1. General method of UV-Vis and fluorescence titration

Path length of the cells used for absorption and emission studies was 1 cm. For UV-Vis and fluorescence titrations, stock solution of **NAPSAL** was prepared (10 μM) in ethanol/water (1/9, v/v) HEPES (0.1M) buffer. Working solutions of **NAPSAL** and $H_2AsO_4^-$ were prepared from their respective stock solutions. Fluorescence measurements were performed using 10 nm x 10 nm slit width. All the fluorescence and absorbance spectra were taken after 5 minutes of mixing of $H_2AsO_4^-$ to **NAPSAL**.

2. Calculation of Quantum Yield

Fluorescence quantum yields (Φ) were estimated by integrating the area under the fluorescence curves using the equation,

where A was the area under the fluorescence spectral curve, OD was optical density of the compound at the excitation wavelength[1] and η was the refractive indices of the solvent. Anthracene was used as quantum yield standard (quantum yield is 0.27 in ethanol)[2] for measuring the quantum yields of **NAPSAL** and [**NAPSAL**-$H_2AsO_4^-$] systems.

3. Single crystal X-ray structure analysis of NAPSAL

Single crystal X-ray diffraction studies on a colorless prismatic crystal obtained after slow evaporation of an methanol solution of **NAPSAL** consist of crystallographically independent molecules that comprise one naphthalene ring connected by a -C=N- group to an *o*-hydroxy benzene unit. Table S1 showed the bond distances and angles for free **NAPSAL** that fall within

the expected ranges. The conformation is stabilized through an extended conjugation and an intra-molecular H bond, O19-H19···N11 (Fig. 1).

4. Calculation for detection limit

To determine the detection limit, fluorescence titration of **NAPSAL** with $H_2AsO_4^-$ was carried out by adding aliquots of micromolar concentration of $H_2AsO_4^-$. The lowest concentration of $H_2AsO_4^-$ that caused a sharp change in the fluorescence emission intensity was recorded as experimental and real detection limit.

However, the detection limit was also calculated using the equation: detection limit = $3\sigma/k$, where σ is the standard deviation of blank, and k is the slope of the plot of emission intensities versus [$H_2AsO_4^-$]. The emission intensities of **NAPSAL** (λ_{em} = 477 nm) were measured 6 times in replicate, and the standard deviation of blank was determined. The emission intensities (at 477 nm) were plotted *vs.* [$H_2AsO_4^-$] to obtain the slope. The value of LOD obtained as 9.0×10^{-8} M using this method.

However, two methods give two values for the LOD. We believe that the LOD obtained directly (Fig. S8, inset, a) is more acceptable than the indirect method using 3σ (Fig. S8, inset, b).

5. Determination of binding constant

Binding interactions of **NAPSAL** with $H_2AsO_4^-$ in HEPES buffered solution (0.1 M, ethanol/water = 1/9, v/v, pH 7.4) have been estimated using the modified Benesi–Hildebrand equation, $(F_{max} - F_0) / (F_x - F_0) = 1 + (1/K)\ (1/[M]^n)$, where F_0, F_x and F_{max} are the emission intensities of **NAPSAL** in the absence of $H_2AsO_4^-$, at an intermediate $H_2AsO_4^-$, and at a concentration of complete interaction, respectively, where K is the binding constant, M is the

concentration of $H_2AsO_4^-$ and n is the number of $H_2AsO_4^-$ ions bound per **NAPSAL** (here, n = 1/2).

Emission intensities of **NAPSAL** (10 µM) in presence of different $H_2AsO_4^-$ concentrations, *viz.* 10, 30, 50, 70, 90, 100, 300 µM have been used for calculation of binding constant.

The equation used is:

$(F_{max} - F_0) / (F_x - F_0) = 1 + (1/K[M]^n)$, where $F_{max} = 245.44$, $F_{min} = 5.76$, n = 1/2.

When 300 µM $H_2AsO_4^-$ is added to **NAPSAL** (10 µM), $F_x = 234.01$,

Now, $(F_{max}-F_0) / (F_x-F_0) = (245.44 - 5.76) / (234.01 - 5.76)$ and $1/ [M]^{1/2} = 1/(300)^{1/2}$

or, $(245.44-5.76) / (234.01-5.76) = 1 + (1/ K(300)^{1/2}$

or, $1.05 = 1 + (1/ 17.32K)$

or, $1.05 = 1 + 0.057/ K$

Similarly, $1.12 = 1 + 0.1/ K$ for 100 µM $H_2AsO_4^-$ where $F_x = 219.93$,

$1.215 = 1 + 0.105/ K$ for 90 µM $H_2AsO_4^-$ where $F_x = 202.93$,

$1.31 = 1 + 0.1196/ K$ for 70 µM $H_2AsO_4^-$ where $F_x = 187.39$,

$1.68 = 1 + 0.14/K$ for 50 µM $H_2AsO_4^-$ where $F_x = 149.93$ and so on.

Thus, plot of $(F_{max} - F_0) / (F_x - F_0)$ *vs.* $1/ [M]^{1/2}$ based on $Y = 1 + P \times X$, yields the slope, P = 7.20.

Thus, $P = 1/K = 7.20\ \mu M^{1/2}$

$1/K = 7.20 \times 10^{-6}\ M^{1/2}$.

So, $K = 1.38 \times 10^5\ M^{-1/2}$.

Experimental

General procedures. High-purity HEPES, *α*-napthyl amine and salisaldehyde were purchased from Sigma Aldrich (India). NaH_2AsO_4 was purchased from Merck (India). Solvents used were of spectroscopic grade. Other chemicals were of analytical reagent grade and had been used without further purification except when specified. Mili-Q Milipore® 18.2 MΩ cm^{-1} water was used throughout the experiments. A JASCO (model V-570) UV–Vis spectrophotometer was used for recording absorption spectra. FTIR spectra were recorded on a JASCO FTIR spectrophotometer (model: FTIR-H20). Mass spectra were performed on a QTOF Micro YA 263 mass spectrometer in ES positive mode. ^{1}H NMR spectra were recorded using Bruker Avance 600 (600MHz) in MeOD. ^{13}C NMR spectra were recorded using Bruker Avance 500 (500MHz) in $CDCl_3$. Melting point measurement was done by VEEGO digital melting point apparatus. Elemental analysis was performed using Perkin Elmer CHN-Analyzer with first 2000-Analysis kit. The steady-state fluorescence emission and excitation spectra were recorded with a Perkin Elmer Precisely LS55 spectrofluorimeter. All pH measurements were performed with Systronics digital pH meter (model 335).

Single crystal X-ray diffraction data were collected at 100 K using graphite-monochromated Mo−Kα radiation (λ = 0.7107 Å) from a fine focus sealed tube. Data were processed and corrected for Lorentz and polarization effects. Multi scan absorption corrections had been performed using the Siemens Area Detector Absorption Correction (SADABS) program. Structure was solved by standard direct methods using Semi-Invariants Representation (SIR 2004) and then refined by full matrix least-squares on F2 using a package of six programs known as per name of the creator, Sheldrick, SHELXL97.[3–5]

Imaging system. The imaging system was composed of an inverted fluorescence microscope (Leica DM 1000 LED), digital compact camera (Leica DFC 420C), and an image processor (Leica Application Suite v3.3.0). The microscope was equipped with a 50 W mercury arc lamp.

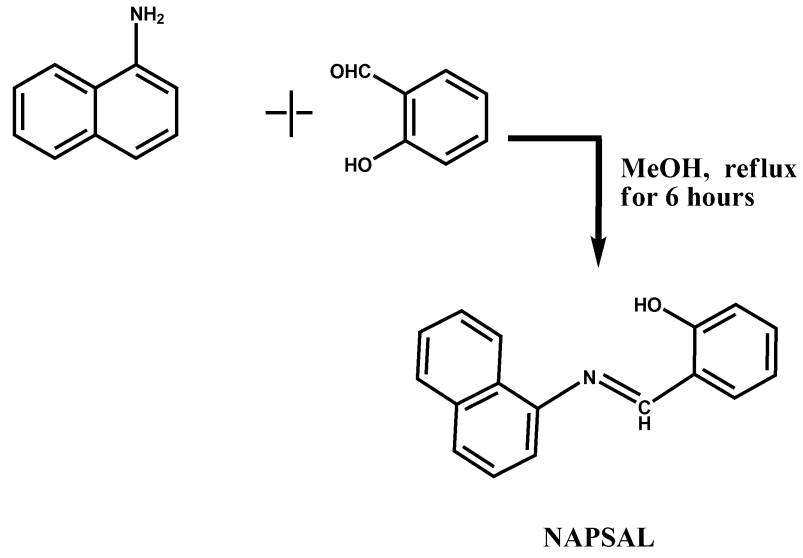
Preparation of cells. Pollen grains were collected from fresh mature buds of *Allamanda puberula* (Aapocynaceae), a common ornamental plant with bell shaped bright yellow flower by crashing stamens on a sterile petriplate and suspending them in normal saline. After crashing, the stamen debris was removed by filtering through a thin layer of non-absorbent cotton and the suspended pollens were collected by centrifugation at 5000 rpm for five minutes. The pollen pellet was then washed twice in normal saline and then incubated in a solution of NaH_2AsO_4 (0.1 mg mL^{-1}) for one hour at ambient temperature. After incubation, they were again washed in normal saline and observed under fluorescence microscope using UV filter in presence and absence of the probe. Both $H_2AsO_4^-$ treated and untreated cells were stained with **NAPSAL** and observed under fluorescence microscope.

