Supporting Information

Dual Chemosensor for the Rapid Detection of Mercury (II) Pollution and Biothiols

Mahnaz D.Gholami[a], Sergei Manzhos[b], Prashant Sonar[a], Godwin A. Ayoko[a], Emad L. Izake[b*]

[a] Queensland University of Technology(QUT), School of Chemistry, Physics and Mechanical Engineering, 2 George street QLD, 4000, Australia

[b] Centre Énergie Matériaux Télécommunications, Institute National de la Recherche Scientifique, 1650, boulevard Lionel-Boulet, Varennes QC J3X1S2 Canada.

[*] Corresponding author e-mail: e.kiriakous@qut.edu.au

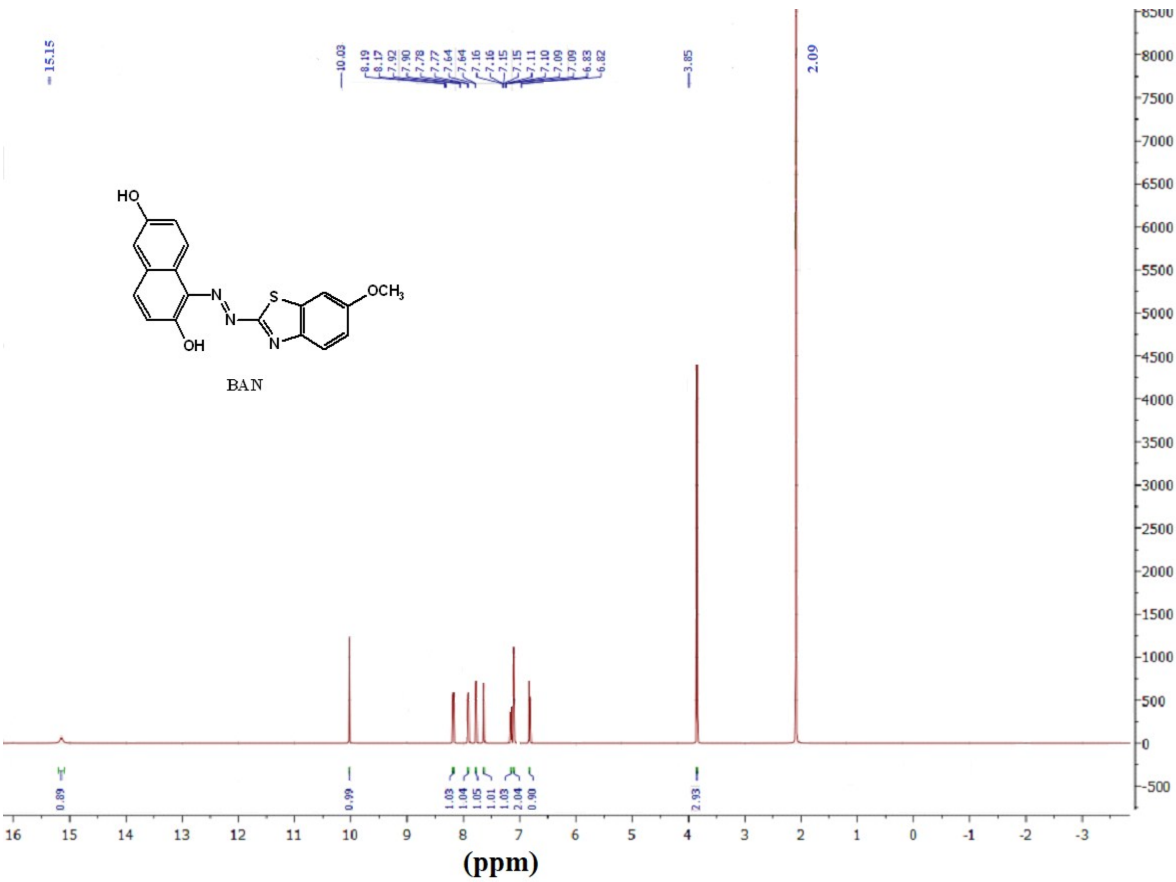


Fig. S1. ^{1}H NMR (600 MHz, DMSO-d$_6$) spectrum of BAN.

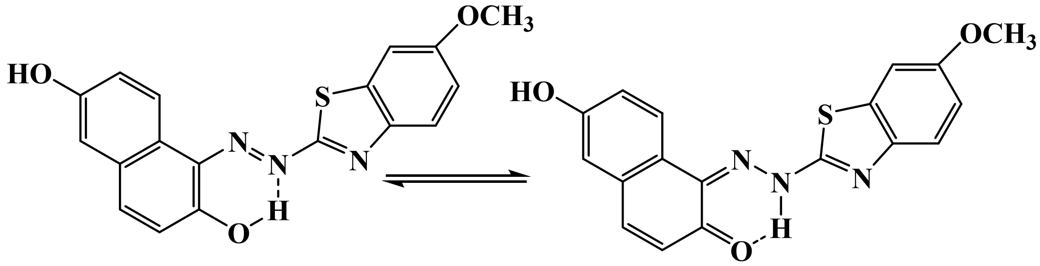


Fig. S2. Azo-hydrazone tautomerism of BAN.

