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Short communication

Highly selective response of bipyridyl-incorporated acetyelene dye for zinc acetate

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ABSTRACT

In this paper, we prepared bpy-modified acetylene dye **2** that contains 2,2'-bipyridine moiety in the center with symmetrically substituted flexible derivatives at both ends. Upon exposure toward various metal salts, **2** revealed a highly selective optical response to Zn^{2+} with AcO^{-} as a counteranion, which is evidenced by large red shift and significant enhancement in emission intensity. Such a peculiar response to single zinc compound, as far as we are aware, has not been reported elsewhere. Compound **2** will find important usefulness in chemo-sensor application due to its highly selective binding to zinc acetate.

1. Introduction

The detection and identification of metal cations and organic/inorganic anions are important in biology, medicine, environmental science, and food science [1–3]. 2,2'-Bipyridine (bpy hereafter) has been incorporated into various chromophores, in which the formation of metal–bpy complexes drastically alters their electronic structures and consequently, the optical properties [4–6]. The widespread usage of bpy building block stems from its facile preparation and efficient capability to bind a wide array of d- and f-block metal elements.

Zinc ion (Zn^{2+}) is the second most abundant transition metal ion in the human body after iron and now recognized as an essential factor in some pathological processes, such as Alzheimer's disease, epilepsy, ischemic stroke, and infantile diarrhea [7,8]. Since Zn^{2+} is spectroscopically silent due to its d-electron configuration, fluorescent chemosensors for the detection of Zn^{2+} have been a focus of intensive researches. Recent articles have focused on various aspects of zinc chemosensors [9–11]. Chromophores incorporating bpy are expected to exhibit well-established ionochromic responses to transition metals.

Herein we present the preparation of a bpy-modified acetylene dye **2**, which can be applied for colorimetric and fluorescent detection of zinc ion with acetate as an anion.

2. Experimental

2.1. Materials

All chemicals were obtained from Aldrich (Sigma-Aldrich Korea, Korea) and used without any purification. The starting compound, 4,4'-bisiodo-2,2'-bipyridine, was prepared by following a previous report in literature [12].

2.2. Syntheses

2.2.1. 4,4-'Diethynyl-2,2'-bipyridine 1

To a 100-mL, round-bottomed flask equipped with a septum and a Teflon-coated magnetic stirring-bar, 4,4'-bisiodo-2,2'-bipyridine (0.273 g 0.873 mmol) in nitrogen-degassed THF (3 ml), (trimethylsilyl)acetylene (0.29 g, 0.42 mL, d 0.695, 2.96 mmol), $PdCl_2(PPh_3)_2$ (0.019 g, 0.026 mmol, 3 mol%), CuI (0.017 g, 0.087 mmol, 10 mol%), and diisopropylamine (3 mL) were successively added. The solution was stirred overnight at room temperature. After the completion of the reaction, the mixture was quenched with water (100 mL) and extracted with CH_2Cl_2 several times. The extracts were combined and concentrated under reduced pressure to yield a crude product.

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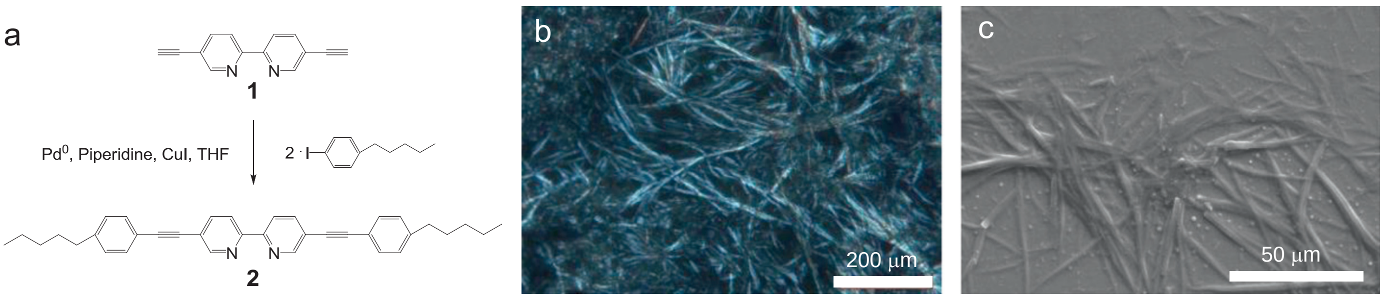

Fig. 1. (a) Synthesis of bipyridyl-incorporated acetyelene dye **2**, (b) POM and (c) SEM images of air-dried thin film made of **2** in CHCl$_3$.

