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A novel dual channel responsive zinc(II) probe

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ABSTRACT

A novel compound, **1**, which is based on a 1,10-phenanthroline scaffold with cofacial BODIPY units, is synthesized via a three-step reaction sequence. It is noteworthy that **1** can be utilized for both visual and turn-off fluorometric detection of Zn^{2+} ions in aqueous acetonitrile solution. The fluorescence response is based on cation-mediated oxidative photoinduced electron transfer (PET). The digital action of a two-input NOR logic gate is also demonstrated.

In supramolecular chemistry, considerable efforts have been devoted to the design and synthesis of functional organic materials, which allow selective and sensitive detection of target metal ions, since metal ions play deleterious and/or essential roles in biological and environmental processes.[1] Among these ions, zinc is one of the most abundant transition metals in many organisms, and it is essential to life by being the only metal which appears in nearly all enzymes. Zinc plays important roles in many biological processes, including regulation of apoptosis, signal transmission, enzyme function, and gene expression.[2a] It is also reported that zinc is associated in a number of pathological processes, such as diabetes[2b] and Alzheimer's disease.[2c] Therefore, designing novel molecular probes which can selectively recognize zinc among other metal ions is a challenging task. It should also be noted that the electronic configuration ($3d^{10}$ $4s^0$) of zinc(II) makes it spectroscopically silent toward many optical detection methods. Fortunately, however, fluorescence spectroscopy offers a highly efficient method for the detection of zinc(II) ions. Thus, many examples of fluorescent zinc(II) sensors have been reported to date in the literature.[3]

Photoinduced electron transfer (PET) is one of the most prominent phenomena in the design of fluorescent molecular probes.[4,5] In principle, PET might occur in two different directions.[5] In the first case, PET takes place from a donor unit to the excited-state fluorophore, which is termed reductive PET. On the other hand, PET might also occur from an excited-state fluorophore to an acceptor unit, which also acts as a receptor. The second case is known as oxidative PET. Both of these processes are accompanied by quenching of the fluorophore emission. Although oxidative PET is well-known,[5] it has been hardly used in chemosensor applications. It is generally observed in bipyridyl fluorophores where the conjugation of bipyridyl and fluorophore units is interrupted by either saturated carbons or by the orthogonal geometry of those units.[6] The fluorescence of the receptor-fluorophore is quenched upon binding of the guest.

Boradiazaindacenes (BODIPYs) are an important class of fluorescent dyes due to their unique photophysical characteristics, which include high molar absorption coefficients, high fluorescence quantum yields, good chemical, thermal, and photostability, and narrow emission band widths. An additional advantage of this class of compounds is that their visible excitation and emission can be tuned by structural modification of the pyrrole core through its rich chemistry. Consequently, these features have made BODIPYs excellent candidates for biological labeling, artificial light harvesters, fluorescent switches, and chemosensors.[7] Additionally, polymeric BODIPYs,[8,9] have recently been added to the repertoire of macromolecular systems, which are now finding an increasing number of applications in both materials and optical imaging fields.

We have previously reported that cation-mediated oxidative PET can be modulated in a very rigid arrangement.[10] We designed a novel compound which was based on a 1,10-phenanthroline scaffold with cofacial BODIPY units attached orthogonally as the

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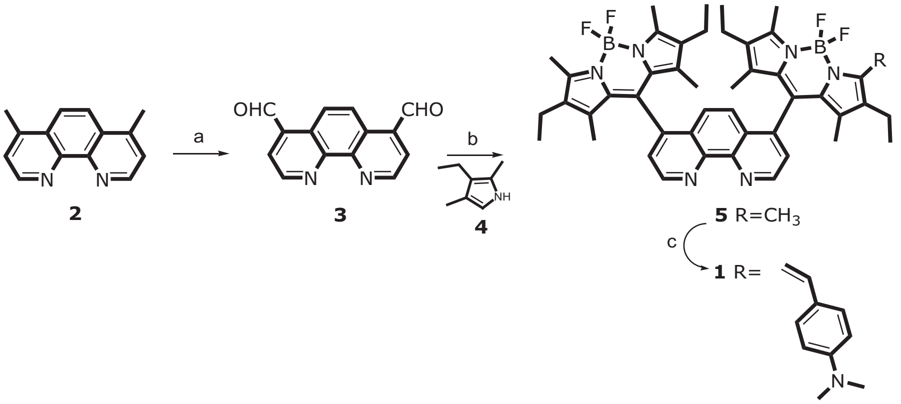

Scheme 1. Reaction conditions: (a) SeO_2, 1,4-dioxane-water (4%, v/v), 100 °C, 60%; (b) TFA, CH_2Cl_2, chloranil, $BF_3 \cdot OEt_2$, 20%; (c) 4-dimethylaminobenzaldehyde (**6**), HOAc, piperidine, benzene, 80 °C, 51%.

