Asian Journal of Chemistry; Vol. 31, No. 5 (2019), 987-992

ASIAN JOURNAL OF CHEMISTRY

https://doi.org/10.14233/ajchem.2019.21684

Pb^{2+} Ion Sensing by Anthracenylimino Compound and its β-Cyclodextrin Complex: A Study by Fluorescence Spectroscopy

M. SUMITHRA[1], R. SIVARAJ[1], P. MOSAE SELVAKUMAR[1] and ISRAEL V.M.V. ENOCH[1,2,*]

[1]Department of Chemistry, Karunya Institute of Technology and Sciences, Coimbatore-641114, India
[2]Nanotoxicology Research Lab, Department of Nanoscience, Karunya Institute of Technology and Sciences, Coimbatore-641114, India

*Corresponding author: E-mail: drisraelenoch@gmail.com

Received: 30 August 2018; *Accepted*: 27 October 2018; *Published online*: 28 March 2019; AJC-19317

This paper describes the Pb^{2+} ion sensing of an anthacenylimino compound in the presence and absence of β-cyclodextrin in aqueous media. The chemosensor is prepared by a simple coupling reaction of an aldehyde and an amine. The compound is characterized using ^{1}H NMR and mass spectrometric techniques. The host-guest complex of the β-cyclodextrin anthracenylimino compound is analyzed using 2D rotating-frame Overhauser effect spectroscopy and its structure is optimized. The stoichiometry of the complex is 1:1. The compound selectively binds Pb^{2+} ion in its free and cyclodextrin-bound forms. The ranges of sensing of the metal ion are calculated and they are similar in magnitude.

Keywords: Anthacenylimine, β-Cyclodextrin, Fluorescent chemosensor, Host-guest complex.

INTRODUCTION

Designing fluorescent probes for the detection of metal ions is attracting much interest because ion-induced changes of fluorescence are a simple, sensitive and instantaneous of sensing. The toxicity of Pb^{2+} ions in the environment is quite apparent [1-5]. Pb^{2+} poisoning records adverse effects in a range of physiological systems *viz.*, brain, liver, kidney, circulatory system, central nervous system and immune system [6,7]. In children, lead exposure can lead to difficulties in mental and physical growth and difficulties in learning. In adults, problems associated with blood pressure, fertility, muscle and joint and memory can effected [8-11]. Lead compounds are found in construction materials, lead acid batteries, ammunition, cable covering and solder [3]. Hence, Pb^{2+} ion sensing is an important aspect of environmental pollution control and toxicity removal. Several fluorescent chemosensors of Pb^{2+} ions have been reported [12-15] and the thrust for newer platforms is still growing.

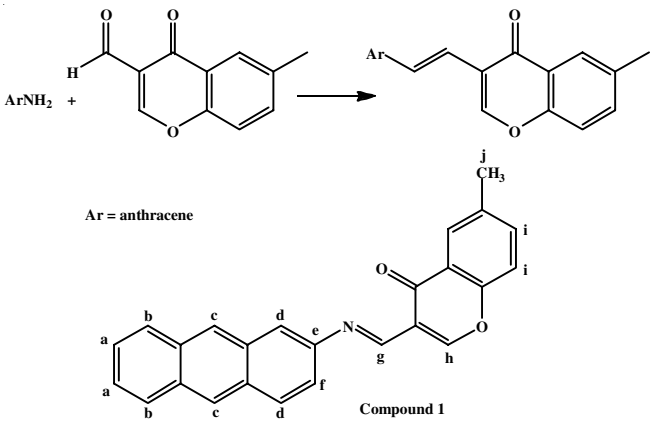
Cyclodextrins, which are tapered cone shaped cyclic oligosaccharides, have a hydrophilic outer surface and a hydrophobic cavity. These molecules can accommodate compounds of appropriate size to fit into their cavity [16-18]. The solubility and stability of molecules get enhanced on complexation by cyclodextrin [19]. Cyclodextrin binding can cause enhanced fluorescence sensing of metal ions [20]. However, the modulations of the sensing of metal ions by complex formation by cyclodextrins and its relationship with the structure of host-guest complex have not been studied. Hence, the study of effect of cyclodextrin on metal ion sensing gains importance. In this paper, we report the Pb^{2+} ion sensing by an anthracenimino derivative of a chromone prepared by a simple method and by its β-cyclodextrin complex.