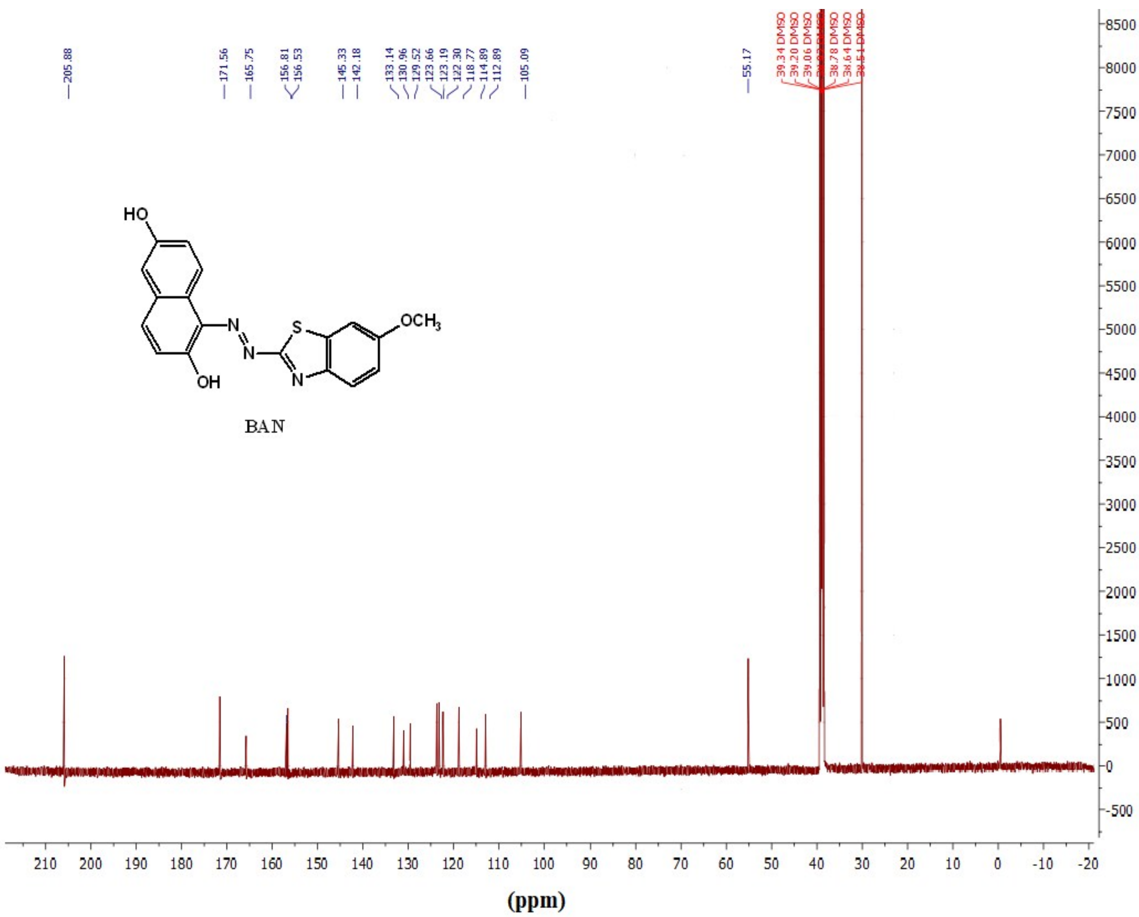


Fig. S3. ${}^{13}C$ NMR (151 MHz, DMSO-d_6) spectrum of BAN.

