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A facile strategy for achieving high selective Zn(II) fluorescence probe by regulating the solvent polarity

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ABSTRACT

A simple Schiff base comprised of tris(2-aminoethyl)amine and salicylaldehyde was designed and synthesized by one-step reaction. Although this compound has poor selectivity for metal ions in acetonitrile, it shows high selectivity and sensitivity detection for Zn(II) ions through adjusting the solvent polarity (the volume ratio of CH_3CN/H_2O). In other words, this work provides a facile way to realize a transformation from poor to excellent feature for fluorescent probes. The bonding mode of this probe with Zn(II) ions was verified by ^1H NMR and MS assays. The stoichiometric ratio of the probe with Zn(II) is 1:1 (mole), which matches with the Job-plot assay. The detection limitation of the probe for Zn(II) is up to 1×10^{-8} mol/L. The electrochemical property of the probe combined with Zn(II) was investigated by cyclic voltammetry method, and the result agreed with the theoretical calculation by the Gaussian 09 software. The probe for Zn(II) could be applied in practical samples and biological systems. The main contribution of this work lies in providing a very simple method to realize the selectivity transformation for poor selective probes. The providing way is a simple, easy and low-cost method for obtaining high selectively fluorescence probes.

1. Introduction

As the second most abundant trace element, Zinc ion is present in the form of divalent cation and it plays very important roles in many biological processes, such as brain fiction, immune function, gene transfection and so on [1–3]. In terms of human health, many mental illnesses have been caused due to the imbalance of Zinc ion including Alzheimer's disease, Parkinson's disease, Epilepsy, etc [4–6]. For the environment, Zinc ion caused a lot of serious environmental pollution due to its widespread use in the electroplating industry [7–9]. Therefore, it is essential for human health and environment to design a highly selective detection probe for Zinc ion and other transition metals ions [10–12].

With the rapid development of chemical technology, researchers have paid much more attention to fluorescence technology [13–15]. What's more, more and more organic fluorescent probes have been designed and synthesized for detecting Zn(II) [16–24]. It is known to all that Schiff bases probes have π electrons in the structure of C=N group which offers the opportunity to combine with metal ions, after chelating with the metal ions, the rigid structure of the probe increases and the fluorescence enhanced. Furthermore, it is beneficial to make Schiff bases become ideal chemical sensors with modifying varieties ligands, especially the ligands consist of oxygen, nitrogen or sulfur atoms [25–30]. On the other hand, Schiff bases are usually simple and low cost and this is the reason why so many researchers are interested in exploring wide varieties of Schiff bases. For example, Yin and co-workers designed and synthesized a new and potential fluorescent probe based on Schiff base recently [31]. This fluorescent probe showed pH dependent dual selectivity for Zn(II) and Al(III), which can detect Zn (II) at pH 7.4 and recognize Al(III) at pH 6.0, respectively. Similar to Yin's research, Kim and co-workers also reported a new Schiff base dual-chemosensor [32]. This chemosensor could detected Co(II) via color change and Zn(II) with turn-on fluorescence. It was worth noting that the detection limit of dual-chemosensor for Co(II) was the lowest one among organic chemosensors for Co(II) compared with before reported. In later studies, Dong and co-workers reported a reversible "turn-on" fluorescent probe for detecting Zn(II) based on CHEF and PET mechanisms [33]. An obvious strongly enhance fluorescence was observed when introducing Zn(II), and the fluorescence of the probe caused by Zn(II) was effectively quenched once adding EDTA which realized the reversible process.

In recent years, many researchers have drawn much more attention

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to tris(2-aminoethyl)amine due to it containing multiple nitrogen atoms and flexible structure so that it can offer reaction sites or binding sites to metal ions. This unique property is beneficial for the synthesis of fluorescent probes and some other advance materials [34–45]. Cheal and co-workers reported a cap-type Schiff base probe based on tris(2-aminoethyl)amine which acted as a fluorescence sensor for Zn(II) and a colorimetric sensor for Fe(II), Cu(II) and Zn(II) [46]. However, although many chemosensors with excellent properties have been reported already, there are more or less some other disadvantages existing, such as poor water solubility, easily affected by other similar ions and so on. In order to solve these problems, variety of ways were brought out by researchers. Generally, modifying with hydrophilic groups or side chains with charge can improve the water solubility [47–49]. Moreover, some research groups even designed and synthesized macromolecules and polymers or nano probes for exploration [50–55]. It is obvious that these methods are very complex and high cost in practical experiments. Beside the above cases, the selectivity for analytes is a crucial factor for fluorescent probes. In fact, many of the original design of the probe is always a low selectivity of the analytes. These probes would be abandoned in practice or modified some groups to redesign the synthetic probe, which could lead to spending more time or effort to improve the selectivity of the probe for designer. Therefore, exploring a simple and economical way to overcome difficulties is a very meaningful and practical exercise.

Here, we synthesized a very simple Schiff base probe comprised of tris(2-aminoethyl)amine and salicylaldehyde groups by one step reaction. This probe could achieved high selectivity and sensitivity to Zn(II) in mixture solution (CH_3CN/H_2O = 1/5, v/v). At the same time, we provided a very simple and low cost method to improve the selectivity of this probe effectively. At the beginning, this probe shows poor selectivity in acetonitrile, which can be response to Ca(II), Mg(II), Cd(II) and Zn(II) ions in fluorescence spectra and show disorganized absorption in the UV spectroscopy. This is a bad phenomenon for a probe. Based on this phenomenon, we tried to explore how to improve the selectivity by a simple method rather than give it up. Next, we found out that adjusting the ratio of water to organic solvent gradually would be able to improve the selectivity of the probe. So the probe could act as a “turn-on” fluorescent probe for Zn(II) finally. In other words, we realized the transformation from poor to excellent selectivity of fluorescent probe by using a very simple method that only changing the solvent polarity. After that, in the further study, we explored the photophysical and electrical properties and the combined mechanism. The results indicate that the probe has high selectivity and sensitivity for Zn (II) in the solution (CH_3CN/H_2O = 5/1, v/v). In addition, the probe can be applied in practical samples and biological systems effectively.

