SUPPLEMENTARY INFORMATION

Colorimetric differentiation of arsenite and arsenate anions using bithiophene sensor with two binding sites: DFT studies and application in food and water samples

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Fig. S19 A linear calibration plot of N7R1–AsO_2^- vs. the amount of AsO_2^- ions for the quantitative analysis of milk, honey and water samples.

S1. Materials and methods

The chemicals, anions, and solvents used in the study were procured from Sigma-Aldrich and TCI and used without further purification. ^{1}H NMR and ^{13}C NMR spectra of the synthesized chemosensor were recorded using JEOL (400 MHz) NMR spectrometer. Infrared spectrum was recorded on Bruker- alpha FT-IR spectrometer with a resolution of 4 cm^{-1}. UV-Vis spectral studies were performed using Analytikjena Specord S600 spectrometer in a 3.5 mL glass cuvette with a path length of 1 cm. The cyclic voltammograms were recorded on an Ivium electrochemical workstation with a scan rate of 20 mV/s and a potential range of −1.5 to +1.5 V. Mass spectrum of the chemosensor was recorded using Xevo QToF, Waters mass spectrometer. The melting point of the synthesized product was recorded using Stuart-SMP3 melting point apparatus.

S2. Synthesis and characterization of chemosensor N7R1

*Synthesis of chemosensor **N7R1** (4,4'-(((1E,1'E)-[2,2'-bithiophene]-5,5'-diylbis(methanylylidene))bis(hydrazin-1-yl-2-ylidene))dibenzonitrile)*

Chemosensor N7R1 was prepared using a Schiff base reaction between 2,2'-bithiophene 5,5'-dicarboxaldehyde (200 mg, 0.899 mmol) and 4-cyanophenylhydrazine (305 mg, 1.799 mmol). Both were dissolved in 20 mL of ethanol. After adding 2–3 drops of glacial acetic acid, the mixture was refluxed for 3 h at 90 °C. The solid formed was filtrated and purified by ethanol wash. Yield: 86%, Melting point: 269 °C. FT-IR (ATR) (cm^{-1}): 3268.36 (N-H), 2204.55 (C≡N), 1600.85 (C=N), ^{1}H NMR (DMSO-d_6, 400 MHz, Me_4Si): 11.074 (s, 2H), 8.130 (s, 2H), 7.660–7.640 (d, 4H), 7.376–7.372 (d, 2H), 7.309 (s, 2H), 7.111–7.091 (d, 4H). ^{13}C NMR (DMSO-d_6, 100 MHz): 148.54, 139.83, 137.06, 135.40, 134.20, 130.05, 125.45, 120.54, 112.56, 100.00. Mass (LC-MS): m/z calculated for $C_{24}H_{16}N_6S_2$: 452.55 Obtained: 451.08 $[M-H]^+$

S3. Binding constant calculation

The binding constants of the chemosensor with the particular anions were calculated from UV-Vis titrations. The fitting of the graph between the $1/(A-A_0)$ *vs.* $1/[\text{Arsenite}]^n$ provides the straight line, and using Benesi-Hildebrand (B-H) equation (Eq. 1), the binding constants can be calculated.

$$\frac{1}{A - A_0} = \frac{1}{A_{max} - A_0} + \frac{1}{K[I^-]^n(A_{max} - A_0)} \qquad \text{(Eq. 1)}$$

where K is the binding constant, [I^-] is the anion concentration, n is the stoichiometric ratio, and A is absorbance.

S4. Limit of detection (LOD) calculation

A linearity graph between absorbance and the concentration of anion was used to calculate LOD. The equation used is

$$LOD = \frac{3 \times \sigma}{S} \qquad \text{(Eq. 2)}$$

where S is the slope and σ is the standard deviation of the calibration curve.