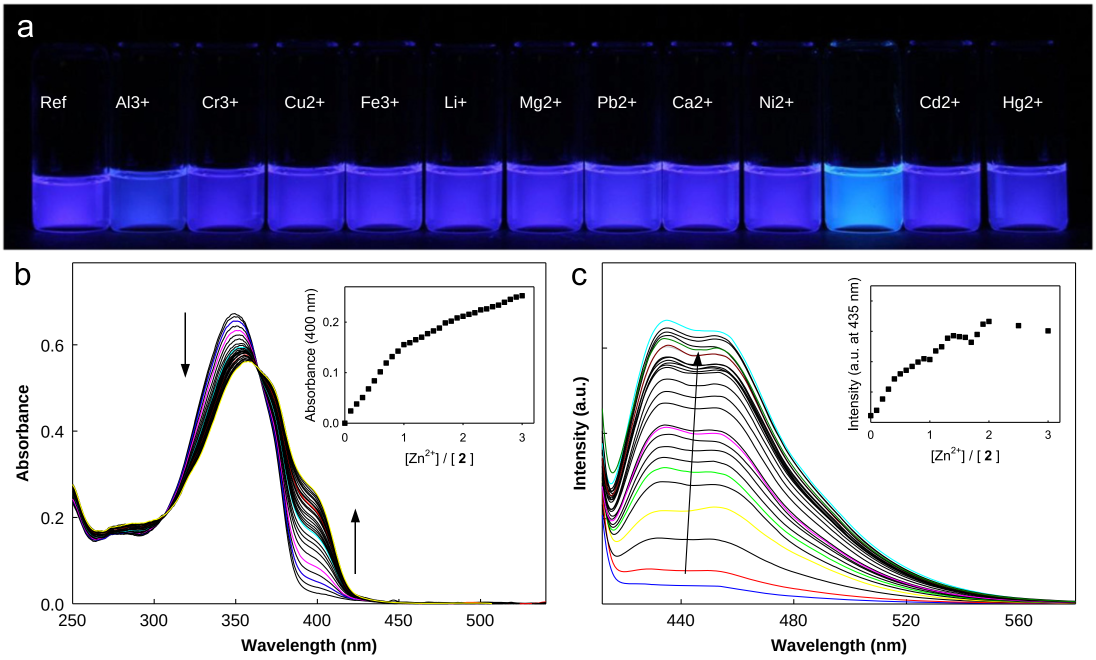

Fig. 2. (a) Photographic image taken under UV light ($\lambda_{excitation}$ = 365 nm) after adding equimolar metal ions to the solutions of **2** (1.0×10^{-4} mol/L) in CHCl$_3$. (b) UV titration curves of **2** (1.0×10^{-7} mol/L) with different amounts of zinc(II) acetate, Zn(AcO)$_2$; the arrows indicate the direction of the change as Zn(AcO)$_2$ was added. The inset indicates the absorbance intensities at 400 nm and (c) PL titration curves of **2** in the presence of different amounts of Zn(AcO)$_2$. All measurements were made with excitation at 400 nm. The inset indicates the emission intensities at 435 nm.

To the stirred solution of trimethylsilyl-protected compound (0.212 g, 0.61 mmol) in CH$_3$OH (20 mL), KF (0.076 g, 1.28 mmol) was added as a solid. After complete consumption, the reaction mixture was concentrated by rotary evaporation to yield a crude residue which was purified by flash chromatography with CH$_2$Cl$_2$/MeOH as an eluent on silica gel. 4,4'-Diethynyl-2,2'-bipyridine **1** was further purified by recrystallization in methanol. ^{1}H NMR (600 MHz, CDCl$_3$): 8.9 (s, 2H), 8.3 (d, 2H), 8.1 (d, 2H), 3.1 (s, 2H); ^{13}C NMR (Bruker Avance II 900 Spectrometer, Korea Basic Science Institute CDCl$_3$): 157.1, 153.0, 141.0, 122.0, and 114.0; m/z (negative MALDI-TOF) 203.1 (M$^+$).