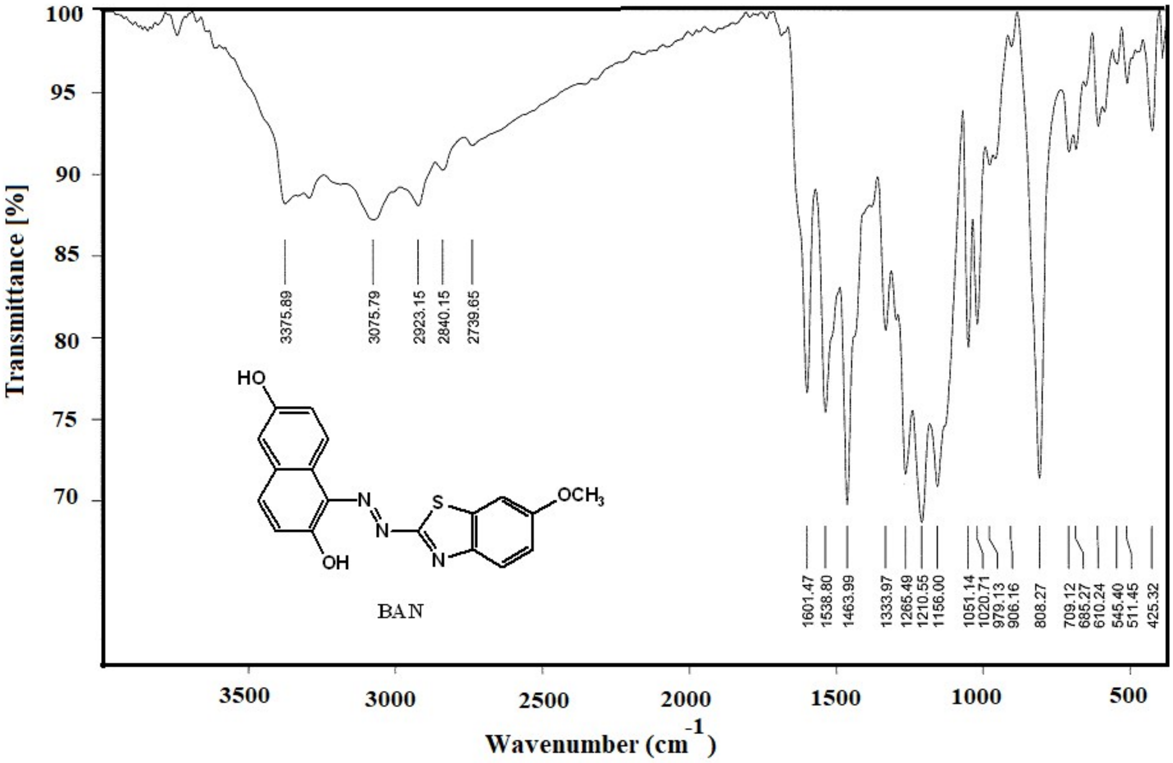


Fig. S4. FTIR spectrum of BAN.

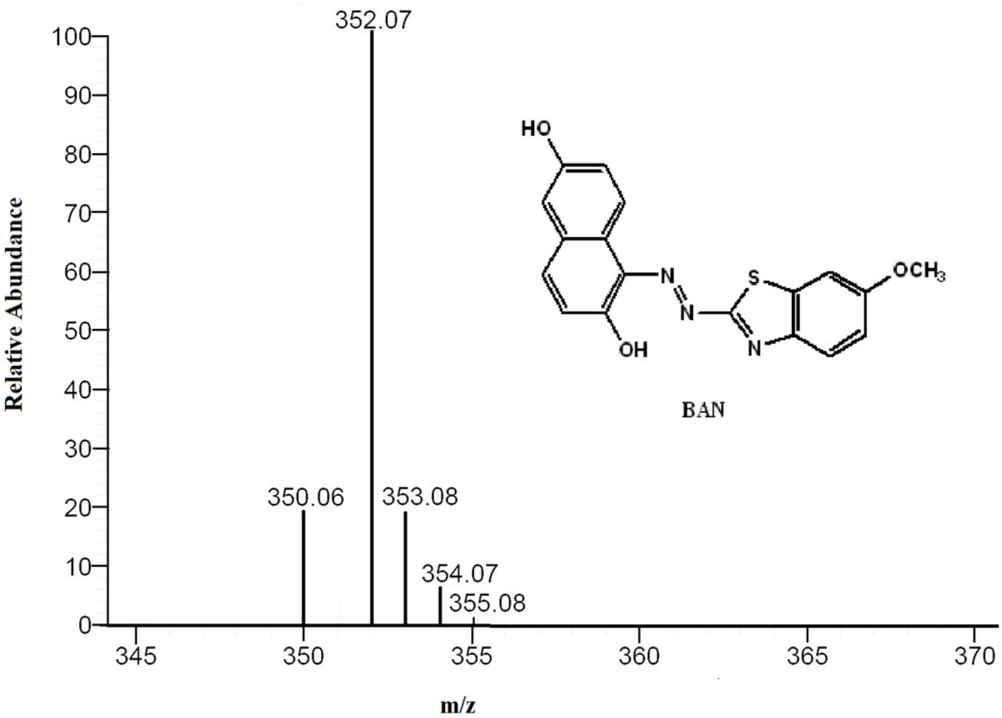


Fig. S5. Mass spectrometry of BAN.

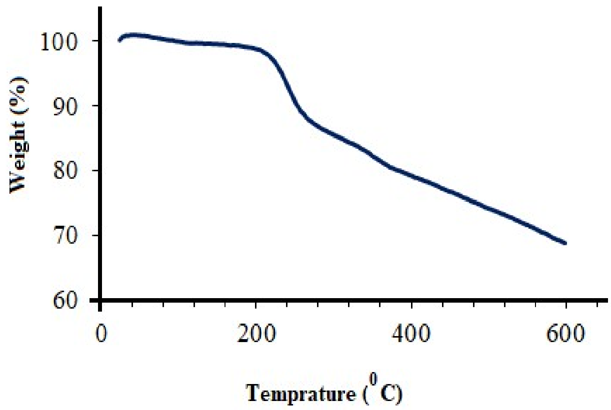


Fig. S6. TGA thermogram of BAN.