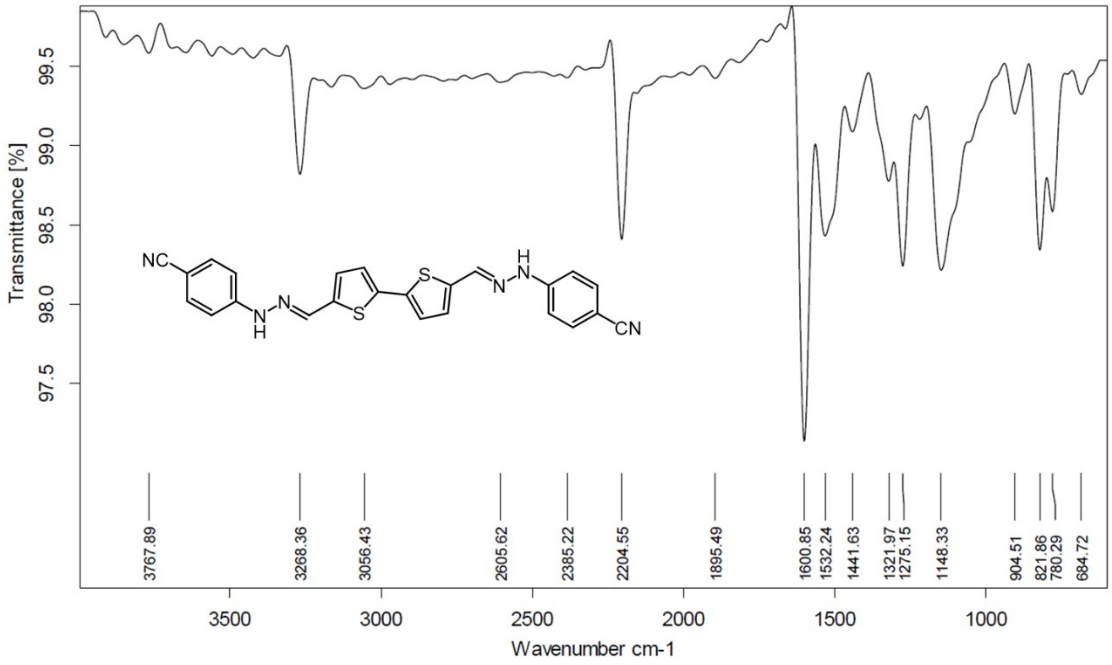

Fig. S1 FT-IR spectrum of chemosensor N7R1.

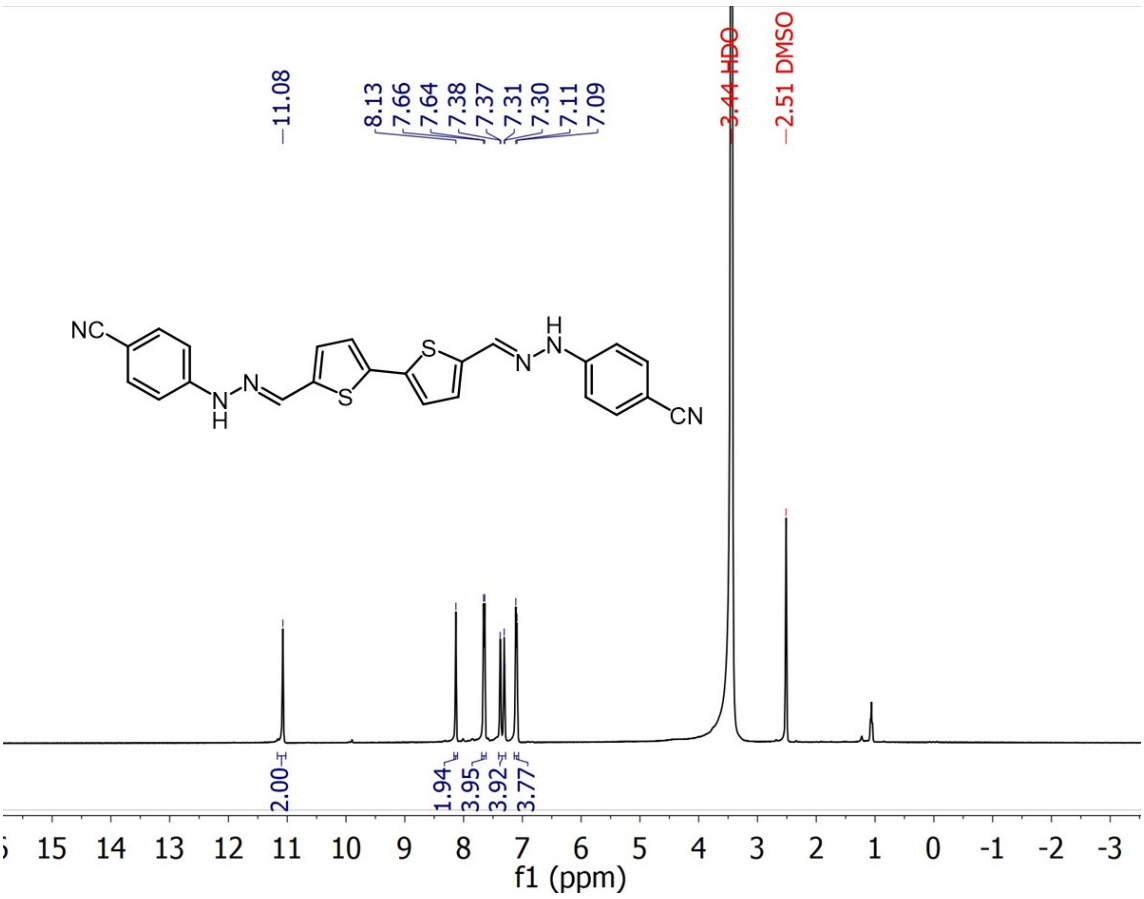

Fig. S2 ^{1}H NMR spectrum of chemosensor N7R1.