2.2.2. Bipyridyl-incorporated acetylene dye 2

4,4'-Diethynyl-2,2'-bipyridine **1** (40.0 mg, 0.196 mmol, FW 204.23) and 1-Iodo-4-n-pentylbenzene (118.2 mg, 0.431 mmol, FW 274.14) were dissolved in toluene (2 mL) and degassed with nitrogen five times. N,N-diisopropylethylamine (2 mL), CuI (9.5 mg, 0.39 mmol, 6 mol%) and PdCl$_2$(PPh$_3$)$_2$ (17 mg, 0.025 mmol, 3 mol%) were successively added and stirred for 24 h at elevated temperature under nitrogen atmosphere. The crude reaction mixture was poured into a 1 L flask containing 5% aqueous NH$_4$OH (250 mL) and hexane (250 mL). The mixture was stirred vigorously to obtain a bright yellow solid. After filteration, the solid was dissolved in a minimum volume of dichloromethane and recrystallized using 250 mL of rapidly stirring hexane to yield analytically pure sample of **2**.

^{1}H NMR (600 MHz, CDCl$_3$): 8.8 (s, 2H), 8.4 (d, 2H), 7.9 (d, 2H), 7.5 (d, 2H), 7.2 (d, 2H), 2.5 (t, 2H), 1.6 (m, 2H), 1.3 (m, 4H), and 0.9 (m, 3H); ^{13}C NMR (Bruker Avance II 900 Spectrometer, Korea Basic Science Institute CDCl$_3$): 154.0, 151.7, 144.2, 139.3, 132.1, 131.7, 128.6, 128.4, 120.7, 120.5, 119.7, 94.1, 85.8, 31.5, 30.9, 29.7, 22.5, and 14.0; m/z (negative MALDI-TOF) 496.1 (M$^+$).

2.3. Experimental procedures

The UV absorbance spectra were obtained from Lambda 7 spectrometer (Perkin Elmer) with a cuvette with 1 cm pathlength and chloroform as solvent. The photoluminescence emission spectra were collected from Perkin Elmer LS-45 spectrofluorophotometer using a cuvette having 1 cm pathlength. In case of metal ion titration, 5 min of standing was allowed, before the measurement, to ensure complete mixing.

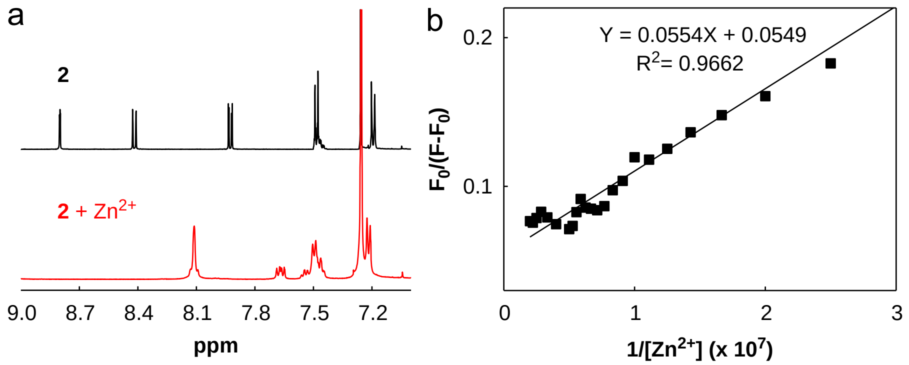

Fig. 3. (a) ^{1}H NMR spectra of **2** before (upper, black) and after (below, red) adding equimolar amount of zinc(II) acetate and (b) the Bensei–Hildebrand plot for **2** with Zn(AcO)$_2$, considering the 1:1 complexation. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

