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A symmetric pseudo salen based turn-on fluorescent probe for sensitive detection and visual analysis of zinc ion

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ABSTRACT

A turn-on fluorescence probe for zinc ion has been synthesized, which contains a symmetric pseudo salen moiety as zinc recognition site. The multidentate salen ligand chelates with zinc ions, and generates the rigidity of the zinc complex, which subsequently results in a dramatic fluorescence enhancement of the probe. Mass spectral and spectroscopic results reveal that the reaction proceeds rapidly in a 1 to 1 stoichiometric manner to form a clean zinc complex. We have demonstrated that the fluorescence probe not only has high selectivity for zinc ion over other biological relevant ions but also shows high sensitivity for zinc ion with a detection limit of 83 nM. A fluorescence test paper has been developed by incorporating the probe on a polyamide fiber paper. The fluorescence color of the test paper became bright green–yellow under UV lamp when water sample containing zinc ions was dropped on it, suggesting its potential application in the measurement of zinc ions.

1. Introduction

As an essential trace element in biological systems, zinc ion (Zn^{2+}) plays an important role in physiological processes, for example, it is a structural or catalytic cofactor for some enzyme and receptor regulation function [1,2]. It is also closely associated with biosynthesis of DNA, RNA and common proteins. Failure of maintain zinc ions homeostasis in body can cause several neurological diseases such as Alzheimer's disease, Parkinson's disease, diabetes, depression and dysplasia [3–5]. Real-time monitoring the uptake, accumulation, trafficking and efflux of zinc ions is of great importance for diagnosis and prophylaxis of such diseases. Therefore, the development of new molecular probes for sensitive and selective detection of zinc ion has been a concern of chemists.

The current methods for zinc ion detection include surface enhanced raman scattering (SERS) [6], electrochemistry [7,8], absorption and fluorescence spectrometry [9]. The method based on SERS uses dithiocarbamate as a substrate and supports the detection of zinc ions at trace level [10]. In recent years, some zinc fluorescent probes have been reported for the detection of zinc ions. These probes generally comprise a chelating moiety and a fluorophore group, which are responsible for the recognition of zinc ions and the generation of fluorescence signal variation, respectively [11–15]. The optical properties of these organic probes are dependent on the substituted groups surrounding the fluorophore moiety. In these probes, the pyrazoline, 2,2′-dipicolylamine (DPA) [16–17], porphyrin [18], bipyridine, quinoline [19–22] and pyridine groups are often used as zinc ion chelators. Some of these probes show cross sensitivity toward other heavy metal ions such as Hg^{2+} and Cd^{2+}, which degrades the selectivity. So, it remains a challenge to develop sensitive and selective fluorescent probes for Zn^{2+}, which has a specific zinc ion chelating ability. Herein, we report a new sensitive and selective fluorescent probe for Zn^{2+} detection, which was synthesized by reacting dansyl chloride with a pseudo salen moiety containing amino groups. Dansyl chloride [23–25] is often used as a derivatizing agent and is intrinsically weakly fluorescent. Upon rapid reaction with the amino groups, a sulfamide derivative formed and its fluorescence property is dependent on the molecular structure. The salicylaldehyde-derived pseudo salen receptor can efficiently bond with zinc ions

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and the dansyl fluorophore provides fluorescence signal. The probe has been demonstrated to selectively and sensitively respond to Zn^{2+} in a wide concentration range.

2. Experimental

2.1. Materials and chemicals

All reagents were purchased from commercial suppliers and used without further purification. Solvents were purified by standard methods prior to use. All the solutions were prepared with water purified by a Millipore water purification system (18.2 MΩ cm). $CaCl_2$, $CuCl_2 \cdot 2H_2O$, $BaCl_2$, $FeCl_3 \cdot 6H_2O$, $MgCl_2 \cdot 6H_2O$, $NiCl_2 \cdot 6H_2O$, $MnSO_4 \cdot 1H_2O$, $CdCl_2 \cdot 2.5H_2O$, $CoCl_2 \cdot 6H_2O$, $ZnCl_2$, $Pb(NO_3)_2$ and$Hg(NO_3)_2$ were used to prepare metal ion stock solutions. $CDCl_3$ were used to record ^1H NMR spectra.

2.2. Apparatus

The UV–vis absorption spectra were recorded with a Shimadzu UV-2550 spectrometer at room temperature. Fluorescence measurements were performed on a Perkin-Elmer LS-55 luminescence spectrometer (Llantrisant, UK) equipped with a quartz cell (1 cm × 1 cm). The slit widths for excitation and emission were both 10 nm. ^1H NMR spectra were recorded on a Brucker Advance 400 NMR spectrometer. Mass spectra were obtained on a Thermo Prpteome X-LTQ MS mass spectrometer in ES positive and negative mode. Photographs were taken by a Canon 350D digital camera. Thin layer chromatography analysis was performed on silica gel plates and column chromatography was conducted over silica gel (mesh 200–300).

