†Electronic Supplementary Information

A bio-relevant supramolecular Co(II)-complex for selective fluorescent sensor of µM range inorganic As(III) in water medium and its intracellular tracking in bacterial systems[†]

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Crystal structural analysis of Co(II)-complex

Single crystal X-ray study shows that Co(II)-complex crystallizes in the $P\bar{1}$ space group. Asymmetric unit of the complex contains one monomeric unit of Co(II) and one guest water molecule. Each Co(II) is coordinated with one n-butylmalonate, one 2,2'-dipyridylamine, two water molecules exhibiting a six coordinated pseudo-octahedral geometry around itself in its solid-state. Six neighbours of each Co(II) ion in its pseudo octahedral geometry are covered by four oxygen atoms (O1, O3 from n-butylmalonate ligand and O1W, O2W from water molecules) and two nitrogen atoms (N2 and N3 from 2,2'-dipyridylamine ligand). The ORTEP diagram of the Co(II)-complex is shown in Fig. S1. The details of crystallographic study is given in Table S1.



Fig. S1 The ORTEP diagram of the Co(II)-complex.

The Co1-N distances are 2.102(4) Å and 2.112(4) Å for N2 and N3 of 2,2'dipyridylamine and the Co1-O distances are 2.086(4) Å, 2.089(4) Å for O1 and O3 of nbutylmalonate ligand, and 2.088(4) Å, 2.149(4) Å for O1W and O2W of coordinated water molecules. Selected bond length and bond angles are given in Table S2 and S3. One guest water molecule (O3W) remains in the non-coordinated form in the crystal lattice of the complex. Due to its versatile metal-binding modes,¹ n-butylmalonate acts as a chelating ligand towards Co(II) in the complex. The bond distances and angles are within the usual range, observed in similar octahedral environments of others Co(II)-complexes.²

The supramolecular self-assembly of Co(II)-complex is manifested through the consequence of hydrogen-bonding and aromatic- π interactions, involving Co(II)-coordinated 2,2'-dipyridylamine, along with coordinated (O1W and O2W) and guest (O3W) water molecules (Table S4). The three-dimensional structure of Co(II)-complex is the outcome of a) a self-complementary O-H···O and N-H···O hydrogen-bonding patterns between successive Co(II)-units through coordinated (O1W and O2W) and non-coordinated guest (O3W) water molecules, b) a supramolecular π ··· π assembly of the aromatic π -systems of 2,2'-dipyridylamine ligands from each Co(II)-units. The presence of two different types of water like the metal coordinated (O1W and O2W) and the guest (O3W) water molecules directs the formation of two different one dimensional hydrogen-bonding polymeric chains of Co(II)-units. Coordinated water molecule (O1W) assists the formation of one polymeric hydrogen-bonded (O1W-H1W1···O4) 1-D chain propagated along crystallographic *a*-axis (Fig. S2).



Fig. S2 Metal coordinated water molecule (O1W) assisted O1W-H1W1···O4 hydrogenbonded polymeric 1-D chain propagated along crystallographic *a*-axis. (Here Co = blue, O = pink, N = light green, C = gray, H = yellow)

The carbonyl oxygen atom (O4) of n-butylmalonate ligand from each monomeric unit of Co(II) are directly participating in the formation of hydrogen-bonded 1-D chain propagated along crystallographic *a*-axis (Fig. S2). The formation of another one dimensional hydrogen-bonded polymeric chain of successive $[Co(n-BuM)(DPA)(H_2O)_2]$ units is supported by the participation of guest water molecule (O3W) (Fig. S3).



Fig. S3 Guest water molecule (O3W) assisted O3W-H1W3 \cdots O2 and N1-H1 \cdots O3W hydrogen-bonded polymeric 1-D chain propagated along crystallographic *b*-axis. (Here Co = blue, O = pink, N = light green, C = gray, H = yellow)

The guest water (O3W) directed self-complementary N1-H1···O3W and O3W-H1W3···O2 hydrogen bonding patterns among successive $[Co(n-BuM)(DPA)(H_2O)_2]$ units dictate the formation of another hydrogen-bonded polymeric 1-D chain propagated along crystallographic *b*-axis (Fig. S3). The carbonyl oxygen atom (O2) of n-butylmalonate ligand from each monomeric Co(II)-unit and hydrogen atoms of N-H bond of 2,2'-dipyridylamine ligands from alternative Co(II)-unit are connected via the guest water (O3W) which leads to the formation of the hydrogen-bonded 1-D chain propagated along crystallographic *b*-axis. Different hydrogen-bonding parameters are given in Table S4.

One coordinated water molecule (O2W) of $[Co(n-BuM)(DPA)(H_2O)_2]$ unit in Co(II)complex interacts with adjacent Co(II) unit through O2W-H1W2···O4 hydrogen-bonding pattern and this leads to the formation of cyclic supramolecular $R_2^2(12)$ synthons between two neighbouring $[Co(n-BuM)(DPA)(H_2O)_2]$ units (Fig. S4).



Fig. S4 One coordinated water molecule (O2W) assisted hydrogen-bonded (O2W-H1W2···O4) cyclic supramolecular $R_2^2(12)$ synthon formation. (Here Co = blue, O = pink, N = light green, C = gray, H = yellow)

The intermolecular hydrogen-bond forming tendency of coordinated (O1W and O2W) and guest (O3W) water molecules along with the presence of hydrogen-bonded (O2W-H1W2···O4) cyclic supramolecular $R_2^2(12)$ motif direct the formation of a two dimensional supramolecular sheet structure parallel to crystallographic *ab*-plane (Fig. S5a). Different

hydrogen-bonding patterns including five self-complementary O-H…O interactions like O1W-H1W1···O4, O3W-H1W3···O2, O1W-H2W1···O2, O2W-H1W2···O4, and O3W-H2W3...O3 and one self-complementary N1-H1...O3W interaction are mainly responsible for the generation the 2-D supramolecular sheet structure parallel to crystallographic *ab*-plane (Fig. S5a). Particularly, the presence of two guest water (O3W) molecules on either side of the coordinated water (O1W) assisted hydrogen bonded 1-D chains propagated along crystallographic a-axis (Fig. S2) is responsible for the generation of supramolecular 2-D sheet structure parallel to crystallographic *ab*-plane (Fig. S5a). The self-complementary hydrogen-bonding interactions (i.e. N1-H1...O3W, O1W-H1W1...O4, O3W-H1W3...O2, O1W-H2W1···O2, O2W-H1W2···O4, and O3W-H2W3···O3) aided 2-D supramolecular sheet structure (Fig. S5a) depict the supramolecular $\pi \cdots \pi$ assembly between adjacent [Co(n-BuM)(DPA)(H₂O)₂] units (Fig. S5b). Cg(1) of one neutral [Co(n-BuM)(DPA)(H₂O)₂] unit interacts with Cg(2) of adjacent [Co(n-BuM)(DPA)(H₂O)₂] unit where Cg(1) is formed by N(2), C(12), C(13), C(14), C(15), C(16) atoms, and Cg(2) is formed by N(3), C(8), C(9), C(10), C(11), C(17) atoms of 2,2'-dipyridylamine (Fig. S5b). Details of the supramolecular $\pi \cdots \pi$ interactions are given in Table S4. Guest and coordinated water assisted selfcomplementary N-H···O and O-H···O hydrogen bonding patterns and corresponding supramolecular $\pi \cdots \pi$ interactions play the crucial role towards the formation of the three dimensional self-assembled supramolecular structure of Co(II)-complex.



