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Water-soluble host-guest system from β-cyclodextrin as a fluorescent sensor for aluminium ion: synthesis and sensing studies

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In the paper, a simple small molecule (L) based on 4-(diethylamino)-2-hydroxy-benzaldehyd and carbohydrazide has been synthesized and characterized, moreover, under ultrasonic conditions, the host-gust system from β-cyclodextrin and L was obtained. According to the hybrid process, the host-guest system showed excellent water solubility. The investigation of fluorescence spectrum revealed that host-guest system exhibited characteristic fluorescence behavior toward Al^{3+} in pure water environment. Upon the addition of Al^{3+}, the host-guest system showed strong blue fluorescence, which resulted from the fluorophore of L after the coordination between β-CD-L and Al^{3+} with high binding constant (k = 3.1626E11 M^{-1}). In addition, the SEM demonstrated that the host-guest system expressed good crystallization behavior. The fluorescence microscope images of onion epidermal cells with β-CD-L-Al^{3+} proved the water-soluble host-guest system showed high ability of cell permeability.

Introduction

In recent years, the detecting and tracking of metal ions has caused extensive concern. Because some metal ions like chromium, cadmium and aluminium *et al* exhibit high toxicity and potential harm to environment and organism, which can be into the biological cycle according to food chain.[1-4] At present, the testing methods of metal ions like electrochemistry, atomic absorption spectrometry and atomic emission spectrometry have been used extensively, however, all these methods require sophisticated equipment, which are not suitable for assays in resource-poor settings or unforeseen accidents. Comparing with the methods, fluorescence probes technique has become an important research tool for sensing metal ions owing to the visualization, sensitivity and high selectivity.[5-9]

Among the metal ions fluorescence probes, the sensors toward aluminium ion have been studied extensively. Aluminium is the third most abundant metallic element in the earth, which accounts for 7.45% of the total of the earth's crust. Despite being a non-essential element in living organism, the detection of aluminium is very necessary and of great interest due to its potential toxicity and extensive application in packing materials, clinical drugs, deodorants and food additives *et al*.[10-12] In addition, aluminium has been proved to be a neurotoxin for a long time, and the abnormal content of aluminium can cause many health hazard such as Alzheimer's disease, osteomalacia and the risk of breast cancer.[13-14] And the excessive use of aluminium ion also leads to environmental pollution, which can have substantially adverse biological and ecological effects.[15-16] So fast detection and quantitative analysis of aluminium ion are very important to natural environment and human health.

Over the years, the fluorescence sensors for aluminium have been synthesized and researched.[17-20] But the sensors are derived from mainly organic small molecules. And the poor solubility of organic sensors in pure water environment limits its application under physiological conditions.[21-23] So the water-soluble fluorescent sensors are an important research subject. Among the water solubility sensor's research methods, the fabrication of host-guest systems is an significant technique. Among the host-guest systems, β-cyclodextrin (β-CD) is an important host molecule owing to its unique structure, which exhibits high water solubility, low toxicity and good biocompatibility and have been widely used in many fields like medicine, chemical engineering and separation technique *et al*.[24-26] And that the β-cyclodextrin derived host-guest system has been have related report,[27-29] but such host-guest fluorescent sensors are relatively scarce in recent years. In addition, the diversity of organic molecules can generate various host-guest system.

In continuation of our research topic based on water-soluble fluorescent sensors in biological organism and environment.[30-31] Herein, An organic fluorescent probe from diethylamine salicylaldehyde has been synthesized and characterized, then by ultrosonic reaction, an host-guest system from β-cyclodextrin and diethylamine salicylaldehyde drivate is prepared systemically. The host-guest system shows high

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water solubility. Simultaneously, the strong binding property between host-guest system and Al^{3+} leads to high sensitivity and selectivity over other metal ions. According to the spectra analysis, the water-soluble fluorescent probe exhibits distinctive fluorescence emission, and the typical spectra characters which can be used to detect Al^{3+} selectively enhance the accuracy and sensitivity. The high water solubility and spectra properties of the probe for Al^{3+} improve the prospects in environment and biological analysis.

