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A “turn-on” fluorescent chemosensor for aluminum ion and cell imaging application

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Abstract

A simple and efficient fluorescent chemosensor for Al^{3+} is reported in the paper. The chemosensor is obtained by dehydration reaction of 2-hydroxy-1-naphthaldehyde and 2-aminophenol. The chemosensor has high selectivity and sensitivity for Al^{3+} and displays fluorescence "off-on" switch signal. The detection limit of the chemosensor for Al^{3+} can reach 1.0×10^{-7} M in DMSO/H_2O (1:9, v/v) solution. The mass spectra and Job's plot analysis confirm the 1:1 stoichiometry between chemosensor and Al^{3+}. Potential utilization of the probe as an intracellular sensor of Al^{3+} in human cancer (HiSa) cells is also examined by confocal fluorescence microscopy.

Keywords: Fluorescence, Chemosensor, Aluminum ion, Naphthalene, Cells imaging

1. Introduction

Aluminum is the third most prevalent (8.3% by weight) metallic element in the earth. It has been widely used in packing materials, clinical drugs, food additives and water purification et al [1-4]. The excess of aluminum can cause many health hazards such as Alzheimer's disease [5,6], Parkinson's disease [7], Osteomalacia [8], and even to the risk of cancer of the breast [9]. Additionally, the World Health Organization (WHO) prescribed the average daily human intake of aluminum as around 3-10 mg with a weekly tolerable dietary intake of 7 $mg \cdot kg^{-1}$ body weight. The WHO has listed Aluminum as a source of food pollution and limited its drinking water concentration to 7.41 mM [10]. Therefore, it is necessary and highly desirable to develop some analytical methods for detecting and controlling the concentration levels of aluminum in the environmental and biological systems.

In the past ten years, several methods used for quantification of aluminum ion are atomic absorption spectrometry (AAS) [11,12], inductively coupled plasma mass spectroscopy (ICPMS) [13], inductively coupled plasma atomic emission spectrometry (ICP-AES) [14], electrochemical method [15,16] and fluorescent chemosensors. Compared with other methods, the fluorescence method can provide a simple and cost-effective detection way together with high sensitivity, good selectivity, short response time, real-time monitoring [17,18]. However, the poor coordination ability of aluminum ion makes it develop slowly. It is because, as a hard acid, aluminum ion prefers to coordinate with hard base such as N and O atoms. Schiff bases (imine) are well known to be good ligands for metal ions [19,20]. Several publications have demonstrated that Schiff bases with proper placement of additional N or O as donor atoms can form stable complexes with transition metal ions and have been used as the ionophore in optical sensors for determining various cations [21-23].

Herein, we designed and prepared a simple chemosensor 1-{[(2-hydroxyphenyl)-imino]methyl}naphthalen-2-ol (HPIN) with Schiff-base unit and naphthalene group. Based on photoinduced electron transfer (PET) mechanism, the weak fluorescence of HPIN happens obvious enhancement with the addition of only Al^{3+}. The mass spectra and Job's plot titration curve are be used to study the bonding ratio of HPIN and Al^{3+}.

In order to develop potential utilization of HPIN, as intracellular sensors, the interaction of HPIN with Al^{3+} in human cancer (HiSa) cells is examined by confocal fluorescence microscopy.

2. Experimental

2.1. Materials and instruments

All chemicals were obtained from commercial suppliers and used without further purification. ^{1}H NMR spectra were recorded on Bruker 300 MHz spectrometers, the chemical shifts (δ) were reported as ppm in DMSO-d_6. IR spectra were recorded with a ThermoFisher Nicolet iS5 FT-IR spectrophotometer as KBr pellets with absorption reported in cm^{-1}. Elemental analyses were measured on a EuroVector EA3000 elemental analyzer. ESI-MS spectra were recorded on an Agilent 6520 Accurate-Mass Q-TOF LC/MS mass spectrometer. UV-visible (UV-Vis) spectra were measured with a Varian 50 BIO spectrophotometer. Fluorescence spectra were recorded on an F-4600 fluorescence spectrophotometer equipped with quartz cuvettes of 1 cm path length at room temperature. Both the excitation and emission slit widths were 5.0 nm.

2.2 UV-vis and fluorescence spectra studies

Stock solutions of various metal ions (1.0 mM) were prepared using nitrate salts. A stock solution of HPIN (1.0 mM) in DMSO was prepared. Double-distilled water was used throughout the experiments. The working solution of HPIN was then diluted to 1.0 μM in DMSO/H_2O (1:9, v/v) solution. In fluorescence titration experiments, each time a 2 mL solution of L (1.0 μM) was filled in a quartz optical cell of 1 cm optical path length, and the ions stock solution were added into the quartz optical cell gradually by using a pipette. The binding constants were obtained from the emission intensity data following the modified Benesi-Hildebrand equation [24] (A):

$$\frac{1}{F - F_{min}} = \frac{1}{K(F_{max} - F_{min})[Al^{3+}]} + \frac{1}{F_{max} - F_{min}}$$

where F_{min}, F, and F_{max} are the emission intensities of the organic moiety considered in the absence of aluminum ion, at an intermediate aluminum concentration, and at a concentration of complete interaction, respectively, and where K is the binding

constant.