Fig. S5 Fig. 2 Crystal packing of Co(II)-complex: Both coordinated (O1W and O2W) and guest (O3W) water molecules assisted hydrogen-bonded (i.e. N1-H1…O3W, O1W-H1W1…O4, O3W-H1W3…O2, O1W-H2W1…O2, O2W-H1W2…O4, and O3W-H2W3…O3)

2-D supramolecular sheet (shown as Fig. 2a) parallel to crystallographic ab-plane depicting a novel supramolecular $\pi \cdots \pi$ assembly (shown as Fig. 2b). (Here Co = blue, O = pink, N = light green, C = gray, H = yellow)

Each $[Co(n-BuM)(DPA)(H_2O)_2]$ unit along with the guest water molecule (O3W) of Co(II)-complex are self-assembled *via* the network of supramolecular cyclic hydrogenbonded motifs (i.e. supramolecular synthons) in solid-state (Fig. S6). An interesting



Fig. S6 $[Co(n-BuM)(DPA)(H_2O)_2]$ unit along with coordinated (O1W) and guest (O3W) water molecules assisted supramolecular cyclic hydrogen-bonded motifs (i.e. supramolecular synthons).

hydrogen-bonded cyclic supramolecular $R_6^4(20)$ motif has been originated through guest water (O3W) directed two N1-H1···O3W interactions and four O-H···O interactions involving guest water (O3W) mediated two O3W-H1W3···O2 and coordinated water (O1W) based two O1W-H2W1···O2 hydrogen-bonding patterns (Fig. S6). Each supramolecular $R_6^4(20)$ synthon connects four [Co(n-BuM)(DPA)(H₂O)₂] units via two guest water (O3W) molecules and several self-complementary hydrogen-bonding patterns (i.e. N1-H1···O3W, O3W-H1W3···O2 and O1W-H2W1···O2) (Fig. S6).

H1 atom of 2,2'-dipyridylamine along with hydrogen atoms i.e. H2W1 and H1W3 of coordinated (O1W) and guest water (O3W) molecules, respectively, act as the hydrogen-

donor in each supramolecular $R_6^4(20)$ synthon. The oxygen atom O2 of n-butylmalonate along with O3W of guest water molecule act as the hydrogen-acceptor in each supramolecular $R_6^4(20)$ synthon. Besides, one coordinated water molecule (O1W) of [Co(n-BuM)(DPA)(H₂O)₂] unit in Co(II)-complex interacts with adjacent Co(II) unit through O1W-H2W1···O2 hydrogen-bonding pattern and this leads to the formation of cyclic supramolecular $R_2^2(12)$ synthons between two neighbouring [Co(n-BuM)(DPA)(H₂O)₂] units (Fig. S6).

These different cyclic hydrogen-bonded motifs ensure the donor acceptor balance within the solid-state architecture of Co(II)-complex.

The placement of guest water molecule (O3W) in the solid-state of Co(II)-complex is really noteworthy (Fig. S7). The guest water (O3W) instigates three diverse non-covalent



Fig. S7 Role of the guest water molecule (O3W) for origination of hydrogen-bonding patterns (i.e. O3W-H1W3···O2, O3W-H2W3···O3 and N1-H1···O3W). The O2W-H1W2···O4 directed cyclic supramolecular $R_2^2(12)$ synthon formation has also given as Fig. S4.

supramolecular interactions involving O3W-H1W3···O2, O3W-H2W3···O3 and N1-H1···O3W hydrogen bonding patterns. Thus every guest water molecule (O3W) connects three surrounding $[Co(n-BuM)(DPA)(H_2O)_2]$ units via two hydrogen atoms (i.e. H1W3 and

H2W3) and one oxygen atom (O3W) in the solid-state of Co(II)-complex (Fig. S7). This specific orientation also favours the donor acceptor balance, thereby directing the three dimensional self-assembled supramolecular architecture of Co(II)-complex. Interestingly, the guest water (O3W) simultaneously acts as two different hydrogen donors (i.e. H1W3 and H2W3) and one hydrogen acceptor (O3W). Two oxygen atoms (O2 and O3) of n-butylmalonate ligand also act as hydrogen acceptor. Hydrogen atom (H1) of N-H bond of 2,2'-dipyridylamine acts as the hydrogen donor.

*CCDC No.	1407706
Formula	C17H23C0N3O6.H2O
Formula Weight	442.33
Crystal System	Triclinic
Space group	<i>P</i> ī (No. 2)
a[Å]	8.1767(7)
<i>b</i> [Å]	10.9491(8)
<i>c</i> [Å]	11.4868(7)
$\alpha[^{o}]$	83.608(4)
β[°]	73.687(3)
γ[°]	88.562(4)
<i>V</i> [Å ³]	980.83(13)
Ζ	2
$D(\text{calc}) [\text{g/cm}^3]$	1.498
$\mu(MoK\alpha)$ [mm ⁻¹]	0.919
<i>F</i> (000)	462
Crystal Size [mm ³]	0.20 imes 0.20 imes 0.40
Temperature [K]	296
Radiation [Å]	МоКа 0.71073
Theta Min-Max [°]	2.8, 27.5
Dataset	-10: 10 ; -13: 14 ; -14: 14
Number of Reflections	19752
Unique Data	4467
R(int)	0.060
Observed data $[I > 2.0 \text{ sigma}(I)]$	3075
N _{ref}	4467
N _{par}	273
R	0.0701
wR2	0.2361
S	1.09
Max. and Av. Shift/Error	0.00, 0.00
Min. and Max. Resd. Dens. [e/Ang ³]	-0.61, 0.78

Table S1.	Crystallographic	data for Co(II)-	complex.
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^{*}These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk.

Bond	Distance	Bond	Distance	Bond	Distance
	(Å)		(Å)		(Å)
Co1-O1	2.086(4)	Co1-O1W	2.088(4)	Co1-O2W	2.149(4)
Co1-O3	2.089(4)	Co1-N2	2.102(4)	Co1-N3	2.112(4)
O1-C7	1.253(6)	O2-C7	1.253(6)	O3-C6	1.258(7)
O4-C6	1.234(7)	N1-C12	1.369(7)	N1-C17	1.362(7)
N2-C12	1.353(7)	N2-C16	1.326(8)	N3-C8	1.359(8)
N3-C17	1.352(7)	C1B-C2	1.49(3)	C2-C3	1.486(13)
C3-C4	1.505(10)	C4-C5	1.494(9)	C5-C6	1.551(8)
C5-C7	1.538(8)	C8-C9	1.344(9)	C9-C10	1.400(12)
C10-C11	1.369(10)	C11-C17	1.392(9)	C12-C13	1.392(8)
C13-C14	1.346(9)	C14-C15	1.383(10)	C15-C16	1.356(9)
C1A-C2	1.55(4)				

Table S2. Selected bond distances (Å) for Co(II)-complex.

Table S3. Selected bond angles (°) for Co(II)-complex.

01-Co1-O1W	92.57(16)	O1-Co1-O2W	86.85(15)
O1-Co1-O3	88.39(14)	O1-Co1-N2	176.96(16)
O1-Co1-N3	93.02(17)	O1W-Co1-O2W	85.05(15)
O1W-Co1-O3	171.31(17)	O1W-Co1-N2	90.43(17)
O1W-Co1-N3	94.02(17)	O2W-Co1-O3	86.37(15)
O2W-Co1-N2	92.89(16)	O2W-Co1-N3	179.05(15)
O3-Co1-N2	88.57(16)	O3-Co1-N3	94.56(16)
N2-Co1-N3	87.29(17)	Co1-O1-C7	125.1(3)
Co1-O3-C6	127.8(3)	Co1-N2-C12	122.5(4)
Co1-N2-C16	119.0(4)	Co1-N3-C8	118.7(4)
Co1-N3-C17	122.8(4)		

Selective Hydrogen bond donor/acceptor scheme (Å, °)					
D-H···A	D-H	Н…А	D····A	D-H···A	
N1-H1····O3W ⁱ	0.86	2.03	2.858(7)	163	
O1W-H1W1····O4 ⁱⁱ	0.80(8)	1.96(8)	2.753(6)	169(8)	
O1W-H2W1····O2 ⁱⁱⁱ	0.86(8)	1.92(8)	2.752(6)	162(7)	
O2W-H1W2····O4 ^{iv}	0.83(5)	1.99(5)	2.815(6)	167(5)	
O3W-H1W3…O2	0.83(9)	1.99(9)	2.728(6)	149(8)	
O3W-H2W3····O3 ^{iv}	0.74(10)	2.15(10)	2.872(7)	167(11)	
	π…π i	nteractions	(Å, °)		
Cg(i)-Cg(j)	Cg-Cg distance	Dihedral angle	Perpendicular distances	Slippage	
		(<i>i</i> , <i>j</i>)	between		
			baricentres (i,j)		
Cg(1)···Cg(2) ^v	3.938(4)	14.8(3)	3.799(3)	1.957	
$Cg(2)\cdots Cg(1)^{v}$	3.938(4)	14.8(3)	3.418(3)	1.041	
Symmetry codes: (i) x,1+y,z; (ii) 1+x,y,z, (iii) 2-x,1-y,1-z; (iv) 1-x,1-y,1-z; (v) 2-x,2-y,1-z					

Table S4. Supramolecular interaction parameters in Co(II)-complex.

