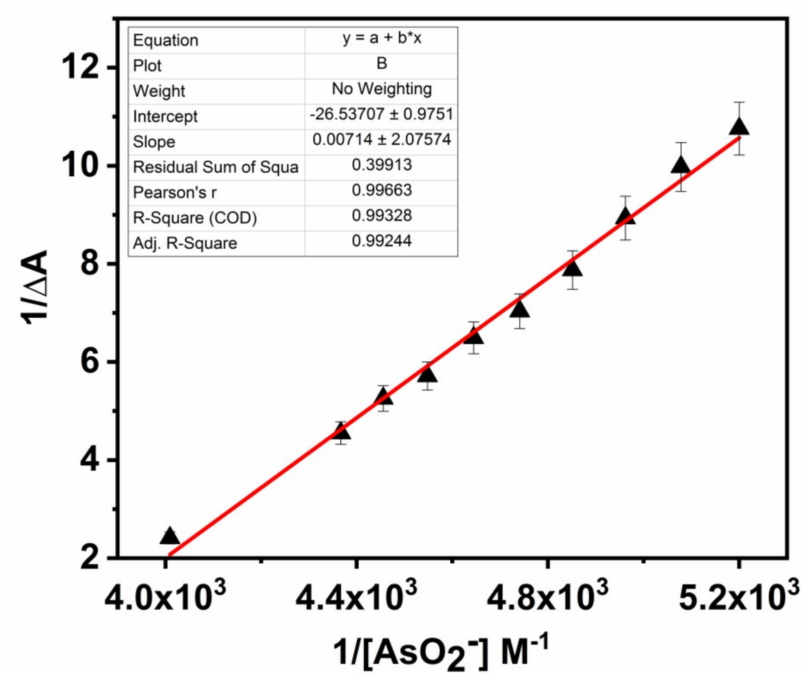


Fig. S5 Linear regression analysis (1/[G] vs 1/ΔA) for the calculation of association constant value by UV-vis titration method. Standard deviations are represented by error bar (n=3).

The association const. (K_a) of NADNP for sensing AsO_2^- was determined from the equation: K_a = intercept/slope. From the linear fit graph, we get intercept =26.53707, slope = 0.00714. Thus, we get, K_a = 26.53707/0.00714 = 3.7 x 10^3 M^{-1}.

b) Determination of the association constants for the formation of NADNP-As^{5+}complex:

Association constant was calculated according to the Benesi-Hildebrand equation. K_a was calculated following the equation stated below.

$$1/(A-A_o) = 1/\{K(A_{max}–A_o) [G]^n\} + 1/[A_{max}-A_o]$$

Here, A_o is the absorbance of receptor in the absence of guest, A is the absorbance recorded in the presence of added guest, A_{max} is absorbance in presence of added $[G]_{max}$ and K_a is the association constant, where [G] is $[AsO_4^{3-}]$. The association constant (Ka) could be determined from the slope of the straight line of the plot of 1/(A-Ao) against $1/[AsO_4^{3-}]$and is found to be:

Binding constant calculation graph (UV-vis method):

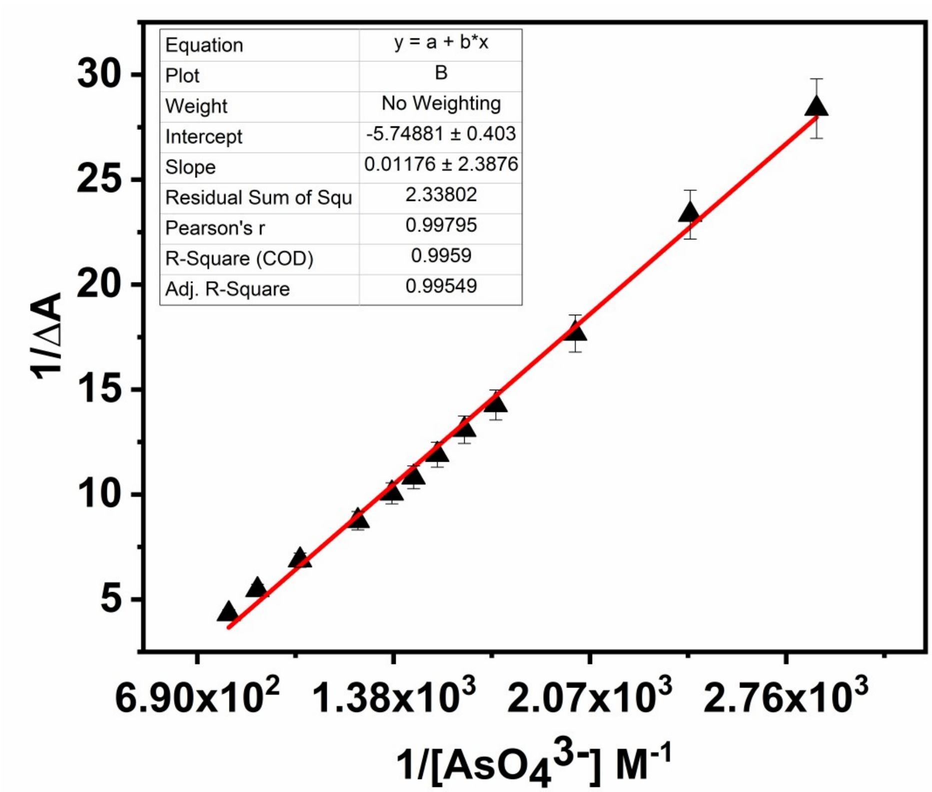


Fig. S6 Linear regression analysis (1/[G] vs 1/ΔA) for the calculation of association constant value by UV-vis titration method. Standard deviations are represented by error bar (n=3).

The association const. (K_a) of NADNP for sensing AsO_4^{3-} was determined from the equation: K_a = intercept/slope. From the linear fit graph, we get intercept =5.74881, slope = 0.01176. Thus, we get, K_a = 5.74881/0.01176= 4.9 x 10^2 M^{-1}.

5. Calculation of limit of detection (LOD) by UV-vis method (NADNP-As^{3+}/As^{5+} complex):

a) Limit of detection (LOD) NADNP with As^{3+}:

The detection limit of the chemosensor NADNP for AsO_2^- was calculated on the basis of UV-vis method. To determine the standard deviation for the absorbance, the absorbance of four individual receptors without AsO_2^- was measured by 10 times and the standard deviation of blank measurements was calculated. The limit of detection (LOD) of NADNP for sensing AsO_2^- was determined from the following equation[2-3]:

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

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.

