Inorganic Chemistry Communications 36 (2013) 72–76

Contents lists available at ScienceDirect

Inorganic Chemistry Communications

journal homepage: www.elsevier.com/locate/inoche

Turn-on selective fluorescent probe for trivalent cations

Hyun Kim [a,*], Kyung Beom Kim [a], Eun Joo Song [a], In Hong Hwang [a], Jin Young Noh [a], Pan-Gi Kim [b], Kwang-Duk Jeong [c], Cheal Kim [a,*]

[a] *Department of Fine Chemistry, Seoul National University of Science and Technology, Seoul 139-743, Republic of Korea*
[b] *Department of Forest & Environment Resources, Kyungpook National University, Sangju, 742-711, Republic of Korea*
[c] *Clean Energy Research Center, Korea Institute of Science and Technology, Seoul, 130-650, Republic of Korea*

ARTICLE INFO

Article history:
Received 12 July 2013
Accepted 22 August 2013
Available online 30 August 2013

Keywords:
Trivalent cations
Pearson's principle
Fluorescent probe
PET process

ABSTRACT

A novel fluorescent sensor **1** (**1** = 10-(2-(((pyridin-2-yl)methylamino)methyl)phenol)methyl-anthracene) for trivalent cations has been synthesized and characterized. Both UV-vis and fluorescence spectroscopic studies demonstrated that the new receptor **1** was highly sensitive and selective toward trivalent cations, while there was no response to monovalent and divalent cations in methanol. Upon binding with trivalent cations, the emission bands of **1** red-shifted for all the trivalent cations from 411 nm to 421 nm and their fluorescence intensities were enhanced. In particular, Fe^{3+} could be obviously discriminated from Fe^{2+}. The binding modes of **1** and the trivalent cations (M^{3+} ions) were found to be 1:1 and confirmed by Job plot, ^{1}H NMR titration and ESI-mass spectrometry analysis.

Cation recognition is an area of growing interest in supramolecular chemistry [1–7]. The recognition and sensing of cationic analytes have emerged as a key research theme within the generalized area. In particular, trivalent cation detection is of significant importance due to its crucial role in a wide range of environmental and biological processes [8–13]. For instance, aluminum is found in its ionic form Al^{3+} in most environmental and biological tissues [14–17]. Al^{3+} which widely exists is considered toxic in biological activities [18,19]. Excessive exposure of the human body to Al^{3+} leads to a wide range of diseases, such as Alzheimer's disease, Parkinson's disease, encephalopathy and osteoporosis [20–25]. The trivalent form of chromium is not only an essential nutrient for humans, but also plays an important role in the metabolism of carbohydrates, lipids, proteins and nucleic acids [26]. The deficiency of chromium is known to lead to a variety of disease, and causes disturbances in the glucose levels and lipid metabolism [27–29]. Gallium akin to aluminum (group 3) is small traces in water, vegetables and fruits. Gallium compounds can cause throat irritation, difficulty breathing and chest pain. In addition, its fumes can cause even very serious conditions such as pulmonary edema and partial paralysis. Indium also belongs to the group 3 and is known to stimulate the metabolism [30–32]. Moreover, it is about to be known that indium compounds damage the heart, kidney and liver [33]. Fe^{3+} is the most compatible material in the enzyme-catalyzed reaction due to rapid oxidation-reduction reaction [34–38]. Also, iron is used as a cofactor of electron transport system [39]. The imbalance of iron in a human body induces the occurrence of many diseases [40–42]. For examples, excess existence of Fe^{3+} is harmful to DNA and protein of an organism by developing the radical species and its deficiency leads to anemia, liver and kidney damages, diabetes, and heart diseases [43,44]. Moreover, it is of great importance to discriminate Fe^{3+} from Fe^{2+} through convenient methods with a simple probe, because the ferrous/ferric (Fe^{2+}/Fe^{3+}) states are one of the important redox pairs in biological systems [45].

In view of the significance of trivalent cations, therefore, there is a great demand to develop selective and sensitive methods for trivalent cation detection and highly desirable to design the probes that presents selective detection for trivalent cations. However, developing such sensors with recognition capability to detect multiple specific analytes such as trivalent cations is a huge challenging task, and surprisingly, only few are known for detection of simultaneously multiple trivalent cations [46,47].

To achieve the huge challenging work, we employed Pearson's principle that hard acids prefer to bind to hard bases and soft acids prefer to bind to soft bases [48]. Therefore, we have attached an anthracene group as a chromophore to a moiety with a phenol group capable of binding to hard metal ions such as the trivalent cations. Indeed, the new receptor **1** was highly sensitive and selective toward only trivalent cations.