Cg(1) is formed by N(2), C(12), C(13), C(14), C(15), C(16) atoms and Cg(2) is formed by N(3), C(8), C(9), C(10), C(11), C(17) atoms of 2,2'-dipyridylamine.

Hirshfeld Surface Analysis

Molecular Hirshfeld surfaces^{3,4} in crystal structure of Co(II)-complex are built up by following the electron distribution calculated as the sum of spherical atom electron densities.⁵ The Hirshfeld surface is characteristic for a particular crystalline architecture and a set of spherical atomic electron densities.⁶ The Hirshfeld surface depicts the possibility of several intermolecular interactions in molecular crystals. The Hirshfeld surface of a molecule is demonstrated by points where the electron density of the molecule under consideration is similar to the contribution from all other molecules. For every such point on that isosurface two distances are defined as d_e , the distance from the point to the nearest nucleus external to the surface, and d_i , the distance to the nearest nucleus internal to the surface. The normalized contact distance (d_{norm}), depending on d_e , d_i , and vdW radii of atom, shown in equation (1), assists to identify the regions of specific significance to intermolecular interactions.³ The value of the d_{norm} is negative or positive when intermolecular contacts are shorter or longer than vdW separations, respectively. Due to the symmetry between d_e and d_i in the expression for d_{norm} , where two Hirshfeld surfaces connect, both will display a red spot identical in color intensity along with size and shape.

$$d_{norm} = (d_i - r_i^{vdw}) / r_i^{vdw} + (de - r_e^{vdw}) / r_e^{vdw}$$
(1)

where, r_i^{vdW} and r_e^{vdW} are the van der Waals radii of the atoms.

Molecular Hirshfeld^{4,7} surfaces and associated 2D-fingerprint plots⁸ were calculated and analysed using the program CrystalExplorer 3.1.⁹ When the structures are read into the program for analysis, CrystalExplorer 3.1 automatically regulates all bond lengths to hydrogen to standard neutron values (C–H = 1.083 Å, N–H = 1.009 Å and O–H = 0.983 Å). For the purpose of this study all the Hirshfeld surfaces were generated using a standard (high) surface resolution. The Hirshfeld surfaces mapped with d_e use a fixed colour scale of 0.65 (red) to 2.2 Å (blue). The *d_{norm}* surfaces are mapped over a fixed colour scale of -0.75 (red) to 1.10 (blue). The fingerprint plots displayed each use the standard 0.4-2.6 Å view with the d_e and d_i distance scales displayed on the graph axes. The connectivity of d_e and d_i is expressed in the form a 2D fingerprint plot.⁸ 2D fingerprint plot offers the different intermolecular contacts within the crystal system.³

Hirshfeld Surface

The Hirshfeld surfaces of Co(II)-complex (Fig. S8) have been mapped over d_{norm} (-0.6 to 1.3 Å), shape index (-0.99 to 0.99 Å) and curvedness (-3.63 to 0.48 Å). The surfaces are transparent for the understanding of the molecular architecture. The crystallographic information on different hydrogen-bonding patterns (Table S4) is expressed through these spots (Fig. S8) where the deep red coloured large circular depressions of surfaces dictate the hydrogen-bonding contacts. H…H contacts are shown by other visible spots in the surfaces (Fig. S8). The leading interactions between N-H (from 2,2'-dipyridylamine), O-H (from both coordinated and guest water molecules) with carbonyl O atoms of n-butylmalonate and guest water molecules (O3W) in Co(II)-complex are given by the red coloured zones in the Hirshfeld surface (Fig. 8). Different moderately weaker and longer contacts except hydrogen bonding patterns are expressed by small extent of area and light coloured on surfaces (Fig. S8).

H...H interactions are given as distinct spikes in the 2D fingerprint plot (Fig. S9). Complementary regions are given in the fingerprint plots where one molecule plays as donor $(d_e > d_i)$ and the other acts as an acceptor $(d_e < d_i)$. The fingerprint plots are separated to explore all significant close contacts between particular atom pairs. Other non-covalent intermolecular interactions like O···H/H···O, H···C/C···H, O···O, N···H/H···N, and C···N/N···C also appear as distinct spikes in 2D fingerprint plot (Fig. S9). These distinct spikes in 2D fingerprint plot (Fig. S9), combined in the full fingerprint (Fig. S9), conveys the impact of the contributions from different interactions towards the formation of crystalline Co(II)-complex. The proportion of O···H/H···O interactions is 22.4 % of the Hirshfeld surfaces for Co(II)complex, The O…H interaction is represented by a spike ($d_i = 1.5988$, $d_e = 1.6108$ Å in the fingerprint plot (Fig. S9), The proportion of C···H/H···C, O···O, N···H/H···N, and C···N/N···C interactions are 7.5%, 1.5%, 1.3%, and 2.1% of the Hirshfeld surfaces of Co(II)-complex. A notable difference among the molecular interactions in the Co(II)-complex with respect to H.H interactions is reflected in the distribution of scattered points in the fingerprint plots, which spread only up to $d_i \approx d_e \approx 1.6$ Å in Co(II)-complex. The contributions of the various contacts, exhibited by Co(II)-complex, have been illustrated in Fig. S9 which clearly shows the minimal effect of other interactions.



Fig. S8 Hirshfeld surface mapped with d_{norm} , d_i , d_e , shape index and curvedness for Co(II)-complex



Fig. S9 Fingerprint plots of Co(II)-complex: Full (middle) and decomposed plots corresponding to all others contacts (i.e. $H \cdots H$, $O \cdots H/H \cdots O$, $C \cdots H/H \cdots C$, $O \cdots O$, $N \cdots H/H \cdots N$, and $C \cdots N/N \cdots C$) involved in the structure [clockwise: from bottom left to bottom right]. The relative contributions of various intermolecular contacts to the Hirshfeld surface area in Co(II)-complex are displayed by schematic representation.

Topological analysis of electron density and theoretical calculations details

In order to understand the nature of water assisted hydrogen bonds and their influence on the 3D self-assembly of Co(II)-complex, partitioning of electron density within clusters including intermolecular interactions were carried out. For this purpose DFT calculations with the GAUSSIAN16 package¹⁰ at the B3LYP/6-311++G(2d,2p) level were engaged. Wave functions obtained this way were further used to perform hard space partitioning of electron density with the use of Bader's quantum theory of atoms (QTAIM) implemented in the AIMAII package.¹¹ Due to high rotational degrees of freedom around the N-C bonds between amino nitrogen and pirydyl substituents in 2,2'-dipyridylamine molecule cluster geometries were not optimized but taken from the crystal structure of Co(II)-complex. The summary of full analysis of the topology of electron density $\rho(\mathbf{r})$ for the examined water assisted hydrogen bonds is given in Table S5.