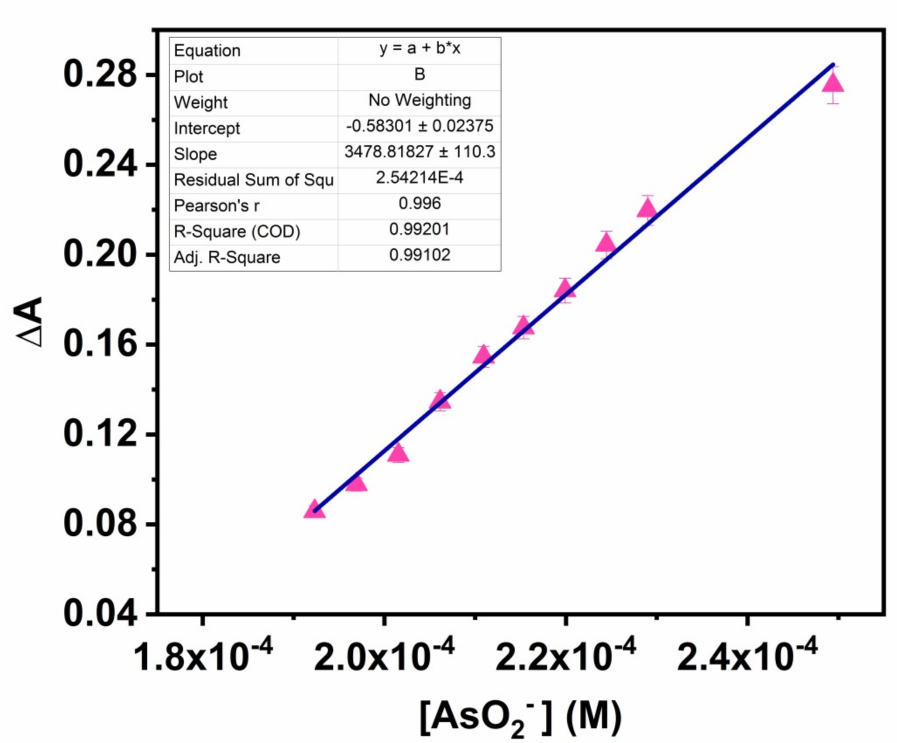


Fig. S8 Linear fit curve of NADNP at 519 nm with respect to AsO_2^- concentration. Standard deviations are represented by error bar (n=3).

For NADNP with As^{3+}:

From the linear fit graph, we get slope = 3478.81827, and SD value is 0.0001.

Thus, using the above formula, we get the Limit of Detection = 1.5×10^{-7} M (0.15 μM). Therefore, NADNP can detect AsO_2^- up to this very lower concentration by UV-vis method.

b) Limit of detection (LOD) NADNP with As^{5+}:

The detection limit of the chemosensor NADNP for AsO_4^{3-} was calculated on the basis of UV-vis method. To determine the standard deviation for the absorbance, the absorbance of four individual receptors without AsO_4^{3-} was measured by 10 times and the standard deviation of blank measurements was calculated. The limit of detection (LOD) of NADNP for sensing AsO_4^{3-} was determined from the following equation[2-3]:

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

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.

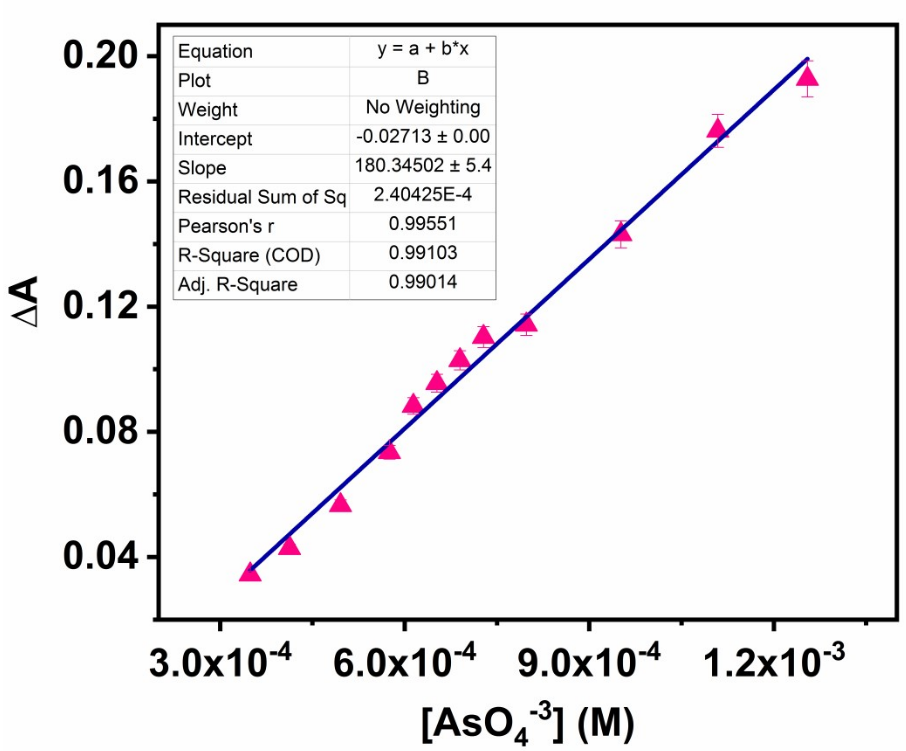


Fig. S7 Linear fit curve of NADNP at 519 nm with respect to AsO_4^{3-} concentration. Standard deviations are represented by error bar (n=3).

For NADNP with As^{5+}:

From the linear fit graph, we get slope = 180.34502, and SD value is 0.00010.

Thus, using the above formula, we get the Limit of Detection = 1.5×10^{-7} M (0.15 μM). Therefore, NADNP can detect AsO_4^{3-} up to this very lower concentration by UV-vis method.

