Rhodamine-naphthalene conjugate as a novel ratiometric fluorescent probe for recognition of Al^{3+}

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Abstract: In this study, a novel chemosensor (HL) for Al^{3+} which contain rhodamine and naphthalene moieties has been designed and synthesized. In the presence of Al^{3+} , the receptor exhibited a strong, increasing fluorescent emission centered at 550 nm at the expense of the fluorescent emission of HL centered at 520 nm. We proposed that the addition of Al^{3+} triggered intramolecular fluorescence resonance energy transfer (FRET) from naphthalene to Rhodamine 6G.

Keywords: fluorescent sensor; rhodamine/naphthalene; Al^{3+} ; ratiometric; FRET/ICT

1. Introduction

As is known, Aluminum (Al) is the third most prevalent and abundant metal in the earth's crust [1]. Compounds of Al are widely dispersed and found in natural waters in food additives, in medicine etc. Nevertheless, as a non-essential element for living systems, high concentration of Al^{3+} can hamper plant performance, kill fish and other species in aquatic ecosystems. Even worse, the Al^{3+} ion existing in natural waters and most plants can enter the human body through water and foods.

Accumulation of excessive amount of Al^{3+} could lead to various neurodegenerative and neurological disorders, like Alzheimer's disease, Guamanian amyotrophic lateral sclerosis and Parkinsonism dementia [2-7]. According to a WHO report, the average daily human intake of Al is approx. 3–10 mg. The tolerable weekly Al intake in the human body is estimated to be 7 mg/kg of body weight [8]. Therefore, owing to its significant impact on the biosphere and human health, it is highly desirable to develop some analytical methods for detecting and controlling the concentration levels of aluminum in the environment.

To date, several methods are available for detection of Al^{3+} . Fluorescent chemosensor with high selectivity, sensitivity and real-time detection have attracted considerable attention. There are more and more Al^{3+} selective fluorescent sensors being reported in recent years [9-17]. However, most of them are mainly based on the change of single emission intensity such as PET which is easy to be affected by instrumental efficiency and environmental condition [18-22]. The design of ratiometric probes which can eliminate these deficiencies through simultaneous recording ratio signals of two emissions at different wavelengths is still challenge.

Fluorescence resonance energy transfer (FRET) is one of important mechanisms which can be applied to the design of ratiometric fluorescent probes. More specifically, FRET is a distance-dependent interaction between the electronic excited states of two different fluorophores in which excitation is transferred from donor moiety to acceptor moiety without photoemission, the transfer efficiency of the excitation primarily depend on the scope of spectral overlap between donor emission with

acceptor absorption and the distance between donor and acceptor [23-30]. With this in mind, it can be conceived that FRET-based fluorescent ratiometric sensor is made up of naphthalene (energy donor) and rhodamine (energy acceptor) moieties.

In this thesis, we have designed and synthesized a novel FRET-based fluorescent ratiometric sensor for Al^{3+} in which rhodamine and naphthalene moieties are linked by glyoxal. In the absence of Al^{3+} , the sensor exhibits fluorescence emission at 520 nm, which is attributed to naphthalene moieties, upon addition of Al^{3+} , the sensor shows a large fluorescence enhancement at 550 nm owing to the ring opened rhodamine moiety. Moreover, the presence of other relevant metal ions has almost no influence on the fluorescence enhancement and the theoretical detection limit for Al^{3+} can reach at $8.06 \times 10^{-8} \text{M}$.

2. Experimental

2.1 General information

2.1.1 Materials and instrumentation

Unless mentioned otherwise, all chemicals for synthesis were purchased from commercial suppliers and used without further purification. ^1H NMR spectra were measured on the JNM-ECS 400MHz instruments using TMS as an internal standard. ESI-MS were determined on a Bruker esquire 6000 spectrometer. UV-Vis absorption spectra were determined on a Shimadzu UV-240 spectrophotometer. Fluorescence spectra were recorded on a Hitachi RF-5301 spectrophotometer equipped with quartz cuvettes of 1 cm path length. The melting point was determined on a Beijing XT4-100x microscopic melting point apparatus. IR spectra were obtained in KBr

disks on a Thermo Mattson FT-IR spectrometer in the 4000-400 cm^{-1} region.

