Electronic Supplementary Material (ESI) for Analytical Methods.
This journal is © The Royal Society of Chemistry 2019

Efficient "Ratiometric" fluorescence chemosensor for selective detection of Hg^{2+} ions based on phosphonates: its live cell imaging and molecular keypad lock applications

Gujuluva Gangatharan Vinoth Kumar[1], Ramaraj Sayee Kannan[2], Thomas Chung-Kuang Yang[4*], Jegathalaprathaban Rajesh[1*], Gandhi Sivaraman[3*]

[1]Chemistry Research Centre, Mohamed Sathak Engineering College, Kilakarai-623 806, Tamil Nadu, India.

[2]Department of chemistry, Thiagarajar College, Madurai-625 009, Tamilnadu, India.

[3] Department of Chemistry, Gandhigram rural institute- Deemed to be university, Gandhigram, Dindigul- 641 602, Tamilnadu, India.

[4] Department of Chemical Engineering and Biotechnology, National Taipei University of Technology, 1 Section 3, Zhong-Xiao East Road, Taipei 10608, Taiwan (ROC).

Supporting information

Supplementary Figures

Fig. S1. (a) ^{1}H NMR spectrum of synthesized sensor **L1**. (b) ^{13}C NMR spectrum of sensor **L1**. (c) ESI-MS spectra of the synthesized sensor **L1**.

Fig. S2. (a) ^{1}H NMR spectrum of synthesized sensor **L2**. (b) ^{13}C NMR spectrum of synthesized sensor **L2**.

Fig. S3. (a) & (b) Colorimetric detection of sensors **L1** and **L2** (30 μM) with 2 equiv. of different metal ions. Sensors, Hg^{2+}, Ni^{2+}, Cu^{2+}, Co^{2+}, Zn^{2+}, Fe^{2+}, and Mn^{2+} (Top left to right), Mg^{2+}, Pb^{2+}, Ag^{+}, Na^{+}, Ca^{2+}, Ba^{2+}, K^{+}, Cd^{2+} and Li^{+} (Bottom left to right).

Fig. S4. (a) Determination of association constant values of Hg^{2+} with **L1** by using Benesi-Hildebrand (B-H) plot analysis from absorption titration (at 434 nm wavelength). (b) Determination of association constant values of Hg^{2+} with **L2** by using B-H plot analysis from absorption titration (at 424 nm wavelength).

Fig. S5. (a) Absorption spectra of the calibration curve of Hg^{2+} with **L1**. (b) Absorption spectra of the calibration curve of Hg^{2+} with **L2**.

Fig. S6. ESI-MS spectra of **L1** with addition of 1 equiv.of Hg^{2+} ion.

Fig. S7. (a) Determination of association constant values of Hg^{2+} with **L1** by using Benesi-Hildebrand (B-H) plot analysis from fluorescence titration (Intensity measured at 520 nm). (b) Determination of association constant values of Hg^{2+} with **L2** by using B-H plot analysis from fluorescence titration (Intensity measured at 545 nm).

Fig. S8. (a) Fluorescence spectra of the calibration curve of Hg^{2+} with **L1**. (b) Fluorescence spectra of the calibration curve of Hg^{2+} with **L2**.

Fig. S9. (a) FTIR spectra of **L1** and **L1** + Hg^{2+} ion. (b) FTIR spectra of **L2** and **L2** + Hg^{2+} ion.

Fig. S10. (a) Sensing results for the colorimetric response of **L1** with Hg^{2+} in tap water, river water and bottled water. (b) Sensing results for the colorimetric response of **L2** with Hg^{2+} in tap water, river water and bottled water.

Fig. S11. (a) & (b) Photograph of the test kits with **L1** and **L2** for sensing Hg^{2+} ion in aqueous solution. (i) Different concentration of Hg^{2+} ion. 0, 1×10^{-3} M and 1×10^{-4} M (From left to right). (ii) Sensing other metal ions (1×10^{-4} M). Sensors, Hg^{2+}, Cu^{2+}, Co^{2+}, Zn^{2+}, Fe^{2+}, Mn^{2+}, Mg^{2+}, Pb^{2+}, Ag^{+}, Na^{+}, Ca^{2+}, Ba^{2+}, K^{+}, Cd^{2+} and Li^{+} (From left to right).

Fig. S12. (a) Color changes of **L1** in the solid state upon addition of aqueous solution of Hg^{2+}. **L1**, **L1**+0.0001 M Hg^{2+}, **L1**+0.001 M Hg^{2+} and **L1**+0.01 M Hg^{2+} (From left to right). (b) Color changes of **L2** in the solid state upon addition of aqueous solution of Hg^{2+}. **L2**, **L2**+0.0001 M Hg^{2+}, **L2**+0.001 M Hg^{2+} and **L2**+0.01 M Hg^{2+} (From left to right).

Supplementary Tables

Table S1. Detection limits of present work to compare with other reported values.

Table S2. Determination of Hg^{2+} ion in real samples.