EXPERIMENTAL

All the chemicals and solvents were purchased from Sigma, India. The solvents were used as received without purifying them further. ^{1}H NMR spectrum was recorded at 400 MHz with Bruker Avance 400 spectrometer using $CDCl_3$ as the solvent and tetramethylsilane as an internal standard. Mass spectrum was recorded using a JOEL GC Mate spectrometer. The β-CD complex of the synthesized compound 3-[(anthracen-2-ylimino)-methyl]-6-methyl-4*H*-chromen-2-one (**1**) was characterized using 2D rotating frame Overhauser effect spectroscopy (ROESY) recorded on a Bruker Avance III 500 MHz spectrometer, under

the spin lock condition. The mixing time was 200 m/s. The UV absorption spectra were recorded on a Jasco V 630 spectrophotometer and the steady state fluorescence spectra on a Jasco FP8300 spectrofluorometer. The samples were taken in quartz cuvettes of 1 cm path length. The spectrofluorometer employed a xenon source lamp. The solutions of the metal ions were made-up in twice-distilled water (pH 7). The test solutions contained 1 % methanol as the final concentration, after making up. All the spectra were recorded at room temperature and the test solutions were prepared just before the spectral measurements.

Compound **1** was prepared by the treatment of 2-aminoanthracene with 3-formyl-6-methylchromone. 2-Aminoanthracene was dissolved in 10 mL of methanol and 3-formyl-6-methylchromone (10 mL methanol) was mixed to it in small portions at room temperature. The mixed solutions were sonicated for 0.5 h and then stirred using a magnetic stir bar for 1 h. A yellow precipitate of **1** was obtained which was filtered at the pump and dried. The product was purified by column chromatography (silica gel) with hexane-petroleum ether (8:2) as the eluent. The pure compound **1** (m.p. 160 °C) was used for spectral measurements. The preparation of **1** is shown in **Scheme-I**.



Scheme-I: Synthesis of compound **1**

The assignment of NMR signals is as follows: ^{1}H NMR ($CDCl_3$), chemical shift relative to TMS in ppm: δ 9.12 (H_c proton of anthracene); δ 8.428.44 (H_c & H_d); δ 8.22 (proton of N=CH moiety); δ 7.067.38 (aromatic protons of chromone moiety, h & c); δ 2.23 (methyl protons i). ^{13}C NMR: δ 141.8 (aromatic carbons e & h); δ 147.2 (carbon g); δ 125-135 (aromatic carbons of anthracene); δ 112-118 (aromatic carbons of chromone i); δ 20.9 (methyl carbon j). Mass spectrum: *m/z*: 363.4071, molecular ion peak.

RESULTS AND DISCUSSION

The ^{1}H NMR spectrum of compound **1** is shown in Fig. 1. The NMR peaks corresponding to various protons are assigned as shown in Fig. 1, which in turn confirm the formation of the compound. The molecular ion peak is seen at *m/z* 363.4071.

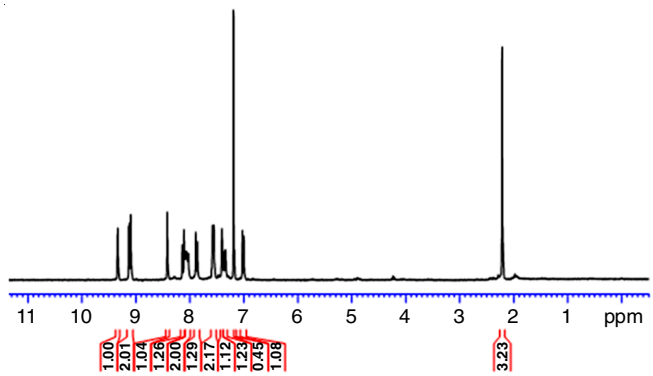


Fig. 1. ^{1}H NMR spectrum of compound **1**

Complexation of compound 1 by β-CD: The complex formation of compound **1** with β-CD was studied using absorption and fluorescence spectroscopy. The absorption spectra of compound **1** at various concentration of β-CD are shown in [Fig. 2(a)] and the fluorescence spectra in [Fig. 2(b)]. Keeping the concentration of compound **1** fixed in the aqueous solution, β-CD was added in stepwise increasing concentration. The absorption spectrum of compound **1** shows a band at 222 nm and a shoulder at around 265 nm. The 222 nm band shows a bathochromic shift gradually at each addition of β-CD and an overall 7 nm shift at the final concentration of the added β-CD. This result is quiet opposite to the small blue shifts usually observed on β-CD complexation of guest molecules, which arises due to the polarity difference between the aqueous solvent microenvironment of the fluorescent molecule in water and the less polarity inside the β-CD cavity [21-23]. However, the actual red shift (bathochromic shift) observed means that the hydroxyl protons of the outer rim of the β-CD molecule interact with the nitrogen of the compound **1** [24,25]. More-