Results and discussion

Spectra investigation

To investigate the fluorescence selectivity of β-CD-L toward various metal ion, the fluorescence selectivity experiments (Al^{3+},Zn^{2+},Cu^{2+},Cd^{2+},Hg^{2+},Mg^{2+},K^{+},Mn^{2+},Cr^{3+},Fe^{3+},Ga^{3+},In^{3+},Sn^{4+}) were conducted in HEPES buffer solution at pH = 7.2. As Shown in Fig. 1 a, in the absence of various metal ions, the host-guest system β-CD-L exhibited rather weak fluorescence in the range from 400 nm to 450 nm in HEPES medium (pH = 7.2). However, upon addition of 2 equivalent metal ions, only the addition of Al^{3+} lead to approximately 25-fold fluorescence enhancement in pure aqueous media. Except for weak fluorescence increase for Cr^{3+} and Zn^{2+}, other metal ions could not arouse obvious fluorescence changes of β-CD-L. It proved that the coordination between Al^{3+} and β-CD-L aroused the large enhancement of fluorescence in pure aqueous media. The fluorescence behavior preliminarily indicated β-CD-L could act as an fluorescence probe for Al^{3+} under physiological pH and pure water conditions. This absolute water solubility experiment condition was the significant advantage of the host-guest system β-CD-L. In addition, according to the histogram (Fig. 1 b), the highly selectivity of β-CD-L for Al^{3+} over other metal ions were indicated more obviously. Further, to illustrate the selectivity of β-CD-L toward Al^{3+} in aqueous media, the fluorescence images under UV light were also made (Fig. 1 b inset). Upon addition of 2 equivalent metal ion, only the solution of β-CD-L with Al^{3+} showed remarkable blue fluorescence under UV light, which indicated β-CD-L could act as a highly selective fluorescent chemosensor for Al^{3+} in absolute aqueous media. Fluorescence titration

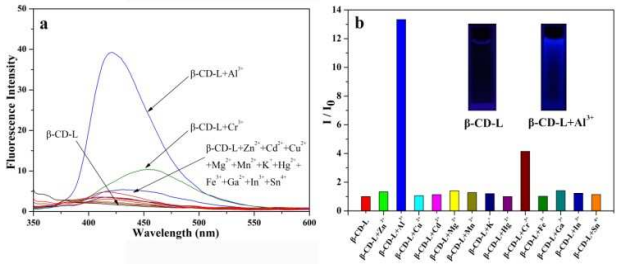


Fig. 1 a. The changes in the fluorescence spectra (excitation at 335 nm, Slit: excitation/emission = 5/5) of β-CD-L (1.25×10^{-5} M) in the presence of different metal ions (1.0×10^{-5} M) in HEPES buffer solution (pH = 7.2). b. the histogram of selectivity for various metal ions.

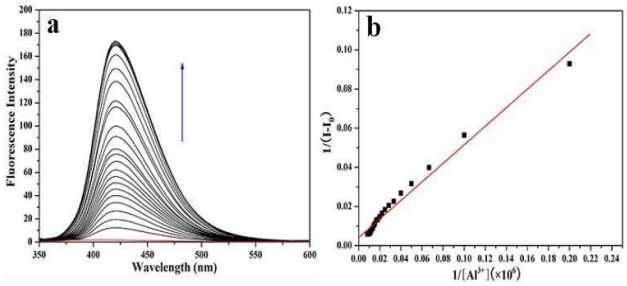


Fig. 2 a. Fluorescence titration spectra of β-CD-L (1.25×10^{-5} M) upon addition of Al^{3+}. (0–5 equiv) in HEPES solution (pH = 7.2). Excitation at 335 nm. b. Fitting of fluorescence titration curve of β-CD-L in HEPES solution (pH = 7.2), R = 0.98962, SD = 0.00295, The binding constant k = 3.1626E11 M^{-1}.

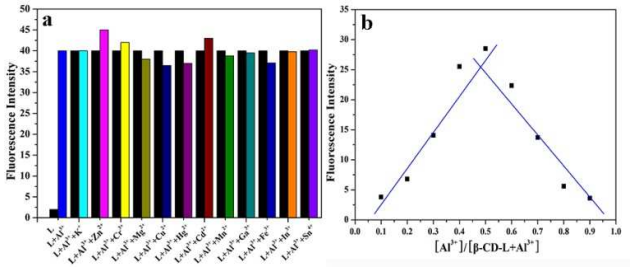


Fig. 3 a. Fluorescence competition experiment between Al^{3+} and other various metal ions in HEPES solution (pH = 7.2). b. The Job plot of β-CD-L (1.25×10^{-5} M) and Al^{3+} in HEPES solution (pH = 7.2).