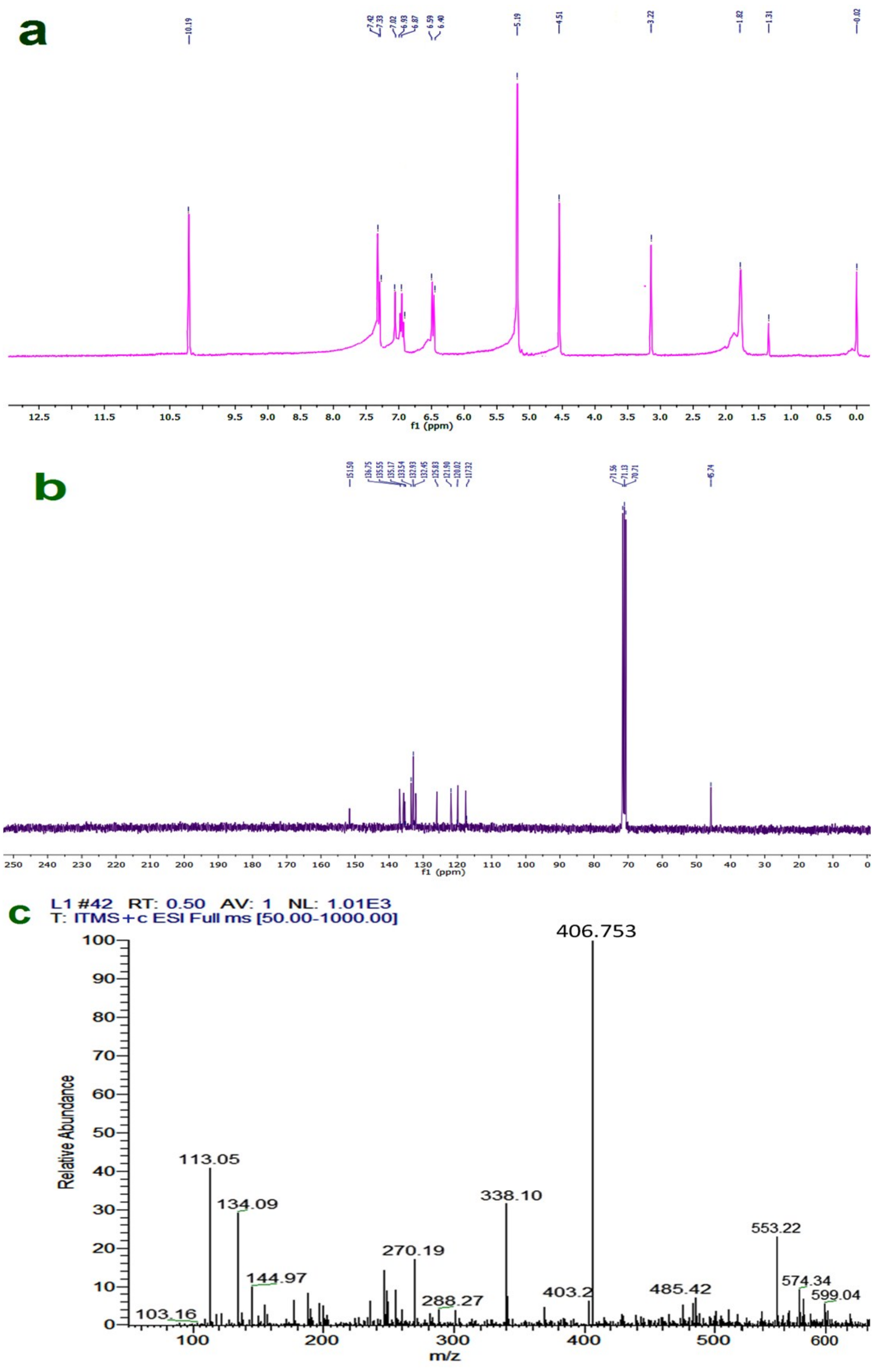
a
10.19
7.42
7.33
7.02
6.93
6.87
6.59
6.40
5.19
4.51
3.22
1.82
1.31
0.02
f1 (ppm)
b
151.50
136.75
135.55
135.17
133.54
132.93
132.45
125.83
121.90
120.02
117.32
71.56
71.13
70.71
f1 (ppm)
c
L1 #42 RT: 0.50 AV: 1 NL: 1.01E3
T: ITMS+c ESI Full ms [50.00-1000.00]
406.753
113.05
134.09
338.10
553.22
270.19
144.97
574.34
599.04
485.42
403.2
288.27
103.16
Relative Abundance
m/z

Fig. S1.