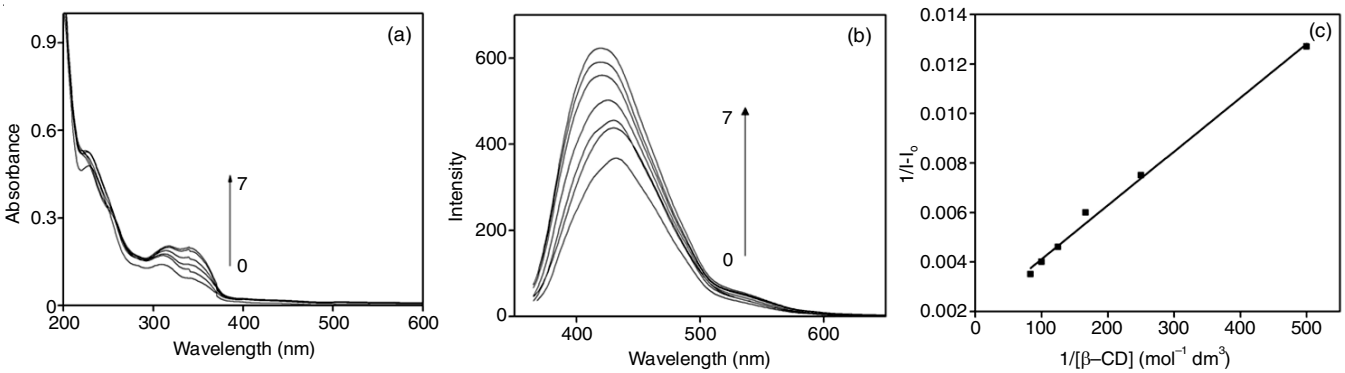


Fig. 2. (a) Absorption spectra and (b) fluorescence spectra of compound **1** at various added amounts of β-CD. (c) Benesi-Hildebrand plot of the binding of **1** to β-CD

over, a continuous hyperchromic shift is observed as a result of the complexation of compound **1** by β-CD.

The spectral shift to longer wavelength due to β-CD addition is more pronounced in absorption spectrum than in fluorescence spectrum which suggests that the complex formation of **1**–β-CD occurs at the ground state itself *i.e.*, the complexation equilibrium **1** + β-CD $\rightleftharpoons$ **1**–β-CD at the excited state is not different from that in the ground state. Aside from the shift of wavelength, the fluorescence spectrum of compound **1** show an enhancement on β-CD addition, this is attributed to the host-guest complex formation. The relaxation from the S_1 state is hindered by encapsulation of compound **1** by the β-CD cavity and hence there is enhancement of fluorescence [26,27].

The fluorescence spectral data were used to do the Benesi-Hidebrand plot [28] [Fig. 2(c)] following the eqn. 1:

$$\frac{1}{I-I_o} = \frac{1}{I'-I_o} + \frac{1}{I'-I_o}\frac{1}{K[\beta-CD]}$$

where I_o, I, I′ represent the initial concentration of 1 before the addition of β-CD, at varying concentration of β-CD and at the largest concentration, respectively. K is the binding constant. The double reciprocal plot with 1/[β-CD] in the x axis shows a linearity suggesting the formation of **1**–β-CD complex in 1:1 stoichiometry (host:guest). The calculated binding constant value was 133.76 M^{-1}.

In order to gain information on the binding mode of **1**–β-CD complex, 2D ROESY spectrum was recorded. The spectrum is shown in Fig. 3. The cross peaks between the internal cavity protons of β-CD (H-3 and H-5) and the aromatic protons shown in figure revealed the possible structure of **1**–β-CD complex.

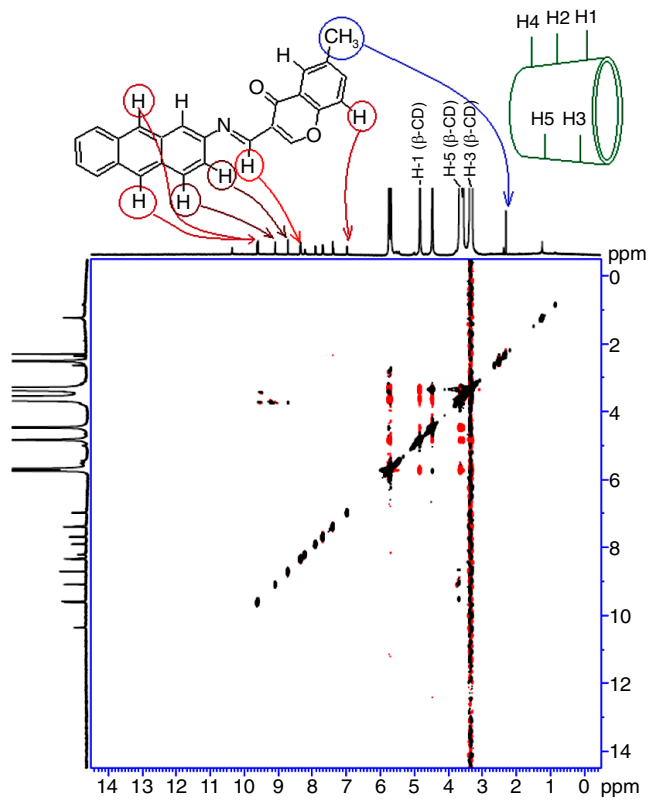


Fig. 3. 2D ROESY of **1**–β-CD complex

Pb^{2+} ion sensing by compound 1: The selective signaling of compound **1** towards various metal ions was examined in CH_3OH–H_2O (0.1/9.9 mL v/v) solution at pH 7.0. The absorption and fluorescence spectra showing the responses to the addition of various metal ions are displayed in Figs. 4(a) and (b) respectively. Upon the addition of Pb^{2+} ions, fluorescence spectrum of compound **1** shows an enhancement of fluorescence in two-fold from the just the fluorescence of compound **1** in solution. Contrast to the observation, all the other metal ions quench the fluorescence of compound **1** which make the compound suitable for sensing Pb^{2+} ions in the solution. The absorption spectrum does not show appreciable difference at the addition of the metal ions. The bar chart showing the intensity of fluorescence of compound **1** with various added metal ions is displayed in Fig. 4(c).

