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A photochromic diarylethene-functionalized fluorescent probe for Cd^{2+} and Zn^{2+} detections



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1. Introduction

With the development of industrialization, metal materials have been used in various fields, such as architecture [1], manufacture [2], transportation [3] etc. The accumulation of ions in environment has broken the balance of ion concentrations in the ecosystem, and the individual has been exposed to the environment which contains a large amount of metal ions [4]. Cadmium, one of the most dangerous heavy metals, can cause human arcinogenicity [5] and toxicity [6], which has been widely utilized in many fields such as agriculture, industry and metallurgy etc. Unfortunately, the bioaccumulation of Cd²⁺ through the food chains can lead great threat to human being and environment. The excessive intake of Cd^{2+} can damage human organs such as liver and kidneys, and be relative to cancer, cardiovascular diseases, heart disease, and diabetes [7-10]. As an essential element which has been found in the human body, zinc, a secondary abundant transition metal in the Earth, takes part in a wide variety of physiological and pathological processes, such as regulators of gene expression, neural signal transmitters and apoptosis [11-13]. Abnormal amount of zinc will lead to several

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ABSTRACT

A novel bifunctional chemosensor **10** constructed with diarylethene and pyridazine unit has been designed and synthesized with excellent photochromic properties upon UV/Vis radiation. The chemosensor **10** shows prominent selectivity and high sensitivity for Cd^{2+} and Zn^{2+} by obvious fluorescent enhancement with a low detection limit in water-acetonitrile solution ($v_{(water)}$: $v_{(acetonitrile)} = 1:9$). The chemosensor **10** could be utilized as a fluorescent sensor for Cd^{2+} with a limit of detection (LOD) of 2.3 × 10⁻⁶ M. With the presence of Zn^{2+} , the fluorescence of the generated zinc complex enhances remarkably and the limit of detection (LOD) for Zn^{2+} is calculated to be 1.1×10^{-5} M by Job's plot titrations. A logic circuit of this chemosensor **10** has been constructed with the input signals of UV and visible light, Cd^{2+} (or Zn^{2+}) and EDTA and the output signal of the emission intensity. In addition, the concentrations of Cd^{2+} or Zn^{2+} in real water are detected quickly and conveniently by this chemosensor.

diseases including prostate cancer [14], Alzheimer's disease [15], and diabetes [16]. The two elements noted above are in the same group [17], so they have similar physical and chemical features. Therefore, exploration of highly selective sensors for Cd^{2+} and Zn^{2+} will produce priceless value for human being.

Amounts of advanced methods including inductively coupled plasma-atomic emission spectrometry (ICP-AES) [17], inductively coupled plasma-mass spectrometry (ICP-MS) [18] and atomic absorption spectroscopy (AAS) [19] have been widely used for analysis of Cd²⁺ and Zn²⁺. Compared to the methods discussed above, fluorescent probes have the advantages of their easy operation, high sensitivity, good selectivity and low cost [20-26], making people explore the ionic sensors in the realm of chemistry and biology. Among the reported fluorescent probes, diarylethene derivatives showing prominent stability for heat and perfect antifatigue character which could be used in ultimate condition and transformed quickly [27-29] are the most promising candidates. The diarylethene exists two formations of open-ring and closedring, which are also identified as non-conjugated formation and conjugated formation. Upon with the irritation of UV light, the diarylethene can change from open-ring formation to closed-ring formation, for the sake of the absorption wavelength becoming longer and the absorption coefficient ascending. With the stimulation of the identified ion, diarylethene molecule can undergo poly-stable conversion [30]. The above properties could be used to design multi-addressable switches. Although many chemosensors







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Scheme 1. The synthetic route and photochromism of 10.

with the diarylethene units have been designed to recognize the ions [31,32], the sensors based on diarylethene to detect Cd^{2+} and Zn^{2+} of the same group have rarely been reported [33].