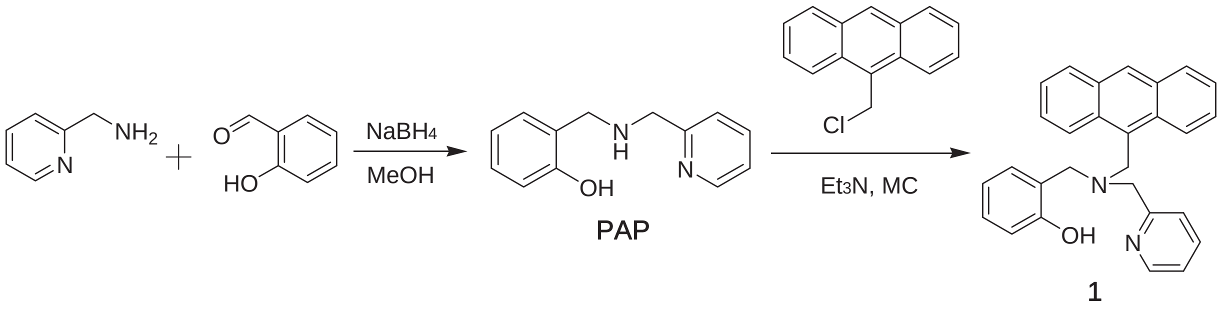
Herein, we report the new simple turn-on fluorescent probe **1** which can detect only trivalent cations in methanol. In contrast, **1** did not respond to monovalent and divalent cations. Furthermore, **1** could discriminate Fe^{3+} from Fe^{2+}. The binding modes of **1** and M^{3+} ions were also studied by Job plot, ^{1}H NMR titration and ESI-mass spectrometry analysis.

Our goal was to design a selective trivalent cation sensor by Pearson' principle. Therefore, the chemosensor **1** was synthesized by reaction of 9-(chloromethyl)anthracene with 2-(((pyridin-3-yl)methylamino) methyl)phenol (**PAP**) acting as a hard base which was made by the

---

[*] Corresponding authors. Tel.: +82 2 970 6693; fax: +82 2 973 9149.
E-mail addresses: eagleyun@naver.com (H. Kim), chealkim@seoultech.ac.kr (C. Kim).

1387-7003/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.inoche.2013.08.025



Scheme 1. Synthetic route of the chemosensor **1**.

condensation of 2-aminomethyl pyridine and 2-hydroxy benzaldehyde as shown in Scheme 1. The anthracene unit acts as a fluorophore [40,49–51] and **PAP** does as a receptor for the hard metal ions such as the trivalent cations. Its molecular structure was confirmed by elemental analysis, ^{1}H NMR,^{13}C NMR and ESI-Mass.

To examine the selectivity of **1** toward metal ions, its spectroscopic properties were measured upon addition of various metal ions such as Na^+, Mg^{2+}, Al^{3+}, K^+, Ca^{2+}, Cr^{3+}, Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Ag^+, Cd^{2+}, Hg^{2+}, Pb^{2+}, Ga^{3+}, In^{3+} and Fe^{2+}in methanol. The emission spectrum of **1**, which was excited at 364 nm, exhibited an emission maximum at 411 nm with a low quantum yield ($\Phi_{free} = 0.02$). The addition of Na^+, Mg^{2+}, K^+, Ca^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Ag^+, Cd^{2+}, Hg^{2+}, Pb^{2+} and Fe^{2+} had no effect on the fluorescence, whereas the addition of trivalent cations (Al^{3+}, Cr^{3+}, Fe^{3+}, Ga^{3+} and In^{3+}) showed the prominent enhancement of the fluorescence ($\Phi = 0.79$, 0.77, 0.72, 0.73 and 0.75, respectively) with a slight red shift of the emission maxima from 411 to 421 nm, as shown in Fig. 1. Such a significant change in emission of **1** in the presence of trivalent cations might be attributed to the strong coordination of trivalent cations to the phenolic hydroxyl group of the **PAP** chelator moiety of **1** by Pearson' principle [52]. The strong binding of the trivalent cations to **1** prevents a PET process from the aliphatic nitrogen center to the excited anthracene, thus resulting in a significant enhancement of fluorescence. These results indicate that the probe **1** exhibits highly selective chemosensor for trivalent cations. To our best knowledge, simultaneous discrimination of three trivalent cations from the monovalent and divalent cations detection was reported only twice [46,47], and this is the first report in which the probe can detect simultaneously five trivalent cations.

In order to understand the binding modes between **1** and the trivalent cations, the fluorescence titration of **1** with M^{3+} was carried out (Fig. S1). In the case of Al^{3+}, with the increase in concentration of Al^{3+} ion, the emission intensity was gradually enhanced with induction period and reached a maximum at 1.4 equiv of Al^{3+} (Fig. 2). More accurate stoichiometry of the Al^{3+}/**1** was determined by Job plot which revealed a 1:1 ratio for **1**:Al^{3+} (Fig. 3). The complexation of Al^{3+} with **1** induced deprotonation of the phenolic hydroxyl group of **1** (Scheme 2), which was confirmed by ESI-mass spectrometry analysis of **1**-Al^{3+} complex (Fig. 4). The $[\mathbf{1} + Al]^{2+}$ complex was calculated to be m/z 215.08 and measured to be m/z 214.80. The 1:1 binding stoichiometries of Cr^{3+}, Fe^{3+}, Ga^{3+} and In^{3+}were also determined by Job plot (Fig. S2). ESI-mass spectrometry analysis of **1** with Cr^{3+} and Fe^{3+} further supported the 1:1 binding stoichiometry (Fig. S3).