In order for compound **1** to function as an effective sensor of Pb^{2+} ions, it must show binding of Pb^{2+} in the solutions containing other metal ions. The experiment to determine such competitive binding was carried out and the results are shown in Fig. 4(d). Compound **1** shows a considerable selectivity of Pb^{2+} in the presence of other metal ions.

The stoichiometry of **1**–Pb^{2+} complex was determined from the Job's plot [Fig. 5(a)] made using the fluorescence intensity data and the relative concentration of Pb^{2+}. The stoichiometry was 2:1 (ligand: Pb^{2+}), which means that two molecules of compound **1** bind to one Pb^{2+} ion. Furthermore, the relationship of the fluorescence response of compound **1** toward Pb^{2+} in the concentration range of solution 1×10^{-5}, 5×10^{-5}, 1×10^{-6}, 5×10^{-6}, 1×10^{-7}, 5×10^{-7}, 1×10^{-8}, 5×10^{-8}, 1×10^{-9}, 5×10^{-9}. The detection limit is determined from the plot of fluorescence intensity as a function of [Pb^{2+}], [Fig. 5(b)] gives the value as 1.4×10^{-8} mol dm^{-3}. The association constant (K_a) of **1**–Pb^{2+} complex is calculated to be 377.35 M^{-1} using the Benesi-Hildebrand plot [28].

Similar to the metal ion selectivity and sensitivity experiments done for **1**–Pb^{2+} in aqueous solution, these were carried out in aqueous β-CD solution also. β-CD was initially added to compound **1** to shift the complexation equilibrium to **1**–β-CD complex side (by adding 1.0×10^{-2} mol dm^{-3} of β-CD). The complex in solution was mixed with various metal ions. The absorption spectra of **1**–β-CD did not show appreciable changes on the addition of metal ions [Fig. 6(a)]. Similar to the enhancement of fluorescence of compound **1** in water, that of **1**–β-CD also gets enhanced on the addition of Pb^{2+} ions, whereas the other metal ions quench the fluorescence [Fig. 6(b)]. The relative intensity of fluorescence of **1**–Pb^{2+} with and without β-CD addition does not show significant difference. This suggests that the binding site and the metal ion chelating atoms are not masked by the β-CD molecule after encapsulating **1**.

The fluorescence intensities of various metal ion added compound **1** in the presence of β-CD are shown in [Fig. 6(c)]. The competitive binding of Pb^{2+} ion by **1**–β-CD in presence of other metal ions is displayed in Fig. 6(d). These results show a trend similar to that observed for **1**–Pb^{2+} binding in water.

The Job's plot of the complex formation of **1**–β-CD–Pb^{2+}, made using fluorescence spectral data [Fig.7 (a)] shows that the stoichiometry of binding is 1:2 (Pb^{2+}:**1**–β-CD). This result