2.1.2 Analysis

The solutions of metal ions (5 mM) were prepared from NaNO_3 , KNO_3 , $\text{Ca}(\text{NO}_3)_2$, $\text{Mg}(\text{NO}_3)_2$, $\text{Al}(\text{NO}_3)_3$, CrCl_3 , FeCl_3 , FeCl_2 , CoCl_2 , $\text{Hg}(\text{NO}_3)_2$, $\text{Ni}(\text{NO}_3)_2$, $\text{Cu}(\text{NO}_3)_2$, $\text{Pb}(\text{NO}_3)_2$, $\text{Zn}(\text{NO}_3)_2$, LiNO_3 , AgNO_3 , $\text{Cd}(\text{NO}_3)_2$, $\text{Mn}(\text{NO}_3)_2$, BaCl_2 respectively, and were dissolved in distilled water. A stock solution of HL (2 mM) was prepared in DMSO. The solution of HL was then diluted 100 times under test. For fluorescence measurements, the excitation and emission slit width was 3 nm, the emission slit width was 1.5 nm

2.1.3. Calculation

The detection limit was calculated based on the fluorescence titration according to the following equation: detection limit $3\sigma/\kappa$. where σ was the standard deviation of blank measurements, and κ was the slope between intensity versus sample concentration [30]

2.2. Synthesis

Rhodamine 6G hydrazide (Fig.S1) was synthesized according to the method reported [31]. The sensor was synthesized as shown in Scheme 1[32-36].

Scheme1

2.2.1. Synthesis of compound Rg-CHO

Rhodamine hydrazide (0.86 g, 2 mmol) was dispersed in 20 mL ethanol, excess of glyoxal (40%, 1.16 g, 8 mmol) was added, and the mixture was stirred for 8 h at room temperature. The precipitate produced was filtered and washed 3 times with 10 mL cold ethanol. After drying under reduced pressure, the reaction yielded 0.77g RG1 as yellow solid. Yield: 76.3%, ^1H NMR (400 MHz; CDCl_3) (Fig.S2) $\delta(\text{ppm}) = 9.40$ (d, 1H, $J=7.5$ Hz, $\text{CH}=\text{O}$), 8.05 (dd, 1H, Ar-H), 7.54 (dd, 2H, Ar-H), 7.27 (d, 1H, $J=7.5$ Hz, $\text{CH}=\text{N}$), 7.18 (m, 1H, Ar-H), 6.37 (s, 2H, xanthene-H), 6.24 (s, 2H, xanthene-H), 3.54 (s, NHCH_2CH_3), 3.24-3.29 (q, $J=7.1$ Hz, 4H, NCH_2CH_3), 1.87 (s, 6H, xanthene- CH_3) 1.29-1.32 (t, $J=7.1$ Hz, 6H, NCH_2CH_3).

2.2.2. Synthesis of 5-bromoacenaphthene

A solution of N-bromosuccinimide (6.00 g, 33 mmol) in DMF (15 mL) was added to a DMF suspension (25 mL) containing acenaphthene (5.13 g, 33 mmol) with stirring at room temperature. After being stirred at room temperature for 2 h, then the solution was poured into cold water. The crude product was obtained via filtration, and the pure 5-bromoacenaphthene was obtained via recrystallization from ethanol. Yield : 73%. Mp: 51-52°C. ¹HNMR (400 MHz, DMSO-*d*₆): (Fig.S3) δ(ppm) =7.75~7.55 (m 3H, Ar-H), 7.37 (d, *J* = 7.4 Hz, 1H), 7.20 (d, *J* = 7.4 Hz, 1H), 3.39~3.33 (m, 1H), 3.31~3.25 (m, 1H).