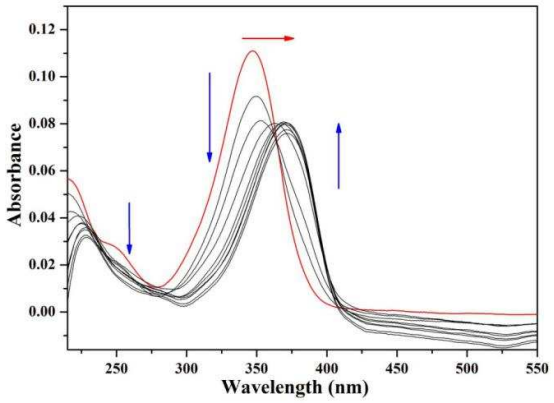


Fig. 4 The Uv-vis absorption spectra of β-CD-L (5.0×10^{-6} M) in HEPES buffer media in the presence of different amounts of Al^{3+} (0–2 equiv).

experiment (Fig. 2 a) of β-CD-L with Al^{3+} was performed in aqueous buffer media at room temperature. Upon addition of Al^{3+}, the fluorescence signal at 425 nm significantly enhanced. It was explicit that the binding between β-CD-L and Al^{3+}

induced the enhancement of fluorescence intensity. It was also clear that the fluorescence enhancement process of water-soluble sensor, which was switched on by coordinative Al^{3+} as the excitation at 335 nm, resulted in the emission of L with a maximum at 425 nm. Moreover, compared with the fluorescence titration spectrum of L with Al^{3+} in Ethanol-H_2O (Fig. S4), the fluorescence of β-CD-L with Al^{3+} exhibited greater enhancement in pure water environment, which demonstrated that the fabrication of host-guest system protected L from the contact of water molecules. As shown in Fig. 2 b, the association constant between β-CD-Land Al^{3+} was estimated to be 3.1626×10^{11} M^{-1} in aqueous media by fitting the data to the Benesi-Hildebrand expression with a good linear relationship (R=0.98962). Additionally, by the Job plot shown in Fig. 3 b, the binding mode between β-CD-L and Al^{3+} was investigated systemically. We could deduce that there was a 1:1 stoichiometry between β-CD-L with Al^{3+}. Moreover, in accordance with the 1:1 stoichiometry, the fluorescent chemosenor was most likely to chelate with Al^{3+} ion via its carbonyl O, imino N and hydroxyl O atoms.

Further, to validate the high selectivity of β-CD-L toward Al^{3+}, the fluorescence competitive experiments of Al^{3+} with other cations were also investigated. 2 equivalent Al^{3+} was added to the aqueous solution of β-CD-L (5.0×10^{-6} M), then equivalent amount of other metal ions (Zn^{2+},Cu^{2+},Cd^{2+},Hg^{2+},Mg^{2+},K^{+},Mn^{2+}, Cr^{3+},Fe^{3+},Ga^{3+},In^{3+},Sn^{4+}) were also injected into the solution. The fluorescence intensities were recorded, respectively. The histogram of fluorescence changes were listed in Fig. 3 a, As shown in histogram, no significant variation in the fluorescence emission of β-CD-L-Al^{3+} was observed by comparison with the fluorescence property with addition of other metal ions. All the results indicated the high selectivity of β-CD-L toward Al^{3+} over other co-existent metal ions in pure aqueous media.

As shown in Fig. 4, the absorption spectrum of β-CD-L in aqueous media exhibited a strong peak at 345 nm, which was ascribed to the absorption of carbonyl group from β-CD-L. With addition of Al^{3+}, the intensity of the absorption peak reduced significantly along with the appearance of new peak at 375 nm with the faint yellow solution, clearly demonstrating the formation of coordination form of β-CD-L with Al^{3+} binding. To evaluate the sensitivity of chemosensor β-CD-L for Al^{3+} in aqueous media, the detection limit of β-CD-L in recognizing

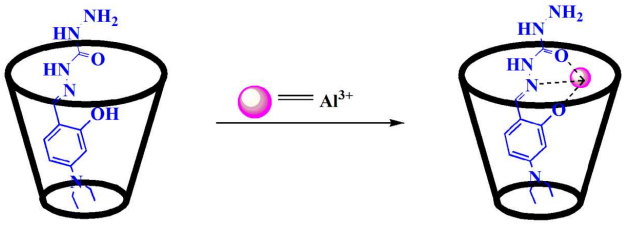


Fig. 5 Models of interactions between host-guest system β-CD-L and Al^{3+} in pure water environment

