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An 8-aminoquinoline derivative as a molecular platform for fluorescent sensors for Zn(II) and Cd(II) ions

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ABSTRACT

The amide derivatives of 8-aminoquinoline with two types of amino acid pendants, i.e. glycine and β-alanine, are evaluated for fluorescence sensing of various metal ions. In Tris-HCl aqueous buffer solution, the derivative containing glycine exhibits selective fluorescence enhancement with Zn^{2+}. The fluorescence turn-on signal at a longer wavelength is a result of the binding between *N*-8-aminoquinolinylglycinamide and Zn^{2+} which is promoted by the deprotonation of the amide proton. However, both Zn^{2+} and Cd^{2+} induce the turn-on signal in ethanol solution. X-ray crystallography of single crystals of both Zn^{2+} and Cd^{2+} complexes formed in ethanol reveals 1-D coordination polymer structures in which the metal ions are tethered with N and O of the amide groups. Simultaneous detection of Zn^{2+} and Cd^{2+} are possible by using paper chromatographic separation and the ligand as a visualizing agent. The fluorescence imaging of either Zn^{2+} or Cd^{2+} in plant tissue is demonstrated. The conjugation of the ligand with dimethylaminophenylacetylene effectively tunes the emission color of the ligand while retaining the sensing selectivity. Therefore, *N*-8-aminoquinolinylglycinamide is a simple yet effective binding probe for Zn^{2+} and Cd^{2+} with excellent fluorescence signal transduction.

1. Introduction

Fluorescent probes are highly useful for in vivo and in vitro analyses of biologically important species including metal ions because of their high sensitivity, possibility for imaging and instrumentless detection [1–4]. Zinc ion (Zn^{2+}) is an essential mineral that affects cell division and differentiation vital for the growth and development of all life forms [5]. Therefore, Zn^{2+} has recently been introduced in many types of dietary supplementary and energy drinks. Fluorescent probes for Zn^{2+} based on w such as quinolone [6], naphthalimide [7], bipyridyl [8], BODIPY [9], fluorescein [10], rhodamine [11], pyrene [12], benzoxazole [13], coumarin [14], and other chromophores [15–24] have been reported. Turn-on fluorescent sensors for Zn^{2+} are particularly interesting for biological imaging [25]. Quinolines are one of the most interesting classes of compounds for such applications as they have low initial fluorescence but they can form highly fluorescent complexes with various metal ions. The prime example is tris-(8-hydroxy quinoline) aluminium (AlQ3) which has been used as a standard green emissive material in studies of organic light-emitting diodes (OLEDs) [26–28].

Fluorescent complexes of Zn^{2+} with 8-aminoquinoline derivatives have also been reported [29–38]. Interestingly, these derivatives contain various groups which are not clear of their roles in binding and selectivity of the probes. Therefore, we decided to investigate the position of N atom of the amide derivatives of 8-aminoquinoline having amino acid pendants i.e. glycine (1) and β-alanine (2) to determine its effect on metal ion sensing selectivity.

2. Experimental section

2.1. Materials and synthesis

8-Aminoquinoline, Boc-glycine, Boc-β-alanine, triethylamine and 4-dimethylaminopyridine (DMAP) were purchased from Merck® (Germany). N-(3-Dimethylaminopropyl)-N-ethylcarbo diimide hydrochloride (EDC·HCl), di-tert-butyl dicarbonate (Boc_2O), ammonium chloride, trifluoroacetic acid and sodium bicarbonate were purchased from Sigma Aldrich (USA). Glycylglycine was purchased from TCI Tokyo Chemical Industry (Japan). In anhydrous reactions, solvent such as dichloromethane was dried before use. All column chromatography

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was run on Merck silica gel 60 (70–230 mesh). Thin layer chromatography (TLC) was performed on Merck F245 silica gel plates. Visualization was performed with a 254 nm ultraviolet lamp. Solvents used for extraction and chromatography such as dichloromethane, hexane and ethyl acetate were commercial grade and distilled before use. Milli-Q water was used in all aqueous experiments unless specified otherwise. The detailed synthesis procedures and characterization data are in the supporting information page S3.

2.2. Measurement of photophysical properties

The UV–vis absorption spectra were acquired from the aqueous solution samples in a 1 cm quartz cell and recorded in the range of 250–600 nm at room temperature. Each solution sample was prepared from a stock solution of the compound in methanol and diluted to the desired concentration with aqueous Tris-HCl buffer pH 7.4 to the desired concentration that the final solution contained less than methanol (1%, v/v). The extinction coefficient (ε) was determined from the solutions with at least 5 different concentrations diluted from 2 stock solutions independently prepared. The fluorescence spectrum was obtained from the solution in a 1.4 mL fluorescence quartz cell with 1 cm optical path length at ambient temperature using an excitation wavelength at the λ_{max} of each fluorophore and recorded in the range of 370–700 nm. The fluorescence quantum yield was determined from the slope of the plot between the integral of emission intensity of the fluorophore solutions at 7 concentrations against the absorbance, always kept below 0.1, in relation to that of quinine sulfate (Φ_F = 0.54) in 0.1 M H_2SO_4 [39,40].

2.3. Fluorescence sensing study

The 10 mM stock solutions of the cation tested were prepared by dissolving their salts LiCl, NaOAc, KCl, $Mg(NO_3)_2$, $Ca(OAc)_2$, $Ba(NO_3)_2$, $Al(NO_3)_3$, $Cr(NO_3)_3$, $FeSO_4$, $Fe(NO_3)_3$, $Co(NO_3)_2$, $Ni(NO_3)_2$, $Cu(OAc)_2$, $Zn(OAc)_2$, $AgNO_3$, $Cd(OAc)_2$, $HgCl_2$ and $Pb(OAc)_2$ in Milli-Q water. The cation stock solution (10 μL) was added to the fluorophore stock solution in methanol (1 mM, 10 μL). The volume of the mixture was adjusted by Tris buffer solution or ethanol to 1 mL to afford the final concentration of 10 μM for the fluorophore and 100 μM for the cation. All final aqueous solutions used for fluorescence measurement contain 1% methanol. The emission spectra were recorded starting from 10 nm longer than the excitation wavelength to 700 nm.