2.2.2. Synthesis of 4-bromo-1, 8-naphthalic anhydride

5-bromoacenaphthene (1.78g, 7.64 mmol) was stirred with the mixture of glacial acetic acid (31ml) and sodium dichromate (5.31 g, 17.81 mmol) under reflux for 5 h. After cooled to the room temperature, then the dark green solution was poured into ice water (65 mL) and the residue was washed until colorless with cold water. And that the solid was stirred in 4% NaOH solution (30 mL) at 50 - 55 °C. After removing the solid via filtration, the filtrate was neutralised with 5 % hydrochloric acid and the white precipitate was formed. The solid obtained via filtration was then purified via recrystallization in glacial acetic acid. Yield: 36 %. Mp: 218 - 220 °C. ¹HNMR (400 MHz, DMSO-*d*₆) (Fig.S4): δ (ppm) 8.66~8.56 (m, 2H), 8.39 (d, *J* = 7.8 Hz, 1 H), 8.29 (d, *J* = 7.85 Hz, 1 H), 8.06 (t, *J* = 7.85 Hz, 1 H)

2.2.3. Synthesis of 4-bromo-N-n-butyl-1, 8-naphthalimide

4-bromo-1, 8-naphthalic anhydride (2.5g, 9 mmol) and n-butylamine (0.85g,

11.65 mmol) were refluxed with stirring for 12 h in ethanol (100 mL) until the mixture became clear. Then most ethanol was removed under reduced pressure and let stand overnight in refrigerator. A yellow solid was observed. Recrystallization from ethanol gave pale gray needles, Yield: 64 %. M.p:109-110°C. ¹HNMR (400 MHz, DMSO-*d*₆) (Fig.S5): δ (ppm) 8.53~8.50 (m, 2H), 8.32~8.30 (d, $J = 7.9$ Hz, 1 H), 8.19~8.17 (d, $J = 7.9$ Hz, 1 H), 7.98~7.94(m, 1 H), 4.04~4.00 (m, 2H), 1.64~1.57 (m, 2H),1.38~1.29 (m, 2H), 0.91 (t, $J = 7.4$ Hz, 3H).

2.2.4. Synthesis of 4-(aminoethylene)amino-N-n-butyl-1,8-naphthlimide (Nap-NH₂)

10 ml of ethylene diamine was dispersed in a round- bottomed flask of 50 ml. With continuous stirring at 50 °C and within an interval of 1 h, 0.8 g (2.41 mmol) of 4-bromo-N-n-butyl-1, 8-naphthalimide was evenly added. After heating at the same temperature for 5h, the mixture was cooled and poured into 20 ml of ice water. The residue was filtered and washed 5times with 10 mL water. Yield: 64% Mp: 130-131 °C. ¹HNMR (400 MHz, CDCl₃) (Fig.S6): δ (ppm) 8.52 (m, 1H),8.43(m, 1H), 8.13(m,1H), 7.64~7.57 (m,1 H), 6.69~6.64(m, 1 H), 6.16 (s,1H), 4.16~4.12 (m, 2H), 3.33~3.16 (m, 4H), 1.64~1.57 (m, 2H),1.38~1.29 (m, 2H),1.34 (s, 2H), 0.91 (t, $J = 7.4$ Hz, 3H).

2.2.5. Synthesis of HL

An ethanol solution (20 mL) of Nap-NH₂ (1 mmol, 0.31 g) was added to another ethanol (20 mL) containing Rg-CHO (1 mmol, 0.47 g). Then the solution was refluxing for 24 h under stirring, the precipitate produced was filtered and washed 3~5 times with 10 mL hot ethanol. After drying under reduced pressure, the reaction

afforded HL as yellow solid. Yield: 54 %. M.p:245~247°C. ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ (ppm) (Fig.S7) 8.55 (d, $J = 8.3$ Hz, 1H), 8.39 (d, $J = 7.8$ Hz, 1H), 8.19 (d, $J = 8.5$ Hz, 1H), 7.96 (d, $J = 7.8$ Hz, 1H), 7.86 (d, $J = 7.2$ Hz, 2H), 7.78~7.76 (m, 2H), 7.62~7.44 (m, 4H), 6.94 (d, $J = 7.5$ Hz, 1H), 6.77 (d, $J = 8.6$ Hz, 1H), 6.27(s, 2H), 6.13(s, 2H), 4.92 (t, $J = 5.3$ Hz, 2H), 3.99 (m, 2H), 3.72 (t, $J = 6.1$ Hz, 2H), 3.54 (q, $J = 6.0$ Hz, 2H), 3.15~3.06 (m, 4H), 1.81 (s, 6H), 1.61~1.52(m, 2H), 1.35~1.26 (m, 2H), 1.16~ 1.21 (t, $J=7.1$ Hz, 6H) 0.91 (t, $J = 7.4$ Hz, 3H). IR (KBr, cm^{-1}) (Fig.S8): 3439, 2949, 1686, 1551, HR-MS (Fig.S9) $[\text{M}+1]^+$ 762.3756, Calcd :762.3767, $[\text{M}+\text{Na}]^+$ 784.3578, Calcd : 784.3587