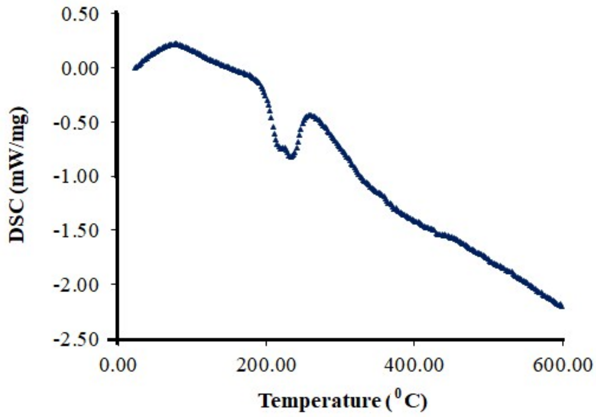


Fig. S7: DSC analysis of BAN.

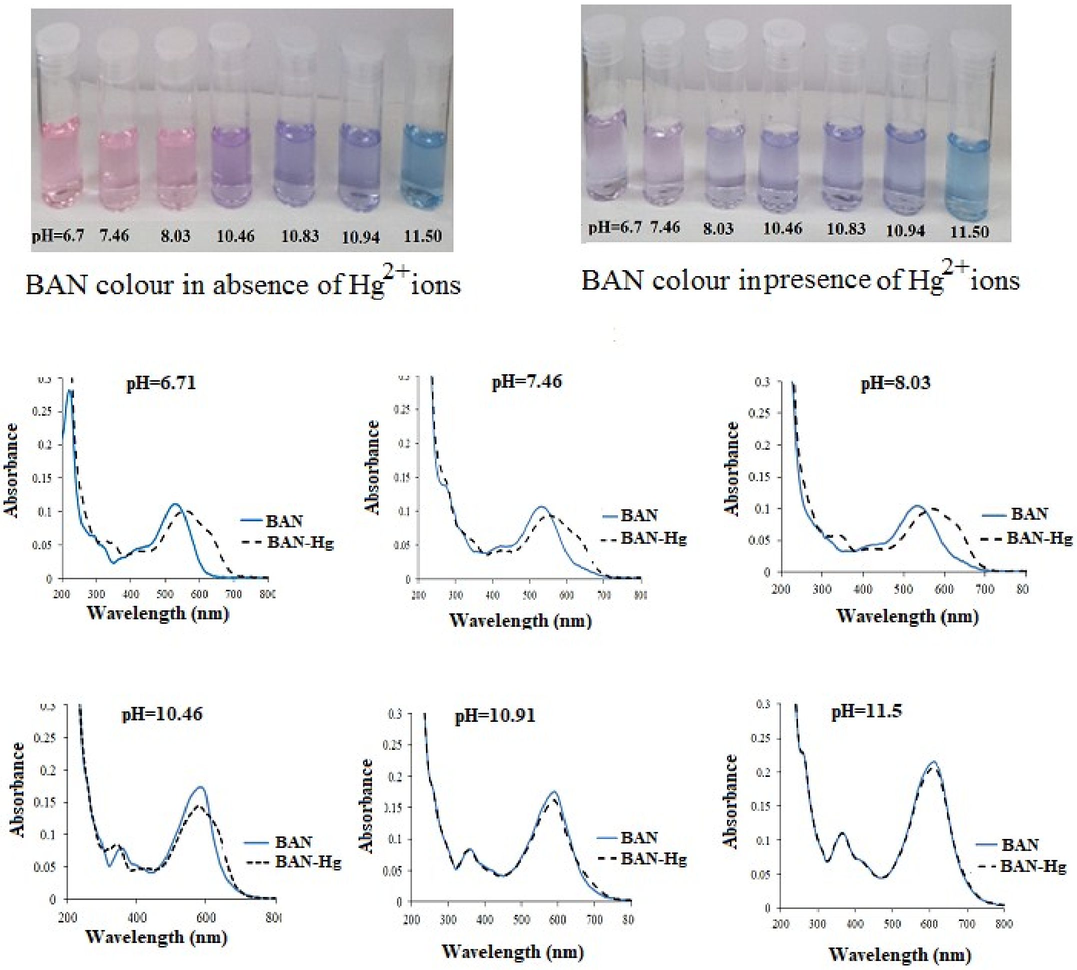


Fig. S8. Colour change and UV-VIS spectra of chemosensor BAN in the absence and presence of Hg^{2+} ions at different values.