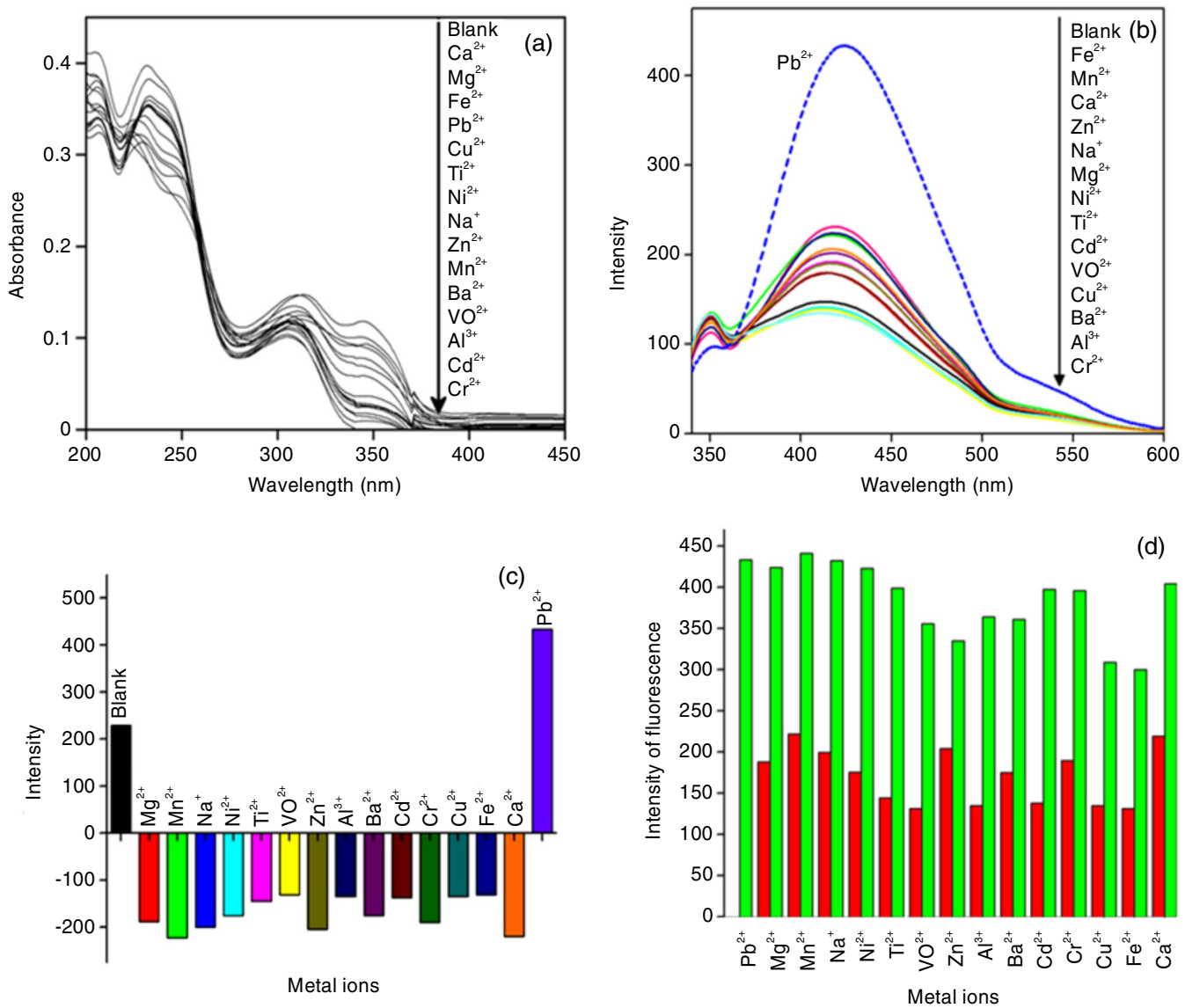


Fig. 4. (a) Absorption and (b) fluorescence spectral response of various metal ion–added compound **1**. (c) Bar chart showing the fluorescence intensities of compound **1** when various metal ions are added. (d) Bar chart showing the competitive binding of Pb^{2+} to compound **1**

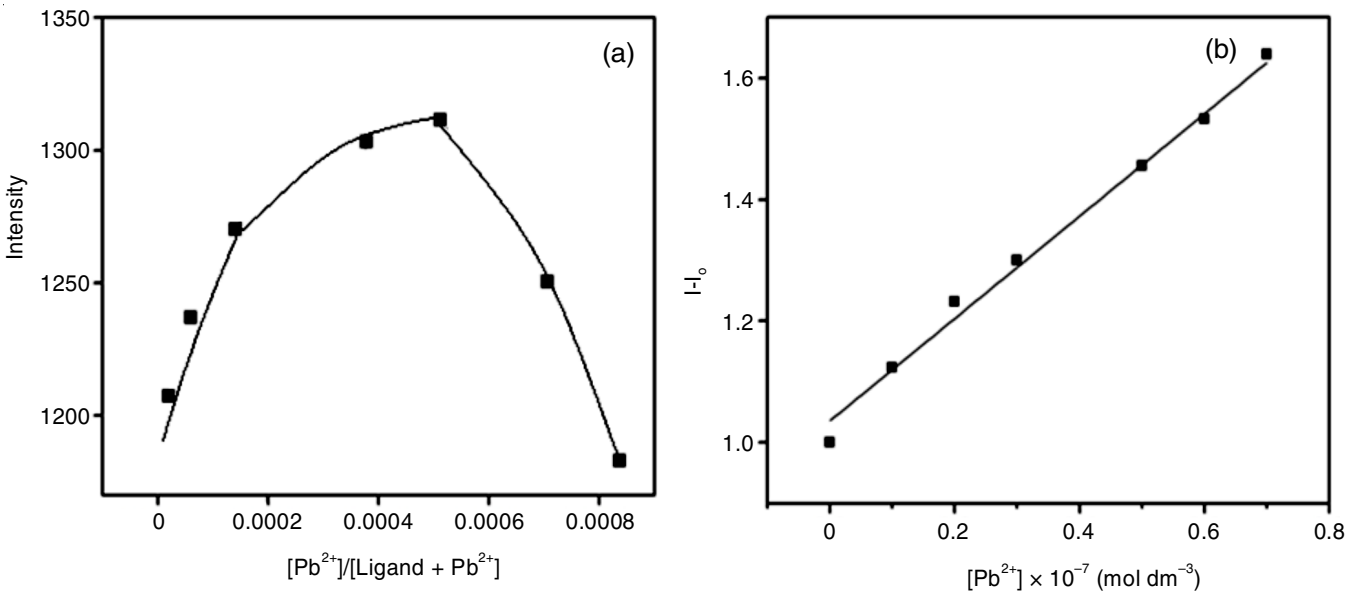


Fig. 5. (a) Job plot showing the stoichiometry of **1**–Pb^{2+} binding. (b) Linear range of detection of Pb^{2+} ions

