

Cite this: *RSC Adv.*, 2016, 6, 77291

A facile Al(III)-specific fluorescence probe and its application in biological systems†

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A facile fluorescence receptor was easily synthesized by an one-step reaction of 3,4-dihydroxybenzaldehyde and hydrazinecarbothioamide. The receptor as a fluorescence probe was used to recognize metal ions by UV-vis and fluorescence techniques. The data of UV-vis and fluorescence spectra display the high sensitivity and selectivity of the receptor for Al(III) ions. When introducing Al(III) ions, the fluorescence of the probe exhibits an obvious enhancement because of inhibiting the photoinduced electron transfer (PET) process. The certain bonding mode of the receptor with Al(III) was verified by ¹H NMR, HRMS-ESI and Job-plot data. The prospective fluorescence "Off-On" signal for Al(III) ions including the color change of the receptor solution was observed. The detection limit of the receptor for Al(III) may reach 10⁻⁷ mol L⁻¹. Noticeably, the probe as a fluorescence "Off-On" switch can detect the trace level of Al(III) in living cells and mouse organs. The work provides a strategy for design simple fluorescence probes for Al(III) and applications in biological systems.

Received 10th July 2016
Accepted 8th August 2016

DOI: 10.1039/c6ra17623b

www.rsc.org/advances

Introduction

Because of its operational simplicity, low cost, instantaneous response and direct visual perception, the fluorescence technique has proved to be a very useful tool for sensing and monitoring metal ions, anions and molecules in an abiotic or biotic systems.¹⁻¹⁰ A typical fluorescence probe is comprised of a substrate (as the recognition site), a chromophore (the optical signal source) and a connection bridge (translating the recognition event into a fluorescence signal).¹¹⁻¹⁵ In order to get ideal probes, a well designed fluorescence receptor is very important, and the receptor needs to possess strong affinity towards the relevant targets.¹⁶⁻¹⁹

Aluminum has been widely used in packing materials, clinical drugs, food additives and water purification because of its rich feature in the earth (the third most prevalent metallic element).²⁰⁻²⁴ However, many health hazards have produced in recent years because of the improper use of aluminum.^{25,26} Under the case, World Health Organization (WHO) drew up the safety dosage of aluminum. And, the organization also revealed aluminum as a source of food pollution and limited the content of aluminum in drinking water to 7.41 mM.²⁷ Therefore,

developed effective aluminum probes with high selectivity and sensitivity in the environmental and biological samples are very urgent for chemist, biologist and medical scientist. In recent years, carbon dots and graphene quantum dots have also been widely used as fluorescence probes for the detection of transition metal ions because of their high fluorescence brightness and sensitivity.²⁸⁻³¹ Compared with transition metal ions, it is challenging to develop excellent fluorescence probes for Al³⁺ because of its poor coordination ability and spectroscopic characteristics.³²⁻³⁴ To date, among reported Al³⁺ fluorescence probes (such as hydrazones, coumarin, calixarene and hydroxyflavone, *etc.*), Schiff base and its derivants as fluorescence receptors are the most effective and prosperous because of their easy preparation and abundant bonding sites (N and O atoms).³⁵⁻⁴⁰ Additionally, due to the isomerization characteristic of C=N bond, the probes based on Schiff base always display a fluorescence "off-on" signal for analytes. Through utilizing the feature, many Al³⁺ fluorescence probes with Schiff base formation have been reported in recent years.⁴¹⁻⁵¹ Meanwhile, these researches mainly focused on improving the parameter values of sensitivity and selectivity for Al³⁺, and a few applications in biological systems. Surprisingly, it is negligible that the C=N bond also is a poor electron group which possesses the strong withdrawing capacity. So, it is interest for designing a fluorescence probe with the withdrawing electron unit (C=N bond of Schiff base) and donating electron groups (such as hydroxyl or amino) because the probe can use to recognize the specific ions based on photoinduced electron transfer (PET) mechanism. Furthermore, considering the human health problem, it is significant to develop a facile fluorescence probe to recognize and detect trace level of Al³⁺ in biological systems.

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† Electronic supplementary information (ESI) available. See DOI: 10.1039/c6ra17623b

Herein, we report a simple receptor as a fluorescence probe to recognize Al^{3+} ions. The receptor ((*E*)-2-(3,4-dihydroxybenzylidene)hydrazine-1-carbothioamide, receptor 1, Fig. 3) was comprised of withdrawing electron unit ($\text{C}=\text{N}$ bond), donating electron groups (hydroxyl) and a connection bridge (benzene ring). As expected, the probe exhibits a fluorescence “turn-on” response only for Al^{3+} ions because of inhibiting photoinduced electron transfer (PET) process from hydroxyl groups to $\text{C}=\text{N}$ bond. Moreover, the detections of the probe for Al^{3+} *in vitro* cells and mouse organs also were investigated.

