



## A highly selective fluorescent sensor for dual detection of Zn<sup>2+</sup> and F<sup>-</sup> based on a new diarylethene



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### ABSTRACT

A new diarylethene derivative with a coumarin unit was synthesized. Its multi-functional fluorescent switching behaviors were investigated by the stimulation of UV/vis light, Zn<sup>2+</sup>/EDTA, and F<sup>-</sup>. The diarylethene was highly selective toward Zn<sup>2+</sup> and F<sup>-</sup> with different fluorescence colors and binding modes. Upon addition of Zn<sup>2+</sup>, its emission peak was blue-shifted by 32 nm and emission intensity was enhanced by 57 fold, due to the formation of a 1:1 metal/ligand complex, accompanied by a fluorescence color change from dull red to green. Moreover, the diarylethene was also selectivity to F<sup>-</sup> with the fluorescence color change from dull red to yellow. The dramatic fluorescence color change made the naked eye detection of Zn<sup>2+</sup> and F<sup>-</sup> possible.

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Fluorescent chemosensors of metal cations and anions were a promising research field in chemistry with potential in ecological, biological, and clinical applications.<sup>1</sup> In particular, the importance of Zn<sup>2+</sup> in the biological domain primarily lies in the fact that it plays important roles in various biological systems such as neurotransmission, signal transduction, and gene expression.<sup>2</sup> However, accumulation of this ion at a high level, even for a short period of time, could cause an imbalance in cellular processes, resulting in many pathological states, such as Wilson's disease, prostate cancer and diabetes.<sup>3</sup> Furthermore, Zn<sup>2+</sup> is also a harmful pollutant for environment especially in water pollution.<sup>4</sup> Meanwhile, fluoride plays an important role in environmental and biological systems.<sup>5</sup> It is becoming more and more popular in many technological developments, for its important role in water supply treatment, osteoporosis treatment, dental care, and even in chemical warfare agents.<sup>6</sup> High levels of F<sup>-</sup> could lead to skeletal fluorosis, mottling of teeth, thyroid, liver, and other organ damages.<sup>7</sup> Thus, it is very important to develop effective chemosensors for the detection of Zn<sup>2+</sup> and F<sup>-</sup>.

Photochromic materials have attracted much attention in recent years because of their potential applications, such as metal ions sensor, molecular switches, logic gates, and information storage.<sup>8</sup> Among various photochromic compounds, diarylethene derivatives are the most promising candidates owing to their excellent thermal stability, fatigue resistance, and rapid response.<sup>9</sup> Furthermore, their

photoswitchable property could undergo conformational change between two isomers with different photophysical properties triggered by light.<sup>10</sup> So far, fluorescent sensors based on diarylethene with various functions have been designed and constructed.<sup>11</sup> However, multi-response fluorescence sensors for both Zn<sup>2+</sup> and F<sup>-</sup> with a photochromic diarylethene were reported rarely. On the other hand, coumarin derivatives have an ideal skeleton structure to construct various fluorescent probes because it possesses desirable photophysical properties such as a large Stokes shift and visible excitation and emission wavelengths.<sup>12</sup> Therefore, it is possible to design and construct a novel fluorescent sensor based on diarylethene with a coumarin unit.

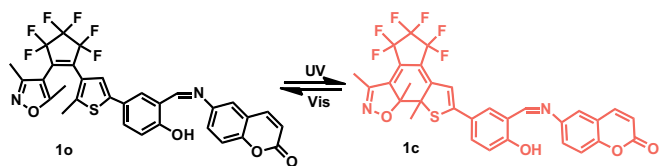
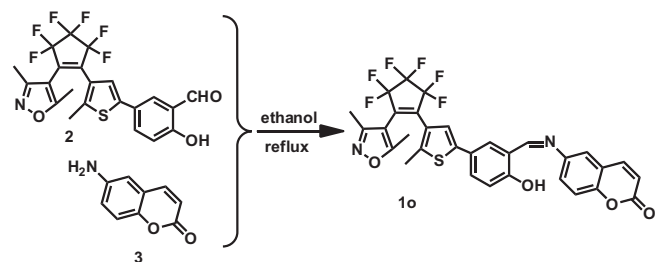
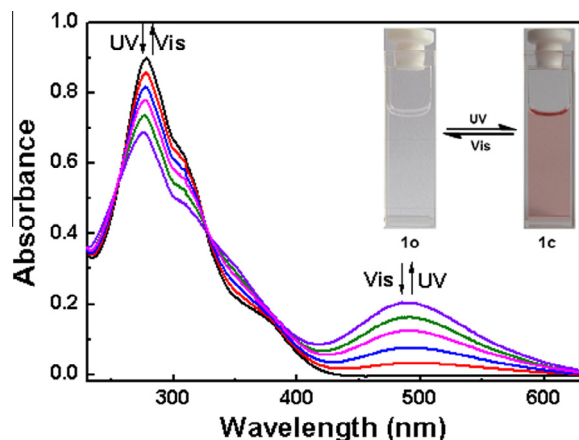
Herein, a novel diarylethene derivative with a coumarin unit was synthesized. The diarylethene named 1-(3,5-dimethyl-4-isoxazolyl)-2-{2-methyl-5-[4-hydroxyl-3-(2-methyleneaminocoumarin)-phenyl]-3-thienyl}perfluorocyclopentene (**10**) was capable of selective and sensitive dual detection of Zn<sup>2+</sup> and F<sup>-</sup> with obvious fluorescence color change, which could be observed by naked eyes. The photochromism of the diarylethene is shown in Scheme 1.