Similarly, *Candida albicans* cells (IMTECH No. 3018) from exponentially growing culture in yeast extract glucose broth medium (pH 6.0, incubation temperature, 37°C) were centrifuged at 3000 rpm for 10 minutes washed twice with 0.1 M HEPES buffer (pH 7.4). Then cells were treated with $H_2AsO_4^-$ (100 µM) for 30 minutes in 0.1 M HEPES buffer (pH 7.4) containing 0.01 % Triton X100 as permeability enhancing agent. After incubation, the cells were washed with HEPES buffer and incubated with **NAPSAL** for 15 minutes. Cells thus obtained were mounted on grease free glass slide and observed under the fluorescence microscope having UV filter. Cells incubated with **NAPSAL** but without $H_2AsO_4^-$ were used as control.

Procedure for intracellular arsenate detection in *Candida albicans* cells grown in arsenic contaminated water collected form Purbasthali, India: *Candida albicans* cells (IMTECH No. 3018) from exponentially growing culture in yeast extract glucose broth medium (pH 6.0, incubation temperature, 37 $^{\circ}$C) were centrifuged at 3000 rpm for 10 minutes, and washed twice with 0.1 M HEPES buffer (pH 7.4). Cells were treated with 1% saline water for cleaning. Then the cells were incubated with 500 µL arsenic contaminated water for overnight. Cells thus obtained were mounted on grease free glass slide and observed under the fluorescence microscope having UV filter. Cells incubated without **NAPSAL** were used as control.

Synthesis of ((Z)-2-((naphthalene-1-ylimimno) methyl) phenol) (NAPSAL)

α-Napthyl amine (0.50 g, 3.49 mmol) and salisaldihyde (0.43 g, 3.49 mmol) were combined in fresh distilled methanol (30 mL) and refluxed for 6 hours (Scheme S1). The reaction mixture was kept at room temperature to form yellow crystals. Crystal structure and packing of **NAPSAL** were shown in Fig.1 and Fig.S17 respectively. Yield, 89%. M. P., 147^{o}C (± 4^{o}C). ^{1}H NMR (600 MHz, MeOD) (ESI, Fig. S18(a) and S18(b)): 7.03 (2H, m, J = 6.0 Hz, a); 7.32 (1H, d, J = 6 Hz, b); 7.45 (1H, m, J = 12 Hz, c); 7.57 (3H, m, J = 12 Hz, d); 7.61 (1H, d, J = 12 Hz, e); 7.82 (1H, d, J = 6 Hz, f); 7.92 (1H, m, J = 6 Hz, g); 8.20 (1H, m, J = 6 Hz, h); 8.73 (1H, s, i); ^{13}C NMR (500 MHz, $CDCl_3$) (ESI, Fig. S19) : δ163.52, 161.16, 146.09, 133.90, 133.33, 132.34, 128.14, 127.85, 126.86, 126.61, 126.43, 125.86, 123.15, 119.43, 119.14, 117.23, 113.94. QTOF – MS ES^{+} (ESI, Fig. S20): $[M + H]^{+}$ = 248.24. Elemental analysis data as calculated for $C_{17}H_{13}NO$ (%): C, 82.57; H, 5.30; N, 5.66. Found (%): C, 82.42; H, 5.21; N, 5.60.



NAPSAL

Scheme S1 Synthesis of **NAPSAL**

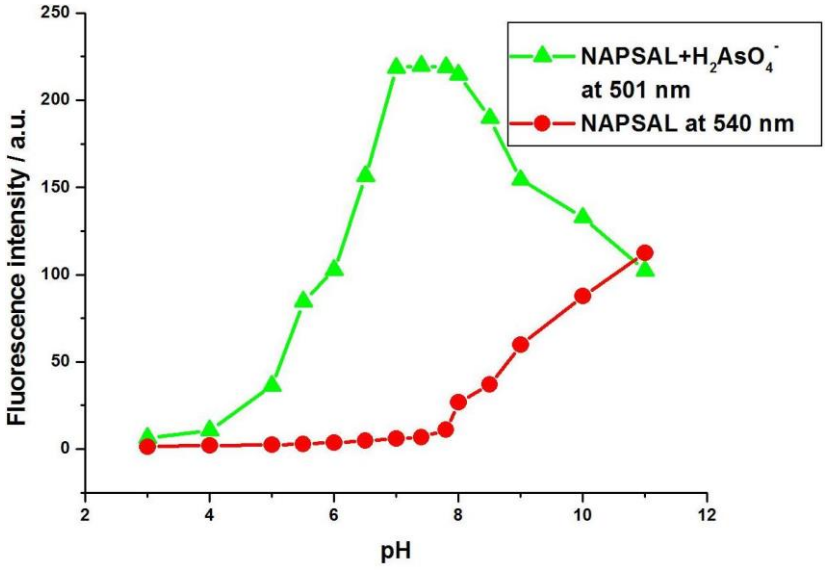


Fig.S1 Variation of emission intensity of **NAPSAL** (10 μM) with $H_2AsO_4^-$ (800 μM) as a function of pH, λ_{ex} = 377 nm.

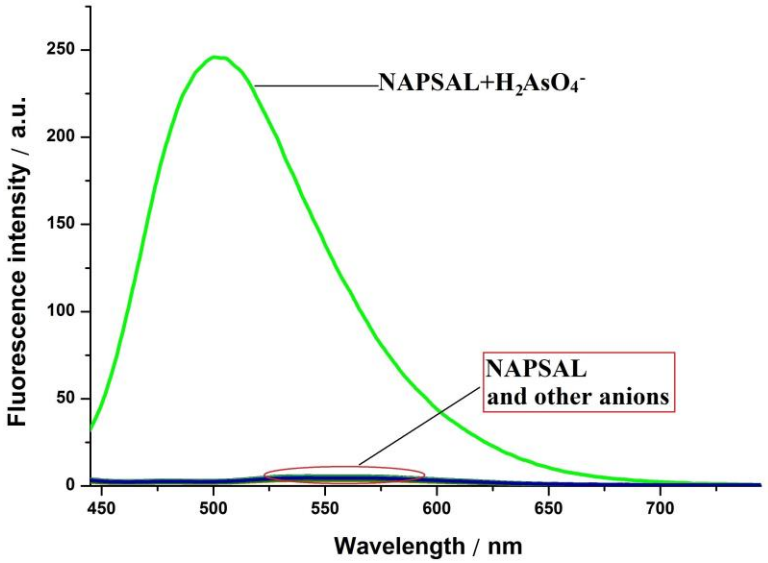


Fig.S2 Fluorescence intensity of the **NAPSAL** (10 μM) in presence of different anions (1000 μM) in HEPES buffered solution (0.1 M, ethanol/water = 1/9, v/v, pH 7.4): where anions = $H_2AsO_4^-$, F^-, Cl^-, Br^-, I^-, N_3^-, NO_2^-, NO_3^-, SCN^-, CN^-, CH_3COO^-, ClO_4^-, $H_2PO_4^-$, λ_{ex} = 377 nm.