6. Job's plot of NADNP with H_2S.

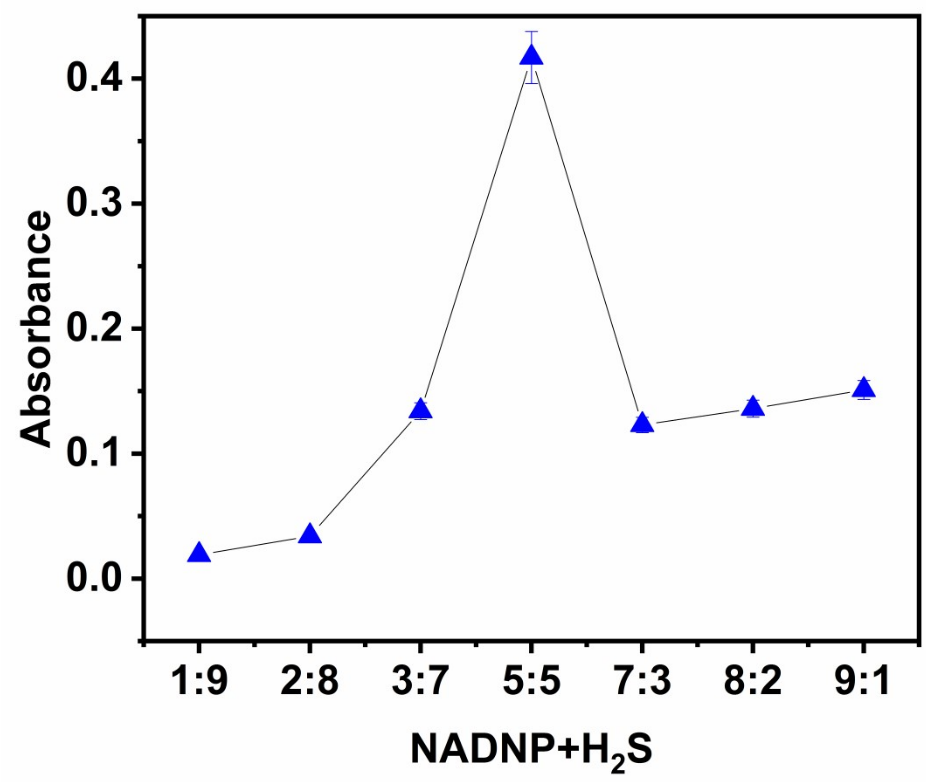


Fig. S9 Job's plot of NADNP (100 μM) with H_2S (100 μM) in DMSO, at neutral pH, by UV-Vis method (at 519 nm), which indicate 1:1 stoichiometry for NADNP with H_2S. Standard deviations are represented by error bar (n=3).

7. Evaluation of the association constants by UV-vis method (NADNP-H_2S complex):

Determination of the association constants for the formation of NADNP-H_2S complex:

Association constant was calculated according to the Benesi-Hildebrand equation. K_a was calculated following the equation stated below.

$$1/(A-A_o) = 1/\{K(A_{max}–A_o) [G]^n\} + 1/[A_{max}-A_o]$$

Here, A_o is the absorbance of receptor in the absence of guest, A is the absorbance recorded in the presence of added guest, A_{max} is absorbance in presence of added $[G]_{max}$ and K_a is the association constant, where [G] is [H_2S]. The association constant (K_a) could be determined from the slope of the straight line of the plot of 1/(A-Ao) against 1/[H_2S]and is found to be:

Binding constant calculation graph (UV-vis method):

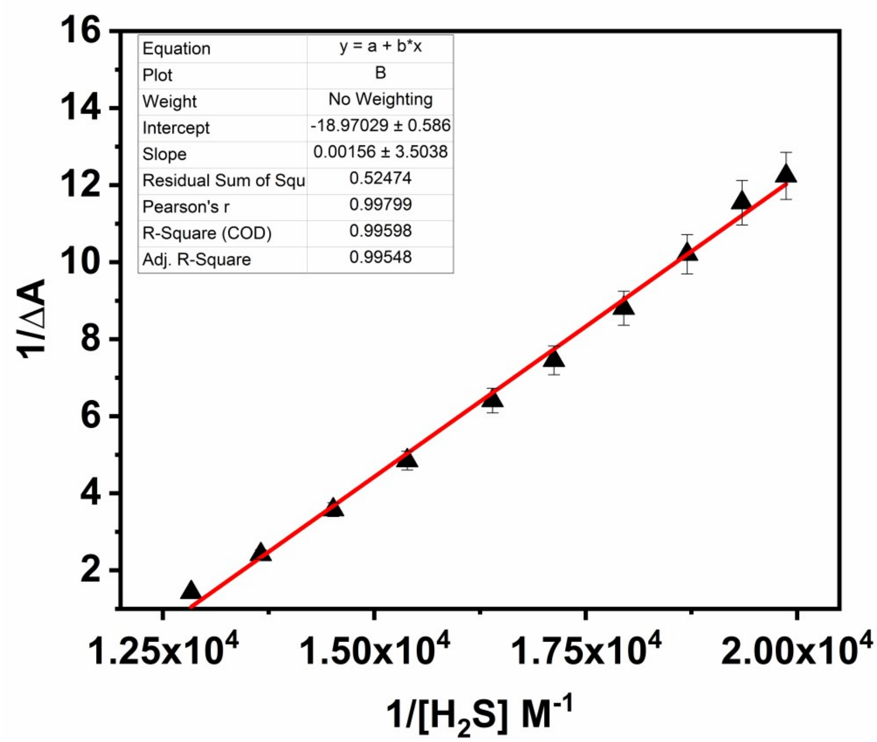


Fig. S10 Linear regression analysis (1/[G] vs 1/ΔA) for the calculation of association constant value by UV-vis titration method. Standard deviations are represented by error bar (n=3).

The association const. (K_a) of NADNP for sensing H_2S was determined from the equation: K_a = intercept/slope. From the linear fit graph, we get intercept =18.97029, slope = 0.00156. Thus, we get, K_a = 18.97029/0.00156= 1.2 x 10^4 M^{-1}.

8. Calculation of limit of detection (LOD) by UV-vis method (NADNP-H_2S complex):

Limit of detection (LOD) NADNP with H_2S:

The detection limit of the chemosensor NADNP for H_2S was calculated on the basis of UV-vis method. To determine the standard deviation for the absorbance, the absorbance 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 NADNP for sensing H_2S was determined from the following equation[2-3]:

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

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.

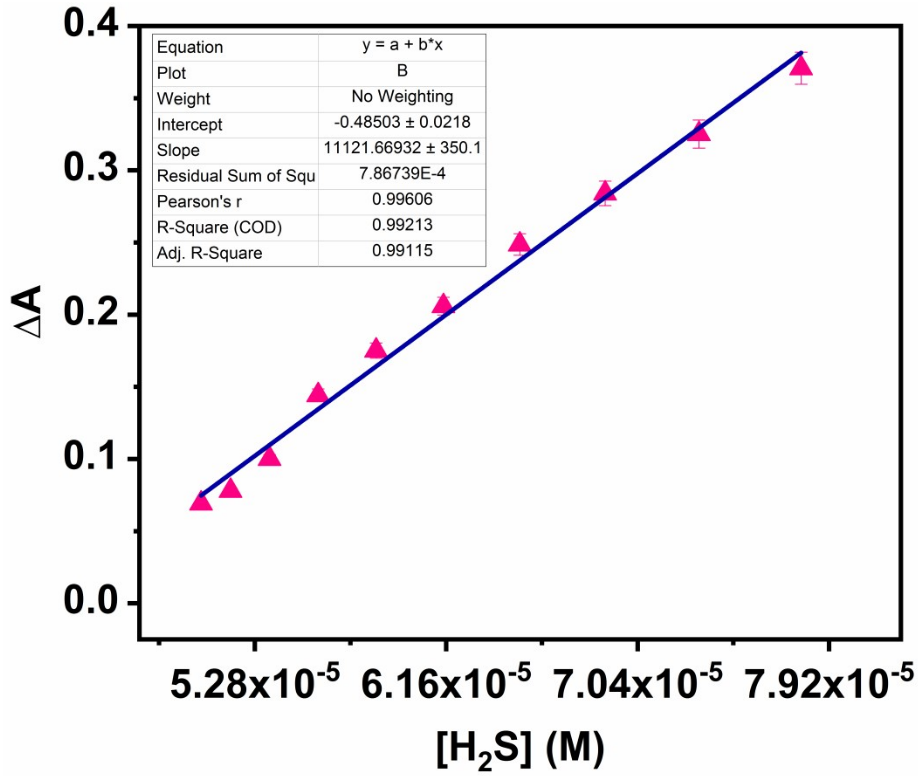


Fig. S11 Linear fit curve of NADNP at 519 nm with respect to H_2S concentration. Standard deviations are represented by error bar (n=3).