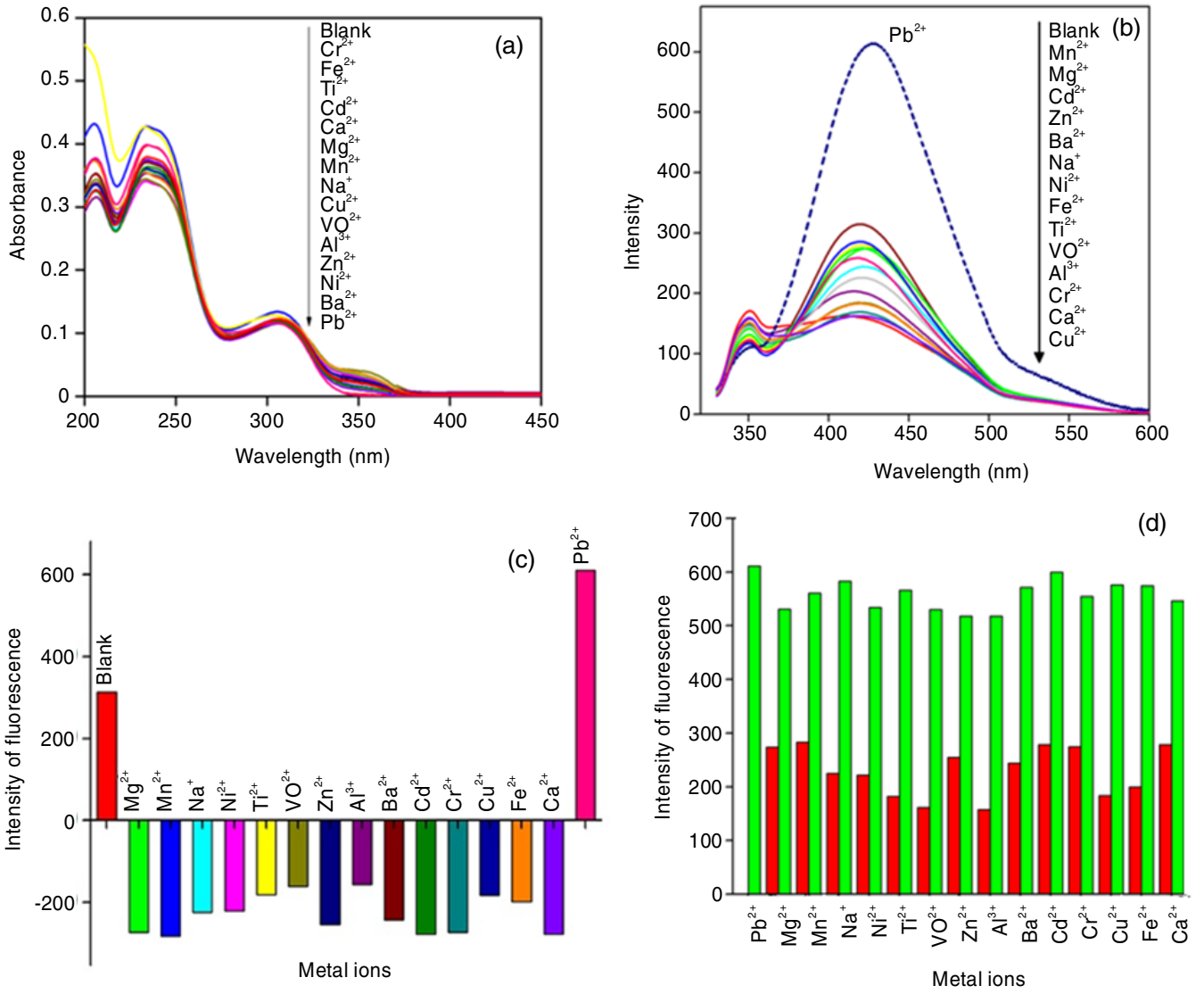


Fig. 6. (a) Absorption and (b) fluorescence spectral response of various metal ion-added **1**–β-CD complex. (c) Bar chart showing the fluorescence intensities of **1**–β-CD complex when various metal ions are added. (d) Bar chart showing the competitive binding of Pb^{2+} to **1**–β-CD complex