In recent decades, chemosensors with special selectivity and high sensitivity for ion detections have been paid more and more attentions due to their extensive applications, including environmental pollution monitoring, medical diagnosis and mineral exploration [34,35] etc. In this work, a novel chemosensor detector for Cd²⁺ and Zn²⁺, based on diarylethene and hydrazinylpyridazine unit connected by Schiff structure, was designed and synthesized in Scheme 1. Schiff base compounds with the lone pair electrons of C=N bond which was a detective site for metal ions exhibited good photochemical properties [36]. Besides, more nitrogen atoms were introduced as chelating sites, such as pyridazine containing two nitrogen atoms [37] and the photochromic diarylethene unit bearing a pyridine unit. Expected as designed, the diarylethene derivative **10** could detect Cd^{2+} and Zn^{2+} in water-acetonitrile solution, with the emission intensity of this sensor dramatically changing comparing alike other diarylethene fluorescence sensors [38,39]. The data characterized by ¹H NMR and ¹³C NMR to describe the structure of **10** was drawn in ESI(Figure S1-S2). With the stimulation of lights and chemical species, we carried out systemically the properties of its photochromism and fluorescence.

2. Experiments

2.1. General procedures and materials

The solvents used in the experiments were analytic, and the reagents purchased from reagent corporations were directly applied. The salt solutions were prepared including HgCl₂, MnCl₂·4H₂O, Al(NO₃)₃·9H₂O, Pb(NO₃)₂, KCl, Cd(NO₃)₂·4H₂O, Ba(NO₃)₂, Sr(NO₃)₂, Cu(NO₃)₂·3H₂O, Ni(NO₃)₃·6H₂O, Zn(NO₃)₂·6H₂O, Fe(NO₃)₃·9H₂O, Cr(NO₃)₃·9H₂O, Co(NO₃)₂·6H₂O, Ca(NO₃)₂·4H₂O, Mg(NO₃)₂·6H₂O. 1 mmol of inorganic ion was weighted and dissolved in water to get the 10 mL aqueous ionic solution (0.1 M). The EDTA solution was made up by mixing ethylene diamine tetraacetic acid disodium salt (Na₂EDTA) (0.2 mmol) and distilled water (2 mL).

UV–Vis spectra were measured with an Agilent 8453 UV–Vis spectrophotometer. Mass spectrometry analysis was operated on an Agilent 1100 ion trap MSD spectrometer. ¹H and ¹³C NMR spectra were recorded on a Bruker AV400 (400 MHz) spectrometer using DMSO-d₆, CDCl₃ and CD₂Cl₂ as the solvents and tetramethylsilane (TMS) as the internal standard. Fluorescence spectra were collected on a Hitachi F–4600 fluorescence spectrophotometer. Infrared spectra (IR) were recorded on a Bruker Vertex–70 spectrometer. The fluorescence quantum yield was measured with an Absolute PL

Quantum Yield Spectrometer QYC11347-11.

2.2. Synthesis of 10

The synthesis route of 1-(2,5-dimethylthiophen-3-yl)-2-{2methylthiophen -5-[5-pyridinyl-2-(methylene)hydrazineyl-6chloropydidazin]-3-yl}perfluorocyclopentene(**10**) was verified in Scheme 1. Based on the reported method [37,38], compound 2 and compound 3 were obtained.

2.2.1. Synthesis of compound 2

The compound 1 (2.0 g, 13.4 mmol) was dissolved in 50 mL 32% ammonia water with a weak nitrogen flow at the same time, then added hydrazine hydrate (4.3 g, 25%, 21.5 mmol). Stirring the mixture was for 3 h at the reflux temperature. Then the reaction was stopped, cooled into room temperature, and put into ice bath with beige solids precipitated, and the precipitated was filtered and vacuum dried to get compound 2 (1.5 g , 10.42 mmol, yield 77.8%). ¹H NMR (DMSO-*d*₆, 400 MHz), δ (ppm): 4.35 (s, 2H), 7.08 (d, *J* = 8.0 Hz, 1H), 7.41 (d, *J* = 8.0 Hz, 1H), 8.20 (s, 1H). The HRMS was shown in Figure S3.