Table S5 Topologica	d analysis of water	r assisted hydrogen bonds	at bond critical points BCPs ^a .
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	<i>ρ</i> (r)	$\nabla^2 \rho(\mathbf{r})$	R _{ij}	d ₁	d ₂	3	G(r _{CP})	V(r _{CP})	V(r _{CP})	Type of interaction
									$/G(\mathbf{r}_{CP})$	
H1W3…O2	0.027	0.099	3.65	1.32	2.33	0.02	0.023	-0.022	1.0	Intermediate
$H2W1\cdots O4^{i}$	0.024	0.089	3.73	1.33	2.37	0.01	0.021	-0.019	0.9	Closed-shell
H1···O3W ⁱⁱ	0.022	0.083	3.89	1.40	2.43	0.03	0.019	-0.017	0.9	Closed-shell
$^{a}\rho(\mathbf{r})/\text{eBohr}$	⁻³ – elect	ron densit	y, $\nabla^2 \rho(\mathbf{x})$	r)/eBoh	r ⁻⁵ – Laj	placian o	of electror	n density, l	R _{ij} /Bohr – b	ond path length,
d ₁ ,d ₂ /Bohr -	- distanc	e between	BCP a	nd atom	s 1 and 2	2, respec	ctively, ε -	- ellipticit	y, G($\mathbf{r}_{ ext{CP}}$) an	nd V(\mathbf{r}_{CP}) are local
kinetic and local potential energy density (eBohr ⁻³), respectively.										
Symmetry codes: (i) x+1,y,z, (ii) x,y+1,z										

Spectral Study:



Fig. S10 UV-absorption spectra of the dilute aqueous solution of Co(II)-complex (i.e. $[Co(II)-complex] = 10^{-4} \text{ M}$) recorded at 298 K and atmospheric pressure.

Density functional theory (DFT) Calculation:

Structure of the molecule was optimized in DFT formalism, with 6-311g(d,p) basis set¹²⁻¹⁴ and B3LYP functional.¹⁵⁻¹⁷ Solvent effects were incorporated using Onsager's SCRF method,¹⁸⁻²⁰ with polarisable continuum model (PCM) approximation.²¹⁻²⁴ With water as solvent, the optimized structure of the molecule is shown in Fig. S11, and the structural parameters are tabulated in Tables S6 and S7. With heptanes as solvent, the optimized structure of the molecule is shown in Fig. S12, and corresponding structural parameters are given in Tables 3 and 4. For MO images, the MaSK software²⁵ was used.



Fig. S11 DFT optimized structure of the Co(II)-complex in water

Bond	Distance	Bond	Distance	Bond	Distance
	(Å)		(Å)		(Å)
Co1-O1	1.93017	Co1-O1W	2.11924	Co1-O2W	2.37374
Co1-O3	1.98901	Co1-N2	1.97721	Co1-N3	2.09815
O1-C7	1.29282	O2-C7	1.23687	O3-C6	1.29461
O4-C6	1.23028	N1-C12	1.38813	N1-C17	1.39083
N2-C12	1.34488	N2-C16	1.35485	N3-C8	1.34993
N3-C17	1.33829	C1-C2	1.53182	C2-C3	1.53454
C3-C4	1.53662	C4-C5	1.53028	C5-C6	1.55154
C5-C7	1.54153	C8-C9	1.38063	C9-C10	1.39869
C10-C11	1.38097	C11-C17	1.40670	C12-C13	1.40709
C13-C14	1.37917	C14-C15	1.39785	C15-C16	1.37869
O1W-H1W	0.96381	O1W-H2W	0.96624	O2W-H3W	0.96897
O2W-H4W	0.96509	N1-H1	1.00976	C1-H1A	1.09372
C1-H1B	1.09481	C1-H1C	1.09478	C2-H2A	1.09574
C2-H2B	1.09713	C3-H3A	1.09472	C3-H3B	1.09722
C4-H4A	1.09090	C4-H4B	1.09516	C5-H5	1.09359
C8-H8	1.08188	С9-Н9	1.08162	C10-H10	1.08328
C11-H11	1.08284	С13-Н13	1.08268	C14-H14	1.08310
C15-H15	1.08138	C16-H16	1.08090		

Table S6. Selected bond distances (Å) for Co(II)-complex in water

Table S7. Selected bond angles (°) for Co(II)-complex in water

O1-Co1-O1W	81.921	O1-Co1-O2W	81.932	01-Co1-O3	91.345
O1-Co1-N2	173.276	O1-Co1-N3	96.319	O1W-Co1-O2W	86.840
O1W-Co1-O3	163.689	O1W-Co1-N2	94.898	O1W-Co1-N3	89.890
O2W-Co1-O3	77.480	O2W-Co1-N2	92.007	O2W-Co1-N3	176.478
O3-Co1-N2	90.168	O3-Co1-N3	105.671	N2-Co1-N3	89.575
Co1-O1-C7	125.969	Co1-O3-C6	124.478	Co1-N2-C12	123.318
Co1-N2-C16	118.097	Co1-N3-C8	119.848	Co1-N3-C17	121.529

The DFT optimized structure of Co(II)-complex in heptane is shown below in Fig. S12.



Fig. S12. DFT optimized structure of Co(II)-complex in heptane

Some important structural parameters of the DFT optimized geometry of Co(II)-complex in heptane are given below.

Bond	Distance	Bond	Distance	Bond	Distance
	(Å)		(Å)		(Å)
Co1-O1	1.91319	Co1-O1W	2.11482	Co1-O2W	2.51768
Co1-O3	1.93205	Co1-N2	1.98024	Co1-N3	2.11276
O1-C7	1.30477	O2-C7	1.22672	O3-C6	1.30730
O4-C6	1.22035	N1-C12	1.38690	N1-C17	1.39016
N2-C12	1.34287	N2-C16	1.35381	N3-C8	1.34906
N3-C17	1.33693	C1-C2	1.53203	C2-C3	1.53429
C3-C4	1.53601	C4-C5	1.53135	C5-C6	1.55192
C5-C7	1.54268	C8-C9	1.38131	C9-C10	1.39744
C10-C11	1.38082	C11-C17	1.40706	C12-C13	1.40788
C13-C14	1.37860	C14-C15	1.39713	C15-C16	1.37887
O1W-H1W	0.96323	O1W-H2W	0.97175	O2W-H3W	0.97157
O2W-H4W	0.96463	N1-H1	1.00858	C1-H1A	1.09421
C1-H1B	1.09465	C1-H1C	1.09454	C2-H2A	1.09613
C2-H2B	1.09769	C3-H3A	1.09354	C3-H3B	1.09725
C4-H4A	1.09129	C4-H4B	1.09560	C5-H5	1.09555
C8-H8	1.08215	C9-H9	1.08161	C10-H10	1.08348
C11-H11	1.08344	С13-Н13	1.08328	C14-H14	1.08341
C15-H15	1.08150	C16-H16	1.08161		

Table S8. Selected bond distances (Å) for Co(II)-complex in heptane

O1-Co1-O1W	78.766	O1-Co1-O2W	80.962	O1-Co1-O3	92.649
O1-Co1-N2	173.232	O1-Co1-N3	96.227	O1W-Co1-O2W	85.775
O1W-Co1-O3	160.350	O1W-Co1-N2	96.901	O1W-Co1-N3	90.441
O2W-Co1-O3	75.365	O2W-Co1-N2	92.350	O2W-Co1-N3	175.658
O3-Co1-N2	89.447	O3-Co1-N3	108.178	N2-Co1-N3	90.214
Co1-O1-C7	125.696	Co1-O3-C6	124.990	Co1-N2-C12	124.111
Co1-N2-C16	117.121	Co1-N3-C8	119.368	Co1-N3-C17	122.023

Table S9.Selected bond angles (°) for Co(II)-complex in heptane

The frontier orbitals of the two DFT optimized structures are shown below. First, the four frontier orbitals of the DFT optimized structure of the Co(II)-complex in water are shown.



Fig. S13 The frontier orbitals of the monomeric Co(II) unit of Co(II)-complex in water.



Next, the frontier orbitals of the DFT optimized structure of Co(II)-complex in heptane are shown below.

LUMO+1

Fig. S14. The frontier orbitals of the monomeric Co(II) unit of Co(II)-complex in heptane.

Next, the energy level diagram of some orbitals near the frontier orbitals is shown. This gives an idea of the nature of orbitals.