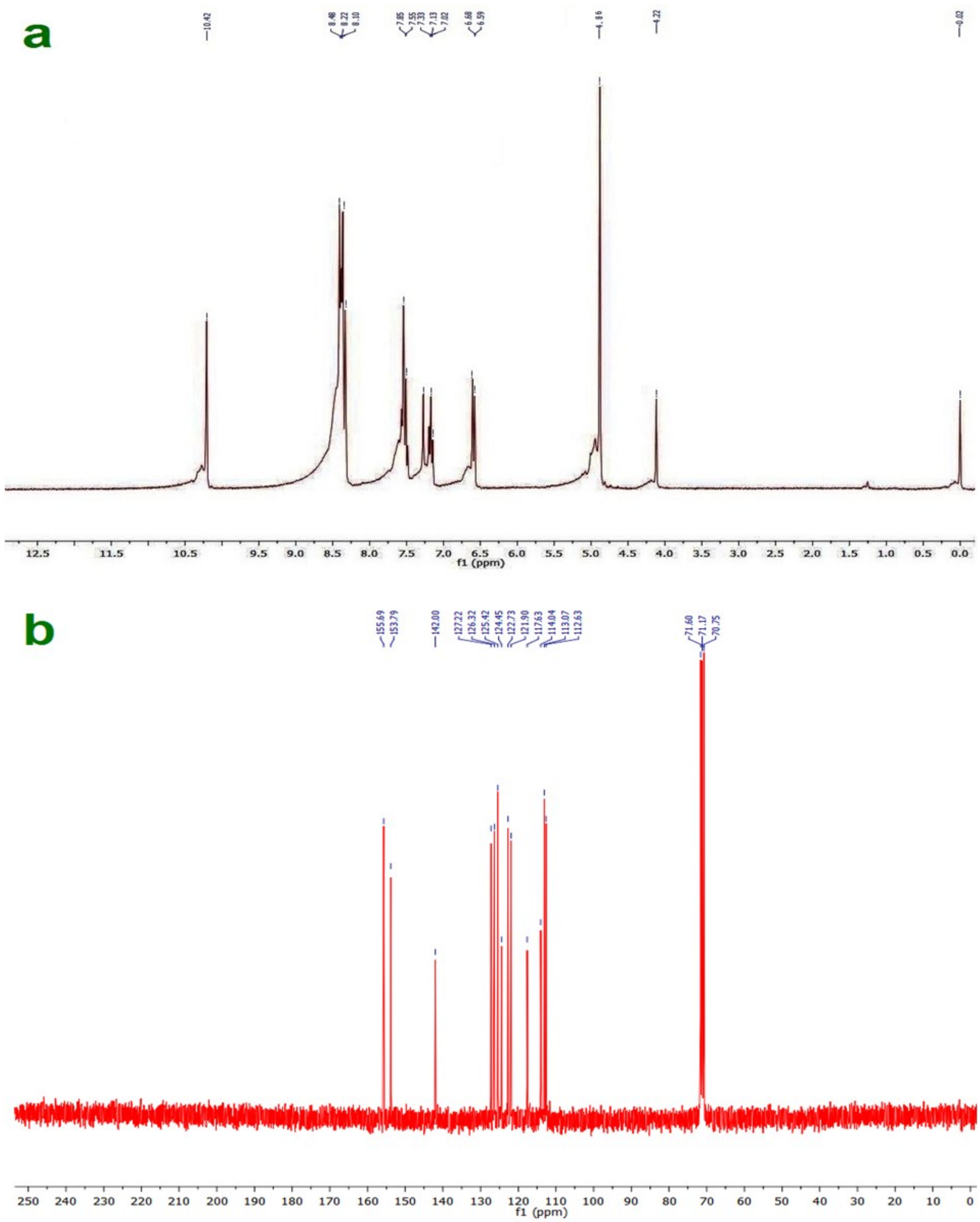
a
10.42
8.48
8.22
8.10
7.85
7.55
7.33
7.13
7.02
6.68
6.59
4.86
4.22
0.02
12.5 11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
b
155.69
153.79
142.00
127.22
126.32
125.42
124.45
122.73
121.90
117.63
114.04
113.07
112.63
71.60
71.17
70.75
250 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

Fig. S2.