2.2.2. Synthesis of compound 10

Diarylethene derivative **10** was constructed via the route in Scheme 1. Compound 2 (0.05 g, 0.1 mmol) and compound 3 (0.014 g, 0.1 mmol) were dissolved in 10 mL absolute methanol, and heated at reflux temperature for 12 h. Then the mixture was descended to room temperature with light yellow power precipitated. The precipitated was washed with methanol and dried to obtain **10** (0.037 g, 0.06 mmol, yield 57.8%). ¹H NMR (CDCl₃, 400 MHz), δ (ppm): 1.88 (s, 3H), 1.97 (s, 3H), 2.43 (s, 3H), 6.73 (s, 1H), 7.34 (s, 1H), 7.43–7.45 (d, J = 8.0 Hz, 1H), 7.71–7.74 (d, J = 12.0 Hz, 1H), 7.83–7.85 (d, J = 8.0 Hz, 1H), 7.91–7.93 (d, J = 8.0 Hz, 1H), 8.79 (s, 1H), 8.20 (s, 1H),10.54 (s, 1H). ¹³C NMR (100 MHz, CDCl₃) δ : 14.46, 14.68, 15.26, 116.51, 120.59, 124.28, 124.57, 124.81, 126.75, 129.34, 130.36, 132.96, 135.16, 137.98, 138.19, 139.96, 142.90, 146.53, 149.44, 152.67, 158.46.

3. Results and discussions

3.1. Photochromism and fluorescent properties of 10

The photochromic properties of **10**, at the concentration of 2.0×10^{-5} M, were studied in water-acetonitrile (v:v = 1:9) at room temperature in Fig. 1A. The maximum absorption peak of **10** was observed at 358 nm ($\varepsilon = 5.2 \times 10^4$ mol⁻¹ L cm⁻¹) due to the π - π * transition [40]. The absorption peak at 358 nm would descend upon the irritation with 297 nm light. Meanwhile, a new absorption peak



Fig. 1. Diarylethene derivative 10 (A) ultraviolet absorption spectrogram. and color change of solution (B) the change of emission intensity.

at 569 nm ($\varepsilon = 1.2 \times 10^4 \text{ mol}^{-1} \text{ L cm}^{-1}$) appeared, accompanied with the color changing from colorless to purple owing to the photocyclization of **10** to **1C**. Reached the photostationary state (PSS), three isosbestic points had been observed at 260 nm, 300 nm, 377 nm respectively, which exhibited a reversible photochromic reaction of two components. Upon irritation with visible light ($\lambda > 500$ nm), the absorption peak changed totally from closed-ring **1C** to open-ring **10** with the color fading from purple to colorless. The quantum yields of open ring $\phi_{\text{o-c}}$ was 0.005, compared with 1,2-bis(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene.

In Figure S4, the water-acetonitrile (v:v = 1:9) solution of diarylethene **10**, at room temperature, was lighted by the alternating UV/Vis light to examine the anti-fatigue properties. The result provided that the diarylethene derivative **10** degraded at the rate of 23.75% after open and close ring 10 times.

The fluorescent properties of **10** were also determined in the water-acetonitrile (v:v = 1:9) solution. The emission peak at 444 nm of **10** was observed with 380 nm light irradiation in Fig. 1B. Upon irritation with 297 nm light, the emission intensity of **10** descended remarkably, because the new isomer **1C** with non-fluorescence was appeared [41]. The PSS reached, the descending

tendency of emission peak had ended. With the emission decrease of *ca*. 62.9%, the diarylethene derivative exhibited high fluorescent modulation efficiency. The residual fluorescence of PSS told the fact that the diarylethene **10** did not completely react into **1C**. Contrarily, the cyclization **1C**, stimulated by visible light ($\lambda > 500$ nm), completely regenerated into open-ring isomer **10**, and the color would be recovered.