3. Results and discussion

3.1 UV-vis analysis

To investigate the binding property of HL and Al^{3+} , the changes in the absorption spectra of HL as a function of the concentration of Al^{3+} are shown in Fig. 1. The spectra of free HL showed an absorption band centered at 440 nm, which should be assigned to the naphthalene moieties, upon the gradual addition of Al^{3+} (0-3.0 equiv.) to a solution of HL, the absorption band at 440 nm exhibited a slightly blue shift ($\Delta\lambda =$ about 10 nm) along with decreasing intensity, Perhaps the reasons for this phenomenon was that the bonding with Al^{3+} and -NH- changed the photophysical properties of ICT fluorophore, consequently, resulting in the reduced of the efficiency of charge transfer from -NH- to -N-n-butyl [37]. In addition, two clear isosbestic points at 430 nm, 463 nm, were observed, which clearly indicated the presence of new complex in equilibrium with the sensor. More importantly, the characteristic

absorption band of rhodamine at about 530 nm was not observed for the free HL, demonstrating its existence in spirolactam form. However, the addition of Al^{3+} led to appeared a new absorption band at about 530 nm with increasing intensity owing to the ring opened rhodamine moieties [38-39]. This indicated that the interaction of HL with Al^{3+} could trigger the formation of the ring-opened form of HL from the spirolactam form.

Fig. 1

3.2. Selectivity studies and effects of metal ions

As shown in Fig. 2, the selectivity of the sensor was investigated upon addition of several metal ions such as Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Hg^{2+} , Pb^{2+} , Mn^{2+} , Fe^{2+} , Ni^{2+} , Cu^{2+} , Fe^{3+} , Co^{2+} , Li^+ , Ag^+ , Ba^{2+} , Cd^{2+} , Zn^{2+} and Al^{3+} , the free sensor displayed fluorescence emission at 520 nm corresponding to naphthalene and the characteristic emission of rhodamine at 550 nm not appeared, which further demonstrated the rhodamine core was in the ring closed isomeric form. Upon addition of Al^{3+} , the fluorescence

emission (L-Al) at 500 nm showed a blue shift compared to the fluorescence emission at 520 nm (HL), combined with decreasing intensity. Moreover, the free the sensor displayed remarkable fluorescence enhancement at 550 nm which belong to the characteristic signal of the ring-opening of the spirolactam. The results further confirmed that the addition of Al^{3+} ions promoted the ring-opened reaction of the rhodamine spirolactam.

Fig. 2

In addition, in order to estimate the practical applicability of HL as a selective fluorescent sensor for Al^{3+} , the competition experiments and fluorescent titrations were carried out. From competition experiments, as shown in Fig. 3, we found that all the coexistent metal ions had no obvious interference with the detection of Al^{3+} . From fluorescent titrations, as shown in Fig. 4, the detection limit was calculated to be

$8.06 \times 10^{-8} \text{ M}$ (Fig. S10). Thus, it meant the sensor HL, having predominant recognition and selectivity, is of a good potential in the detection of Al^{3+} .

Fig. 3

Fig. 4

3.3. The complexation of HL with Al^{3+}

In order to further validate the stoichiometry of HL and Al^{3+} , Job's method for

fluorescence measurement was carried out. The total concentration of HL and Zn^{2+} was $20\ \mu\text{M}$. $X_L = ([\text{HL}]/([\text{Al}^{3+}] + [\text{HL}])$. As shown in Fig. 5, the maximum point appeared at a mole fraction of 0.5. The result has indicated that it was a 1:1 stoichiometry of the binding mode of HL and Al^{3+} which was further confirmed by the appearance of a peak at $m/z\ 832.98$ assignable to $[\text{HL} + \text{Al}^{3+} - 2\text{H} + \text{CH}_3\text{CH}_2\text{OH}]^+$ in the ESI/MS (Fig. S11).