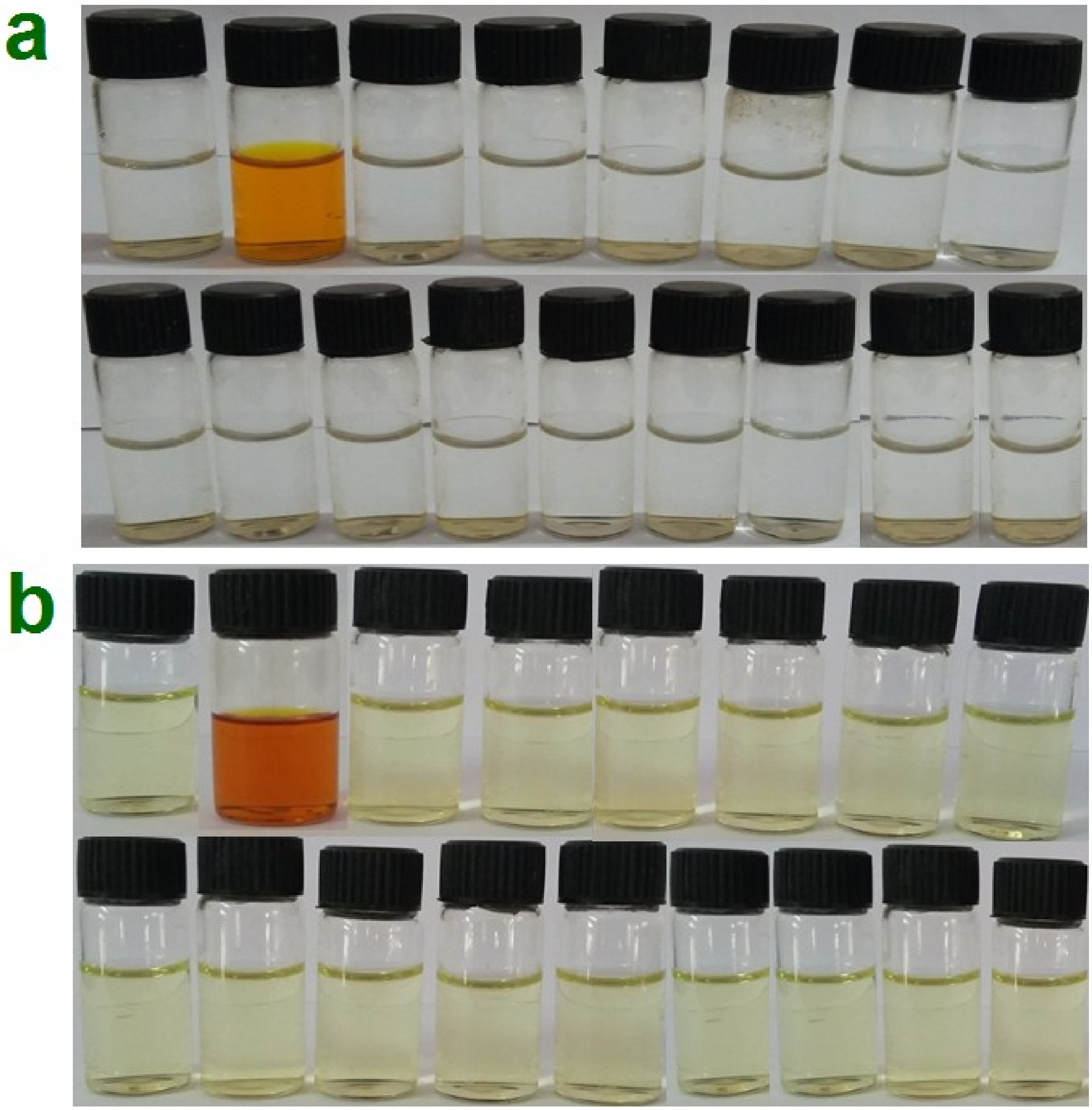

Fig. S3.

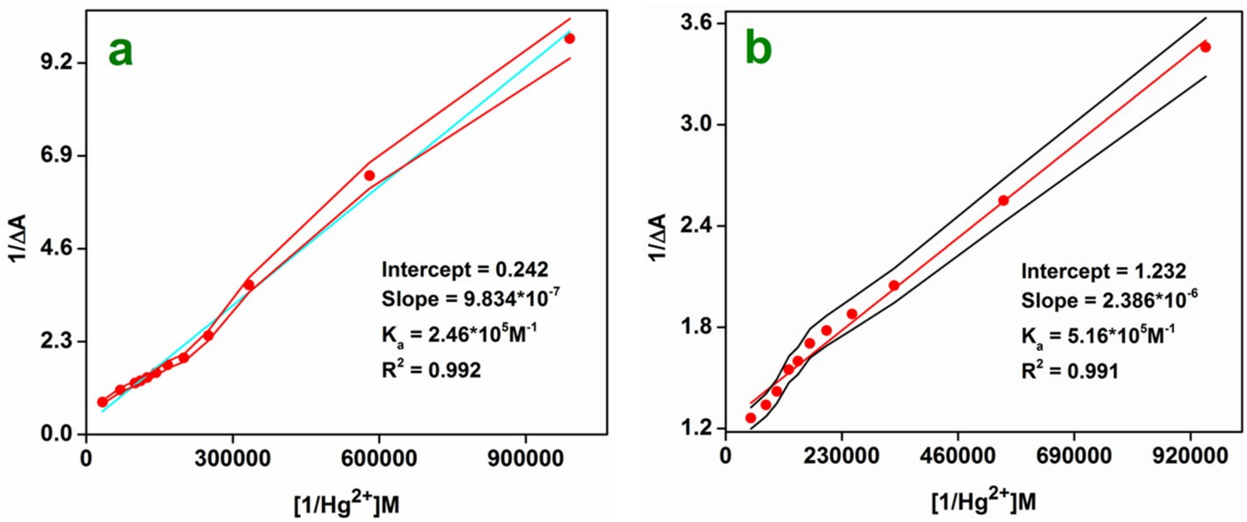
a
Intercept = 0.242
Slope = 9.834*10-7
Ka = 2.46*105M-1
R2 = 0.992
1/ΔA
[1/Hg2+]M
b
Intercept = 1.232
Slope = 2.386*10-6
Ka = 5.16*105M-1
R2 = 0.991
1/ΔA
[1/Hg2+]M

Fig. S4.