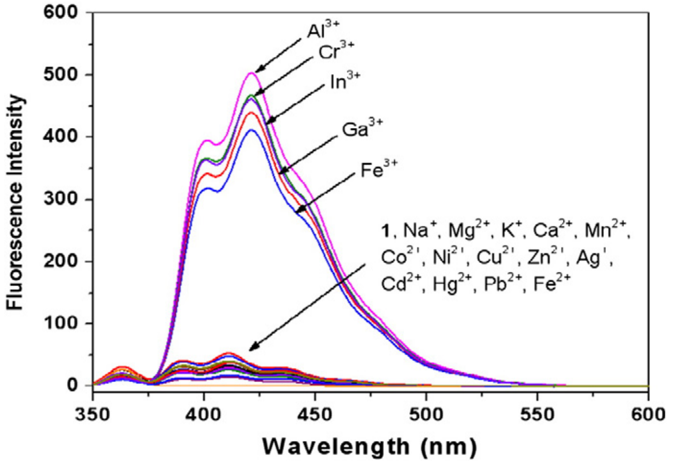


Fig. 1. Fluorescence spectra of **1** (5.0×10^{-6} M) upon addition of 2 equiv of Na^+, Mg^{2+}, Al^{3+}, K^+, Ca^{2+}, Cr^{3+}, Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Ag^+, Cd^{2+}, Hg^{2+}, Pb^{2+}, Ga^{3+}, In^{3+} and Fe^{2+} in methanol ($\lambda_{ex} = 364$ nm).

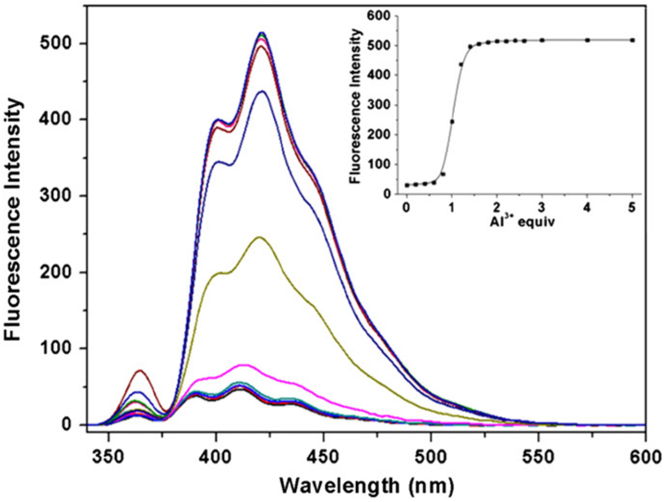


Fig. 2. Fluorescence spectra of **1** (5.0×10^{-6} M) in the presence of different concentration of Al^{3+}. Inset: the fluorescence at 421 nm of **1** as a function of the Al^{3+} concentration. ($\lambda_{ex} = 364$ nm).

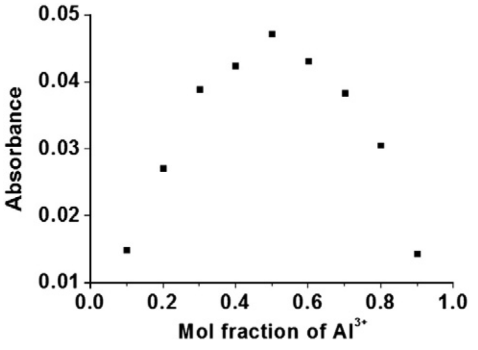
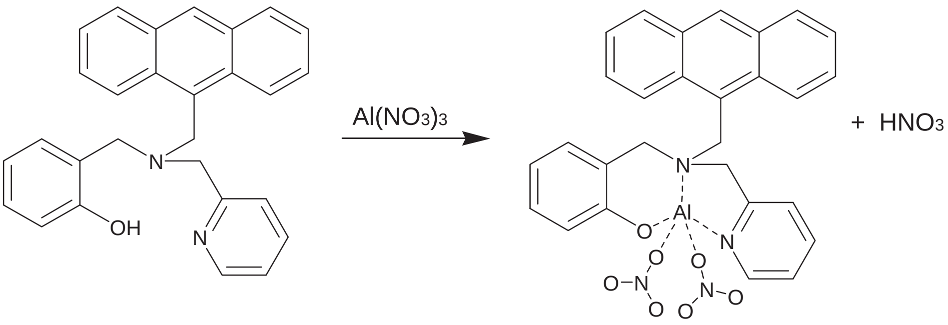


Fig. 3. Job plot of **1** with Al^{3+}.



Scheme 2. Proposed structure of a 1:1 complex of **1** and Al^{3+}.

The binding abilities of the trivalent cations with **1** were determined from modified Benesi-Hildebrand equations (Fig. S4) and the detection limits for each M^{3+} ion were obtained using the method of a signal-to-background (S/B) ratio (Fig. S5) [53]. These values are shown in Table 1. All trivalent cations showed similar binding abilities to **1** ($K_a = 1.0 \times 10^5$– 1.7×10^5) and Fe^{3+} had the lowest detection limit (0.6 μM), indicating that **1** detects Fe^{3+} most sensitively among the trivalent cations.

