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Two new isomerous fluorescent chemosensors for Al³⁺ based on photoinduced electron transfer



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HIGHLIGHTS

- Two new isomerous PET fluorescent chemosensors (*L* and *L*') has been developed.
- Both chemosensors exhibited "turnon" for Al³⁺ in CH₃CN.
- The selectivity of *L*′ for Al³⁺ was improved compared to *L*.

G R A P H I C A L A B S T R A C T



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ABSTRACT

Two new isomerous PET fluorescent chemosensors (L and L') for Al³⁺ have been designed, synthesized and characterized. The two chemosensors exhibited fluorescence enhancement upon binding Al³⁺ in CH₃₋ CN by PET inhibition processes from both the sulfur and the nitrogen donors to anthracene. The job's plot, Benesi-Hildebrand plot and ¹H NMR titration experiments indicate that both chemosensors form a 1:1 complex with Al³⁺. The binding constants were calculated to be $(1.432 \pm 0.186) \times 10^5$ and $(1.427 \pm 0.970) \times 10^5$, respectively. Furthermore, the lowest detection limit for Al³⁺ in CH₃CN was determined to be 4.8×10^{-7} M and 2.2×10^{-7} M, respectively.

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Introduction

In recent years, fluorescent chemosensors for the detection of various biologically and environmentally relevant ions have attracted significant interest due to their potential applications in a wide variety of fields [1]. But most of these chemosensors were developed for the detection of transition and heavy metal ions such as Zn^{2+} , Cd^{2+} , Cu^{2+} , Hg^{2+} and Cr^{3+} [2]. It is well-known that aluminum is the most abundant metallic element in the earth's crust and widely used in industrial materials, food additives, water purification, and cooking utensils [3]. However, excessive aluminum to

human body may damage the central nervous system to cause human illnesses like dementia, Parkinson's disease, and Alzheimer's disease [4]. Thus, the development of chemosensors for the facile detection of Al³⁺ in biologically and environmentally important samples is still in high demand.

In the last decade, many methods such as atomic absorption spectrometry, atomic emission spectrometry, inductively coupled plasma atomic emission spectrometry and electrochemical methods have been used for aluminum detection [5]. But these methods are relatively complex and need expensive instruments. Comparatively, fluorescent chemosensors are widely used because of their advantages such as high sensitivity, selectivity, versatility, rapid response time and relatively simple handling [1]. However, compared to transition metal ions, the detection of Al³⁺ has been

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greatly limited due to its weak coordination and strong hydration ability [6]. So far, only a few of fluorescent chemosensors for Al³⁺ have been designed with moderate success [7]. Therefore, it is a challenging work to develop some high selective and sensitive chemosensors for Al³⁺ in environmental monitoring and biological assays.

Recently, Zeng and co-workers reported a successful PET chemosensor by using 1,2-dihydroxyanthraquinone as the fluorophore and S_2N podand moiety together with the hydroxyl of 1,2-dihydroxyanthraquinone as binding sites [7m]. In this paper, we have designed and synthesized two new isomerous PET chemosensors L and L' for the detection of Al^{3+} using anthracene as the fluorophore and only S_2N podand moiety as the chelating unit. Studies show that the two chemosensors L and L' had selectivity for Al^{3+} .

Experimental

Materials, instruments and methods

Materials

All the materials for the synthesis were purchased from commercial suppliers and used without further purification. All of the solvents used were of analytical reagent grade. Fresh anhydrous CH₃CN was distilled. Double distilled water was used for spectral detection.

Instruments

¹H NMR and ¹H NMR titrations experiments were obtained on a Bruker 300 spectrometer with TMS as internal standard at room temperature. ¹³C NMR were carried out on a Bruker 400 spectrometer. Mass spectra were recorded on a LC-MSD-Trap-XCT instrument by electrospray ionization (ESI). UV–vis absorption spectra were recorded on a TU-1900 double-beam UV–vis spectrophotometer. Fluorescence emission spectra were recorded on a FluoroMax-4 spectrofluorometer with 5 nm slit for both excitation and emission. The Fourier transform infrared (FT-IR) spectra were obtained in the range of 400–4000 cm⁻¹ as KBr pellets on a Bruker VECTOR 22 spectrometer. Microanalysis (C, H, N, S) was performed on a Perkin–Elmer 240 elemental analyzer. Melting points were determined on an X-4 microscope electron thermal apparatus.