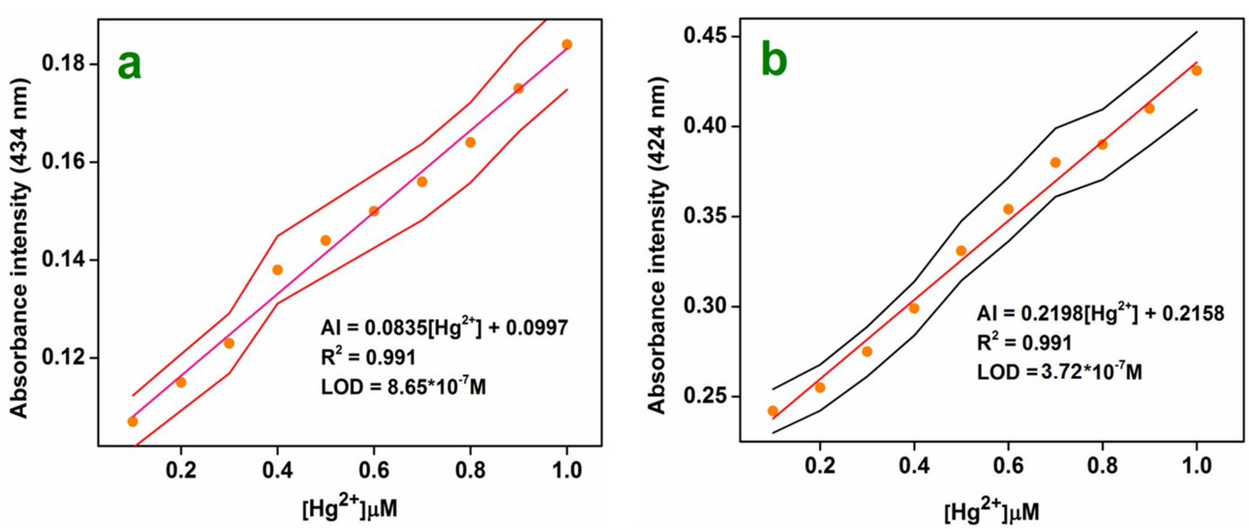
a
AI = 0.0835[Hg2+] + 0.0997
R2 = 0.991
LOD = 8.65*10-7M
Absorbance intensity (434 nm)
[Hg2+]μM
b
AI = 0.2198[Hg2+] + 0.2158
R2 = 0.991
LOD = 3.72*10-7M
Absorbance intensity (424 nm)
[Hg2+]μM

Fig. S5.

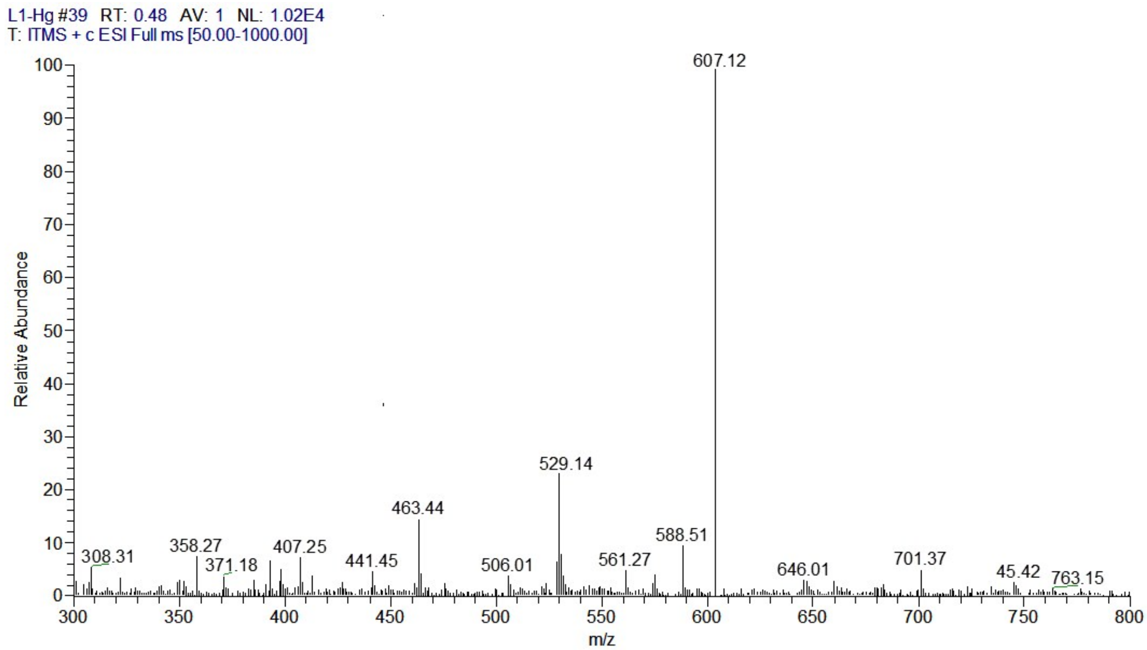
L1-Hg #39 RT: 0.48 AV: 1 NL: 1.02E4
T: ITMS + c ESI Full ms [50.00-1000.00]
607.12
529.14
463.44
588.51
308.31
358.27
371.18
407.25
441.45
506.01
561.27
646.01
701.37
45.42
763.15
Relative Abundance
m/z

Fig. S6.

