Inorganic Chemistry Communications 33 (2013) 6–9

Contents lists available at SciVerse ScienceDirect

Inorganic Chemistry Communications

journal homepage: www.elsevier.com/locate/inoche

A fluorescent and colorimetric sensor for Al^{3+} based on a dibenzo-18-crown-6 derivative

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ARTICLE INFO

Article history:
Received 14 February 2013
Accepted 18 March 2013
Available online 28 March 2013

Keywords:
Aluminum ion recognition
Dibenzo-18-crown-6 derivative
Ratiometric
Fluorescent
Chemosensor

ABSTRACT

A new receptor based on a dibenzo-18-crown-6 derivative is successfully synthesized and characterized. This receptor reveals selective recognition toward Al^{3+} ion, along with colorimetric and fluorometric dual-signaling responses based on internal charge transfer (ICT). Also, it can serve as a highly selective chemodosimeter for Al^{3+} with naked-eye detection.

Fluorescent chemosensors are widely used as powerful tools to detect neutral and ionic species owing to their high sensitivity, selectivity, versatility, and relatively simple handling [1]. In this regard, the design and synthesis of chemosensors are currently of great interest [2–11]. On the other hand, aluminum is the most abundant metal in the Earth's crust and has been extensively used in modern life [12]. However, Al^{3+} is neurotoxic to humans and has been found to induce many health issues, such as Alzheimer's disease and Parkinson's disease [13]. Thus, the development of sensors for facile detection of Al^{3+} is of great importance in environmental monitoring and biological applications. Compared with the detections of other transition-metal ions, limited examples of Al^{3+} fluorescence sensors based on small molecules have been reported through an internal charge-transfer (ICT) mechanism [14,15], and most of the detections are due to photoinduced electron transfer (PET) process [2,3,16]. Herein, a new chemosensor **1** with 2,3-diphenylquinoxaline as fluorophore and 18-crown-6 moiety as chelating unit has been reported, which exhibits high selectivity for Al^{3+} ions. The Al^{3+} detection process gives rise to large changes in the absorption spectra (from colorless to yellow), which is clearly visible to the naked eye. Meanwhile, upon the binding of **1** with Al^{3+}, a distinct emission red shift based on the ICT mechanism with slight emission enhancements could be observed. These results might provide explicit information to qualitative and quantitative detection of Al^{3+} ions in future application.

The synthetic route of **1** was outlined in Scheme 1. Compound **3** was prepared by following the literature method [17]. The reaction of **3** with benzil in ethanol under a nitrogen atmosphere gave **1** in the yield of 30%. Compound **1** was then characterized by ^1H NMR, ESI-MS, IR, elemental analysis and X-ray diffraction analysis.

The metal affinity of **1** toward a variety of cations: K^+, Na^+, Ca^{2+}, Mg^{2+}, Al^{3+}, Cu^{2+}, Co^{2+}, Ni^{2+}, Fe^{2+}, Hg^{2+}, Mn^{2+}, Cr^{3+}, Cd^{2+}, Ag^+, Zn^{2+}, La^{3+}, Eu^{3+}, and Td^{3+} was investigated by absorption and fluorescence spectroscopy in CH_3CN solution. As shown in Fig. 1, without any metal ion, **1** showed an absorption band centered at 366 nm and at 258 nm. Upon addition of Al^{3+}, the absorption band at 366 and 238 nm diminished, while new bands at 271 and 418 nm were observed. The presence of well-defined isosbestic points at 398 and 265 nm indicates the formation of stable complex between **1** and Al^{3+}. The color of the solution changes from colorless to light yellowish-green upon addition of Al^{3+} as shown in Fig. 1b, which allows the detection of Al^{3+} ions by naked-eyes.