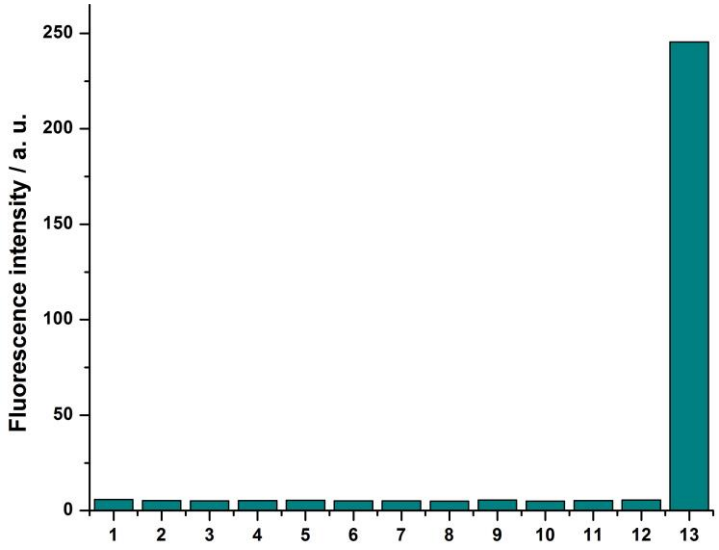


Fig.S3 Fluorescence intensity of the **NAPSAL** (10 μM) in presence of different cations (1000 μM) in HEPES buffered solution (0.1 M, ethanol/water = 1/9, v/v, pH 7.4): where cations = **NAPSAL (1)**, Na^+ **(2)**, K^+ **(3)**, Li^+ **(4)**, Ca^{2+} **(5)**, Mg^{2+} **(6)**, Co^{2+} **(7)**, Ni^{2+} **(8)**, Fe^{2+} **(9)**, Zn^{2+} **(10)**, Hg^{2+} **(11)**, Pb^{2+} **(12)**, $H_2AsO_4^-$ **(13)** , λ_{ex} = 377 nm, λ_{em} = 501 nm.

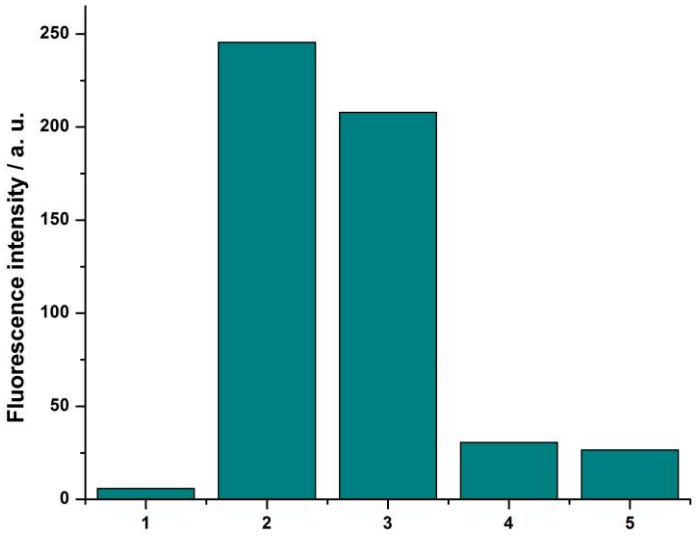


Fig.S4 Fluorescence intensity of the **NAPSAL** (10 μM) in presence of different As species (1000 μM) in HEPES buffered solution (0.1 M, ethanol/water = 1/9, v/v, pH 7.4): where As species = **NAPSAL** (1), $H_2AsO_4^-$ (2), $H_2AsO_3^-$ (3), monomethylarsonic acid (MMA) (4), dimethylarsonic acid (DMA) (5), λ_{ex} = 377 nm, λ_{em} = 501 nm.

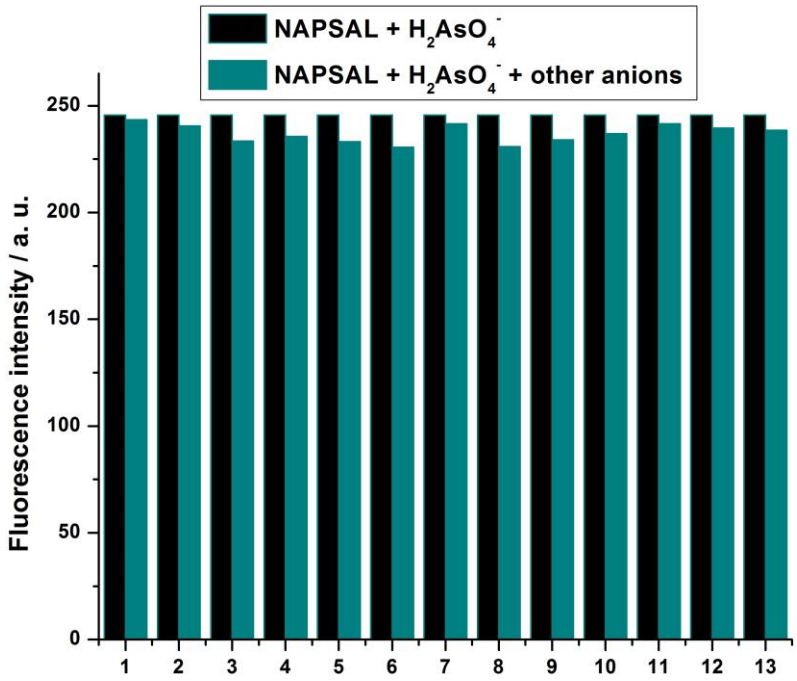


Fig.S5 Anion selectivity of **NAPSAL** (10 µM) in HEPES buffer (0.1 M; EtOH–H_2O, 1:9 v/v; pH 7.4. Black bars represent the emission intensity of [**NAPSAL**-$H_2AsO_4^-$] system and red bars show the fluorescence intensity of [**NAPSAL**-$H_2AsO_4^-$] system in presence of 1000 µM of different anion: F^- **(1)**, Cl^- **(2)**, Br^- **(3)**, I^- **(4)**, N_3^- **(5)**, NO_2^- **(6)**, NO_3^- **(7)**, SCN^- **(8)**, CN^- **(9)**, CH_3COO^-**(10)**, SO_4^{2-} **(11)**, ClO_4^- **(12)**, HPO_4^{2-} **(13)** , λ_{ex} = 377 nm, λ_{em} = 501 nm.

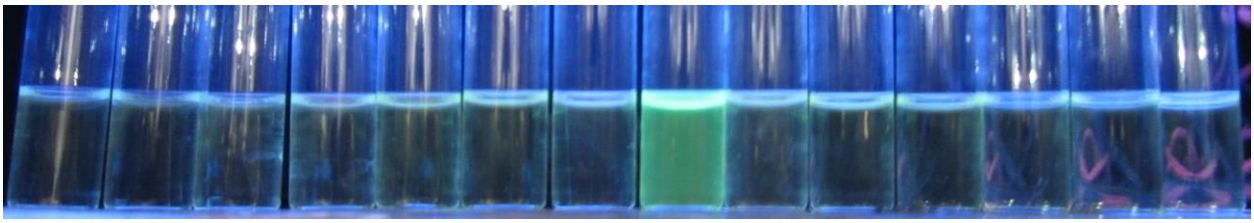


Fig.S6 Photographs of **NAPSAL** (10 µM) and under hand held UV lamp in presence of different anions (500 µM): (from left to right), F^- **(1)**, Cl^- **(2)**, Br^- **(3)**, I^- **(4)**, **NAPSAL (5)**, N_3^- **(6)**, CH_3COO^- **(7)**, $H_2AsO_4^-$ **(8)**, NO_3^- **(9)**, SCN^- **(10)**, CN^- **(11)**, ClO_4^- **(12)**, $H_2PO_4^-$ (**13**), NO_2^- **(14)**.

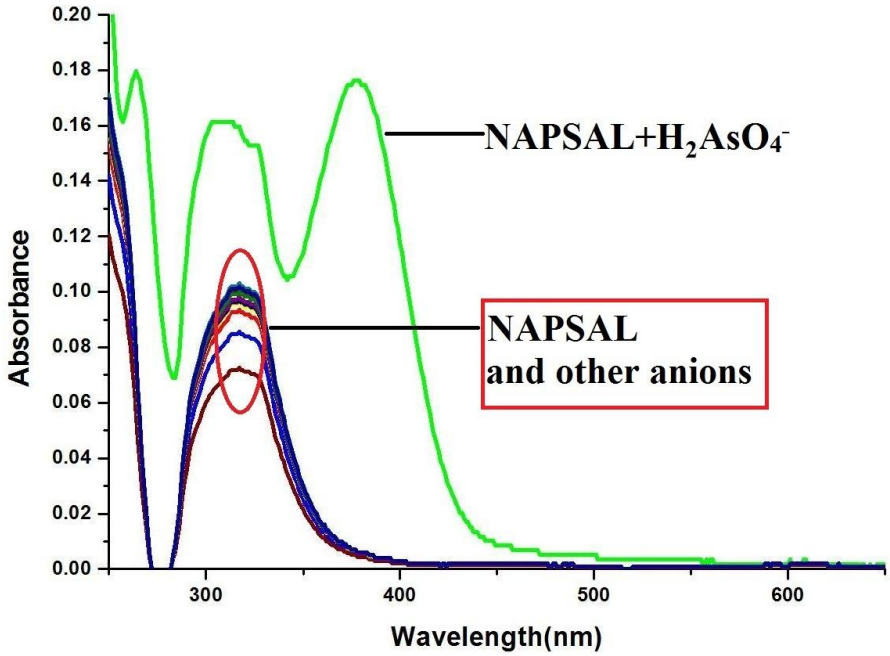


Fig.S7 Absorbance of the **NAPSAL** (10 μM) in presence of different anions (1000 μM) in HEPES buffered solution (0.1 M, ethanol/water = 1/9, v/v, pH 7.4): where anions = $H_2AsO_4^-$, F^-, Cl^-, Br^-, I^-, N_3^-, NO_2^-, NO_3^-, SCN^-, CN^-, CH_3COO^-, ClO_4^-, $H_2PO_4^-$.