For NADNP with H_2S:

From the linear fit graph, we get slope = 11121.66932, and SD value is 0.0004.

Thus, using the above formula, we get the Limit of Detection = 1.7×10^{-7} M (0.17 μM). Therefore, NADNP can detect H_2S up to this very lower concentration by UV-vis method.

9. pH titration study:

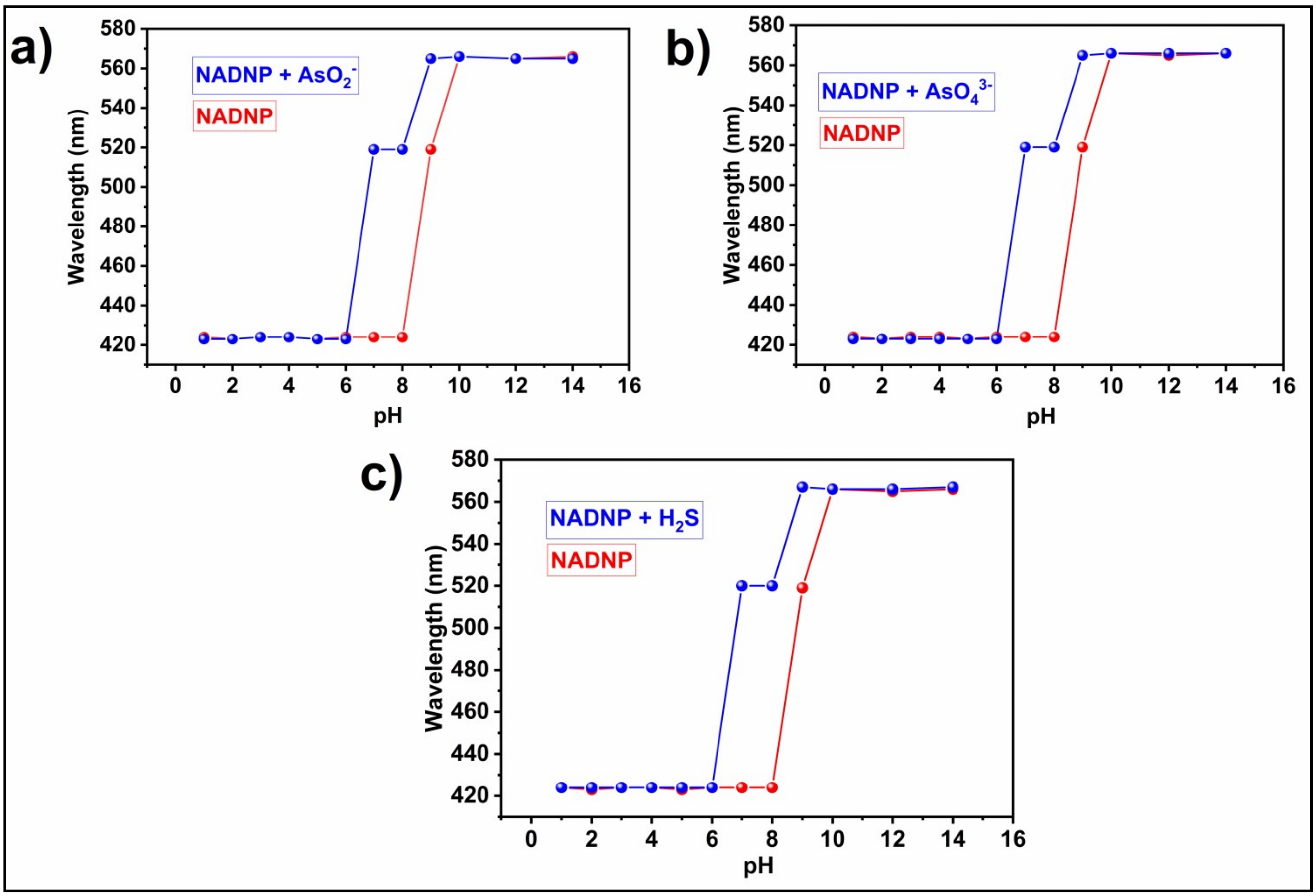


Fig. S12 a) Effect of pH on the wavelength of NADNP (10^{-5} M) in the absence of AsO_2^- (redline) and in the presence of AsO_2^- (5 x 10^{-3} M, blue line). b) Effect of pH on the wavelength of NADNP (10^{-5} M) in the absence of AsO_4^{3-} (redline) and in the presence of AsO_4^{3-} (5 x 10^{-3} M, blue line). c) Effect of pH on the wavelength of NADNP (10^{-5} M) in the absence of H_2S (redline) and in the presence of H_2S (10^{-3} M, blue line).