2.3. Synthesis of compounds 2,2′-(1E,1′E)-(2,2-azanediylbis(ethane-2,1-diyl)bis(azan -1-yl-1-ylidene))bis(methan-1-yl-1-ylidene) dipnenol, TAS

Diethylenetriamine (2 mmol, 200 mg) was dissolved in CH_3OH (6 ml) at room temperature, salicylaldehyde (2.5 mmol, 310 mg) was then added to form a clear solution. The solution was further stirred for 2 h at room temperature. The solvent was then removed under reduced pressure to obtain the crude product, which was further purified by column chromatography on silica (CH_2Cl_2: CH_3OH=9:1) to yield pure yellow oil product TAS (430 mg, 70.5% yield).

2.4. Synthesis of compounds [5-(dimethylamino)-N,N-bis(2-((E)-2-hydroxybenzy lideneamino)ethyl)naphthalene-1-sulfonamide], DS-TAS

A portion (200 mg, 0.6 mmol) of compound TAS was mixed with dansyl chloride (205 mg, 0.7 mmol) in 6 mL of CH_2Cl_2 and several drops of pyridine were added, followed by stirring for 2 h at room temperature. The reaction mixture was then filtered and the filtrate was dried by rotary evaporator under reduced pressure. The resulting residue was subjected to column chromatography on silica (CH_2Cl_2:CH_3OH=30:1) and finally a yellow–green solid, DS-TAS (261.1 mg, 80.2% yield). ESI-MS: 543.14 (M^-). ^1H NMR (400 MHz, $CDCl_3$) δ 12.82 (s, 2H), 8.47 (d, J=8.5 Hz, 1H), 8.2–8.12 (m, 2H), 7.96 (s, 2H), 7.47–7.42 (m, 1H), 7.37 (ddd, J=7.8, 6.8, 3.8 Hz, 1H), 7.22 (ddd, J=8.4, 7.3, 1.7 Hz, 2H), 7.05 (d, J=7.1 Hz, 1H), 7.01 (dd, J=7.6, 1.6 Hz, 2H), 6.84 (d, J=8.3 Hz, 2H), 6.77 (td, J=7.5, 1.1 Hz, 2H), 3.64–3.54 (m, 7H), 2.80 (d, J=4.8 Hz, 5H).

2.5. Fluorescence experiments

A stock solution of DS-TAS (1 mM) in ethanol was prepared. The working solution of DS-TAS (500 nM) was prepared by diluting 1 μL of the DS-TAS stock solution in 2 mL ethanol. The metal ion solutions were added into the mixture followed by recording the fluorescence spectra. Equimolar solutions of DS-TAS and Zn^{2+} were prepared first for the Job's plot experiment. The two solutions were then mixed in standard volume and proportion in order to keep the total concentration of probe and Zn^{2+} constant of 500 nM. All fluorescence spectra were recorded in the range from 420 nm to 750 nm using a 360 nm excitation wavelength and a 500 nm/min scan rate.

2.6. Preparation of fluorescence test paper

2 μL of DS-TAS (5 μM) was dripped on a piece of polyamide fiber paper to form a spot about 5 mm in diameter, followed by drying under air. The spot was nearly colorless under a 365 nm UV lamp. In order to detect Zn^{2+}, 2 μL of Zn^{2+} with different concentrations from 0.5 μM to 5 μM was dropped on the center of the spot. Then after the spot was air-dried under room temperature, the indicating paper was put under a UV lamp with excitation wavelength of 365 nm to observe the change of fluorescence color.

3. Results and discussion

3.1. Characterization of DS-TAS

The fluorescence probe, DS-TAS, was obtained in high yield through a simple two-step reaction modified from a literature [26], as shown in Scheme S1. The probe contains two functional segments, the pseudo salen moiety as the analyte-sensitive receptor and dansyl moiety as fluorophore reporter, whose fluorescence quantum yield is dependent on the conformation of salen moiety. The chemical structure is confirmed by ESI-MS (Fig. S1) and ^1H NMR (Fig. S2). The ESI-MS spectrum shows a peak at m/z 543.14 in negative mode which matches perfectly with the calculated molecular weight of [DS-TAS].

3.2. Spectroscopic properties of DS-TAS

The UV–vis spectrum of the probe in ethanol shows two absorption bands at 254 and 320 nm. The spectrum changes gradually upon the addition of zinc ion as shown in Fig. 1. The two absorption bands decrease and finally disappear as the amount of Zn^{2+} added increases, accompanied by the appearance of three new absorption peaks at 225, 270 and 360 nm. The new absorption peaks gradually increase and finally reach their plateaus when one molar equivalent of Zn^{2+} was added. The red shift of the absorption bands can be attributed to the zinc coordination and the formation of a planar complex. It can be seen that four isosbestic points at 250, 262, 291 and 335 nm produced, which correspond to the clear formation of zinc complex. The well-defined isosbestic points clearly indicate the formation of a new complex in equilibrium with the free DS-TAS ligand. The appearance of the absorption band at 360 nm indicates the formation of DS-TAS–Zn complex and isomerisation of the C=N bond. DS-TAS contains both hydroxyl and C=N groups that are well-known to be involved in metal ions coordination. Upon addition of Zn^{2+}, the acidities of phenolic hydroxyl is enhanced and therefore an excited-state intra/inter molecular proton transfer (ESPT) channel might be opened. A new absorption band at 360 nm arising from