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## Luminescent properties and logic nature of a crown Schiff base responding to sodium ion and zinc ion

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## ABSTRACT

An N-salicylidenaniline (SA), compound **1** with 15-crown-5 moiety, was synthesized. Coordinations with Na<sup>+</sup> or/and Zn<sup>2+</sup> induced obvious changes in fluorescence spectra. When the solvent changed from ethanol to acetonitrile, compound **1** and its complexes exhibited noticeable fluorosolvatochromism. However, the spectral changes all could express the AND logic function in these two solvents. The changes in fluorescence spectra were interpreted as photoinduced electron transfer (PET) and charge transfer transition (CT) mechanisms.

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## 1. Introduction

Following the concept of molecular logic proposed by Aviram in 1988 [1], a large number of significant logic functions were exploited [2–7]. NOT, AND, OR, and XOR are the most basic but most important logic operations. Many other logic functions such as NAND, NOR, INHIBIT, even many complex integrated logic can also be obtained by the specific combinations of above four basic logic gates. Thanks to the pioneering work by De Silva on a fluorescent AND logic gate based on PET mechanism [2], more PET molecular systems were designed for fluorescent AND logic operation [8–15]. Recently, PET type AND gates mainly concern Na<sup>+</sup> and various phosphate species [12], K<sup>+</sup> and F<sup>-</sup> [13], and Na<sup>+</sup> and transition metal ions [15]. In our previous work, we have developed several logic functions using N-salicylidenaniline (SA) as the response molecule [16–21]. However, a single AND logic gate of SA has not still been reported. Herein, we will present what we have achieved on developing a PET type AND gates.

In general, AND logic gives an output of 1 only if both inputs are held at 1 each. Therefore, one molecular system that can perform a PET type AND logic gate must contain a fluorophore and two PET donors. SA molecule is a kind of active material for its excellent luminescence and remarkable coordination properties with

transition metal ions [22,23]. In essence, SA molecule is a good fluorophore with a  $\pi$ -conjugation system. In addition, after coordination with transition metal ions, the PET action from oxygen and nitrogen to the  $\pi$ -conjugation chromophore will be prevented. Consequently, enhanced fluorescence can be observed. Summarily, SA molecule is a fluorophore containing a PET donor. In order to obtain a PET molecular system for AND logic function, we merely need to modify SA molecule with another PET donor.

Crown group is a well known PET donor. After coordination with special metal ion, the electron-rich elements in crown group will be bound. Hence, the PET action from crown donor towards the fluorophore is stopped and high fluorescence will be obtained. Taking this into account, we introduced 15-crown-5 group into the SA molecular skeleton. Consequently, compound **1** was prepared as shown in Scheme 1. The experimental results demonstrated that the stimulations of Na<sup>+</sup> and Zn<sup>2+</sup> induced considerable fluorescent changes whether in ethanol or in acetonitrile. As a result, an AND logic operation was expressed.

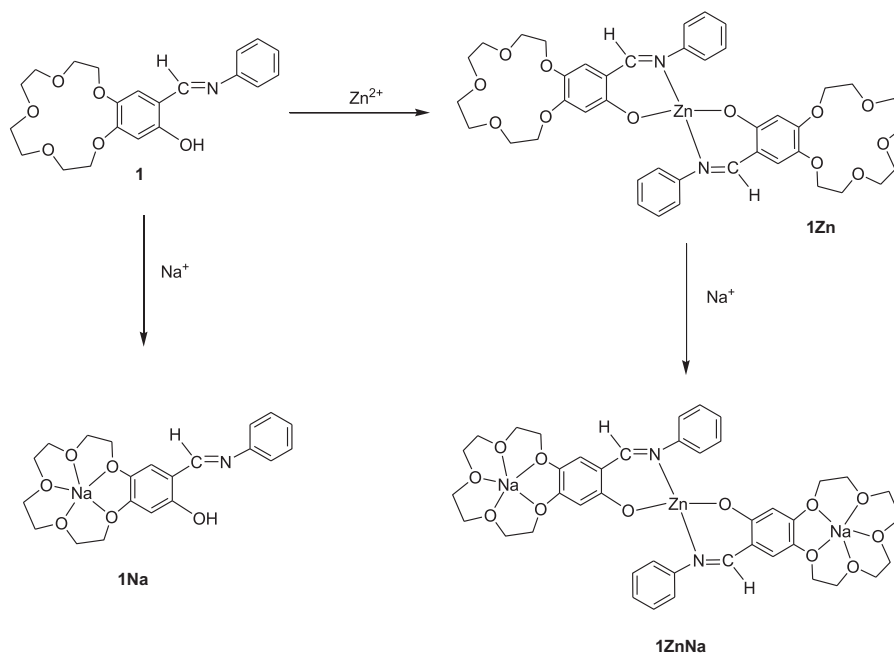
## 2. Experimental

## 2.1. General

Low-resolution mass spectra were measured on Agilent 7890A-5975C GC-MS using electron impact (EI) ionization at 70 eV. <sup>1</sup>H NMR spectra were recorded at 400 MHz on Bruker AV-400 instrument. <sup>13</sup>C NMR spectra were recorded at 100 MHz. High-resolution

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**Scheme 1.** The molecular structures of compounds **1** and the complex with  $\text{Na}^+$  and  $\text{Zn}^{2+}$ .

mass spectra were taken on an Agilent 1200–6520 Q-TOF electro spray mass spectrometer. The fluorescence spectra were determined with a FluoroMax-4 (JobinYvon) fluorimeter.