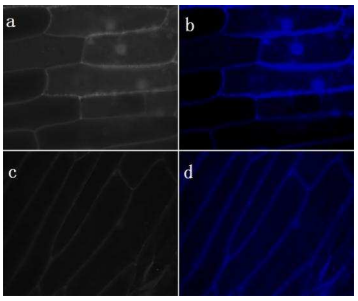


Fig. 6 The fluorescence microscope images of onion epidermal cells with β-CD-L and Al^{3+} (b,d) under pure water environment showed intense blue fluorescence and did not show any fluorescence in the absence of Al^{3+} (a,c).

Al^{3+} was also tested using fluorescence spectra (Fig. S5). The fluorescence titration profile of β-CD-L (1.0×10^{-5} M) with Al^{3+} demonstrated the detection of Al^{3+} in aqueous media was at the part 10^{-7} M (0.1 ppM). Under the condition, the fluorescence intensities of chemosensor β-CD-L solution was still proportional to the amount of Al^{3+} in pure water environment. In addition, the reversibility between β-CD-L with Al^{3+} in pure water solution was also checked (Fig. S6). EDTA was conducted as an coupling reagent owing to the large binding constant of EDTA and Al^{3+}, EDTA was added to the water solution of β-CD-L treated with Al^{3+}, as shown in Fig. S6, the fluorescence intensity of β-CD-L-Al^{3+} showed no significant variation, which illustrated that the coordination between β-CD-L and Al^{3+} was irreversible.

Based on the fluorescence and Uv-vis spectra analysis, the water-soluble host-guest system exhibited high selectivity and sensitivity for Al^{3+}, and the sensing process was shown in Fig. 5, The organic molecule L, which inclused in β-CD, could coordinate with Al^{3+} in pure aqueous environment and showed intense blue fluorescence. The host-guest system was highly selective fluorescent sensor toward Al^{3+} in pure aqueous environment.

Cell fluorescence microscopy

The fluorescence microscope images with β-CD-L (Fig. 6 a,c) and β-CD-L-Al^{3+} (Fig. 6 b,d) under pure water environment were tested to demonstrate its application in tracking aluminium ion in biological systems. The onion epidermal cells were from fresh onion inner surface. And the onion epidermal was soaked in β-CD-L water solution for 5 min, then the soaked onion epidermal was observed under fluorescent microscope (Fig. 6 a,c). Moreover, suitable Al^{3+} solution was added to the onion epidermal cells handled with β-CD-L water solution, the onion epidermal cells fluorescence signal was recorded (Fig. 6 b,d). As shown in Fig. 9 , The onion epidermal cells showed intense blue fluorescence, and the nuclei of cells was also labeled clearly. No obvious fluorescence was observed when the cells were not treated with Al^{3+}. The results suggested the host-guest system β-CD-L could permeate the

cytoderm and plasma membrane of onion epidermal cells and give specific blue fluorescence signal in the nucleus only in the presence of Al^{3+}, which demonstrated that the water-soluble host-guest guest β-CD-L could be acted as an fluorescence sensor for Al^{3+} in biological system.

Experimental

Carbohydrazide and 4-diethylamino salicylaldehyde was purchased from aladdin reagent corporation. All the chemicals were of reagent grade and were used without further purification.

All spectroscopic measurements were performed in HEPES buffer solution (pH = 7.2).

Stock solutions (1×10^{-3} M) of metal ions (metal nitrate) were prepared using in two-distilled water. The stock solution of sensor (0.5×10^{-3} M) was prepared in two-distilled water. In titration experiments, each time a 50 μL solution of sensor β-CD-L was filled in a quartz optical cell of 1cm optical path length. Then equal amount of Al^{3+} stock solution (10 μL) was added to the compound solution with micro-pippet. Spectral data was recorded at 1 min after addition. In fluorescence selectivity experiment, the test samples were prepared by placing appropriate amounts of metal ion stock into 2 mL HEPES buffer solution of sensor β-CD-L (1.25×10^{-5} M). For fluorescence measurements, the excitation wavelength is at 335 nm. In Uv-vis spectrum, each time a 20 μL solution of sensor β-CD-L (0.5×10^{-3} M) was filled in a quartz optical cell of 1cm optical path length. Then 0–2 equiv amount of Al^{3+} stock solution (10 μL) was added to the compound solution with micro-pippet. Spectral data was recorded after addition.

