ORGANIC LETTERS

2011
Vol. 13, No. 19
5274–5277

Highly Selective and Sensitive Fluorescent Turn-on Chemosensor for Al^{3+} Based on a Novel Photoinduced Electron Transfer Approach

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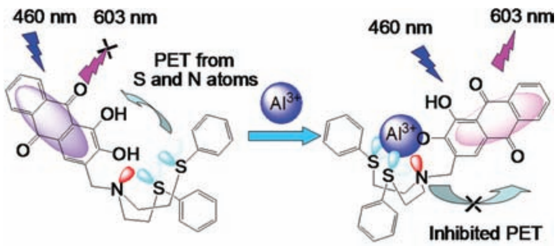
Received August 7, 2011

ABSTRACT



A photoinduced electron transfer (PET)-based chemosensor possessing dual PET processes by simultaneously introducing both nitrogen and sulfur donors was achieved. The fluorescence signal of the free chemosensor is in a normal-off state due to the sulfur donor being insensitive to environmental pH stimuli. As a result, the device can be used over a wide pH span of 3−11. Upon binding Al^{3+}, a significant fluorescence enhancement with a turn-on ratio over 110-fold was triggered by the inhibition of PET processes from both the sulfur and the nitrogen donors to the fluorophore.

The heightened concern for environmentally and biologically relevant species such as Al^{3+}, Pb^{2+}, Hg^{2+}, Cu^{2+}, and F^- has stimulated active research on the potential impact of their toxic effects. The molecular design and synthesis of chemosensors to detect such species is currently of great interest.[1] In this regard, chemosensors with high selectivity and sensitivity to these species are especially important.[2] Al^{3+} which widely exists in the environment due to acidic rain and human activities is considered toxic in biological activities.[3] The incremental increase of Al^{3+} concentrations in the environment is detrimental to growing plants.[4] Excessive exposure of the human body to Al^{3+} leads to a wide range of diseases, such as Alzheimer's disease, osteoporosis, etc.[5] According to a WHO report, the average daily human intake of aluminum is approximately 3−10 mg per day.[6] Due to the potential impact of Al^{3+} ions on human

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10.1021/ol202054v

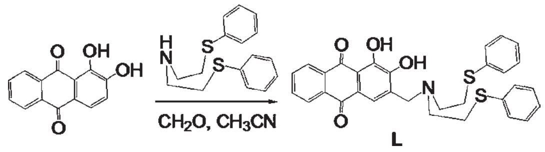
health and the environment, highly selective and sensitive chemosensors for Al^{3+} are hence highly demanded.

Known methods for aluminum detection, such as graphite furnace atomic absorption spectrometry and inductively coupled plasma atomic emission spectrometry, are generally expensive and time-consuming in practice. Comparatively, optical detection, particularly fluorescence methods, shows unique potential for high sensitivity. Compared to transition metals, the detection of Al^{3+} has always been problematic due to the lack of spectroscopic characteristics and poor coordination ability.[7] To the best of our knowledge, only a few fluorescent chemosensors have been reported for detection of Al^{3+} with moderate success to date.[3b,8] The majority of the reported Al^{3+} sensors, however, have limitations such as tedious synthetic efforts[8b−g] and/or lack of practical applicability in aqueous solutions.[8a−f] Thus, it is still highly desirable to develop new or improved methods for the selective evaluation of Al^{3+} ions in aqueous environments.

The photoinduced electron transfer (PET) process has been widely exploited for the sensing of anions as well as for cations.[9] Generally, PET sensors based on nitrogen donors are highly sensitive to environmental pH stimuli, because the degree of nitrogen protonation is strongly pH dependent.[9] This pH sensitivity is unfavorable to obtaining reproduciable and reliable signals for most PET sensors used in a wide pH span. To obtain highly sensitive Al^{3+} chemosensors in a wide pH span, novel chemosensors with dual PET processes are desirable by simultaneously introducing a nitrogen donor[10] and pH inert donors to ensure the PET processes are always 'ON' in both acidic and basic media. This design enables the fluorescence signal of the free chemosensor to be always 'OFF', leading to remarkable signal turn-on ratios over a wide pH span before and after binding of a guest species.

Based on this idea, we report a successful PET chemosensor **L** by using 1,2-dihydroxyanthraquinone as the fluorophore and a conjugated S_2N podand moiety as the chelating unit. The S_2N podand moiety together with the hydroxyl of 1,2-dihydroxyanthraquinone serves as an ionophore by providing a coordinating site. The free chemosensor **L** shows no fluorescence emission over a very wide pH span (pH 1−12). Upon binding of a Al^{3+} cation, a significant fluorescence enhancement with turn-on ratios over 110-fold was achieved.