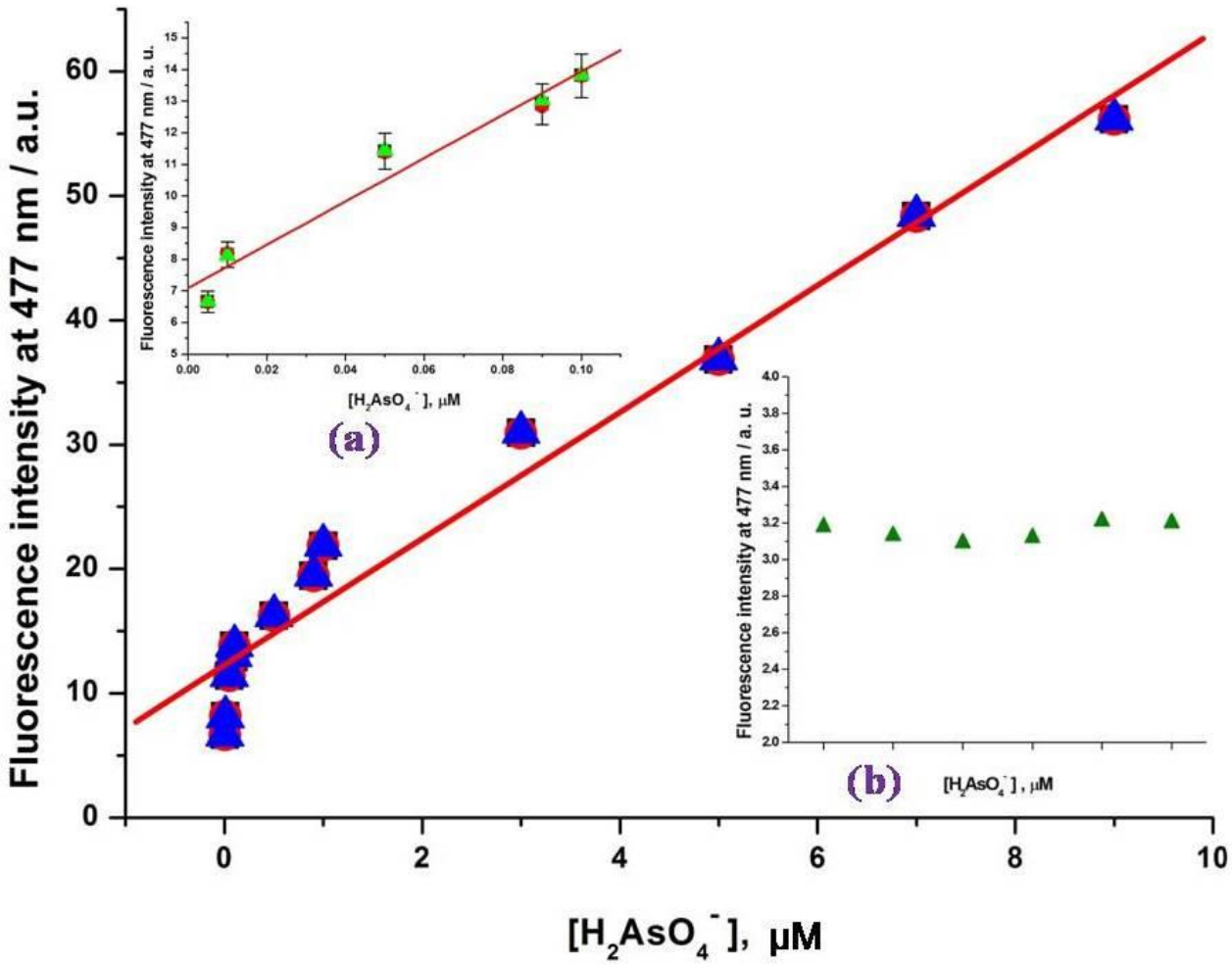


Fig.S8 Plot of emission intensity of **NAPSAL** (10 μM) with increasing concentration of $H_2AsO_4^-$ (0.005, 0.01, 0.05, 0.09, 0.1, 0.5, 0.9, 1, 3, 5, 7, 9 μM) (3 replicate measurements) in HEPES buffered (0.1 M, ethanol/water = 1/9, v/v, pH 7.4), inset: (a) plot of emission intensity of **NAPSAL** (10 μM) upon gradual addition of $H_2AsO_4^-$ (0.005, 0.01, 0.05, 0.09, 0.1 μM) (3 replicate measurements), (b) emission intensities of **NAPSAL** (10 μM) at 477 nm in 6 replicate measurements (λ_{ex} = 377 nm) for finding 3σ.

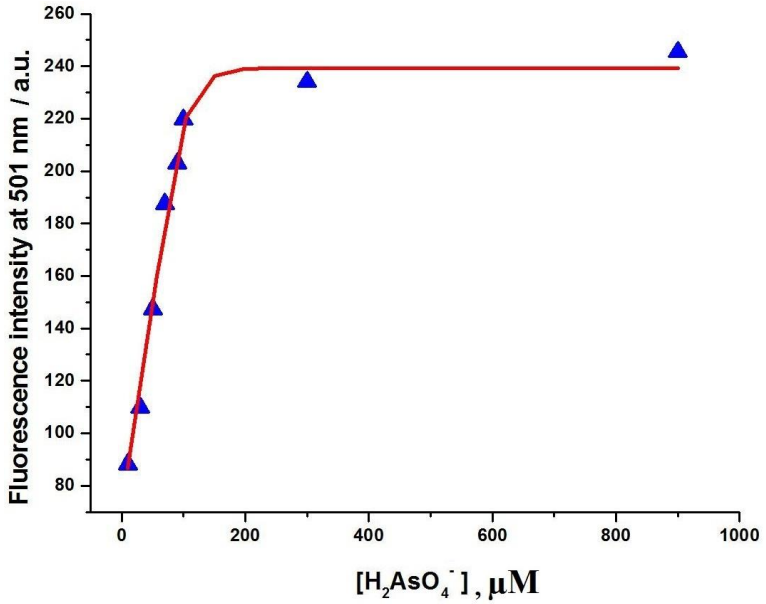


Fig.S9 Plot of emission intensity of **NAPSAL** (10 μM) with increasing concentration of $H_2AsO_4^-$ (10, 30, 50, 70, 90, 100, 300, 900 μM) in HEPES buffered (0.1 M, ethanol/water = 1/9, v/v, pH 7.4), λ_{ex} = 377 nm, λ_{em} = 501 nm.

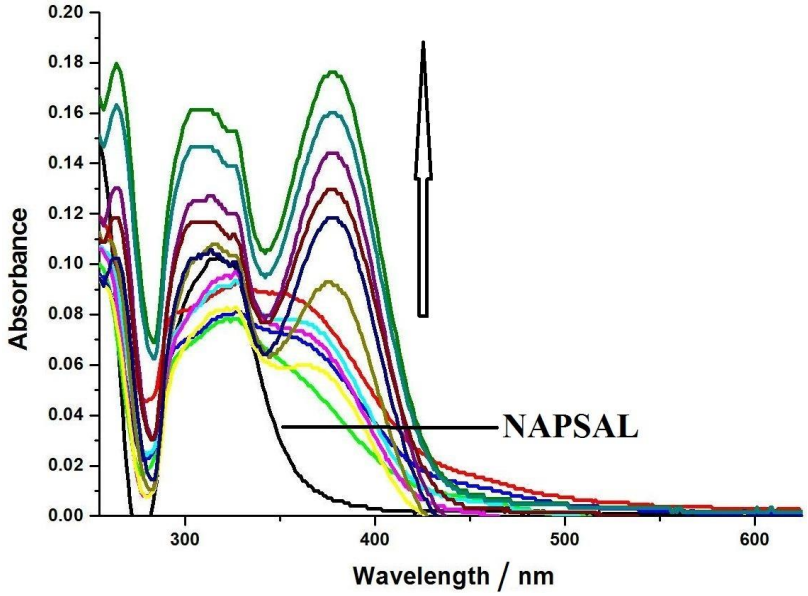


Fig.S10 Changes of the absorption spectra of **NAPSAL** (10 μM) upon gradual addition of $H_2AsO_4^-$ (0, 10, 20, 30, 40, 50, 60, 70, 80, 90, 250, 500, 900 μM) in HEPES buffered (0.1 M, ethanol/water = 1/9, v/v, pH 7.4).