Results and discussion

UV-vis studies of receptor 1 and metal ions

The interactions of receptor 1 with various metal ions (Zn^{2+} , Pb^{2+} , Ni^{2+} , Na^+ , Mn^{2+} , Mg^{2+} , K^+ , Hg^{2+} , Fe^{2+} , Fe^{3+} , Cu^{2+} , Cr^{3+} , Co^{2+} , Cd^{2+} , Ca^{2+} , Ag^+ and Al^{3+}) were studied by UV-vis absorption spectra in mixed media ($\text{H}_2\text{O}/\text{DMSO} = 2/3$, v/v), respectively. As shown in Fig. 1, the absorption peak of receptor 1 is at 335 nm. The absorption spectra of receptor 1 exhibit an obvious blue-shifted and enhancement in intensity with the addition of Cu^{2+} , Fe^{3+} , Hg^{2+} and Pb^{2+} , respectively. Different from the above four transition metal ions, the absorption peak of receptor 1 displays a red-shifted only in the present of Al^{3+} . Meanwhile, the introduction of other metal ions does not induce obvious change of the absorption peak of receptor 1 in wavelength or intensity aspects. These results show that the receptor 1 has a unique response and high selectivity for Al^{3+} . The change processes of the absorption spectra with the increase of Al^{3+} were listed in Fig. S1.† From Fig. S1,† we can find that the absorption peak of receptor 1 displays an obvious change from 350 nm to 360 nm, and the isosbestic point is 352 nm, which indicates the formation of a complex between receptor 1 and Al^{3+} .

Fluorescence studies of receptor 1 and metal ions

In order to confirm the selectivity of receptor 1 for Al^{3+} , the fluorescence technique was used to investigate the interactions

of receptor 1 with various metal ions, respectively. The fluorescence spectra of receptor 1 in the present of metal ions were shown in Fig. 2. From Fig. 2, the receptor 1 has a weak fluorescence emission at 410 nm because of the intramolecular photoinduced electron transfer from hydroxyl groups to $\text{C}=\text{N}$ unit of Schiff base. An obvious enhancement of fluorescence intensity of receptor 1 is observed by only introducing Al^{3+} . While introducing Hg^{2+} , Cu^{2+} , Fe^{3+} and Pb^{2+} metal ions, the fluorescence of receptor 1 is quenched, respectively. The fluorescence of receptor 1 has not an obvious change in the present of other metal ions, respectively. Based on the experimental facts, we believe the receptor can detect Al^{3+} as a high selectivity probe. Meanwhile, the sensitivity of receptor 1 for Al^{3+} is also studied by the titration method at 445 nm (Fig. S2†). With the increase of Al^{3+} , the emission peak exhibits a red-shifted from 410 nm to 445 nm with the gradual enhancement of fluorescence intensity (Fig. S2†). The detection limit of receptor 1 for Al^{3+} is up to 10^{-7} mol L^{-1} , which is low enough as a fluorescence probe to detect Al^{3+} in environmental and biological samples.³¹ Notably, the plot of relative intensity to the concentration of Al^{3+} ions possesses a good linear relation and reproducibility (Fig. S2†). The linear independent constant (R^2) is up to 0.9945 within the range of 10^{-7} to 10^{-5} mol L^{-1} for Al^{3+} . Compared with electrochemical technique for detection Al^{3+} , the advantages of the fluorescence probe lie in its low cost, fast analysis and wide application.⁵²

Fluorescence spectra of the probe in different pH solutions also were investigated by the titration method (Fig. S3†). In pH < 5.0 media, the emission peak of receptor 1 at 405 nm has no obvious changes because of the protonation of N and O atoms weakening the conjugated extend, which results in the blue-shifted of fluorescence spectra.⁵³ The wavelength and intensity of the probe exhibit a red-shifted and enhancement form pH 5.0 to pH 7.0. And, the fluorescence of the probe with an outstanding reduction in pH > 8.0 media may be due to the dissociation of the hydroxyl and amino protons.⁵⁴ The result indicates that the pH value has an obvious effect for the fluorescence of the probe. The acid (pH < 5.0) or alkali (pH > 8.0)