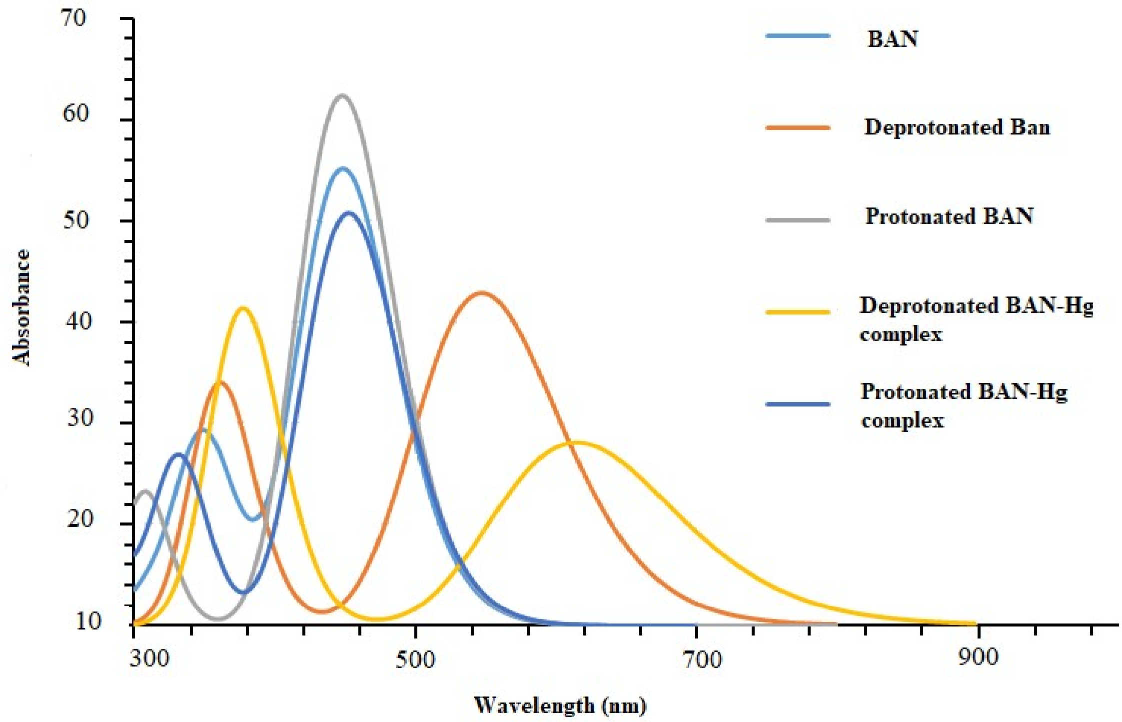


Fig. S9. Computed absorption spectra of BAN and deprotonated BAN (a Gaussian broadening of 0.25 eV HWHM is applied).

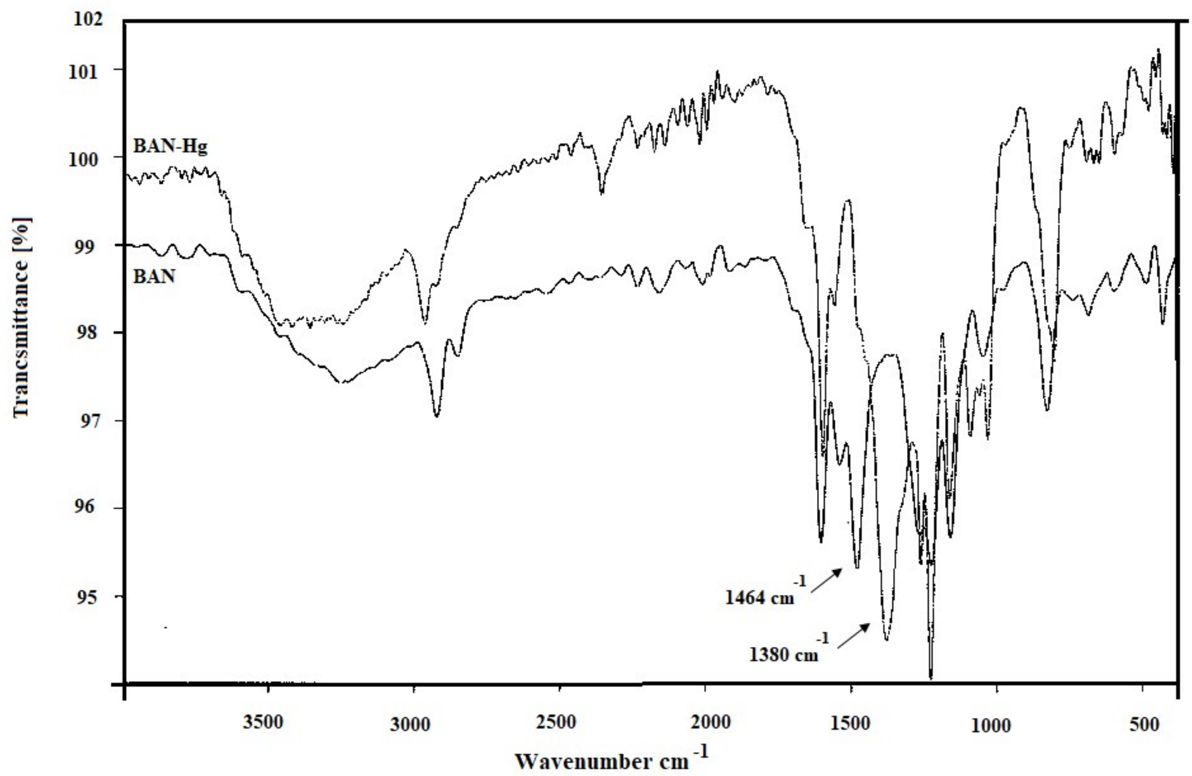


Fig. S10. FT-IR Spectra of BAN and BAN - Hg^{2+} complex.