Fig. 5

Since the formation of 1: 1 ligand-metal complexes were confirmed by Job's plot analysis and ESI/MS, in combination with the fluorescence titration, the binding constant values ($K_{\text{L-Al}} = 2.31 \times 10^4$) was calculated based on the modified Benesi–Hildebrand equations (Fig. S12) [40].

$$1/(F_x - F_0) = 1/(F_{\text{max}} - F_0) + (1/K[\text{C}])(1/(F_{\text{max}} - F_0))$$

where F_0 , F_x , and F_{max} were the ratio of the emission intensities (at 550 nm) and the emission intensities (at 520 nm) of the organic moiety considered in the absence of metal ion, at an intermediate metal ion concentration, and at a concentration of

complete interaction, respectively, and where K was the binding constant concentration.

3. The proposed mechanism

Based on the above experiments and some reported fluorescent probes which shared some similarities to HL, the Fluorescence (or Forster) resonance energy transfer (FRET), coupled with intramolecular charge transfer (ICT) was proposed to explain the fluorescence responses of the sensor to Al^{3+} . The sensing mechanism is schematically illustrated in Scheme 2 [26, 29, 41-43]. Up addition of Al^{3+} , the binding with -NH- and Al^{3+} resulted in the reduced of the efficiency of intramolecular charge transfer (ICT) from -NH- to -N-n-butyl, as result, the fluorescence emission exhibited a blue shift ($\Delta\lambda$ = about 20 nm). In addition, the fluorescence emission at 500 nm weaken compared to the fluorescence emission at 520 nm (HL) and a new emission band with a maximum at 550 nm appeared which were attribute to the FRET process, namely, the addition of Al^{3+} triggered the ring-opening of the spirolactam, thus, the excitation energy is passed from the donor (naphthalene moiety) to the acceptor (the ‘opened-up’ rhodamine moiety) and then a significant enhancement of the characteristic fluorescence of rhodamine at 550 nm emerged at the expense of the fluorescent emission at 500 nm.

Scheme 2

4. Conclusion

In summary, we have successfully developed a novel ratiometric chemosensor based on an asymmetric bis-Schiff base containing rhodamine and naphthalene moieties. Up addition of Al^{3+} , the fluorescence emission exhibited a blue shift along with decreasing intensity and a new emission appeared at 550 nm which were attributed to FRET, coupled with ICT. More importantly, the theoretical detection limit for Al^{3+} can reach at 10^{-8}M level which is sufficiently low to enable the detection of micromolar concentrations of Al^{3+} in many chemical and biological systems.

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References

- [1] Sen, S.; Mukherjee, T.; Chattopadhyay, B.; Moirangthem, A.; Basu, A.; Marek, J. *Analyst* 2012, 137, 3975-3981.
- [2] Tavakoli, O.; Yoshida, H. *Environ Sci Technol* 2005, 39, 2357-2363.
- [3] Weller, D.G.; Gutierrez, A.J.; Rubio, C.; Revert, C.; Hardisson, A. *J Agr Food Chem* 2010, 58, 10452-10457.
- [4] Perl, D.P.; Gajdusek, D.C.; Garruto, R.M.; Yanagihara, R.T.; Gibbs, C.J. *Science* 1982, 217, 1053-1055.
- [5] Valeur, B.; Leray, I. *Coord Chem Rev.* 2000, 205, 3-40.
- [6] Perl, D.P.; Brody, A.R. *Science* 1980, 208, 297-299.
- [7] Fasman, G.D.; *Coord Chem Rev* 1996, 149, 125-165.
- [8] Krejpcio, Z.; Wojciak, R.W.; *Pol J Environ Stud* 2002, 11, 251-254.
- [9] Qin, J.C.; Li, T.R.; Wang, B.D.; Yang, Z.Y.; Fan, L. *Synth Metals* 2014, 195, 141-146.
- [10] Das, S.; Dutta, M.; Das, D. *Anal. Methods* 2013, 5, 6262-6285.
- [11] Lohani, C. R.; Kim, J.M.; Chung, S.Y.; Yoon, J.Y.; Lee, K.H.; *Analyst* 2010, 135, 2079-2084.
- [12] Han, T.Y.; Feng, X.; Tong, B.; Shi, B.J.; Chen, L.; Zhi, J.G.; Dong, Y.P. *Chem. Commun* 2012, 48, 416-418.
- [13] Kumar, A.; Kumar, V.; Upadhyay, K. K.; *Analyst* 2013, 168, 1891-1897.
- [14] Shi, X.Y.; Wang, H.; Han, T.Y.; Feng, X.; Tong, B.; Shi, J.B.; Zhi, J.; Dong, Y.P. *J. Mater. Chem* 2012, 22, 19296-19302.