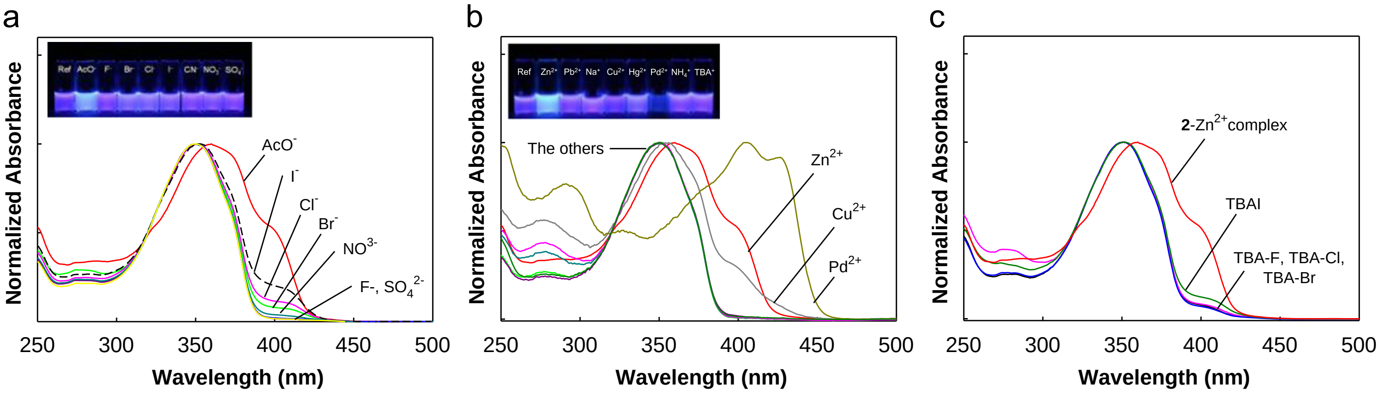

Fig. 4. (a) UV spectra after adding equimolar zinc salts to the solution of **2** (5.0×10^{-7} mol/L) in CHCl$_3$. Legends indicate counter-anions of the zinc salts. (b) UV spectra after adding equimolar acetate salts to the solution of **2** (5.0×10^{-8} mol/L) in CHCl$_3$. Legends indicate metal cations of the salts. The insets in (a) and (b) show photos under UV light after adding the corresponding salts and (c) UV spectra of **2**-Zn^{2+} complex after adding 4 equiv. of tetrabutylammonium salts of F$^-$, Cl$^-$, Br$^-$, and I$^-$.

3. Results and discussion

In an effort to access Zn^{2+}-specific sensor, we prepared bpy-incorporated acetylene dye **2** using a Pd-catalyzed reaction of the Heck-Cassar-Sonogashira-Hagihara-type [13], in which 4,4'-diethynyl-2,2'-bipyridine **1** was reacted with 4-iodo-pentyl benzene (Fig. 1a). The molecular structure of **2** resembles the repeating unit of poly(*p*-phenyleneethynylene)s, which is characterized by high fluorescence quantum yield from the electron-withdrawing effect of the –C≡C– unit ($\lambda_{max}=350$ nm, $\lambda_{em}=410$ nm, $\phi_{350}=0.36$). We found that good solubility of **2** in many common solvents such as CH$_2$Cl$_2$ and CHCl$_3$ may be due to the existence of two symmetrically substituted flexible tails. Its rigid rod character exhibits an anisotropic texture similar to that of liquid crystal when observed under crossed-polarizers. Hence, in POM image, it reveals long and fibrous threads which form randomly arranged networks (Fig. 1b). The surface of air-dried thin film made of **2** was imaged by SEM (Fig. 1c), showing numerous wire-like structures containing the width ranging from several nanometers and the lengths of several hundreds of micrometers.

Dye **2** was exposed to various metal ions, and its fluorescence response was captured under UV illumination. As noted, it exhibits significant color changes exclusively to Zn^{2+} (Fig. 2a). In UV–vis absorption spectra, **2** gives two characteristic absorption bands at 275 nm (n–σ* trasnsition) and 350 nm (π–π* ligand-centered transition). Upon the addition of Zn^{2+} ions to the solution of **2** (1.0×10^{-7} M) in chloroform, the obvious ionochromic effects were observed (Fig. 2b). The binding of Zn^{2+} causes red shift in the absorption spectrum relative to those of the metal-free analog. Absorbance at 400 nm, which is the typical d–π* transition, MLCT (metal to ligand charge transfer) of the **2**–Zn^{2+} complex, gradually increases with a well-defined isosbestic point at 363 nm. The appearance of only one isosbestic point strongly suggests the existence of only one binding state, most likely a bidentate binding structure, i.e., Zn^{2+} chelation with both nitrogen atoms of the bpy group [14,15]. Meanwhile, the absorbance at 400 nm increases with two distinctive slopes corresponding to the ratio of Zn^{2+} concentration to the concentration of **2** at 0–1.0 and 1.0–3.0 (Fig. 2b inset). Such a stepwise change in the absorbance can be attributed to the formation of **2**–Zn^{2+}complex in the ratio of 1:1. Upon the addition of low concentrations of Zn^{2+} ($<1.0\times10^{-7}$ M), the formation of **2**–Zn^{2+} complex becomes dominant, after which the stacking of aromatic moieties in **2** occurs leading to a retarded increase in absorbance.