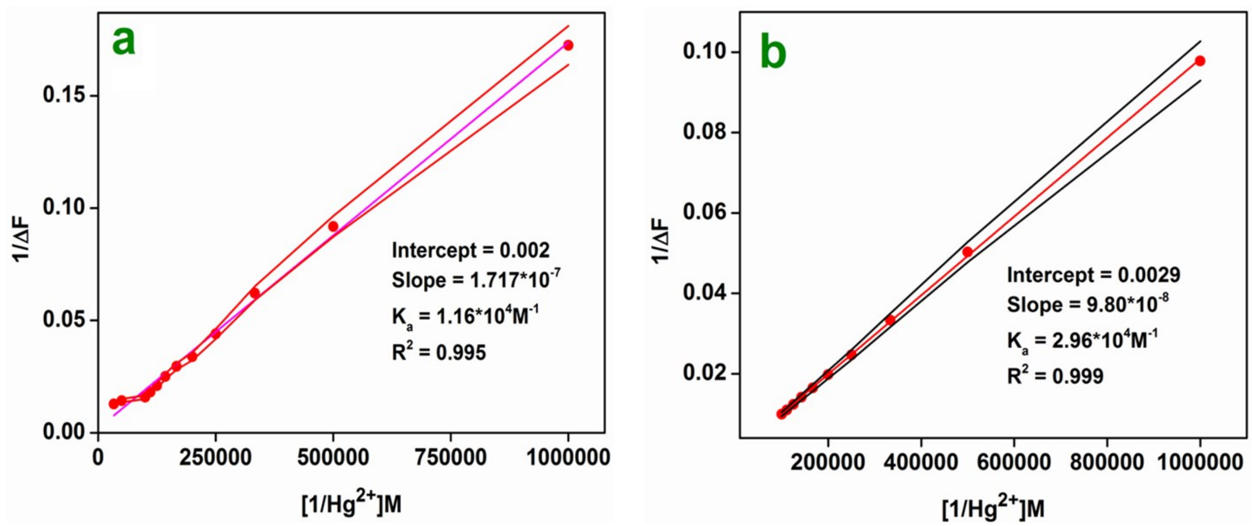
a
Intercept = 0.002
Slope = 1.717*10-7
Ka = 1.16*104M-1
R2 = 0.995
1/ΔF
[1/Hg2+]M
b
Intercept = 0.0029
Slope = 9.80*10-8
Ka = 2.96*104M-1
R2 = 0.999
1/ΔF
[1/Hg2+]M

Fig. S7.

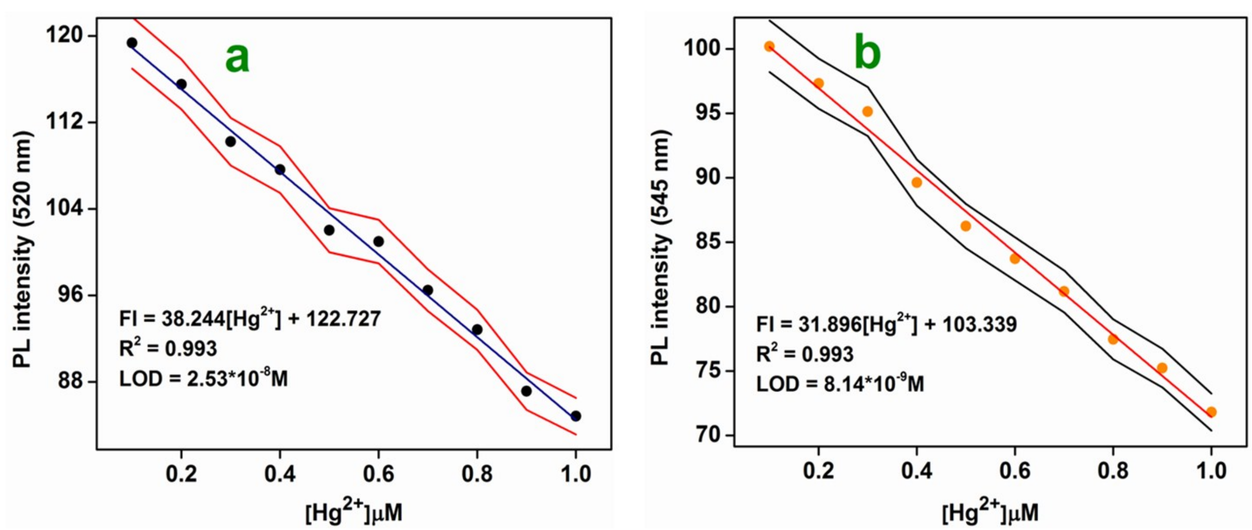
a
FI = 38.244[Hg2+] + 122.727
R2 = 0.993
LOD = 2.53*10-8M
PL intensity (520 nm)
[Hg2+]μM
b
FI = 31.896[Hg2+] + 103.339
R2 = 0.993
LOD = 8.14*10-9M
PL intensity (545 nm)
[Hg2+]μM

Fig. S8.

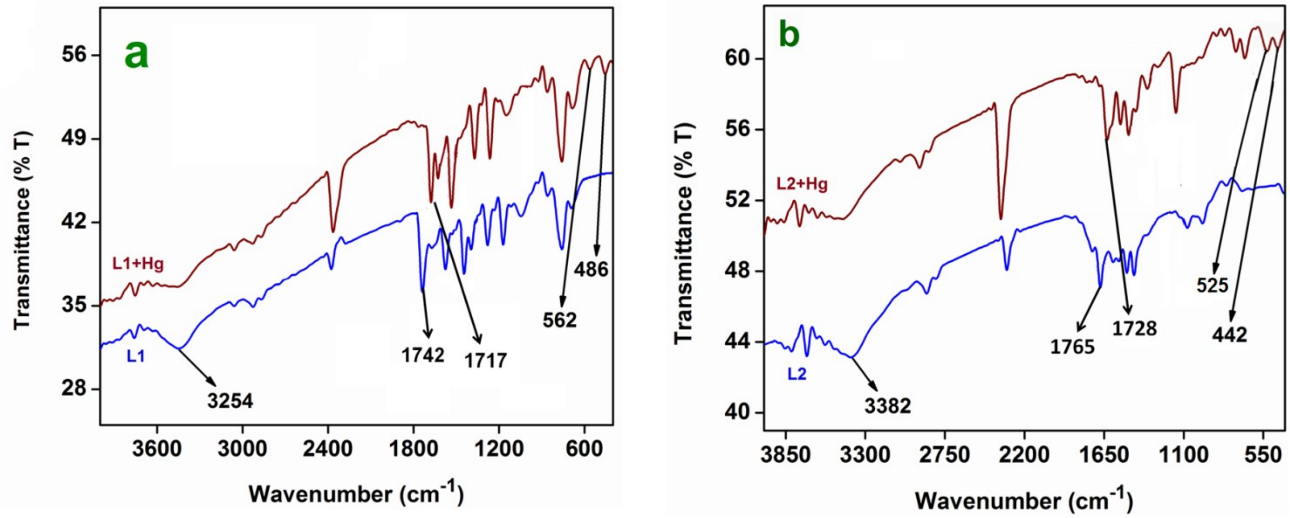

Fig. S9.