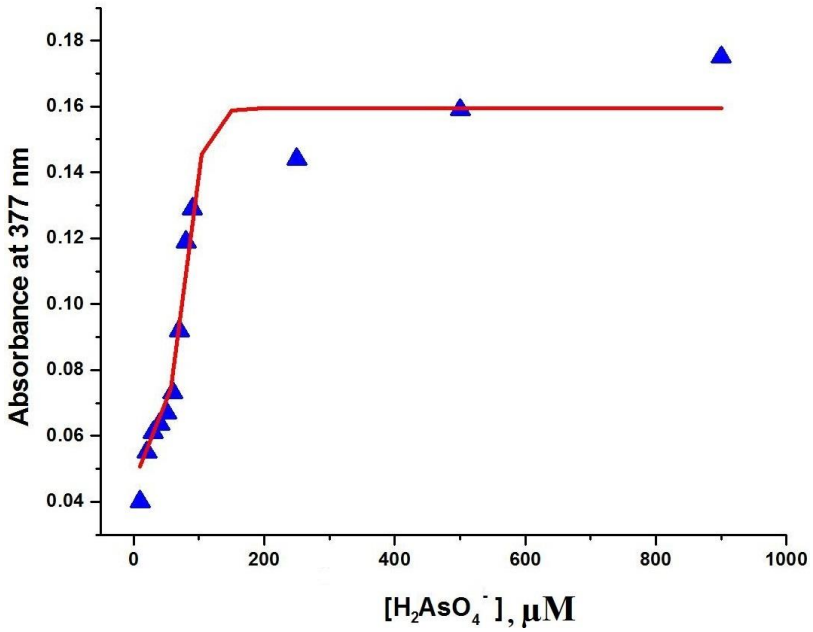


Fig.S11 Plot of absorbance of **NAPSAL** (10 μM) with increasing concentration of $H_2AsO_4^-$ (0, 10, 20, 30, 40, 50, 60, 70, 80, 90, 250, 500, 900 μM) in HEPES buffered (0.1 M, ethanol/water = 1/9, v/v, pH 7.4).

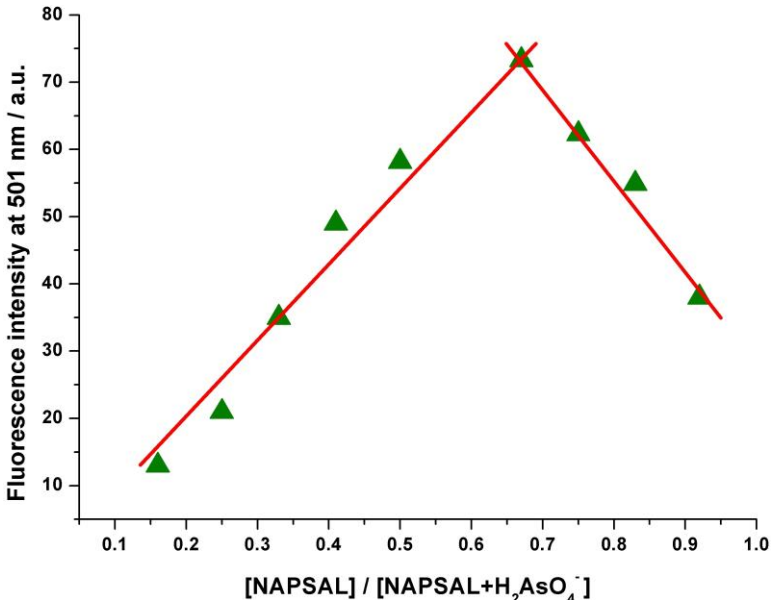


Fig.S12 Job's plot (stoichiometry determination of the [**NAPSAL**-$H_2AsO_4^-$] complex) in HEPES buffer (0.1 M, ethanol/water = 1/9, v/v, pH 7.4).

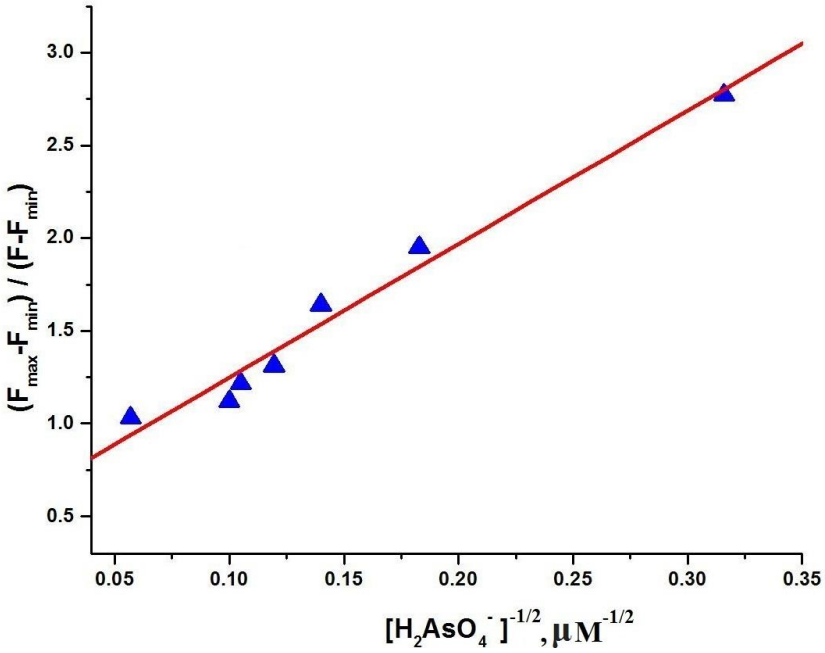


Fig.S13 Determination of binding constant between **NAPSAL** and $H_2AsO_4^-$ in HEPES buffered (0.1 M, ethanol/water = 1/9, v/v, pH 7.4), λ_{ex} = 377 nm, λ_{em} = 501 nm.

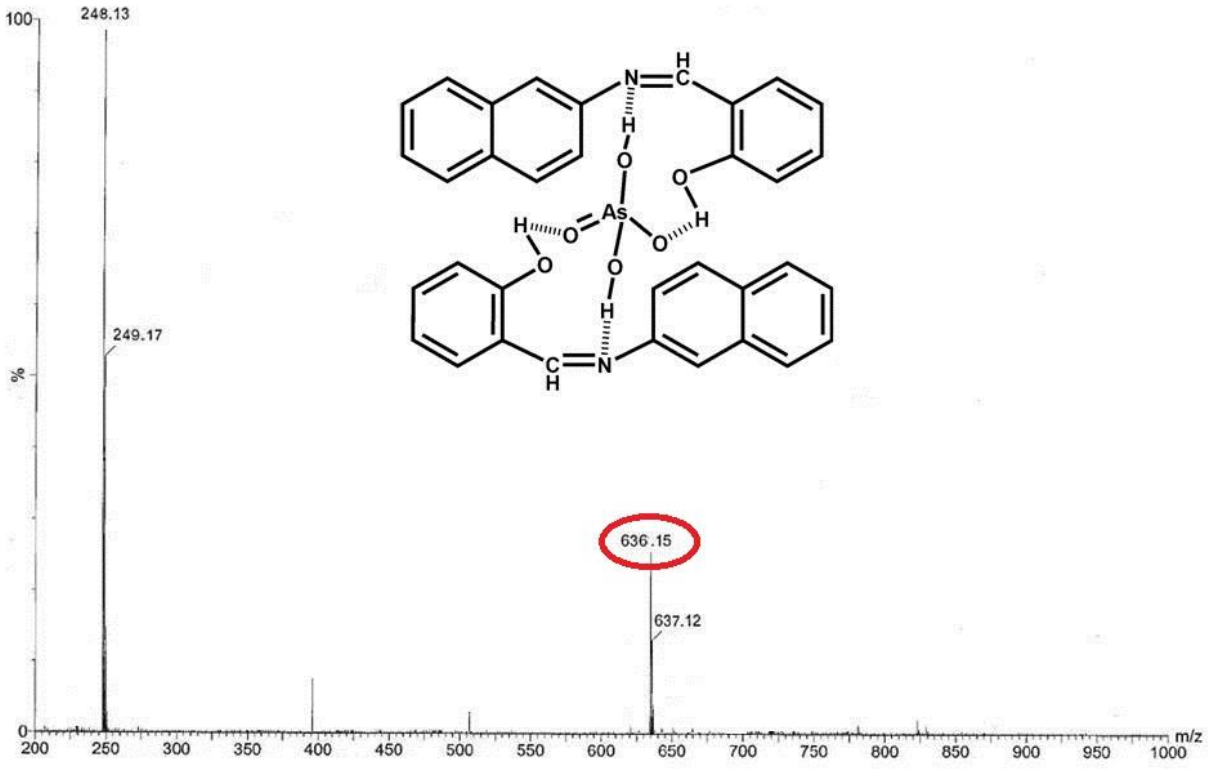


Fig.S14 QTOF-MS spectrum of **NAPSAL**-$H_2AsO_4^-$ adduct in MeOH.

