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A quinoline-functionalized amphiphilic fluorogenic probe for specific detection of trivalent cations

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Shengyang Tao* [a], Ying Wei [a], Chan Wang [b], Zhaoqi Wang [a], Pan Fan [a], Da Shi[a], Baojun Ding[a] and Jieshan Qiu[c]

A novel fluorescent probe, which has an amphiphilic structure and can selectively detect and distinguish trivalent metal cations, was synthesized. The probe has a hydrophobic quinoline head and a hydrophilic pyridinium tail. This amphiphilic molecular structure makes the molecule exhibit ideal solubility and sensitivity in three kinds of solvents, including EtOH, CH_3CN and H_2O. The ideal cross-reactivity of this probe in different solvents provided it ability to distinguish Fe^{3+}, Cr^{3+}, Al^{3+}, Ru^{3+} and Au^{3+} through PCA method. The detection limits of the probe to trivalent metal cations reach micromolar range.

Introduction

Detection of various trivalent metal cations (M^{3+}) is an important task for chemists since many M^{3+} ions play crucial roles in the environment and human daily physiological activity[1, 2]. For instance, Al^{3+} is abundantly found in nature. Aluminum compounds have been widely used in water purification, pharmaceuticals and food. Metallic aluminum also is processed into kitchenware. In recent years, it has been found that the over dose of Al^{3+} in human body can cause series diseases, such as Alzheimer's disease, osteoporosis, headache, memory loss and gastrointestinal problems[3-5]. Chromium in its trivalent form is one of the most important heavy metal elements. It is an essential mineral element in human health and has a huge impact on the metabolism of carbohydrates, proteins and fats[6, 7]. Lack of Cr^{3+} can disturb glucose levels and lipid metabolism[8, 9]. Meanwhile, Cr^{3+} from mining and electroplate industries leads to serious pollutions of water, solid and agriculture[10-12]. As the second most abundant metal in the Earth's crust, Fe^{3+} is a familiar nutrition element for people who even do not understand chemistry. It exists in cellular tissues, and has significant biological importance in lots of biochemical processes, especially in electron transfer and oxygen transport reactions[13-15].

Different equipment can detect M^{3+} metal ions, including X-Ray Photoelectron Spectrometer (XPS), Inductive Coupled Plasma Emission Spectrometer (ICP), and Atomic fluorescence spectroscopy (AFS) [16-18]. Compared with these expensive and complicated methods, luminescence chemosensor is facile and highly sensitive. It usually gives a quick response to trace amount of M^{3+} cations[19-21]. Various sensors based on fluorescent indicators have been developed, such as naphthalene, rhodamine, porphyrin, BODIPY and fluorescein[22-26]. Some Al^{3+}, Cr^{3+} and Fe^{3+} selective fluorogenic probes have been reported[27-31]. However, there are still problems in this field. First, most fluorescent molecules contain polycyclic aromatic structure, so the solubility of them in many solvents is not high[32-36]. Therefore, developing new sensing molecules, which can be applied in different solvents, including water, will be useful for detecting M^{3+} cations. Then, to get a selective detectability, probe molecules are usually designed with complex structure which is difficult to be synthesized, and one probe only can be used for one special M^{3+}. This greatly increase the cost for detection. Finally, the reported fluorescent probes for M^{3+} can distinguish the M^{3+} from M^{2+} and M^{+}, but for each individual M^{3+}, they don't show a significant distinction. So developing a new fluorescent probe, which can be employed universally for selectively detecting and distinguishing M^{3+}, is quite necessary.

Herein, we reported a new amphiphilic fluorogenic probe for specific detection of five kinds of trivalent cations, including Al^{3+}, Fe^{3+}, Cr^{3+}, Ru^{3+} and Au^{3+} in acetonitrile, water and ethanol. The fluorescence probe shows cross-reactivity in the three solvents. Therefore, this amphiphilic fluorogenic probe can not only distinguish M^{3+} from M^{2+} and M^{+} ions, but also accurately identify various M^{3+} through principal component analysis (PCA). The detection limits of the probe to trivalent metal cations reach micromolar range. The PCA data exhibit about 99.99% of the total variance to identify the five M^{3+} ions.