Methods

Stock solutions of metal ions were prepared from their chloride or nitrate salts in distilled water. High concentration of the stock solutions of L and L' (200 µM) were prepared in freshly distilled CH₃CN, respectively. When studying the fluorescence sensing behaviors of L or L' to metal ions, 75 µL stock solution of L or L'was put into a 3 mL quartz cuvette, then 60 µL one of the stock solutions of the metal salts was added to the above solution and mixed. Fluorescence quantum yields of complexes Al-L and Al-L'were determined by comparison of the integrated area of the emission spectrum in CH₃CN. The optically matching solution of anthracene (ethanol, $\Phi = 0.27$) was used as standard, the concentration of the reference was adjusted to match the absorbance of the test sample at the wavelength of excitation [8].

Syntheses

Synthesis of compounds A, 1(1') and 2(2')

Compounds **A** [9], $\mathbf{1}(\mathbf{1}')$ [10] and $\mathbf{2}(\mathbf{2}')$ [10] were synthesized according to the literature procedure.

Synthesis of the intermediate compound 3

Compound **3** was synthesized by an improved method according to the literature [11]. N,N-bis(2-chloroethyl)amine hydrogen-

chloride (0.274 g, 1.55 mmol), intermediate compound 2 (0.600 g, 3.1 mmol), anhydrous sodium carbonate (0.494 g, 4.66 mmol) and DMF (25 mL) were added into a 100 mL three-necked flask. The reaction mixture was stirred at 120 °C under nitrogen atmosphere for 4 h. After cooling to room temperature, the reaction mixture was poured into distilled water (20 mL), and filtered off. The residue was dissolved in dichloromethane (15 mL) and washed with water (15 mL \times 3). The organic phase was separated and dried with anhydrous MgSO₄. The organic solvent was removed under reduced pressure. The crude product was purified by column chromatography (SiO₂, chloroform/methanol, 60:1, v/v). The product was obtained as gray yellow solid in 81% yield (0.571 g). m.p.: 193197 °C. ¹H NMR (300 MHz, CDCl₃, ppm) δ: 7.70 (m, 6H *J* = 28.8 Hz), 3.22 (t, 4H, *J* = 13.2 Hz), 3.16 (t, 6H, *J* = 15.6 Hz), 3.01 (m, 4H, I = 22.2 Hz). ¹³C NMR (400 MHz, CDCl₃, cm⁻¹): δ 167.79, 137.40, 133.97, 133.60, 130.26, 127.40, 119.30, 47.49, 31.32, 23.89. IR (KBr plate, cm⁻¹): 3402, 2927, 1759, 1704, 1643, 1601, 1581, 1531, 1434, 1379, 1360, 1358, 1176, 1261, 1143, 1174, 1004, 863, 816, 800, 788, 778, 733, 702, 666, 620, 564, 500. Anal. Calcd. for C₂₂H₂₁N₃O₄S₂: C, 58.00, H, 4.65, N, 9.22, S, 14.08; found: C, 58.21, H, 4.59, N, 9.28, S, 14.13. EI-MS: 456.1 [M + H]⁺.