Depending on the excitation wavelength, varying emission spectra were observed. Photoluminescence spectra in the presence of Zn^{2+} after excitation at $\lambda=350$ nm and $\lambda=400$ nm revealed emission peaks located at $\lambda=410$ nm and $\lambda=455$ nm, respectively. The first peaks is attributed to the π–π* ligand-centered absorption of **2**, while the latter is the characteristic d–π* MLCT absorption band of **2**–Zn^{2+} complex. Along with a large red shift of 45 nm from 410 nm to 455 nm, a significant enhancement in emission intensity is accompanied (by 14-fold increase) (Fig. 2c). This coordination-driven photophysical process has been frequently referred to as chelation-enhanced fluorescence (CHEF) [16,17]. A red shift from the ion binding results from the planarization of the bipyridyl unit extending the effective conjugation length in conjunction with perturbation of the electronic system. An exclusive and selective fluorescence response to Zn^{2+} may be due to the closed-shell configuration of Zn^{2+} and diamagnetic property,

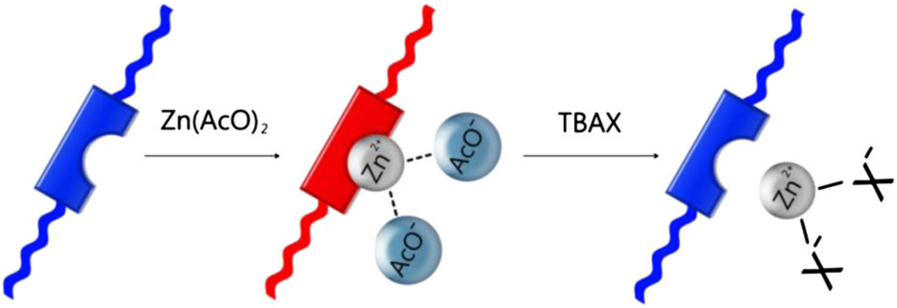

Fig. 5. Schematic representation of optical responses of **2** after adding zinc acetate, followed by addition of tetrabutylammonium halides (TBAX).

which is found to be different from those of other divalent d^{10} ions, such as Cd^{2+} and Hg^{2+}, that exhibit lowered emission due to the so-called "heavy ion effect".

In ^1H NMR spectrum of **2** (Fig. 3a), all the signals for aromatic protons were sharp and easily-identified with a complete integral ratio. Upon the complexation with Zn^{2+}, the aromatic signals are merged and shifted to lower field with respect to those in the free ligand. The shifted signal at $\delta = 8.1$ ppm, attributed to the 3,3'-protons, provides an obvious evidence to support the coordination of the 2,2'-bipyridyl in **2** [18]. Titrations with zinc ions allows us to determine the binding constant of **2**–Zn^{2+}. The value (K_b) is derived to be $9.2 \times 10^6\ M^{-1}$ by the Benesi–Hildebrand equation according to 1:1 complexation (Fig. 3b). High value of K_b clearly indicates a strong binding of **2** to zinc ions.