2. Experimental

2.1. Materials and instruments

Unless otherwise stated, all chemical reagents were obtained from commercial suppliers and used without further purification. Solvents used were purified and dried by standard methods prior to use. Tris(2-aminoethyl)amine and salicylaldehyde were purchased from Aladdin Industrial Corporation (Shanghai, China). Other routine solvents were purchased from Beijing Chemical Plant (Beijing, China). Metal ions were all nitrates and provided from Alfa Aesar (Tianjin, China). ^{1}H NMR and ^{13}C NMR spectra were measured on a Bruker ARX600 spectrometer with chemical shifts reported as ppm (TMS as an internal standard). High-resolution mass spectra (HRMS) were acquired on an Agilent 6510 Q-TOF LC/MS instrument (Agilent Technologies, Palo Alto, CA) equipped with an electrospray ionization (ESI) source. UV–Vis spectra were measured with a Hitachi 5300 absorption spectrophotometer. Fluorescence spectra were acquired with a Hitachi F-4600 fluorescence spectrophotometer, the excitation and emission slit widths both were 5.0 nm. Confocal laser scanning microscopy (CLSM) imaging was taken on a confocal laser scanning biological microscope (FV1000-IX81, Olympus, Japan). The fluorescence imaging assays were recorded by the fluorescence microscopy (Olympus 1 × 71). Cyclic voltammetry (CV) measurement was determined on a three-electrode AUTOLAB (model PGSTAT30) workstation in a solution of Bu_4NClO_4 (0.10 M) in acetonitrile at a scan rate of 50.0 mV/s at room temperature. The geometries and electron density distributions of the HOMO and LUMO energy levels of the probe and Zn(II) were calculated by density functional theory (DFT). Gaussian 09 software was used to calculate the DFT/B3LYP/6–31G (d, p) level.

2.2. Synthesis of the receptor

To 2.00 mL anhydrous ethanol containing tris(2-aminoethyl)amine (0.29 g, 2.00 mmol), salicylaldehyde (0.49 g, 4.00 mmol) in anhydrous ethanol (6.00 mL) was added and the mixture was stirred at room temperature for 4 h. Then, the resulting yellow solid was filtered off, recrystallized with anhydrous ethanol and dried in vacuo to obtain the desired receptor (N′,N′-bis[(2-salicylidene)aminoethyl]ethane- 1,2-diamine, 0.55 g, 78%). ^{1}H NMR (*d*-CH_3CN, 600 MHz) δ 10.14 (s, 2H), 13.71 (s, 2H), 8.04 (s, 2H), 7.31 (t, J = 12.0, 6.0 Hz, 2H), 6.88 (d, J = 12.0 Hz, 2 H), 6.72 (t, J= 6.0, 6.0 Hz, 2 H), 6.51 (t, J = 6.0, 6.0 Hz, 2 H), 3.57 (t, J = 6.0, 6.0 Hz, 4H), 2.85 (t, J = 12.0, 6.0 Hz, 4H), 2.18 (b, 6H); ^{13}C NMR (*d*-CH_3CN, 150 MHz) δ 165.88, 161.21, 131.80, 131.32, 118.55, 116.95, 57.91, 56.60, 55.35, 39.76; HRMS-ESI for $C_{20}H_{26}N_4O_2$ (m/z) 355.2122 [M + 1].

2.3. Fluorescence and UV–Vis measurements of the receptor with metal ions

All used water was the redistilled water. The receptor was dissolved in acetonitrile as the stock solutions (1.00×10^{-2} mol/L). The working solution was obtained by diluting method and placed in a quartz cuvette with 1 cm path. The total volume of working solution was 2.00 mL. The UV–Vis and fluorescence measurements were carried out by the titration method and the added volume did not exceed 3% of the total. After the mixed solutions were waited for 15 min, the new spectra were measured. All of the experiments were performed at barometric pressure and room temperature.

2.4. Assay of practical sample

The syrup sample was brought from the supermarket. Then, the working samples were prepared by a diluting method to be 1/14、1/10、1/8、1/6、1/4、1/3、1/2、2/3、3/4 of original volume. After that, these diluents acted as stock solutions of practical samples.

2.5. Cells culture and imaging

Human breast cancer cells (MCF-7) were cultured in DMEM medium containing 10% FBS routinely under a humidified atmosphere containing 5% CO_2, and then harvested for subculture using trypsin (0.05%, Gibco/Invitrogen) at 37 °C. HeLa cells were subcultured onto a 35 × 35 mm Petri dish with a glass bottom, then allowed to grow for 24 h for attachment. After that, 1.00 mL of DMEM medium containing 10% 10^{-5} mol/L compound (R) was used to incubate the HeLa cells at 37 °C for 3 h. The medium was replaced and phosphate-buffered saline (PBS, pH 7.4) was used to wash the cells thrice. And the quantities of Zn (II) (1.0×10^{-5} mol/L and 2.0×10^{-5} mol/L) in PBS buffer solutions were added into the dish and the cells were cultured at 37 °C for 1 h, respectively. The media were replaced and phosphate-buffered saline (PBS, pH 7.4) was used to wash the cells thrice. Then fresh media with cytoplasm located dye (Lyso tracker red) were added and incubated. After washing thrice with PBS, the images of the cells were recorded on confocal laser scanning microscopy.