2.3 Preparation of HPIN and HPIN/Al^{3+} complex [25,26]

The fluorescent chemosensor 1-{[(2-hydroxyphenyl)imino]methyl}naphthalen-2-ol (HPIN) was designed and synthesized in one step as shown in Scheme 1. 2-Hydroxy-1-naphthaldehyde (1.72g, 10.0 mmol) in 50 ml absolute ethanol was added drop wise into a solution of 2-aminophenol (1.09 g, 10.0 mmol) in 50 ml absolute ethanol under stirring. And then, the reaction mixture was further stirred for 4 h at room temperature until an orange-yellow precipitate appeared. The resulting precipitate was filtered and washed 2 times with ice ethanol. The solid obtained was recrystallized from ethanol to give orange-yellow crystals. Yield: 85%, m.p.: 252-253 °C. Anal. Calc. for $C_{17}H_{13}NO_2$: C, 77.55; H, 4.98; N, 5.32. Found: C, 78.27; H, 5.02; N, 5.09. IR (KBr pellet, cm^{-1}): 3427 (OH), 1632 (C=N); ^1H NMR (DMSO-d_6, δ_H, ppm): 10.32 (s, 1H), 9.51 (d, 1 H), 8.40 (d, 1 H), 7.95 (d, 1 H), 7.82 (d, 1 H), 7.69 (d, 1 H), 7.51 (t, 1 H), 7.29 (t, 1 H), 7.11 (d, 1 H), 7.01 (m, 2H), 6.79 (d, 1 H). ESI-MS (*m/z)*: $[M+H]^+$= 264.1018.

A mixture of HPIN (0.26 g, 1.0 mmol) and $Al(NO_3)_3 \cdot 9H_2O$ (0.38 g, 1.0 mmol) in 10 mL of methanol was stirred and refluxed for 5 h. The reaction mixture was concentrated by rotary evaporation and cooled to precipitate solid. The solid was collected on a Buchner funnel, washed thoroughly with methanol and dried at ambient temperature to obtain yellow brown solid. Yield 68%. IR (KBr pellet, cm^{-1}): 3423 (OH), 1621 (C=N), 1384 (NO_3). ESI-MS (*m/z)*: $[(M-2H)+Al(III)]^+$=288.0584, $[(M-2H)+Al(III)+H_2O]^+$=306.0701, $[(M-2H)+Al(III)+CH_3OH]^+$=320.0859, $[(M-2H)+Al(III)+H_2O+Na]^+$=329.0862, $[(M-2H)+Al(III)+2H_2O+Na]^+$=347.0969, $[(M-2H)+Al(III)+H_2O+CH_3OH+Na]^+$=361.1125, $[(M-2H)+Al(III)+H_2O+NO_3+2]^+$=370.1126.

2.4 Cells culture and imaging

Under a humid atmosphere containing 5% CO_2, SiHa cells were grown in DMEM medium containing 10% FBS routinely, then harvested for subculture using trypsin (0.05%, Gibco/Invitrogen) at 37 °C. SiHa cells were incubated onto a 35 mm ×35 mm Petri dish with a glass bottom, then allowed to grow for 24 h for attachment, after which 1 mL of DMEM medium containing 10% 5 μM compound HPIN was used to

incubated the SiHa cells at 37 ºC for 5 h. The medium was replaced and phosphate-buffered saline (PBS, pH =7.4) was used to wash the cells thrice. And two equivalent metal ion in PBS buffer solution were added into the dish and the cells were cultured at 37 ºC for 1 h. The medium was replaced and phosphate-buffered saline (PBS, pH =7.4) was used to wash the cells thrice. Then fresh medium with cytoplasm located dye (Lyso tracker red) was added and incubated. After washing thrice with PBS, the images of the cells were recorded on confocal laser scanning microscopy.

3. Results and discussion

3.1 UV-Vis absorption and fluorescence emission spectra of HPIN with Al^{3+}

Firstly, the interaction of HPIN with Al^{3+} was investigated by UV-Vis absorption spectrum. ***Fig.S1*** shows the change of the UV-vis spectrum of HPIN with addition of Al^{3+} in DMSO/H_2O (1:9, v/v) solution. As can be seen from ***Fig.S1***, Upon the addition of Al^{3+}, the absorption intensities of HPIN peaks about 450 nm (n-π* transition from imine) and 310 nm (π-π* transition from naphthalene) all gradual decrease with the solution color from blue to yellow under λ_{365} nm irradiation (**Scheme 1**). Next, the fluorescence response behavior of HPIN with Al^{3+} was also examined in DMSO/H_2O (1:9, v/v) solution. As shown in **Fig.1**, the HPIN almost not shows fluorescence peak at 524 nm when it is excited at 440 nm in DMSO/H_2O (1:9, v/v) solution. However, upon the addition of Al^{3+}, the fluorescence intensity of HPIN at 524 nm shows a significant fluorescence enhancement. The fact displays that HPIN is a "turn-on" fluorescence probe for Al^{3+} and 20-fold enhancement of fluorescence intensity at 524 nm can obtain only at Al^{3+}/HPIN (1/1) condition. Based on the fluorescence titration, the binding constant of HPIN for Al^{3+} has been estimated using the Benesi-Hildebrand equation (A). The stability constant is determined as 2.2×10^4, that is within the range 10^3-10^9 of those reported for Al^{3+}-binding sensors [27-29].

To reflect the high sensitivity, the detection limit was evaluated by using the method of gradually decreasing concentration of Al^{3+}. When the concentration of Al^{3+}

decreases to 0.1μM，an observable stripping peak was observed. When further decreasing the concentration, the stripping peak almost disappears. So, the detection limit is evaluated to be 1.0×10^{-7} M, which enables to meet the detection of Al^{3+} in many chemical and biological systems [30,31]. Noticeable, it is a good linear relation for relative intensities of HPIN to Al^{3+} concentrations (**Fig.2**).