Experimental

Chemicals

8-hydroxyquinoline, 1,12-dibromododecane, pyridine, ethyl acetate, tetrabutylammonium bromide, petroleum ether, acetonitrile, methanol, dichloromethane, sodium hydroxide and magnesium sulfate anhydrous, were purchased from Beijing Chemical Company. Other reagents including ethanol absolute, aluminium nitrate, aluminium chloride, ruodium chloride, iron (Ⅲ) nitrate, iron (Ⅲ) chloride, chromium (Ⅲ) nitrate, chromium (Ⅲ) chloride, gold (Ⅲ) chloride, silver nitrate, potassium nitrate, sodium nitrate, sodium perchlorate, potassium iodide, calcium chloride anhydrous, cobalt nitrate, zinc chloride , magnesium nitrate, nickel chloride, copper nitrate were purchased from Aladdin. Mercuric chloride was purchased from Sinopharm Chemical Reagent Co., Ltd. Chlorates of trivalent metal ions were dissolved in water and EtOH. Perchlorates of trivalent metal ions were dissolved in CH3CN. Metal nitrates were used for preparation of perchlorates. All chemicals were used without further purification. Perchlorate were prepared from our laboratory.

Synthesis of $QC_{12}Br$

8-hydroxyquinoline (0.74 g, 5 mmol) was dissolved in dichloromethane (20 mL). To this, 10% aqueous sodium hydroxide, tetrabutylammonium bromide (0.16 g, 0.5 mmol) and 1,12-dibromododecane (1.64 g, 5 mmol) were added under stirring. The resulting mixture was stirred at room temperature for 24 hours. After the reaction was complete, the layers were separated and the organic layer washed with water. The solution was dried over anhydrous magnesium sulfate, and then filtered. The solvent was removed by rotary evaporation at reduced pressure. The crude product was purified by silica gel column chromatography with ethyl acetate/petroleum ether = 1/1 (volume ratio) as an eluent to yield the desired product. Yield: 40%; yellow solid.

^{1}H NMR ($CDCl_3$): 8.94-8.95 (d, 1H, J=4 Hz), 8.10-8.12 (d, 1H, J=8 Hz), 7.40-7.46 (m, 2H), 7.35-7.39 (d, 1H, J=16 Hz), 7.05-7.07 (d, 1H, J=8 Hz), 4.21-4.25 (t, 2H, J_1=J_2=8 Hz), 3.38-3.41 (t, 2H, J_1=4 Hz, J_2=8 Hz), 2.00-2.05 (m, 2H), 1.81-1.86 (m, 2H), 1.48-1.56 (m, 2H), 1.28-1.41 (m, 14H). MS (EI) = 392.2 (M^{+}).

Synthesis of $QC_{12}PyBr$ (probe 1)

The obtained QC12Br (1.05 g, 2.7 mmol) was dissolved in acetonitrile (50 mL), and pyridine (3 mL) was added dropwise under vigorous stirring. The resulting mixture was refluxed for 24 h, and then cooled to room temperature. The crude product was concentrated on a rotary evaporator and purified by silica gel column chromatography with dichloromethane/methanol = 10/1(volume ratio) as an eluent, affording the desired product. Yield: 80%; beige solid.