Fig. S15 Energy level diagram of DFT optimized structures of Co(II)-complex in water and in heptanes. Orbitals with some Co electron density (esp. d) is mixed, are coloured black. Ligand π orbitals are coloured red.

SOMO at -0.2076 au comprises of Co d with less on the nearest neighbour atoms viz. O3, O2W, N3 and less on O1W. The HOMO at -0.2152 au is mostly Co d with neighbouring O3 and O1W. The HOMO-1 at -0.2242 au is a combination of Co d with π density on O1 – O4, and less on N1. HOMO-2 at -0.2313 au is also Co d with density on O1, O3 and O1W. HOMO-3 at -0.2380 au is again Co d with near neighbour O atoms, and some density on N1. HOMO-4 at -0.2443 au is Co d mixed with electron density on O1–O4 and C5–C7, less on N1. HOMO-5 at -0.2520 au and HOMO-6 at -0.2650 au are very similar, with more density on O1 to O4, and some on O3W. HOMO-7 at -0.2758 au is very similar to HOMO-5, with some density on O2W instead of O3W. HOMO-7 at -0.2766 au is similar to HOMO-6. HOMO-8 at at -0.2799 au is mostly π density on O3W, O1 and O2. HOMO-9 at -0.2870 au is similar to HOMO-8 but with some Co d density. HOMO-10 at -0.2898 au is similar to HOMO-8. HOMO-11 at -0.2930 au is similar to HOMO-9, but with no O3W, little O2W, and

some σ density between C4, C5 and C7. The next MO at -0.3007 au comprises of σ density between C3, C4, C6 and C7, with Co d and π density on O1, O2, O3, O4, with some density on O2W and N2.

The LUMO at -0.0605 au is a mixture of π density on the pyridines and Co d. LUMO+1 at -0.0540 au has some σ density on the butane chain. LUMO+2 at -0.0517 au is similar to LUMO. LUMO+3 at -0.0366 au is just π density on the pyridines. LUMO+4 at -0.0257 au is a mixture of Co d and near neighbour atoms (N2, N3, O1W, O1, O3). LUMO+5 at -0.0096 au is a mixture of π density on the pyridines and some on Co.

For DFT optimized structure in heptanes, the SOMO at -0.2067 au is a mixture of Co d with O3, O4 and O1W π density. The HOMO at -0.2106 au comprises Co d and π density on O3, O4, N3, O1W, O2W and less on O1 and N2. HOMO-1 at -0.2206 is very similar to SOMO. HOMO-2 at -0.2253 au is a mixture of Co d with π density on O1 to O4. HOMO-3 at -0.2305 au is similar to HOMO-2, with more density on the O atoms. HOMO-4 at -0.2435 au is similar to HOMO-3, with some π density on N1, less on the pyridines and little on O3W. HOMO-5 at -0.2491 au is mostly π density on the pyridines, N1 and O2, and less on O1, O3, O4 and on Co d. HOMO-6 at -0.2554 au is Co d with π density on O1 to O4, σ density on C5 to C6, C7, and some on O3W and N1 (π). HOMO-7 at -0.2618 au has a lot of density on O3W, with less on the 4 O atoms, little on Co d, and on C4. HOMO-8 at -0.2687 au is σ density on C5 to C6, π density on O3 and O4, and less on Co d. HOMO-9 at -0.2719 au is a mixture of Co d and π density on the 4 O atoms, with less on C4 and O2W. HOMO-10 at -0.2776 au is a mixture of Co d with σ density on the 4 O atoms, and on O1W and O2W. HOMO-11 at -0.2879 au is a mixture of density along C4 to C6 bonds with less on the O atoms and on Co d, with little on O2W. The next MO at -0.2957 au is similar, with some density on O3W as well.

The LUMO at -0.0704 au, and LUMO+1 at -0.0623 au are both mostly π pyridine with less density on Co. LUMO+2 at -0.0513 au comprises Co d and π density on O1, O3, O1W and N2, with little on N3. LUMO+3 at -0.0479 au is just π density on the pyridines. LUMO+4 at -0.0243 au is similar to LUMO+2, with less on pyridines instead of on N3. LUMO+5 at -0.0163 au is mostly π density on the pyridines, with less on Co.

From the above data, we can draw a couple of broad conclusions:

- (1) The DFT optimized structures, in water and in heptanes, are close to the structure obtained from single crystal x-ray diffraction analysis. This may be because the complex has both hydrophilic and hydrophobic regions.
- (2) The frontier orbitals are mainly metal-ligand (or M–L) type orbitals, in both water and in heptanes mediums. Position of the HOMO appears unchanged in both, while the LUMO seems a little more stabilised in heptanes medium. Therefore, the major low energy electronic transitions (in UV-Visible or in fluorescence) involve M-L to M-L type transitions.

Next, the theoretical UV-Vis absorption spectra of the Co(II)-complex are presented.



Fig. S16 Theoretical UV-VIS spectrum of the Co(II)-complex in water medium.

Table S10. TDDFT results of a few low lying electronic transitions for the Co(II)-complex in water. Counting is from Homo (H), LUMO (L), SUMO (S). Only transitions with oscillator strength > 0.005 are tabulated. Components whose percentage in the transition is < 10% are not mentioned.

Water			
medium			
$\Delta E (eV)$	λ (nm)	Oscillator	Major components
		strength	
3.4111	363.47	0.0063	$H \to L (31.86), H-1 \to S_{\beta} (15.09), H-1 \to L (0.96)$
3.8429	322.63	0.0086	$H \rightarrow L+1 (32.32), H-2 \rightarrow S_{\beta} (15.25), H \rightarrow L+2 (13.90)$
3.8646	320.82	0.0136	$H-1 \rightarrow L (61.00), H \rightarrow L+2 (11.66)$
3.9197	316.31	0.0113	$H-1 \rightarrow L+1 (53.23)$
4.0712	304.54	0.0458	$\text{H-1} \rightarrow \text{L} (34.01), \text{H-3} \rightarrow \text{H-1} \rightarrow \text{L} (16.70)$
4.1283	300.33	0.006	H-1→L+1 (26.87), H-2→L (20.81)
4.1747	296.99	0.0141	$H-1 \rightarrow L+2 (20.62)$
4.2669	290.57	0.0105	$H \rightarrow L+3 (37.98), H-2 \rightarrow L (13.60)$
4.3217	286.89	0.0569	$H \rightarrow L+3 (29.55)$
4.3386	285.77	0.0278	H-1→L+2 (23.57), H-3→L (12.85), H-1→L+1 (11.38)
4.3522	284.88	0.0337	H-1→L+1 (47.71), H-4→L (15.00)
4.4339	279.63	0.0899	H-4 \rightarrow L (24.53), H-3 \rightarrow H-1 \rightarrow S _{β} (13.72)
4.5052	275.20	0.0215	$H-4 \rightarrow S_{\beta} (40.05), H-2 \rightarrow L+1 (16.15)$
4.5059	275.16	0.0063	H-2→L+1 (43.09), H-4→ S _β (25.60)
4.5294	273.73	0.0146	$H-2 \rightarrow L+1 (22.51), H-2 \rightarrow L+2 (20.08), H-3 \rightarrow L (14.28),$
			$H-2 \rightarrow L+2 (14.21)$
4.5828	270.54	0.0918	$H-3 \rightarrow L (14.20), H-3 \rightarrow L+1 (13.60), H-4 \rightarrow L (12.99),$
			$H-4 \rightarrow S_{\beta} (11.86)$
4.6619	265.95	0.0118	$H-4 \rightarrow L+2 (23.35), H-2 \rightarrow L+2 (12.59)$
4.7389	261.63	0.0123	$H-6 \rightarrow L+1 (19.63), H-5 \rightarrow L (17.27), H-5 \rightarrow L+1 (17.04),$
			$H-6 \rightarrow L (13.11)$
4.7678	260.05	0.0142	$H-4 \rightarrow L (24.22), H-3 \rightarrow L+2 (19.22), H-4 \rightarrow L+2 (12.13)$
4.7878	258.96	0.0529	$H-1 \rightarrow L+3 (38.62)$
4.8592	255.15	0.0650	$H-3 \rightarrow L+1 \ (13.88)$
4.9490	250.52	0.0063	$H-3 \rightarrow L+2 \ (76.43)$
4.9741	249.26	0.0180	$H \rightarrow L+4 \ (11.24)$
4.9992	248.01	0.0190	$H-2 \rightarrow L+3 (13.25)$
5.0110	247.42	0.0201	$H \rightarrow L+5 \ (26.65), H-5 \rightarrow S_{\beta} \ (16.65), H \rightarrow L+4 \ (13.45)$
5.0197	247.00	0.0318	$H-5 \rightarrow S_{\beta}$ (39.07), $H-2 \rightarrow L+3$ (15.24)
5.0320	246.39	0.0683	$H \rightarrow L+4 (49.25), H-3 \rightarrow L+1 (13.86)$
5.1140	242.44	0.0075	$H-5 \rightarrow L+1 (27.44), H-5 \rightarrow L (17.61)$
5.2289	237.11	0.0076	$H \rightarrow L+6 (36.31), S \rightarrow L+6 (33.59)$
5.2466	236.31	0.0083	$H-5 \rightarrow S_{\beta} (18.38)$
5.2607	235.68	0.0056	$H-2 \rightarrow L+3 (18.22)$
5.2799	234.82	0.0094	$H-6 \rightarrow L (32.79), H-5 \rightarrow L+2 (16.14)$
5.3706	230.86	0.0061	$H \rightarrow L+5 (44.61)$