In addition, fluorescence properties of **1** in the presence of the above mentioned metal ions in CH_3CN solution were investigated. As shown in Fig. 2, the free receptor **1** exhibits a strong emission band around at 400 nm upon excitation at 334 nm. Addition of K^+, Na^+, Ca^{2+}, Mg^{2+}, Cu^{2+}, Co^{2+}, Ni^{2+}, Mn^{2+}, Cr^{3+}, Cd^{2+}, Ag^+, Zn^{2+}, Fe^{2+}, La^{3+}, Eu^{3+}, and Td^{3+} induced almost no changes in the emission profiles. However, addition of Hg^{2+} quenched the fluorescence to some extent. Only the addition of Al^{3+} ions to the solution of **1** resulted in a prominent red shift of the fluorescence maximum of about 75 nm from 400 nm to 475 nm. Meanwhile, the ratio of emission intensities at 475 and 400 nm ($I_{475\ nm}/I_{400\ nm}$) changed from 30.36 to 0.04 upon addition of Al^{3+}. The significant red shift observed suggests that Al^{3+} likely interacts with the electron donor **1** through the intramolecular charge transfer (ICT) mechanism [14,15]. The experimental observations are confirmed quantitatively by the DFT calculation results. As shown in Fig. S1, the LUMO of complex

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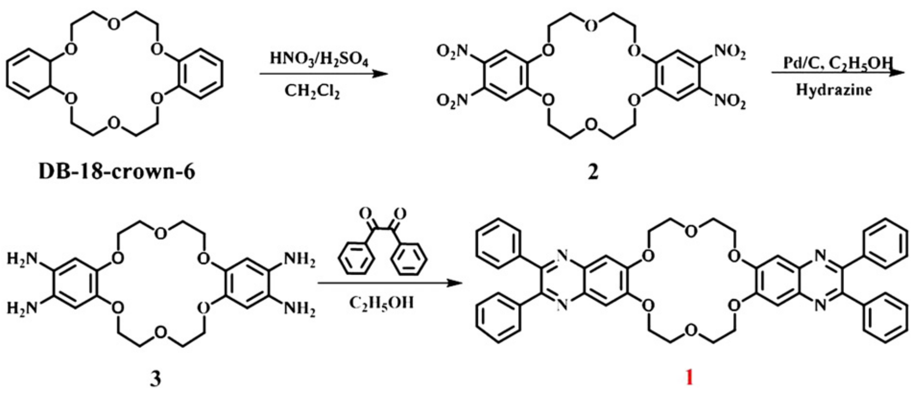
http://dx.doi.org/10.1016/j.inoche.2013.03.020



Scheme 1. The structure and synthesis of **1**.

stabilizes more strongly than HOMO after the coordination of Al^{3+} ion, resulting in a red shift of fluorescence spectra [18].

The fluorescence titration spectra of Al^{3+} to **1** (50 μM) are shown in Fig. 3a. Gradually increasing concentrations of Al^{3+} caused the decrease of the emission band at 400 nm, while a new peak around 475 nm with fluorescence enhancement up to 30-fold reached a plateau after 1 equiv. of Al^{3+} was added. Also, a new isoemissive point at 456 nm appeared, implying the formation of a well-defined complex between Al^{3+} and **1**. The solution of **1** with 1 equiv. Al^{3+} converted the visual emission color from purple to cyan when excited with a hand-held 365 nm UV-lamp (Fig. 3b). The saturation behavior of the fluorescence intensity after 1 equiv. of Al^{3+} reveals that the Al^{3+} receptor has a 1:1 stoichiometry (Fig. 4). These results were further confirmed by Job's plot, which indicates that a binding stoichiometry of the complex formed between **1** and Al^{3+} is 1:1. Based on the above fluorescence titration studies, the association constant (Ks) of 1 for Al^{3+} ions was found to be 3.28×10^4 (Fig. S2).

To explore practical applicability of **1** as an Al^{3+} selective receptor, cross-contamination experiments were conducted in the presence of Al^{3+} at a concentration of 50 μM mixed with other metal ions at a concentration of 0.5 mM. As shown in Fig. S3, the results clearly suggest that the selectivity of **1** towards Al^{3+} was almost unaffected by other competitive ions (10 equiv.).