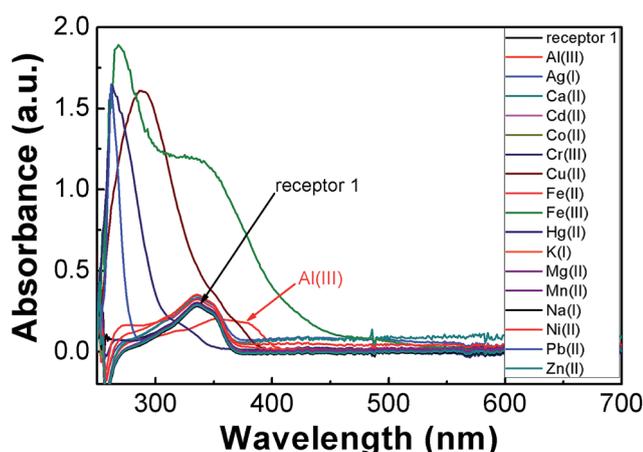


Fig. 1 The UV-vis absorption spectra of receptor 1 and receptor 1 (1.0×10^{-5} mol L^{-1}) with various metal ions (5.0×10^{-4} mol L^{-1}) in mixed media ($\text{H}_2\text{O}/\text{DMSO} = 2/3$, v/v), respectively.

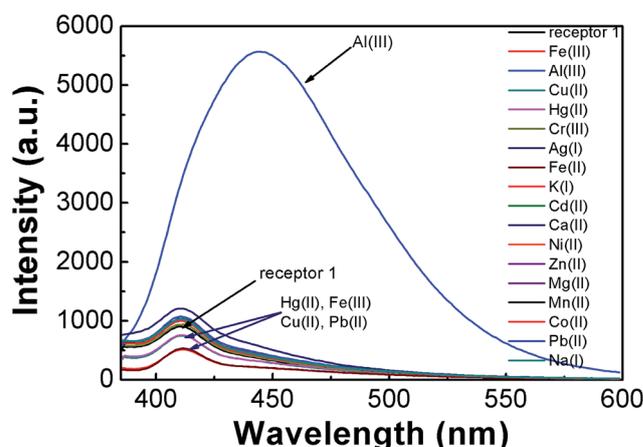


Fig. 2 The fluorescence spectra of receptor 1 (5.0×10^{-6} mol L^{-1}) and introducing various metal ions (3.0×10^{-5} mol L^{-1}) to receptor 1 in mixed medium ($\text{H}_2\text{O}/\text{DMSO} = 2/3$, v/v), respectively.

media can both inhibit the fluorescence of the probe. Although the fluorescence of the probe in pH = 7.0 medium obtains a certain recovery, it is lower than that in present of Al^{3+} , which indicates the detection of the probe for Al^{3+} has no apparent effect during pH 5.0–8.0 range.

The sensing mechanism and bonding mode

For fluorescence probes, the response signals for analytes mainly included the following mechanisms, such as photo induced electron transfer (PET), intramolecular charge transfer (ICT), chelation enhanced fluorescence (CHEF) and twisted intra-molecular/intermediate charge transfer (TICT), *etc.* In this work, the fluorescence of the probe is inhibited because of photoinduced electron transfer action from rich electronic group (hydroxyl group) to lack electronic body (C=N bond of Schiff base). When introducing Al^{3+} , the process of PET is destroyed by the connection of receptor 1 and Al^{3+} . Accordingly, the “turn-on” response signal of the probe for Al^{3+} is observed with the color change of the solutions by naked eyes (Fig. 3).

In order to explore the action mode of receptor 1 with Al^{3+} , other two receptors (2 and 3) were prepared and applied to detect the Al^{3+} in Fig. S4.† As can be seen from Fig. S4,† we can obtain other two receptors have similar structures with receptor 1, but the two receptors have all no fluorescence changes in the present of Al^{3+} , respectively. Combining with the ^1H NMR titration data (Fig. S5†), only a change of chemical shift was the hydroxyl groups, which indicates oxygen atoms of hydroxyl participate in the complexation with Al^{3+} . Next, the specific mode of receptor 1 with Al^{3+} was verified by HRMS-ESI data (Fig. 3). Based on these cases, we believe the bonding ratio of receptor 1 with Al^{3+} is 1 : 1 (mol) mode, which also was verified by the Job-plot experiment (Fig. S6†). In the Job-plot testing, the fluorescence intensity of receptor 1 with Al^{3+} (5 : 5, mol) was highest in different ratios.