5.4547	227.30	0.0054	$\text{H-7} \rightarrow \text{L} (79.51)$
5.4840	226.08	0.0060	$H-6 \rightarrow L (84.56)$
5.4937	225.69	0.0070	$H-5 \rightarrow L+2 (38.83)$
5.5084	225.08	0.0069	$H-6 \rightarrow L+2 (46.89), H-6 \rightarrow L+1 (21.51)$
5.5914	221.74	0.0098	$H-9 \rightarrow L (16.78), H-9 \rightarrow L+1 (13.70)$
5.6091	221.04	0.0054	$H-7 \rightarrow L+2 (60.02), H-7 \rightarrow L+1 (23.31)$
5.6795	218.30	0.0089	$H-1 \rightarrow L+6 (11.73), H-5 \rightarrow L+1 (11.41)$
5.6894	217.92	0.0060	$H-10 \rightarrow S_{\beta} (20.07)$
5.6990	217.55	0.0090	$H-3 \rightarrow L+3 (10.08)$
5.7038	217.37	0.0069	$H-1 \rightarrow L+6 (58.04)$
5.7290	216.41	0.0676	$H-7 \rightarrow L+2 (22.63)$
5.7469	215.74	0.0073	H-8→ L (18.94), H-2→ L+4 (11.36)
5.7483	215.69	0.0063	$H-5 \rightarrow L+2 (22.61), H-7 \rightarrow L+2 (12.13)$
5.7693	214.90	0.0075	$H-8 \rightarrow L (33.95), H-10 \rightarrow L (11.53)$

Theoretical FTIR spectra of the Co(II)-complex were calculated in water and in heptanes media. They are shown below.



Fig. S17 Theoretical FTIR spectrum of the Co(II)-complex, optimized in water medium.



Fig. S18 Theoretical FTIR spectrum of the Co(II)-complex, optimized in heptane medium.

Sensing Activity:

Detection Limit:



Fig. S19. Detection limit: Plot of I *vs* [As(III)], where, I = Fluorescent intensity of the water solution of Co(II)-probe in presence of As(III) (i.e. As(OH)₃) and [As(III)] = Added amount of As(III) source (i.e. As(OH)₃) into the water solution of the Co(II)-probe.

This plot of I *vs* [As(III)] depicts the detection limit of fluorescent Co(II)-probe towards inorganic As(III) source in aqueous solution. The plot based on the fluorescence spectroscopic investigation shows that the detection limit of fluorescent Co(II)-probe towards toxic inorganic As(III) source (i.e. As(OH)₃) in aqueous solution is 0.49 μ M.



Fig. S20. The linear response range of Co(II)-probe for the sensing of toxic inorganic As(III)source (i.e. As(OH)₃) in water medium.

The plot of $I/I_0 vs$ [As(III)], (where, I_0 = Fluorescent intensity of the water solution of pure Co(II)-probe, I = Fluorescent intensity of the water solution of Co(II)-probe in presence of

As(III) source and [As(III)] = added amount of toxic inorganic As(III) source (i.e. As(OH)₃) into the water solution of the Co(II)-probe), shows that the linear response range of Co(II)-probe in As(III) sensing from 0.49 μ M to 390.24 μ M.

Fluorescence spectroscopic result of Co(II)-probe (i.e. Co(II)-complex) in presence of different water solution of As(OH)₃ with different concentrations given in Fig. 3.

Each reading has been taken just after the mixing of As(OH)₃ with Co(II)-probe in water medium.

Evaluation of Fluorescence Quantum Yield:

$$\Phi_{\text{Sample}} = \Phi_{\text{ref}} \times \frac{\text{OD}_{\text{ref}} \times A_{\text{sample}} \times \eta^2_{\text{sample}}}{\text{OD}_{\text{sample}} \times A_{\text{ref}} \times \eta^2_{\text{ref}}}$$

Here, Φ = Fluorescence Quantum Yield, OD = Optical density, A = Area under the fluorescence spectral curve, η = Refractive index of the solvent. The fluorescence quantum yield (Φ) of the Co(II)-probe was evaluated in absence and in presence of As(OH)₃ in water solution. The 2-aminopyridine was used as the standard for measuring the fluorescence quantum yield (Φ = 0.6 in 0.1 (N) H₂SO₄).^{26,27} The fluorescence quantum yield (Φ) of the Co(II)-probe was evaluated as 0.019 and 0.477 in absence and in presence of As(III)-source (i.e. [As(OH)₃] = 696.05 µM), respectively.

Alike concentrations of As(OH)₃ are also taken for other selective metal ions like Li⁺, Na⁺, K⁺, Ca²⁺, Mg²⁺, Fe²⁺, Mn²⁺, Cu²⁺, Ni²⁺, Cd²⁺, Zn²⁺, Sn²⁺, Cr³⁺, Sb³⁺, Pb²⁺ and anions like F⁻, Cl⁻, Br⁻, SO₄²⁻, N₃⁻, BF₄⁻, Cr(VI)-oxo anions and PO₄³⁻ along with other arsenic sources like inorganic As(V)-oxo anion and organic arsenic species like Cacodylic acid and the fluorescence spectroscopic results are collected as the plot of I/I₀ vs concentration of different metal ions (Fig. S21).



Fig. S21 Fluorescence spectroscopic patterns of the water solution of Co(II)-probe in presence of different ions and other arsenic-sources at variable concentrations (where I_0 = Fluorescence intensity of the water solution of Co(II)-probe and I = Fluorescence intensity of Co(II)-probe in presence of different ions and other arsenic-sources with variable concentrations in water medium. Here, [Co(II)-probe] = 1×10^{-4} (M),)

The fluorescence spectroscopic results (i.e. $I/I_0 vs$ Concentration plot, Fig. S21) endorse that the Co(II)-probe is a critical fluorescent sensor for only inorganic As(III)-species i.e. As(OH)₃ over versatile ions and other Arsenic-species including As(V)-oxoanions and organic Arsenic-species (Cacodylic acid) at micromolar concentration level in water medium.

