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# A multi-functional fluorescent sensor for Zn<sup>2+</sup> and HSO<sub>4</sub><sup>-</sup> based on a new diarylethene derivative

Shiqiang Cui, Shouyu Qiu, Ruimin Lu, Shouzhi Pu\*

Jiangxi Key Laboratory of Organic Chemistry, Jiangxi Science and Technology Normal University,

Nanchang 330013, PR China

\*Corresponding author: E-mail: <u>pushouzhi@tsinghua.org.cn</u> (S. Pu); Tel./Fax: +86-791-83831996.

**Abstract:** A new photochromic diarylethene derivative with a hydralazine unit was designed and synthesized. It was not only acted as a  $Zn^{2+}$  sensor with the fluorescent color change from dark blue to bright orange, but also acted as a fluorescent sensor for  $HSO_4^-$  with the fluorescent color change from dark blue to bright blue,. Furthermore, the derivative also exhibits multi-addressable switching properties by the stimulations of lights and chemical reagents. Based on these characteristics, two combinational logic circuits were constructed with the emission intensity as the output signals, and the UV/vis lights, chemical species as the input signals.

Keywords: Photochromic diarylethene; Fluorescent sensor; Multi-addressable; Logic circuit.

#### 1. Introduction

The development of fluorescent sensors for the recognition of cations or anions has attracted great research interests due to their important role in biological, clinical and environmental applications.<sup>1-7</sup> Zinc is the second most abundant transition metal as well as essential ingredient to preserve life with 2-4 g distributed throughout the human body.<sup>8,9</sup> It plays a vital role in many biological processes such as brain function and pathology, gene transcription, immune function, and mammalian reproduction,<sup>10,11</sup> as well as it is involved in the pathological processes in many diseases including Alzheimer's disease,<sup>12</sup> epilepsy,<sup>13</sup> and ischemic stroke.<sup>14</sup> Meanwhile, among various anions, the hydrogen sulfate ion (HSO<sub>4</sub><sup>-</sup>) is of great significance as it is established role in biological and industrial areas.<sup>15</sup> The HSO<sub>4</sub><sup>-</sup> eventually dissociates at high pH to generate toxic sulfate radical ion,<sup>16</sup> which causes irritation of the skin, eyes, and even respiratory paralysis.<sup>17-19</sup> For these reasons, the effective and selective detection of Zn<sup>2+</sup> and HSO<sub>4</sub><sup>-</sup> ions is of great significance for biochemistry, environmental science and medicine. The development of highly selective fluorescent sensors for Zn<sup>2+</sup> and HSO<sub>4</sub><sup>-</sup> is still a great challenge, although some fluorescent sensors for Zn<sup>2+</sup> and HSO<sub>4</sub><sup>-</sup> have been reported, respectively.<sup>20-28</sup>

In recent years, photochromic compounds have attracted much attention for their potential applications in data recording and storage,<sup>29-31</sup> multi-photon devices,<sup>32,33</sup> photo-elctronic devices,<sup>34</sup> fluorescent sensors,<sup>35-38</sup> molecular logic gates,<sup>39-42</sup> and so forth. Among the reported photochromic compounds for distinguishing ions, diarylethenes are the most promising materials because of their fast response, high cyclization/cycloreversion quantum yields, excellent thermal stability, and outstanding fatigue resistance.<sup>43-46</sup> Up to date, many single-identified fluorescent sensors based on diarylethene for cations have been extensively studied.<sup>47-49</sup> However, the multi-identified fluorescent sensors based on diaryelthene have not been reported. Therefore, the multiple functional fluorescent sensors for cations and anions also have attracted more attention.<sup>50-54</sup>