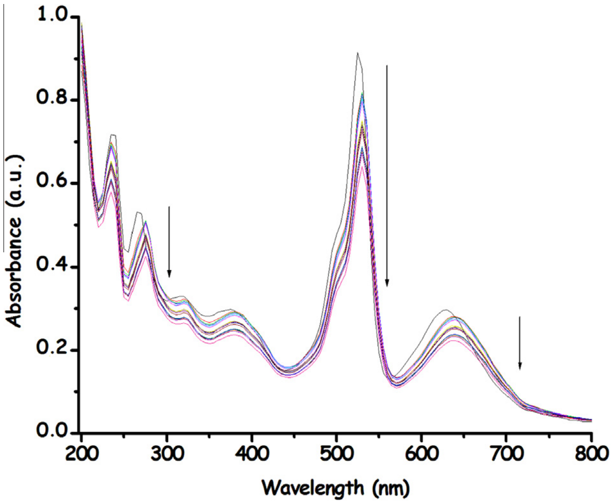

Figure 1. UV–vis absorption spectra of **1** (5×10^{-5} M) in 10% aqueous CH_3CN (v/v) solution upon addition of Zn^{2+} ions (0.0–5×10^{-3} M).

receptor and fluorophore units, respectively. This design afforded a turn-off fluorescent Cd(II) probe. We wondered if a simple modification could allow us to tailor the selectivity of this probe from Cd(II) to Zn(II) (vide infra). It is important to note that these analytes, Cd(II) and Zn(II), are in the same group of the periodic table and they show very similar properties. Removing the possible disruptive effects of other metal ions such as Cd(II), Cu(II), and Ni(II) was also critical in the design.

In this Letter, we report our research concerning the design, synthesis, and properties of novel material **1** based on 1,10-phenanthroline and BODIPY units. It is noteworthy that **1** can be utilized as a selective dual channel (colorimetric and fluorometric) responsive Zn^{2+} probe in aqueous solution. The fluorescence response of **1** is based on cation-mediated oxidative PET. Importantly, the modulation of BODIPY emission in a highly rigid arrangement by cation-mediated oxidative PET in aqueous solution was achieved to afford a highly selective fluorescent Zn^{2+} probe. Interestingly, the digital action of **1** as a two-input NOR[6a,b] logic gate was also illustrated.

The synthesis of the target compound was carried out via a three-step sequence. Initially, 4,7-dimethyl-1,10-phenanthroline (**2**) was treated with SeO_2 in refluxing 1,4-dioxane-water to afford bisaldehyde **3** in 60% yield according to a known procedure (Scheme 1).[11] Next, condensation of **3** with 2,4-dimethyl-3-ethylpyrrole (**4**) in the presence of a catalytic amount of trifluoroacetic acid (TFA) resulted in the formation of a dipyrromethane, which was then oxidized by chloranil to generate the corresponding dipyrromethene. Complexation with $BF_3 \cdot OEt_2$ provided **5**, albeit in 20% yield (Scheme 1). Finally, Knoevenagel-type condensation of **5** with 4-dimethylaminobenzaldehyde (**6**) afforded the target compound. Compound **1** was initially characterized on the basis of ^1H and ^{13}C NMR spectroscopy and elemental and MALDI-TOF analysis, which firmly established the structure (see Supporting information, Figs. S4–S6).

The absorption profile of **1** was examined in solution. The UV–vis spectrum of **1** in 10% aqueous CH_3CN (v/v) solution was characterized by absorption bands centered at 234, 264, 320, 374, 524, and 629 nm with extinction coefficients (ε) of 177401, 125588,

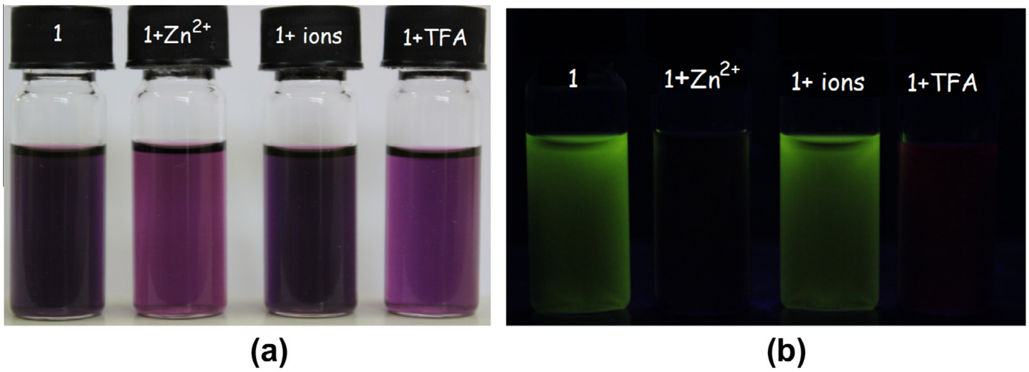

Figure 2. (a) Chromogenic and (b) fluorogenic responses of **1** (5×10^{-5} M) to Zn^{2+} ions and TFA (0.0–5×10^{-3} M) in 10% aqueous CH_3CN (v/v) solution under room light and UV illumination (365 nm), respectively.

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