Selectivity Study:

A comparative fluorescence spectral study of the water solution of Co(II)-probe in absence and in presence of different metal ions and As(III)-species (where [As(OH)₃] = 148.94 μ M and [Mⁿ⁺] = 148.94 μ M) have been recorded (Fig. S22). Initially, 148.94 μ M of each metal ion solution has been mixed to the water solution of Co(II)-probe ([Co(II)-probe] = 10⁻⁴ M), and then after recording the fluorescence emission spectral data of this mixture of Co(II)-probe and respective metal ion, further 148.94 μ M water solution of As(III)-species i.e. As(OH)₃ has also been added to each of the mixture, containing respective metal ions and Co(II)-probe, to collect the fluorescence spectral pattern of the water solution of Co(II)-probe with respective metal ions and As(OH)₃. Each reading has been taken just after the addition of each metal ion or/and As(III)-species into the water solution of Co(II)-probe. These fluorescence spectroscopic measurements (Fig. S22) establish that the Co(II)-probe is extremely specific towards toxic inorganic $As(OH)_3$ sensing in presence of other metal ions in water medium. This is also given by the histogram as Fig. S23.





S35





Fig. S22 Fluorescence spectra of Co(II)-probe in absence and in presence of different metal ions or/and As(OH)₃, where I₀ = Fluorescence intensity of Co(II)-probe and I = Fluorescence intensity of Co(II)-probe with other metal ions or/and As(OH)₃ in water medium (Here, [Probe 1] = 1×10^{-4} (M), [Mⁿ⁺] = 148.94 µM, [As(OH)₃] = 148.94 µM, Mⁿ⁺ = Li⁺, Na⁺, K⁺, Ca²⁺, Mg²⁺, Mn²⁺, Ni²⁺, Cu²⁺, Fe²⁺, Cd²⁺, Cr³⁺, Cr(VI)-oxoanion, Pb²⁺, Sb³⁺, Sn²⁺, Zn²⁺, along with other arsenic sources like inorganic As(V)-oxo anion and organic arsenic species like Cacodylic acid)



Fig. S23 Comparative histogram based assessment of fluorescence intensity ratios of the water solution of Co(II)-probe in presence of different metal ions or/and As(III)-species. This is the histogram of the spectral results shown in **Fig. S22**.

A relative comparison of the fluorescence spectral results of Co(II)-probe in absence and in presence of different anions and As(OH)₃ as the source of As(III) (where [As(OH)₃] = 148.94 μ M and [anion] = 148.94 μ M) have also been recorded (shown in Fig. S24). Here, initially, 148.94 μ M of each anion solution has been added to the water solution of Co(II)probe ([Co(II)-probe] = 10⁻⁴ M) and then after obtaining the fluorescence emission spectra of this mixture, further 148.94 μ M water solution of As(OH)₃ has also been added to each mixture, containing respective anions and Co(II)-probe. Then, again fluorescence spectra of the water solution of Co(II)-probe with respective anions and As(OH)₃ has also been collected. Each reading has been taken just after the addition of each anion and As(OH)₃ into the water solution of Co(II)-probe. These fluorescence spectroscopic measurements (Fig. S24) show that the aqueous solution of Co(II)-probe is extremely specific towards the sensing of As(OH)₃ in presence of other anions in water medium. This is also given by the histogram as Fig. S25.







Fig. S24 Fluorescence spectra of Co(II)-probe in absence and in presence of different anions or/and As(OH)₃, where I₀ = Fluorescence intensity of Co(II)-probe and I = Fluorescence intensity of Co(II)-probe with other anions or/and As(OH)₃ in water medium (Here, [Probe 1] = 1×10^{-4} (M), [Anion] = 148.94μ M, [As(OH)₃] = 148.94μ M, and Anion = F⁻, Cl⁻, Br⁻, SO₄²⁻, N₃⁻, BF₄⁻, PO₄³⁻ and Cr(VI)-oxo anions)



Fig. S25 Comparative histogram based assessment of fluorescence intensity ratios of the water solution of Co(II)-probe in presence of different anions or/and As(III)-species. This is the histogram of the spectral results shown in Fig. S24.

Solid State Infrared spectroscopic study:



Fig. S26 Solid-state Infrared spectra of solid Co(II)-probe and the dried (using $CaCl_2$ based closed desiccator) sample of the water solution of Co(II)-probe and $As(OH)_3$.

ESI-MS study:



Fig. S27 ESI-MS spectra of the water solution of Co(II)-probe.



Fig. S28 ESI-MS spectra of the water solution of Co(II)-probe and As(OH)₃.

DFT level theoretical study of As(OH)3 sensing activity

To understand the binding mode of $As(OH)_3$ units with the Co(II)-probe, two such units were placed close to the carboxylate groups of the Co(II)-probe. The whole structure was subject to geometry optimization, with 6-311G(d,p) basis set and B3LYP functional at DFT level using Gaussian 09 program suite. Solvent effect was included via Onsager's SCRF model, with polarisable continuum approximation. Water was taken as the solvent. The optimum structure was viewed from different angles and is shown below. The two As(OH)₃ units are seen to be bounded by hydrogen bonds to the free carboxylate units of the Co(II)probe.



Fig. S29 The optimum structure of two $As(OH)_3$ units hydrogen bonded with the Co(II)probe was viewed from different angles.

The binding energy however is very small. It was calculated as 0.0067 hartree = 0.1823 eV = 4.208 kcal/mol

Bond	Distance	Bond	Distance	Bond	Distance
	(Å)		(Å)		(Å)
Co1-O1	1.96707	Co1-O1W	2.16029	Co1-O2W	2.00169
Co1-O3	2.26303	Co1-N2	1.96454	Co1-N3	1.98313
O1-C7	1.28794	O2-C7	1.23993	O3-C6	1.28672
O4-C6	1.23957	N1-C12	1.39296	N1-C17	1.39361
N2-C12	1.34357	N2-C16	1.35267	N3-C8	1.35273
N3-C17	1.34354	C1-C2	1.53217	C2-C3	1.53471
C3-C4	1.53747	C4-C5	1.53443	C5-C6	1.55650
C5-C7	1.53481	C8-C9	1.37987	C9-C10	1.40017
C10-C11	1.38152	C11-C17	1.40403	C12-C13	1.40454
C13-C14	1.38132	C14-C15	1.40048	C15-C16	1.37893
O1W-H1W	0.95864	O1W-H2W	0.98666	O2W-H3W	0.97065
O2W-H4W	0.96311	N1-H1	1.01078	C1-H1A	1.09388
C1-H1B	1.09490	C1-H1C	1.09481	C2-H2A	1.09655
C2-H2B	1.09708	C3-H3A	1.09380	C3-H3B	1.09714
C4-H4A	1.09298	C4-H4B	1.09322	C5-H5	1.09626
C8-H8	1.08084	C9-H9	1.08217	C10-H10	1.08375
C11-H11	1.08296	C13-H13	1.08321	C14-H14	1.08359
C15-H15	1.08195	C16-H16	1.08457	As1-OAs1	1.80172
As1-OAs2	1.80411	As1-OAs3	1.81322	As2-OAs1	1.94547
As2-OAs2	1.77243	As2-OAs3	1.82742		
Some hydrogen bonds					
O5H-O3	1.74805	O6H-O4	1.75244	O8H-O1	1.76836
O9H-O2	1.81120				

Table S11 Some selected the bond lengths found in theoretical analysis

Table S12 Some selected the bond angles found in theoretical analysis

O1-Co1-O1W	83.475	O1-Co1-O2W	83.114	O1-Co1-O3	84.131
O1-Co1-N2	173.973	O1-Co1-N3	95.200	O1W-Co1-O2W	93.029
O1W-Co1-O3	165.469	O1W-Co1-N2	97.221	O1W-Co1-N3	87.507
O2W-Co1-O3	77.963	O2W-Co1-N2	90.868	O2W-Co1-N3	178.157
O3-Co1-N2	94.324	O3-Co1-N3	101.156	N2-Co1-N3	90.814
Co1-O1-C7	134.067	Co1-O3-C6	125.351	Co1-N2-C12	121.821
Co1-N2-C16	118.882	Co1-N3-C8	119.616	Co1-N3-C17	121.422
O5-As1-O6	97.958	O5-As1-O7	93.242	06-As1-07	96.268
08-As2-09	91.707	O8-As2-O10	129.902	O9-As2-O10	85.716

Here for example O5H means the hydrogen that is connected to O5 (and is part of a H bond between O5 and O3). Similarly, for other atoms.