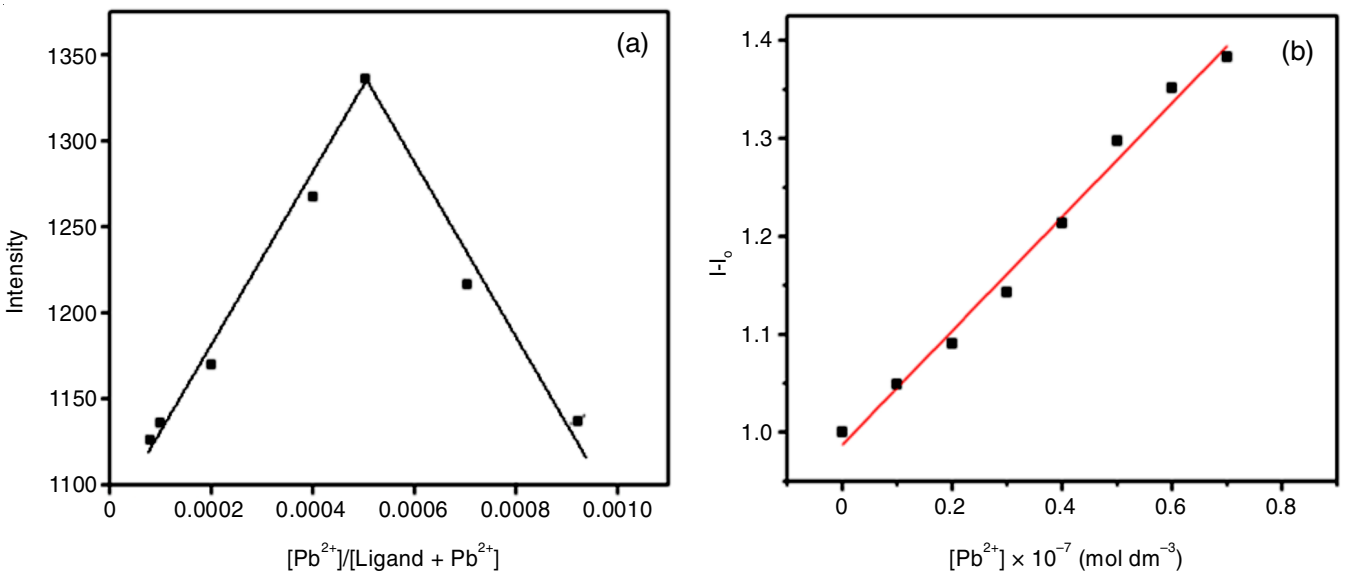


Fig. 7. (a) Job plot showing the stoichiometry of **1**–β-CDPb^{2+} binding. (b) Linear range of detection of Pb^{2+} ions by **1**–β-CD

also suggests that the encapsulation by β-CD does not affect the metal ion binding by compound **1**. The association constant of **1**–β-CD–Pb^{2+} complex is 1639 M^{-1}. The range of detection of Pb^{2+} ions by **1**–β-CD is 1.2×10^{-8} mol dm^{-3} derived from the plot shown in Fig. 7 (b).

Conclusion

An anthracenyliminochromone compound is synthesized by a simple coupling of an aminoanthracene and a formylchromone. The compound forms an inclusion complex with β-cyclodextrin with a stoichiometry of 1:1. The binding constant is 133.76 M^{-1}, which reveals that the complex is formed with weak binding of the guest molecule to the host. The compound shows Pb^{2+} ion selectivity in water and aqueous β-cyclodextrin media, the metal binding site of the chemosensor being outside the cavity of β-cyclodextrin. The linear range of detection of Pb^{2+} ions by the compound and its host-guest complex are down to the concentrations *viz.*, 1.4×10^{-8} mol dm^{-3} and 1.2×10^{-8} mol dm^{-3} respectively. This work demonstrates the possibility of metal ion detection by chemosensors being encapsulated by host molecule, with the metal ligating groups standing outside the host.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