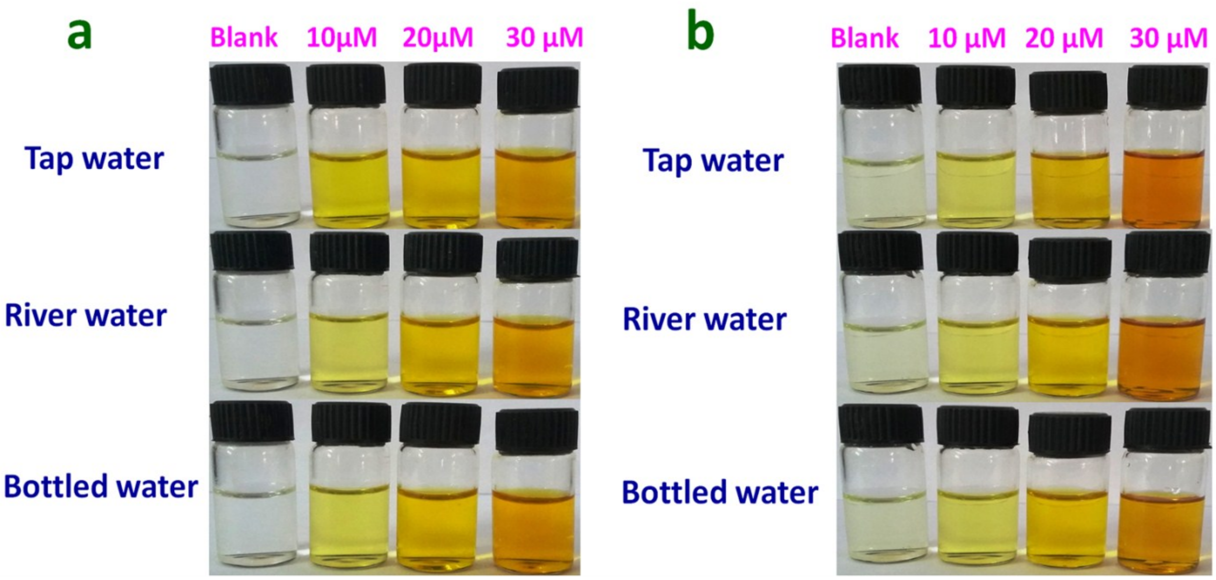

Fig. S10.