Fluorescence imaging in live cells of receptor 1 for Al^{3+}

The interaction of receptor 1 with Al^{3+} in live cells was investigated by confocal laser scanning microscope (CLSM). Firstly,

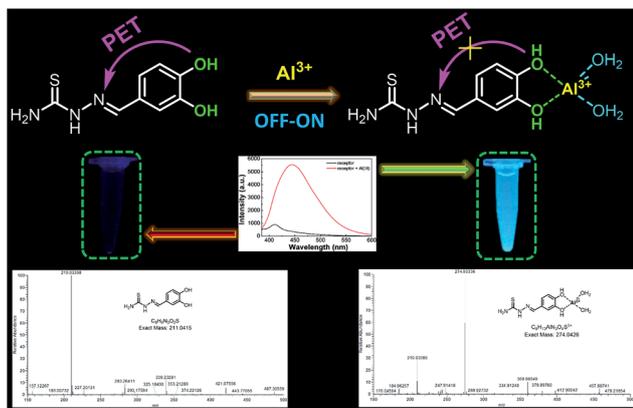


Fig. 3 The sensing mechanism of the probe for Al^{3+} , the bonding mode of receptor 1 with Al^{3+} and HRMS-ESI (negative) graphs, and the color change of receptor 1 solution without or with Al^{3+} .

the HepG-2 cells were cultured with receptor 1 at 37 °C for 1 h or 3 h, and then, the five equivalents of Al^{3+} were added to the mixture 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. 4, the blue fluorescence of receptor 1 can be observed only in the present of Al^{3+} , and the staining region has well overlap with the cytoplasm located dye (Lyso tracker red). Compared with receptor 2, the receptor 1 in live cells can be illumined by introducing Al^{3+} . While, due to shorter incubation time of receptor 1 with HepG-2 cells (1 h), the fluorescence imaging is not bright (Fig. S7†). These results show that receptor 1 can detect Al^{3+} in living cells as a biocompatible and effective fluorescence probe.

Fluorescence imaging in mouse organs of receptor 1 for Al^{3+}

In order to further develop the application in biological field, fluorescence imaging of the probe for Al^{3+} was performed in mouse organs (Fig. 5). As shown from Fig. 5, typical *ex vivo* biophotonic images of mouse main organs (heart, liver, spleen, lung, kidney and brain) at 1 h post injection of receptor 1/ Al^{3+} were investigated. In this experiment, propidium iodide (PI) is used as a located dye for these organs. The blue fluorescence is observed at various organs of mouse by introducing Al^{3+} to these organs with receptor 1, which indicates receptor 1 as a suitable “off-on” probe may apply to detect Al^{3+} *in vivo*.

Live subject statement

These authors state that all experiments were performed in compliance with the relevant laws and institutional guidelines (Animal Ethical Committee, Shanxi Medical University) and this work has been approved by the IAEC (Institutional Animal Ethical Committee) constituted as per the Rules and

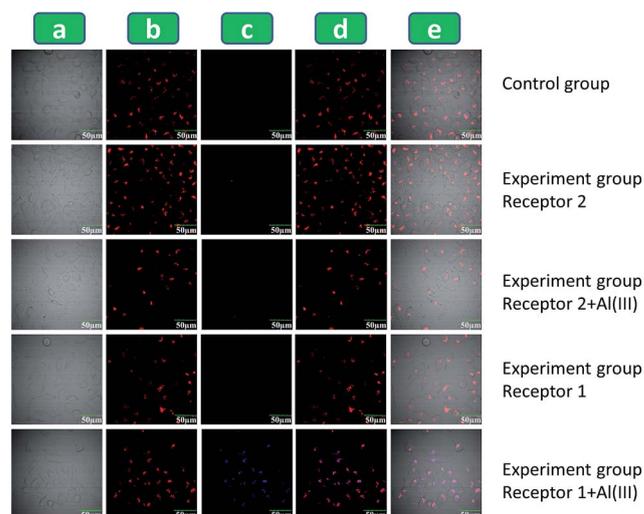


Fig. 4 Fluorescence imaging of HepG-2 cells with receptor 1, 2 and Al^{3+} . (a) is bright image, (b) is fluorescence image of cytoplasm located dye (Lyso tracker red), (c) is fluorescence image of receptors or receptors/ Al^{3+} , (d) is merged image of located dye and receptors or receptors/ Al^{3+} , (e) is merged bright image and fluorescence image of located dye and receptors or receptors/ Al^{3+} .