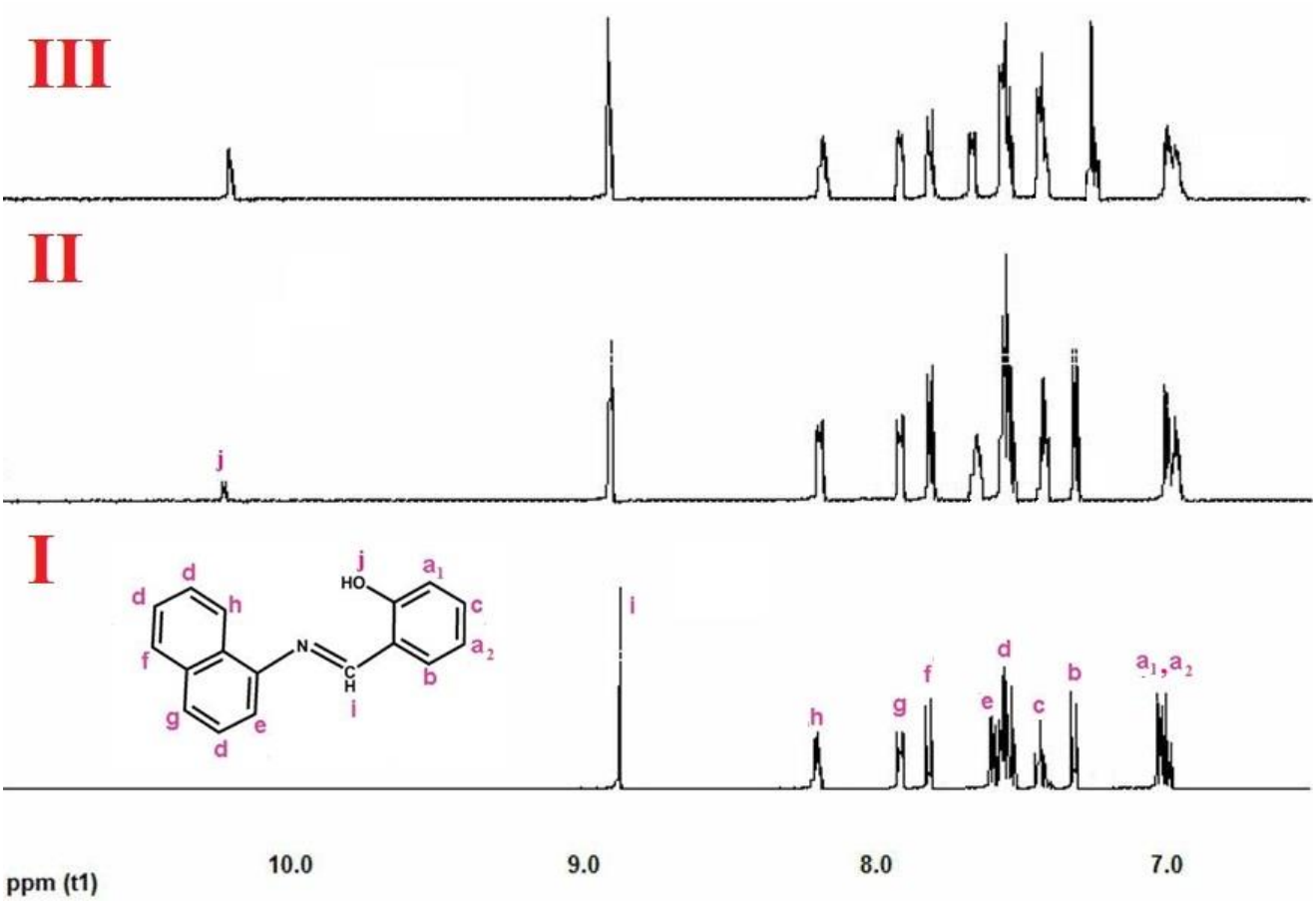


Fig.S15 Mode of interaction between **NAPSAL** and $H_2AsO_4^-$ as evident from ^1H NMR titration in MeOD: (I) **NAPSAL**; (II) **NAPSAL** with 1.0 equivalent of $H_2AsO_4^-$; (III) **NAPSAL** with 2.0 equivalent of $H_2AsO_4^-$.

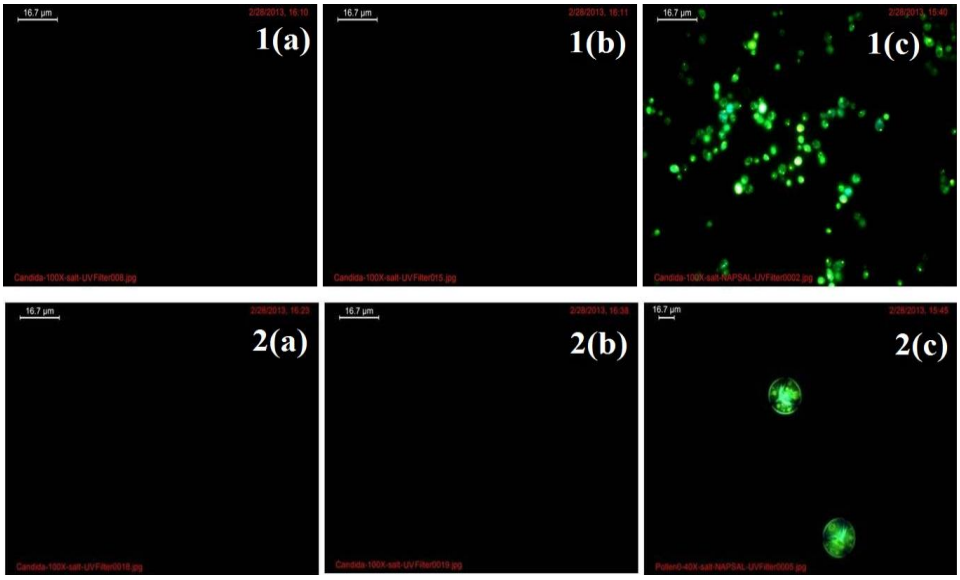


Fig.S16 Fluorescence microscope images of (**1**) *Candida albicans* cells (IMTECH No. 3018) and (**2**) *Allamandapuberula* (Aapocynaceae) cells: without **NAPSAL** under 100× objective lens (a), cells loaded with **NAPSAL** for 30 minutes under 100× objective lens (b), **NAPSAL** stained cells pre-exposed to $H_2AsO_4^-$ for 30 minutes under 40× objective lens, all the photographs were taken under UV filter; incubation temperature, 37 °C.