^{1}H NMR ($CDCl_3$): 9.52-9.53 (d, 2H, J=4 Hz), 8.95-8.96 (d, 1H, J=4 Hz), 8.50-8.54 (t, 1H, J_1=J_2=8 Hz), 8.12-8.17 (t, 3H, J_1=8 Hz, J_2=12 Hz), 7.43-7.49 (m, 2H), 7.38-7.40 (d, 1H, J=8 Hz), 7.07-7.09 (t, 1H, J=8 Hz), 5.00-5.03 (t, 2H, J_1=8 Hz, J_2=4 Hz), 4.21-4.25 (t, 2H, J_1=J_2=8 Hz), 1.96-2.07 (m, 4H), 1.23-1.53 (m, 16H). ^{13}C NMR (500 MHz, $CDCl_3$), δ (TMS, ppm):26.00, 29.35, 31.96, 62.12, 69.06, 108.83, 119.39, 121.53, 126.85, 128.43, 129.51, 136.17, 140.13, 142.65, 145.14, 149.07, 154.71. MS (EI) = 392.2 (M^{+}). Elemental analysis: calcd (%): C, 66; H, 7.4; N, 5.9; found (%): C, 62.12; H, 7.68; N, 5.52.

Preparation of the fluorometric metal ion titration solution

Stock solutions (1×10^{-2} M) of the Al^{3+}, Fe^{3+}, Cr^{3+}, Ru^{3+}, Au^{3+}, K^{+}, Na^{+}, Ag^{+}, Ca^{2+}, Co^{2+}, Cu^{2+}, Hg^{2+}, Mg^{2+}, Ni^{2+}, Zn^{2+} and Fe^{2+} using their salts were prepared in EtOH, CH_3CN and H_2O . The solution of probe 1 (1×10^{-4} M) was prepared in EtOH, CH_3CN and H_2O. Each time, a 2 mL solution of probe 1 was added to a quartz cuvette of 1 cm optical path length, and different stock solutions of cations were gradually added into the quartz cuvette by micro-syringe addition.

Preparation of the adsorptive metal ion titration solution

Stock solutions (1×10^{-2} M) of the Al^{3+}, Fe^{3+}, Cr^{3+}, Ru^{3+} and Au^{3+} using their perchlorate salts were prepared in CH_3CN. Moreover, the solutions of Al^{3+} using nitrate salt were prepared in H_2O and EtOH. The solution of probe 1 (1×10^{-4} M) was prepared in the same way as in the case of fluorescence titration. Each time, a 2 mL solution of probe 1 was added to a quartz cuvette of 1 cm optical path length, and different stock solutions of cations were gradually added into the quartz cuvette by micro-syringe addition.

General procedure for drawing Job's plot by UV-vis adsorption

Stock solution of same concentration of probe 1 and M^{3+} (where M = Al^{3+}, Fe^{3+}, Cr^{3+}, Ru^{3+} and Au^{3+}) were prepared in the order of 10^{-3} M in EtOH, CH_3CN and H_2O. The adsorption spectra in each case with different *host-guest* ratio (0:10, 1:9, 2:8, 3:7, 4:6, 5:5, 6:4, 7:3, 8:2, 9:1, 10:0) but equal in volume was recorded.

Characterization

Element contents (C, O, N) were performed on 0.0001mg/vario EL III. The fluorescence emission measurements were carried out using a fluorescence spectrometer (Perkin-Elmer, LS55). Both excitation and emission slit widths were fixed at 5 nm and 10 nm. The emission data were collected in the region of 390 to 700 nm. UV–visible absorption spectra were recorded using a Perkin-Elmer Lambda 35 spectrometer. ^{1}H-NMR spectra was measured on a Varian INOVA 400M spectrometer with chemical shifts reported as ppm ($CDCl_3$ as internal standard). MS data were obtained by means of a Finnigan MAT 112b. All the spectroscopic measurements were performed in at least triplicate.

Results and discussion

The synthesis of fluorescent probe 1 is shown in Fig. 1. The process is facile and the overall yield is 32% (see ESI). The molecular structure and purity of probe 1 is established from different spectroscopic studies like ^{1}H NMR, MS and elemental analysis. To increase the solubility of the fluorogenic probe in water and ethanol, one end of the molecule is a pyridinium salt, which is designed for the hydrophilic head, and the other end is a quinoline group as the hydrophobic tail. There is a 12-carbon chain as a spacer between the head and tail , which is used for preventing the interaction of the fluorescent tail and quaternary ammonium head. Quinoline is an aromatic ligand that cancoordinate with various metal ions and shows a strong fluorescence[37]. For example, 8-hydroxyquinoline aluminium (Alq_3) is a well-known fluorescent material for fabricating optoelectronic devices[38-40]. The quinoline moiety in the amphiphilic molecule contains donor atoms (oxygen and nitrogen), which displays a certain affinity to metal ions, so the coordination interaction can form between the two parts (quinolone tail and metal ions).

