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A novel sensitive sensor for Cu²⁺ and multi-switch based on a diarylethene with a 2-(2'-hydroxyphenyl)benzothiazole unit

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Abstract: A new asymmetrical photochromic diarylethene with a 2-(2'-hydroxyphenyl)benzothiazole unit has been synthesized. It underwent reversible cyclization and cycloreversion reactions upon alternating irradiation with lower energy UV (297 nm, 25 μ W/cm²) and visible light, while it could induce intramolecular proton transfer reaction upon irradiation with higher energy UV light (254 nm, 92 μ W/cm²) with distinct color change. The absorption maximum of the closed-ring isomer was redshifted from 539 nm to 660 nm and the color changed from purple to cyan when the diarylethene was stimulated with base. Furthermore, addition of acid enhanced its fluorescence intensity by 5.5 fold and the emission peak was blueshifted from 596 nm to 570 nm with a concomitant color change from light orange to bright green, while base could efficiently quench its fluorescence intensity. Finally, the diarylethene was highly selective towards Cu²⁺ with significant absorption and fluorescence changes, which makes the 'naked-eye' detection of Cu²⁺ possible.

Keywords: Diarylethene; Photochromism; Fluorescence switch; Multi-switch; Copper(\Box) recognition.

1. Introduction

Photochromism is reversible transformations between two isomers with different characteristics induced by alternating illumination with UV and visible light. During the past few decades, many photochromic materials have attracted numerous attentions because of their potential applications in photonic devices and optical memory media.¹ Among various types of photochromic compounds, diarylethenes are most promising candidates for optoelectronic applications owing to their excellent thermal stability, remarkable fatigue resistance, higher conversion rate, and rapid response.² Based on these properties, many functional diarylethene molecules, which possess multi-responsive, fluorescence probing, ion recognition, and chemosensing abilities have been designed and constructed in the past few years.³

It is a hot topic in current chemical research for designing and synthesizing multiple responsive switching molecules, and integrating switchable unit into a function molecule is an effective method to construct a multiple responsive switching molecule, whose properties can be efficiently tuned by the switchable unit. Diaryelthene is an ideal molecule for switchable unit because it could be transformed distinctly from one form to the other through photoirradiation. Generally, conventional switches of diarylethenes include photochromic switches,⁴ fluorescence switches,⁵ and pH switches.⁶ So far, many multi-switching molecules based on diarylethene skeletons have been developed. For example, Tian *et al.* constructed a donor-photochromic bridge-acceptor (D-P-A) system based on electron-donating triphenylamine/diethylphenylamine and electron-accepting dicyanovinyl group at each end of dithienylethene. Its fluorescence was sharply enhanced through the nucleophilic reactions between dicyanovinyl group and $CN^{-,7}$ In a previous work, we designed and synthesized a multi-addressable molecular switch, in which a 2-benzothiazyl group was appended to diarylethene core via a salicylidene

Schiff base. Its fluorescence emission wavelength and intensity sensitively responded to both pH and cation stimuli. On the basis of these properties, two logic circuits with four inputs and one output were constructed on a single molecule.⁸ Additionally, cation sensors based on photochromic diarylethenes also have achieved much progress, and some functionalities such as crown ether,⁹ rhodamine,¹⁰ pyridine,¹¹ quinoline, and imidazole derivatives¹² have been successfully incorporated into diarylethene systems as ion recognition units.

Copper ion is an essential trace element, and it plays an important role in the human body and plant tissues during life processes.¹³ However, copper ion could cause neurodegenerative diseases, such as Alzheimer's and Wilson's diseases at high concentrations.¹⁴ In addition, it is also a widespread metal pollutant in nature. Sometimes copper ion exhibits high toxicity even at submicromolar concentration for certain microorganisms.¹⁵ Due to the dual properties of copper ion, much attention has been paid to the development of chemosensors of Cu^{2+,16} In past several decades, many works focused on designing highly selective fluorescence sensors for Cu²⁺ based on diarylethene^{10,17}. However, colorimetric sensors for convenient detection of Cu²⁺ are rarely reported.¹⁸2-(2'-Hydroxyphenyl)benzothiazole (HBT) group is a fascinating functional group because the phenolate and the nitrogen atoms in the benzothiazolyl could be used as proton donors /acceptors.¹⁹ Therefore, it could be used as reactive sites for acid/base or metal ion stimuli. According to the unique physicochemical properties of HBT group, we believe that introducing a HBT unit into a diarylethene skeleton will form a multi-responsive molecule. In this work, we designed and synthesized a new asymmetrical diarylethene with HBT unit. Its photochromism and fluorescence properties were studied systemically. The photochromic process of diarylethene 1 is shown in Scheme 1.