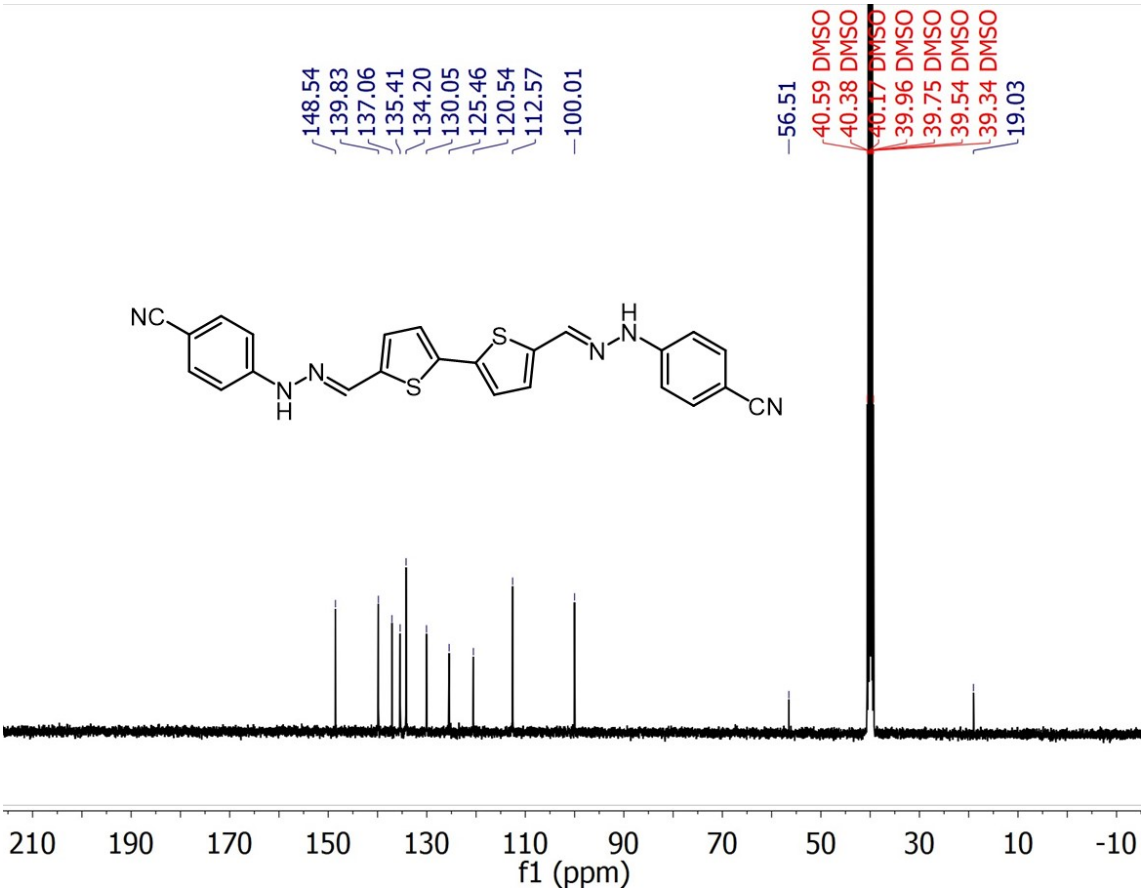

Fig. S3 ^{13}C NMR spectrum of chemosensor N7R1.