The most important criterion for a selective cation probe is the ability to detect a specific cation in the existence of other competing ions, although **1** revealed a remarkable selectivity for trivalent cations against monovalent and divalent metal ions (Fig. 1). To further examine the selectivity of **1** for trivalent cations, therefore, we investigated the fluorescence intensity in the presence of trivalent cations mixed with monovalent and divalent ones. First of all, the change of fluorescence intensity of **1** was measured in the presence of the trivalent cation Ga^{3+} mixed with various metal ions (Fig. 5). Compared to the intensity obtained with the trivalent cation Ga^{3+}, the emission spectra were almost identical in the presence of Na^+, Mg^{2+}, Al^{3+}, K^+, Ca^{2+}, Cr^{3+}, Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Ag^+, Cd^{2+}, Hg^{2+}, Pb^{2+}, In^{3+} and Fe^{2+}, except for Cu^{2+} that inhibited about 75% of the fluorescence. Nevertheless, it still had a sufficient turn-on ratio for the detection of Ga^{3+} in the presence of Cu^{2+}. These results indicate that the presence of monovalent and divalent cations did not disturb the detection of the trivalent cation Ga^{3+} with **1**. Again, this might be attributed to the strong complexation of trivalent cations with **1** by Pearson's principal that hard acids (M^{3+}) prefer to bind the hard base (the oxygen atom of the phenol group of **1**). Competition experiments of Al^{3+}, Cr^{3+}, Fe^{3+}, and In^{3+} were also carried out in the presence of potentially competitive metal ions (Fig. S6). Fe^{3+}, In^{3+} and Al^{3+} showed similar selective patterns to that of Ga^{3+}, while less selective property was displayed for Cr^{3+}. In particular, it is worthwhile to mention that Fe^{3+}can be obviously discriminated from Fe^{2+}. Based on competition experiments, **1** could be used as a selective fluorescent sensor for trivalent cation detection in the presence of most competing metal ions such as monovalent and divalent cations.

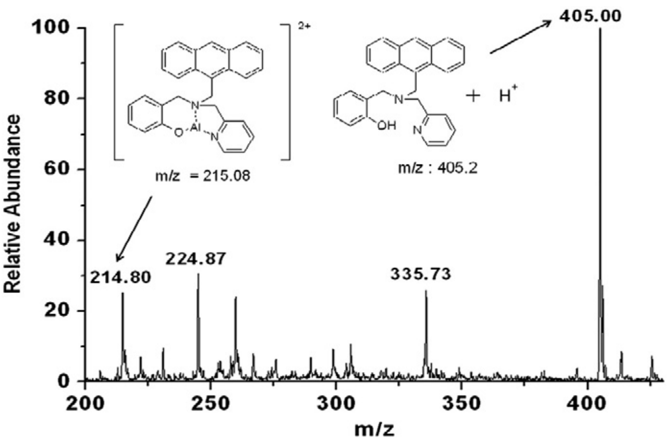


Fig. 4. Positive-ion electrospray ionization mass spectrum of **1** (1.0×10^{-4} M) upon addition of 1 equiv of Al^{3+} in methanol.

In order to further inquire into the spectral characteristics of **1**, we investigated UV-vis absorption changes with respect to each M^{3+}. As shown in Fig. 6, the UV-vis spectrum of **1** exhibited absorption bands at 332, 348, 366 and 386 nm. Upon addition of Al^{3+}, the absorption peaks at 332, 348, 366 and 386 nm decreased obviously, whereas new prominent bands at 337, 353, 371 and 391 nm were developed with red shift. The well-defined isosbestic points at 335, 341, 351, 359, 369, 379 and 389 nm represent a clean conversion of **1** into the **1**-Al^{3+} complex. The spectral characteristic behaviors of **1** toward Cr^{3+}, Fe^{3+}, Ga^{3+} and In^{3+} were also conducted by UV-vis spectroscopy, respectively, and similar results were obtained (Fig. S7).

The ^1H NMR investigation was performed in CD_3OD to understand the nature of interaction between sensor **1** and Al^{3+}. As shown in Fig. 7, significant spectral changes were observed. Upon addition of Al^{3+} ion to receptor **1**, H_a, H_b, H_c and H_d of anthracene protons and H_e of pyridyl group showed downfield shifts. The shift of pyridyl moiety protons suggests N-metal coordination. H_f, H_g and H_h of methylene protons also showed significant downfield shifts, indicating the strong coordination of nitrogen atoms with Al^{3+}. In a similar way, all signals corresponding to aromatic protons shifted. Most of the phenol group peaks at 6.7–7.2 ppm were shifted to 6.6-7.1 ppm. These obvious changes of the chemical shifts indicated that **1** could form a stable complex with Al^{3+}. There was no shifts in the position of proton signals on further addition of metal ions (>1.0 equiv) which confirms 1:1 complexation between Al^{3+} and **1**. These results are consistent with the formation of 1:1 ligand-to-metal complex supported by Job plot and ESI-mass spectrometry analysis.

Furthermore, we examined the selectivity of **1** toward metal ions in various solvents. Any significant selectivity was not observed, except in DMSO which similar results were obtained as observed in methanol (Fig. S8).

