



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



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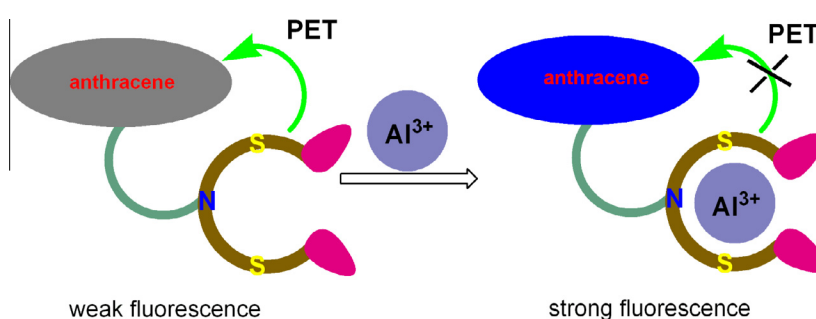
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HIGHLIGHTS

- Two new isomeric PET fluorescent chemosensors (**L** and **L'**) has been developed.
- Both chemosensors exhibited “turn-on” for Al³⁺ in CH₃CN.
- The selectivity of **L'** for Al³⁺ was improved compared to **L**.

GRAPHICAL ABSTRACT



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ABSTRACT

Two new isomeric PET fluorescent chemosensors (**L** and **L'**) for Al³⁺ have been designed, synthesized and characterized. The two chemosensors exhibited fluorescence enhancement upon binding Al³⁺ in CH₃CN 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 Zn²⁺, Cd²⁺, Cu²⁺, Hg²⁺ and Cr³⁺ [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 Al^{3+} have been designed with moderate success [7]. Therefore, it is a challenging work to develop some high selective and sensitive chemosensors for Al^{3+} 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 isomeric 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 CH_3CN was distilled. Double distilled water was used for spectral detection.

Instruments

^1H NMR and ^{13}C NMR titrations experiments were obtained on a Bruker 300 spectrometer with TMS as internal standard at room temperature. ^{13}C 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 CH_3CN , 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 CH_3CN . 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], **1(1')** [10] and **2(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 MgSO_4 . The organic solvent was removed under reduced pressure. The crude product was purified by column chromatography (SiO_2 , chloroform/methanol, 60:1, v/v). The product was obtained as gray yellow solid in 81% yield (0.571 g). m.p.: 193.197 °C. ^1H NMR (300 MHz, CDCl_3 , 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, $J = 22.2$ Hz). ^{13}C NMR (400 MHz, CDCl_3 , 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 $\text{C}_{22}\text{H}_{21}\text{N}_3\text{O}_4\text{S}_2$: 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 $[\text{M} + \text{H}]^+$.

Synthesis of the intermediate compound **3'**

This compound was prepared from N,N-bis(2-chloroethyl)amine hydrogenchloride 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.: 120.123 °C. ^1H NMR (300 MHz, CDCl_3 , 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). ^{13}C NMR (400 MHz, CDCl_3 , 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 $\text{C}_{22}\text{H}_{21}\text{N}_3\text{O}_4\text{S}_2$: 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 $[\text{M} + \text{H}]^+$.

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 CH_3CN (8 mL). The reaction mixture was allowed to reflux for 12 h. After cooling to room temperature, K_2CO_3 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, CDCl_3 , 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). ^{13}C NMR (400 MHz, CDCl_3 , 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 $\text{C}_{37}\text{H}_{31}\text{N}_3\text{O}_4\text{S}_2$: 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 $[\text{M} + \text{H}]^+$.

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, CDCl_3 , 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,

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