The binding constant between sensor and Al^{3+} was calculated by the linear Benesi-Hildebrand expression.[32,33]

$$I_0 / (I-I_0) = I_0 / [L] + I_0 / [L].Ks.[M]$$

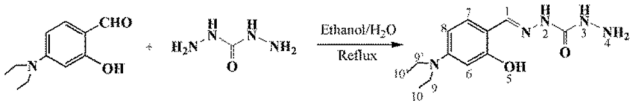
Where I is the change in the fluorescence intensity at 425 nm, Ks is the stability constant, [L] and [M] are the concentration of β-CD-L and Al^{3+}, respectively. I_0 is the fluorescence intensity of L in the absence of Al^{3+}. On the basis of the plot of $1 / (I-I_0)$ versus $1 / [Al^{3+}]$, the stability constant can be obtained.

Physical measurement

^{1}HNMR and ^{13}CNMR spectra were recorded on a Bruker Avance III 400 spectrometer with TMS as an internal standard. The melting points of the compound were determined on a Beijing XT4-100X microscopic melting point apparatus. The UV-Vis spectra were recorded on a Perkin-Elmer Lambda-35 UV-Vis spectrophotometer. Fluorescence spectra were obtained on a Cary Eclipse spectrophotometer at room temperature. The Scanning Electron Microscopy was tested on FEI Quanta 200. The fluorescence image of onion epidermal cells was tested using BX61 fluorescence microscope.

Synthesis of compounds 4-diethylaminobenzaldehyde-carbohydrazide schiff-base (L). and β-cyclodextrin-4-diethylaminobenzaldehyde-4-aminoantipyrine schiff-base (β-CD-L)

The synthetic route of 4-diethylaminobenzaldehyde-carbohydrazide schiff-base was shown in Scheme 1. An ethanol ethanol/H_2O solution (1:1, 10 mL) of carbohydrazide (1 mmol, 0.09 g) was added to another (10 mL) solution containing 4-diethylaminobenzaldehyde (1 mmol, 0.193 g), Then the solution was reflux for 6 h and cooled to room temperature. The mixture was filtered and dried under vacuum. Recrystallization from C_2H_5OH/H_2O (V:V = 1:1) gave the target product 4-diethylaminobenzaldehyde-carbohydrazide schiff-base (L), which was dried under vacuum. Yield, 62%. m.p.: 215–217 °C. ^{1}HNMR (Fig. S1 a, DMSO–d_6 400MHz): δ 10.379 (2H, s, –N^4–H), δ 10.061 (1H, s, –N^3–H), δ 8.211 (1H, s, –N^2–H), δ 8.054 (1H, s, –O^5–H), δ 7.714 (1H, s, –C^1–H), δ 7.347—7.235 (1H, m, –C^6–H), δ 6.200–6.257 (1H, m, –C^8–H), δ 6.098–6.125 (1H, m, –C^7–H), δ 3.402 (4H, m, –$C^{9,9'}$–H), δ 1.107–1.122 (6H, m, –$C^{10,10'}$–H). ^{13}CNMR (Fig. S1 b, DMSO–d_6 400MHz): δ=158.58, δ=157.32, δ=152.93, δ=150.41, δ=130.75, δ=108.49, δ=104.47, δ=98.55, δ=44.70, δ=13.50. EI-MS (Fig. S2): m/Z=233, $[M-NH_2-O]^+$



Scheme 1 The synthetic route of 4-diethylaminobenzaldehyde-carbohydrazide schiff-base (L)

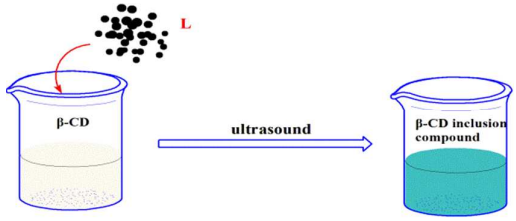


Fig. 7 The preparation process of β-cyclodextrin derived host-guest system β-CD-L