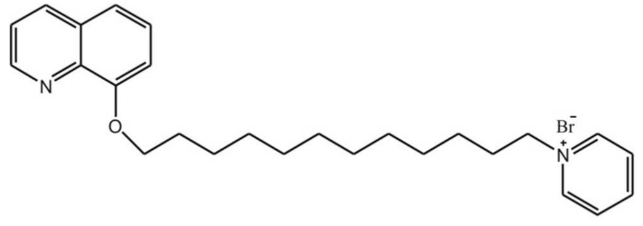

Fig. 1 Probe 1

Due to the amphiphilic structure, the probe 1 has a good solubility in EtOH, CH_3CN and H_2O. The fluorescent property of the probe 1 is firstly researched by adding different metal ions in its absolute ethanol solution. As shown in Fig. 2, the probe 1 exhibits no fluorescence (λ_{exc}=365 nm) in the 400 nm to 700 nm range. A strong blue-green emission is observed at 502 nm when trivalent ions (M^{3+}) are added, such as Fe^{3+}, Al^{3+}, Cr^{3+}, Ru^{3+} and Au^{3+}. When M^{2+} or M^{+} metal ions are added, there is no obvious change in the fluorescence intensity. It

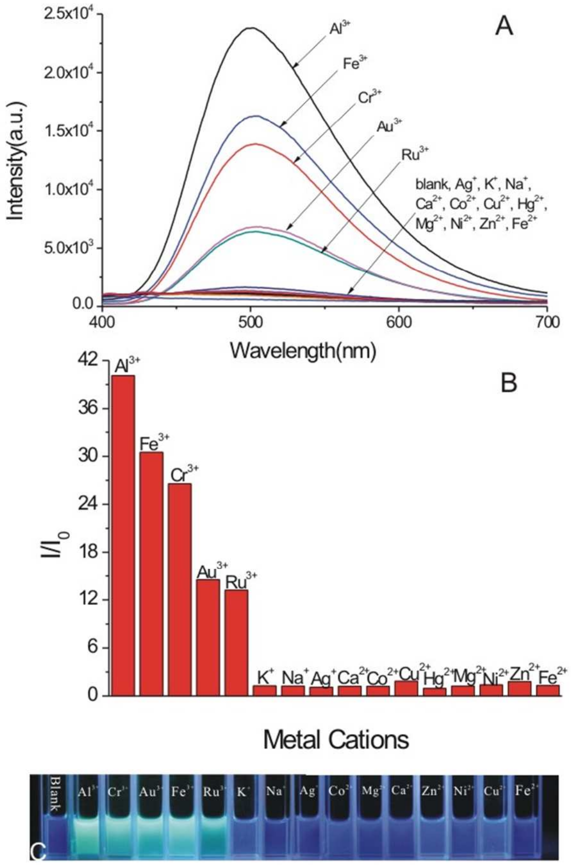

Fig. 2 (A) Fluorescence spectra of probe 1 (10^{-4} M) upon addition of 1 eq. of Al^{3+}, Fe^{3+}, Cr^{3+}, Ru^{3+}, Au^{3+}, K^{+}, Na^{+}, Ag^{+}, Ca^{2+}, Co^{2+}, Cu^{2+}, Hg^{2+}, Mg^{2+}, Ni^{2+}, Zn^{2+} and Fe^{2+} in absolute ethanol . (B) Fluorescence response of spectra of probe 1 (10^{-4} M) in ethanol absolute solution to various cations (1 equivalent). (c) Photographs of above solutions taken under UV light. Excitation is at 365 nm.