Hydralazine was primarily synthesized by Ciba as an anti-hypertensive compound and has long been known to possess de-methylating activity.<sup>55,56</sup> It was first approved by the U.S. Food and Drug Administration as an anti-hypertensive drug in 1952.<sup>57</sup> Today, it has vital place in clinical practice as a third-line antihypertensive regimen in patients with complicated hypertension, an antihypertensive in intensive care unit settings, and a second-line therapeutic for chronic heart failure, or because of its safety profile in pregnancy hypertension.<sup>57-62</sup> Recently, two fluorogenic chemosensors for  $Co^{2+}$  based on hydralazine have been reported.<sup>63,64</sup> However, fluorescent sensors for special ions of interest based on diarylethene with hydralazine unit have not been reported previously. In this work, a new fluorescent sensor for  $Zn^{2+}$  and  $HSO_4^-$  based on a diarylethene containing hydralazine unit was constructed. The photophysical and photochemical behaviors of the diarylethene derivative (**10**) were investigated systematically. The synthetic route and photochromism of **10** are shown in Scheme 1.



Scheme 1. Synthetic route and photochromism of 10.

#### 2. Experimental

#### 2.1. General methods

All reagents were purchased from Aldrich and used without further purification. All solvents used were

spectral grade and purified by distillation before use. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were collected on a Bruker AV400 spectrometer by using tetramethylsilane (TMS) as an internal standard and with DMSO-*d*<sub>6</sub> as the solvent. Infrared spectra (IR) were performed on a PerkinElmer Spectrum spectrometer. Mass spectra were recorded with an Agilent 1100 ion trap MSD spectrometer. Melting point was measured on a WRS-1B melting point apparatus. Fluorescence spectra were measured with a Hitachi F-4600 fluorescence spectrophotometer, and the slit width was 5 nm for both excitation and emission. Absorption spectra were measured on an Agilent 8453 UV/vis spectrophotometer. The fluorescence quantum yield was obtained on an Absolute PL Quantum Yield Spectrometer QY C11347-11. Elemental analysis was carried out with a PE CHN 2400 analyzer. Photoirradiation were performed on a MUA-165 UV lamp and a MVL-210 visible lamp.

#### 2.2. Synthesis of 10

The synthetic route of 10 is shown in Scheme 1. Compound 2 was synthesized through Suzuki coupling reaction according to the previous report,<sup>65</sup> after the formyl in compound **2** was protected with glycol, 3 obtained. Compound compound was 4 was synthesized from 3-Bromo-2-methyl-5-phenylthiophene, according to the reported work.<sup>66</sup> Subsequently, compound **3** was lithiated in THF at 195 K, and then compound 4 was added. After reacting for 1 h, the reaction product was hydrolyzed to give diarylethene 5. The experimental procedures and characterized data are showed in Supporting Information (Experimental procedures details, Fig. S1-S2).

A mixture of **5** (0.28 g, 0.5 mmol) and 1-(pthalazine-4-yl)hydrazine (0.064 g, 0.5 mmol) were dissolved in 10.0 mL in anhydrous methanol. After stirring and refluxing for 2 h, the mixture was cooled to room temperature and a green precipitate was obtained. The crude product was purified by recrystallization with ethanol to give the target diarylethene **10** (0.23 g, 66% yield) as a light green solid. Mp. 426-427 K. <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ , TMS),  $\delta$  (ppm): 2.03 (s, 3H), 2.06 (s, 3H), 7.36 (d, 1H, J = 12.0 Hz), 7.44 (d, 2H, J = 16.0 Hz), 7.52 (s, 1H), 7.65 (d, 2H, J = 8.0 Hz), 7.84 (s, 1H), 8.16 (d, 1H, J = 8.0 Hz), 8.21 (d, 2H, J = 8.0 Hz), 8.29 (m, 1H), 8.75 (d, 1H, J = 8.0 Hz), 8.88 (s, 1H), 8.95 (d, 1H, J = 8.0 Hz), 8.98 (s, 2H). <sup>13</sup>C NMR (100 MHz, DMSO- $d_6$ , TMS),  $\delta$  (ppm): 13.5, 13.6, 116.7, 119.3, 121.0, 122.0, 123.5, 123.9, 124.4, 124.5, 124.6, 124.8, 127.3, 127.6, 128.7, 129.7, 132.0, 133.3, 135.3, 139.7, 140.7, 141.2, 141.3, 143.9, 147.3, 148.83, 157.2. IR (KBr, v, cm<sup>-1</sup>): 3025, 2698, 2488, 1621, 1602, 1472, 1390, 1334, 1272, 1184, 1111, 1092, 1051, 1026, 987, 919, 804, 764, 739, 720, 700, 688, 662; Anal. calcd for C<sub>35</sub>H<sub>23</sub>F<sub>6</sub>N<sub>5</sub>S<sub>2</sub> (%): C, 60.77; H, 3.35; N, 10.12, found: C, 60.78; H, 3.34; N, 10.11. HRMS-ESI, m/z =692.1414 [M+H<sup>+</sup>]<sup>+</sup> (calcd, 692.1377) (Fig. S3-S6).