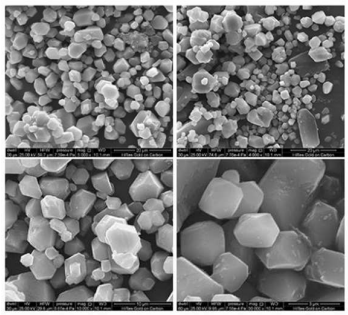


Fig. 8 The SEM graph of host-guest system β-CD-L

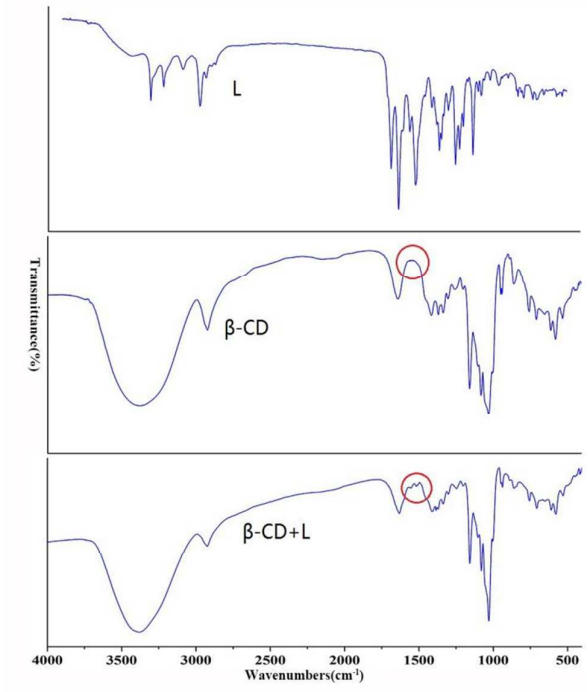


Fig. 9 The IR spectra of L, β-CD and β-CD-L

The schematic diagram of β-cyclodextrin derived host-guest system β-CD-L was listed in Fig. 7. 1 mmol β-cyclodextrin was dissolved in pure two-distilled water, then 1 mmol 4-diethylaminobenzaldehyde-carbohydrazide schiff-base (L) was added to water solution of β-cyclodextrin. The suspended mixture reacted for 26 h under ultrasound condition and 40 ℃. Then the suspended mixture undergo transmutation from mixture to aqueous solution. After cooling to room temperature, the solution was concentrated by vacuum distillation. The solid host-guest system β-CD-L was dried and was characterized by scanning electron microscope (SEM), IR spectrum and Uv-vis spectrum. According to SEM observation (Fig. 8), β-CD-L exhibited regular polygon morphology, simultaneously, the host-guest system β-CD-L has a good solubility in water. Moreover, make a comparison of IR spectra of L, β-CD and β-CD-L (Fig. 9), IR spectrum of β-CD-L showed obvious difference. The several vibration bands at 1500 cm^{-1} were attributed to the characteristic bands of L in the in the cavity of β-CD. But the IR characteristic bands from L were shielded by β-CD because of the fabrication of host-guest system. In addition, the Uv-vis spectra of L and β-CD-L were tested to demonstrate the formation of host-guest system (Fig. S3). The Uv-vis spectrum showed β-CD-L exhibited same absorption with L, which proved the constitute of the host-guest system between L and β-CD. Such the methods explained that the host-guest system β-CD-L were prepared successfully.

Conclusions

In summary, we have developed water-soluble β-cyclodexrin derived host-guest system fluorescent chemosensor for Al^{3+}. It exhibits high selectivity and sensitivity toward Al^{3+} over other metal ions in pure aqueous media. The host-guest system with addition of Al^{3+} in pure aqueous media showed specific fluorescence and intense blue fluorescence under the combined action of 4-(diethylamino)-2-hydroxy -benzaldehyd and carbohydrazide shiff-base with Al^{3+}. Moreover, according to the investigation, 1:1 stiochiometry compound between β-CD-L and Al^{3+} is formed. Additionally, the high binding constant was existent. Its fluorescence property was also investigated in a biological system. In onion epidermal cells, the host-guest system showed high fluorescence imaging property with Al^{3+}, and this observation demonstrated that the probe was cell permeable. The excellent selectivity of host-guest system with Al^{3+} in pure aqueous media indicated its potential application value tracking of aluminium ion.