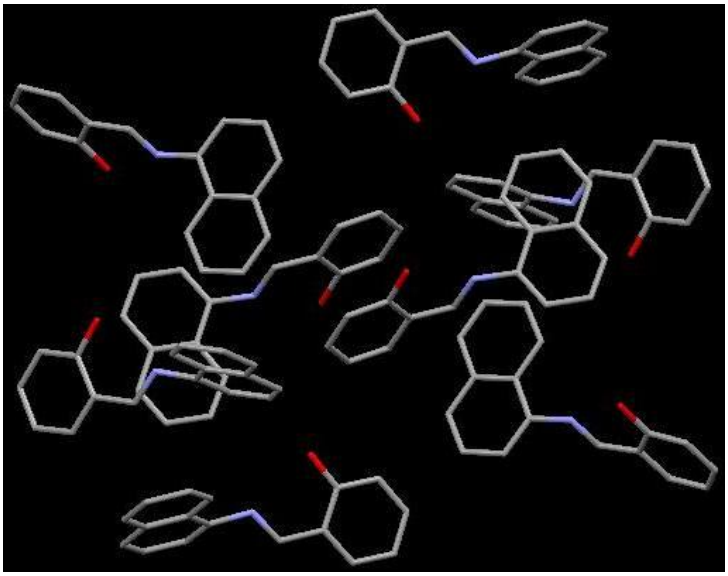


Fig.S17 Crystal packing of **NAPSAL**

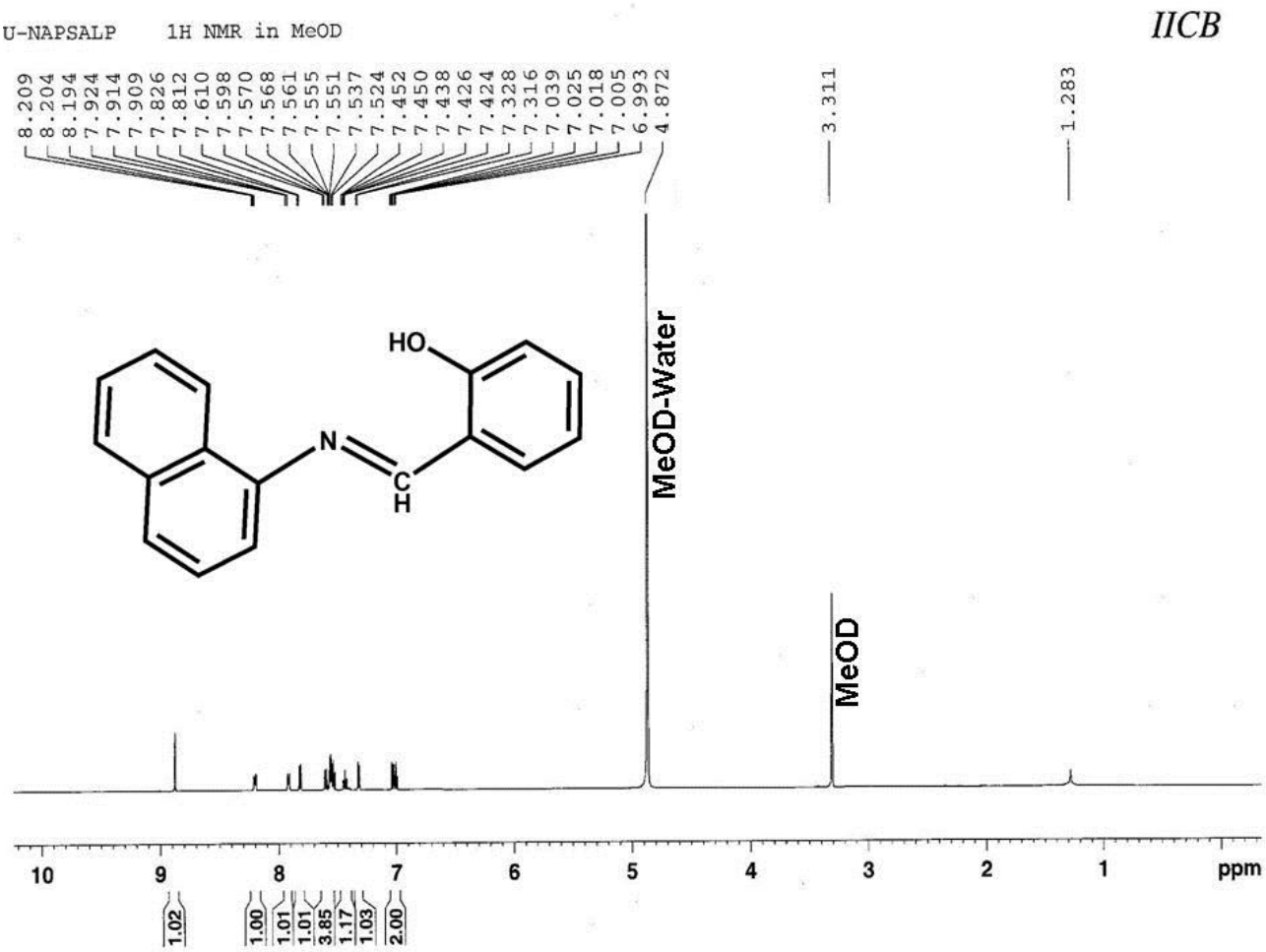


Fig. S18(a) ^{1}H NMR spectrum of **NAPSAL** in MeOD

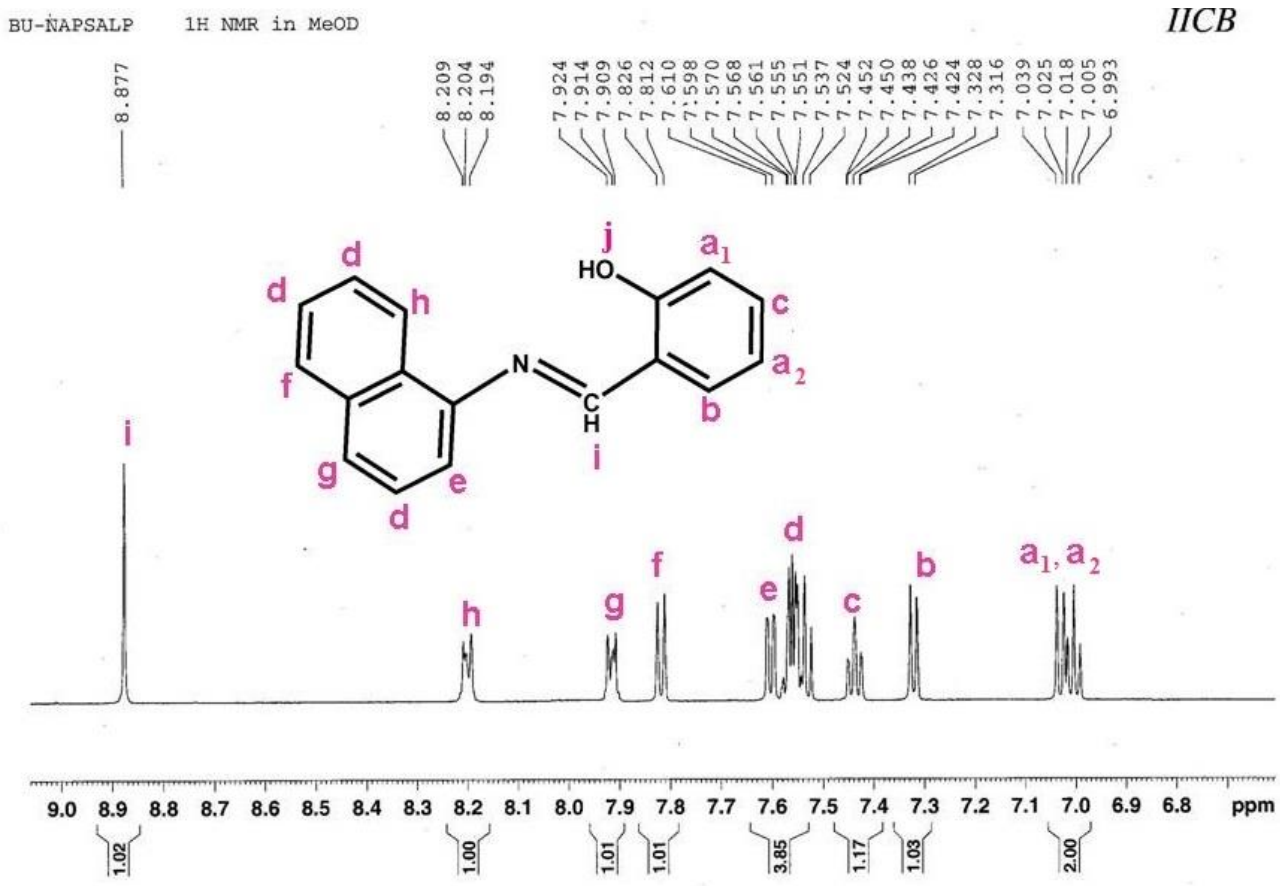


Fig. S18(b) ^{1}H NMR spectrum (expansion) of **NAPSAL** in MeOD

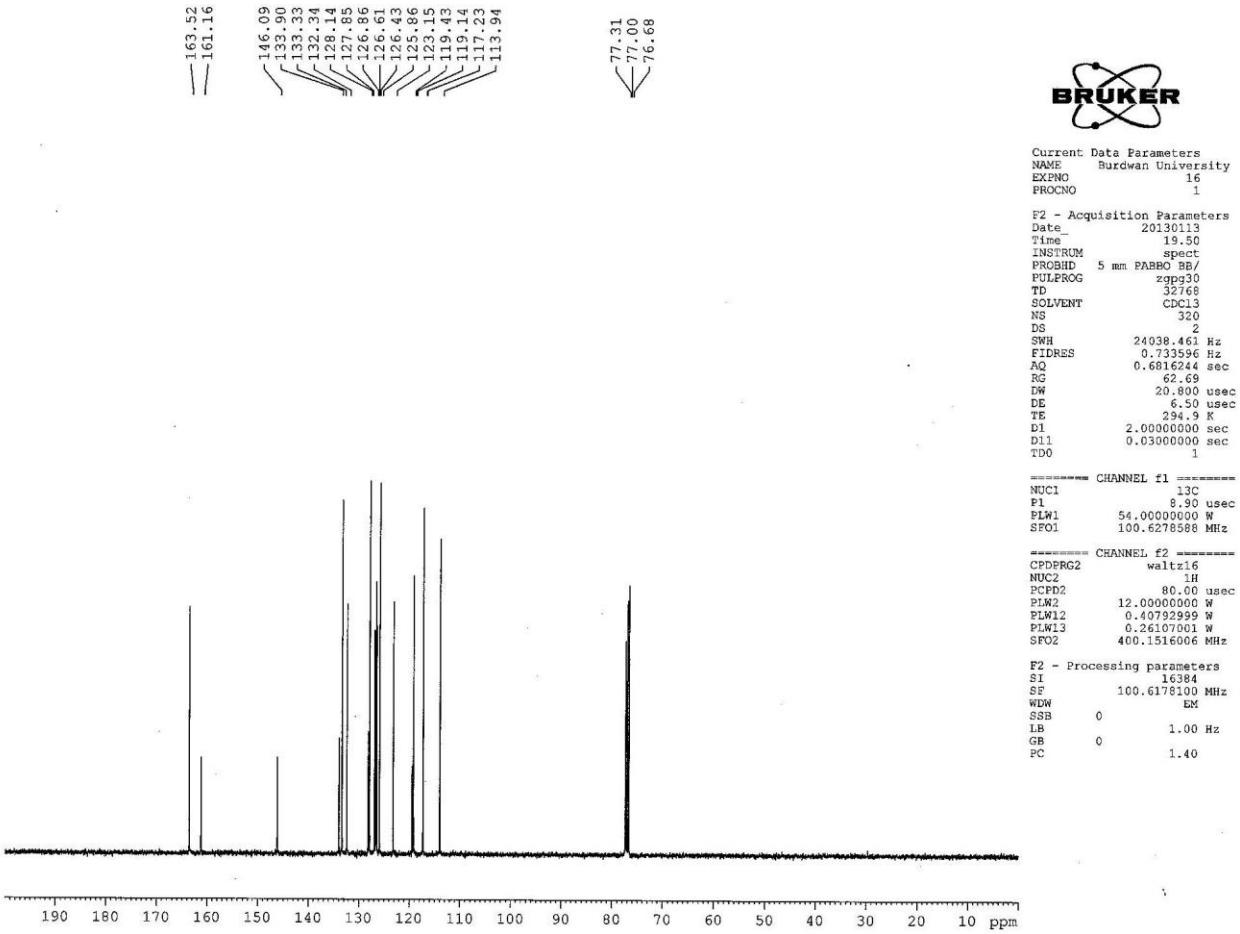


Fig. S19 ^{13}C NMR spectrum of **NAPSAL** in $CDCl_3$

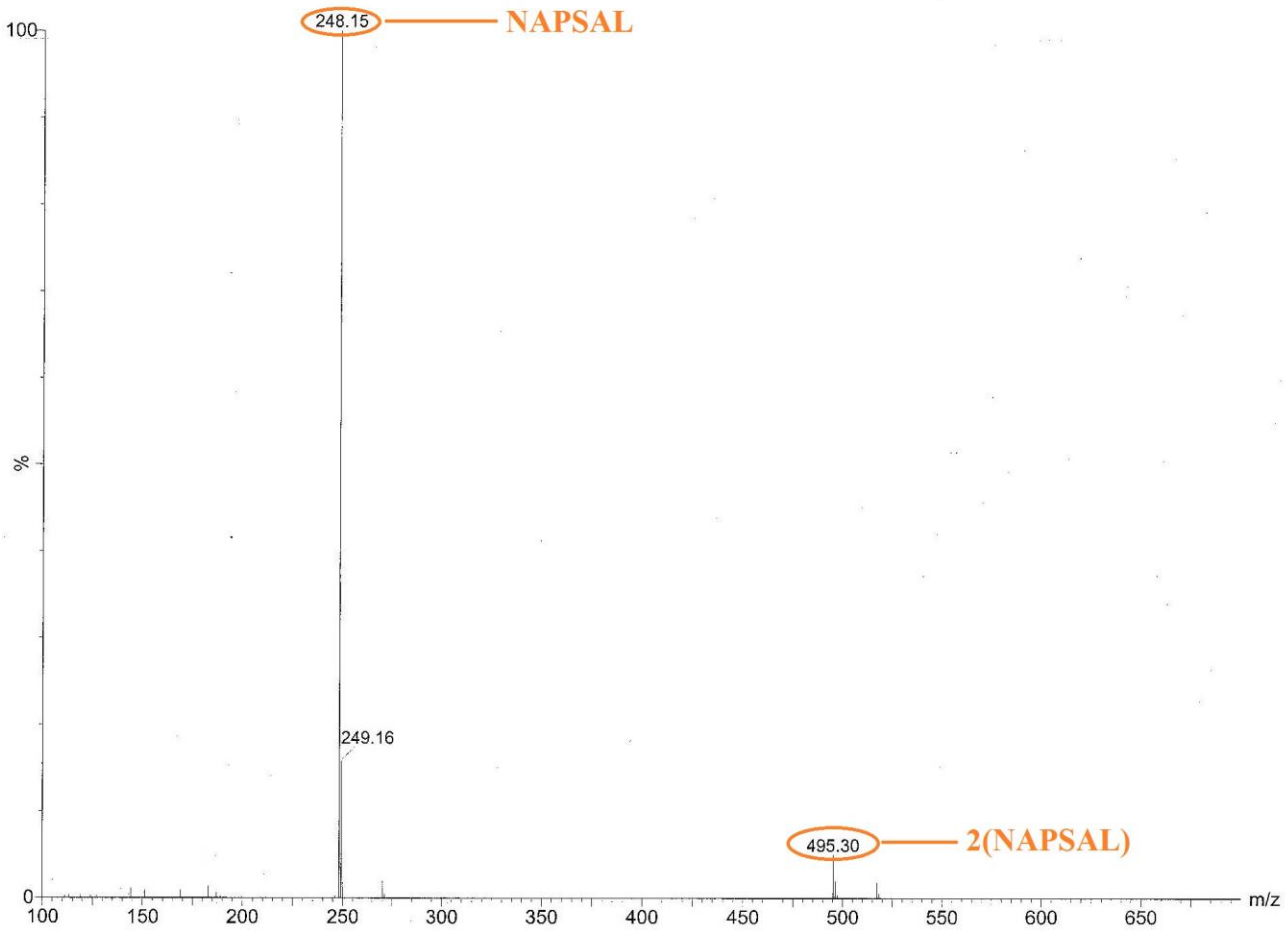


Fig. S20 QTOF-MS spectrum of **NAPSAL** in MeOH.

Table S1. Crystal parameters of **NAPSAL**

Empirical formula	$C_{17}H_{13}NO$
Formula weight	247.28
Temperature	100 K
Wavelength	0.71073 Å
Crystal system	orthorhombic
Space group	*Pbca*
Unit cell dimensions	a = 10.4675 (7) Å, b = 12.2615 (8) Å, c = 19.3299 (11) Å
Volume	2480.9 (3) $Å^3$
Z	8
Density (calculated)	1.324 Mg m^{-3}
Absorption coefficient	0.08 mm^{-1}
F(000)	1040
Crystal size	0.51 × 0.23 × 0.14 mm
Θ range for data collection	2.8–27.5°
Index ranges	h = 0→13, k = 0→16, l = 0→25