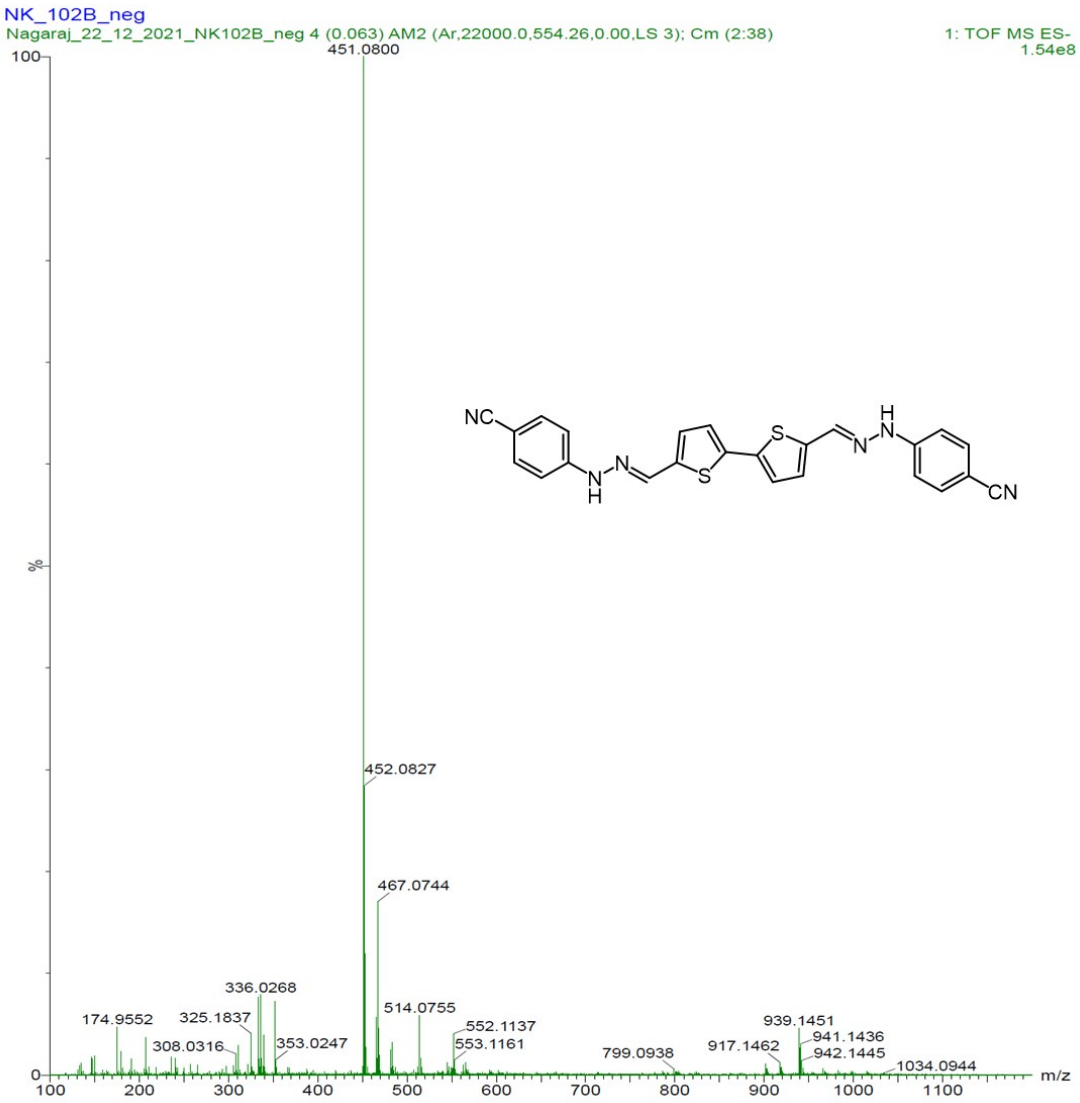

Fig. S4 LC-MS spectrum of chemosensor N7R1.

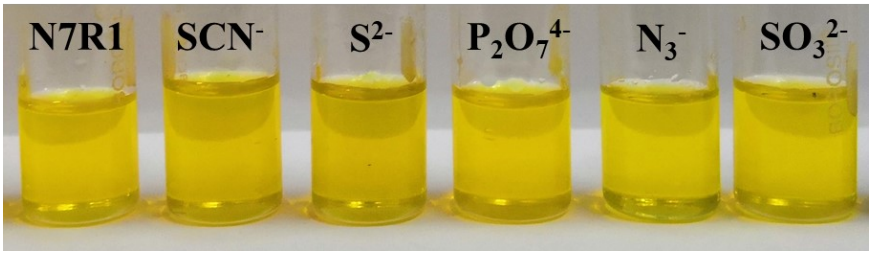

Fig. S5 Color changes of chemosensor N7R1 (2×10^{-5} M) in DMSO/H_2O (9:1, v/v) on adding two equivalences of anions SCN^-, S^{2-}, $P_2O_7^{4-}$, N_3^-, and SO_3^{2-} (1×10^{-2} M in water).

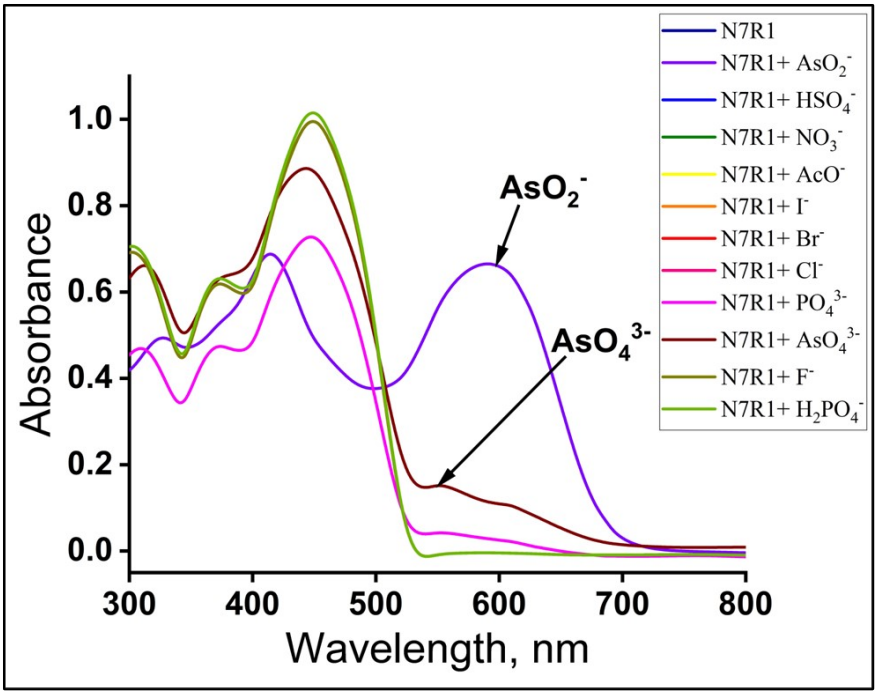

Fig. S6 UV-Vis absorption spectra of chemosensor N7R1 in DMSO/H_2O (9:1, v/v) in the presence of 2 equivalences of different anions.

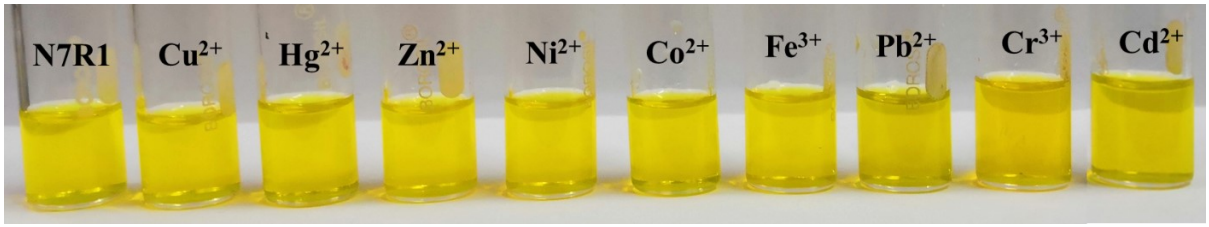

Fig. S7 Color changes of chemosensor N7R1 (2×10^{-5} M) in DMSO/H_2O (9:1, v/v) on adding two equivalences of various metal ions (1×10^{-2} M in water).