Synthesis of the intermediate compound 3'

This compound was prepared from N,N-bis(2-chloroethyl)amine hydrogench-loride and intermediate compound **2**′ through the similar procedure to **3**. The product was obtained as light yellow solid in 78% yield (0.550 g). m.p.: 120123 °C. ¹H NMR (300 MHz, CDCl₃, ppm) δ : 7.70 (d, 4H *J* = 7.8 Hz), 7.56 (t, 2H, *J* = 9.6 Hz), 3.21 (t, 10H, *J* = 12.6 Hz), 2.98 (t, 4H, *J* = 12.6 Hz). ¹³C NMR (400 MHz, CDCl₃, cm⁻¹): δ 168.07, 145.69, 133.10, 131.77, 128.60, 123.37, 120.84, 47.40, 32.89, 23.99. IR (KBr plate, cm⁻¹): 3301, 2920, 2803, 2751, 1767, 1697, 1603, 1487, 1436, 1380, 1335, 1322, 1291, 1254, 1193, 1178, 1161, 1125, 1050, 1007, 975, 886, 829, 736, 669, 614, 600, 510. Anal. Calcd. for C₂₂H₂₁N₃O₄-S₂: C, 58.00, H, 4.65, N, 9.22, S, 14.08; found: C, 58.14, H, 4.62, N, 9.54, S, 14.15. EI-MS: 456.1 [M + H]⁺.

Synthesis of L

9-Bromomethylanthracene (A) (0.108 g, 0.4 mmol), intermediate compound **3** (0.182 g, 0.4 mmol), anhydrous K_2CO_3 (0.116 g, 0.8 mmol) were added in CH₃CN (8 mL). The reaction mixture was allowed to reflux for 12 h. After cooling to room temperature, K₂CO₃ was removed by filtration. The yellow filtrate was evaporated to dryness under reduced pressure. The resulting solid was purified by column chromatography (petroleum ether/ethyl acetate, 7:3, v/v). The product was obtained as light yellow solid in 85.8% yield (136 mg). m.p.: 203-206 °C. ¹H NMR (300 MHz, CDCl₃, ppm) δ: 8.51 (d, 2H, J=9.0 Hz), 8.363 (s, 1H), 7.97 (d, 2H, J = 7.8 Hz), 7.49 (m, 6H, J = 43.2 Hz), 7.15 (t, 2H, J = 9.6 Hz), 6.88 (d, 2H, J = 8.4 Hz), 4.70 (s, 2H), 3.11 (d, 6H, J = 5.1 Hz), 3.05 (m, 4H, J = 24.3 Hz), 2.99 (t, 4H, J = 7.2 Hz). ¹³C NMR (400 MHz, CDCl₃, cm⁻¹): δ 167.94, 167.76, 137.67, 133.53, 133.33, 131.26, 131.22, 129.49, 129.03, 128.64, 128.04, 126.87, 126.15, 125.03, 124.79, 118.77, 52.60, 51.17, 29.30, 23.81. IR (KBr plate, cm⁻¹): 3451, 3049, 2933, 2864, 2808, 1765, 1706, 1599, 1580, 1457, 1439, 1380, 1340, 1261, 1179, 1114, 1098, 1055, 1007, 887, 864, 800, 733, 669, 634, 555, 526, 501. Anal. Calcd. for C₃₇H₃₁N₃O₄S₂: C, 68.81, H, 4.84, N, 6.51, S, 9.93; found: C, 68.79, H, 4.81, N, 6.48, S, 9.96. EI-MS: 646.2 [M + H]⁺.

Synthesis of L'

This compound was prepared from 9-bromomethylanthracene (**A**), intermediate compound **3**' through similar procedure to **L**. The product was obtained as yellow solid in 80.2% yield (0.118 g). m.p.: 7375 °C. ¹H NMR (300 MHz, CDCl₃, ppm) δ : 8.43 (d, 2H, *J* = 9.0 Hz), 8.33 (s, 1H), 7.95 (d, 2H, *J* = 7.8 Hz), 7.47 (m,

