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Supplementary

## A hydrazine-based thiocarbamide probe for colorimetric and turn-on

## fluoremetric detection of $PO_4^{3-}$ and $AsO_3^{3-}$ in semi-aqueous medium

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Scheme S1 Synthesis of HTP



Fig S1. FT-IR spectrum of HTP.



Fig S2. <sup>1</sup>H NMR of HTP in DMSO- $d_6$ 



Fig S3 ESI-MS spectrum of HTP



Fig. S4. 2D supramolecular structure of HTP

Table S1 interactions in HTP

D-H···A	D-H	H···A (Å)	D····A (Å)	<d-< th=""><th>Symmetry</th></d-<>	Symmetry
	(Å)			H···A	
	(11)			(°)	
N4-H4S2	0.859	2.726	3.513	152.88	1.5-x,-
					1/2+y,1/2-z
N2-H2··· S1	0.861	2.586	3.416	162.17	1-x,3-y,1-z
C8-H8S2	0.930	2.933	3.700	140.74	1.5-x,-
					1/2+y,1/2-z
С9-Н9S1	0.932	2.879	3.721	151.07	1-x,3-y,1-z
H1-O1N1	0.821	1.969	2.690	146.13	



Fig. S5(a). Jobs plot for addition of  $AsO_3^{3-}$  with HTP in solution



Fig. S5(b). Jobs plot for addition of  $PO_4^{3-}$  with HTP in solution

## Determination of binding constant

The binding constant value of arsenite and phosphate with **HTP** has been determined from the emission intensity data following the modified Benesi–Hildebrand equation,  $1/\Delta F = 1/\Delta F_{max}$  + $(1/K[C])(1/\Delta F_{max})$ . Here  $\Delta F = F - F_{min}$  and  $\Delta F$  max =  $F_{max} - F_{min}$ , where  $F_{min}$ , F, and  $F_{max}$  are the emission intensities of **HTP** considered in the absence of anions, at an intermediate anions concentration, and at a concentration of complete saturation where K is the binding constant and [C] is the anions concentration respectively. In this report we represent  $F_{min}$  as  $F_0$ . From the plot

of  $(F_{max}-F_0)/(F-F_0)$  against  $[C]^{-1}$  for anions, the value of K has been determined from the slope. The association constant (K<sub>d</sub>) as determined by fluorescence titration method for HTP with PO<sub>4</sub><sup>3-</sup> is found to be  $5.2 \times 10^4 \text{ M}^{-1}$  (error < 10%) and for HTP with AsO3<sup>3-</sup> is found to be  $1.0 \times 10^5 \text{ M}^{-1}$  (error<10%)



Fig S6(a) Benesi–Hildebrandplot for addition of AsO<sub>3</sub><sup>3-</sup> with HTP



Fig S6(b) Benesi-Hildebrand plot for addition of PO<sub>4</sub><sup>3-</sup> with HTP

## **Determination of detection limit:**

The detection limit was calculated based on the fluorescence titration. To determine the S/N ratio, the emission intensity of HTP without any analyte was measured by 10 times and the standard deviation of blank measurements was found to be 0.206

The limit of detection (LOD) of HTP for  $PO_4^{3-}$  and  $AsO_3^{3-}$  was determined from the following equation:  $LOD = K \times \sigma$  Where K = 3 in this case and  $\sigma = (Sb_1)/(S)$ ;  $Sb_1$  is the standard deviation of the blank solution; S is the slope of the calibration curve.

For AsO<sub>3</sub><sup>3-</sup>, From the graph we get slope =  $3.9547 \times 10^7$ , and Sb<sub>1</sub>value is 412.948 (**Fig. S7**). Thus using the formula we get the LOD =  $5 \times 10^{-9}$  M.

For PO<sub>4</sub><sup>3-</sup>, From the graph we get slope =  $1.8122 \times 10^7$ , and Sb<sub>1</sub>value is 412.948 (**Fig. S8**). Thus using the formula we get the LOD =  $34 \times 10^{-9}$  M.