Scheme 1. Photochromism of diarylethene 10.

2. Experimental

2.1. General methods

All solvents were purified by distillation before use. ¹H NMR and ¹³C NMR spectra were recorded on a Bruker AV400 (400 MHz) spectrometer with DMSO- d_6 as the solvent and tetramethylsilane as an internal standard. Infrared spectra (IR) were recorded on a Bruker Vertex-70 spectrometer. Melting point was measured on a WRS-1B melting point apparatus. Absorption spectra were measured using an Agilent 8453 UV/VIS spectrophotometer. Photoirradiation was carried out using an SHG-200 UV lamp, a CX-21 ultraviolet fluorescence analysis cabinet, and a BMH-250 visible lamp. The light intensity was 25 μ W/cm² for UV (297 nm) light, 92 μ W/cm² for UV (254 nm) light and 13.5 mW/cm² for visible light, respectively. Fluorescence spectra were measured using a Hitachi F-4600 spectrophotometer, and the breadths of excitation and emission slit were both selected 5 nm. Fluorescence quantumn yield was measured with an Absolute PL Quantumn Yield Spectrometer QY C11347-11. Expect for Mn²⁺, K⁺, and Ba²⁺ (their counterions were chloride ions), other metal ions were obtained by the dissolution of their respective metal nitrates (0.10 mmol) in distilled water (10.00mL). Stock solution of NaOH (0.1 mol L⁻¹) were prepared in deionized water.

2.2 Synthesis of 10

The synthetic route for diarylethene **1O** is shown in Scheme 2. First, the diarylethene salicylaldehyde derivative **2** was prepared by the reported method.²⁰ In a 100 mL flask, diarylethene **2** (0.49 g, 1.00

mmol) and thiol aniline (**3**) (0.13 g, 1.00 mmol) were dissolved in anhydrous ethanol (50.0 mL) containing 0.02 equiv acetic acid. The mixture was stirred at 350 K under reflux for 24 h. Then, the reaction was allowed to slowly cool to the room temperature. Then the crude product was purified by recrystallization. The yellow soil powder was filtered off and washed with EtOH. Pure diarylethene **10** (0.27 g) was obtained in 45% yield after vacuum drying. M.p. 198-199 °C; IR (KBr, v, cm⁻¹): 541, 644, 687, 760, 808, 847, 896, 956, 1067, 1128, 1198, 1273, 1436, 1505, 1598, 3062; ⁻¹H NMR (400 MHz, DMSO-*d*₆, ppm): δ 2.09 (s, 3H, -CH₃), 2.14 (s, 3H, -CH₃), 2.36 (s, 3H, -CH₃), 7.15 (d, 1H, phenyl-H, *J* = 8.0 Hz), 7.45 (d, 2H, phenyl-H, *J* = 8.0 Hz), 7.47 (s, 1H, thiophene-H), 7.56 (t, 1H, phenyl-H, *J* = 8.0 Hz), 7.72 (d, 1H, phenyl-H, *J* = 8.0 Hz), 8.11 (d, 1H, phenyl-H, *J* = 8.0 Hz), 8.15 (d, 1H, phenyl-H, *J* = 8.0 Hz), 8.44 (s, 1H, phenyl-H), 11.78 (s, 1H, -OH). ¹³C NMR (100 MHz, DMSO-*d*₆, TMS): δ =10.2, 11.7, 14.0, 103.9, 117.8, 119.3, 121.7, 122.3, 124.2, 124.3, 124.9, 125.1, 126.4, 129.4, 134.9, 140.6, 141.6, 151.4, 156.2, 158.1, 163.5, 170.2; HRMS-ESI (*m*/*z*): [M+H]⁺ Calcd. For (C₂₈H₁₈F₆N₂O₂S₂), 593.0792, found: 593.0709.



Scheme 2. Synthetic route to diarylethene 1O.

3. Results and discussion

3.1 Photochromism of 1



Fig. 1. Absorption spectral changes of 1 by photoirradiation in acetonitrile $(2.0 \times 10^{-5} \text{ mol } \text{L}^{-1})$ at room

temperature.