- [15] He, L.; Liu, C. J.; Xin, H. *Sensors Actuat Chem-B* 2015, 213, 181-187.
- [16] Hsieh, W.H.; Wan, C.F.; Liao, D.J.; Wu, A.T. *Tetrahedron Lett* 2012, 53, 5848-5851.
- [17] Tiwari, K.; Mishra, M.; Singh, V. P. *RSC Adv* 2013, 3, 12124-12132.
- [18] Guha, S.; Lohar, S.; Sahana, A.; Banerjee, A.; Safin, D.A.; Babashkina, M.G.; Mitoraj, M.P.; Bolte, Garcia, M. Y.; Mukhopadhyay, S.K.; Das, D. *Dalton Trans* 2013, 42, 10198-10207.
- [19] Goswami, S. A.; Das, K.; Aich, K.; Manna, A.; Fun, H. K.; Quah, C. K. *Supramol. Chem* 2014, 2, 94-104.
- [20] Ye, X.P.; Sun, S.B.; Li, Y.D.; Zhi, L.H.; Wu, W.N.; Wang, Y. J. *Lumin* 2014, 155, 180-184.
- [21] Sahana, A.; Banerjee, A.; Lohar, S.; Sarkar, B.; Mukhopadhyay, S.K.; Das, D. *Inorg. Chem* 2013, 52, 3627-3633.
- [22] Qin, J.C.; Yang, Z.Y. *Synth Metals* 2015, 209, 570-576
- [23] Wang, C.C.; Liu, Y.Q.; Cheng, J.Y.; Song, J.H.; Zhao, Y.F.; Ye, Y. E. *J. Lumin.* 157 (2015) 143-148.
- [24] Georgiev, N. I.; Asiri, A. M.; Qusti, A. H.; Alamry, K. A.; Bojinov, V. B. *Dyes and Pigment* 2014, 102, 35-45.
- [25] Sahana, A.; Banerjee, A.; Lohar, S.; Banik, A.; Mukhopadhyay, S. K.; Safin, D. A.; Babashkina, M. G.; Bolte, M.; Garcia, Y.; Das, D. *Dalton Trans.* 2013, 42, 13311-13314.
- [26] Q, J.C.; Yang, Z.Y.; Wang, G.Q; G.Q.; Li, C.R. *Tetrahedron Lett* 2015, 56,

- [27] Sen, B.; Pal, S.; Lohar, S.; Mukherjee, M.; Mandal, S. K.; Khuda, A. R.; Chattopadhyay, P. RSC Adv 2014, 4, 21471-21478.
- [28] Mi, Y.S.; Liang, D.M.; Chen, Y.T.; Luo, X.B.; Xiang, J.N. RSC Adv 2014, 4, 42337-42345.
- [29] Yu, C.W.; Wen, Y.Y.; Qin, X.; Zhang, J. Anal. Methods 2014, 6, 9825-9830
- [30] Lohani, C. R.; Kim, J. M.; Chung, S.Y.; Yoon, J.; Lee, K. H.; Analyst 2010, 135, 2079-2084
- [31] Chen, Y.T.; Mu, S.Y. Journal of Lumin. 2014,145, 760-766.
- [32] Tian, M.Z.; Peng, X.J.; Fan, J.L.; Wang, J.Y.; Sun, S.G. Dyes Pigments 2012, 95, 112-115.
- [33] Du, J.J.; Fan, J.L.; Peng, X.J.; Sun, P.P.; Wang, J.Y.; Li, H.L.; Sun, S.G. Org. Lett 2010,12, 476-479.
- [34] Zhang, C.L.; Liu, Z.P.; Li, Y.L.; He, W.J.; Gao. X.; Guo, ZJ. Chem. Commun. 2013, 49, 11430-11432
- [35] Liu, B.; Tian, H. Chem. Commun., 2005, 3156-3158
- [36] Wang, J.X.; Xu, Z.G.; Zhao, Y.; Qiao, W. H.; Li, Z.G.; Dyes Pigments 2007,74, 103-107
- [37] Langdon-Jones, E. E.; Symonds, N.O.; Yates, S. E.; Hayes, A. J.; Lloyd, D.; Williams, R. Coles, S. J.; Horton, P.N.; Pope, S. J.A. Inorg. Chem. 2014, 53, 3788-3797
- [38] Lee, M.H.; Giap, T. V.; Kim, S. H.; Lee, Y. H.; Kang, C.; Kim, J. S. Chem.