Acknowledgements

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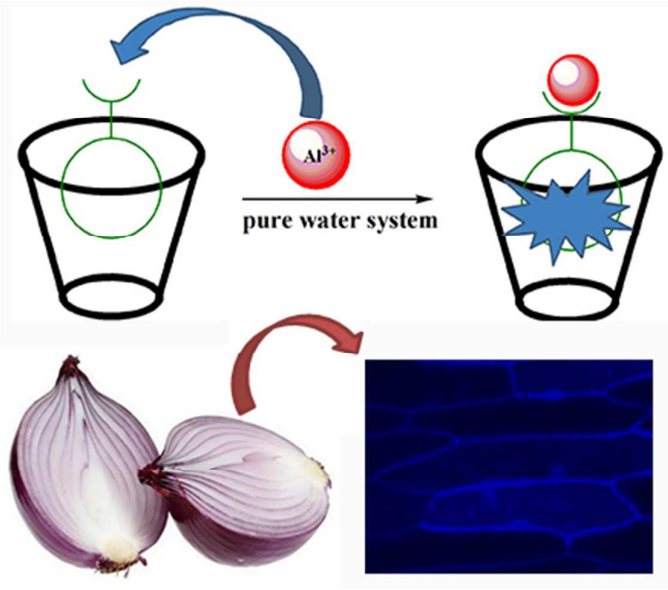
Notes and references

1 C. Orvig and M. J. Abrams, *Chem. Rev.*, 1999, **99**, 2201–2204.
2 V. Gomez and M. P. Callao, TrAC, *Trends Anal. Chem.*, 2006, **25**, 1006–1015.
3 A. K. Singh, V. K. Gupta and B. Gupta, *Anal. Chim. Acta.*, 2007, **585**, 171–178.
4 E. Àlvarez, M. L. Fernández-Marcos, C. Monterroso and M. J. Fernández-Sanjurjo, *Forest Ecol. Manag.*, 2005, **211**, 227.
5 P. de Silva, H. Q. Nimal Gunaratne, T. Gunnlaugsson, A. J. M. Huxley, C. P. McCoy, J. T. Rademacher and T. E. Rice, *Chem. Rev.*, 1997, **97**, 1515–1566.
6 S. Goswami, A. K. Das, A. K. Maity, A. Manna, K. Aich, S. Maity, P. Saha and T. K. Mandal, *Dalton Trans.*, 2014, **43**, 231-239.
7 B.D. Wang, J. Hai, Z.C. Liu, Q. Wang, Z.Y. Yang, S.H. Sun, *Angew. Chem. Int. Ed.*, 2010, **49**, 4576–4579.
8 Y. X. Li, Z. C. Liu, W. P. Zhu, H. Fu, Y. J. Ding, J. P. Xie, W. J. Yang, L. L. Li, C. Cheng, *J. FLuoresce.*, 2015, 25, 603–611.
9 P. Das, A. Ghosh, M. K. Kesharwani, V. Ramu, B. Ganguly, A. Das, *Eur. J. Inorg. Chem.*, 2011, **2011**, 3050−3058.
10 M. G. Soni, S. M. White, W. G. Flamm and G. A. Burdock, *Regul. Toxicol. Pharm.*, 2001, **33**, 66-79.
11 J. R. Lakowicz, *Kluwer Academic Publishers, New York*, 2002, 4.
12 R. L. Blaylock, *Curr. Inorg. Chem.*, 2012, **2**, 46.
13 A. M. Gomes da Costa, E. M. Nogami, J. V. Visentainer, N. E. de Souza and E. E. Garcia, J. Agr. Food. Chem., *2009*, **1**, 196–200.