#### 3. Results and discussion

#### 3.1 Photochromic and fluorescent properties of 10

The UV-vis absorption spectral and color changes of **10** induced by photoirradiation were measured in THF ( $2.0 \times 10^{-5} \text{ mol } \text{L}^{-1}$ ) at room temperature. As shown in Fig. 1A, **10** exhibited a maximum absorption band centered at 403 nm ( $\varepsilon = 4.02 \times 10^4 \text{ mol}^{-1} \text{ L cm}^{-1}$ ), which was resulted from  $\pi \to \pi^*$ transition.<sup>67</sup> Upon irradiation with 297 nm light, the colorless solution turned into cyan and a new visible absorption band centered at 607 nm ( $\varepsilon = 1.76 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ ) appeared and increased due to the formation of the closed-ring isomer **1c**.<sup>68</sup> Simultaneously, the absorption band centered at 403 nm decreased evidently. Reversely, upon irradiation with visible light ( $\lambda > 500$  nm), the absorption spectrum was recovered to that of **10**, accompanied by the cyan solution was bleached completely. In the photostationary state (PPS), a clearly isosbestic point was observed at 440 nm, indicating that this is a unimolecular process.<sup>69</sup> The quantum yields of cyclization and cycloreversion were determined to be 0.24 and 0.014, respectively, using 1,2-bis(2-methyl-5-phenyl-3-thienyl) perfluorocyclopentene as reference.<sup>70</sup> The fatigue resistance of **10** was tested in THF through alternating irradiation with UV and visible lights at room temperature. The results showed that the coloration/decoloration cycles of **10** could be repeated for 20 times with 6.2% degradation (Fig. S7).



**Fig. 1.** The absorption (A) and fluorescence (B) spectra changes of **1o**  $(2.0 \times 10^{-5} \text{ mol } \text{L}^{-1})$  upon alternating irradiation with UV/vis lights in THF, when excited at 400 nm.

The fluorescent properties of **1o** were also examined. As shown in Fig. 1B, the emission peak of **1o** was observed at 491 nm with 400 nm excitation. The absolute fluorescence quantum yield of **1o** was determined to be 0.002. Upon irradiation with 297 nm light, the emission intensity of **1o** decreased remarkably, due to the non-fluorescence isomer **1c** was formed. When the PPS was reached, the emission of **1o** was decreased by *ca*. 89.2%, indicating that the diarylethene exhibited high fluorescence modulation efficiency. The residual fluorescence in the PSS may be attributed to the incomplete cyclization reaction and the existence of the open-ring isomer with parallel conformation.<sup>71</sup> Inversely, the open-ring isomer **1o** could be regenerated and the original emission spectrum could be recovered upon irradiation with visible light ( $\lambda > 500$  nm).