The absorption spectra changes of **1** in acetonitrile solution $(2.0 \times 10^{5} \text{ mol } \text{L}^{-1})$ under irradiation with UV and visible light at appropriate wavelength are shown in Fig. 1. The open-ring isomer of 1 was colorless in solution with an intense absorption band at 295 nm (ε , 4.60 × 10⁴ L mol⁻¹ cm⁻¹) corresponding to the $\pi \rightarrow \pi^*$ transitions. Upon irradiation with UV light ($\lambda = 297$ nm, 25 μ W/cm²), a new absorption band at 539 nm (ε , 2.24 × 10³ L mol⁻¹ cm⁻¹) was observed, indicating the formation of the closed-ring isomer 1C with color change from colorless to light purple. The photostationary state (PSS) was achieved after 10 was irradiated for 30 min, and the conversion was estimated to ca. 40% by ¹H NMR analysis. The original absorption spectrum could recover completely upon irradiation with visible light ($\lambda \ge 500$ nm). The result indicated that the closed-ring isomer (1C) could be reversed back to the open-ring isomer (10). The coloration–decoloration cycles of 1 could be repeated more than 100 times with negligible degradation (Fig. S1, Supporting information (SI)). The cyclization and cycloreversion quantum yields determined in acetonitrile of 1 were by using 1,2-bis(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene as a reference,²¹ and the values were measured as 0.02 and 0.59, respectively. Compared to the precursor compound 2^{20} , the cyclization

quantum yield of 1 ($\Phi_{1, O-C} = 0.02$) was much lower than that of 2 ($\Phi_{2, O-C} = 0.10$), while the cycloreversion quantum yield of 1 ($\Phi_{1, C-0} = 0.59$) was much higher than that of 2 ($\Phi_{2, C-0} = 0.08$). The results shown that the benzothiazolyl group at the terminal phenol could remarkably inhibit the photocyclization of 10, but notably increase the ring-opening reaction of 1C. Additionally, it is worth noting that the light purple solution of 1C could be changed to red upon further irradiation with high energy UV light ($\lambda = 254$ nm, 92 μ W/cm²). Upon illumination with 254 nm light, the absorption band of 1C at 539 nm hypochromatically shifted to 483 nm accompanied with the molar absorption coefficient sharply increased from ε (1C, 2.24 ×10³ L mol⁻¹ cm⁻¹) to ε' (1C', 1.24 × 10⁴ L mol⁻¹ cm⁻¹) (Fig. 2A). It was possible that the closed-ring isomer of 1C underwent intramolecular proton transfer from the phenol to the benzothiazolyl group, inducing the structure of 1C to change from the enol form to ketone form (Scheme 3).²² After photoirradiation with 254 nm light for 20 min, the PSS of 1C' was arrived. Subsequently, the absorption band of 1C' at 483 nm gradually decreased when it was irradiated with appropriate visible light ($\lambda \ge 500$ nm). Unfortunately, the red color solution of 1C' could not be bleached entirely after irradiation with visible light for 2 hrs (Fig. 2B). The results indicated that the ketone form closed-ring isomer of 1C' was stable and less photoactive to visible light.²³ In order to determine the structure of ketone form (1C'), the 2-(2'-hydroxyphenyl) benzothiazole (HBT) group was synthesized. Fig. S2 shows the absorption spectral change of HBT group induced by 254 nm UV light. The results demonstrated that the original peak at 272 nm and 349 nm gradually decreased when irradiation with 254 nm light. It is worth noting that the process is irreversible. In addition, the 1 H NMR change of HBT group illuminated by 254 nm UV light was also obtained. As shown in Fig. S3, a new signal peak appeared at 5.22 ppm (N–H), while the integral area of the signal peak at 12.80 ppm (O-H) was become lower than before photoirradiation. The results demonstrated that the hydroxy

proton (O–H) of HBT group was transfer to the benzothiazolyl group (N–H) during this process. Moreover, the MS-ESI date shown that **10** and **1C'** with the same molecular weight (Fig. S4, SI), which further verified only photo-induced intramolecular proton transfer reaction was take place during the process of **10** changed to **1C'**.



Fig. 2. Absorption spectral changes of **1C** by photoirradiation in acetonitrile $(2.0 \times 10^{-5} \text{ mol } \text{L}^{-1})$: (A) absorption spectral changes of **1C** upon irradiation with 254 nm light; (B) absorption spectral changes



of $1C^\prime$ upon alternating irradiation with visible light and 254 nm light.

