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Exploiting the deprotonation mechanism for the design of ratiometric and colorimetric Zn²⁺ fluorescent chemosensor with a large red-shift in emission

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Abstract—The design, synthesis, and photophysical evaluation of a new naphthalimide-based fluorescent chemosensor, *N*-butyl-4-[di-(2-picolyl)amino]-5-(2-picolyl)amino-1,8-naphthalimide (**1**), were described for the detection of Zn²⁺ in aqueous acetonitrile solution at pH 7.0. Probe **1** showed absorption at 451 nm and a strong fluorescence emission at 537 nm ($\Phi_F=0.33$). The capture of Zn²⁺ by the receptor resulted in the deprotonation of the secondary amine conjugated to 1,8-naphthalimide so that the electron-donating ability of the N atom would be greatly enhanced; thus probe **1** showed a 56 nm red-shift in absorption (507 nm) and fluorescence spectra (593 nm, $\Phi_F=0.14$), respectively, from which one could sense Zn²⁺ ratiometrically and colorimetrically. The deprotonated complex, [(1-H)/Zn]⁺, was calculated at *m/z* 619.1800 and measured at *m/z* 618.9890. In contrast to these results, the emission of **1** was thoroughly quenched by Cu²⁺, Co²⁺, and Ni²⁺. The addition of other metal ions such as Li⁺, Na⁺, K⁺, Mg²⁺, Ca²⁺, Fe³⁺, Mn²⁺, Al³⁺, Cd²⁺, Hg²⁺, Ag⁺, and Pb²⁺ produced a nominal change in the optical properties of **1** due to their low affinity to probe **1**. This means that probe **1** has a very high fluorescent imaging selectivity to Zn²⁺ among metal ions.

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1. Introduction

Chemosensors that convert molecular recognition into highly sensitive and easily detected signals have been actively investigated in recent years. A ratiometric and colorimetric fluorescent probes combine the sensitivity of fluorescence with the convenience and aesthetic appeal of a colorimetric assay.¹ In particular, ratiometric measurements have the important features that they permit signal rationing, and thus increase the dynamic range and provide built-in correction for environmental effects.²

The design of fluorescent probes for Zn²⁺ is actively investigated,³ as this metal ion is a critical trace element, playing significant roles in biological processes such as regulators of enzymes,⁴ structural cofactors in metalloproteins, neural signal transmission,⁵ and gene expression.⁶ It is also known that a disorder of zinc metabolism is closely associated with many severe neurological diseases such as Alzheimer's disease (AD), amyotrophic lateral sclerosis (ALS), Guam

ALS-Parkinsonism dementia, Parkinson's disease, hypoxia-ischemia, and epilepsy.⁷ However, up to now, most of the Zn²⁺ fluorescent probes are intensity-responsive based on PET quenching mechanism.⁸ Only a few ratiometric and colorimetric fluorescent probes for Zn²⁺ have been found in the literature. And still many efforts for a Zn²⁺ fluorescent probe should be made among the issues, such as easy synthesis, visible light excitation, large red-shift in emission for Zn²⁺ sensing, and no pH interference in the physiological pH range.

To carry out ratiometric measurements of Zn²⁺ and get quantitative readouts, various mechanisms, which can cause a large shift in emission or excitation spectra have been introduced into Zn²⁺ sensors such as excimer,⁹ FRET,¹⁰ ICT,¹¹ ES IPT,¹² two fluorophore approach,¹³ conformational restriction,¹⁴ time-resolved fluorescence techniques,¹⁵ and self-assembly strategy.¹⁶ Herein, we represent another new mechanism to design a ratiometric fluorescent probe for Zn²⁺ based on deprotonation mechanism.

The secondary amines conjugated to 1,8-naphthalimide could be deprotonated by Cu(II)^{1c} or F⁻,¹⁷ and as a result, large red shifts in both absorption and fluorescence spectra were obtained, from which one could sense Cu²⁺ or F⁻ colorimetrically and ratiometrically. In addition, the

Keywords: Ratiometric; Zn²⁺ Fluorescent chemosensor; Naphthalimide; Deprotonation.

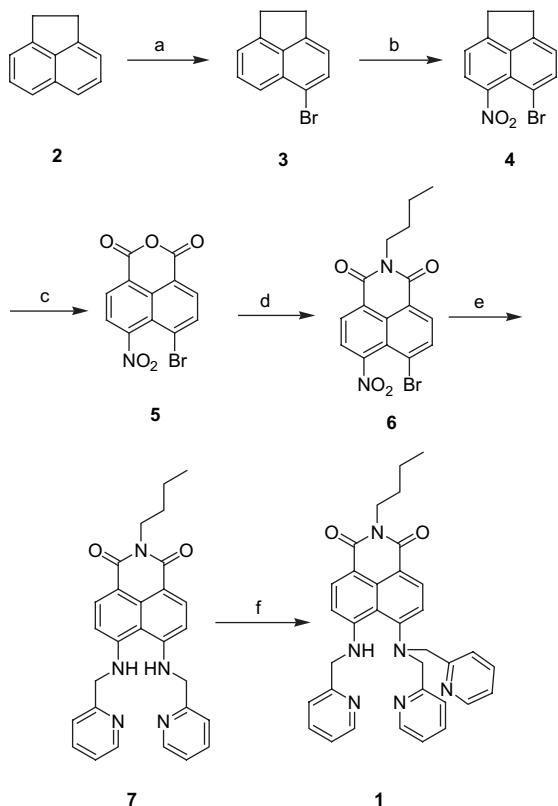
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deprotonation of NH in amide or thiourea was believed to be the basis of F⁻ sensing in recent research.¹⁸ Based on the same deprotonation mechanism, which should not be a privilege confined to Cu²⁺ or F⁻, we introduced the well-known Zn²⁺ receptor tris(2-pyridylmethyl)-amine (TPA) into 1,8-naphthalimide fluorophore and easily obtained fluorescent probe **1**, *N*-butyl-4-[di-(2-picolyl)amino]-5-(2-picolyl)amino-1,8-naphthalimide. The capture of Zn²⁺ by the receptor resulted in the deprotonation of the secondary amine of **1**, which caused the ratiometric UV and fluorescence changes.