14 Y. Matsui, T. Matsushita, S. Sakuma, T. Gojo, T. Mamiya, H. Suzuoki and T. Inoue, *Environ. Sci. Technol.*, 2003, **22**, 5175–5180.
15 Y. Kawanishi, K. Kikuchi, H. Takakusa, S. Mizukami, Y. Urano, T. Higuchi and T. Nagano, *Angew. Chem., Int. Ed.*, 2000, **112**, 3580.
16 S. Deo and H. A. Godwin, J. Am. Chem.Soc., 2000, 122, 174.
17 (a)J. Kumar, M. J. Sarma, P. Phukan and D. K. Das, *Dalton Trans.*, 2015, **44**, 4576-4581.(b)S. Goswami, S. Paul, A. Manna, *RSC Adv.*, 2013, **3**, 10639-10643. S. Goswami, A. Manna, S. Paul, A. K. Maity, P. Saha, C. H. Quah and H. K. Fun, *RSC Adv.*, 2014, **4**, 3472-34576. S. Goswami, S. Paul, A. Manna, *RSC Adv.*, 2013, **3**, 25079-25085. S. Goswami, K. Aich, S. Das, A. k. Das, D. Sarkar, S. Panja, T. K. Mondal and S. Mukhopadhyay, *Chem. Commun.*, 2013, **49**, 10739-10741.
18 (a)A. Dhara, A. Jana, N. Guchhait, P. Ghosh and S. K. Kar, *New. J. Chem.*, 2014, **38**, 1627-1634. (b)S. Goswami, A. Manna, S. Paul, K. Aich, A. K. Das and S. Chakraborty, *Dalton Trans.*, 2013, **42**, 8078-8085. S. Goswami, A. K. Das, K. Aich, A. Manna, H. K. Fun and C. K. Quah, *Supramol. Chem.*, 2014, **26**, 94-106. S. Goswami, K. Aich, A. K. Das, S. Manna and S. Das, *RSC Adv.*, 2013, **3**, 2412-2416.
19 A. Sahana, A. Banerjee, S. Lohar, A. Banik, S. K. Mukhopadhyay, D. A. Safin, M. G. Babashkina, M. Bolte, Y. Garcia and D. Das, *Dalton Trans.*, 2013, **42**, 13311-13314
20 B. Sen, S. Pal, S. Lohar, M. Mukherjee, S. K. Mandal, A. R. Khuda, B. P. Chattopadhyay, *RSC Adv.*, 2014, **4**, 21471-21478.
21 C. H. Chen, D. J. Liao, C. F. Wan and A. T. Wu, *Analyst*, 2013, **138**, 2527-2530.
22 N. A. Kumar, V. Kumar, R. Prajapati, S. K. Asthana, K. K. Upadhyay and J. Z. Zhao, *Dalton Trans.*, 2014, **43**, 5831-5839
23 H. D. Xiao, K. Chen,N. N. Jiang, D. D. Cui, G. Yin, J. Wang and R. Y. Wang, *Analyst*., 2014, **139**, 1980-1986.
24 (a)G. Chen and M. Jiang, *Chem. Soc. Rev.*, 2011, **40**, 2254–2266. (b) K. N. Jayaprabha and P. A. Joy, *RSC Adv.*, 2015, **5**, 22117-22125. (c) F. Hapiot, S. Tilloy, and E. Monflier, *Chem. Rev.*, 2005, **3**, 767-781.
25 Y. W Yang, Y. Chen, Y. Liu, *Inorg. Chem.*, 2006, **45**, 3014–3022
26 Y. J. Yao, X. W. Liu, T. Liu, J. Zhou, J. Zhu, G. Sun and D. N. He, *RSC Adv.*, 2015, **5**, 6305-6310.
27 C. R. Palomero, M. L. Soriano and M. Valcárcel, *Analyst*, 2015, **140**, 3431-3438.
28 L. Szente and J. Szemán, *Anal. Chem.*, 2013, **85**, 8024–8030.
29 Z. Chen, Q. Wang, X. Wu, Z. Li and Y. B. Jiang, *Chem. Soc. Rev.*, DOI: 10.1039/c4cs00531g
30 Z. C. Liu, Z. Y. Yang, Y. X. Li, T. R. Li, B. D. Wang, Y. Li, X. L. Jin, *Inorg. Chim. Acta.*, 2013, **395**, 77–80.
31 Z. C. Liu, Y. X. Li, Y. J. Ding, Z. Y. Yang, B. D. Wang, Y. Li, T. R. Li, W. Luo, W. P. Zhu, J. P. Xie, C. J. Wang, *Sensor. Actuat. B-Chem.*, 2014, **197**, 200–205.
32 H. A. Benesi, J. H. Hildebrand, *J. Am. Chem. Soc.*, 1949, **71**, 2703–2707.
33 B.D. Wang, J. Hai, Z.C. Liu, Q. Wang, Z.Y. Yang, S.H. Sun, *Angew. Chem. Int. Edit.*, 2010, **27**, 4576–4579.



In the paper, a simple small molecule derived from 4-(diethylamino)-2-hydroxy-benzaldehyd and carbohydrazide has been synthesized and characterized, moreover, under ultrasonic conditions, an water-soluble host-gust system from β-cyclodextrin and L was obtained. It exhibited characteristic fluorescence behavior toward Al^{3+} in pure water environment. The fluorescence microscope images of onion epidermal cells with β-CD-L-Al^{3+} proved the water-soluble host-guest system showed high ability of cell permeability.