#### 3.2 Selectivity of **10** towards $Zn^{2+}$

In order to study the selectivity of 10 towards  $Zn^{2+}$ , the interaction between 10 and various metal ions

including  $Zn^{2+}$ ,  $Cd^{2+}$ ,  $Al^{3+}$ ,  $Cr^{3+}$ ,  $Fe^{3+}$ ,  $Ba^{2+}$ ,  $Mn^{2+}$ ,  $Hg^{2+}$ ,  $Pb^{2+}$ ,  $Ca^{2+}$ ,  $Sr^{2+}$ ,  $Mg^{2+}$ ,  $Ni^{2+}$ ,  $Co^{2+}$ ,  $Cu^{2+}$ ,  $Fe^{2+}$ , and K<sup>+</sup> were investigated in THF solution. As shown in Fig. 2, when 35.0 equiv.  $Zn^{2+}$  were added, the fluorescence of **10** at 594 nm was enhanced greatly, accompanied by the fluorescent color changed from blue to bright orange. The enhancement of emission intensity was attributed to the formation of **10**- $Zn^{2+}$  (**10'**) complex. When **10** was coordinated with  $Zn^{2+}$ , due to the stable complexation between **10** and  $Zn^{2+}$  prohibited the PET process, a large CHEF effect was observed. Furthermore, the stable chelation of **10** and  $Zn^{2+}$  inhibited the C=N isomerization and rigidification of fluorophore structure.<sup>63,64</sup> There were no changes in fluorescence of **10**, when the same amounts of other ions were added. These results indicated that the diarylethene **10** could act as a fluorescent sensor for  $Zn^{2+}$  with prominent selectivity.



**Fig. 2.** Changes in the fluorescence of **1o** induced by the addition of various metal ions (35.0 equiv.) in THF ( $2.0 \times 10^{-5}$  mol L<sup>-1</sup>,  $\lambda_{ex} = 400$  nm): (A) fluorescence spectral changes; (B) emission intensity changes; (C) photos of fluorescence.

Subsequently, a fluorometric titration experiment was carried out in THF  $(2.0 \times 10^{-5} \text{ mol L}^{-1})$  at room temperature to investigate the fluorescence responsive of 10 to  $Zn^{2+}$ . As shown in Fig. 3A, the emission intensity at 594 nm increased when  $Zn^{2+}$  was increased from 0 to 35.0 equiv., followed by a plateau with further titration. Compared to **10**, the emission peak has a redshift of 103 nm, and the emission intensity of 10' was enhanced by 9.5 fold at the plateau. A notable fluorescent color was changed from dark blue to bright orange. The absolute fluorescence quantum yield of **10'** was determined to be 0.023. To examine the coordination process of **10** with  $\mathbf{Zn}^{2+}$  was reversible or not, the chelating agent EDTA was added to the solution of 10'. The fluorescence spectrum of 10' recovered immediately to that of 10, when 70.0 equiv. EDTA were added. The result suggested that the complexation-decomplexation reaction between **10** and  $Zn^{2+}$  was reversible. Upon irradiation with 297 nm light, the emission intensity of 10' decreased and the fluorescent color changed from bright orange to light yellow, due to the closed-ring isomer  $1c-Zn^{2+}(1c')$  complex was formed. In the PSS, the emission intensity was quenched by ca. 66.8%, indicating that 1c' also exhibited strong fluorescence modulation efficiency (Fig. 3B). The emission intensity of **10'** could be recovered upon irradiation with visible light ( $\lambda > 500$  nm). Furthermore, the fluorescence responsive of 1c to  $Zn^{2+}$  was also investigated. As shown in Fig. S8A, Compared to 1c, the emission intensity increased about 16.5 fold when  $Zn^{2+}$  was increased from 0 to 35.0 equivalents. The absolute fluorescence quantum yield of **1c'** was determined to be 0.003.



**Fig. 3.** (A) The fluorescence changes of **1o** ( $2.0 \times 10^{-5}$  mol L<sup>-1</sup>,  $\lambda_{ex} = 400$  nm) induced by Zn<sup>2+</sup>; (B) the fluorescence changes of **1o'** upon irradiation of UV/vis lights.