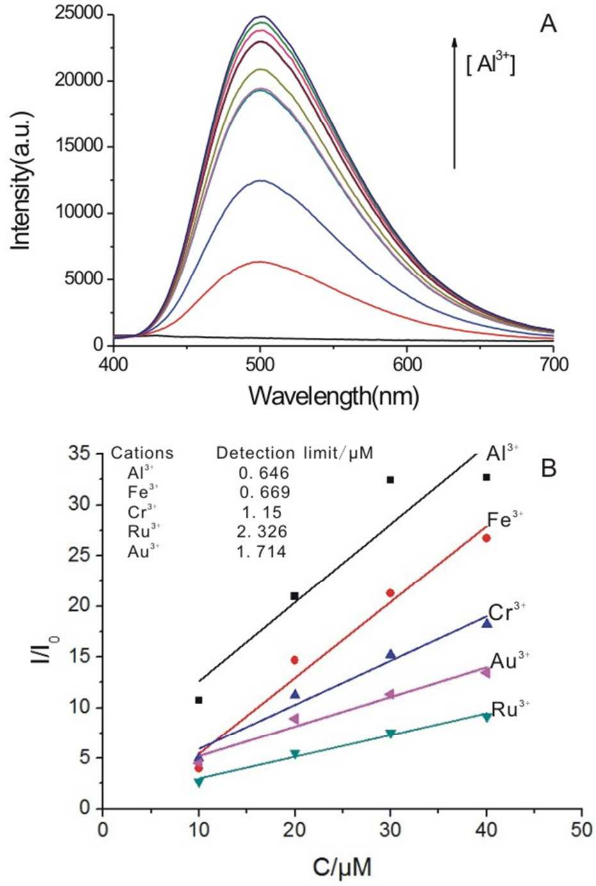

Fig. 3 (A) Change in fluorescence spectra of 1 (10^{-4} M) in ethanol absolute solution when titrated with Al^{3+} (0 to 1 equivalent). (B) Fluorescence intensity ratio as function of Al^{3+}, Fe^{3+}, Cr^{3+}, Ru^{3+} and Au^{3+} in ethanol absolute solution (excitation is at 365 nm).

indicates that the probe 1 has a selective response to M^{3+} metal ions over other competing ions (M^{2+} and M^{+}). From the fluorescence titration experiments, the detection limits (DL) of the probe 1 for Al^{3+}, Fe^{3+}, Cr^{3+}, Ru^{3+} and Au^{3+} are evaluated and determined to be 0.646, 0.669, 1.15, 2.326 and 1.714 μM, using the equation $DL = K \times Sb_1/S$, where $K = 3$, Sb_1 is the standard deviation of the blank solution and S is the slope of the calibration curve[41-43]. These values are also depicted in Fig. 3. The detection limits of probe 1 to M^{3+} ions reach micromolar range. According to the fluorescence titration results, the stoichiometry of probe 1 to metal ions is different. Using Al^{3+} as representativeness ion, a maximum fluorescence enhancement at 502 nm is got when 1 equivalent Al^{3+} has been added. The further increase in concentration of Al^{3+} ions (2 equiv.) cannot lead to a larger fluorescence intensity. So stoichiometry of probe 1 to Al^{3+} is 1:1 (Fig. 4). Cr^{3+}, Ru^{3+} and Au^{3+} exhibit the similar results with Al^{3+} (nearly 1:1 stoichiometry). For Fe^{3+}, the stoichiometry are 2:1 (probe 1 to Fe^{3+}). These fluorescence results agree with the UV-vis data.