8H, J = 43.2 Hz), 7.07 (m, 2H, J = 9.6 Hz), 4.63 (s, 2H), 3.17 (s, 6H), 3.08 (d, 4H, J = 6.9 Hz), 2.98 (d, 4H, J = 6.9 Hz). ¹³C NMR (400 MHz, CDCl₃, cm⁻¹): δ 168.01, 167.94, 145.48, 132.65, 131.20, 131.25, 128.99, 128.39, 128.18, 128.03, 126.02, 124.96, 124.64, 123.04, 120.85, 52.34, 50.97, 30.92, 23.94. IR (KBr plate, cm⁻¹): 3459, 3050, 2941, 1771, 1704, 1610, 1523, 1436, 1378, 1294, 1252, 1436, 1378, 1294, 1177, 1108, 1051, 1007, 978, 886, 840, 736, 670, 611, 590, 511. Anal. Calcd. for C₃₇H₃₁N₃O₄S₂: C, 68.81, H, 4.84, N, 6.51, S, 9.93; found: C, 68.85, H, 4.80, N, 6.53, S, 9.89. EI-MS: 646.2 [M + H]⁺.

Result and discussion

Our research involves the design, synthesis, and evaluation of the two isomerous fluorescent chemosensors *L* and *L'*. The detailed experimental procedures were shown in Scheme 1 and all new compounds were characterized by NMR, IR, ESI/MS and elemental analysis. The single crystals of *L* and *L'* were obtained by solvent evaporation method in dichloromethane and acetone, respectively (Scheme 1, Supplementary Figs. 9 and 10).

UV-vis and fluorescence spectral changes of **L** induced by Al^{3+}

The UV–vis spectra of the chemosensor L in CH₃CN exhibited three obvious absorption peaks at 255, 367 and 387 nm. To investigate the binding property of L toward Al³⁺, titration experiments were carried out as shown in Fig. 1A. Upon addition of Al³⁺, the absorption peaks at 367 and 387 nm gradually decreased and the absorption peak at 233 nm gradually increased while the absorption peak at 255 nm remained constant along with the increase of the Al³⁺ concentration. Meanwhile, a high energy (LE) shoulder developed at 280 nm. Moreover, three clear isobestic points at 269, 358 and 392 nm were observed. Furthermore, the changes of this absorption peaks were likely due to the coordination of Lwith Al³⁺ [12]. According to the linear Benesi–Hildebrand expression [13], the linear relationship assumed a 1:1 binding model with the K_a of (1.432 ± 0.186) × 10⁵ from the titration experiments (Supplementary Fig. 11).

The chemosensor **L** exhibited a weak fluorescence at 413 nm in CH₃CN (Φ = 0.006) as shown in Fig. 1B, which could be attributed to the two PET processes from the nitrogen donor and the sulfur donors to the anthracene fluorophore. Upon binding Al³⁺, a significant



Scheme 1. (a and b) Synthesis of L and L' and (c) X-ray single crystal structures for L and L'.



Fig. 1. (A) UV-vis spectra and (B) fluorescence spectra of L (5 μ M) in CH₃CN upon the addition of Al³⁺. Inset: (A) the photos of the solution of L before and after addition of 10 equiv of Al³⁺ under visible light. (B) (a) the plot of the fluorescence intensity (413 nm) vs the concentration of Al³⁺; (b) the photos of the solution of L before and after addition of 10 equiv Al³⁺ under visible light.

increase of fluorescence intensity at 413 nm was observed by the inhibition of PET processes ($\Phi = 0.013$). The inset in Fig. 1a showed the dependence of the fluorescence intensity at 413 nm on the Al³⁺ concentration, which suggested the chemosensor *L* exhibited an efficient fluorescence response. The 1:1 stoichiometry between *L* and Al³⁺ was also obtained from Job's plot (Supplementary Fig. 12). The corresponding detection limit was found to be 4.8×10^{-7} M by plotting the fluorescence intensity at 413 nm *versus* the concentration of Al³⁺ (Supplementary Fig. 13) [14].