Scheme 3. Structural and color changes among different forms of 1 with different UV light in

acetonitrile $(2.0 \times 10^{-5} \text{ mol } \text{L}^{-1})$.

3.2 Multi-photochromism of 1 with stimulation of base/acid

Diarylethene 1 also exhibited multi-responsive characteristics when it was stimulated with base/acid

and light. In acetonitrile, the deprotonated $10-H^+$ was obtained after the addition of NaOH solution (8.0 μ L, C = 0.10 mol L⁻¹). The absorption maximum of **10** at 295 nm gradually decreased, when NaOH solution was added (0 to 20.0 equiv). Meanwhile, two new absorption bands appeared at 345 and 427 nm with color change from colorless to yellow. The results demonstrated that the deprotonated **10-H**⁺ was formed (Fig. 3A).^{20,24} Neutralization with hydrochloric acid (HCl, 5.0 μ L, $C = 0.10 \text{ mol L}^{-1}$) recovered the absorption spectrum of 10. In acetonitrile, diarylethene $10-H^+$ also underwent photoisomerization upon alternating UV and visible light. Upon irradiation with 297 nm UV light, the original absorption bands of **10-H**⁺ at 295 nm, 345 nm, and 427 nm decreased. Simultaneously, a new visible absorption band centered at 660 nm (ε , 6.90 × 10³ L mol⁻¹ cm⁻¹) increased due to the formation of a closed-ring isomer $1C-H^+$ accompanied with color change from yellow to cyan (Fig. 3B). The colored solution could be bleached completely upon irradiation with visible light ($\lambda \ge 500$ nm), suggesting the closed-ring isomer $1C-H^+$ returned to the open-ring isomer $1O-H^+$. The quantum yields of cyclization and cycloreversion of 10-H⁺ were determined to 0.03 and 0.26, respectively. Compared to 10, the cyclization quantum yield of 10-H⁺ showed negligible change, but the cycloreversion quantum yield notably decreased. After 50 repeated cycles, no remarkable decomposition of 10-H⁺ was detected by UV/Vis spectral analysis, indicating **10-H**⁺ has good fatigue resistance.



Fig. 3. Absorption spectral and color changes of 1 by NaOH/HCl and light stimuli in acetonitrile (2.0×10^{-5} mol L⁻¹) at room temperature: (A) absorption spectral changes of 10 upon addition of NaOH/HCl,



(B) absorption spectral changes $10-H^+$ by photoirradiation.

Fig. 4. Absorption spectral and color changes of 1C in acetonitrite $(2.0 \times 10^{-5} \text{ mol L}^{-1})$ with the stimulation of NaOH and HCl.

Moreover, the colored isomer of **1C** also could be transformed to deprotonated **1C-H⁺** via the stimulation of base. During the addition of NaOH (0 to 20.0 equiv) to the solution containing **1C**, the light purple color of solution changed to cyan due to the formation of deprotonated **1C-H⁺**, whose absorption maximum was remarkably redshifted from 539 nm to 660 nm (Fig. 4). The results were well consistent with the absorption spectrum of **1O-H⁺** in PSS upon irradiation with 297 nm light. Compared to **1C**, the absorption maximum of **1C-H⁺** was bathochromically shifted by 121 nm. The color and absorption spectrum of **1C-H⁺** could be converted back to **1C** by neutralization with HCl (12.5 equiv.).The structure and color changes between neutral and deprotonated states induced by base/acid and light are described in Scheme 4.



Scheme 4. Structural changes between 10, 10-H⁺, 1C, and 1C-H⁺.