Reflections collected	42766
Independent reflections	3081
Absorption correction	colorless
Refinement method	full-matrix least-squares on F2

Table S2: Changes in chemical shifts (δ ppm) values of **NAPSAL** during ^{1}H NMR titration with $H_2ASO_4^-$.

Protons	δ (ppm)		
	free **NAPSAL**	with 1.0 eq. $H_2ASO_4^-$	with 2.0 eq. $H_2ASO_4^-$
a_1, a_2	7.03	7.01	7.01
b	7.32	7.29	7.26
c	7.45	7.44	7.43
d	7.57	7.56	7.56
e	7.61	7.65	7.67
f	7.82	7.81	7.81
g	7.92	7.91	7.91
h	8.20	8.19	8.18
i	8.87	8.90	8.91
j	------	10.0	10.2

Table S3. Determination of $H_2AsO_4^-$ in the spiked drinking water samples

Drinking water source	$H_2AsO_4^-$ added (μM)	$H_2AsO_4^-$ found (μM)	Errors (%)
Tap water (Burdwan town)	10	10.2 ± 0.2	0.2
Tap water (Durgapur city)	15	14.9 ± 0.5	0.1
Tap water (Kolkata)	25	25.3 ± 0.2	0.3
Tap water, Kanchrapara, 24 Parganas (N)	35	34.7 ± 0.2	0.3
Tap water (Bankura town)	45	44.6 ± 0.4	0.4

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