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A simple fluorescent probe for Zn(II) based on the aggregation-induced emission

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ABSTRACT

A aggregation-induced emission-based fluorescent probe **1** for Zn^{2+} was designed and simply synthesized by condensation of salicylaldehyde with aqueous hydrazine. The experimental conditions were first optimized. It was found that N, N-Dimethylformamide (DMF) was the best solvent for the Zn^{2+}-triggered aggregation of compound **1** compared with other solvents. The emission intensity was gradually increased, accompanied by the simultaneous red shift of the maximum emission peak with increasing Zn^{2+} concentrations. A red shift about 45 nm was achieved when Zn^{2+} concentration is 100 μM. Compared with other Zn^{2+} fluorescent sensors based on aggregation-induced emission (AIE), compound **1** can detect a lower concentration of Zn^{2+} with a detection limit of 0.1 μM. Compound **1** also exhibited good selectivity toward Zn^{2+}. The aggregation was verified by the dynamic light scattering (DLS) results, with a Zn^{2+} concentration-dependent size observed. It was also directly confirmed by TEM analyses.

1. Introduction

Following iron, zinc ranks the second in abundance among the transition metals in the human body, and plays vital roles in many biological processes such as cellular metabolism, gene expression, and immune function [1–3]. Zn^{2+} is also believed to be an essential factor in some pathological processes, including Alzheimer's disease, epilepsy, and ischemic stroke [4,5]. Therefore, it is important to monitor Zn^{2+} in many scientific fields and clinical situations.

In the past few years, many traditional analytical techniques such as atomic absorption spectrometry [6], flame atomic absorption spectroscopy [7], inductively coupled plasma–atomic emission spectrometry [8], mass spectrometry [9], and cyclic voltammetry methods [10] have been employed to detect the concentration of Zn^{2+}. Though these techniques are sensitive, selective, and accurate for Zn^{2+} detection, most of them are rather complicated, time-consuming, and expensive as well as inadequate for on-line monitoring. Owing to the advantages of simplicity and inexpensive instrumentation, there are many methods such as spectrophotometric and fluorophotometric methods reported for the determination of trace amounts of zinc. Up to now, a variety of Zn^{2+}-selective fluorescent probes have been reported, most of which are based on photoinduced electron transfer (PET) [11–14], internal charge transfer (ICT) [13,15–17], and fluorescence resonance energy transfer (FRET) [18–22]. In recent years, various aggregation-induced emission (AIE) active compounds have been synthesized [23,24,27], and several Zn^{2+}-selective fluorescent turn-on probes based on aggregation-induced emission have also been developed [24,25].

Although the synthesis and optical property of 1,2-bis(2-hydroxybenzylidene) hydrazine have been previously reported [26], its analytical recognition characteristics are not investigated up to date. It was found that it is practically nonluminescent in the solution state, but becomes highly emissive as nanoparticle suspensions in poor solvents, demonstrating a novel phenomenon of AIE [27]. By taking advantage of the AIE feature of 1,2-bis(2-hydroxybenzylidene) hydrazine **1** (Scheme 1), herein we report a new fluorescence turn-on probe **1** for Zn^{2+}. Compound **1** exhibited good selectivity and sensitivity toward Zn^{2+}.

2. Experimental

2.1. General

Chemicals were purchased from commercial suppliers and used without further purification. Double-distilled water was used throughout all experiments. Thin layer chromatography (TLC) was carried out using silica gel HSGF254, which were obtained from the Qingdao Ocean Chemicals (Qingdao, China). NMR spectra were

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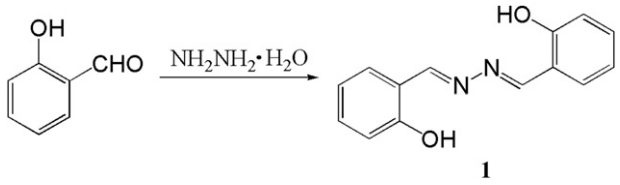

Scheme 1. Synthetic routes of compound **1**.

recorded on a Bruker DRX-400 spectrometer operating at 400 MHz. LC-MS analyses were performed using an Agilent 1100 HPLC/MSD spectrometer. All fluorescence measurements were carried out on a Hitachi-F4500 fluorescence spectrometer with excitation slit set at 5 nm and emission at 5 nm. Dynamic light scattering (DLS) characterization was performed using a Zetasizer Nano ZS90 DLS system. The morphology and particle size distribution of particles were characterized using a Jeol JEM-2010 transmission electron microscopy.