UV-vis and fluorescence spectral changes of L' induced by Al^{3+}

The UV–vis spectra of the chemosensor L' exhibited a typical anthracene absorption peak at 255 nm in CH₃CN as shown in Fig. 2A. Upon addition of Al³⁺, the absorption band at 205 nm gradually increased while the absorption peak at 255 nm remained constant. These changes were likely attributed to the coordination of L' with Al³⁺ [12]. According to the linear Benesi–Hildebrand expression [13], the linear relationship suggested a 1:1 binding model with the K_a of $(1.427 \pm 0.970) \times 10^5$ from the titration experiments (Supplementary Fig. 14).

The fluorescence spectral changes of L' (5 µM) induced by Al³⁺ were conducted in CH₃CN as shown in Fig. 2B. Upon addition of different concentrations of Al³⁺, a significant enhancement of the fluorescence intensity at 395, 416 and 443 nm was observed by the inhibition of PET processes. The quantum yield of the complex in CH₃CN was calculated to be 0.021, which was higher than that of the free ligand (Φ = 0.009). The inset in Fig. 2a also suggested that the chemosensor L' (416 nm) exhibited an efficient fluorescence response toward Al³⁺. To further confirm the stoichiometry between Al³⁺ and L', a Job's plot obtained from emission data also showed a 1:1 complex (Supplementary Fig. 15). The detection limit of the chemosensor L' for Al³⁺ was about 2.2 × 10⁻⁷ M (Supplementary Fig. 16) [14].

¹H NMR titration experiments

To further investigate the binding model between *L* and *L'* with Al^{3+} , ¹H NMR titration experiments were carried out in $CDCl_3/CD_3$ -OH (17:3, v/v). As shown in Fig. 3A, upon adding 1 equiv of Al^{3+} to *L* solution, the peaks of the protons H_a , H_b , H_c , H_d and H_e around binding sites were obviously shifted downfield by 0.75, 0.48, 0.30, 0.20, 0.14 ppm from δ 4.71, 2.66, 3.10, 6.91, 7.17 to 5.46,



Fig. 2. (A) UV-vis spectra and (B) fluorescence spectra of L' (5 μ M) in CH₃CN upon the addition of Al³⁺. Inset: (A) the photos of the solution of L' before and after addition of 10 equiv of Al³⁺ under visible light. (B) (a) the plot of the fluorescence intensity (416 nm) vs the concentration of Al³⁺; (b) the photos of the solution of L' before and after addition of 10 equiv of Al³⁺ under visible light.



Fig. 3. ¹H NMR spectra of L (A) and L' (B) with and without Al(NO₃)₃ in CDCl₃:CD₃OD = 17:3 (v/v).

3.14, 3.40, 7.11, 7.31 ppm, respectively. Upon adding 1 equiv of Al^{3+} to L' solution (Fig. 3B), the peaks of the protons H_a , H_b , H_c , H_d and H_e around binding sites were also obviously shifted downfield by 0.53, 0.20, 0.13, 0.08, 0.03 ppm from δ 4.63, 2.98, 3.14, 7.09, 7.38 to 5.16, 3.18, 3.27, 7.17, 7.41 ppm, respectively. When adding more than 1 equiv of Al^{3+} , the chemical shift of the protons of L and L' stopped changing, which confirmed again that L and L' toward Al^{3+} ions formed a 1:1 complex, respectively.

Selection and competition experiments

To evaluate the selectivity of the chemosensors L and L' toward Al³⁺ ions in CH₃CN, fluorescence spectra changes were recorded after 3 min when 10 equiv of each of these metal ions such as Na⁺, K⁺, Ca²⁺, Mg²⁺, Al³⁺, Cd²⁺, Zn²⁺, Fe²⁺, Fe³⁺, Mn²⁺, Co²⁺, Ni²⁺, In³⁺, Cr³⁺, Cu²⁺, Hg²⁺, Pb²⁺, and Ag⁺ were added. As can be seen from Fig. 4, Na⁺, K⁺, Ca²⁺, Mg²⁺, Cd²⁺, Zn²⁺, Fe²⁺, Mn²⁺, Co²⁺, Ni²⁺, In³⁺,