On the basis of the above studies of optical measurement and Job's plot, probable sensing processes for **1** to Al^{3+} were proposed (Fig. 6). The bonding mode of **1** was confirmed by ^{1}H NMR titrations experiment. The chemical shifts for the key protons in the crown moieties (Ha and Hb) of **1** were assigned as 4.36, and 4.00 ppm, respectively (Fig. 5a), based on the previous report regarding related compounds. After addition of 0.4 equiv. Al^{3+}, the signals shifted downfield from 4.00 to 4.04, and 4.36 to 4.39, respectively. With further addition of Al^{3+} up to 1 equiv.,

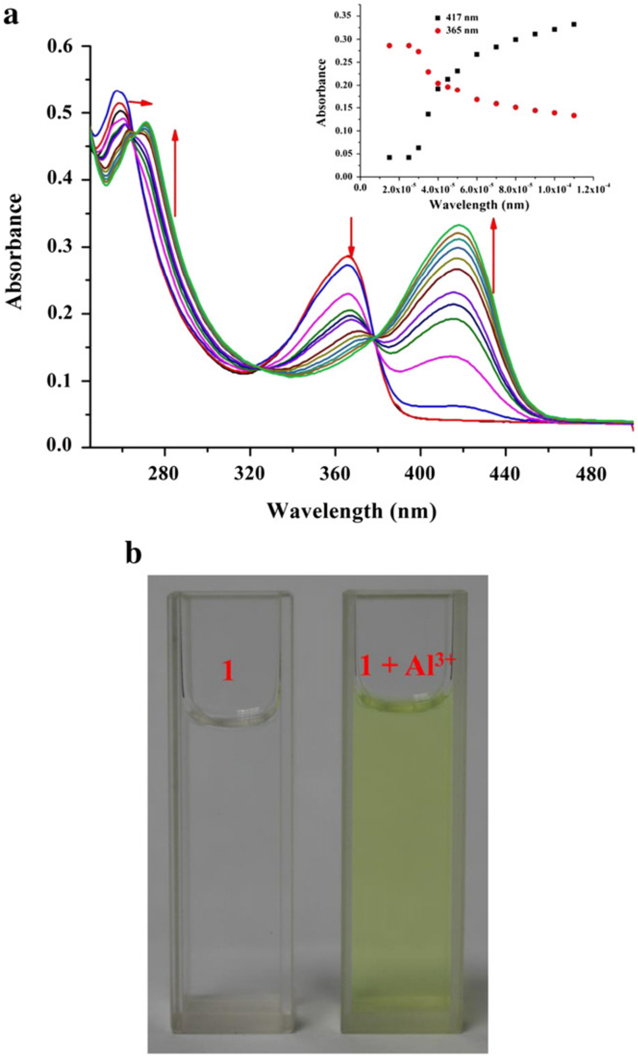


Fig. 1. (a) UV–vis spectra of 1 (5 μM) with increasing amounts of Al(ClO$_4$)$_3$ (0–2.5 equiv.). Inset: absorbance of **1** at 365 (circles) and 417 (squares) nm as a function of Al^{3+} concentration. (b) Color changes of **1** in CH$_3$CN solution upon addition of Al^{3+}.