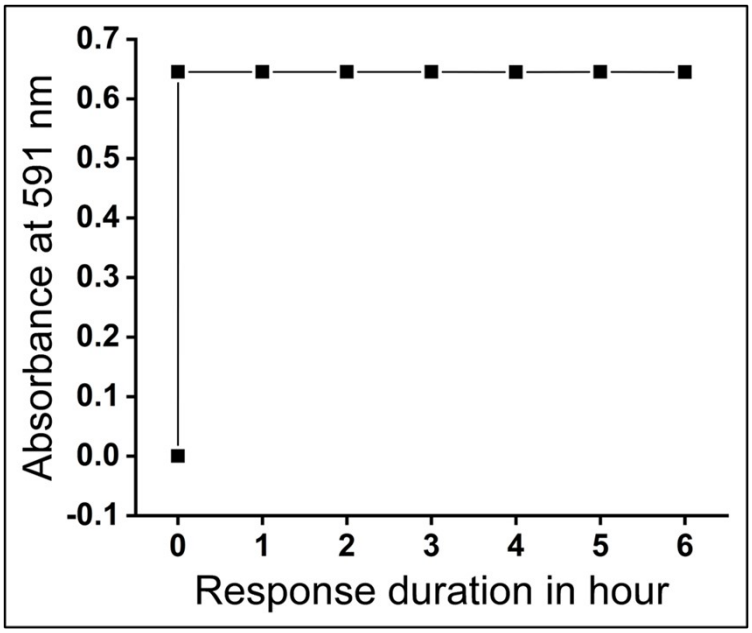

Fig. S8 Absorption intensity of N7R1 (2×10^{-5} M) in DMSO/H_2O (9:1, v/v) on adding two equivalences of arsenite ions (1×10^{-2} M in water) in various intervals of time.

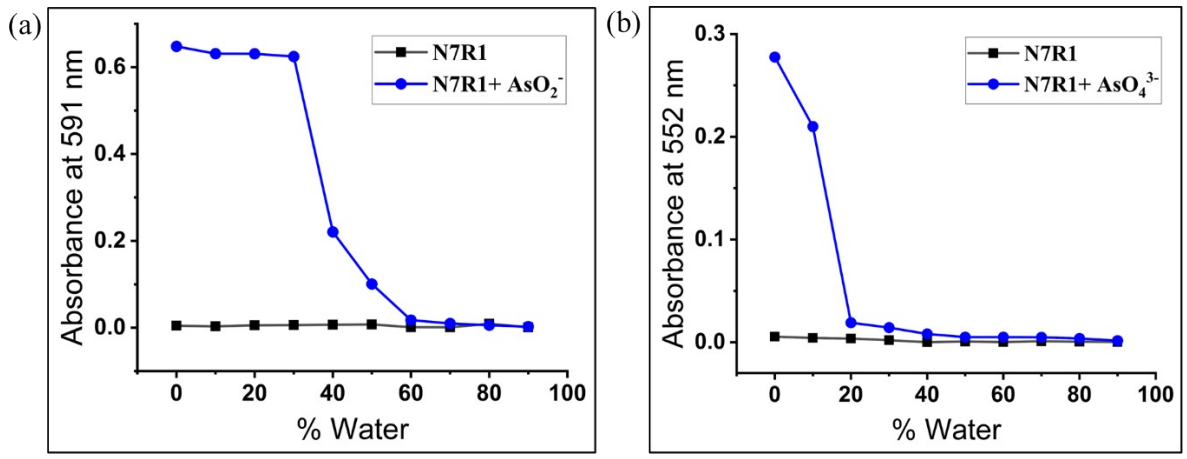

Fig. S9 UV-Vis spectral response of (a) N7R1 and N7R1+ AsO_2^- and (b) N7R1 and N7R1+ AsO_4^{3-} in various percentages of water content in DMSO.

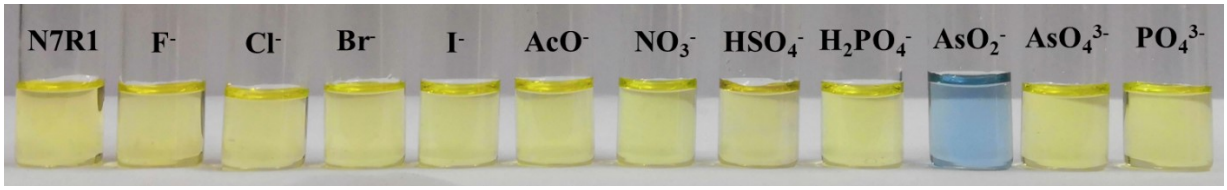

Fig. S10 Color changes of chemosensor N7R1 (1×10^{-5} M) in DMSO/H_2O (7:3, v/v) on adding two equivalences of anions (1×10^{-2} M in water).