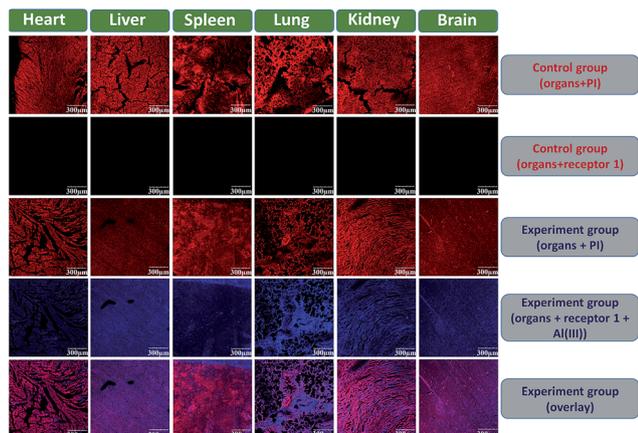


Fig. 5 Fluorescence images of major organs, including heart, liver, spleen, lung, kidney and brain collected from the control untreated mouse and the injected (Al^{3+} or receptor 1, $5.0 \times 10^{-5} \text{ mol L}^{-1}$) mice at 1 h post-injection. No noticeable abnormality or lesion was observed in organs of mouse.

Regulations of Ministry of Animal Husbandry, Government of China. The authors also state that informed consent was obtained for any experimentation with human subjects and Animal Ethical Committee, Shanxi Medical University.

Conclusions

In summary, we develop a simple fluorescence “off-on” probe for Al^{3+} with high selectivity and sensitivity. The probe was comprised of pyrocatechol and thiosemicarbazide and easily synthesized by a one step. Due to destroying the PET action by introducing Al^{3+} , the fluorescence of the probe exhibits an outstanding increase. The bonding mode (1/1, mol) of the receptor with Al^{3+} was verified by HRMS-ESI and Job plot data. The probe with good biocompatible and high specific for Al^{3+} can detect Al^{3+} ions in cells and organs systems. The contribution of the work lies in not only providing a new platform for applications of fluorescence probes of Al^{3+} , but also proposing a strategy for designing and preparing easy Schiff base probes.

Experimental

Materials and characterization

Unless otherwise stated, all chemical reagents were obtained from commercial suppliers and used without further purification. Hydrazinecarbothioamide, benzaldehyde with different hydroxyl groups were purchased from Aldrich (Steinheim, Germany). All metal ions were nitrates and provided by Alfa Aesar (Tianjin, China). ^1H NMR and ^{13}C NMR were measured on a Bruker ARX400 spectrometer with chemical shifts reported as ppm (TMS as an internal standard). Elemental analyses were performed on a Vario EL elemental analysis instrument (Elementar Co.). High-resolution mass spectra (HRMS) were acquired with an Agilent 6510 Q-TOF LC/MS instrument (Agilent Technologies, Palo Alto, CA) equipped with an electrospray ionization (ESI) source. Fluorescence spectra were acquired

with a Hitachi F-4600 fluorescence spectrophotometer, and the excitation and emission slit widths were both 5.0 nm. UV-vis spectra were measured with a Hitachi 5300 absorption spectrophotometer. Confocal laser scanning microscopy (CLSM) imaging was taken on a confocal laser scanning biological microscope (FV1000-IX81, Olympus, Japan).

Procedures for synthesis of receptors

0.46 g (5.0 mmol) hydrazinecarbothioamide was added to a suspension of 0.69 g (5.0 mmol) 3,4-dihydroxybenzaldehyde in 30 mL ethanol, and the reaction mixture was stirred at 80°C for 5 h. After filtrating the insoluble precipitate and removing a mass of ethanol, the residue was precipitated with dichloromethane (50 mL) and the precipitate was collected by centrifugation. The crude product was purified by precipitation for twice from ethanol to dichloromethane. The final product (receptor 1) as solid was obtained through centrifugation and drying under vacuum. Receptor 2 and 3 were prepared according to the similar method.

Receptor 1 (deep yellow powder, yield 43.2%). ^1H NMR (*d*-DMSO, 400 MHz) δ 11.20 (s, 1H), 9.46 (s, 1H), 8.98 (s, 1H), 8.03 (s, 1H), 7.89 (s, 1H), 7.71 (s, 1H), 7.18 (s, 1H), 7.02 (d, 1H), 6.76 (s, 1H); ^{13}C NMR (*d*-DMSO, 100 MHz) δ 177.18, 148.00, 145.40, 144.62, 125.86, 120.79, 114.90, 112.75; element analysis for $\text{C}_8\text{H}_9\text{N}_3\text{O}_2\text{S}$ (mol. wt: 211.04) calcd C, 45.49; H, 4.29; N, 19.89; O, 15.15; found: C, 45.52; H, 4.33; N, 19.95; O, 15.23; HRMS-ESI (positive) for $\text{C}_8\text{H}_9\text{N}_3\text{O}_2\text{S}$ (*m/z*) 211.91026 [$\text{M} + 1$].