Scheme 1. Structure and the Synthesis of the Chemosensor **L**



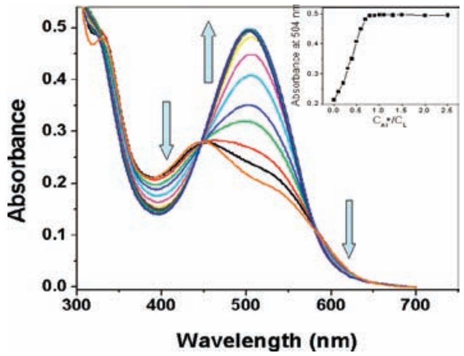


Figure 1. UV−vis spectra of **L** (50 μM) with increasing amounts of $Al(NO_3)_3$ (0−2.5 equiv). Inset: absorbance of **L** at 505 nm as a function of $C_{Al^{3+}}/C_L$.

The synthesis of **L** is shown in Scheme 1. 1,2-Dihydroxyanthraquinone reacted with *N*,*N*-bis(2-phenylthioethyl)-amine in the presence of paraformaldehyde in acetonitrile yielded **L** in 53% yield. The structure of **L** was confirmed by its NMR, MS spectra and elemental analysis (Figures S1−S4).

The spectroscopic properties of the chemosensor **L** were investigated in an ethanol−water (1:1, v/v) solution. As illustrated in Figure 1, the free chemosensor **L** exhibited a maximal absorption at 446 nm ($\varepsilon = 4.24 \times 10^3\ M^{-1}\ cm^{-1}$). Upon addition of Al^{3+} ions (0−2.5 equiv), the absorbances at 395 and 600 nm decreased gradually while the absorbance at 446 nm remained constant along with the increase of the Al^{3+} concentration. In contrast, a significant increase was observed for the absorption band at 504 nm. The presence of three clear isosbestic points at 446, 579, 650 nm implies the conversion of the free chemosensor **L** to the only Al^{3+} complex. Moreover, the absorbances at 395, 504, 600 nm remained constant in the presence of more than 1 equiv of Al^{3+} ions, indicating the formation of a 1:1 complex between **L** and the Al^{3+} ion. This is in perfect agreement with a 1:1 stoichiometry for the Al^{3+} complex determined by Job's plot yielded from UV−vis absorption

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(Figure S5). High-resolution mass spectra (HRMS) provided additional evidence for the formation of a 1:1 complex of **L**·Al^{3+} (Figure S6).

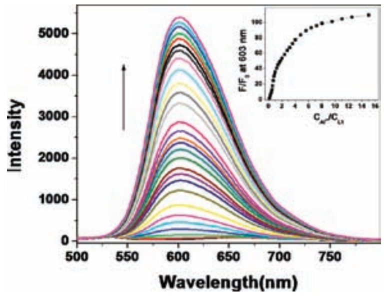

Figure 2. Fluorescent titration spectra of **L** (50 μM) in the presence of different concentrations of $Al(NO_3)_3$. Inset: the fluorescence at 603 nm of **L** as a function of the Al^{3+} concentration. λ_{ex} = 460 nm.

Figure 2 shows the fluorescence spectrum of the free chemosensor **L** and those in the presence of an incremental amount of Al^{3+} in a H_2O–ethanol solution (1:1, v/v). The fluorometric titration reaction curve showed a steady and smooth increase with the increase of the Al^{3+} concentration. A turn-on ratio over 110-fold was triggered with the addition 16 equiv of Al^{3+}. The inset in Figure 2 shows the dependence of the emission intensity ratio (F_i/F_0) at 603 nm on the Al^{3+} concentration. The chemosensor exhibited an efficient fluorescence response. An over 35-fold increase in fluorescence intensity was observed with the addition of 1 equiv of Al^{3+} ions. The association constant (K_a) of **L** with Al^{3+} was 8.84×10^3 M^{-1} (R = 0.9934), as obtained by nonlinear least-squares analysis (Figure S7). From the changes in Al^{3+}-dependent fluorescence intensity (Figure S8), the detection limit was estimated to be 5.0×10^{-7} M, indicating that the limit of detection of **L** to Al^{3+} met the limit for drinking water according to the China EPA standard (0.05 mg L^{-1}, 1.85 mM). Sufficient fluorescence enhancement was observed for **L** after the addition of Al^{3+} in the presence of different counteranions (Cl^-, Br^-, I^-, CO_3^{2-}, SO_4^{2-}, PO_4^{2-}, ClO_4^-, NO_2^-, PF_6^-, AcO^-, and BF_4^-) (Figure S9), suggesting that the chemosensor **L** can be used as a selective fluorescent sensor for Al^{3+} in the presence of a wide range of the environmentally relevant anions.