3.2 The binding mode and action mechanism of HPIN with Al^{3+}

To explore the binding mode between HPIN and Al^{3+} complex, binding analysis was carried out by the Job's plot method (**Fig.3**). The total concentration of HPIN and Al^{3+} was 1.0 μM in the experimental process and the concentration of HPIN and Al^{3+} changed correspondingly. As can be seen from **Fig.3**, the maximum mole fraction of HPIN to Al^{3+} is 0.5, which established a 1:1 binding stoichiometry of HPIN to Al^{3+}. The 1:1 coordination stoichiometry was further confirmed from ESI-MS spectra, where some peaks at m/z 288.0584 with 7% abundance, assignable to $[(M-2H)+Al(III)]^+$, $[(M-2H)+Al(III)+H_2O]^+$, m/z, 306.0701 (observed with 3% abundance) and $[(M-2H)+Al(III)+CH_3OH]^+$, m/z, 320.0859, (observed with 30% abundance 288.0584 ($[HPIN-2H+Al]^+$) were clearly observed (**Fig.S2** and **S3**). Additionally, Compared the IR spectra of the complex with HPIN (**Fig.S4** and **S5**), we can see two differences: (i) the stretch vibration of imine group (C=N) at 1632 cm^{-1}, which was a strong and sharp absorption band, changed to 1621 cm^{-1}, a mild and broad band; (ii) The new intense absorption band at 1384 cm^{-1} corresponding to the NO_3 stretching vibration appeared. These differences suggest that the imine groups and NO_3 group took part in the coordination with Al^{3+}. From these data, it may be deduced that the possible coordination modes of HPIN/Al^{3+} complex is 1:1 binding stoichiometry.

Based on the above results, the supposed action mechanism of HPIN with Al^{3+} is listed in **Scheme 1**. Due to the photoinduced electron transfer from the nonbonding electron pair from nitrogen atom to the fluorophore (naphthyl ring), the fluorescence of HPIN is restrained. So, the fluorescence of HPIN is "off" state. When introducing Al^{3+} to HPIN probe, the restrained fluorescence of HPIN is released owing to the binding of Al^{3+} with nitrogen and oxygen atoms, which will destroy the PET process in HPIN [32-36]. In the fact, the fluorescence of HPIN is "on" state with the addition

of Al^{3+}. In other word, HPIN can be used to determine Al^{3+} with fluorescence "off-on" response.

3.3 Selectivity of HPIN probe for Al^{3+}

For a chemosensor, the selectivity for analytes is one of the most important parameters. Hence, the interactions of HPIN with other metal ions were studied by fluorescence technique. From **Fig.4**, the fluorescence intensity of HPIN takes place a significant enhancement with only addition of Al^{3+} in many metal ions (Na^{+}, K^{+}, Ca^{2+}, Al^{3+}, Mg^{2+}, Mn^{2+}, Zn^{2+}, Co^{2+}, Pb^{2+}, Cu^{2+}, Cd^{2+}, Ni^{2+}, Ag^{+}, Fe^{3+}, Cr^{3+}, Ba^{2+}, Bi^{3+}, Hg^{2+}, Sr^{2+}, Ga^{3+}, In^{3+}). And, compared with other metal ions, the relative intensity of HPIN (1.0×10^{-6} mol/L) can reach 19-fold enhancement in one equiv. Al^{3+} (1.0×10^{-6} mol/L, **Fig.S6**), which displays HPIN has a high selectivity for Al^{3+}.

In view of interference factors in practical applicability, the fluorescence competitive experiments of HPIN/Al^{3+} with other various metal ions were also investigated, respectively (**Fig.5**). As can be seen from **Fig.5**, the fluorescence emission intensity of HPIN/Al^{3+} solution containing other metal ions (Na^{+}, K^{+}, Ca^{2+}, Mg^{2+}, Mn^{2+}, Zn^{2+}, Co^{2+}, Pb^{2+}, Cu^{2+}, Cd^{2+}, Ni^{2+}, Ag^{+}, Fe^{3+}, Cr^{3+}, Ba^{2+}, Bi^{3+}, Hg^{2+}, Sr^{2+}, Ga^{3+}, In^{3+}) did not show significant variation by comparison with the fluorescence intensity of HPIN/Al^{3+} solution, respectively. These results suggest that HPIN may be used for the selective detection of Al^{3+} ion in practical sample with a little interference.

3.4 Cell Imaging in Vitro

Biological application of HPIN to detect Al^{3+} was investigated by confocal laser scanning microscope (CLSM). Firstly, the SiHa cells were cultured with compound HPIN at 37 °C for 5 h, and then, the two equivalent Al^{3+} were added the system and sequentially cultured the cells for 1 h. The fluorescence imaging was taken, where Lyso tracker red was used as a cytoplasm located dye. As shown in **Fig.6**, the cytoplasm regions of SiHa cells are stained by HPIN/Al^{3+} and well overlay with cytoplasm located dye (Lyso tracker red). Obviously, the cells can be illumed by introducing Al^{3+} to SiHa cells with HPIN. Based on control experiments, we can obtain a fact that HPIN can be used to detect and tract Al^{3+} in intracellular with

"off-on" fluorescence signal.

4. Conclusion

In summary, a simple and facile chemosensor HPIN for Al^{3+} with fluorescence "off-on" signal was obtained. The chemosensor displays high selectivity and sensitivity for Al^{3+} in DMSO/H_2O (v/v=1/9). Based on these experimental data, the work has the following features: (1) the fluorescence receptor is simple and easily prepared; (2) the receptor HPIN has higher sensitivity and selectivity for Al^{3+} and may be used to determine Al^{3+}; (3) it is a fluorescence "off-on" probe; (4) the detection of HPIN for Al^{3+} may be realized in biological system. In view of above points, the work not only obtains a facile chemosensor for Al^{3+}, but also provides a new strategy for designing simple fluorescence receptors for metal ions recognition.

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Appendix. Supplementary data

Other fluorescence spectroscopy (PDF) and characteristic data associated with this article can be found in the online version, at doi:

References

[1] M.G. Soni, S.M. White, W.G. Flamm, G.A. Burdock, Safety evaluation of dietary aluminum, Regul. Toxicol. Pharmacol. 33 (2001) 66-79.

[2] R. Azadbakht, T. Almasi, H. Keypour, M. Rezaeivala, A new asymmetric Schiff base system as fluorescent chemosensor for Al^{3+} ion, Inorg. Chem. Commun. 33 (2013) 63-67.