3.2 Fluorescence properties of 1

Like most diarylethenes have been reported,²⁵ diarylethene **1** exhibited notable fluorescence in acetonitrile (2.0×10^{-5} mol L⁻¹). Its fluorescence spectrum was measured at room temperature, and the result is shown in Fig. 5A. The emission peak of **10** was observed at 596 nm when excited at 380 nm. The fluorescence quantum yield of **10** was determined to be 0.003. Upon irradiation with 297 nm UV light, the emission intensity at 596 nm decreased gradually along with the photoisomerization due to the production of the weakly fluorescent closed-ring isomer **1C**. After exposure to UV light ($\lambda = 297$ nm) for 30 min, the emission intensity of **10** was quenched to ca. 88%. The residual fluorescence in the PSS may be attributed to the incomplete cyclization reaction and the existence of parallel conformation.²⁶ Back irradiation with visible light of appropriate wavelength ($\lambda > 500$ nm) regenerated the open-ring isomer **10** and recovered the original emission spectrum. It should be noted that the fluorescence of **10** could be modulated by acid/base stimulation. Fig. 5B shows the emission spectral changes of **10** by alternating addition of acid and base in acetonitrile ($C = 2.0 \times 10^{-5}$ mol L⁻¹). Addition of acid (HCl, 9.6 µL, C = 0.10 mol L⁻¹) to **10** produced the protonated diarylethene **10**+H^{+,27}. The emission peak hypochromatically shifted from 596 (**10**) nm to 570 (**10**+H⁺) nm, and its fluorescence

emission intensity was enhanced significantly by 5.5 fold with a concomitant change of color from light orange to bright green. The absolute fluorescent quantum yield of the $10+H^+$ was determined to be 0.01. The fluorescence spectrum of $10+H^+$ could return to the initial state 10 by neutralizing with base (NaOH, 9.6 µL, C = 0.10 mol L⁻¹). Similar to 10, the emission intensity of $10+H^+$ also could be modulated by illumination UV/Vis light (Fig. 5C). Upon irradiation with 297 nm light, the emission intensity of $10+H^+$ was quenched to ca. 53% when arrived at the PSS. Compared to 10, the fluorescent modulation efficiency of $10+H^+$ was significantly improved, which may be attributed to the intermolecular charge transfer.²⁸ Furthermore, base could also tune the fluorescence properties of 1. Upon addition of base (NaOH, 0 to 20.0 equiv.), the emission intensity of 10 was distinctly quenched to 74% due to the formation of deprotonated compound $10-H^+$ (Fig. 5D). The emission intensity of 10 could be restored to the initial state via neutralizing with acid (HCl, 5.0 µL, C = 0.10 mol L⁻¹). The results indicated that an efficient multi-responsive fluorescence switch could be constructed based on diarylethene 1 using acid/base and light as stimuli.





Fig. 5. Emission spectral changes and photos of 1 by stimulation of acid/base and light in acetonitrile
(2.0 × 10⁻⁵ mol L⁻¹) excited at 380 nm: (A) emission intensity changes of 10; (B) emission intensity changes of 10 with the stimulation of HCl; (C) emission intensity changes of 10+H⁺ by photoirradiation; (D) emission intensity changes of 10 with the stimulation of NaOH.

3.3 Photochromism and fluorescence response to Cu²⁺

Furthermore, diarylethene **1** shows high selectivity to Cu^{2+} with obvious absorption spectral and color changes. Upon addition of Cu^{2+} (0 to 10.0 equiv.), the absorption maximum of **10** at 295 nm gradually increased and a new visible absorption appeared at 420 nm due to the formation of **10**- Cu^{2+} complex accompanied with distinct color change from colorless to light yellow (Fig. 6A). The subsequent addition of excess of EDTA did not recover its original color and absorption spectrum, indicating that the sensing process of **10** in response to Cu^{2+} was irreversible. Interestingly, the closed-ring isomer **1C** also showed obvious selectivity towards to Cu^{2+} . When Cu^{2+} was added to the solution of **1C**, the absorption intensity at 539 nm decreased and reached a plateau after 10.0 equiv of Cu^{2+} was added. Meanwhile, a new absorption band at 420 nm was detected by UV/Vis absorption and the solution color changed from purple to light yellow. The results indicated that the closed-ring isomer **1C** could be transformed into **10**- Cu^{2+} complex, and the absorption spectrum of **1C**- Cu^{2+} was well consistent with

the absorption of 10-Cu²⁺. The sensing process of 1C in response to Cu²⁺ could not recover the original color after addition of excess of EDTA (Fig. 6B). In addition, the light yellow solution of 10-Cu²⁺ could not turn purple when irradiated with 297 nm UV light for more than 30 min, suggesting that the 10-Cu²⁺ complex exhibited no photochromism. The reason might be attributed to the high-affinity binding of diarylethene 1 with Cu²⁺, which restricted the interconversion efficiency from the parallel to the anti-parallel conformation of 10-Cu²⁺.²⁹ These results indicated that the 'naked-eye' sensor for Cu²⁺ based on diarylethene 1 could be constructed in acetonitrile.