Fig. S7(a) LOD plot for Arsenite



Fig S7(b) LOD plot for phosphate



**Fig S8(a)** Interference study of probe HTP with phosphate ion in the presence of foregin metal ion



**Fig S8(b)** Interference study of probe HTP with arsenite ion in the presence of foregin metal ion



Fig. S9. Effect of pH on fluorescence intensity of receptor HTP, HTP-PO<sub>4</sub><sup>3-</sup> and HTP-AsO<sub>3</sub><sup>3-</sup>



Fig. S10(a) Decay profile of HTP and HTP-AsO<sub>3</sub><sup>3-</sup>



Fig. S10(b) Decay profile of HTP and HTP-  $PO_4^{3-}$ 



**Fig S11.** <sup>1</sup>H NMR of **HTP**-AsO<sub>3</sub><sup>3-</sup> in DMSO-d<sub>6</sub>



**Fig S12.**<sup>1</sup>H NMR of HTP-PO<sub>4</sub><sup>3-</sup> in DMSO-d<sub>6</sub>



Fig S13(a) ESI-MS spectrum of HTP-AsO3<sup>3-</sup>



Fig S13(b) ESI-MS spectrum of HTP-PO4<sup>3-</sup>

Table S2 Frontier molecular orbitals contributions of HTP

MO	Paracresoldiformyl	thiohydrazide
LUMO+10	48	52
LUMO+9	48	52
LUMO+8	12	88
LUMO+7	58	42
LUMO+6	62	38
LUMO+5	14	86
LUMO+4	33	67
LUMO+3	7	93
LUMO+2	17	83
LUMO+1	55	45
LUMO	62	38

НОМО	5	95
HOMO-1	58	42
HOMO-2	1	99
HOMO-3	29	71
HOMO-4	21	79
HOMO-5	20	80
HOMO-6	46	54
HOMO-7	26	74
HOMO-8	51	49
HOMO-9	39	61
HOMO-10	76	24

Table S3 Frontier molecular orbitals contributions of HTP-Phosphate

MO	phosphate	Paracresoldiformyl	thiohydrazide
LUMO+10	0	32	67
LUMO+9	0	61	39
LUMO+8	0	16	83
LUMO+7	0	36	64
LUMO+6	0	99	1
LUMO+5	0	57	43
LUMO+4	0	58	41
LUMO+3	1	7	93
LUMO+2	0	77	23
LUMO+1	0	58	41
LUMO	0	65	55
HOMO	94	1	5
HOMO-1	7	67	26
HOMO-2	91	5	4
HOMO-3	83	1	17
HOMO-4	12	2	86
HOMO-5	5	30	66
HOMO-6	4	23	87
HOMO-7	8	4	69
HOMO-8	87	2	9
HOMO-9	70	54	28
HOMO-10	3	14	43

Table S4 Frontier molecular orbitals contributions of HTP-Arsenite

MO	phosphate	Paracresoldiformyl	thiohydrazide

LUMO+10	13	7	79
LUMO+9	35	1	64
LUMO+8	10	84	6
LUMO+7	63	13	24
LUMO+6	2	1	97
LUMO+5	0	30	70
LUMO+4	0	100	0
LUMO+3	0	39	60
LUMO+2	0	62	38
LUMO+1	0	57	43
LUMO	0	64	36
HOMO	0	54	46
HOMO-1	3	8	90
HOMO-2	92	2	6
HOMO-3	0	11	89
HOMO-4	0	41	59
HOMO-5	2	5	93
HOMO-6	69	2	30
HOMO-7	5	26	70
HOMO-8	24	26	50
HOMO-9	1	48	51
HOMO-10	4	19	76



Fig. S14: Calibration plot between emission intensity of the probe HTP at 560 nm vs phosphate ion for the quantitative analysis of phosphate ion in water.



Fig. S15: Calibration plot between emission intensity of the probe HTP at 560 nm vs arsenite ion for the quantitative analysis of arsenite ion in water.