[3] Z.C. Liu, Z.Y. Yang, Y.X. Li, T.R. Li, B.D. Wang, Y. Li, X.L. Jin, An effective mutli-wavelength emissive aluminum ion fluorescence chemosensor based on 3-[1′-(2′-hydroxy-α-methylbenzylidene-imino)]-2-(*p*-*N*,*N*-dimethylaminophenyl)-1,2-dihydroquinazolin-4-(3H)-one, Inorganica Chimica Acta. 395 (2013) 77-80.

[4] A.J. Blotcky, D. Hobson, J.A. Leffler, E.P. Rack, R.R. Recker, Determination of trace aluminum in urine by neutron activation analysis, Anal. Chem. 48 (1976) 1084-1088.

[5] T.P. Flaten, Aluminium as a risk factor in Alzheimer's disease, with emphasis on drinking water. Brain Res. Bull. 55 (2001) 187-196.

[6] D. P. Perl, A. R. Brody, Alzheimer's disease: X-Ray spectrometric evidence of aluminum accumulation in neurofibray tangle-bearing neurons, Science 208 (1980) 297-299.

[7] D. P. Perl, D. C. Gajdusek, R. M. Garruto, R. T. Yanagihara, C. J. Gibbs, Intraneuronal aluminum accumulation in amyotrophic lateral sclerosis and Parkinsonism-dementia of gauam, Science 217 (1982) 1053-1055.

[8] G.C. Woodson, An interesting case of osteomalacia due to antacid use associated with stainable bone aluminum in a patient with normal renal function, Bone 22 (1998) 695-698.

[9] P.D. Darbre, Aluminium, antiperspirants and breast cancer, J. Inorg. Biochem. 99 (2005) 1912-1919.

[10] Z. Krejpcio, R.W. Wojciak, The influence of Al^{3+} ions on pepsin and trypsin activity in vitro, Polish Journal of Environmental Studies 11 (2002) 251-254.

[11] T.A. Zafar, D. Teegarden, C. Ashendel, M.A. Dunn, C.M. Weaver, Aluminum negatively impacts calcium utilization and bone in calcium-deficient rats. Nutr. Res. 24(2004) 243-259.

[12] C. Guo, G.W. Hsu, C. Chuang, P. Chen, Aluminum accumulation induced testicular oxidative stress and altered selenium metabolism in mice, Environ.

Toxicol. Phar. 27 (2009) 176-181.

[13] B. Deng, J. Feng, J. Meng, Speciation of inorganic selenium using capillary electrophoresis– inductively coupled plasma-atomic emission spectrometry with on-line hydride generation, Anal. Chim. Acta 583 (2007) 92-97.

[14] P. Olmedo, A. Pla, A.F. Hernández, O. López-Guarnido, L. Rodrigo, F. Gil, Validation of a method to quantify chromium, cadmium, manganese, nickel and lead in human whole blood, urine, saliva and hair samples by electrothermal atomic absorption spectrometry, Anal. Chim. Acta 659 (2010) 60-67.

[15] R.S. Maharia, R.K. Dutta, R. Acharya, A. Reddy, Heavy metal bioaccumulation in selected medicinal plants collected from Khetri copper mines and comparison with those collected from fertile soil in Haridwar, India, J. Environ. Sci. Health B 45 (2010) 174-181.

[16] S. Kameo, K. Nakai, N. Kurokawa, T. Kanehisa, A. Naganuma, H. Satoh, Metal components analysis of metallothionein2 III in the brain sections of metallothionein-I and metallothionein-II null mice exposed to mercury vapor with HPLC/ICP/MS, Anal. Bioanal. Chem. 381 (2005) 1514.

[17] F. Yu, X. Han, L. Chen, Fluorescent probes for hydrogen sulfide detection and bioimaging, Chem. Commun. 50 (2014) 12234-12249.

[18] R. Wang, C. Yu, F. Yu, L. Chen, C. Yu, Molecular fluorescent probes for monitoring pH changes in living cells, TrAC Trends Anal. Chem. 29 (2010) 1004-1013.

[19] Y. Xu, J. Meng, L. Meng, Y. Dong, Y. Cheng, C. Zhu, A highly selective fluorescence-based polymer sensor incorporating an (*R*,*R*)-salen moiety for Zn^{2+} detection, Chem. Eur. J. 16 (2010) 12898-12903.

[20] R. Joseph, J.P. Chinta, C.P. Rao, Lower rim 1,3-diderivative of calix[4]arene-appended salicylidene imine (H_2L): experimental and computational studies of the selective recognition of H_2L toward Zn^{2+} and sensing phosphate and amino acid by [ZnL], J. Org. Chem. 75 (2010) 3387-3395.

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

(2010) 7229-7231.

[22] D. Maity, T. Govindaraju, Pyrrolidine constrained bipyridyl-dansyl click fluoroionophore as selective Al^{3+} sensor, Chem. Commun. (2010) 4499-4501.

[23] R. Azadbakht, J. Khanabadi, A novel aluminum-sensitive fluorescent nano-chemosensor based on naphthalene macrocyclic derivative, Tetrahedron 69 (2013) 3206-3211.

[24] H.A. Benesi, J.H. Hildebrand, A spectrophotometric investigation of the interaction of iodine with aromatic hydrocarbons, J. Am. Chem. Soc. 71 (1949) 2703-2707.

[25] D. Sharma, S.K. Sahoo, R.K. Bera, R. Kamal, Spectroscopic and computational study of a naphthalene derivative as colorimetric and fluorescent sensor for bioactive anions, J Fluoresc 23 (2013) 387-392.

[26] S. Das, D. Karak, S. Lohar, A. Banerjee, A. Sahana, D. Das, Interaction of a naphthalene based fluorescent probe with Al^{3+}: experimental and computational studies, Anal. Methods 4 (2012) 3620-3624.

[27] Y.K. Jang, U.C. Nam, H.L. Kwon, I.H. Hwang, C. Kim, A selective colorimetric and fluorescent chemosensor based-on naphthol for detection of Al^{3+} and Cu^{2+}, Dyes Pigment. 99 (2013) 6-13.