The frontier MOs of the Co(II)-probe with two attached $As(OH)_3$ are presented below.

SOMO

SOMO-1 (HOMO)



HOMO-1

HOMO-2





LUMO+2

LUMO+3

Fig. S30 The frontier MOs of the Co(II)-probe with two attached As(OH)₃. Comparing with the MOs of the Co(II)-probe alone, it is seen that the MOs appear to be similar, with minor variation in electron density for the frontier orbitals. This may mean that the there is little charge transfer between the two As(OH)₃ units and the Co(II)-probe. In fact, that happens to be the case. Mulliken population analysis reveals that the two As(OH)₃ units take away about 0.224 units of charge. In other words, the two As(OH)₃ units are very loosely bound to the Co(II)-probe, as per the binding energy estimation given above (about 4 kcal/mole).

Studies with Living systems: Intracellular tracking of As(III) in bacterial systems

Arsenic resistant bacteria *Bacillus aryabhattai* NCBI GenBank accession number KY098771 and arsenic non-resistant bacteria *Bacillus subtilis* were used for the study. Arsenic resistant *Bacillus sp.* was grown in nutrient broth medium containing 50 mM As(III) solution. Non arsenic resistant *Bacillus sp.* was grown in nutrient broth medium without any arsenic stress. Both the cultures were incubated at 37 °C overnight. Both the bacteria were isolated from the medium by centrifugation at 6000 rpm for 5 min and washed thrice with normal saline water for removal of growth medium. Arsenic non-resistant *Bacillus sp.* was incubated in 50 mM As(III) solution for 30 min and then washed thrice with normal saline water. Both the bacterial strains were incubated in 10^{-4} M Co(II)-probe solution for 10 min. Then the bacterial samples with probe solution were dropped cast in a glass slide and covered with a coverslip and observed under Fluorescence microscope (EVOS FL Auto Invitrogen) in DAPI filter. Bacterial cells, treated with As(III)-solution, without the Co(II)-probe were used as the control.

Detection of arsenic was carried out using Co(II)-probe on both arsenic-resistant bacteria (Bacillus aryabhattai) and arsenic non-resistant bacteria (Bacillus subtilis). For control samples both the bacterial strains were treated without the Co(II)-probe. Under fluorescence microscope using DAPI filter both the bacterial strains containing Co(II)-probe appeared blue. This infers that As(III) gets internalize into bacterial cells and probe successfully binds with the arsenic inside the cell. Control samples without the Co(II)-probe were not visible under DAPI filter, thereby images were taken under phase contrast microscopy. Both fluorescence microscopy and phase contrast microscopy revealed that the arsenic-resistant bacteria (Bacillus aryabhattai), isolated in the laboratory of Dr. Sarkar, were able to resist the arsenic stress by internalization and were intact and live even when treated with the Co(II)probe as observed under DAPI filter. Whereas, arsenic non-resistant Bacillus subtilis was distorted when incubated in 50 mM As(III) for 30 mins, as they couldn't withhold the arsenic stress. Still Arsenic(III) was incorporated into the distorted cells of Bacillus subtilis and Co(II)-probe was able to detect the presence of arsenic in those cells, and therefore, blue clumps were observed. The Co(II)-probe successfully able to cross the cell membrane and detect the presence of arsenic intracellularly for both the strains. Detailed description and observation of the study were listed in Table S13.

Bacterial type	Growth conditions	Incubation conditions with As(III)	Incubation conditions with a probe	Observation under microscope
Arsenic resistant <i>Bacillus sp.</i>	Nutrient broth with 50 mM As(III) at 37 °C overnight	Only washed with normal saline water	Not given	Not visible under Fluorescence microscope. Under Phase contrast microscope intact bacteria was observed. Control 1(Fig. 5a)
Arsenic resistant <i>Bacillus sp.</i>	Nutrient broth with 50 mM As(III) at 37 °C overnight	Only washed with normal saline water	10 ⁻⁴ M probe for 10 min	Intact blue fluorescent bacteria visible under DAPI filter of Fluorescence microscope. Sample1 (Fig. 5b)
Non-arsenic resistant <i>Bacillus sp.</i>	Nutrient broth without As(III) at 37 °C overnight	50 mM As(III) for 30 min at 37 °C; then washed with normal saline water	Not given	Not visible under Fluorescence microscope. Under Phase contrast microscope distorted bacteria was observed due to arsenic stress. Control 2 (Fig. 5c)
Non-arsenic resistant <i>Bacillus sp.</i>	Nutrient broth without As(III) at 37 °C overnight	50 mM As(III) for 30 min at 37 °C; then washed with normal saline water	10 ⁻⁴ M probe for 10 min	Blue fluorescent bacterial clumps were visible under DAPI filter of Fluorescence microscope. Sample 2(Fig. 5d)

Table S13. Observation under the microscope with	ith a detailed description
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Cell viability assay by MTT

The percentage viability of HeLa cells was evaluated by MTT assay²⁸ after being exposed to Co(II)-probe and As(III) for 24 h. One set of HeLa cells (1×10^4 cells/well) were seeded in 96-well plate and treated with different concentration of Co(II)-probe (0, 10^{-2} , 10^{-8} , 10^{-10} , 10^{-12} and 10^{-15} M) and other set with combination of As(III) (10^{-2} M) and Co(II)-probe (0, 10^{-2} , 10^{-8} , 10^{-10} , 10^{-12} and 10^{-15} M) for 24 h. Another set of cells were also incubated with As(III) at a concentration of 10^{-2} M only for 24 h. MTT solution was then added to each well and incubated for the next 4 h. The intracellular formazan crystals formed were solubilized with dimethyl sulfoxide (DMSO) and the absorbance of the solution was measured at 595 nm by using a microplate reader (Thermo scientific, Multiskan ELISA, USA). Samples were placed in triplicate for each set of experiment. The cell viability ratio was calculated by the following formula:



(Mean experimental absorbance / Mean control absorbance) \times 100 %.

Fig. S31 Cell viability graph of HeLa cells when treated with Co(II)-probe and As(III) for 24h.

Cell viability experiment was performed to evaluate the cytotoxic potency of As(III), Co(II)probe and As(III) collectively with Co(II)-probe on HeLa cells. Data revealed that there were no significant changes occurred in percentage of surviving HeLa cells when treated with Co(II)-probe at 1.00E-15 M concentration (Fig. S31a) but had a gradual cytotoxic effect on HeLa cells when treated with a combination of Co(II)-probe and As(III) solution (Fig. S31b) as compared to that of the untreated control set of cells. The Co(II)-probe was found to be nontoxic on HeLa cells survivability and almost 100% cells were found viable when incubated with 10⁻¹⁵ M concentration.



Fig. S32 Cell viability graph showing the survival of HeLa cells when treated with As(III) at a concentration of 10^{-2} M for 24 hrs.

Fig. S30 demonstrated the viability of HeLa cells when treated with As(III) at the concentration of 10^{-2} M for 24 h. Only 11% cells were found viable, while at the same concentration of Co(II)-probe ([Co(II)-probe] = 10^{-15} M) in combination with As(III) at concentration (10^{-2} M) showed only about 25% of viability due to As(III) which plays important role to impart toxicity to the cells when incubated with Co(II)-probe. MTT data (Table S14) express the biocompatibility and non toxic behavior of Co(II)-probe which could effortlessly use for As(III)-sensing within living system such as cell lines.

	Cell Viability (%)		
Probe - Concentration	Co(II)-Probe	Co(II)-Probe+ As(III)*	
Control	100	100	
1.00E-15 M	100	24.69415	
1.00E-12 M	58.58632	23.65202	
1.00E-10 M	34.32261	22.97236	
1.00E-8 M	28.6135	17.78432	

Table S14. Showing the percentage of viable cells evaluated by MTT assay on HeLa cells

* As(OH)₃ has been used at the concentration of 1.00E-2 M (10⁻² M)

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