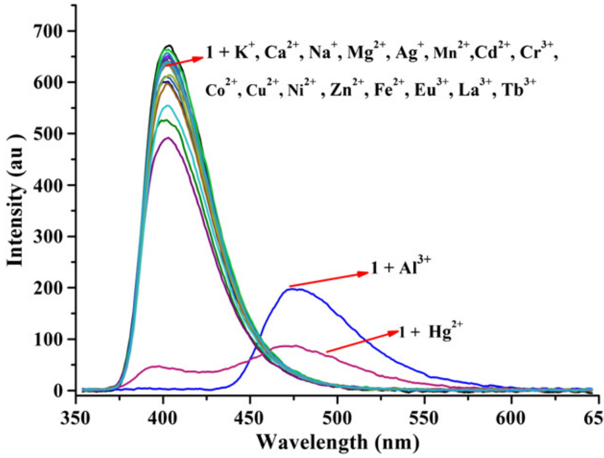


Fig. 2. Fluorescence spectra of 1 (50 μM) after adding metal salts (10 equiv.) of K$^+$, Na$^+$, Ca^{2+}, Mg^{2+}, Cu^{2+}, Co^{2+}, Ni^{2+}, Mn^{2+}, Cr^{3+}, Cd^{2+}, Ag$^+$, Zn^{2+}, Fe^{2+}, Al^{3+}, La^{3+}, Eu^{3+}, and Td^{3+} in CH$_3$CN solution. The excitation wavelength was 334 nm.

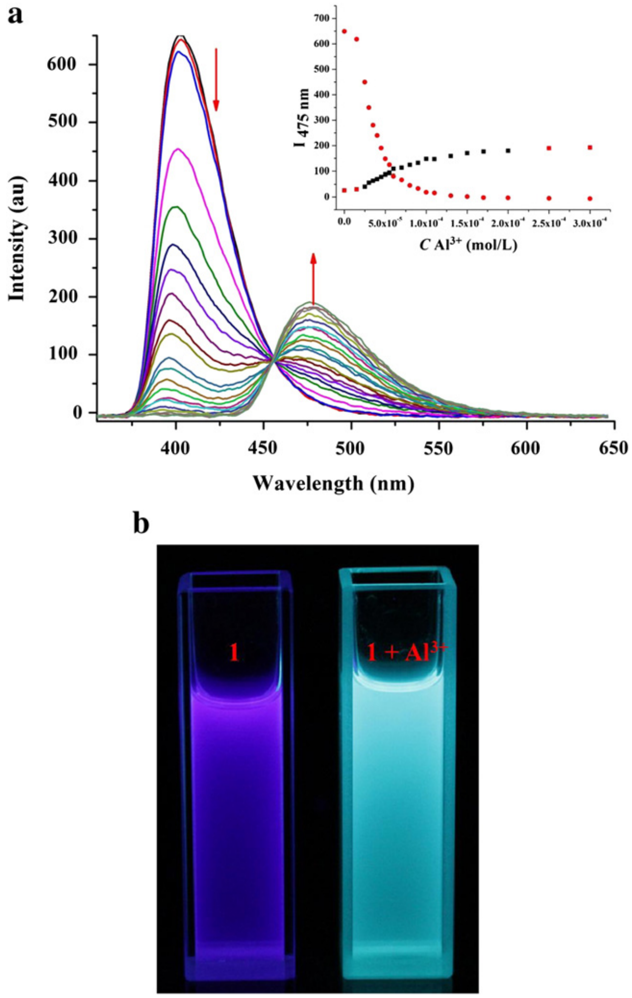


Fig. 3. (a) Fluorescence (λ ex = 334 nm) titrations of **1** (50 μM) with Al^{3+} (from 0 to 2 equiv.) in CH_3CN. The excitation and emission slit widths were 2.5 nm and 5 nm, respectively. Inset: Fluorescence intensity at 400 and 475 nm as a function of $[Al^{3+}]$. (b) Fluorescence images under 365 nm UV-light.

the signals of Ha and Hb stop shifting and stabilized at $\delta = 4.49$ and 4.07 ppm, respectively. These results suggest that Al^{3+} interacts with the oxygen atom of **1** in the 18-crown moieties and forms stable complex with 1:1 stoichiometry [19]. Significantly, the proposed bonding mode for **1** to Al^{3+} is consistent with the fluorescence studies. Binding of Al^{3+} to the 18-crown moieties (the electron acceptor in the push–pull system) is in accordance with the red shift (75 nm) in the fluorescence spectra. The proposed mode of **1** and Al^{3+} is displayed in Fig. 6.