3.2. The ions detection of diarylethene 10

In order to investigate the response of **10** to various metal ions including K⁺, Ba²⁺, Hg²⁺, Sr²⁺, Cr³⁺, Fe³⁺, Mg²⁺, Mn²⁺, Ca²⁺, Ni²⁺, Pb²⁺, Sn²⁺, Co²⁺, Cu²⁺, Cd²⁺ and Zn²⁺, they were added respectively in water-acetonitrile solution (v:v = 1:9) to observe the alternation of emission peak intensity and fluorescent color. As shown in Fig. 2, excited by the 380 nm UV light, the emission peak intensity and fluorescent color. As shown in Fig. 2, excited by the 380 nm UV light, the emission peak intensity and fluorescent color of **10** remarkably changed. When 5.0 equiv. Cd²⁺ were added, the fluorescence of **10** at 482 nm was enhanced greatly, and the fluorescent color turned from dark to cyan. Meanwhile, when 5.0 equiv. Zn²⁺ was added, the fluorescence of **10** at 493 nm was enhanced remarkably and the color altered



Blank Cd²⁺ Zn²⁺ Hg²⁺ Al³⁺ Cu²⁺ Ca²⁺ Mn²⁺ K⁺ Mg²⁺ Sr²⁺ Pb²⁺ Ba²⁺ Co²⁺ Ni²⁺ Fe³⁺ Cr³⁺ Ag⁺ Sn²⁺

Fig. 2. Diarylethene derivative **10** at the water-acetonitrole solution (v:v = 1:9) (A) the emission intensity stimulated by different metal ions; (B) selectivity of bar chart for metal ions; (C) emission color after adding different ions.



Fig. 3. Diarylethene derivative 10 at the water-acetonitrole solution (v:v = 1:9) altered by Cd^{2+} (A)absorption spectra and color change of 10 (B) absorption spectra and color change of 1C.

from dark to orange yellow. The change stimulated by other ions would not be observed with naked eyes in Fig. 2B. The enhancement of emission intensities contributed to this reason that diarylethene **10** combined with Cd^{2+} or Zn^{2+} respectively to form **10–Cd**²⁺(**10'**) complex or **10–Zn**²⁺(**10''**) complex. The result manifested that the diarylethene derivative **10** could be viewed as a fluorescent sensor for Cd^{2+} and Zn^{2+} with eminent selectivity in Fig. 2C.

3.3. The features of **10** toward Cd^{2+}

With the addition of Cd²⁺, the absorption peak at 403 nm slowly



Fig. 4. Ultraviolet absorption spectrum and color change of 10'at the water-acetonitrile solution (v:v = 1:9) lighted by UV/Vis.

increased with the peak at 358 nm descending as the complex $10-Cd^{2+}(10')$ appeared, and the color of the solution turned from colorless to pale brown. The quantum yield of **10'** was 0.040. As the excessive EDTA was added into **10'** solution, the state of solution recovered to the primary state as it was shown in Fig. 3A. Accompanied with the addition of excessive Cd^{2+} into **1C** solution, the solution altered from purple to pale brown due to the decrease of the absorption peak at 371 nm and the increase of the absorption peak at 408 nm. Shown in Fig. 3B, the color of **1C**–Cd²⁺(**1C'**) would recover to the initial state with the excessive addition of EDTA.

The photochromic properties of **10'** were further studied. As is shown in Fig. 4, the compound of **10'**, lighted by ultraviolet light at 297 nm, appeared a new absorption peak at 581 nm which would be increased gradually with the passage of irritation going on. As reached the PSS, two absorptive points were observed at 355 nm and 421 nm, respectively. The closed-ring isomer **1C'** would be produced at the same time, and the color of solution altered from yellow to brown. By contrary, the solution of **1C'**, stimulated by visible light ($\lambda > 500$ nm), changed gradually to open-ring isomer **10'**, and the color of solution altered from brown to dark yellow.

With the accumulation of Cd^{2+} ions, the fluorescent titration experiment would be studied at the water-acetonitrile solution (v:v = 1:9) of the compound **10** (2.0×10^{-5} mol L⁻¹) at the room temperature to obtain the change of fluorescent spectrum. As shown in Fig. 5A, with the addition of Cd^{2+} into the water-acetonitrile solution of **10**, the emission peak shifted red gradually from 442 nm to 485 nm and the emission intensity ascended with the increase of Cd^{2+} . The emission intensity would continue to become higher until the concentration of Cd^{2+} was added to the 3.6 equiv, with the emission peaks altering from 471 nm to 485 nm.