The synthetic route for **10** was shown in Scheme 2. The compound **2** was synthesized through the similar methods according to the previous Letter.<sup>13</sup> To a stirred anhydrous ethanol solution of compound **2**, compound **3** was added and refluxed to give the diarylethene derivative **10**. The structure of **10** was confirmed by elemental analysis, NMR, and IR (Supplementary Information (SI)).

The UV–vis absorption spectral and color changes of **10** induced by photoirradiation were measured in acetonitrile (2.0 × 10<sup>-5</sup> mol L<sup>-1</sup>) at room temperature. As shown in Figure 1, the absorption maximum of the open-ring isomer **10** was observed

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Scheme 1. Photochromism of **1o**.Scheme 2. Synthetic route for **1o**.

**Figure 1.** Absorption spectral and color changes of **1o** upon alternating irradiation with UV and visible light in acetonitrile ( $2.0 \times 10^{-5}$  mol L $^{-1}$ ).

at 278 nm ( $\epsilon_{\text{max}} = 4.49 \times 10^4$  L mol $^{-1}$  cm $^{-1}$ ) corresponding to  $\pi$ - $\pi^*$  transition.<sup>14</sup> Upon irradiation with 297 nm light, the absorption intensity at 278 nm gradually decreased and a new absorption band centered at 485 nm ( $\epsilon_{\text{max}} = 1.02 \times 10^4$  L mol $^{-1}$  cm $^{-1}$ ) was observed due to the formation of the closed-ring isomer **1c**,<sup>15</sup> accompanied by a solution color changed from colorless to red. Alternatively, upon irradiation with visible light ( $\lambda > 500$  nm), the absorption spectrum recovered to the initial state and the red solution was bleached entirely. With 1,2-bis(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene as a reference compound,<sup>16</sup> the cyclization and cycloreversion quantum yields of **1o** were determined to be 0.17 and 0.032, respectively.

The emission spectral changes of **1o** upon irradiation UV/vis were measured in acetonitrile. As shown in Figure S1 (SI), with 410 nm light as excitation, the emission peak of **1o** was observed at 598 nm and the fluorescence quantum yield of **1o** was determined to be 0.009. Upon irradiation with 297 nm light, the emission intensity of **1o** decreased remarkably, accompanied by an obvious fluorescent color changed from dull red to dark. At the photostationary state (PSS), the fluorescence intensity of **1o** was quenched to 53%, due to the formation of the non-fluorescent closed-ring isomer **1c**.<sup>17</sup> The residual fluorescence in the PSS may be attributed to

the incomplete cyclization reaction and the existence of open-ring isomers with a parallel conformation.<sup>18</sup>