To make sure the binding mode between **10** and  $Zn^{2+}$ , a Job's plots analysis was calculated by using the emission intensity at 594 nm as a function of the molar fraction of **10**. As shown in Fig. 4A, the intensity approached the maxima when the molar fraction of [**10**] / ([ $Zn^{2+}$ ] + [**10**]) was about 0.5, indicating that **10** was bound to  $Zn^{2+}$  with a binding stoichiometry of 1 : 1. The HRMS peaks at 754.0507 *m/z* assigned to [**10**-H<sup>+</sup>+Zn<sup>2+</sup>]<sup>+</sup> (calcd. 754.0501) was observed (Fig. S9), which provided another evidence for the formation of a 1 : 1 complex between **10** and  $Zn^{2+}$ . The relationship between  $F_0 / (F-F_0)$  and  $[Zn^{2+}]^{-1}$  were obtained from the fluorescence titration profiles for the plots measured at 594 nm and the association constants ( $K_a$ ) of **10** and  $Zn^{2+}$  could be calculated with the Benesi-Hildebrand equation.<sup>72</sup> Based on the 1 : 1 binding mode and the fluorescence titration data, the  $K_a$  was determined to be  $6.0 \times 10^3$  L mol<sup>-1</sup> (Fig. S10A). According to the reported method,<sup>73</sup> the detection limit was calculated to be  $9.47 \times 10^{-6}$  mol L<sup>-1</sup> for Zn<sup>2+</sup> (Fig. S11A). Based on these facts, the proposed binding mode between **10** and Zn<sup>2+</sup> was shown in Scheme 2.



Fig. 4. Job's plot showing the 1 : 1 complex of 10 with  $Zn^{2+}$  (A), and the 1 : 1 complex of 10 with  $HSO_4^{-}$  (B).



Scheme 2. Structure fluorescence color changes of 10 induced by Zn<sup>2+</sup> and HSO<sub>4</sub><sup>-</sup>.

#### 3.3 Fluorescent response of **10** toward $HSO_4^-$

The fluorescence selectivity of **10** toward various anions (HSO<sub>4</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, SO<sub>3</sub><sup>2-</sup>, H<sub>2</sub>PO<sub>4</sub><sup>-</sup>, HPO<sub>4</sub><sup>2-</sup>, PO<sub>4</sub><sup>3-</sup>, HCO<sub>3</sub><sup>-</sup>, CO<sub>3</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup>, NO<sub>2</sub><sup>-</sup>, SCN<sup>-</sup>, CN<sup>-</sup>, CH<sub>3</sub>COO<sup>-</sup>, F<sup>-</sup>, CI<sup>-</sup>, Br<sup>-</sup>, and  $\Gamma$ ) was measured in THF. As shown in Fig. 5, only HSO<sub>4</sub><sup>-</sup> caused notable emission intensity and fluorescent color changes. When HSO<sub>4</sub><sup>-</sup> was added, the emission intensity at 491 nm was enhanced by 46.7 fold, along with the fluorescent color change from dark blue to bright blue. There were no changes in the emission intensity upon addition of other anions. The results suggested that **10** could also be used as a fluorescent sensor for HSO<sub>4</sub><sup>-</sup> in THF with high selectivity.



Fig. 5. Changes in the fluorescence of 10 induced by the addition of various anions (50.0 equiv.) in THF ( $2.0 \times 10^{-5}$  mol L<sup>-1</sup>,  $\lambda_{ex} = 400$  nm): (A) fluorescence spectral changes; (B) emission intensity changes; (C) photos of fluorescence.

The fluorometric titration experiment with  $HSO_4^-$  was also carried out in THF at room temperature. As shown in Fig. 6A, when  $HSO_4^-$  was increased from 0 to 50.0 equivalents, the emission intensity of **1o** at 491 nm gradually increased due to the formation of **1o**- $HSO_4^-$  (**1o''**), followed by a plateau with further titration. Compared with **1o**, the emission intensity of **1o''** was enhanced 46.7 fold at the plateau, accompanied by a notable fluorescent color changed from dark blue to bright blue. At the plateau, the absolute fluorescence quantum yield of **1o''** was determined to be 0.032. Upon irradiation with 297 nm light, the emission intensity of **1o''** was quenched dramatically, accompanied by the fluorescent color change from bright blue to dark blue, due to the formation of the non-fluorescence isomer **1c**- $HSO_4^-$  (**1c''**). At the PSS, the emission intensity of **1o''** was quenched by ca. 91% (Fig. 6B), indicating that