## 2.2. Preparation of **1**

Compound **1** was prepared *via* seven-step as shown in Scheme 2. **1a–f** was synthesized according to the known methods [24–27]. Compounds **1** were synthesized by the condensation of aniline with **1f** according to standard procedures as previously reported [28]. The details of preparation and analytical data are as follows:

**1f–1.** 100 mg of **1f** (0.32 mmol) was dissolved in 30 mL of absolute ethanol and 54 mg aniline (0.58 mmol) was added. The mixture was refluxed for 2 h. After removal of the solvent in vacuo, the residue was recrystallized twice from diethyl ether and yielded yellow crystals (55 mg, 44%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , TMS):  $\delta$  13.60 (s, 1H), 8.46 (s, 1H), 7.41 (dd,  $J=7.6$  and 8 Hz, 2H), 7.24 (3H), 6.87 (s, 1H), 6.49 (s, 1H), 4.17 (t,  $J=4$  Hz, 2H), 4.11 (t,  $J=4.4$  Hz, 2H), 3.92 (tt,  $J=2.8$  and 4.8 Hz, 4H), 3.76 (8H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  160.96, 159.50, 154.89, 148.28, 141.79, 129.37, 126.32, 120.91, 118.02, 111.18, 101.60, 71.11, 70.90, 70.72, 70.21, 69.81, 69.10, 68.25. GC–MS (EI): 387 ( $\text{M}^+$ ), 315, 255, 182, 154, 104. UV ( $\text{CHCl}_3$ )  $\lambda_{\text{max}}$ : 294 nm, 356 nm, 452 nm (broad). HRMS ( $m/z$ ) [ $\text{M}+\text{H}$ ] $^+$ , 388.1757, calcd for: 388.1755.

## 3. Results and discussion

### 3.1. Spectral analysis

The fluorescence spectra were respectively investigated in ethanol and in acetonitrile. In these two kinds of solvent, the stimulations of  $\text{Na}^+$  and  $\text{Zn}^{2+}$  all could induce dramatic fluorescence changes, however, there was some noticeable difference. Detailed spectral changes would be particularly discussed in the following sections.

#### 3.1.1. Ethanol system

**Action of  $\text{Zn}^{2+}$  (IN1).** SA molecules can be bound with various transition metal ions. Especially, their zinc complexes often display strong fluorescence emission, which can be used as a detectable output signal for molecular devices. So, we introduced  $\text{Zn}^{2+}$  ion as the first input signal. In ethanol solution, compound **1** exhibited a weak fluorescence centered at 410 nm with a little tail spread over towards red (dash line in Fig. 1). Coordination took place instantly when  $\text{Zn}^{2+}$  was added into the system. The  $^1\text{H}$  NMR of the compound **1** in the presence of  $\text{Zn}^{2+}$  provided further evidence for the coordination. As can be seen from Fig. S1 (shown in the Electronic Supplementary Information file), after addition of  $\text{Zn}^{2+}$ , the chemical shift at 9.80 ppm assigned to the proton of the phenol group disappeared, which indicated that the phenol group had been deprotonated. In addition, signals in the region from 8.00 ppm to 6.00 ppm were shifted upfield and became broad. These difference in the  $^1\text{H}$  NMR indicated that the change of the electron density owing to the through-bond electronic effects, in other words, compound **1** had coordinated with  $\text{Zn}^{2+}$ . As a result, the complex **1Zn** (shown in Scheme 1) was produced. Remarkable glaucous emission at 504 nm was observed by adding a small amount of  $\text{Zn}^{2+}$ . Then, the fluorescence intensity of complex **1Zn** gradually increased until the  $\text{Zn}^{2+}$  amount reached the coordination concentration.

After titration with  $\text{Zn}^{2+}$ , compound **1** would coordinate with  $\text{Zn}^{2+}$ . Thus, the PET process from oxygen and nitrogen to the  $\pi$ -conjugation fluorophore would be reduced. Consequently, enhanced fluorescence was observed [29]. The complex **1Zn** showed an obvious dual emission character. Dual fluorescence can result due to the excited state intramolecular proton transfer (ESIPT) or twisted intramolecular charge transfer (TICT) state [30]. After coordination, the phenolic group of compound **1** was deprotonated. Hence, there was no possibility that the complex could undergo ESIPT. Consequently, the observed dual fluorescence may be due to TICT character. There was a possibility that the charge transfer took place from the nitrogen and oxygen to the  $\text{P}\pi$  electron system of the benzene. In the dual fluorescence spectrum, the shorter wavelength peak (around 410 nm) arose due to emission from the locally excited (LE) state and the longer wavelength peak (around 500 nm) arose due to emission from the TICT state.

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