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Research paper

A simple Schiff-base fluorescence probe for the simultaneous detection of Ga^{3+} and Zn^{2+}

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ABSTRACT

A new Schiff-base sensor **1**, based on fluorene and salicylaldehyde, has been prepared for the fluorescent detection of Ga^{3+} and Zn^{2+} by different emissions. The sensing behaviors of **1** with Ga^{3+} and Zn^{2+} were studied by using photophysical experiments, NMR titration, and ESI-mass spectrometry analysis. Moreover, turn-on fluorescence of **1** toward Ga^{3+} and Zn^{2+} caused by photo-induced electron transfer (PET) was explained by density functional theory (DFT) calculations. In particular, the detection limit of **1** for Ga^{3+} was down to nano-molar concentration (10 nM), which is the lowest one among those previously reported for organic-probes for sensing Ga^{3+} by fluorescence.

1. Introduction

The development of efficient probes for the detection of metal ions has received considerable attention due to their important roles in medicine, living systems and the environment [1]. Although gallium does not occur in nature, gallium salt is often found in diaspora, sphalerite, germanite, bauxite, zinc ores and coal. Moreover, it is employed in semiconductor devices, usually in the form of gallium arsenide and gallium nitride which in turn is used in light emitting diodes (LEDs) [2]. Gallium has no known physiological function in the human body, but is known to be highly toxic and carcinogenic for animals and humans [3]. Exposure to chronic poisoning of gallium causes serious disease, including gastrointestinal discomfort, coma, anemia, leucopenia, skin cancer, other internal cancers and sometimes death [4,5]. For these reasons, it is of considerable importance to develop probes for detection of gallium. However, probe for Ga^{3+} is very rare compared to those for other metal ions. Only a few probe for Ga^{3+} have been reported [6–11]. In addition, the discrimination of Ga^{3+} from Al^{3+} is very difficult because of their similar chemical properties [12,13]. Therefore, the achievement of specific Ga^{3+} sensing is a great challenge.

Zinc is not only an essential trace element but also the second most abundant transition metal ion in the human body and plays an important role in several biological processes, such as DNA synthesis, gene transcription, regulation of metallo-enzymes, neural signal transmission and cellular metabolism [14–16]. Apart from its biological role, deficiency of zinc causes acrodermatitis, while exposure to high levels of zinc causes serious neurological disorders like Alzheimer's and Parkinson's diseases and Friedreich's ataxia [17–20]. Meanwhile, Ga^{3+} sometimes inhibits the detection of Zn^{2+}, while the discrimination of Zn^{2+} from Ga^{3+} is a challenge. These issues indicate the urgent need to develop sensors that are capable of detecting zinc [21–25].

Among the various detecting methods such as inductively coupled plasma atomic emission spectrometry, atomic absorption spectroscopy and electrochemical methods [26–28], fluorescent probes have been regarded as useful tools for sensing biologically important metal ions because of their advantages such as, low cost, facile sample preparation, the simplicity and high sensitivity [29–34].

Fluorene-based compounds with short-wavelength fluorescence have been widely chosen as a signaling agent [35–37]. In addition, Schiff-base derivatives with π electrons in the C=N group offer a good chance for chelation with metal ions [38–40]. Therefore, we expected that the probe having fluorene moiety and Schiff-base would show unique fluorescent properties and the good chelation with metal ions.

Bifunctional sensors to detect more than one analyte by distinct signal responses have attracted researcher's attention and were found to be a more efficient method compared with sensors for single-ion. Some bifunctional sensors have been reported such as Hg^{2+}/Fe^{3+} [41], Cu^{2+}/F^- [42], Zn^{2+}/Co^{2+} [43], CN^-/F^- [44], Al^{3+}/Cr^{3+} [45,46] and Hg^{2+}/I^- [47]. However, there is no report that both Ga^{3+} and Zn^{2+} could be detected via a single molecule, to the best of our knowledge.

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Herein, we report a multifunctional fluorescence probe **1** based on combination of fluorene and salicylaldehyde for Ga^{3+} and Zn^{2+}. **1** showed discernible fluorescence emissions in the presence of Ga^{3+} and Zn^{2+} over other metal ions. Importantly, **1** can discriminate Ga^{3+} from Al^{3+}. The sensing mechanisms of Ga^{3+} and Zn^{2+} were supported by theoretical calculations.

2. Experimental

2.1. Materials and equipment

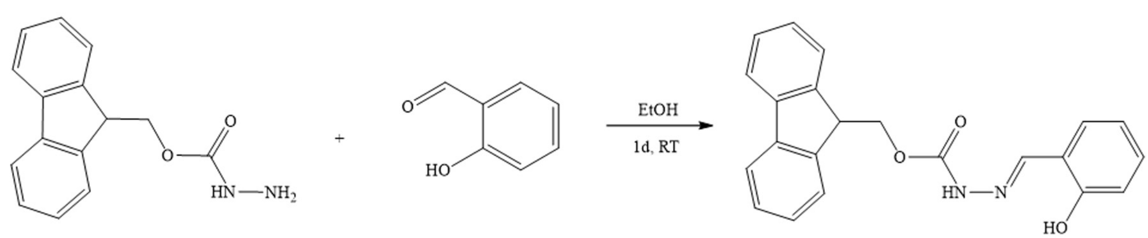
All the solvents and reagents (analytical grade and spectroscopic grade) were obtained from Sigma-Aldrich and used as received. ^{1}H NMR and ^{13}C NMR measurements were performed on a Varian 400 MHz and 100 MHz spectrometer, and chemical shifts were recorded in ppm. Electrospray ionization mass spectra (ESI-MS) were collected on a Thermo Finnigan (San Jose, CA, USA) LCQTM Advantage MAX quadrupole ion trap instrument. Absorption spectra were recorded at room temperature using a Perkin Elmer model Lambda 25 UV/Vis spectrometer. The emission spectra were recorded on a Perkin-Elmer LS45 fluorescence spectrometer. Elemental analysis for carbon, nitrogen and hydrogen was carried out by using a Vario micro cube elemental analyzer (ELEMENTAR) in laboratory center of Seoul National University of Science and Technology, Korea.