Fig. 5. Diarylethene derivative **10** at the water-acetonitrile solution (A) emission intensity and fluorescent color with the addition of Cd^{2+} or EDTA (B) titration cure of **10** added Cd^{2+} and linear relationship between emission intensity and the concentrations of Cd^{2+} .



Fig. 6. Fluorescent switch of 10' at the water-acetonitrile solution (v:v = 1:9).

Continuing to add the Cd^{2+} ion, the emission intensity would not change. A new complex $10-Cd^{2+}$ (10') would be produced with the fluorescent color of the solution altering from dark to cyan. Excessive EDTA added into the solution of $10-Cd^{2+}$ (10'), the fluorescent spectrum and fluorescent color would recover to the initial state, which indicated that EDTA could dissociate the Cd^{2+} from 10'. Further, the relationship between Cd^{2+} and emission intensity was studied in Fig. 5B. The result indicated that the emission intensity was positively correlated with the concentration of Cd^{2+} at a certain concentration range. Thus, the complex 10could be considered as a chemosensor to detect the ion of Cd^{2+} .

The emission intensity of **10'** was further studied. As verified in Fig. 6, upon the irritation with ultraviolet at 297 nm, the emission intensity of **10'** at 501 nm descended gradually, and the fluorescent color of solution became dark yellow from orange. When reached the PSS, the emission peak intensity decreased from 411.8 to 203.2, along with the formation of closed-ring **1C'**. Correspondingly, when exposed to visible light ($\lambda > 500$ nm), the formation of closed-ring **1C'** would recover to the formation of open-ring **10**.

Furthermore, the fluorescent titration experiment was studied at the room temperature to investigate the relation between the water-acetonitrile of **1C** and Cd^{2+} . As shown in Fig. 7, the Cd^{2+} ion was added into the water-acetonitrile solution of **1C** on the dropwise. The emission peak intensity, changing with the addition of Cd^{2+} , would ascend gradually with red shift. After Cd^{2+} was added 2.1 equiv., the emission peak intensity got the maximum, and the excessive Cd^{2+} did not make the intensity change. Red-shift of the emission peak altered from 445 nm to 500 nm in accompany with the color becoming dark cyan from dark. After addition of excessive EDTA, the fluorescent peak intensity and color recovered to the statement of **1C**.



Fig. 7. Fluorescent switch of 1C' at the water-acetonitrile solution (v:v = 1:9).



Fig. 8. Anti-interference experiment and error bars of it between **10** $(2.0 \times 10^{-5} \text{ M})$ at the water-acetonitrile solution and different metal ions (5.0 equiv.) Black Blank: **10** and different metal ions; Red Blank.

The anti-interference experiment was operated at the room temperature to examine fluorescent selectivity of **10** toward various metal ions (5.0 equiv. of **10**) such as Ca²⁺, Sn²⁺, K+, Pb²⁺, Mg²⁺, Cr³⁺, Co²⁺, Hg²⁺, Mn²⁺, Fe³⁺, Cu²⁺, Ba²⁺, Ni²⁺, Ag⁺, Al³⁺, Sr²⁺ in water-acetonitrile solution. When the Cd²⁺(5.0 equiv.) ion was added into **10** solution coexisted with various metal ions, the emission intensity was enhanced by Sn²⁺ and Ba²⁺, also quenched by Co²⁺, Cu²⁺, Ni²⁺ in Fig. 8. The results showed that most metal ions did not interfere the detection of Zn²⁺ and Cd²⁺, except the metal ions of Co²⁺, Cu²⁺ and Ni²⁺.