Receptor 2 (light yellow powder, yield 45.7%). ^1H NMR (*d*-DMSO, 400 MHz) δ 11.22 (s, 1H), 9.45 (s, 1H), 9.02 (s, 1H), 8.19 (s, 1H), 8.17 (s, 1H), 8.11 (s, 1H), 7.38 (d, 1H), 6.36 (d, 1H), 6.31 (s, 1H); ^{13}C NMR (*d*-DMSO, 100 MHz) δ 177.19, 161.12, 158.89, 145.38, 130.39, 110.98, 107.71, 102.14; element analysis for $\text{C}_8\text{H}_9\text{N}_3\text{O}_2\text{S}$ (mol. wt: 211.04) calcd C, 45.49; H, 4.29; N, 19.89; O, 15.15; found: C, 45.55; H, 4.32; N, 19.81; O, 15.24; HRMS-ESI (positive) for $\text{C}_8\text{H}_9\text{N}_3\text{O}_2\text{S}$ (*m/z*) 211.94012 [$\text{M} + 1$], 233.92894 [$\text{M} + \text{Na}$].

Receptor 3 (white powder, yield 41.8%). ^1H NMR (*d*-DMSO, 400 MHz) δ 11.15 (s, 1H), 9.44 (s, 1H), 8.05 (s, 1H), 7.90 (s, 1H), 7.82 (s, 1H), 7.22–7.16 (m, 3H), 6.84 (t, 1H); ^{13}C NMR (*d*-DMSO, 100 MHz) δ 178.52, 157.53, 143.95, 135.30, 129.44, 118.90, 117.17, 112.94; element analysis for $\text{C}_8\text{H}_9\text{N}_3\text{OS}$ (mol. wt: 195.05) calcd C, 49.22; H, 4.65; N, 21.52; O, 8.19; found: C, 48.95; H, 4.68; N, 22.32; O, 8.41; HRMS-ESI (positive) for $\text{C}_8\text{H}_9\text{N}_3\text{OS}$ (*m/z*) 196.22038 [$\text{M} + 1$].

Fluorescence and UV-vis measurements

All used water was redistilled water. All these receptors were dissolved in DMSO as the stock solutions ($1.0 \times 10^{-2} \text{ mol L}^{-1}$). The working solutions were prepared by diluting method with mixed media ($\text{H}_2\text{O}/\text{DMSO} = 2/3$, v/v). The working solutions were placed in a quartz cuvette with 1 cm path. The total volume of working solutions is 2.0 mL. The UV-vis and fluorescence measurements used titration experiments and the volume added did not exceed 3% of the total. After the mixture solution was shaken for 30 s, the new spectra were measured. All of the experiments were performed at room temperature.

Cells and organs imaging of mouse

Human liver carcinoma cells (HepG-2) were cultured in DMEM medium containing 10% FBS routinely under a humidified atmosphere containing 5% CO₂, and then harvested for subculture using trypsin (0.05%, Gibco/Invitrogen) at 37 °C. HepG-2 cells were subcultured onto a 35 mm × 35 mm Petri dish with a glass bottom, then allowed to grow for 24 h for attachment. After that, 1 mL of DMEM medium containing 10% 20 μM receptor (1 or 2) was used to incubate the HepG-2 cells at 37 °C for 3 h. The media were replaced and phosphate-buffered saline (PBS, pH = 7.4) was used to wash the cells thrice. And five equivalents of Al³⁺ in PBS buffer solution were added into the dish and the cells were cultured at 37 °C 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.

The mice that come from the animal laboratory of Shanxi Medical University were firstly injected with 100 μL of 1.0 × 10⁻⁴ mol L⁻¹ Al³⁺. After 1 h, 100 μL (1.0 × 10⁻⁴ mol L⁻¹) receptor 1 was injected by tail intravenous and acted for 1 h. After the anatomical and histological section, the fluorescence images of heart, liver, spleen, lung, kidney and brain organs were recorded on confocal laser scanning microscopy. Untreated mice were used as the control.