Commun 2010, 46, 1407-1409.

- [39] Wu, Y.X.; Li, J.B.; Liang, L.H.; Lu, D.Q.; Zhang, J. G.; Mao, J. Zhou, L.Y.; Zhang, X.B.; Tan, W.H.; Shen, G. L.; Yu. R.Q. Chem. Commun 2014, 5, 2040-2042.
- [40] Benesi, H.A.; Hildebrand, J.H. J. Am. Chem. Soc 1949, 71, 2703-2707.
- [41] Pal, S.; Sen, B.; Lohar, S.; Mukherjee, M.; Banerjee, S.; Chattopadhyay, P.; Dalton Trans 2015,44,1761-1768.
- [42] Mahato, P.; Saha, S.; Suresh, E.; Liddo, R.D.; Parnigotto,P.P.; Maria Teresa Conconi, M.T.; Kesharwani, M.K.; Ganguly, B.; Das. A. Inorg. Chem. 2012, 51, 1769-1777
- [43] Zhang, J.F.; Zhou, Y.; Yoon, J. Y.; Kim, Y.M.; Kim, S. J.; Kim, J.S.; Org. Lett 2010, 17, 3852-3855

Figure captions

Fig. 1 Changes in the absorption spectra of HL (10 μ M) in ethanol at room temperature as a function of added Al^{3+} (0-1.0 equiv)

Fig.2. Fluorescence spectra of HL (20 μ M) upon the addition of metal salts (1.0 equiv of Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Pb^{2+} , Mn^{2+} , Fe^{2+} , Ni^{2+} , Fe^{3+} , Co^{2+} , Hg^{2+} , Li^+ , Ag^+ , Ba^{2+} , Cu^{2+} , Cd^{2+} , Zn^{2+} and Al^{3+} in ethanol (λ_{ex} =440nm, slit widths: 3nm/1.5 nm).

Fig. 3 Fluorescence intensity of HL and its complexation with Al^{3+} in the presence of various metal ions in ethanol, Red bar: HL (20 μ M) and HL with 1.0 equiv. of Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Pb^{2+} , Mn^{2+} , Cu^{2+} , Fe^{2+} , Ni^{2+} , Fe^{3+} , Hg^{2+} , Co^{2+} , Li^+ , Ag^+ , Ba^{2+} , Cd^{2+} , Zn^{2+} stated. Green bar: 20 μ M of HL and 1.0 equiv. of Al^{3+} ; 20 μ M of HL and 1.0 equiv. of Al^{3+} with 1.0 equiv. of metal ions stated in ethanol (λ_{ex} =440 nm, slit widths: 3 nm /1.5nm)

Fig. 4 Fluorescence spectra of the sensor HL (20 μ M) in ethanol upon the addition of Al^{3+} (0-1equiv.). (λ_{ex} =440 nm, slit widths: 3 nm /1.5nm. Inset: color of HL (right) and HL+ Al^{3+} system (left) under UV lamp.

Fig. 5 Job's plot for determining the stoichiometry of HL and Al^{3+} in ethanol ($X_{\text{Al}}=[\text{Al}^{3+}]/([\text{Al}^{3+}] + [\text{HL}])$, the total concentration of HL and Al^{3+} was 20 μ M).

Scheme1 Synthesis of HL, Reagents and conditions: (a) DMF, NBS, at room temperature, 2h. (b) glacial acetic acid, sodium dichromate, reflux, 5 h, 4% NaOH at 50 - 55 $^{\circ}\text{C}$, 5 % HCl, neutralization (c) EtOH, n-butylamine, reflux, 12h (d) ethylene diamine , at room temperature, 5 h (e) EtOH, reflux, 12h

Scheme 2 Proposed mechanism for detection of Al^{3+} by HL