10. Partial HRMS of the mixed assay systems:

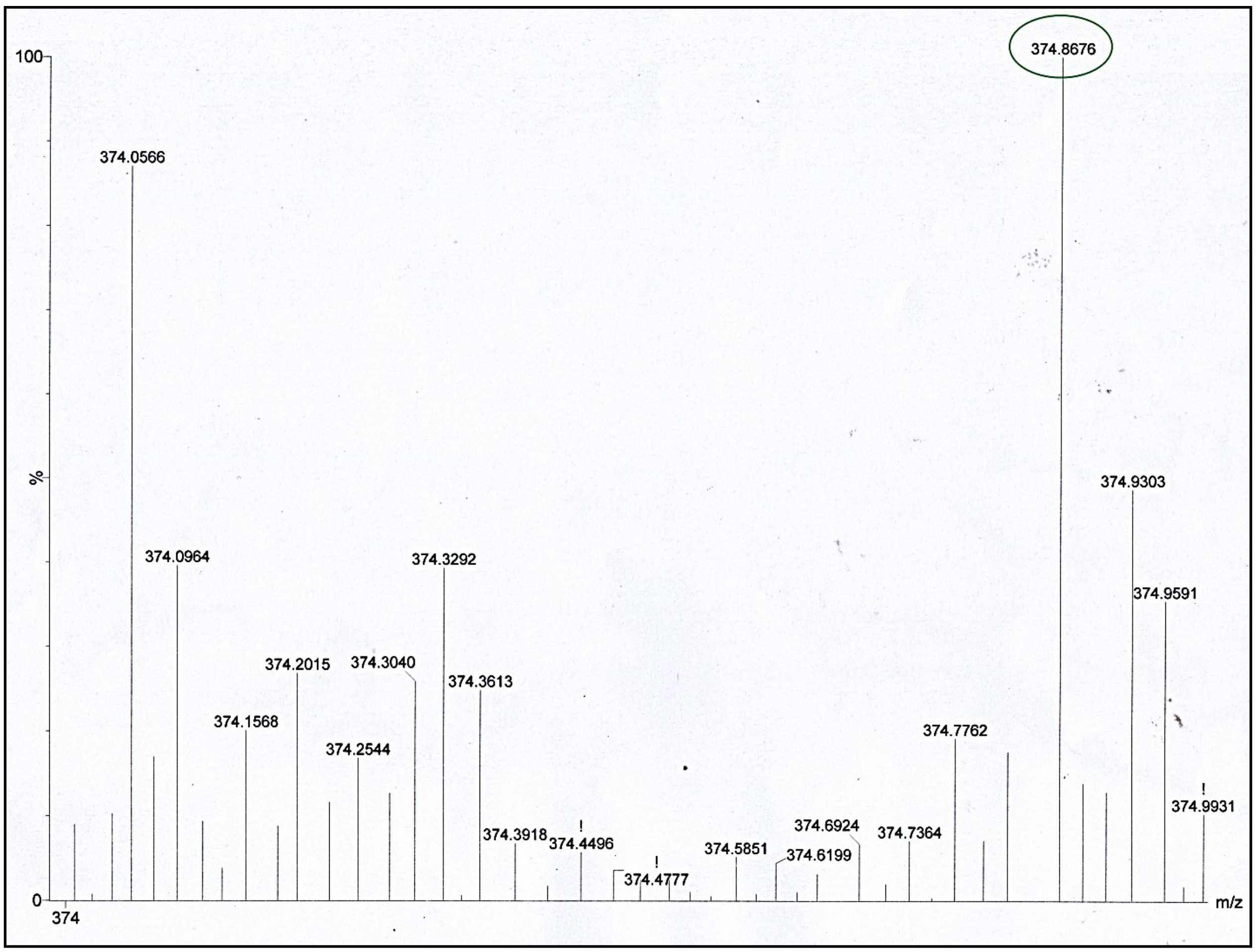


Fig. S13 Partial HRMS spectra of NADNP with AsO_2^- in MeOH.

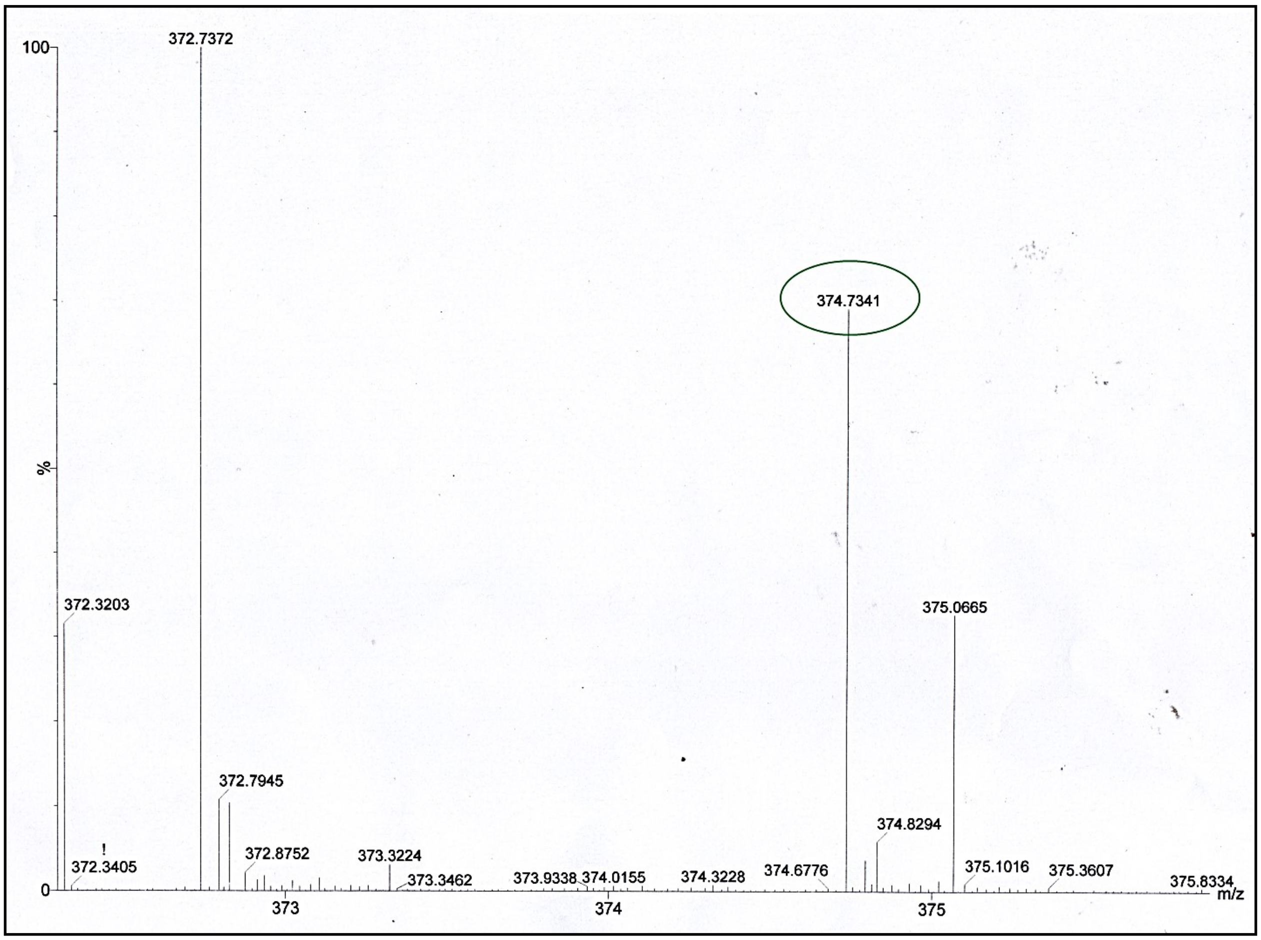


Fig. S14 Partial HRMS spectra of NADNP with AsO_4^{3-} in MeOH.