Acknowledgements

The work described in this paper was supported by the National Nature Science Foundation (No. 21571116 and 21371110), the Youth Science Foundation of Shanxi Province (No. 2014021006, and 2016021054) and the Program for the Outstanding Innovative Teams of Higher Learning Institutions of Shanxi (2013). The authors of Haiying Lei and Haipeng Diao contributed equally to this work.

Notes and references

- 1 F. Yu, X. Han and L. Chen, *Chem. Commun.*, 2014, **50**, 12234.
- 2 M. Formica, V. Fusi, L. Giorgi and M. Micheloni, *Coord. Chem. Rev.*, 2012, **256**, 170.
- 3 X. Lou, D. Ou, Q. Li and Z. Li, *Chem. Commun.*, 2012, **48**, 8462.
- 4 R. Wang, C. Yu, F. Yu, L. Chen and C. Yu, *TrAC, Trends Anal. Chem.*, 2010, **29**, 1004.
- 5 S. Das, S. Guha, A. Banerjee, S. Lohar, A. Sahana and D. Das, *Org. Biomol. Chem.*, 2011, **9**, 7097.
- 6 Y. Zhou and J. Yoon, *Chem. Soc. Rev.*, 2012, **41**, 52.
- 7 K. Tayade, S. K. Sahoo, B. Bondhopadhyay, V. K. Bhardwaj, N. Singh, A. Basu, R. Bendre and A. Kuwar, *Biosens. Bioelectron.*, 2014, **61**, 429.
- 8 G. Sivaraman, T. Anand and D. Chellappa, *Anal. Methods*, 2014, **6**, 2343.
- 9 K. M. Vengaiyan, C. D. Britto, G. Sivaraman, K. Sekar and S. Singaravadivel, *RSC Adv.*, 2015, **5**, 94903.
- 10 O. Sunnapu, N. G. Kotla, B. Maddiboyina, S. Singaravadivel and G. Sivaraman, *RSC Adv.*, 2016, **6**, 656.
- 11 R. Shen, X. Pan, H. Wang, L. Yao, J. Wu and N. Tang, *Dalton Trans.*, 2008, **27**, 3574.
- 12 A. P. de Silva, H. Q. N. Gunaratne, T. Gunnlaugsson, A. J. M. Huxley, C. P. McCoy, J. T. Rademacher and T. E. Rice, *Chem. Rev.*, 1997, **97**, 1515.
- 13 S. Das, M. Dutta and D. Das, *Anal. Methods*, 2013, **5**, 6262.
- 14 G. Sivaraman and D. Chellappa, *J. Mater. Chem. B*, 2013, **1**, 5768.
- 15 G. Sivaraman, T. Anand and D. Chellappa, *RSC Adv.*, 2012, **2**, 10605.
- 16 W. Cao, X. J. Zheng, J. P. Sun, W. T. Wong, D. C. Fang, J. X. Zhang and L. P. Jin, *Inorg. Chem.*, 2014, **53**, 3012.
- 17 N. H. Yin and L. H. Feng, *Spectrochim. Acta, Part A*, 2016, **153**, 1.
- 18 L. Fan, J. C. Qin, T. R. Li, B. D. Wang and Z. Y. Yang, *Sens. Actuators, B*, 2014, **203**, 550.
- 19 W. H. Ding, W. Cao, X. J. Zheng, W. J. Ding, J. P. Qiao and L. P. Jin, *Dalton Trans.*, 2014, **43**, 6429.
- 20 M. G. Soni, S. M. White, W. G. Flamm and G. A. Burdock, *Regul. Toxicol. Pharmacol.*, 2001, **33**, 66.
- 21 J. H. Lee, H. Y. Kim, S. J. Kim, J. Y. Noh, E. J. Song, C. Kim and J. H. Kim, *Dyes Pigm.*, 2013, **96**, 590.
- 22 R. Azadbakht, T. Almasi, H. Keypour and M. Rezaeivala, *Inorg. Chem. Commun.*, 2013, **33**, 63.
- 23 S. Goswami, A. Manna, S. Paul, K. Aich, A. K. Das and S. Chakraborty, *Dalton Trans.*, 2013, **42**, 8078.
- 24 Z. C. Liu, Z. Y. Yang, Y. X. Li, T. R. Li, B. D. Wang, Y. Li and X. L. Jin, *Inorg. Chim. Acta*, 2013, **395**, 77.
- 25 D. P. Perl, D. C. Gajdusek, R. M. Garruto, R. T. Yanagihara and C. J. Gibbs, *Science*, 1982, **217**, 103.
- 26 P. D. Darbre, *J. Inorg. Biochem.*, 2005, **99**, 1912.
- 27 Z. Krejpcio and R. W. Wojciak, *Pol. J. Environ. Stud.*, 2002, **11**, 251.
- 28 R. Z. Zhang and W. Chen, *Biosens. Bioelectron.*, 2014, **55**, 83.
- 29 X. H. Gao, Y. Z. Lu, R. Z. Zhang, S. J. He, J. Ju, M. M. Liu, L. Li and W. Chen, *J. Mater. Chem. C*, 2015, **3**, 2302.
- 30 J. Ju and W. Chen, *Biosens. Bioelectron.*, 2014, **58**, 219.
- 31 X. H. Gao, C. Du, Z. H. Zhuang and W. Chen, *J. Mater. Chem. C*, 2016, **4**, 6927.
- 32 K. K. Upadhyay and A. Kumar, *Org. Biomol. Chem.*, 2010, **8**, 4892.
- 33 K. Soroka, R. Vithanage, D. A. Philips, B. Walker and P. K. Dasgupta, *Anal. Chem.*, 1987, **59**, 629.
- 34 X. Sun, Y. W. Wang and Y. Peng, *Org. Lett.*, 2012, **14**, 3420.
- 35 Y. Zhao, Z. Lin, H. Liao, C. Duan and Q. Meng, *Inorg. Chem. Commun.*, 2006, **9**, 966.
- 36 A. Sahana, A. Banerjee, S. Das, S. Lohar, D. Karak, B. Sarkar, S. K. Mukhopadhyay, A. K. Mukherjee and D. Das, *Org. Biomol. Chem.*, 2011, **9**, 5523.
- 37 R. S. Sathish, A. G. Raju, G. N. Rao and C. Janardhana, *Spectrochim. Acta, Part A*, 2008, **69**, 282.
- 38 A. B. Othman, J. W. Lee, Y. D. Huh, R. Abidi, J. S. Kim and J. Vicens, *Tetrahedron*, 2007, **63**, 10793.
- 39 C. Jiang, B. Tang, R. Wang and J. Yen, *Talanta*, 1997, **44**, 197.