Reversibility is a prerequisite in developing novel chemosensors for practical application. The reversibility of the recognition process of **L** was performed by adding an Al^{3+} bonding agent, Na_2EDTA. The addition of Na_2EDTA to a mixture of **L** and Al^{3+} resulted in diminution of the fluorescence intensity at 603 nm, which indicated the regeneration of the free chemosensor **L**. The fluorescence was recovered by the addition of Al^{3+} again (Figure S10). Such reversibility and regeneration are important for the fabrication of devices to sense the Al^{3+} ion.

The response of **L** to other metal ions was also studied. As shown in Figure 3, the addition of 8 equiv of Ag^+, Ca^{2+}, Cd^{2+}, Co^{2+}, Cr^{3+}, Cu^{2+}, Fe^{3+}, Hg^{2+}, K^+, Mg^{2+}, Na^+, NH_4^+, Ni^{2+}, and Zn^{2+} has no obvious effect on the fluorescence emission, whereas Pb^{2+} responded with a slight increase in the fluorescent intensity at 626 nm. In stark contrast, the addition of Al^{3+} resulted in a significant enhancement of the emission intensity positioned at 603 nm. Thus, **L** can function as a highly selective fluorescence chemosensor for Al^{3+}.

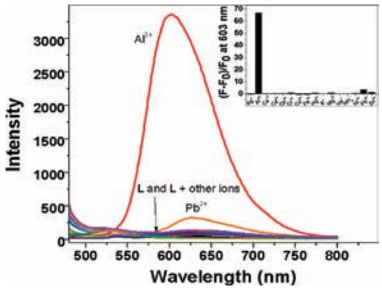

Figure 3. Fluorescence spectra of **L** (50 μM) in the presence of several relevant metal ions (8 equiv for each metal ion). Inset: histogram representing the fluorescence enhancement and quenching of **L** in the present of metal ions. λ_{ex} = 460 nm.

To explore the possibility of using **L** as a practical ion-selective fluorescent chemosensor for Al^{3+}, competition experiments were carried out, in which **L** (50 μM) was first mixed with 10 equiv of various metal ions including Ca^{2+}, Cd^{2+}, Co^{2+}, Cr^{3+}, K^+, Mg^{2+}, Na^+, NH_4^+, Ni^{2+}, and Zn^{2+}, followed by adding 10 equiv of Al^{3+}. Fluorescence emission spectroscopy was used to monitor the competition events. As can be seen from Figure 4, in the presence of Ca^{2+}, Cd^{2+}, Co^{2+}, Cr^{3+}, K^+, Mg^{2+}, Na^+, NH_4^+, Ni^{2+}, Zn^{2+}, the emission spectra were almost identical to that obtained in the presence of Al^{3+} alone. In the case of Ag^+, Cu^{2+}, Fe^{3+}, Pb^{2+}, and Hg^{2+}, the emission intensities diminished to a different extent to that obtained in the presence of Al^{3+} alone, but they still had a sufficient turn-on ratio for the detection of Al^{3+}. Therefore, **L** was shown to be a promising selective fluorescent sensor for Al^{3+} in the presence of most competing metal ions.

For practical applications, the proper pH condition of the chemosensor **L** was evaluated. The inset of Scheme 2 shows the dependence of the fluorescence intensity of **L** on pH values with and without the addition of Al^{3+} in EtOH/H_2O (1:1, v/v). As expected, the fluorescence of unbonded **L** was almost 100% quenched over a wide pH span of 1–12. A PET sensor based on nitrogen donors was highly sensitive to environmental pH stimuli due mainly to the protonation degree of the nitrogen being strongly dependent on environmental pH.[9] The quenching of fluorescence of **L** even at low pH conditions indicated that the lone electron pairs of the sulfur donors played an important role in the modulation of the PET processes[11] (Scheme 2). In neutral and acidic media, although the