Then, we intuitively learned that the counteranion of zinc ion significantly affects the binding behavior of **2** [19]. When eight different zinc salts were added to the solution of **2**, surprisingly, only zinc(II) acetate, $Zn(AcO)_2$, exhibited an emission change under UV light (Fig. 4a inset). When the response of **2** to equimolar zinc salts was examined by absorption spectroscopy, only $Zn(AcO)_2$ induced a red shift (Fig. 4a). In comparison, there are no obvious changes in UV spectra of **2** upon addition of other zinc salts, such as ZnF_2, $ZnCl_2$, $ZnBr_2$, ZnI_2, $Zn(CN)_2$, $Zn(NO_3)_2$, and $ZnSO_4$. The effect of counteranions on spectral properties is ascribed to the different coordinating abilities between the counteranions and zinc(II) ion. It is known that the alkalescence of acetate anion, AcO^-, is stronger that other anions [20]. In case of AcO^-, the nature of the coordination bonds between zinc(II) ion and AcO^- is fortified, since complexation of Zn^{2+} with anions is enhanced in an aprotic environment like $CHCl_3$. This, in turn, will induce an effective binding, leading to an ionochromic response of **2**. Such response offers remarkable properties in terms of selectivity and sensitivity because it can selectively respond in the presence of both Zn^{2+} cation and AcO^- anion. Upon further investigation, we observed a distinctive emission enhancement only by $Zn(AcO)_2$, which can be differentiated from all other metal acetates. Though $Pd(AcO)_2$ and $Cu(AcO)_2$ exhibited their inherent colors in the absorbance spectra, no such emission change as that of $Zn(AcO)_2$ was observed. In case of $Pd(AcO)_2$, it exhibited a slightly lowered emission only after standing for several days. Such discriminate interaction of dye **2** toward zinc acetate finds important usefulness in chemo-sensor application due to its highly selective binding to a single ionic zinc compound. Meanwhile, the addition of exogenous anions, as tetrabutylammonium salts of F^-, Cl^-, Br^-, I^-, and CN^-, to **2**–Zn^{2+} complex induced a significant fluorescence decrease, accompanied by a blue shift in UV spectra (Fig. 4c). UV measurements represent the decomplexation of species (local $\lambda_{max} = 350$ nm). The decrease in fluorescence was observed after adding excess amount (4 equiv.) of these anions, with no differentiation noticed among tested anions.

The visual emission changes of **2** in the presence of $Zn(AcO)_2$ and the effective decomplexation of **2**–Zn^{2+} complex after adding excess amount of tetrabutylammonium halides are schematically represented in Fig. 5.

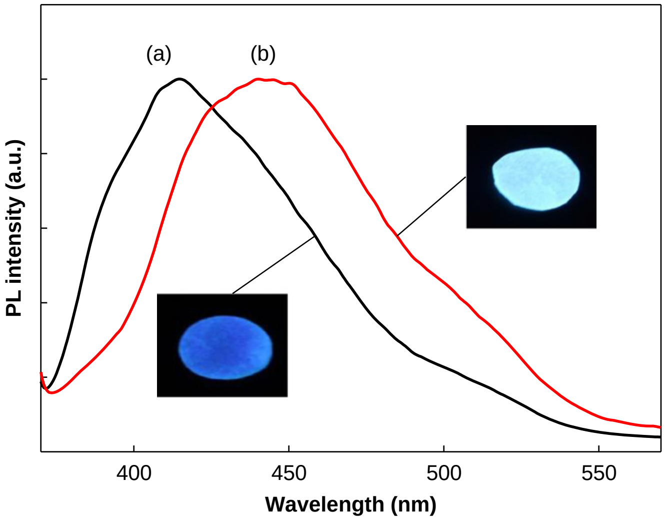

Fig. 6. PL spectra of **2**-coated filter papers (a) before and (b) after dipping into the chloroform solution containing zinc acetate. Photo images, under UV light, of the corresponding samples are also shown.

To examine the potential applications of **2** as ready to use, dipstick experiments were carried out using coated filter papers which had been prepared following the previous method [21]. When the paper was introduced into the chloroform solution containing $Zn(AcO)_2$, we instantly observed a color change in its fluorescence, which can also be evidenced in the photoluminescence spectra (Fig. 6). Development of sensitive "dipstick" tests for zinc is attractive, since instant qualitative information is obtained with no special equipment.

In summary, we prepared bpy-modified acetylene dye **2** which contains 2,2'-bipyridine moiety in the center with symmetrically substituted flexible derivatives at both ends. Upon exposure toward various metal salts, **2** revealed a highly selective optical response to Zn^{2+} with AcO^- as a counteranion, which is evidenced by a large red shift and a significant enhancement in emission intensity. Such a peculiar response to a single zinc compound, as far as we are aware, has been reported elsewhere. Subsequent efforts will follow as an effort to prepare water-soluble analog, which finds useful for bio-application in aqueous medium.

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