To further explore the formation of the ligand-to-metal complex, NMR titration has been adopted. The ^1H NMR spectra of probe 1 recorded in CD_3CN shows obvious changes of signals upon the increase of Al^{3+} concentrations (Fig. 5). The most significant shifts of the signals of probe 1 are observed in the quinoline moiety, especially two β protons. The chemical shift of the β_1 proton at the ortho-position of ether bond moves from 7.5 to 8.1 ppm, following the addition of Al^{3+}. Meanwhile, the β_2 proton, at the ortho-position of nitrogen atom shows a similar behavior. Its chemical shift varies from 8.5 to 9.0 ppm. These chemical shifts stop changing when the 1:1 stoichiometry (probe 1 to Al^{3+}) is reached. When the Al^{3+} is continuously added, from 1:1 to 1:2 stoichiometry, the NMR spectra vary little. These data strongly indicate the direct involvement of the quinolone moiety in Al^{3+} coordination process, and 1:1 complex is formed, which is in accord with the UV-vis data (see ESI). Then, the downfield shift of these should be caused by the coordination-induced deshielding effect. Metal ions coordinate with nitrogen atom and oxygen atom[44]. We believed that the coordination between the probe and metal ion caused the intramolecular valence electrons transition and level changes, so that the fluorescence enhancement. However, oxygen atom of the probe may involve in the formation of ether bond, it will reduce the negative electrical. For fluorescence enhancement, it is needed to take metal ions with more positive

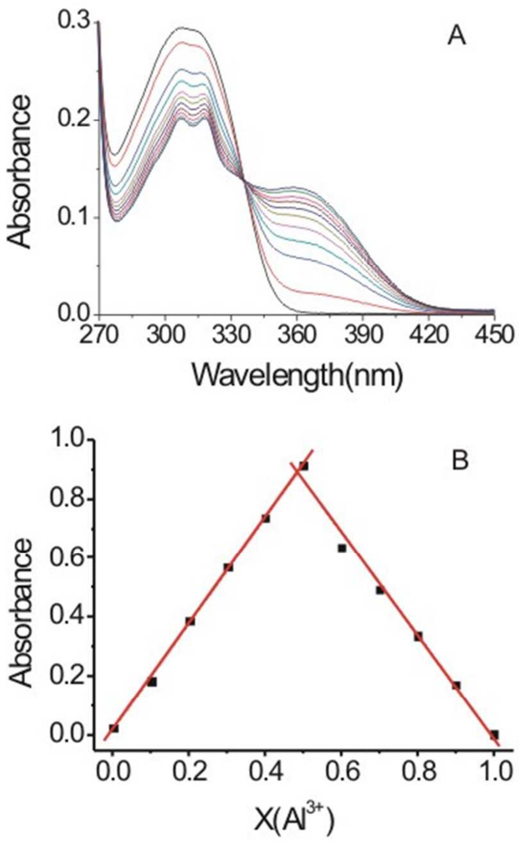

Fig. 4 (A) Adsorption spectra of 1 (10^{-4} M) in ethanol absolute solution when titrated with Al^{3+} (0, 2, 4, 6, 8, 10, 12,14,16,18, 20 μL). (B) Job's plot of 1 and Al^{3+} in the same medium according to the absorbance at 365 nm

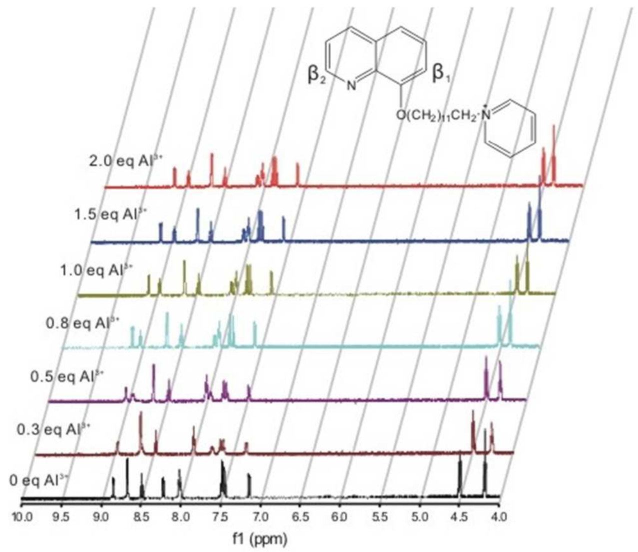

Fig. 5 ^1H NMR spectra of probe 1 and probe 1 + 0.3, 0.5, 0.8, 1.0, 1.5, 2.0 eq. of Al^{3+} in CD_3CN from the bottom to the top respectively.