3.4. The characters of **10** toward Zn^{2+}

As shown in Figure S5A, when the ion of Zn^{2+} was added in the solution of **10**, the absorption peak at 358 nm would be descended, and a new peak at 403 nm would occur with the reason of the formation of complex of $10-Zn^{2+}(10'')$ whose quantum yield was 0.029. With the increase of Zn^{2+} , the new peak would ascend until the 16 equiv. ion of Zn^{2+} was added. Two clear isosbestic points were observed at 314 nm and 382 nm at the same time, accompanied with the color changing from colorless to dark yellow. Then, when excessive EDTA was added into the 10'' solution, the solution could recover to initial state. When 16 equiv. Zn^{2+} was added into the **1C** solution, the color turned from purple to earthy yellow in Figure S5B, with the reason that the absorption peaks at 371 nm descended and 576 nm ascended. The $1C-Zn^{2+}(1C'')$ solution would recover to the state of **1C** after the addition of excessive EDTA.

The photochromic properties of **10**" were further studied. Upon the irritation of 297 nm light, the **10**" solution altered to the closedring isomer **1C**" with a new absorption peak at 581 nm, and the color changed from dark yellow to brown with naked-eye observation. Using the stimulation of visible light ($\lambda > 500$ nm), compound **1C**" totally altered to open-ring isomer **10**", with the color changing to yellow in Figure S6.

When the solution of Zn^{2+} was added into the water-acetonitrile solution of **10** on the drop-wise, the emission peak of **10** at the state of open-ring shifted red gradually with the enhancement of peak. The emission peak intensity, altered from 422 nm to 498 nm, reached the top, as the Zn^{2+} was added at the concentration of 4.8 equiv. shown in Figure S7A. With the complex **10–Zn^{2+}(10'')** generating, the color of the solution became orange yellow from dark. After adding excessive EDTA in **10**'' solution, the fluorescent spectrum and fluorescent color recovered to **10**. The result was further analyzed that at a certain concentration rang the emission intensity at 486 nm was linear with the concentration of Zn^{2+} in Figure S7B. The results discussed above proved that complex **10** could be considered as a chemosensor for Zn^{2+} .

The emission peak intensity of complex **10**" decreased steadily when stimulated by ultraviolet light. Reaching PSS, the emission peak intensity descended from 174.4 to 106.6 because of the new formation of closed-ring **10**". The color of the solution altered from orange to dark yellow in Figure S8. Exposed to the visible light ($\lambda > 500$ nm), the emission peak intensity of **1C**" could recover to the initial statement.

The fluorescent titration experiment, depicted in Figure S9, was carried out in the water-acetonitrile solution of **1C** adding Zn^{2+} ion on the drop. As the addition of Zn^{2+} into the water-acetonitrile of **1C**, the emission peak shifted to higher with the enhancement of intensity. The peak reached the maximum, as the addition of Zn^{2+} reached 4.0 equiv., with the formation of complex **1C**–**Zn**²⁺(**1C**"). The color of solution became dark yellow from dark. After the excessive EDTA was added, the fluorescent color and the emission intensity returned to the original.

Ca²⁺, K+, Pb²⁺, Cr³⁺, Ba²⁺, Co²⁺, Sn²⁺, Mn²⁺, Fe³⁺, Mg²⁺, Cu²⁺, Ag⁺, Ni²⁺, Al³⁺, Sr²⁺ and Hg²⁺ were added into the solution of **10** to examine the interference of them with the detection of Zn²⁺ ion. As shown in Figure S10., when Zn²⁺ (5.0 equiv.) was added into **10** solution containing various metal ions, the emission intensity was increased by Cd²⁺, quenched by Co²⁺, Cu²⁺, Ni²⁺, and inhibited by Fe³⁺.