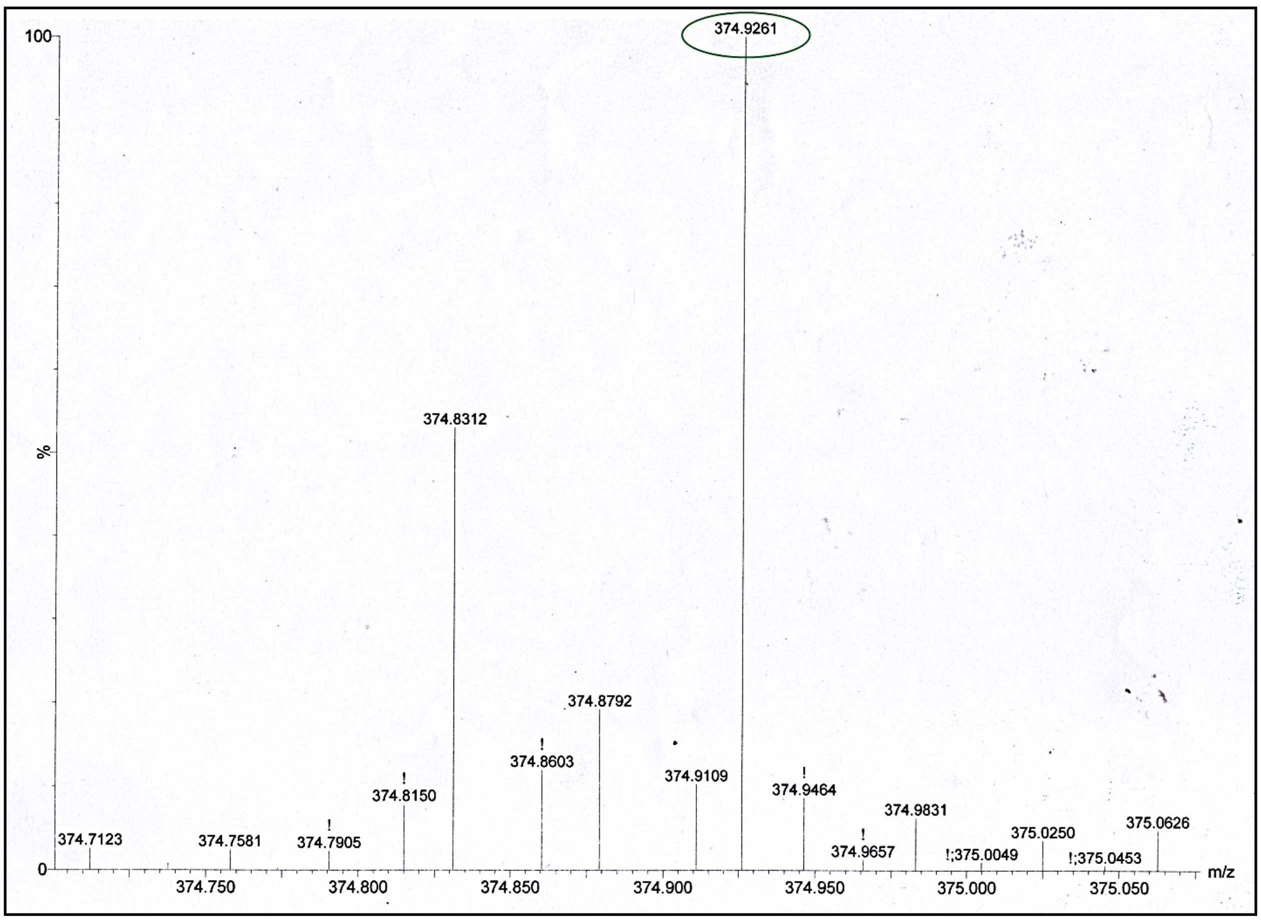


Fig. S15 Partial HRMS spectra of NADNP with H_2S in MeOH.

11. DFT Study

Table S3 Details of Geometry Optimization in Gaussian 09 Program.

Details	NADNP	NADNP-Na$^+$
Calculation method	B3LYP	B3LYP
Basis set	6-31+G (d)	6-31+G (d)
E (B3LYP) (a.u.)	-1250.004713	-1411.756065
Charge, Multiplicity	0, 1	0, 1

Table S4 Details of Solvent Single Point Calculation in Gaussian 09 Program.

Details	NADNP	NADNP-Na$^+$
Calculation method	B3LYP	B3LYP
Basis set	6-31+G (d,p)	6-31+G (d,p)
E(B3LYP) (a.u.)	-1250.05654907	-1411.81140693
Charge, Multiplicity	0, 1	0, 1
Solvent (SMD)	DMSO	DMSO

TDDFT- Calculation

Table S5 TDDFT results of complex Probe at B3LYP/6-31+G(d,p) (SMD=DMSO)//B3LYP/6-31+G(d) level. Total no. of states in the calculation: 20.

Complex	λ(nm)[a]	*f*[b]	Δ*E*(cm^{-1})[c]	Transitions[d]
NADNP	482.86	0.6222	20709.898	HOMO → LUMO+1 (99%)
NADNP-Na$^+$	570.83	0.4573	17518.36	HOMO → LUMO+1 (99%)

[a]Wavelength of the transition. [b]The oscillator strength of the transition. [c]Excitation energies for each transition. [d]Molecular orbitals involved in the transitions.

Table S6. Energies of HOMO and LUMO+1 (HOMO = Highest Occupied Molecular Orbital and LUMO = Lowest Unoccupied Molecular Orbital)

Species	E_{HOMO} (a.u.)	E_{LUMO+1} (a.u.)	Δ*E*(a.u.)	Δ*E*(eV)	Δ*E*(kcal/mol)
NADNP	-0.21146	-0.10492	0.10654	2.899	66.9
NADNP-Na$^+$	-0.19238	-0.10053	0.09185	2.499	57.6

Table S7 Cartesian coordinates (in Å) of the complexes NADNP and NADNP-Na^+ at B3LYP/6-31+G(d) level of theory.

NADNP

8	1.122912000	-0.419973000	-0.157043000
6	2.452868000	-0.212713000	-0.110735000
6	3.026584000	1.074320000	-0.068858000
6	2.190871000	2.253126000	-0.073592000
7	0.890346000	2.203564000	-0.116160000
7	0.241522000	3.403645000	-0.114333000
6	-1.112454000	3.499981000	-0.155515000
6	-1.925788000	2.333495000	-0.202951000
6	-3.299890000	2.412087000	-0.245124000
6	-3.928084000	3.670210000	-0.241735000
7	-5.386161000	3.751143000	-0.286539000
8	-6.013473000	2.688487000	-0.326043000
8	-5.904375000	4.869886000	-0.282393000
6	-3.185070000	4.835084000	-0.196517000
6	-1.790427000	4.763985000	-0.153579000
7	-1.082741000	6.031519000	-0.107717000
8	-1.732739000	7.074564000	-0.109123000
8	0.166814000	6.014710000	-0.068344000
6	4.472507000	1.193857000	-0.020673000
6	5.161875000	2.435833000	0.023639000
6	6.542571000	2.494727000	0.068662000
6	7.318522000	1.315802000	0.072156000
6	6.683426000	0.092669000	0.029846000
6	5.268406000	0.001928000	-0.016898000
6	4.623845000	-1.268174000	-0.060511000
6	3.259149000	-1.377358000	-0.106144000
1	0.666633000	0.455933000	-0.155799000
1	2.676258000	3.230626000	-0.039682000
1	0.764887000	4.280400000	-0.081360000
1	-1.443203000	1.365976000	-0.205523000
1	-3.904963000	1.513760000	-0.280986000
1	-3.670920000	5.802040000	-0.193999000
1	4.615856000	3.372806000	0.023006000
1	7.033174000	3.464015000	0.101685000
1	8.402609000	1.374974000	0.107768000
1	7.261377000	-0.828818000	0.031621000
1	5.239542000	-2.164558000	-0.057089000
1	2.759884000	-2.340517000	-0.139621000