2.2. Synthesis of compound *1*

Compound **1** was synthesized according to a reported method (Scheme 1) [28]. To a solution of aqueous hydrazine (13 mg, 2.25 mmol) in methanol (20 mL) was added salicylaldehyde (549 mg, 4.50 mol) over a period of 1 h. Then the mixture was refluxed for 4 h. The solution was concentrated to give crude solid, which was recrystallized methanol and dried in vacuo to get 421 mg (78%) of compound **1** as a pale yellow solid. ^{1}H NMR (400 Hz, $CDCl_3$): 6.97 (t, J = 7.2 Hz, 2H), 7.04 (d, J = 8.0 Hz, 2H), 7.35–7.42 (m, 4H), 8.72 (s, 2H), 11.34 (brs, 2H); ^{13}C NMR (100 Hz, $CDCl_3$): δ 117.16, 119.72, 132.55, 133.44, 159.81, 164.70; ESI-MS: calcd for $C_{14}H_{12}N_2O_2$ m/z 240.3, found $(M + H)^+$: 241.1.

2.3. Procedures for metal ion sensing

A 11.11 μM stock solution of **1** was prepared by dissolving **1** in DMF. A standard stock solution of Zn^{2+} (10 mM) was prepared by dissolving an appropriate amount of zinc nitrate in water and

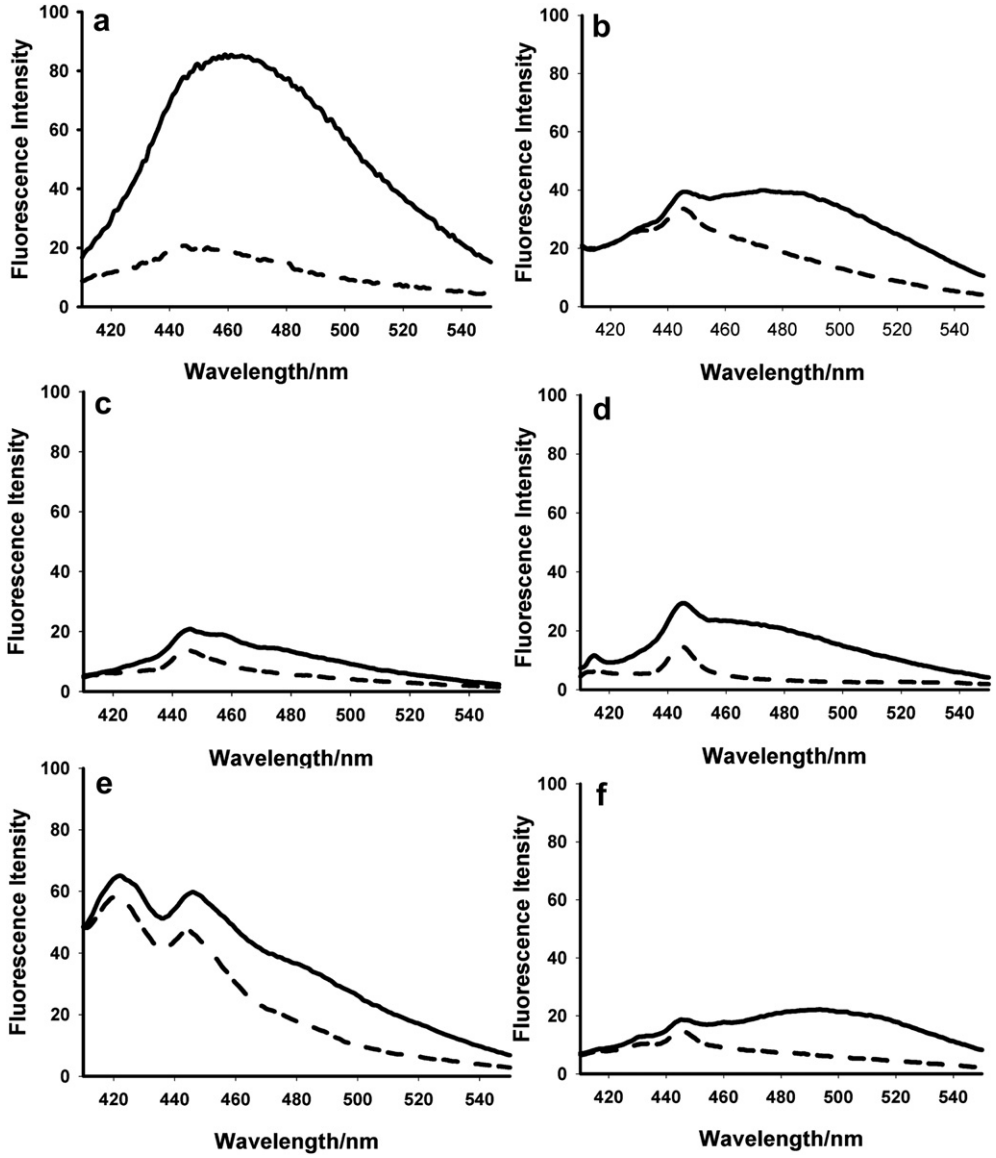

Fig. 1. Fluorescence emission spectra of the fluorescence chemosensor exposed to various solvents (dotted line: compound **1**; solid line: compound **1** with Zn^{2+}): a) DMF; b) DMSO; c) CH_3OH; d) THF; e) C_2H_5OH; f) CH_3CN. λ_{ex} = 400 nm.