REFERENCES

1. C. Hou, Y. Xiong, N. Fu, C.C. Jacquot, T.C. Squier and H. Cao, *Tetrahedron Lett.*, **52**, 2692 (2011); https://doi.org/10.1016/j.tetlet.2011.03.075.
2. D.A. Gildlow, *Occup. Med.*, **54**, 76 (2004); https://doi.org/10.1093/occmed/kqh019.
3. H.W. Mielke and P.L. Reagan, *Environ. Health Perspect.*, **106(Suppl.1)**, 217 (1998).
4. Q. Wang, S. Zhang, H. Ge, G. Tian, N. Cao and Y. Li, *Sens. Actuators B Chem.*, **207**, 25 (2015); https://doi.org/10.1016/j.snb.2014.10.096.
5. K. Aggarwal and J.M. Khurana, *J. Lumin.*, **167**, 146 (2015); https://doi.org/10.1016/j.jlumin.2015.06.027.
6. Y.W. Fen, W.M.M. Yunus and N.A. Yusof, *Sens. Actuators B Chem.*, **171-172**, 287 (2012); https://doi.org/10.1016/j.snb.2012.03.070.
7. Y. Lu, X. Li, G.K. Wang and W. Tang, *Biosens. Bioelectron.*, **39**, 231 (2013); https://doi.org/10.1016/j.bios.2012.07.045.
8. H.G. Preuss, G. Jiang, J.W. Jones, P.O. Macarthy, P.M. Andrews and J.A. Gondal, *J. Am. Coll. Nutr.*, **13**, 578 (1994); https://doi.org/10.1080/07315724.1994.10718451.
9. A. Skoczynska, J. Wrobel and R. Andrzejak, *Toxicology*, **162**, 157 (2001); https://doi.org/10.1016/S0300-483X(01)00355-9.
10. M.J.J. Ronis, T.M. Badger, S.J. Shema, P.K. Roberson and F. Shaikh, *Toxicol. Appl. Pharmacol.*, **136**, 361 (1996); https://doi.org/10.1006/taap.1996.0044.
11. D.A. Daggett, E.F. Nuwaysir, S.A. Nelson, L.S. Wright, S.E. Kornguth and F.L. Siegel, *Toxicology*, **117**, 61 (1997); https://doi.org/10.1016/S0300-483X(96)03555-X.
12. K.P. Nandre, A.L. Puyad, S.V. Bhosale and S.V. Bhosale, *Talanta*, **130**, 103 (2014); https://doi.org/10.1016/j.talanta.2014.06.064.
13. M. Wang, F. Wang, Y. Wang, W. Zhang and X. Chen, *Dyes Pigm.*, **120**, 307 (2015); https://doi.org/10.1016/j.dyepig.2015.04.035.
14. E.J. Antony, M. Raj, R.Q. Paulpandi, M.S. Paulraj and I.V.M.V. Enoch, *J. Fluoresc.*, **25**, 1031 (2015); https://doi.org/10.1007/s10895-015-1588-z.
15. B.K. Datta, C. Kar, A. Basu and G. Das, *Tetrahedron Lett.*, **54**, 771 (2013); https://doi.org/10.1016/j.tetlet.2012.11.114.
16. S. Chandrasekaran, N. Sudha, D. Premnath and I.V.M.V. Enoch, *J. Biomol. Struct. Dyn.*, **33**, 1945 (2015); https://doi.org/10.1080/07391102.2014.980323.
17. C. Sowrirajan, S. Yousuf and I.V.M.V. Enoch, *Aust. J. Chem.*, **67**, 256 (2014); https://doi.org/10.1071/CH13364.
18. S. Chandrasekaran, Y. Sameena and I.V.M.V. Enoch, *J. Mol. Recognit.*, **27**, 640 (2014); https://doi.org/10.1002/jmr.2387.
19. C.R. Palem, S. Patel and V.B. Pokharkar, *PDA J. Pharm. Sci. Technol.*, **63**, 217 (2009).
20. R.Q. Paulpandi, S. Ramasamy, M.S. Paulraj, F.G. Díaz Baños, G. Villora, J.P. Cerón-Carrasco, H. Pérez-Sánchez and I.V.M.V. Enoch, *RSC Adv.*, **6**, 15670 (2016); https://doi.org/10.1039/C6RA01202G.
21. I.V.M.V. Enoch, R. Rajamohan and M. Swaminathan, *Spectrochim. Acta A*, **77**, 473 (2010); https://doi.org/10.1016/j.saa.2010.06.021.
22. Z.H. Qi, L. Zhu, H. Chen and W. Qi, *J. Incl. Phenom. Molec. Recognit. Chem.*, **27**, 279 (1997); https://doi.org/10.1023/A:1007914329584.
23. S. Sortino, J.C. Scaiano, G.D. Guidi and S. Monti, *Photochem. Photobiol.*, **70**, 549 (1999); https://doi.org/10.1111/j.1751-1097.1999.tb08250.x.
24. I.V.M.V. Enoch and S. Yousuf, *J. Solution Chem.*, **42**, 470 (2013); https://doi.org/10.1007/s10953-013-9965-1.
25. I.V.M.V. Enoch and M. Swaminathan, *J. Incl. Phenom. Macrocycl. Chem.*, **53**, 149 (2005); https://doi.org/10.1007/s10847-005-2633-3.
26. C. Dall'asta, G. Ingletto, R. Corradini, G. Galaverna and R. Marchelli, *J. Incl. Phenom. Macrocycl. Chem.*, **45**, 257 (2003); https://doi.org/10.1023/A:1024572426577.
27. Y.-H. Chiu and J.-H. Liu, *J. Polym. Sci. A*, **48**, 3368 (2010); https://doi.org/10.1002/pola.24121.
28. H.A. Benesi and J.H. Hildebrand, *J. Am. Chem. Soc.*, **71**, 2703 (1949); https://doi.org/10.1021/ja01176a030.