In conclusion, we have developed a new simple chemosensor **1** by the combination of an anthracene group as a chromophore moiety and a phenol group as a binding moiety toward hard metal ions such as the trivalent cations. The chemosensor **1** showed excellent turn-on fluorescence signals with high sensitivity and selectivity in the presence

Table 1
Association constants and detection limits for **1** with trivalent cations.

Cation	Ka	Detection limit / μM
Al^{3+}	1.4×10^5	2.4
Cr^{3+}	1.7×10^5	1.6
Fe^{3+}	1.4×10^5	0.6
Ga^{3+}	1.0×10^5	2.4
In^{3+}	1.4×10^5	2.0

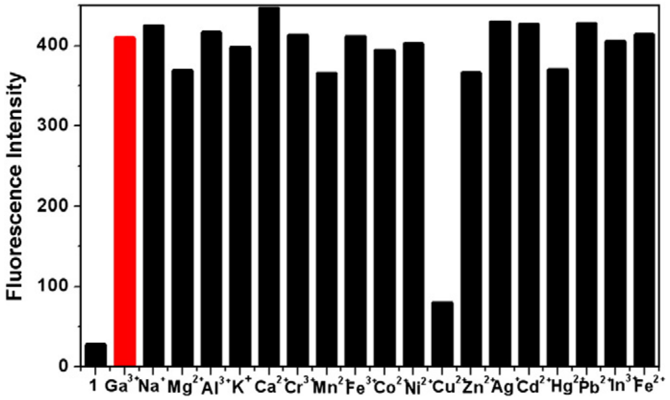


Fig. 5. Fluorescence intensity of **1** induced by various metal cations. Red bar represents emission intensity of **1** in the presence of 3 equiv of Ga^{3+}. Black bars stand for fluorescence change that occurs upon additionof 3 equiv of Na^{+}, Mg^{2+}, Al^{3+}, K^{+}, Ca^{2+}, Cr^{3+}, Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Ag^{+}, Cd^{2+}, Hg^{2+}, Pb^{2+}, In^{3+} and Fe^{2+} in the presence of Ga^{3+}.

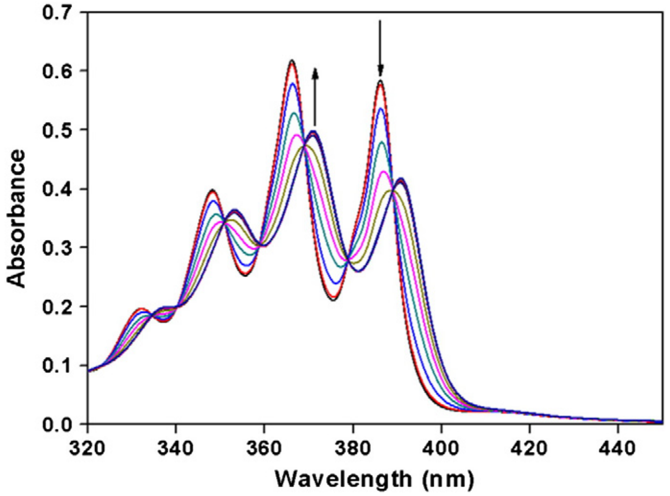


Fig. 6. UV-vis absorption spectra of **1** (6.0×10^{-5} M) upon addition of Al^{3+} in methanol.

of trivalent cations (Al^{3+}, Cr^{3+}, Fe^{3+}, Ga^{3+} and In^{3+}) in methanol, while monovalent and divalent cations had no effect on the fluorescence emission. The optical mechanism of **1** was proposed to be a PET process from the tertiary aliphatic nitrogen to the excited anthracene. The fluorescence probe had detection ability in the μM range and detected Fe^{3+} most sensitively among the trivalent cations. More importantly, Fe^{3+}could be obviously discriminated from Fe^{2+} by **1**. Therefore, **1** could be used as an optical sensor for the trivalent cations. Future study will focus on enhancing the water solubility of receptor and its potential applications in biological chemistry.

Acknowledgements

Financial support from Converging Research Center Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (2012001725, 2012008875 and 2013 K000334) is gratefully acknowledged. We thank Prof. MiSookSeo (EwhaWomans University) for ESI-Mass running.

Appendix A. Supplementary material

Supplementary data (experimental procedures and additional experimental data) associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.inoche.2013.08.025.