10" exhibited relatively strong fluorescence modulation efficiency in THF. Reversely, upon irradiation with visible light ( $\lambda > 500$  nm), the open-ring isomer 10" was regenerated and the original emission intensity was recovered. In addition, the fluorometric titration of 1c with HSO<sub>4</sub><sup>-</sup> was also performed under the same conditions (Fig. S8B). The emission intensity increased about 15.4 fold, when HSO<sub>4</sub><sup>-</sup> was increased from 0 to 50.0 equivalents, and the emission intensity remained constant with further titration. The absolute fluorescence quantum yield of 1c" was determined to be 0.009.



**Fig. 6.** The fluorescence change of **1o**  $(2.0 \times 10^{-5} \text{ mol L}^{-1}, \lambda_{ex} = 400 \text{ nm})$  induced by HSO<sub>4</sub><sup>-</sup> (A), and the fluorescence change of **1o''** upon irradiation of UV/vis light (B).

The Job's plot analysis was also performed to study the binding mode between **10** and HSO<sub>4</sub><sup>-</sup>. As shown in Fig. 4B, when the molar fraction of  $[10] / ([HSO_4^-] + [10])$  was about 0.5, the maximum value achieved, indicating that the stoichiometry between **10** with HSO<sub>4</sub><sup>-</sup> was 1 : 1. From the Benesi–Hildebrande equation, the binding constant of **10** with HSO<sub>4</sub><sup>-</sup> was calculated to be  $2.65 \times 10^2$  L mol<sup>-1</sup> based on the 1 : 1 binding mode (Fig. S10B). Additionally, the fluorescence titration profile demonstrates that **10** has a detection limit of  $1.3 \times 10^{-5}$  mol L<sup>-1</sup> for HSO<sub>4</sub><sup>-</sup> (Fig. S11B). According to the previous report,<sup>74,75</sup> the proposed binding mode between **10** and HSO<sub>4</sub><sup>-</sup> is *via* intermolecular hydrogen-bonding and is shown in Scheme 2.



Scheme 3 Structure, color, and fluorescence changes of **10** induced by Zn<sup>2+</sup>/EDTA, HSO<sub>4</sub><sup>-</sup>, and UV/vis lights.

#### 3.4 Application in logic circuits

The emission intensity of **10** could be modulated by the stimuli of UV/vis lights and chemical. The multi-addressable fluorescence switching behaviors of **10** are shown in Scheme 3. On the basis of the facts mentioned above, two molecular logic circuits were constructed, one has four inputs (In1: 297 nm light, In2:  $\lambda > 500$  nm visible light, In3: Zn<sup>2+</sup>, and In4: EDTA) and one output (Output 1: the change in the emission intensity at 594 nm), the other has three inputs (In1: 297 nm light, In2:  $\lambda > 500$  nm visible light, and In5: HSO<sub>4</sub><sup>¬</sup>) and one output (Output 2: the change in the emission intensity at 491 nm). As shown in Fig. 7, the emission intensity of **10** at 491 nm was regarded as an initial value. When the emission intensity at 594 nm was 9.5 fold lager than the initial value, the output could be regarded as 'on' state with a Boolean value of '1', otherwise, it was regarded as 'off' state with a Boolean value of '1', otherwise, it was regarded as on-off-on colorimetric switching behavior. Subsequently, there would read a string of four inputs and write one output. For example,

when the string is '0, 0, 1, and 0', the corresponding input signals of In1, In2, In3, and In4 are 'off, off, on, and off'. Under these conditions, **1o** was converted to **1o'** with the addition of  $Zn^{2+}$ , and its emission intensity at 594 nm is increased significantly. As a result, the output signal Output 1 was 'on', and the Boolean value was '1'. Similarly, different combinational strings could result different outputs. All possible logic strings concluded the logic circuit are concluded and shown in Table 1.