2.2. Synthesis of sensor 1

The sensor **1** was prepared by the reaction of 9-fluorenylmethyl carbazate (0.25 g, 1.0 mmol) and salicylaldehyde (161.4 μL, 1.5 mmol) in ethanol. Two drops of HCl were added into the reaction solution and it was stirred for 1 day at room temperature. A white precipitate was filtered, washed several times with ethanol and diethyl ether, and dried in vacuum. Yield: 0.32 g (88%). The ^{1}H NMR spectra (Fig. S1) were recorded in CD_3CN, and the descriptions of the signals include: s = singlet, d = doublet, t = triplet and m = multiplet (400 MHz, 25 °C): δ = 11.10 (s, 1H), 9.42 (s, 1H), 8.12 (s, 1H), 7.80 (d, 2H, *J* = 7.6 Hz), 7.70 (d, 2H, *J* = 7.6 Hz), 7.46 (t, 2H, *J* = 7.2 Hz), 7.38 (t, 2H, *J* = 7.2 Hz), 7.32 (t, 2H, *J* = 6.4 Hz), 6.95 (t, 2H, *J* = 7.6 Hz), 4.54 (d, 2H, *J* = 6.8 Hz), 4.34 (t, 1H, *J* = 6.4 Hz); ^{13}C NMR (100 MHz, CD_3CN, 25 °C, Fig. S2): δ = 158.02, 155.31, 146.11, 142.29, 140.30, 137.41, 127.83, 126.28, 122.11, 120.54, 118.58, 67.96, 47.08. Anal. calcd for $C_{22}H_{18}N_2O_3$: C, 73.73; H, 5.06; N, 7.82%. Found: C, 73.92.; H, 5.15.; N, 7.76.%. LRMS (ESI): *m*/*z* calcd. for $C_{22}H_{18}N_2O_3 + H^+$: 360.14; found 360.10.

2.3. Fluorescence titrations

For Ga^{3+}, a stock solution (5 mM) of the sensor **1** was prepared in dimethylformamide (DMF) and 6 μL of the sensor **1** (5 mM) was diluted to 2.994 mL acetonitrile (CH_3CN) to make final concentration of 10 μM. Then, 0.15–4.80 μL of the stock solution of Ga



Scheme 1. Synthesis of **1**.

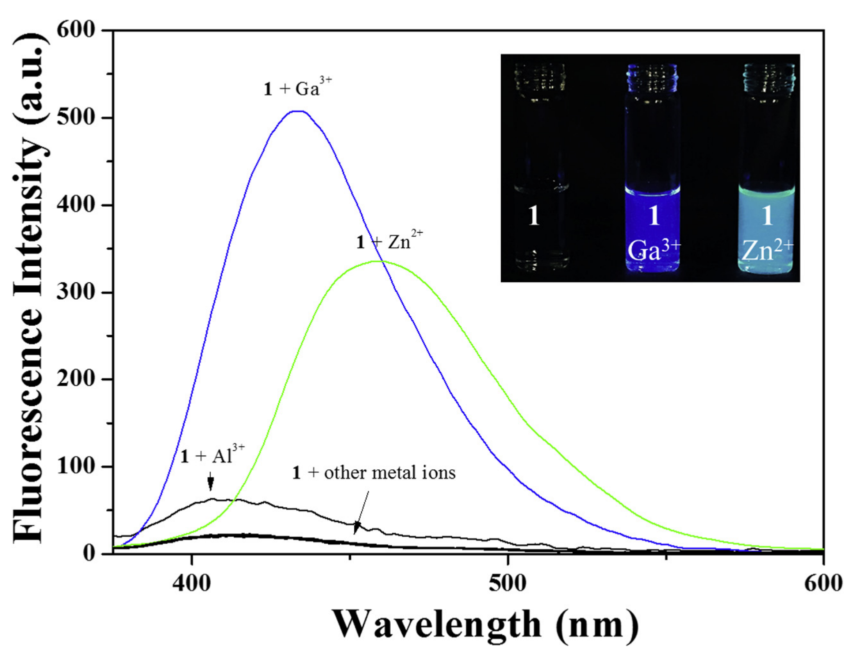


Fig. 1. Fluorescence spectral changes of **1** (10 μM) in the presence of 3.6 equiv of different metal ions in CH_3CN solution. Inset: Picture of the fluorescence corresponding to **1**, **1**-Ga^{3+} and **1**-Zn^{2+} (excitation: 300 nm).