3.5. Mechanism of **10** to Cd^{2+} and Zn^{2+}

The Job's plot of UV–Vis titration of **10** toward Cd^{2+} and Zn^{2+} was put forward to further elucidate the interaction between **10**

and Cd^{2+} or Zn^{2+} in the water-acetonitrile solution (v:v = 1:9). As shown in Fig. 9A, when the molar ratio of $[Cd^{2+}]/([Cd^{2+}]+[10])$ reached the point of 0.5, the emission intensity got the top, which showed that the combination ratio between compound 10 and Cd²⁺ was 1:1. Meanwhile, the association constant (Ka) between **10** and Cd^{2+} in the water-acetonitrile solution (v:v = 1:9) was $1.7 \times 10^4 \text{ mol}^{-1} \text{ L} (\text{R} = 0.99439)$ [42] in Fig. 9B by the equation of Benesi-Hildebrand, Based on the method reported above, the limit of detection for Cd^{2+} could reach 2.3 × 10⁻⁶ mol L⁻¹ [42] in Fig. 9C. Similarly, Figure S11A manifested the stoichiomical relation between **10** and Zn^{2+} in the water-acetonitrile solution (v:v = 1:9) would be obtained by the Job's plot. With the alteration of molar ratio of $[Zn^{2+}]/([Zn^{2+}]+[10])$ achieving the point of 0.5, the emission intensity ascended on the top, exhibiting that the stoichiomecal ratio between **10** and Zn^{2+} was 1:1. Based on the equation of Benesi-Hildebrand noted above, the association constant (Ka) between the **10** and Zn^{2+} in the water-acetonitrile solution (v:v = 1:9) was $4.9 \times 10^3 \text{ mol}^{-1} \text{ L}(\text{R} = 0.99103)$ in Figure S11B. The limit of detection (LOT) for Zn^{2+} could reach 1.1×10^{-5} mol L⁻¹ demonstrated in Figure S11C.

In order to further research the binding formation, the ESI-MS, titration experiments and IR spectra of **10**, **10'** and **10**" were operated. The 1 : 1 coordination stoichiometry of **10** with Cd^{2+} or Zn^{2+} was further confirmed by the ESI mass spectrometry (ESI-MS) analysis (Figure S12). As shown in Figure S12A, a characteristic peak at 849.7 m/z for $[Cd^{2+}+10+2NO_3^{-}-H^+]$ (calcd 850.4) was observed. Meanwhile, Figure S12B manifested a characteristic peak at 799.8 m/z which was for $[Zn^{2+}+10+2NO_3^{-}-H^+]$ with the calculation of 800.4. ¹H NMR titration experiments were done in CDCl₃ to investigate the binding mode of **10** with Cd^{2+} or Zn^{2+} . A new peak at 4.692 appeared as shown in Figure S13., when Cd^{2+} ion was



Fig. 9. Diarylethene derivative **10** at the water-acetonitrile solution (v:v = 1:9) (A) the complex ration and linear relationship between **10** and Cd^{2+} (B) association constant and linear relationship of association constant between **10** and Cd^{2+} (C) LOD and linear relationship of **10** for Cd^{2+} .

added. In order to exclude the influence of water, deuterium oxide was titrated in the solution of **10**. As few deuterium was added, a new peak at 4.692 appeared in Figure S14, which indicated that the new peak was the peak of deuterium oxide and Cd^{2+} ion did not influence the shift of **10**. After the addition of Zn^{2+} ion to the **10** solution, a new peak at 4.692 was examined shown in Figure S15, and as the addition of deuterium oxide a new peak at 4.692 was also observed in Figure S14. This phenomenon also showed that the new peak was the peak of deuterium oxide and Zn^{2+} ion did not influence the shift of **10**. In addition, IR spectrum was carried out to detect the binding sites shown in Figure S16. After adding the ions of Cd^{2+} or Zn^{2+} respectively, a new peak at 2400 cm⁻¹ appeared, manifesting that a triple bind would form. According to what had been discussed above, the binding mode between **10** and Cd²⁺ or Zn^{2+} was verified in Scheme 2.