- 40 T. Anand, G. Sivaraman, A. Mahesh and D. Chellappa, *Anal. Chim. Acta*, 2015, **853**, 596.
- 41 Y. J. Lee, C. Lim, H. Suh, E. J. Song and C. Kim, *Sens. Actuators, B*, 2014, **201**, 535.
- 42 D. Maity and T. Govindaraju, *Inorg. Chem.*, 2010, **49**, 7229.
- 43 Y. W. Choi, G. J. Park, Y. J. Na, H. Y. Jo, S. A. Lee, G. R. You and C. Kim, *Sens. Actuators, B*, 2014, **194**, 343.
- 44 D. Maity and T. Govindaraju, *Chem. Commun.*, 2010, 4499.
- 45 C. Gou, S. H. Qin, H. Q. Wu, Y. Wang, J. Luo and X. Y. Liu, *Inorg. Chem. Commun.*, 2011, **14**, 1622.
- 46 R. Azadbakht and J. Khanabadi, *Tetrahedron*, 2013, **69**, 3206.
- 47 R. Azadbakht and S. Rashidi, *Spectrochim. Acta, Part A*, 2014, **127**, 329.
- 48 S. K. Shoorra, A. K. Jain and V. K. Gupta, *Sens. Actuators, B*, 2015, **216**, 86.
- 49 V. K. Gupta, A. K. Singh and N. Mergu, *Electrochim. Acta*, 2014, **117**, 405.
- 50 M. Mukherjee, B. Sen, S. Pal, S. Banerjee, S. Lohar and P. Chattopadhyay, *RSC Adv.*, 2014, **4**, 64014.
- 51 S. Pal, B. Sen, M. Mukherjee, M. Patra, S. L. Ganguly and P. Chattopadhyay, *RSC Adv.*, 2015, **5**, 72508.
- 52 Z. N. Yan, H. X. Wang, C. Y. Xu, X. L. Wen and B. X. Gu, *J. Mol. Liq.*, 2014, **190**, 185.
- 53 D. Sarkar, A. Pramanik, S. Biswas, P. Karmakar and T. K. Mondal, *RSC Adv.*, 2014, **4**, 30666.
- 54 R. Bhowmick, R. Alam, T. Mistri, K. K. Das, A. Katarkar, K. Chaudhuri and M. Ali, *RSC Adv.*, 2016, **6**, 11388.