References

[1] Z. Xu, J. Yoon, D.R. Spring, Fluorescent chemosensors for Zn^{2+}, Chem. Soc. Rev. 39 (2010) 1996–2006.
[2] A.P. de Silva, H.Q.N. Gunaratne, T.A. Gunnlaugsson, J.M. Huxley, C.P. MeCoy, J.T. Rademacher, T.E. Rice, Signaling recognition events with fluorescent sensors and switches, Chem. Rev. 97 (1997) 1515–1566.
[3] J.F. Zhang, Y. Zhou, J. Yoon, J.S. Kim, Recent progress in fluorescent and colorimetric chemosensors for detection of precious metal ions (silver, gold and platinum ions), Chem. Soc. Rev. 40 (2011) 3416–3429.
[4] E.L. Que, D.W. Domaille, C.J. Chang, Metals in neurobiology: probing their chemistry and biology with molecular imaging, Chem. Rev. 108 (2008) 1517–1549.
[5] H.N. Kim, M.H. Lee, H.J. Kim, J.S. Kim, J. Yoon, A new trend in rhodamine-based chemosensors: applications of spirolactam ring-opening to sensing ions, Chem. Soc. Rev. 37 (2008) 1465–1472.
[6] Y. Xiao, A.A. Rowe, K.W. Plaxco, Electrochemical detection of parts-per-billion lead via an electrode-bound DNAzyme assembly, J. Am. Chem. Soc. 129 (2007) 262–263.
[7] H.N. Kim, W.X. Ren, J.S. Kim, J. Yoon, Fluorescent and colorimetric sensors for detection of lead, cadmium, and mercury ions, Chem. Soc. Rev. 41 (2012) 3210–3244.

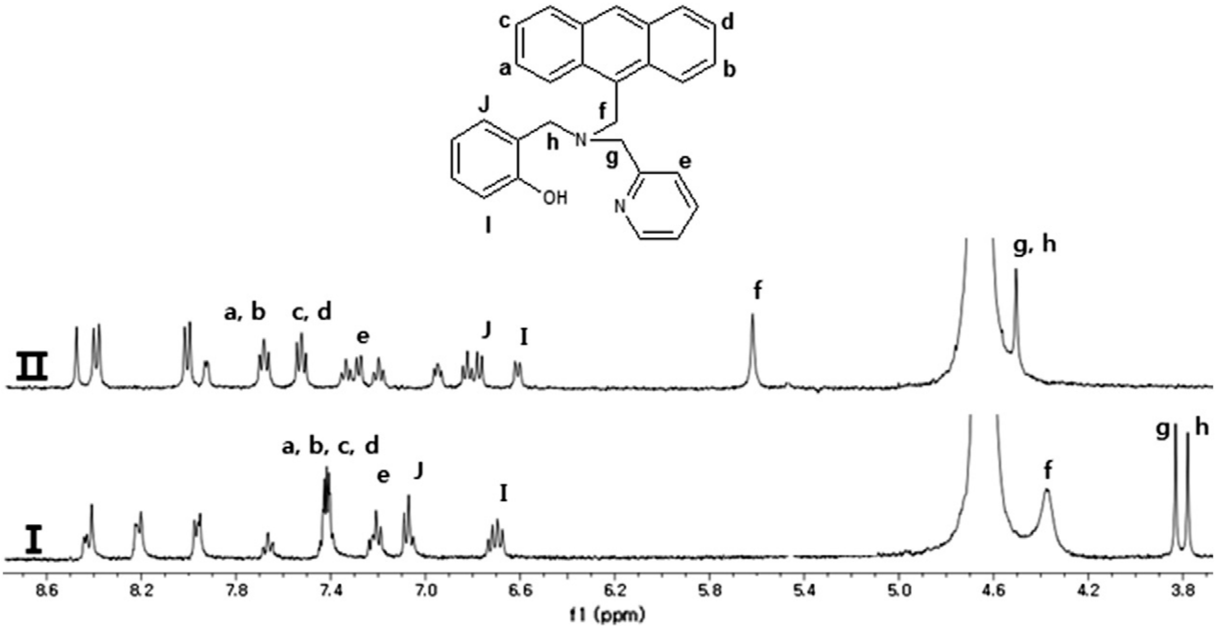


Fig. 7. ^{1}H NMR spectra of **1** with 0 and 1.0 equiv of Al^{3+} in CD_3OD: (I) **1**; (II) **1** with 1 equiv of Al^{3+}.

[8] T. Kawano, T. Kadono, T. Furuichi, S. Muto, F. Lapeyrie, Aluminium-induced distortion in calcium signaling involving oxidative burst and channel regulations in tobacco BY-2 cells, Biochem. Biophys. Res. Commun. 308 (2003) 35–42.

[9] L. Prodi, F. Balletta, M. Mantalti, N. Zaccheroni, Luminescent chemosensors for transition metal ions, Coord. Chem. Rev. 205 (2000) 59–83.

[10] S. Kabehie, M. Xue, A.Z. Stieg, M. Liong, K.L. Wang, J.I. Zink, Heteroleptic copper switches, J. Am. Chem. Soc. 132 (2010) 15987–15996.

[11] D. Astruc, E. Boisselier, C. Ornelas, Dendrimers designed for functions: from physical, photophysical, and supramolecular properties to applications in sensing, catalysis, molecular electronics, photonics and nanomedicine, Chem. Rev. 110 (2010) 1857–1959.

[12] J. Wu, W. Liu, J. Ge, H. Zhang, P. Wang, New sensing mechanisms for design of fluorescent chemosensors emerging in recent years, Chem. Soc. Rev. 40 (2011) 3483–3495.

[13] V. Amendola, L. Fabbrizzi, F. Forti, M. Licchelli, C. Mangano, P. Pallavicini, A. Poggi, D. Sacchi, A. Taglieti, Light-emitting molecular devices based on transition metals, Coord. Chem. Rev. 250 (2006) 273–299.