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

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

[30] L. Mei, Y. Xiang, N. Li, A.J. Tong, A new fluorescent probe of rhodamine B derivative for the detection of copper ion , Talanta 72 (2007) 1717-1722.

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

[32] S. Sinha, R.R. Koner, S. Kumar, J.M. Monisha, P.V. Kazi, S. Ghosh,

Imine containing benzophenone scaffold as an efficient chemical device to detect selectively Al^{3+} , RSC Adv. 3 (2013) 345-351.

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

[34] 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 andplatinum ions), Chem. Soc. Rev. 7 (2011) 3416-3429.

[35] A. Ajayaghosh, P. Carol, S. Sreejith, A ratiometric fluorescence probe for selective visual sensing of Zn^{2+}, J.Am. Chem. Soc. 127 (2005) 14962-14963.

[36] A.P. de Silva, H.Q. Gunaratne, T. Gunnlaugsson, A.J. Huxley, C.P. McCoy, J.T. Rademacher, T.E. Rice, Signaling recognition events with fluorescent sensors and switches, Chem. Rev. 97 (1997) 1515-1566.

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The scheme and figures captions

Scheme 1. The probable bonding model of HPIN with Al^{3+} and the color change of HPIN (2.0×10^{-5} mol/L) solution by introducing Al^{3+} (2.0×10^{-4} mol/L).

Fig. 1. Fluorescence spectra of HPIN (1.0×10^{-6} mol/L) in DMSO/H_2O (1:9, v/v) solution upon the addition of Al^{3+} (0, 0 mol/L; 1, 1.0×10^{-7} mol/L; 2, 2.0×10^{-7} mol/L; 3, 3.0×10^{-7} mol/L; 4, 4.0×10^{-7} mol/L; 5, 5.0×10^{-7} mol/L; 6, 6.0×10^{-7} mol/L; 7, 7.0×10^{-7} mol/L; 8, 8.0×10^{-7} mol/L; 9, 9.0×10^{-7} mol/L; 10, 1.0×10^{-6} mol/L; 11, 1.2×10^{-6} mol/L 12, 1.5×10^{-6} mol/L, respectively.) with an excitation of 440 nm.

Fig.2. Characteristic fluorescence response by the introduction of Al^{3+} to the HPIN (1.0×10^{-6} mol/L) in DMSO/H_2O (1:9, v/v) solution. The concentrations of Al^{3+} are from 1.0×10^{-7} to 1.0×10^{-6} mol/L.

Fig.3. Job plot of HPIN and Al^{3+} in DMSO/H_2O solution (1:9, v/v). The total concentration of HPIN and Al^{3+} is 1.0×10^{-6} mol/L.

Fig.4. Fluorescence spectra of HPIN (1.0×10^{-6} mol/L) in DMSO/H_2O (1:9, v/v) solution by adding metal ions (1.0×10^{-6} mol/L), respectively.

Fig.5. Characteristic fluorescence response of HPIN (1.0×10^{-6} mol/L) with Al^{3+} in the presence of other metal ions (Na^+, K^+, Ca^{2+}, Mg^{2+}, Mn^{2+}, Zn^{2+}, Co^{2+}, Pb^{2+}, Cu^{2+}, Cd^{2+}, Ni^{2+}, Ag^+, Fe^{3+}, Cr^{3+}, Ba^{2+}, Bi^{3+}, Hg^{2+}, Sr^{2+}, Ga^{3+}, In^{3+}, respectively) in DMSO/H_2O (1:9, v/v) solution.

Fig.6. Fluorescence imaging of SiHa cells with HPIN. a) is bright image, b) is fluorescence image of cytoplasm located dye (Lyso tracker red), c) is fluorescence image of HPIN and Al^{3+}, d) is fluorescence image of HPIN, e) is merged image of located dye and HPIN/Al^{3+}, f) is merged bright image and fluorescence image of located dye and HPIN/Al^{3+}.