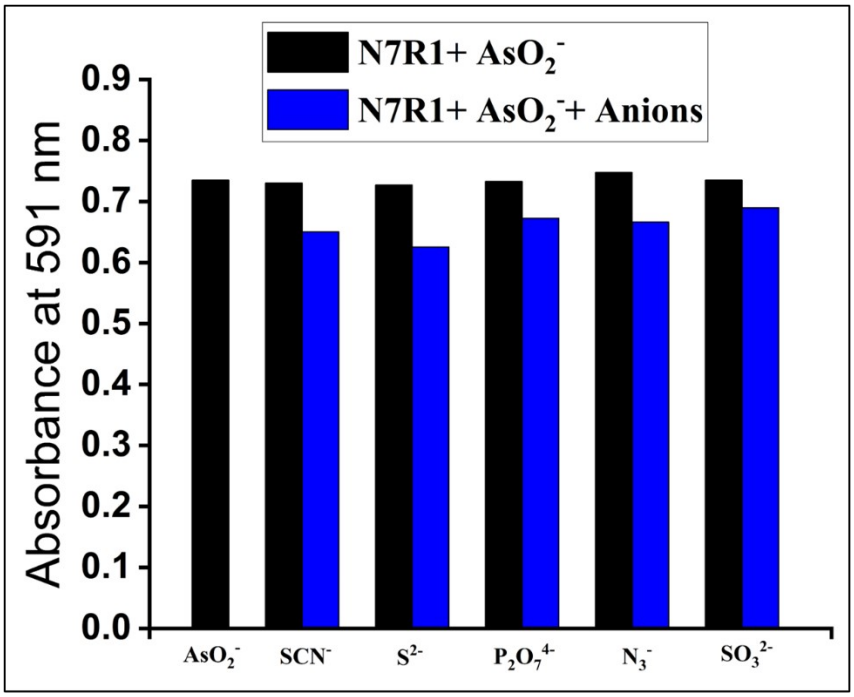

Fig. S11 Effects of absorbance in the presence of 3 equiv. of different anions in DMSO/H_2O (7:3, v/v) solution of N7R1 (2 × 10^{-5} M) Black bar: N7R1 + AsO_2^- ion, Blue bar: N7R1 + AsO_2^-+ competing anions.

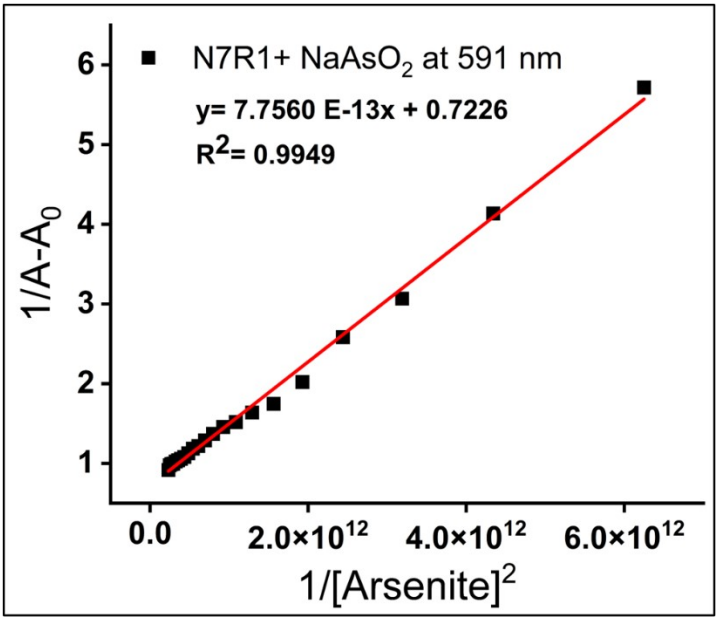

Fig. S12 B-H plot for N7R1–AsO_2^- complex in DMSO/H_2O (9:1, v/v).

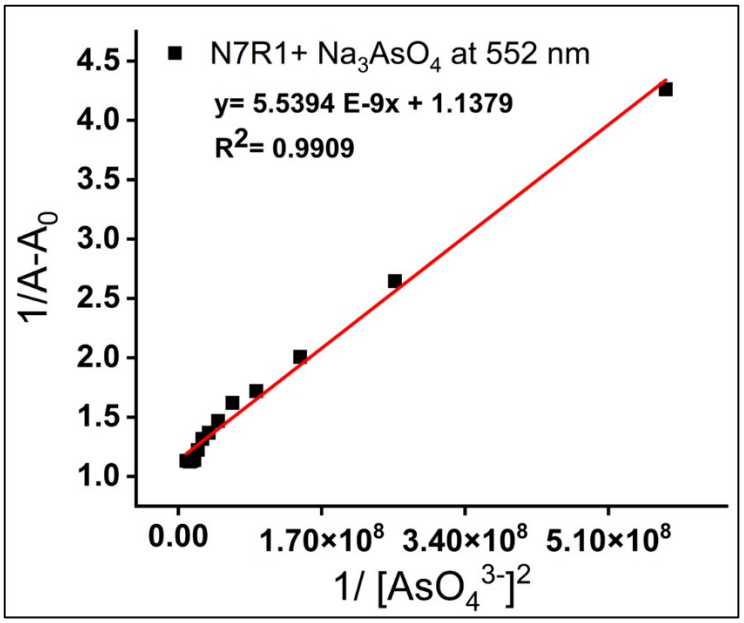

Fig. S13 B-H plot for N7R1–AsO_4^{3-} complex in DMSO/H_2O (9:1, v/v).