[14] T.H. Ma, M. Dong, Y.M. Dong, Y.W. Wang, Y. Peng, A unique water-tuning dual-channel fluorescence-enhanced sensor for aluminum ions based on a hybrid ligand from a 1,1-binaphthyl scaffold and an amino acid, Chem. Eur. J. 16 (2010) 10313–10318.

[15] F.K.W. Hau, X. He, W.H. Lam, V.W.W. Yam, Highly selective ion probe for Al^{3+} based on Au(I)···Au(I) interactions in a bis-alkynyl calix[4]arene Au(I) isocyanide scaffold, Chem. Commun. 47 (2011) 8778–8780.

[16] K.K. Upadhyay, A. Kumar, Pyrimidine based highly sensitive fluorescent receptor for Al^{3+} showing dual signalling mechanism, Org. Biomol. Chem. 8 (2010) 4892–4897.

[17] M. Dong, Y.M. Dong, T.H. Ma, Y.W. Wang, Y. Peng, A highly selective fluorescence-enhanced chemosensor for Al^{3+} in aqueous solution based on a hybrid ligand from BINOL scaffold and β-amino alcohol, Inorg. Chim. Acta 381 (2012) 137–142.

[18] D. Maity, T. Govindaraju, A differentially selective sensor with fluorescence turn-on response to Zn^{2+} and dual-mode ratiometric response to Al^{3+} in aqueous media, Chem. Commun. 48 (2012) 1039–1041.

[19] Y. Lu, S. Huang, Y. Liu, S. He, L. Zhao, X. Zeng, Highly selective and sensitive fluorescent turn-on chemosensor for Al^{3+} based on a novel photo-induced electron transfer approach, Org. Lett. 13 (2011) 5274–5277.

[20] X. Sun, Y.W. Wang, Y. Peng, A selective and ratiometric bifunctional fluorescent probe for Al^{3+} ion and proton, Org. Lett. 14 (2012) 3420–3423.

[21] S. Kim, J.Y. Noh, K.Y. Kim, J.H. Kim, H.K. Kang, S.W. Nam, S.H. Kim, S. Park, C. Kim, J. Kim, Salicylimine-based fluorescent chemosensor for aluminum ions and application to bioimaging, Inorg. Chem. 51 (2012) 3597–3602.

[22] J. Lee, H. Kim, S. Kim, J.Y. Noh, E.J. Song, C. Kim, J. Kim, Fluorescent dye containing phenol-pyridyl for selective detection of aluminum, Dyes Pigments 96 (2013) 590–594.

[23] H.M. Park, B.N. Oh, J.H. Kim, W. Qiong, I.H. Hwang, K.D. Jung, C. Kim, J.K., Fluorescent chemosensor based-on naphthol-quinoline for selective detection of aluminum ions, Tetrahedron Lett. 52 (2011) 5581–5584.

[24] J. Kang, H.K. Kang, H. Kim, J. Lee, E.J. Song, K.D. Jeong, C. Kim, J. Kim, Fluorescent chemosensor based on bispicolylamine for selective detection of magnesium ions, Supramol. Chem. 25 (2013) 65–68.

[25] D. Maity, T. Govindaraju, Conformationally constrained (coumarin–triazolyl–bipyridyl) click fluoroionophore as a selective Al^{3+} sensor, Inorg. Chem. 49 (2010) 7229–7231.

[26] J.Y. Jung, S.J. Han, J. Chun, C. Lee, J. Yoon, New thiazolothiazole derivatives as fluorescent chemosensors for Cr^{3+} and Al^{3+}, Dyes Pigments 94 (2012) 423–426.

[27] A.K. Singh, A. Panwar, S. Kumar, S. Baniwal, Chromium(III)-selective electrode based on a macrocyclic compound, Analyst 124 (1999) 521–525.

[28] M. Elavarasi, M.L. Paul, A. Rajeshwari, N. Chandrasekaran, A.B.. Mandal, Studies on fluorescence determination of nanomolar Cr(III) in aqueous solutions using unmodified silver nanoparticles, Anal. Methods 4 (2012) 3407–3412.

[29] M. Ezer, S.A. Elwood, J.B. Simeonsson, A new scheme for trace determination of chromium using electrothermal atomization-laser induced fluorescence spectrometry, J. Anal. At. Spectrom. 16 (2001) 1126–1130.

[30] A. Safavi, M. Sadeghi, A PVC-membrane bulk optode for gallium(III) ion determination, Talanta 71 (2007) 339–343.

[31] J. Kimura, H. Yamada, H. Ogura, T. Yajima, T. Fukushima, Development of a fluorescent chelating ligand for gallium ion having a quinoline structure with two Schiff base moieties, Anal. Chim. Acta 635 (2009) 207–213.

[32] F. Fages, B. Bodenant, T. Weil, Fluorescent, siderephore-based chelators. Design and synthesis of a trispyrenyl trishydroxamate ligand, an interamolecular excimer-forming sensing molecule which responds to Iron(III) and Gallium(III) metal cations, J. Org. Chem. 61 (1996) 3956–3961.

[33] J.A.J. Pardoe, A.J. Downs, Development of the chemistry of indium in formal oxidation states lower than +3, Chem. Rev. 107 (2007) 2–45.