The fluorescence spectra and fluorescent color changes of **1o** induced by metal ions including Zn $^{2+}$ , Ni $^{2+}$ , K $^{+}$ , Ca $^{2+}$ , Hg $^{2+}$ , Cd $^{2+}$ , Sr $^{2+}$ , Mg $^{2+}$ , Co $^{2+}$ , Mn $^{2+}$ , Ba $^{2+}$ , Pb $^{2+}$ , Cu $^{2+}$ , Fe $^{3+}$ , Cr $^{3+}$ , and Al $^{3+}$  are shown in Figure 2. It could be seen that the emission intensity of **1o** was notably enhanced upon addition of 260 equiv Zn $^{2+}$ . The addition of other cations, such as Ni $^{2+}$ , K $^{+}$ , Ca $^{2+}$ , Hg $^{2+}$ , Cd $^{2+}$ , Sr $^{2+}$ , Mg $^{2+}$ , Co $^{2+}$ , Mn $^{2+}$ , Ba $^{2+}$ , Pb $^{2+}$ , Cu $^{2+}$ , Fe $^{3+}$ , Cr $^{3+}$ , and Al $^{3+}$ , resulted in no obvious change. When Zn $^{2+}$  was added to the solution of **1o**, the emission peak blue shifted from 598 nm to 566 nm and the emission intensity enhanced by 57 fold (Fig. 2A and B). At the same time, an evident fluorescent color changed from dull red to green, which could be observed by naked-eyes, due to the formation of **1o**-Zn $^{2+}$  (**1o'**) complex (Fig. 2C). The results indicated that the diethylene could serve as a naked-eye fluorescence sensor for detection of Zn $^{2+}$  in acetonitrile.

To further evaluate the responsive nature of **1o** stimulated by Zn $^{2+}$ , the fluorescence titration experiment was carried out in acetonitrile ( $2.0 \times 10^{-5}$  mol L $^{-1}$ ) at room temperature. As depicted in Figure 3, the fluorescence of **1o** increased when Zn $^{2+}$  increased from 0 to 260 equiv, followed by a plateau with further titration. The emission peak of **1o** was blue-shifted by 32 nm and intensity enhanced by 57 fold, accompanied by a notable fluorescence color change from dull red to green. The inset of Figure 3A depicted the effect of Zn $^{2+}$  concentration on the emission intensity at 566 nm. The results indicated that the fluorescence intensity and the concentration of Zn $^{2+}$  have a good linear relationship. Furthermore, the fluorescence quantum yield of **1o'** was determined to be 0.059. To examine whether the coordinating processes of **1o** with Zn $^{2+}$  was reversible or not, excess of EDTA (0.1 mol L $^{-1}$ ) was added to the solution of **1o'**. The fluorescence spectrum of **1o** recovered immediately due to the complexation/decomplexation reaction between **1o** and Zn $^{2+}$ . It should be noted that **1o'** exhibited remarkable fluorescence switch property upon irradiation with UV/vis light (Fig. 3B). The emission intensity of **1o'** quenched dramatically upon irradiation with 297 nm light due to the formation of the closed-ring isomer of **1c'**. At PSS, the fluorescence intensity of **1o'** was quenched to 15%, accompanied by the green fluorescence disappeared gradually. Reversely, the fluorescence of **1o'** could be recovered by irradiating the closed-ring isomer **1c'** with visible light ( $\lambda > 500$  nm). The fluorescence enhanced mechanisms could be explained by the stable chelation of **1o** with the Zn $^{2+}$  inhibiting the C=N isomerization and rigidification of fluorophore structure.<sup>19</sup>

To determine the stoichiometry between **1o** and Zn $^{2+}$ , Job's plot analysis was performed according to the reported method.<sup>20</sup> As shown in Figure 4. The maximum value was achieved when the molar fraction of [Zn $^{2+}$ ]/([Zn $^{2+}$ ] + [1o]) was about 0.5, which demonstrated the 1:1 stoichiometry between **1o** with Zn $^{2+}$ . Based on the 1:1 stoichiometry and fluorescence titration data, the association constants ( $K_a$ ) of **1o** with Zn $^{2+}$  was calculated from the slope and intercept of the linear plot was found to be  $2.6 \times 10^3$  L mol $^{-1}$  ( $R = 0.991$ ). The detection limit was calculated to be  $1.18 \times 10^{-5}$  mol L $^{-1}$  for Zn $^{2+}$  (Fig. S2, SI). In order to confirm the coordination between **1o** and Zn $^{2+}$ ,  $^1\text{H}$  NMR monitored experiments were performed in CDCl $_3$ . As shown in Figure 7B, after the Zn $^{2+}$  (in distilled water) was added to **1o**, the proton of CH=N displayed a remarkable downfield shifted from 8.55 ppm to 8.61 ppm with an addition of 260 equiv Zn $^{2+}$ , indicating the binding mode of Zn $^{2+}$ -N was formed. On the other hand, the formation of Zn $^{2+}$ -O between the Zn $^{2+}$  and the -OH groups of **1o** resulted in the resonance signal of -OH proton disappeared. The results indicated that Zn $^{2+}$  may coordinate with N of C=N, and the O of -OH. The proposed binding mode between **1o** and Zn $^{2+}$  was shown in Scheme 3.

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