NADNP-Na^+

8	1.365843000	-0.776921000	-0.916342000
6	2.567266000	-0.460688000	-0.622608000
6	2.983098000	0.876239000	-0.250860000
6	2.089743000	1.980448000	-0.280279000
7	0.783673000	1.983673000	-0.489652000
7	0.252757000	3.271955000	-0.574005000
6	-1.043183000	3.508204000	-0.299263000
6	-1.811842000	2.528136000	0.408273000
6	-3.153459000	2.702040000	0.665511000
6	-3.802808000	3.871674000	0.226916000
7	-5.225429000	4.044178000	0.483153000
8	-5.819084000	3.117214000	1.047364000
8	-5.758457000	5.096671000	0.122195000
6	-3.098580000	4.870035000	-0.426556000
6	-1.737998000	4.707770000	-0.687541000

7	-1.074941000	5.789819000	-1.384009000
8	-1.739198000	6.758900000	-1.752599000
8	0.154630000	5.692759000	-1.587622000
6	4.382093000	1.125743000	0.111626000
6	4.874764000	2.372343000	0.579355000
6	6.211855000	2.562369000	0.894983000
6	7.138573000	1.511117000	0.776092000
6	6.688921000	0.274804000	0.348977000
6	5.330980000	0.060030000	0.020803000
6	4.885670000	-1.239375000	-0.392470000
6	3.582664000	-1.490998000	-0.688045000
11	-0.466384000	0.182014000	1.217016000

1	2.541100000	2.961898000	-0.126479000
1	0.772664000	4.018152000	-1.035406000
1	-1.282577000	1.681056000	0.831074000
1	-3.714250000	1.964090000	1.227921000
1	-3.595987000	5.777541000	-0.744344000
1	4.206552000	3.214639000	0.722775000
1	6.539762000	3.536992000	1.248201000
1	8.184330000	1.665862000	1.026565000
1	7.380141000	-0.561226000	0.262628000
1	5.623615000	-2.037536000	-0.455429000
1	3.245664000	-2.478563000	-0.990054000

12. Quantitative analysis of Arsenite , Arsenate and H_2S in water sample:

For the quantitative anlysis ,water samples were collected from ground level sources and unused well. Unknown concentrations of arsenite, arsenate, and H_2S were spiked into these water samples in equal volumes (300µL) to prepare artificial arsenite, arsenate, and H_2S contaminated water, respectively.

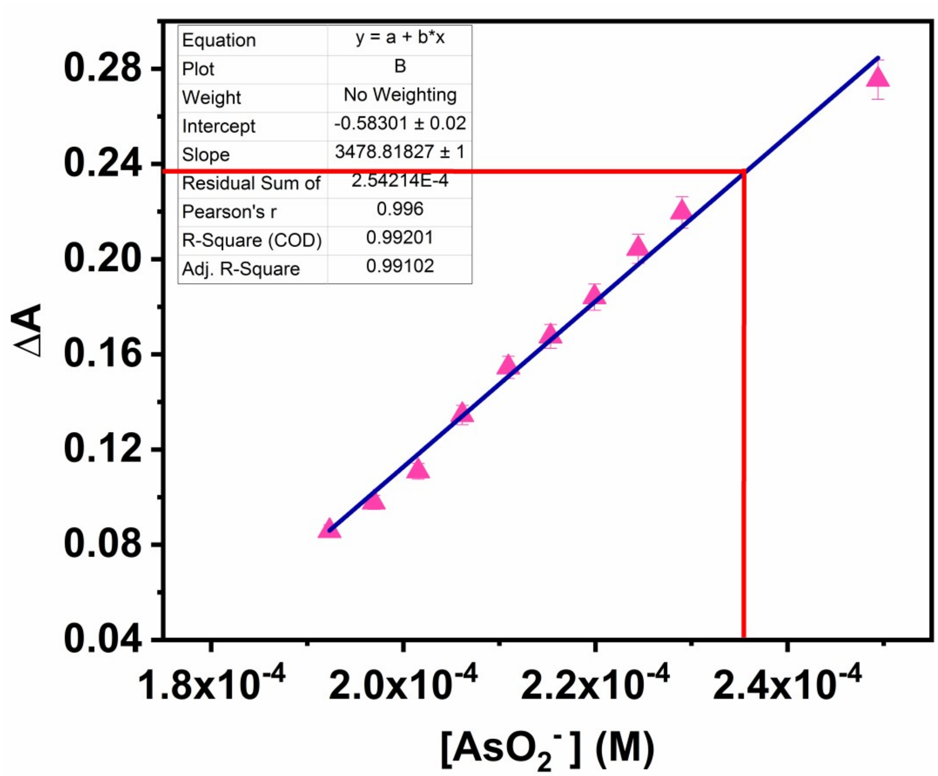


Fig. S16 Estimation of unknown concentration (2.35 x 10^{-4} M) of Arsenite (red line) in artificially arsenite contaminated ground level water from the standard absorbance curve.