Scheme 1

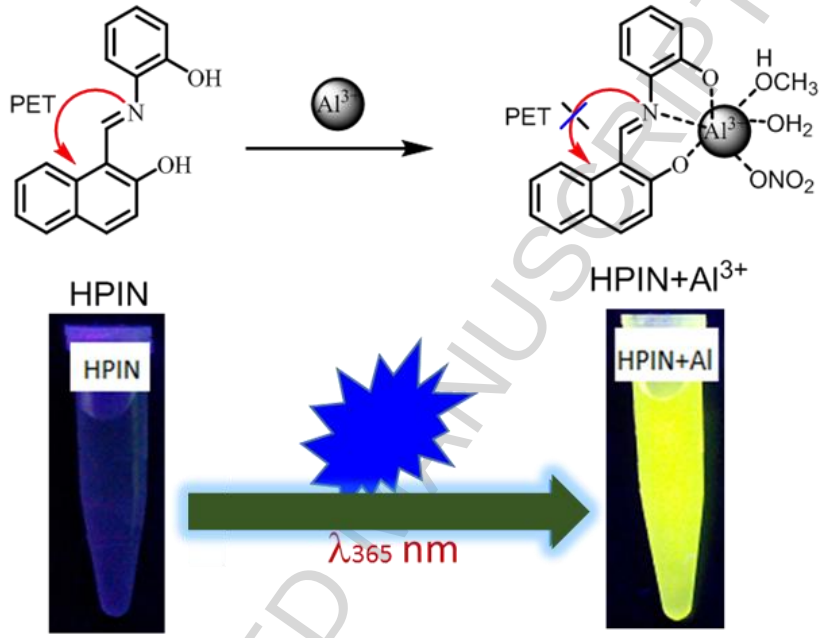


Fig.1

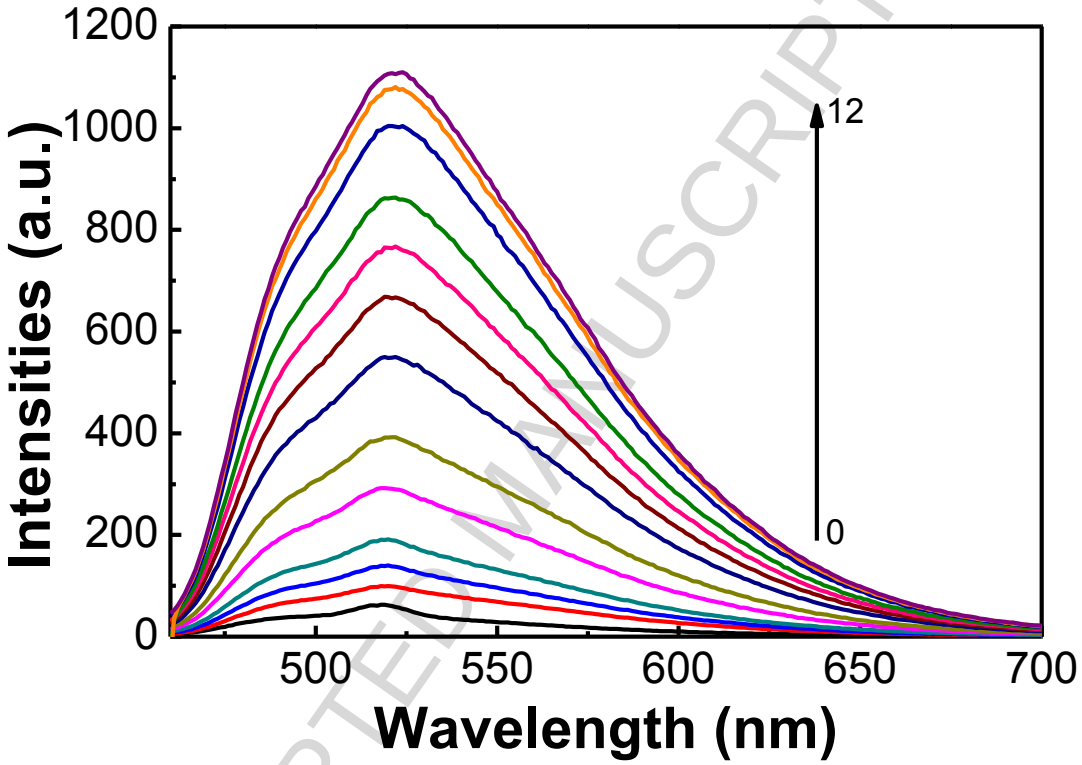


Fig.2

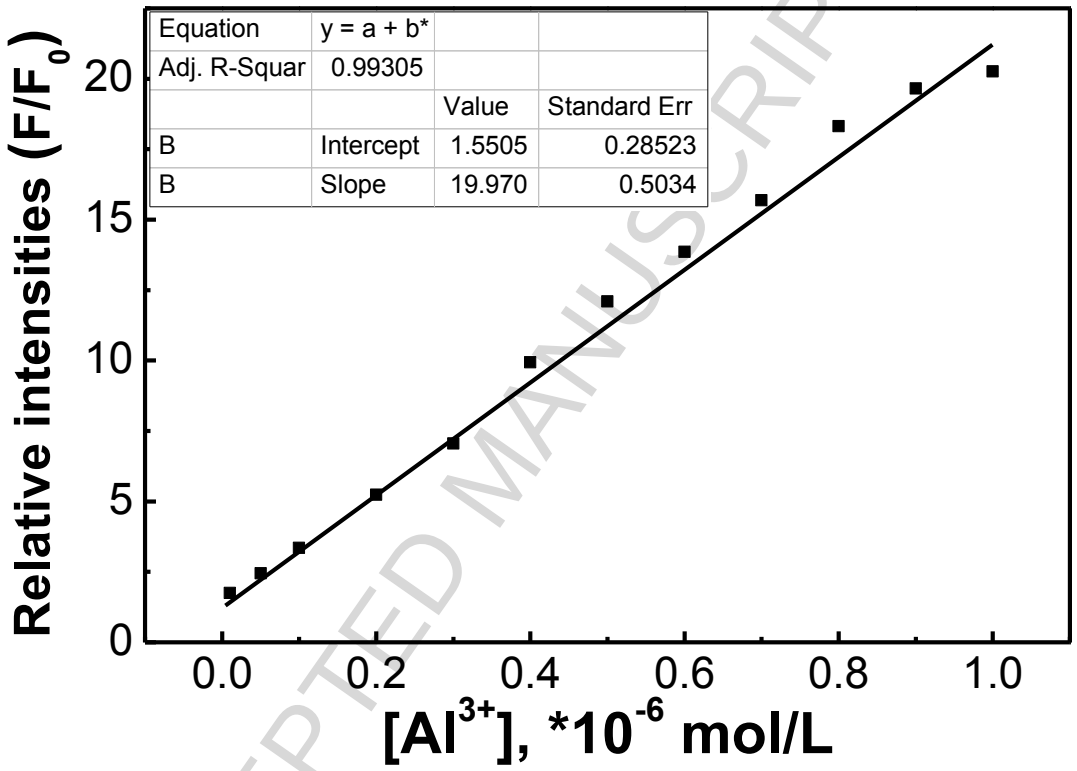


Fig.3

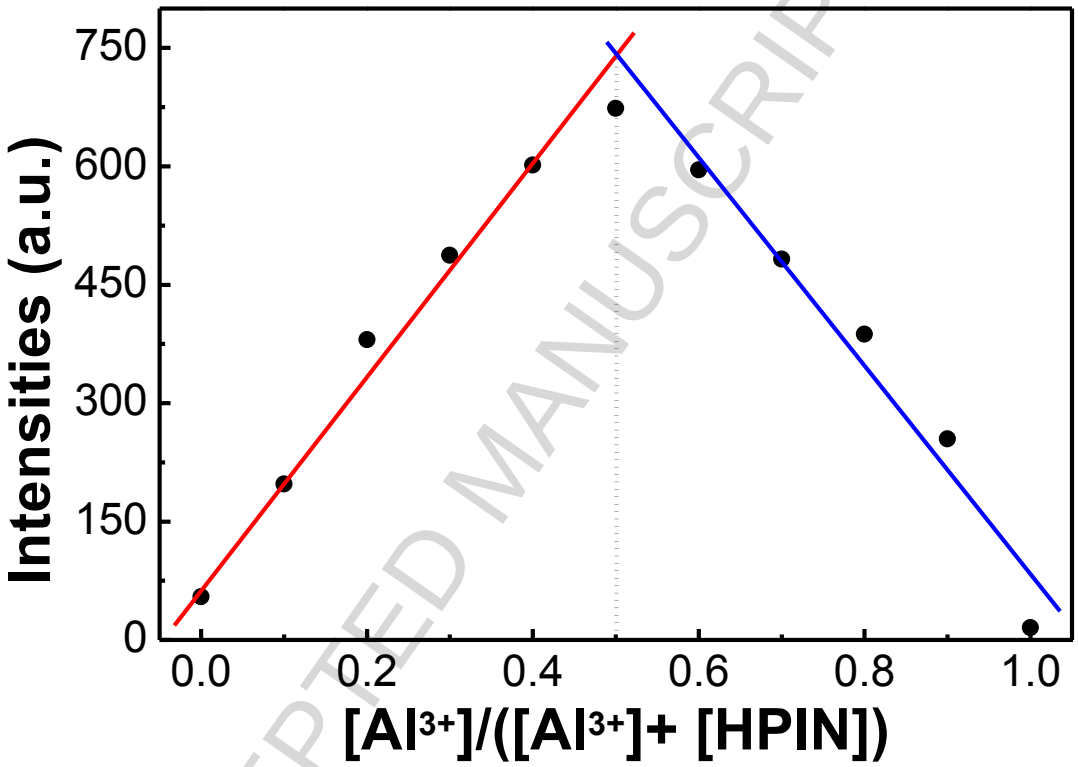


Fig.4

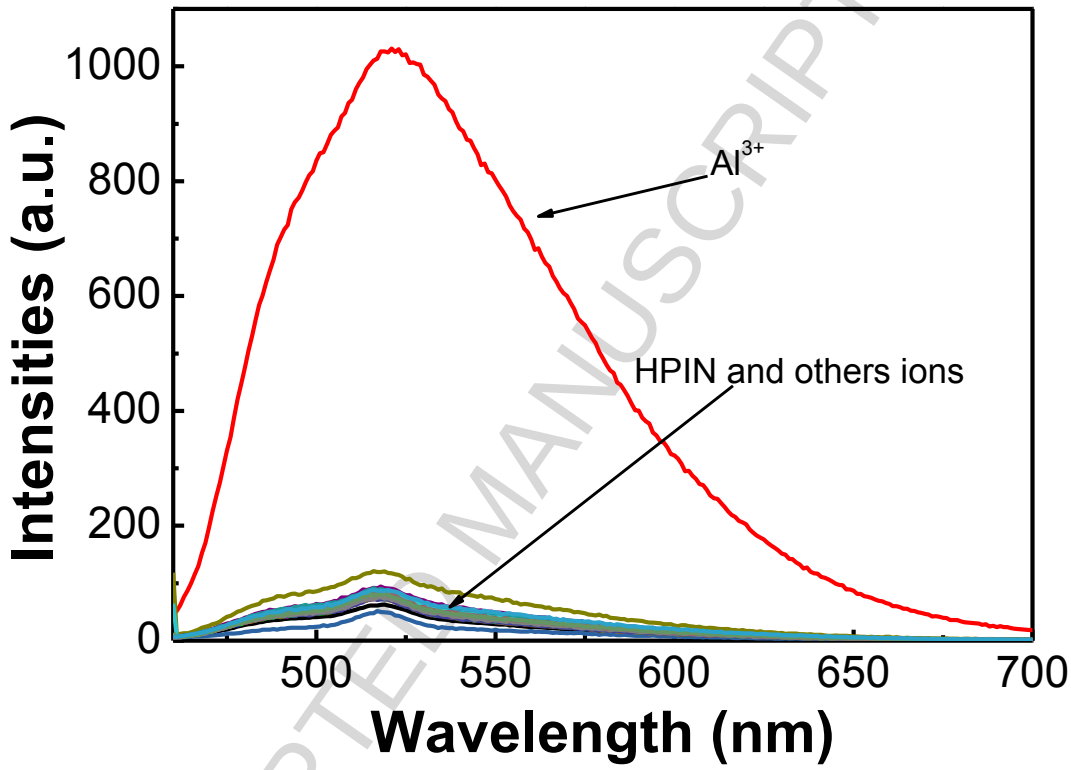


Fig. 5