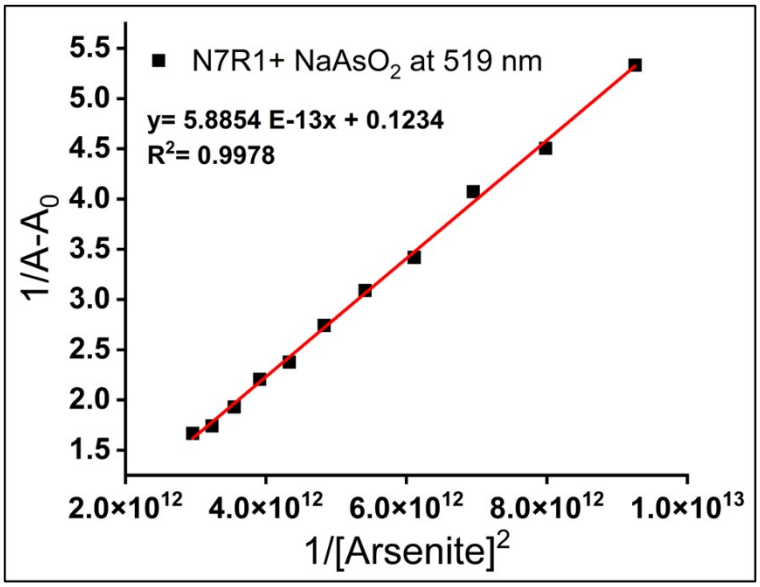

Fig. S14 B-H plot for N7R1–AsO_2^- complex in DMSO/H_2O (7:3, v/v).

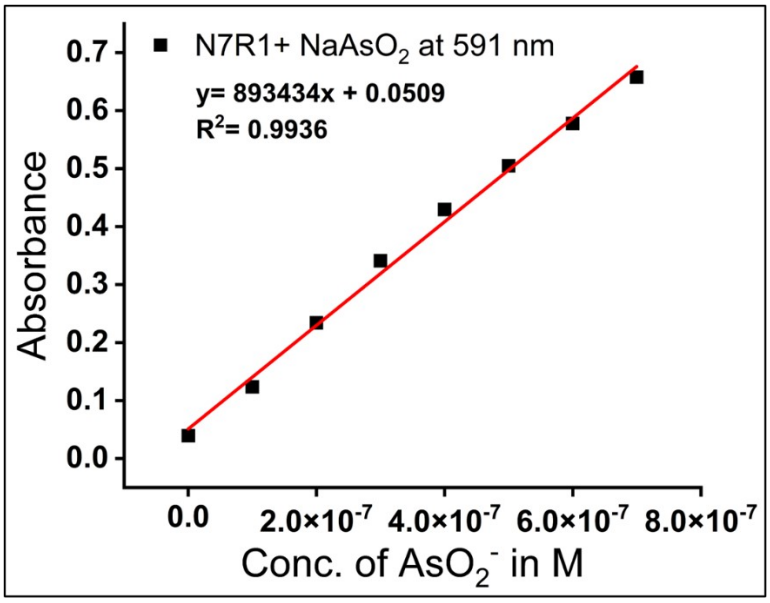

Fig. S15 Calibration curve for N7R1–AsO_2^- complex in DMSO/H_2O (9:1, v/v)

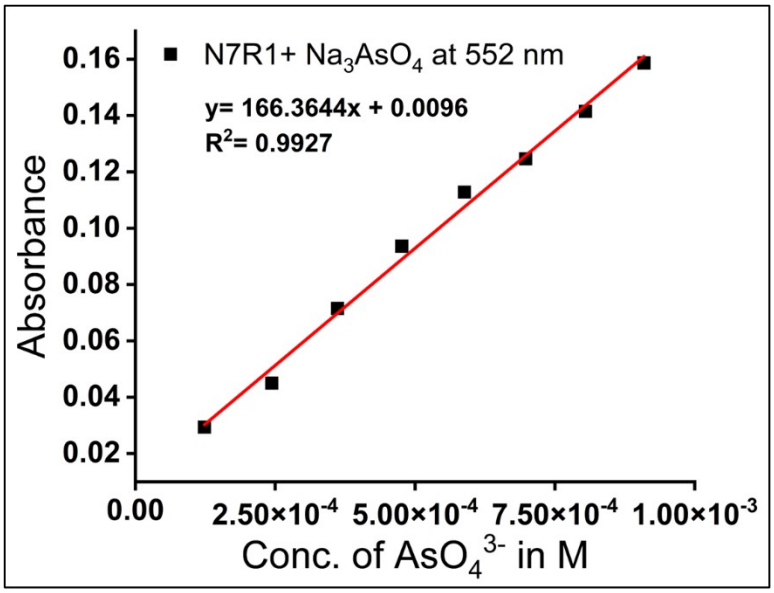

Fig. S16 Calibration curve for N7R1– AsO_4^{3-} complex in DMSO/H_2O (9:1, v/v)