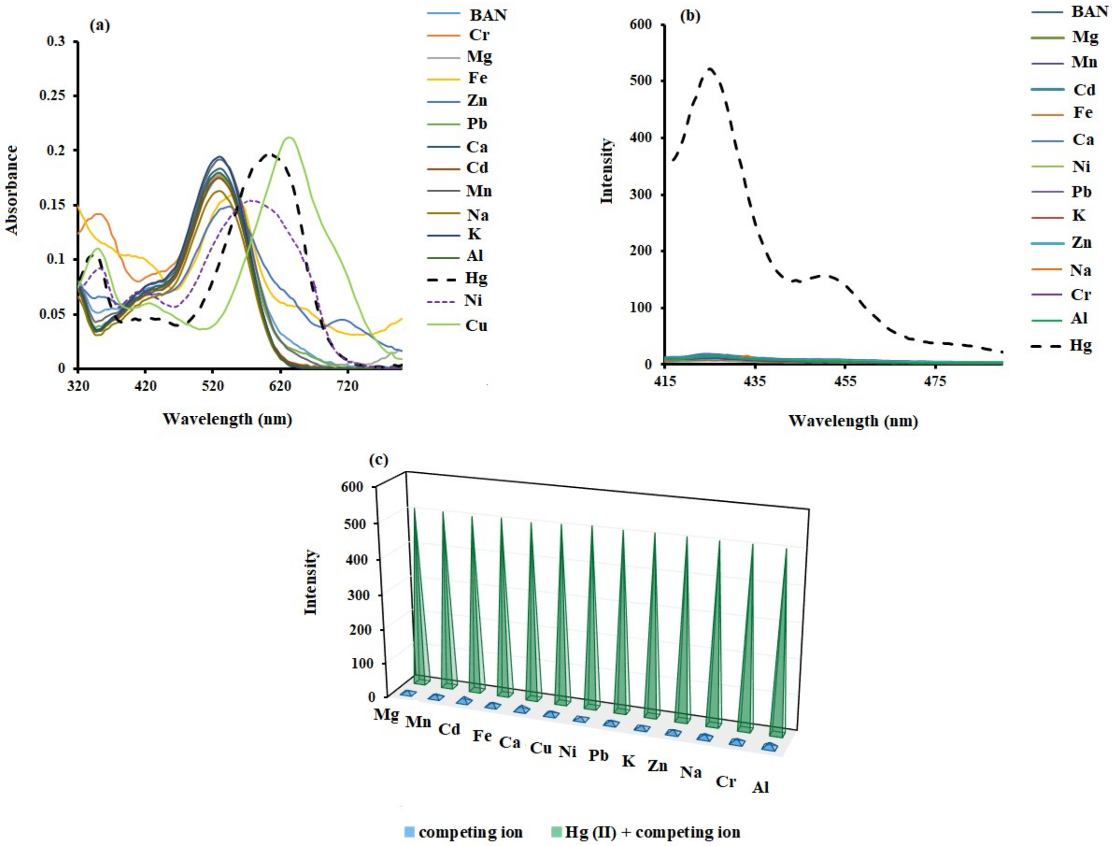


Fig. S11. (a) UV–Vis spectra of BAN (1×10^{-5} M) after the addition of 13 metal ions (5×10^{-5} M), (b) Fluorescence emission spectra of BAN (1×10^{-5} M) after the addition 13 metal ions (5×10^{-5} M). (c) The fluorescence emission of BAN (1×10^{-5} M) when interacted with 13 different metal ions (5×10^{-5} M) in the absence and the presence of 5×10^{-6} M Hg^{2+} ions. The excitation wavelength was set at λ_{ex}= 252 nm and the fluorescence emission recorded at 425 nm

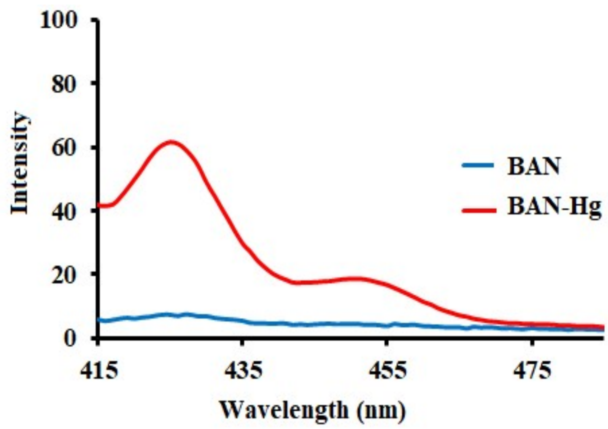


Fig. S12. Fluorescence emission spectra of BAN (1×10^{-7} M) before and after interaction with blank and spiked tap water (Hg^{2+} concentration = 5×10^{-8} M) at pH 8. The excitation wavelength was set at λ_{ex}= 252 nm.