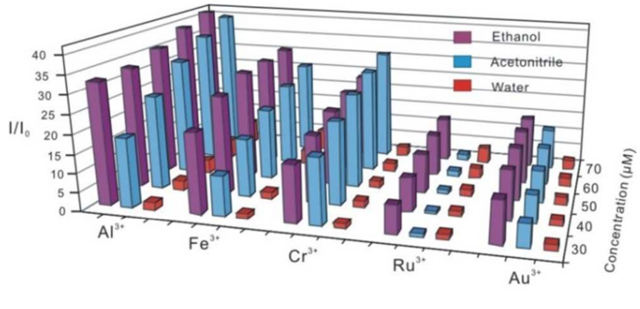

Fig. 6 Fluorescence intensity ratio of probe 1 with the addition of Al^{3+}, Fe^{3+}, Cr^{3+}, Ru^{3+} and Au^{3+} to water, ethanol absolute and acetonitrile, respectively (concentration ranging from 30 to 70 μM). Excitation is at 365 nm.

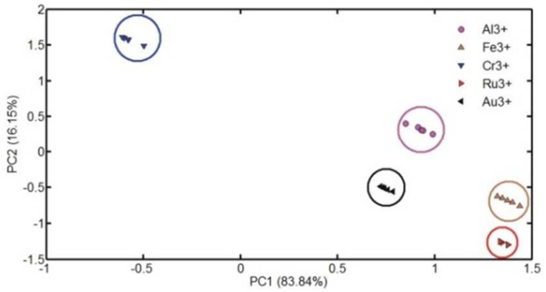

Fig. 7 Two-dimensional PCA score plot for discrimination of different trivalent metal ions at same concentrations (20 μM). PCA score plot of the two PCs describing approximately 99.99% of the total variance.

charge to coordinate with the probe. While, fewer positive charges of the divalent metal ions may be insufficient to enable fluorescence enhancement. The fluorescence enhancement efficiencies, I/I_0, upon the concentration of Al^{3+}, Fe^{3+}, Cr^{3+}, Ru^{3+} and Au^{3+} in all the three solvents (EtOH, CH_3CN, H_2O) are collected and displayed in Fig. 6. I_0 and I stand for the maximum emission in the absence and presence of metal ions, respectively. In acetonitrile solution, when different M^{3+} ions are added, the maximum emission wavelength shifts to 510 nm, and the largest fluorescence enhancement is 11.3 to 39.9 times for different M^{3+}, which is close to the results in ethanol (12.2 to 41.1 times). But Ru^{3+} ion leads a poorer enhancement in acetonitrile, which is less than 2 times. In water, the maximum emission wavelength is 507 nm, and all the M^{3+} ions exhibit the smallest promotion in the fluorescence intensity, which is only 2.4 to 6.7 times. This phenomenon may be caused by the partly hydrolysis of metal ions, which hinders the combination of the probe 1 and metal ions. According to the above data, in only one specific solvent (such as ethanol), the small difference in sensitivity makes the present probe hard to identify various trivalent metal ions, especially Fe^{3+}, Al^{3+} and Cr^{3+}. So, the cross-reactivity of fluorescence probe 1 featured in the three solvents is quite important. This character of it approximates a sensor array that produces a fingerprint pattern recognition from all the sensing elements to distinguish the target ions from each other.