 Cr^{3+} , Cu^{2+} , Hg^{2+} had no obvious effect on the fluorescence emission of L except that Pb^{2+} , Ag^+ and Fe^{3+} showed little enhancement. Compared to L, Cu^{2+} , Cr^{3+} , Fe^{3+} and Fe^{2+} had a slight increase in the fluorescence intensity positioned at 443 nm of L'. In stark contrast, the addition of Al^{3+} caused a significant fluorescence enhancement of L and L'. Moreover, L' had better selectivity for Al^{3+} than L due to a more efficient PET mechanism. These results suggested that both L and L' had good selectivity for Al^{3+} over other metal ions with little interference in CH_3CN .

To further evaluate the selectivity of L and L' as the fluorescent chemosensor for Al³⁺ in practice, competition experiments were carried out by adding 10 equiv of Na⁺, K⁺, Ca²⁺, Mg²⁺, Cd²⁺, Zn²⁺, Fe²⁺, Fe³⁺, Mn²⁺, Co²⁺, Ni²⁺, Cu²⁺, Hg²⁺, Pb²⁺, Ag⁺ in the presence of 10 equiv of Al³⁺ under the above conditions. As shown in Fig. 5, competitive metal ions had no obvious interference with the detection of Al³⁺ ions. In addition, the fluorescence behaviour of the two chemosensors L and L' in different ratios of CH₃CN/



Fig. 4. Fluorescence spectra of L (A) and L' (B) (5 μ M) upon addition of 10 equiv of various metal ions in CH₃CN (λ_{ex} = 367 nm).



Fig. 5. Metal-ion response for L (A) and L' (B) (5 µM) in the absence (F₀) and presence (F) of 10 equiv of various metal ions in CH₃CN. Bars represent the fluorescence intensity changes (F- F_0). The gray bars represent the changes of the fluorescence intensity after the addition of various metal ions, the black bars represent the changes of the fluorescence intensity that occurs upon the subsequent addition of 10 equiv of AI^{3*} to the above solution.

H₂O solution was investigated under the same measurement conditions (Supplementary Fig. 17). Moreover, the selectivity of L and L' toward Al³⁺ was also studied in CH₃CN/H₂O (9/1) solution (Supplementary Fig. 18). These data indicated that the chemosensors L and L' displayed excellent selectivity toward Al³⁺ in CH₃CN and CH₃CN/H₂O (9/1) solution.

In addition to cation binding properties, the selectivity of toward various anions the chemosensors **L** and **L**' $(F^-,Cl^-,Br^-,I^-,AcO^-,ClO_4^-,H_2PO_4^- \mbox{ and }HSO_4^-)$ was also conducted in the presence of 10 equiv of Al³⁺ in CH₃CN under the above conditions (Supplementary Fig. 19). Among the various anions, only F⁻ and ClO_4^- had little effect on the fluorescence emission of Al-L. But in Al-L' solution, these anions remained practically unchanged. Besides, the selectivity of the chemosensors L and L' toward various anions was also studied in CH₃CN/H₂O (9/1) solution (Supplementary Fig. 20). All the results suggested that L and L' could be used as selective fluorescent chemosensors for Al³⁺ with little interference of the environmentally relevant anions.

Conclusions

In conclusion, we have successfully developed two new isomerous turn-on fluorescent chemosensors for Al³⁺ based on PET processes. Moreover, the two chemosensors (L and L') exhibited good selectivity for Al³⁺ over other metal ions with little interference. More importantly, the fluorescence intensity of L' was improved in comparison to L due to a more efficient PET mechanism. In addition, both **L** and **L**' for Al^{3+} had a quite lower detection limit. Hence, our present study opens up the new possibility of more PET chemosensors for some specific ions based on anthracene.

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Appendix A. Supplementary material

Characterization data including ¹H and ¹³C NMR, MS, UV-vis, fluorescence spectra and X-ray crystallographic data in CIF format of L (CCDC 907002) and L' (CCDC 902859). Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.saa.2013.06.006.

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