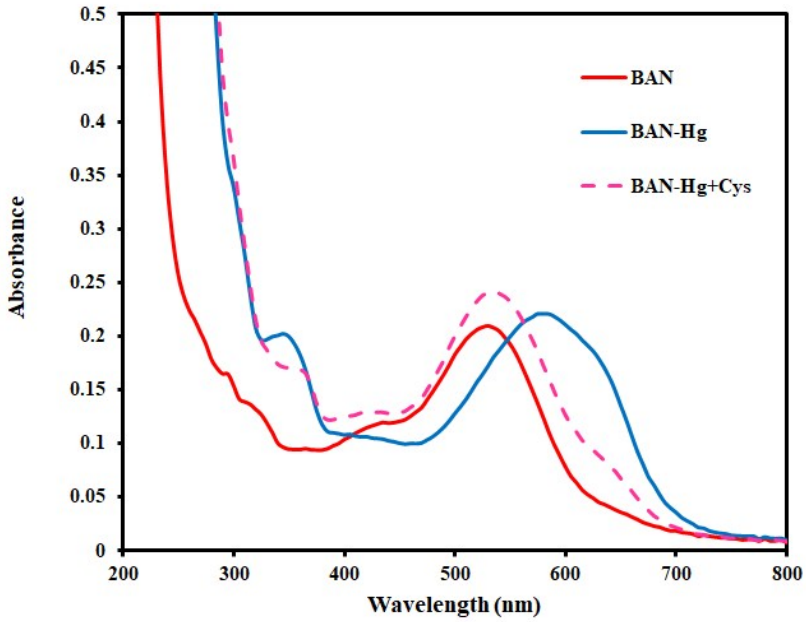


Fig. S13. The UV-Vis spectra of a) BAN dye (5×10^{-6} M in ACN: H_2O, 1:1 v/v), b) BAN-Hg^{2+} complex and c) The BAN-Hg^{2+} complex after the addition of cysteine.

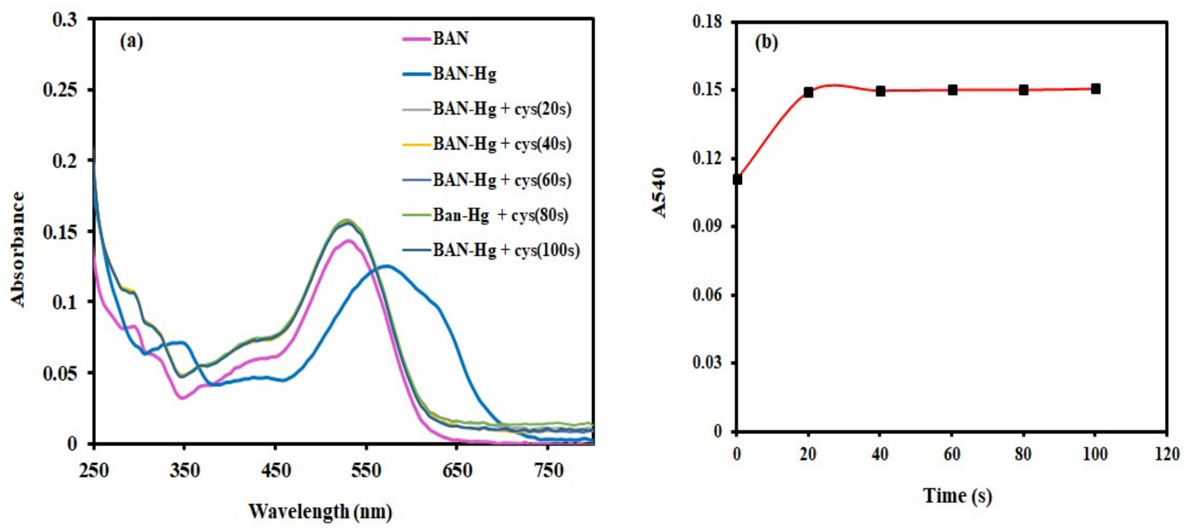


Fig. S14. (a) The UV-Vis spectra of BAN-Hg^{2+} complex (5×10^{-6} M in ACN: H_2O, 1:1 v/v) after addition of cysteine during 100 s, (b) Plotted absorbance at 540 nm against time (s).

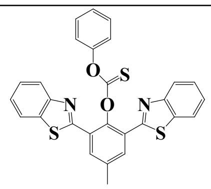
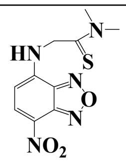
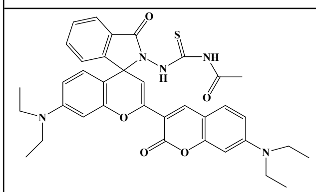
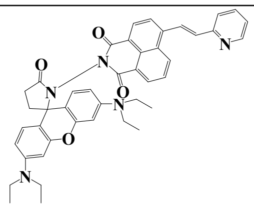
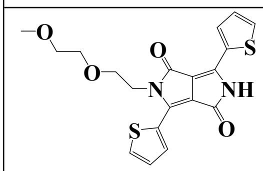
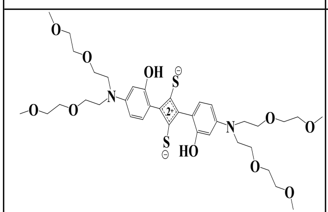
Determination of Quantum yield