To observe identification ability of the probe 1 to these trivalent metal ions, we perform further experiments for measuring the fluorescence enhancement in the three solvents, and principal component analysis (PCA) is used to analyse the measured data. The PCA, an important chemometric method, is usually used to decompose complex optical fingerprint patterns and repeating experiments into simplified components. PCA is a non-supervised mathematical method that can transform a number of correlated variables into uncorrelated variables called principal components (PCs). The first PC (PC1) provides the highest degree of variance, and other PCs follow in the order of decreasing variance. Then, the PCA concentrates the most significant characteristics of the data into a lower dimensionally space without losing much information. As a result, just principal component 1 (PC1) and principal component 2 (PC2) can be plotted graphically to allow the description of the discriminatory power of the fluorescent probe. In Fig. 7, the two-dimensional PCA score plot two-dimensional PCA plot for Fe^{3+}, Al^{3+}, Cr^{3+}, Ru^{3+} and Au^{3+} to the three solvents of EtOH, CH_3CN and H_2O is illustrated. The discriminating features of five metal cations are significant, and replacement of solvents has few effects to the intrinsic differences of the cations. Therefore, the fluorescent signals from the same metal cations in different solvents are classified in the same group. The PCA plot exhibits an excellent discrimination of the five trivalent metal cations. The two components, PC1 and PC2, carry about 99.99% of the total variance. In this PCA plot (Fig. 7), the fluorescent probe 1 corresponding type of trivalent metal ions are aggregated into five groups, and each M^{3+} cation can be clustered into a tight distinct group, demonstrating the good reproducibility of the response for each cation. This result indicates that the amphiphilic fluorescent probe can detect and identify the trivalent metal ions.

Conclusions

In summary, we report the synthesis and characterization of afluorescent probe for the selective detection of five trivalent metal cations, Fe^{3+}, Cr^{3+}, Al^{3+}, Ru^{3+} and Au^{3+}. The probe has a hydrophobic quinoline head and a hydrophilic pyridinium tail. This amphiphilic molecular structure makes the molecule exhibit ideal sensitive performance in three kinds of solvents, including EtOH, CH_3CN and H_2O. Job's plot from UV-vis data showed that Fe^{3+} was found to form 2:1 ligand-to-metal complexes with probe 1, whereas the formation of 1:1 complexes was observed for Al^{3+}, Cr^{3+}, Ru^{3+} and Au^{3+}. NMR titration further proves this interference and indicats that nitrogen and oxygen atoms at the quinoline moiety take part in the coordination process. The various sensitivity of the probe in three solvents provides a cross-reactivity to detect and identify the five M^{3+} cations, which approximates a sensor array that selectively distinguish the target ions from each other. The principal component analysis is used to analyze the measured data. This method shows excellent discrimination and good reproducibility for each cations. The design thought of the amphipilic fluorescent probe, together with the PCA method, may benefit for constructing chemo- and bio- sensor systems.

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Notes and references

[a] Department of Chemistry, Dalian University of Technology, Liaoning, China. E-mail: taosy@dlut.edu.cn; Fax: +86 411 84986035.

[b] Assistant researcher of Chinese Academy of Sciences, Yantai Shandong Center for Integrated Technology Transfer Center, Shandong, China.

[c] Carbon Research Laboratory, Liaoning Key Lab for Energy Materials and Chemical Engineering, State Key Lab of Fine Chemicals, School of Chemical Engineering, Dalian University of Technology, Dalian, Liaoning. P. R. China

† Electronic Supplementary Information (ESI) available: Detailed synthesis and characterization of 1; Fluorescence and UV titrations of 1 with trivalent metal cations. See DOI: 10.1039/b000000x/

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A quinoline-functionalized amphiphilic fluorogenic probe for specific detection of trivalent cations

Shengyang Tao*[a], Ying Wei[a], Chan Wang[b], Zhaoqi Wang[a], Pan Fan[a], Da Shi[a], Baojun Ding[a] and Jieshan Qiu[c]

A quinoline-functionalized amphiphilic fluorogenic probe was synthesized which selectively detects trivalent ions viz. Al^{3+}, Fe^{3+}, Cr^{3+}, Ru^{3+} and Au^{3+} through a fluorescence turn on signal