2.4. NMR titration

A solution of **1** (10.0 mg, 0.05 mmol) in $(CD_3)_2SO$ (0.4 mL) and a solution of $Zn(OAc)_2$ (0.1 mmol) in $(CD_3)_2SO$ (0.2 mL) were prepared. The calculated volumes of $Zn(OAc)_2$ solution at designated equivalents were added titrimetrically to the solution of **1**. After thorough mixing, ^{1}H NMR spectra were recorded.

2.5. Synthesis of complexes

A ethanol solution (1 mL) of $Zn(NO_3)_2{\cdot}6H_2O$ (13.4 mg, 0.045 mmol) was added dropwise to a solution of 1 (10 mg, 0.050 mmol) in ethanol (1 mL) with stirring to give a light yellow solution and left in dark to stand at room temperature for slow evaporation. Pale yellow block shaped single crystals of **Zn-1** were formed in about five days.

Colorless block shaped crystals of **Cd-1** suitable for X-ray structure determination were prepared by following the procedure described above for **Zn-1** and $Cd(NO_3)_2{\cdot}4H_2O$ (13.8 mg, 0.045 mmol) was used instead of $Zn(NO_3)_2{\cdot}6H_2O$.

2.6. X-ray structure determination

Single crystal X-ray diffraction data for both complexes were recorded using a Bruker D8 QUEST CMOS diffractometer with graphite-monochromatic Mo Kα radiation (λ = 0.71073 Å) at 296(2) K. Data reductions and absorption corrections were performed with the SAINT and SADABS software packages [41], respectively. Using Olex2 [42], the structure was solved with the ShelXT [43] structure solution program using intrinsic phasing and refined with the ShelXL [44] refinement package using least squares minimisation. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms of the organic molecules were generated geometrically. Crystallographic figures were prepared using Olex2 [42] and ORTEP-3 for Windows [45]. A summary of crystallographic data and structure refinements, selected bond lengths and bond angles, and hydrogen bonds geometry for **Zn-1** and **Cd-1** complexes are given in Tables S2–S4, respectively, in the Supporting Information. Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center. CCDC 1542601 (**Zn-1**) and 1542602 (**Cd-1**), contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

2.7. Fluorescence imaging of plant tissues

A sprout (5 mm) closest to the root of 4 days old Chinese cabbage (Brassica rapa.) seedling was cut longitudinal-section into two half. The samples were incubated with $Zn(OAc)_2$ aqueous solution (100 μM) for 40 min, and then placed in ethanol for 40 min to remove chlorophyll. For comparison, one sample was left in distilled water and the other sample was left in fresh ethanol for 10 min. These two samples were placed side by side (5 mm apart) on a microscope slide (25 × 75 mm^2) and separately closed with two cover slides (22 × 22 mm^2). The prepared sample slide was mounted on a confocal laser scanning fluorescence microscope (Nikon, Eclipse-C1 Ti series). The fluorescence image was acquired by using the excitation and detection wavelengths of 488 and 525 nm, respectively. A solution of 1 in methanol (100 μM, 10 μL) was introduced into each sample at the edge of the cover slide and the fluorescence image was acquired again. For detecting of Cd^{2+}, the similar procedure was performed but the samples were incubated in Cd $(OAc)_2$ aqueous solution (100 μM instead of the $Zn(OAc))_2$ solution.

2.8. Naked eye detection of Zn^{2+} and Cd^{2+} on paper-based sensors

A microwell plate style array of circular hydrophilic detection area with 3.0 mm diameter and 1.0 cm center-to-center distance (Fig. 7a) was created on a filter paper sheet (Whatman No. 1, 21 × 29.7 cm^2) by a wax-printing technique (Xerox Phaser 8860) and a common graphic software to create hydrophobic pattern of black wax ink. The printing pattern was heated at 200 °C for 120 s on a hot plate to define the hydrophobic barriers and hydrophilic detection area [46]. For selectivity test, various metal ions (0.1 mM, 1.0 μL) were pipetted into the detection circles. After air drying, the solution of 1 in methanol (1.0 mM, 1.0 μL) was added on top of the metal ion area and allowed for air dry. The fluorescence images of the samples were photographically recorded by a digital camera under black light (365 nm) illumination.

The simultaneous detection of Zn^{2+} and Cd^{2+}, was performed with chromatographic separation on filter paper strip (Whatman No. 1, 9.5 × 3.0 cm^2) with multi-channelled hydrophilic/hydrophobic pattern (Fig. 7b) created on a filter paper by the wax-printing technique. Each hydrophilic channel was 1.0 mm wide and 9.5 cm long having a circular reservoir (3.0 mm diameter) at 2.0 cm from the bottom of the filter paper. The channels were 5.0 mm separated from each other with the hydrophobic wax barrier generated by the heating technique described above. Each of $Zn(OAc)_2$ and $Cd(OAc)_2$ aqueous solution (1 mM, 1 μL) was separately pipetted onto the surface of the reservoir area. For the third spot, both solutions were spotted on top of each other. Then, the strip was placed in a closed chamber containing CH_3NH_2 4% (v/v) in Milli-Q water as the mobile phase. After the development and an air