	Output 1			
In1 (UV light)	In2 (Vis light)	In3 $(Zn^{2+})$	In4 (EDTA)	$\lambda_{em} = 594 \text{ nm}$
0	0	0	0	0
1	0	0	0	0
0	1	0	0	0
0	0	1	0	1
0	0	0	1	0
1	1	0	0	0
1	0	1	0	0
1	0	0	1	0
0	1	1	0	1
0	1	0	1	0
0	0	1	1	0
1	1	1	0	1
1	1	0	1	0
1	0	1	1	0
0	1	1	1	0
1	1	1	1	0

Table 1 Truth table for all possible strings of four binary-input data and the corresponding output digit.



Fig. 7. The combinational logic circuit equivalent to the truth table given in Table1: In1 (297 nm light), In2 ( $\lambda > 500$  nm light), In3 (Zn<sup>2+</sup>), In4 (EDTA) and Output 1 (fluorescence at 594 nm).

In another combinational logic circuit (Fig. 8), when the emission intensity at 491 nm was 46.7 fold larger than the initial value, the output signal Output 2 was regarded as 'on' state. Under the stimuli of the three inputs, **10** also showed "on-off-on" fluorescence switching behaviors. Consequently, **10** could read a string of three inputs and write one output. All possible logic strings of the combinational logic circuit are concluded and listed in Table 2.

Input			Output 2
In1 (UV)	In2 (Vis)	In5 $(HSO_4)$	$\lambda_{\rm em} = 491 \ \rm nm$
0	0	0	0
0	0	1	1
1	0	0	0
0	1	0	0
1	0	1	0
0	1	1	1
1	1	0	0
1	1	1	1

Table 2. Truth table for all possible strings of three binary-input data and the corresponding output digit.



**Fig. 8.** The combinational logic circuit equivalent to the truth table given in Table2: In1 (297 nm light), In2 ( $\lambda > 500$  nm light), In5 (HSO<sub>4</sub><sup>-</sup>) and Output 2 (fluorescence at 491 nm).

#### 4. Conclusion

In summary, a novel diarylethene derivative with a hydralazine unit was designed and synthesized. It exhibited high selectivity toward  $Zn^{2+}$  and  $HSO_4^-$ , respectively. The fluorescent spectral studies revealed that  $Zn^{2+}$  could induce the emission peak for 103 nm redshift, and the emission intensity enhanced 9.5 fold, accompanied by the fluorescent color change from dark blue to bright orange. The

added  $HSO_4^-$  could induce the emission intensity enhanced 46.7 fold, accompanied by the fluorescent color changed from dark blue to bright blue. Furthermore, based on the multi-addressable fluorescence switching characteristics, two logic circuits were constructed with the emission intensity as output signals and the UV/vis lights,  $Zn^{2+}/EDTA$ , or  $HSO_4^-$  as input signals. This work will be helpful for a new approach to design fluorescent sensors for the detection of multiple ions, and to construct multi-state diarylethene for logic circuits.

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# **Graphical Abstract**

# A multi-functional fluorescent sensor for $Zn^{2+}$ and $HSO_4^-$ based on a

# new diarylethene derivative

Shiqiang Cui, Shouyu Qiu, Ruimin Lu, Shouzhi Pu\*

Jiangxi Key Laboratory of Organic Chemistry, Jiangxi Science and Technology Normal University,

Nanchang 330013, China

\*Corresponding author: E-mail: pushouzhi@tsinghua.org.cn (S. Pu); Tel./Fax: +86-791-83831996.



# Highlights

> This paper reports a new diarylethene with a hydralazine unit that was designed and synthesized for the first time. > The diarylethene could act as a fluorescent sensor for  $Zn^{2+}$  and  $HSO_4^-$ . > The diarylethene also could be used to construct molecular logic circuits.