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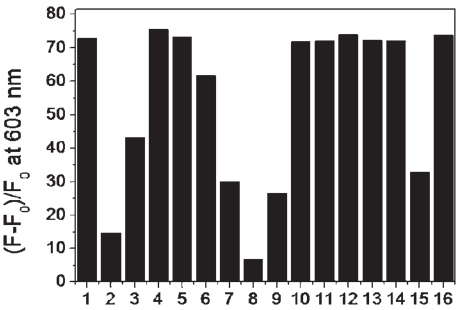
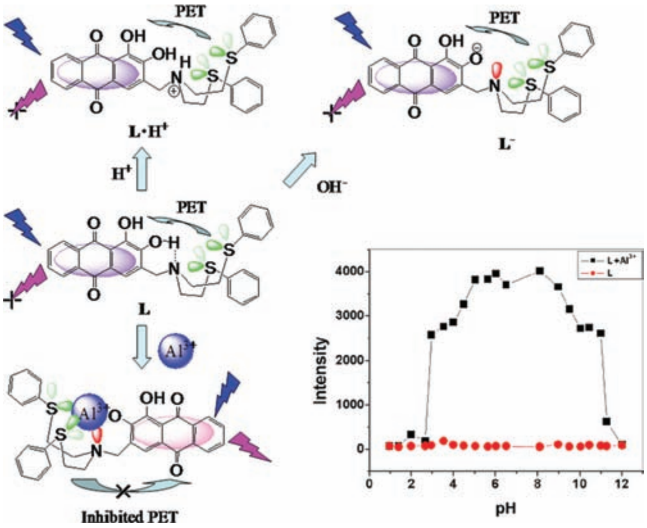


Figure 4. Change ratio ($(F - F_0)/F_0$) of fluorescence intensity of **L** (50 μM) at 603 nm in various mixtures of metal ions ($Al(NO_3)_3$ 5×10^{-4} mol/L and one other metal ion 5×10^{-4} mol/L). (1) Al^{3+}; (2) $Al^{3+} + Ag^{+}$; (3) $Al^{3+} + Ca^{2+}$; (4) $Al^{3+} + Cd^{2+}$; (5) $Al^{3+} + Co^{2+}$; (6) $Al^{3+} + Cr^{3+}$; (7) $Al^{3+} + Cu^{2+}$; (8) $Al^{3+} + Fe^{3+}$; (9) $Al^{3+} + Hg^{2+}$; (10) $Al^{3+} + K^{+}$; (11) $Al^{3+} + Mg^{2+}$; (12) $Al^{3+} + Na^{+}$; (13) $Al^{3+} + NH_4^{+}$; (14) $Al^{3+} + Ni^{2+}$; (15) $Al^{3+} + Pb^{2+}$; (16) $Al^{3+} + Zn^{2+}$.

Scheme 2. Possible PET Processes of **L** under Different pH Conditions[a]



[a] Inset: Effect of pH on the emission intensity of **L** and its Al^{3+}-complex at 603 nm in ethanol/H_2O (1:1, v/v): red circle, 50 μM **L**; black square, 50 μM **L** + 5×10^{-4} mol/L Al^{3+}.

PET process from a nitrogen donor to the fluorophore was blocked by intramolecular hydrogen bonding or by protonation of the nitrogen donor, the PET derived from the sulfur donors to the fluorophore is always switched on and resulted in the fluorescence being 100% quenched ('**L**•H$^+$' and '**L**' in Scheme 2). Under basic conditions, the PET processes from both the nitrogen donor and the sulfur donors to the fluorophore were switched on due to the deprotonation of the phenol hydroxy, leading to the complete quenching of the fluorescence ('**L**$^-$' in Scheme 2). After bonding with Al^{3+}, the phenol O, N, and S donors are likely to coordinate to the Al^{3+} ion. The PET processes derived from the lone electron pairs of both the nitrogen and sulfur donors to the fluorophore were fully blocked and triggered strong fluorescence enhancements over a wide pH range of 3–11.

In conclusion, we have developed a novel chemosensor **L** based on multiple PET processes from both the nitrogen donor and the sulfur donors to the 1,2-dihydroxyanthroquinone fluorophore by a facile one-step Mannich reaction. The fluorescence signal of the free chemosensor is always off due to the sulfur donor being insensitive to environmental pH stimuli. The device can be used within a wide pH span of 3–11. The chemosensor **L** shows an excellent turn-on fluorescence signal with high sensitivity in the presence of Al^{3+}, allowing its reversible detection in the presence of a wide range of environmentally relevant competing metal ions and anions. This strategy may provide a general way for designing new PET sensors to detect other environmentally and biologically relevant species.

Acknowledgment. This work was sponsored by the NCET-09-0894, NNSFC (20972111, 21074093, 21004044), SRF for ROCS, SEM, the NSFT (08JCYBJC-26700). and the State Key Lab. Elemental-Organic Chemistry at Nankai University (No. 1011).

Supporting Information Available. Experimental details; synthesis of **L**; the emission spectra of **L** with Al^{3+} salts with different counteranions; Job's plot; the measurement of the detection limit; the reversible binding nature of Al^{3+} with **L**; ^{1}H and ^{13}C NMR spectra of **L** or other electronic format. This material is available free of charge via the Internet at http://pubs.acs.org.