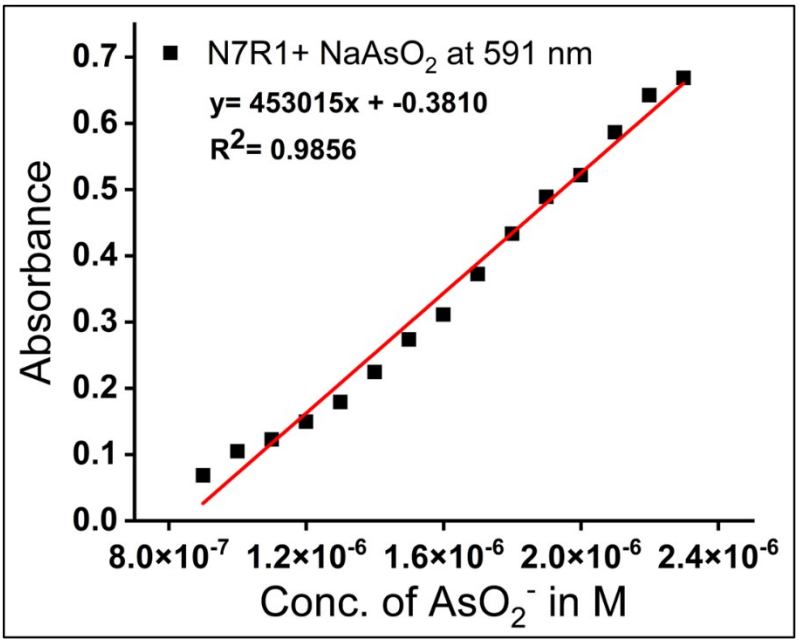

Fig. S17 Calibration curve for N7R1–AsO_2^- complex in DMSO/H_2O (7:3, v/v).

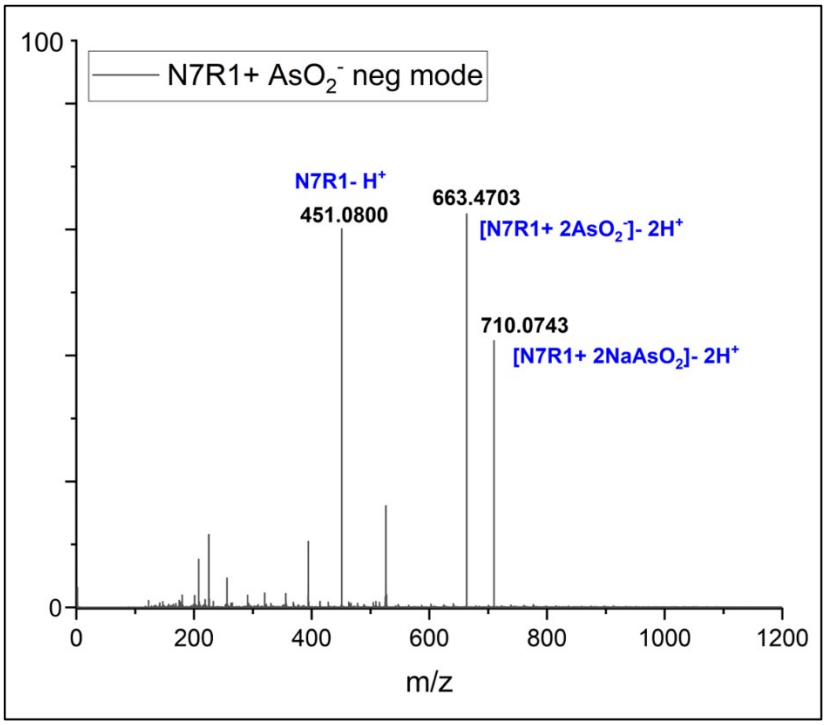

Fig. S18 LC- MS spectrum of N7R1- AsO_2^- complex in negative mode.

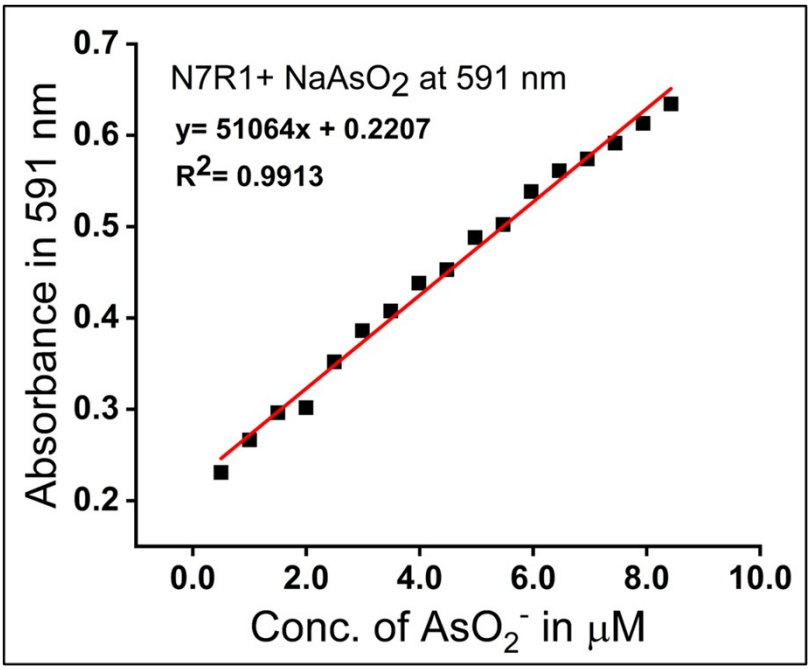

Fig. S19 A linear calibration plot of N7R1–AsO_2^- vs. the amount of AsO_2^- ions for the quantitative analysis of milk, honey and water samples.