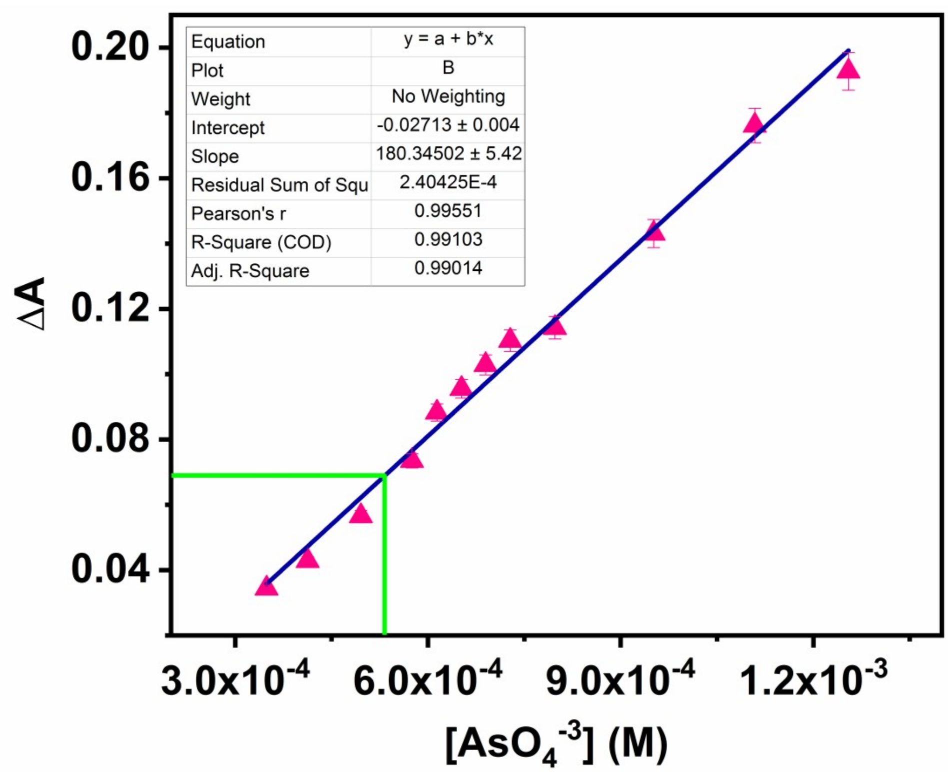


Fig. S17 Estimation of unknown concentration (5.32 x 10^{-4} M) of Arsenate (green line) in artificially arsenate contaminated ground level water from the standard absorbance curve.

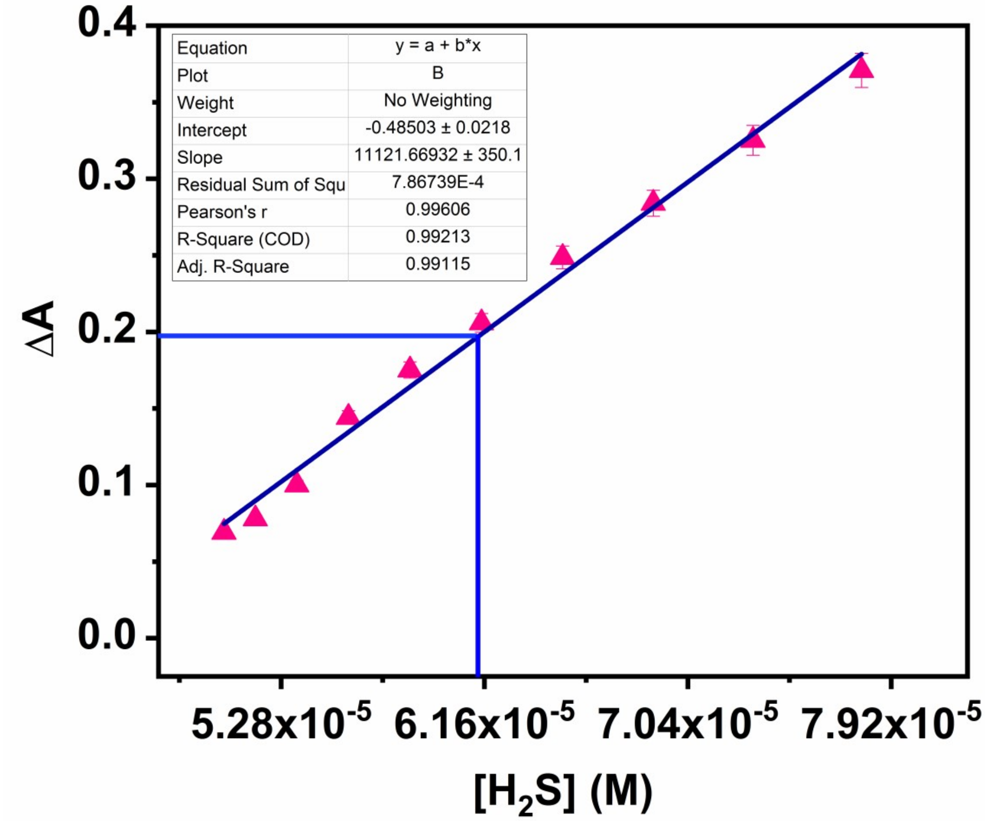
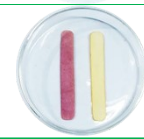
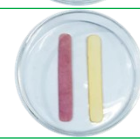
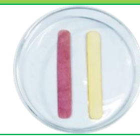
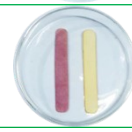


Fig. S18 Estimation of unknown concentration (6.13 x 10^{-5} M) of H_2S (blue line) in artificially H_2S contaminated water of unused well from the standard absorbance curve.

Concentration of probe solution	Volume of spiked H_2S solution of unknown strength with the unknown contaminated sample	Images of paper strips	Concentration of H_2S
10 µM	500 µL		6.70×10^{-5} M
10 µM	300 µL		6.13×10^{-5} M
10 µM	200 µL		5.92×10^{-5} M

13. Statistic evaluation of the paper strip:

Table S3. Statistic evaluation of the paper strip

Concentration of probe solution	Volume of spiked arsenite solution of unknown strength with the unknown contaminated sample	Images of paper strips	Concentration of arsenite
10 µM	500 µL		2.42 x 10^{-4} M
10 µM	300 µL		2.35 x 10^{-4} M
10 µM	200 µL		2.25 x 10^{-4} M

14. Spiked recovery experiment:

Table S4. Determination of H_2S in tap water samples with the probe NADNP.

Sample	Added H_2S (µM)	Found H_2S (µM)	Recovery (%)
Ground Water	10	9.8±0.2	98
	15	14.8±0.3	98.6

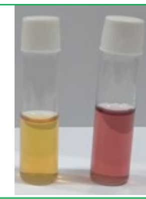
[a] Standard deviation calculation for three measurements.

Table S5. Determination of AsO_2^- in tap water samples with the probe NADNP.

Sample	Added AsO_2^- (µM)	Found AsO_2^- (µM)	Recovery (%)
Ground Water	10	9.4±0.3	94
	15	14.7±0.3	98

[a] Standard deviation calculation for three measurements.

Concentration of probe solution	**Volume of spiked H_2S solution of unknown strength with the unknown contaminated sample**	**Images of paper strips**	**Images of solutions**	**Concentration of H_2S**
10 µM	500 µL			6.70×10^{-5} M
10 µM	300 µL			6.13×10^{-5} M

10 µM	200 µL			5.92 x 10^{-5} M
Concentration of probe solution	**Volume of spiked arsenite solution of unknown strength with the unknown contaminated sample**	**Images of paper strips**	**Images of solutions**	**Concentration of arsenite**
10 µM	500 µL			2.42 x 10^{-4} M
10 µM	300 µL			2.35 x 10^{-4} M
10 µM	200 µL			2.25 x 10^{-4} M

15. Sensor Sensitivity between solutions and paper strips:

Table S6. Sensor Sensitivity between solutions and paper strips.