The luminescence quantum yield was measured using anthracene ($\phi_f = 0.27$ in ethanol) as a reference dye. Both the BAN compound and the reference were excited at the same wavelength (λ_{ex}=252 nm), maintaining nearly equal absorbance (~0.1), and the emission spectra were obtained at 425 nm. The quantum yield is calculated according to the following equation:

$$\emptyset_S = \emptyset_R\left[\frac{A_S}{A_R}\right]\left[\frac{Abs_R}{Abs_S}\right]\left[\frac{n_S^2}{n_R^2}\right]$$

where A is the integrated intensity of the luminescence, Abs is absorbance at the excitation wavelength, n is the refractive index of the solvent and ϕ is fluorescence quantum yield.

Table S1. Comparison of optical probes for Hg^{2+} ions.

Chemosensor	Detection mode	LOD	LOQ	Comments	Ref
	Fluorescence	55nM	NA	Requires complex synthesis procedures. LOD is above the maximum allowable level of Hg^{2+} in drinking water.	1
	Fluorescence	50 nM	NA	LOD is above the maximum allowable level of Hg^{2+} in drinking water.	2
	UV–vis	188 nM	NA	LOD is above the maximum allowable level of Hg^{2+} in drinking water.	3
	Fluorescence	27nM	NA	Suffers from interferes by Fe^{3+} ions. LOD is above the maximum allowable level of Hg^{2+} in drinking water.	4
	Fluorescence	11 nM	NA	The LOD satisfies the maximum allowable level of Hg^{2+} in drinking water. The screening time for Hg^{2+} ions is 30 min.	5
	Fluorescence	1.2 nM	NA	The LOD is below the maximum allowable level of Hg^{2+} in drinking water. The screening time for Hg^{2+} ions is 30 min.	6

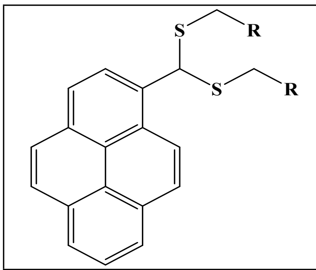
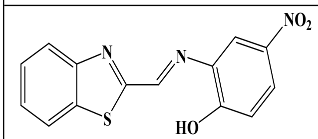
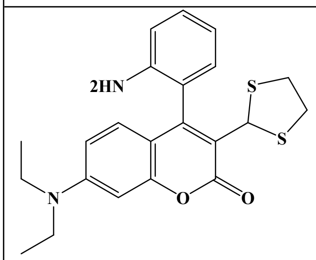
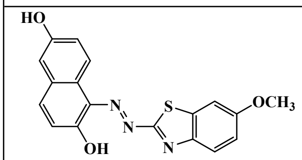
	Fluorescence	1.8 nM	NA	The LOD is below the maximum allowable level of Hg^{2+} in drinking water. The screening time for Hg^{2+} ions is 30 min.	7

Table S1. Continued.

Chemosensor	Detection mode	LOD	LOQ	Comments	Ref
	UV–vis	150 nM	510 nM	The LOD is above the maximum allowable level of Hg^{2+} in drinking water.	8
	Fluorescence	27 nM	NA	The LOD is above the maximum allowable level of Hg^{2+} in drinking water.	9
 BAN	Fluorescence	9.45 nM	50 nM	Spontaneous detection. Can be used as a paper based sensor. The LOD satisfies the maximum allowable level of Hg^{2+} in drinking water.	
	UV–vis	470 nM	2500 nM		

References

1 J. Xu, Z. Xu, Z. Wang, C. Liu, B. Zhu, X. Wang, K. Wang, J. Wang and G. Sang, *Luminescence*, 2018, **33**, 219-224.
2 K. Wang, X. Mao, L. Cao, G. Lv, X. Dong, Y. He and Y. Wei, *J. Fluoresc.*, 2017, **27**, 1739-1745.
3 D. S. Lim, S. Y. Park, K. S. Hwang and S.-K. Chang, *Tetrahedron Lett.*, 2018, **59**, 1819-1822.
4 J. Liu and Y. Qian, *J. Lumin.*, 2017, **187**, 33-39.
5 K. Nie, B. Dong, H. Shi, Z. Liu and B. Liang, *Anal. Chem.*, 2017, **89**, 2928-2936.
6 G. Wang, W. Xu, H. Yang and N. Fu, *Dyes Pigm*, 2018, **157**, 369-376.
7 Y. Gao, T. Ma, Z. Ou, W. Cai, G. Yang, Y. Li, M. Xu and Q. Li, *Talanta*, 2018, **178**, 663-669.
8 B. K. Momidi, V. Tekuri and D. R. Trivedi, *Inorg. Chem. Commun.*, 2016, **74**, 1-5.
9 S.-L. Pan, K. Li, L.-L. Li, M.-Y. Li, L. Shi, Y.-H. Liu and X.-Q. Yu, *Chem. Commun.,* 2018, **54**, 4955-4958.