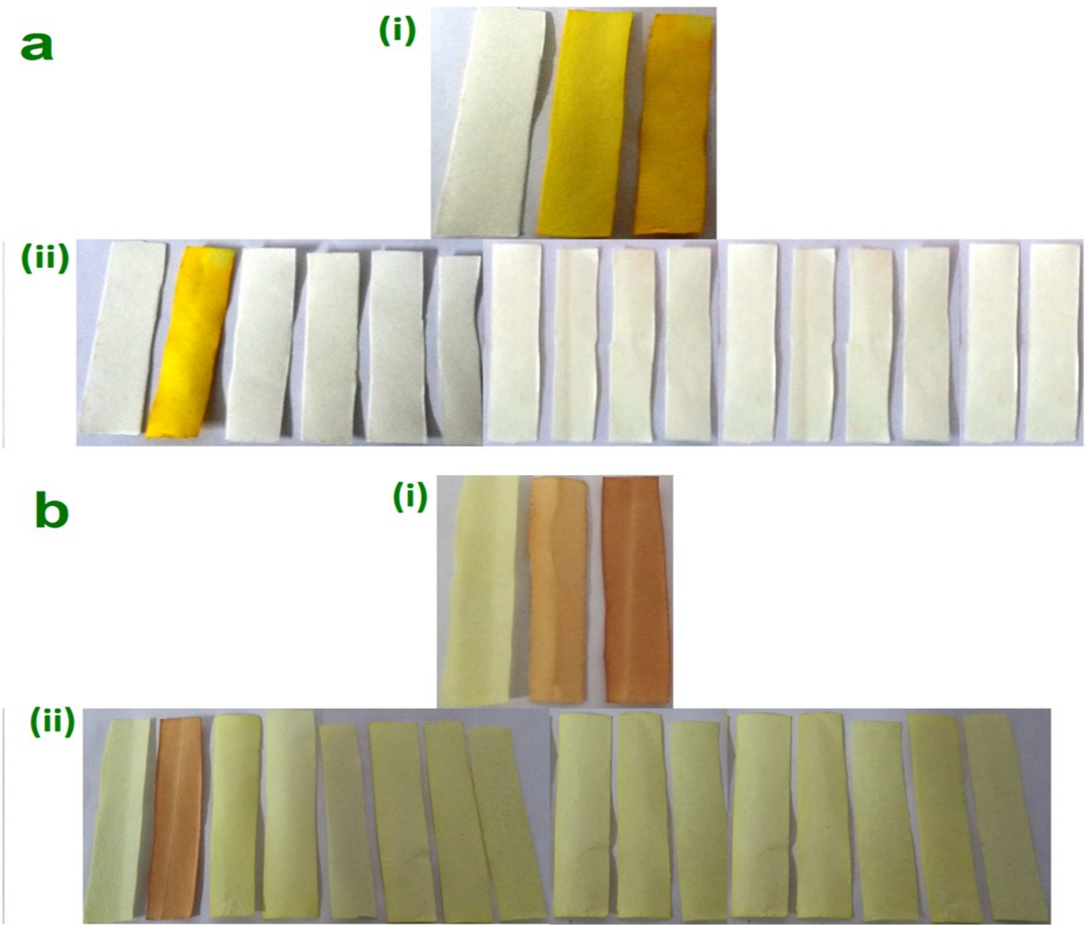

Fig. S11.

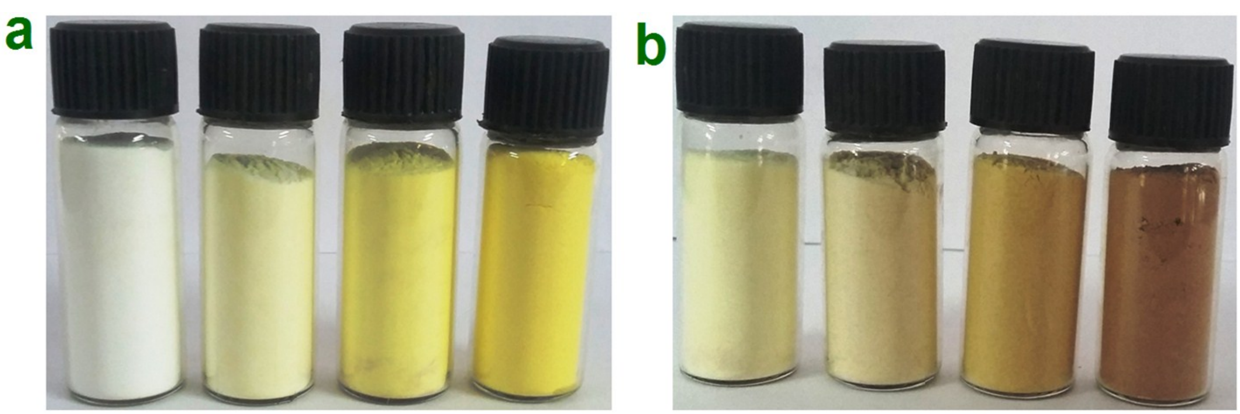

Fig. S12.

Table S1

Chemosensors	Selectivity	Method	Solvent system	Detection limit	References
Calix[4]arenediazacrown ether based	Hg^{2+}	Colorimetric	Water/MES	1×10^{-5}	[33]
Azobenzene based	Hg^{2+}	Colorimetric and Fluorescent	$DMSO/H_2O$	0.5×10^{-6}	[34]
Schiff base	Hg^{2+}	Fluorescence	DMF/H_2O	1.5×10^{-5}	[35]
DCF-Coumarin based	Hg^{2+}	Fluorescence	$DMSO/H_2O$	4.3×10^{-6}	[36]
Benzothiadiazole based	Hg^{2+}	Fluorescence	CH_3CN/H_2O	1.6×10^{-7} & 5×10^{-7}	[37]
BODIPY based	Hg^{2+}	Fluorescence	HEPES	7.7×10^{-8}	[38]
Benzimidazole and Coumarin based	Hg^{2+}	Fluorescence	HEPES/DMSO	7.0×10^{-8}	[39]
α-aminophosphonate based	Hg^{2+}	Fluorescence	$MeOH/H_2O$	2.53×10^{-8} & 8.14×10^{-9}	Present work

Table S2

Sensor	**Sample**	**Hg^{2+} spiked (μM)**	**Found Hg^{2+} mean[a] ± SD[b] (μM)**	**Recovery (%)**
	Tap water 1	10	9.6 ± 0.08	96
	Tap water 2	20	17.95 ± 0.05	89.8
	Tap water 3	30	31.7 ± 0.1	105.7
	River water 1	10	8.95 ± 0.06	89.5
L1	River water 2	20	19.5 ± 0.12	97.5
	River water 3	30	28.15 ± 0.15	93.8
	Bottled water 1	10	9.2 ± 0.08	92
	Bottled water 2	20	18.25 ± 0.12	91.25
	Bottled water 3	30	28.5 ± 0.13	95
	Tap water 1	10	7.18 ± 0.16	71.8
	Tap water 2	20	17.2 ± 0.09	86
	Tap water 3	30	27.68 ± 0.1	92.23
	River water 1	10	9.53 ± 0.14	95.3
L2	River water 2	20	20.48 ± 0.8	102.4
	River water 3	30	28.35 ± 0.06	94.5
	Bottled water 1	10	9.4 ± 0.11	94
	Bottled water 2	20	21.5 ± 0.20	107.5
	Bottled water 3	30	30.57 ± 0.15	101.9

[a]mean of three determination. [b]SD, standard deviation.