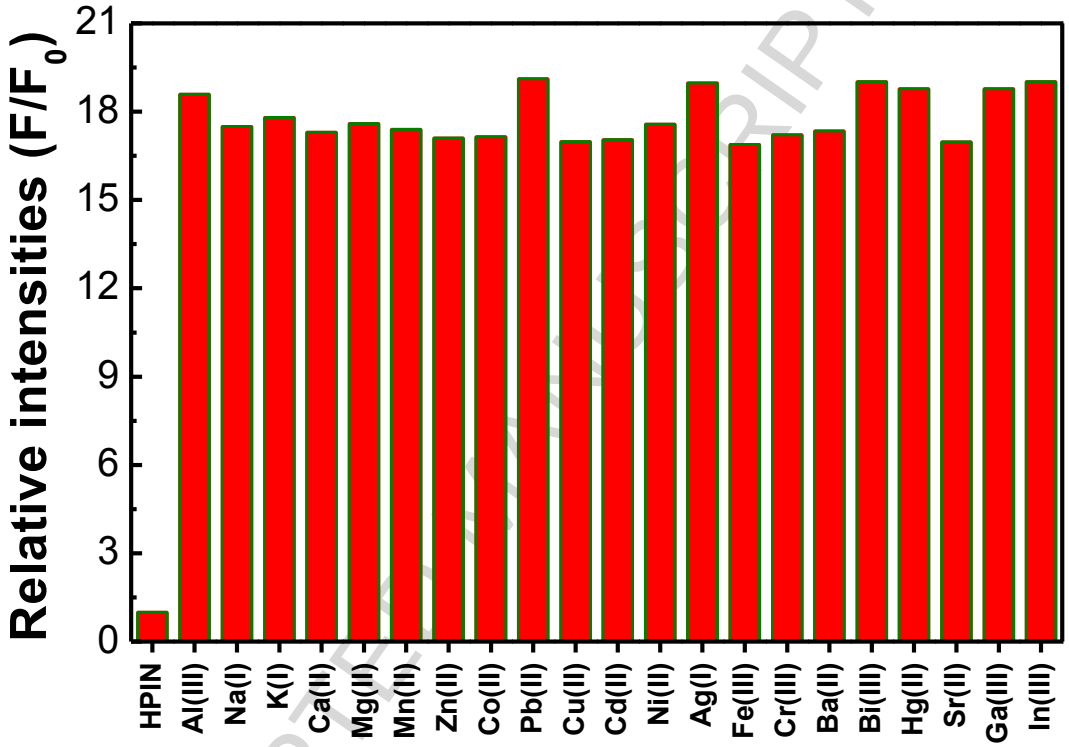
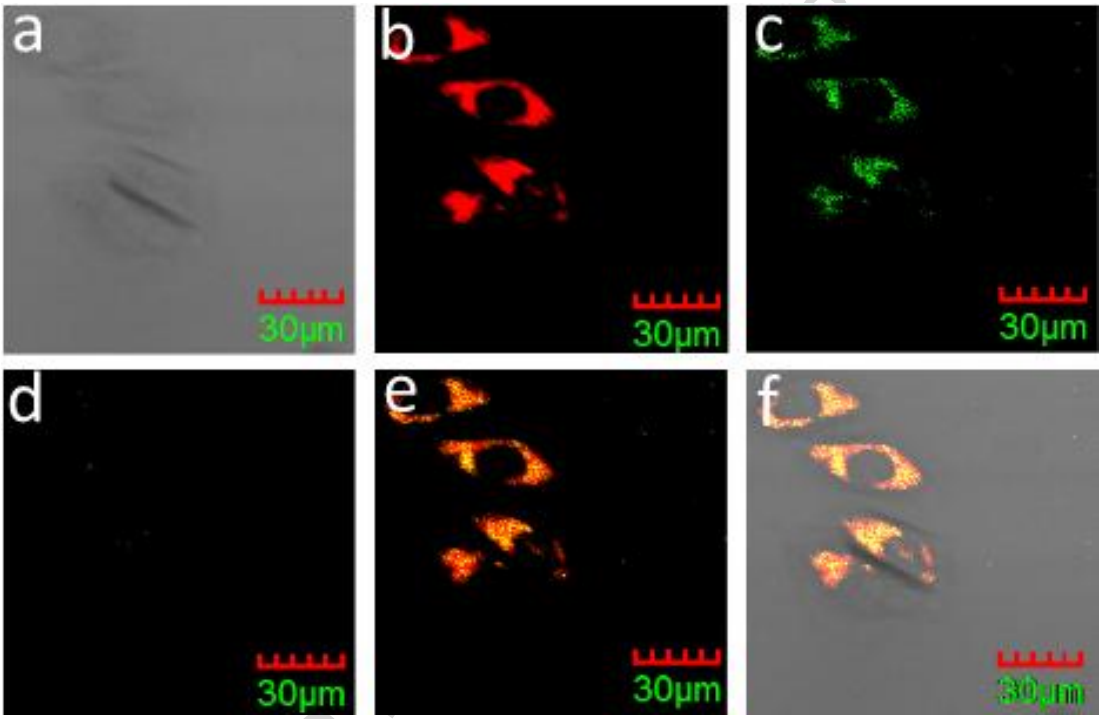
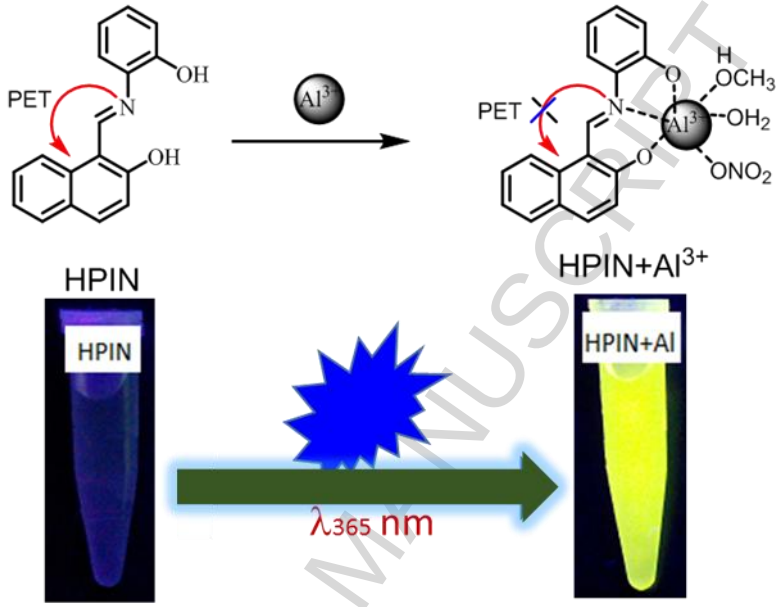


Fig. 6



Graphical Abstract



Highlights

A simple and efficient chemosensor HPIN is designed and synthesized.

The chemosensor has high selectivity and sensitivity for Al^{3+}.

It is a fluorescence “off-on” switch for Al^{3+}.

The coordination mode of HPIN with Al^{3+} is a 1:1 binding stoichiometry.

Potential utilization of HPIN as intracellular sensors of Al^{3+} was examined.