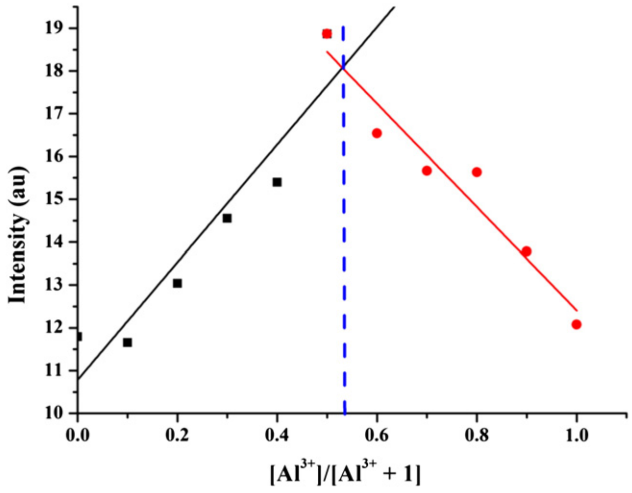


Fig. 4. Job's plots for **1** with Al^{3+} $[\mathbf{1}] + [Al^{3+}] = 10^{-4}$ M.

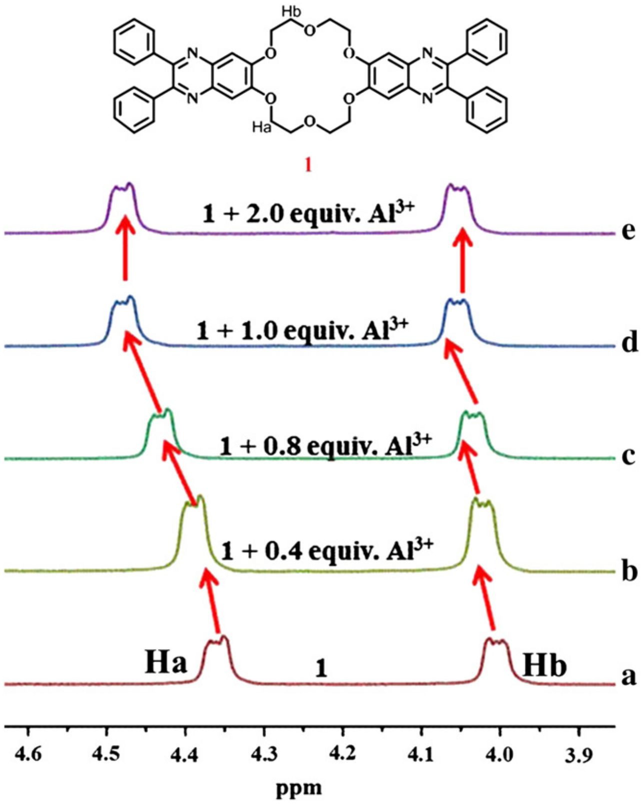


Fig. 5. ^1H NMR (400 MHz) spectra of **1** (5×10^{-3} M) in CD_3CN/DMSO-d6 (0.1/0.4, v/v) with addition of $Al(ClO_4)_3$.

In conclusion, we have successfully designed and synthesized a new receptor **1** that shows colorimetric and fluorometric dual-signaling responses for Al^{3+} ions. The detection process gives rise to a color change that is clearly visible to the naked eye (from colorless to yellow). Furthermore, both the colorimetric and fluorometric detection exhibit high selectivity towards to Al^{3+} over other tested cations. The bonding mode has been further confirmed by ^1H NMR and Job's plot.

Acknowledgements

This work was supported by the NSF of China (21031002 and 51073079), National Basic Research Program of China (2012CB821700) and the Natural Science Fund of Tianjin, China (10JCZDJC22100 and 11JCYBJC04100).

Appendix A. Supplementary material

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.inoche.2013.03.020.

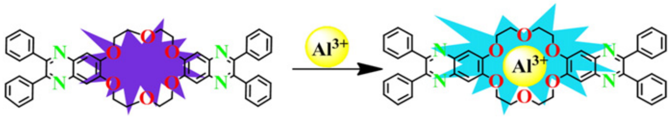


Fig. 6. The proposed **1**–Al^{3+} binding mode in solution.

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