[34] S. Sen, S. Sarkar, B. Chattopadhyay, A. Moirangthem, A. Basu, K. Dhara, P. Chattopadhyay, A ratiometric fluorescent chemosensor for iron: discrimination fo Fe^{2+} and Fe^{3+} and living cell application, Analyst 137 (2012) 3335–3342.

[35] J. Mao, L. Wang, W. Dou, X. Tang, Y. Yan, W. Liu, Tuning the selectivity of two chemosensors to Fe(III) and Cr(III), Org. Lett. 9 (2007) 4567–4570.

[36] R. Wang, F. Yu, P. Liu, L. Chen, A turn-on fluorescent probe based on hydroxylamine oxidation for detecting ferric ion selectively in living cells, Chem. Commun. 48 (2012) 5310–5312.

[37] Y. Xinag, A. Tong, A new phodamine-based chemosensor exhibiting selective Fe$^{\mathrm{III}}$-amplified fluorescence, Org. Lett. 8 (2006) 1549–1552.

[38] N.R. Chereddy, S. Thennarasu, A.B.. Mandal, Incorporation of triazole into a quinoline-rhodamine conjugate imparts iron(III) selective complexation permitting detection at nanomolar levels, Dalton Trans. 41 (2012) 11753–11759.

[39] L. Huang, F. Hou, J. Cheong, P. Xi, F. Chen, D. Bai, Z. Zeng, Selective off-on fluorescent chemosensor for detection of Fe^{3+} ions in aqueous media, Org. Biomol. Chem. 10 (2012) 9634–9638.

[40] Q. Mei, C. Jiang, G. Guan, K. Zhang, B. Liu, R. Liu, Z. Zhang, Fluorescent grapheme oxide logic gates for discrimination of iron (3+) and iron (2+) in living cells by imaging, Chem. Commun. 48 (2012) 7468–7470.

[41] E.L. Que, D.W. Domaille, C.J. Chang, Metals in neurobiology: probing their chemistry and biology with molecular imaging, Chem. Rev. 108 (2008) 1517–1549.

[42] D.Y. Lee, N. Singh, D.O. Jang, Ratiometric and simultaneous estimation of Fe^{3+} and Cu^{2+} ions: 1,3,5-substituted triethylbenzene derivatives coupled with benzimidazole, Tetrahedron Lett. 52 (2011) 3886–3890.

[43] S.K. Sahoo, D. Sharma, R.K. Bera, G. Criponi, J.F. Callan, Iron(III) selective molecular and supramolecular fluorescent probes, Chem. Soc. Rev. 41 (2012) 7195–7227.

[44] Q. Mei, C. Jiang, G. Guan, K. Zhang, B. Liu, R. Liu, Z. Zhang, Iron(III) selective molecular and supramolecular fluorescent probes, Chem. Commun. 48 (2012) 7468–7470.

[45] A. Mitra, B. Ramanujam, C.P. Rao, 1-(D-Glucopyranosyl-2′-deoxy-2′-iminomethyl)-2-(hydroxynaphthalene as chemo-sensor for Fe^{3+} in aqueous HEPES buffer based on colour changes observable with the naked eye, Tetrahedron Lett. 50 (2009) 776–780.

[46] A. Barba-Bon, A.M. Costero, S. Gil, B. Parra, J. Soto, R. Martinez-Manez, F. Sancenon, A new selective fluorogenic probe for trivalent cations, Chem. Commun. 48 (2012) 3000–3002.

[47] S. Gowami, K. Aich, A.K. Das, A. Manna, S. Das, A naphthalimide-quionline based probe for selective, fluorescence ratiometric sensing of trivalent ions, RSC Adv. 3 (2013) 2412–2416.

[48] R.G. Pearson, Hard and soft acids and basis, J. Am. Chem. Soc. 85 (1963) 3533–3539.

[49] J.H. Kim, I.H. Hwang, S.P. Jang, J. Kang, S. Kim, I. Noh, Y. Kim, C. Kim, R.G. Harrison, Zinc sensors with lower binding affinities for cellular imaging, Dalton Trans. 42 (2013) 5500–5507.

[50] H.G. Lee, J.H. Lee, S.P. Jang, H.M. Park, S.J. Kim, Y. Kim, C. Kim, R.G. Harrison, Zinc selective chemosensor based on pyridyl-amide fluorescence, Tetrahedron 67 (2011) 8073–8078.

[51] H.G. Lee, J.H. Lee, S.P. Jang, I.H. Hwang, S.J. Kim, Y. Kim, C. Kim, R.G. Harrison, Zinc selective chemosensor based on quinoline and the flexible dipicolylamine, Inorg. Chim. Acta 394 (2013) 542–551.

[52] K. Ghosh, I. Saha, Selective sensing of Zn (II) ion by a simple anthracene-based tripodal chemosensor, Tetrahedron Lett. 51 (2010) 4995–4999.

[53] A.L. Garner, K. Koide, Oxidatin state-specific fluorescent method for Palladium(II) and Platimum(IV) based on the catalyzed aromatic claisen rearrangement, J. Am. Chem. Soc. 130 (2008) 16472–16473.