3.6. The practical application

3.6.1. The detection of actual water

The application of **10** to detect the ions of Cd^{2+} or Zn^{2+} was

operated. The method that was used to measure the contents of Cd^{2+} or Zn^{2+} in actual water was reported [43,44]. Water samples were filtered with 0.2 mm membranes to filter the precipitation. Then, different contents of Cd^{2+} or Zn^{2+} were added in the actual water sample to prepare different concentration gradients. In order to compare the experimental data, the parallel testes were carried out. The ions of Cd^{2+} or Zn^{2+} were dissolved into deionized water to prepare samples with the concentrations similar to the actual concentrations before and determine the standard curve. Fluorescence of the two samples in the corresponding gradient was investigated, and the actual value was calculated by comparing the two data of same concentrations. One sample was conducted three times and calculated the average data, and the Recover (%), RSD (%) and Relative error (%) were obtained. The results were shown in Table 1 and Table 2.

3.6.2. Application for logic gate

Discussed the properties of the diarylethene derivative above, the fluorescent emission intensity could be effectively adjusted by Cd^{2+} (or Zn^{2+})/EDTA and UV/Vis light in water-acetronitrile



Scheme 2. Photochromism, color and fluorescence alteration of 10 stimulated by Cd^{2+}/Zn^{2+} and UV/Vis lights.

Table 1

Concentration of Cd²⁺ in practical samples.

Sample	Cd^{2+} spiked (µmol L ⁻¹)	Cd^{2+} recovered (µmol L ⁻¹)	Recover (%)	RSD (%)	Relative error (%)
Yao Lake	6	6.02	100.33	±2.51	0.33
	10	10.17	101.70	±4.28	1.7
	16	16.01	100.06	±1.82	0.0625
Tap Water	6	5.87	97.83	±3.01	-2.17
	10	10.13	101.30	±3.11	1.3
	16.0	15.82	98.88	±2.37	-0.1125

Table 2

Concentration of Zn²⁺ in practical samples.

Sample	Zn^{2+} spiked (µmol L ⁻¹)	Zn^{2+} recovered (µmol L ⁻¹)	Recover (%)	RSD (%)	Relative error (%)
Yao Lake	6.0	5.93	99.83	±3.56	-1.17
	10.0	9.95	99.50	±3.65	-0.5
	16.0	15.93	99.56	±2.32	-0.438
Tap Water	6.0	5.99	99.83	± 1.04	-0.17
	10.0	9.98	99.80	±2.25	-0.2
	16.0	16.01	100.06	±1.01	-0.0625



Fig. 10. Logic circuits constructed by 10 and the symbols: In1 (UV light), In2 (visible light), In3 (Zn²⁺ or Cd²⁺), In4 (EDTA).

solution to create a logic gate (Fig. 10). The four input signals were In1: 297 nm UV light, In2: $\lambda > 500$ nm visible light, In3: Cd²⁺ (or Zn²⁺), and In4: EDTA, and the fluorescent emission intensity of **10**

at 485 nm (or 498 nm) was the output signal. When the emission intensity was 2-fold enhancement than the original state, output signal could be looked up as 'on' with a Boolean value of '1'.

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Input	Output					
InA (UV)	InB (Vis)	$InC(Zn^{2+}orCd^{2+})$	InD (EDTA)	λ em = 498 nm or 485 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		

Otherwise, it was thought as 'off' state with a Boolean value of '0'. Stimulated by those four signals, the diarylethene derivative **10** presented on-off-on colorimetric switchable behavior. Taking strings of '0, 0, 1, and 0' for instance, they relate to input signals of 'In A, In B, In C, and In D' with the state of 'off, off, on, and off'. Under those operation, **10** was converted to **10–Cd²⁺** (or **10–Zn²⁺**) stimulated by Cd²⁺ (or Zn²⁺) with the emission intensity ascending remarkably, resulting in the output signal 'on' and Boolean value '1'. Similarly, different operations could get various outputs. All possible logic circuits were listed in Table 3.

4. Conclusion

A novel diarylethene with pyridazine unit, showing high sensitivity and selectivity for Cd^{2+} and Zn^{2+} in water-acetonitrile (v:v = 1:9), was designed and synthesized. In addition, the applications of logic gate and the detection of Cd^{2+} or Zn^{2+} in real water were realized by the novel diarylethene fluorescent sensor. These works would be beneficial to the researchers of fluorescent sensors based on diarylethene unit.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.tet.2020.131618.

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