2. Results and discussions

2.1. Synthesis

The synthesis of **1** is shown in Scheme 1. The intermediate, compound **5**, was synthesized from acenaphthene following a literature procedure.¹⁹ Compound **6** was prepared in 40.2% yield by the condensation of **5** with butylamine and was subsequently converted into compound **7**, which we have reported as a ratiometric Cu²⁺ fluorescent sensor,^{1b} through reaction with 2-aminomethylpyridine. Probe **1** was easily synthesized by conjugating picolyl chloride and compound **7** in 56.5% yield.



Scheme 1. Synthesis of **1**. (a) NBS, DMF, room temperature, 82.4%; (b) fuming HNO₃, AcOH, 10–15 °C, 53.1%; (c) Na₂Cr₂O₇·2H₂O, AcOH, reflux, 51.7%; (d) *n*-C₄H₉NH₂, C₂H₅OH, reflux, 40.2%; (e) 2-aminomethylpyridine, CH₃OC₂H₄OH, CH₃CN, reflux, 85%; (f) picolyl chloride, CH₃CN, K₂CO₃, N₂, reflux, 56.5%.

2.2. ESIMS analysis

Probe **1** showed absorption at 451 nm and a strong fluorescence emission at 537 nm in acetonitrile–water (80:20)

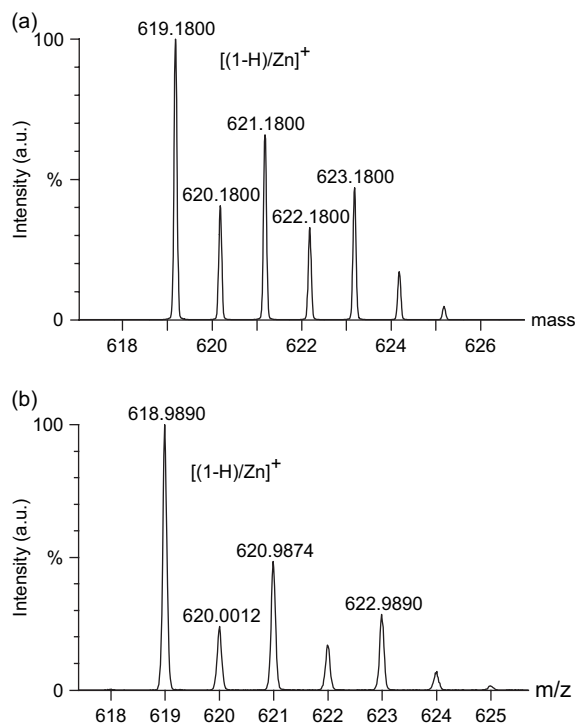


Figure 1. Electrospray mass spectrum of **1**-Zn sample in acetonitrile–water (80:20) solution at pH 7.0 maintained with HEPES buffer (50 mM). [**1**]=10 μM, [Zn²⁺]=30 μM. (a) The calculated pattern of the most abundant complex [(1-H)/Zn]⁺, C₃₄H₃₁N₆O₂Zn, *m/z*=619.1800. (b) The measured pattern of the most abundant complex [(1-H)/Zn]⁺, C₃₄H₃₁N₆O₂Zn, *m/z*=618.9890.

solution. The capture of Zn²⁺ by the receptor resulted in the deprotonation of the secondary amine so that the electron-donating ability of the N atom conjugated to the naphthalene ring would be greatly enhanced; thus probe **1** showed large red shifts in absorption and fluorescence spectra. The ESIMS analysis revealed single-charged complex [(1-H)/Zn]⁺ that is formed due to the interaction of **1** with 1 equiv of Zn²⁺ (Fig. 1). The [(1-H)/Zn]⁺ complex was calculated at *m/z* 619.1800 and measured at *m/z* 618.9890. This indicated the formation of a **1**/Zn²⁺ adduct of 1:1 stoichiometry.

2.3. The effect of pH

The influence of pH on the fluorescence of **1** was first determined by fluorescence titration in acetonitrile–water (80:20) solution (Fig. 2). The fluorescence of **1** at 537 nm remained unaffected between pH 13 and 4.21, and then gradually decreased from pH 4.21 to 1.77; below pH 1.77, no change in fluorescence was observed, leading to a sigmoid curve. Its pK_a value was 3.0. The fluorescence quenching was most likely caused by the photo-induced electron transfer (PET) from the fluorophore to protonated pyridine.²⁰ de Silva had found the similar phenomenon in the design of an ‘off-on-off’ fluorescent PET sensor.²¹ The influence of pH on the deprotonation of **1** induced by Zn²⁺ was then investigated by means of the absorption and fluorescence measurements for a solution of 1 equiv of **1** and 2 equiv of Zn²⁺. When 2 equiv of Zn²⁺ was added to an acidic solution of **1** (pH=2), the absorbance at 451 nm steadily decreased,

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