Fig. 6. Absorption spectral and color changes of **1O** (A) and **1C** (B) upon addition of Cu^{2+} (0–10.0 equiv.) in acetonitrile ($2.0 \times 10^{-5} \text{ mol } L^{-1}$).

It is noteworthy that the fluorescence properties of **1** could be modulated by metal ions. The binding ability of **10** with different ions, such as metal ions Cu^{2+} , Al^{3+} , Fe^{3+} , Cr^{3+} , Mn^{2+} , K^+ , Ca^{2+} , Mg^{2+} , Co^{2+} , Ni^{2+} , Ba^{2+} , Cd^{2+} , Hg^{2+} , Sr^{2+} , Zn^{2+} , Pb^{2+} (Fig. 7), and anions F⁻, Cl⁻, Br⁻, Γ , NO_3^- , NO_2^- , SO_4^{2-} , HSO_4^- , SO_3^{2-} , CO_3^{2-} , HCO_3^- , CH_3COO^- , and SCN^- (Fig. S5, SI) were tested by fluorescence spectroscopy in acetonitrile. It is clearly seen that **10** exhibits highly selective for Cu^{2+} . As shown in Fig. 7, the emission intensity change of **10** (2.0×10^{-5} mol L⁻¹) induced by the addition of different metal ions (10.0 equiv.). It can be seen that the fluorescence emission intensity of **10** was notably decreased only

when Cu^{2+} was added. Except that Al^{3+} , Cd^{2+} , and Zn^{2+} can slightly enhance the emission intensity, other cations, such as Fe³⁺, Cr³⁺, Mn²⁺, K⁺, Ca²⁺, Mg²⁺, Co²⁺, Ni²⁺, Ba²⁺, Hg²⁺, Sr²⁺, and Pb²⁺ lead to negligible decrease in the emission intensity of **10**. The fluorescence intensity of **1** declined remarkably after the Cu²⁺ concentration increased from 0 to 10.0 equiv. followed by a plateau with further titration, and the emission intensity of **10** at 596 nm was remarkably quenched to ca. 11% (Fig. 8). The results may be attributed to the ligand-to-metal charge transfer, in which the charge was transferred from the ligand towards the coordinating metal ion.³⁰ The inset of Fig.8 depicts the effect of Cu^{2+} concentration on the emission intensity at 596 nm. A linear relationship was observed between the fluorescence intensity of **10** and Cu²⁺ concentration in the range of 0 to 4.0 equiv., indicating that **10** could be potentially used as a colorimetric fluorescent probe for Cu²⁺.



Fig. 7. The $(F-F_0)/F_0$ ratio of diarylethene **1O** at 596 nm in acetonitrile $(2.0 \times 10^{-5} \text{ mol } \text{L}^{-1})$ in the

presence of respective metal ions (10.0 equiv.).



Fig. 8. Emission intensity changes of **1O** induced by Cu^{2+} in acetonitrile $(2.0 \times 10^{-5} \text{ mol } \text{L}^{-1})$ (Inset shows its emission intensity changes along with the addition of Cu^{2+} from 0 to 14.0 equiv.).

In order to confirm the stoichiometry between **10** and Cu^{2+} , a Job's plot was performed in acetonitrile according to the reported method,³¹ and the results are depicted in Fig. 9A. It can be easily calculated that the complex rations of compounds between **10** and Cu^{2+} is 1:1. The binding sites for Cu^{2+} to coordinate with diarylethene **1** are probably the -OH group of phenol and the N atom of benzothiazole. (Scheme 5).³² In addition, the 1:1 binding stoichiometry was further confirmed by ESI-Mass analysis. As shown in Fig. 9B, the free **10** had a main peak at 593.0 *m/z* for $[10+H]^+$. When excess amounts of Cu^{2+} were added into **10**, a new peak at 654.9 *m/z* was observed due to the formation of $[10-Cu^{2+}-H]^+$. Additionally, the association constant (*K*_a) of **10** with Cu^{2+} was obtained using the liner Bensi-Hildebrand expression, and the value of *K*_a was found to be 3.6×10^6 L mol⁻¹ (Fig. S6, SI). The result further confirmed that **10** bound to Cu^{2+} with a higher affinity.



Fig. 9. Job's plot showing the 1:1 complex between 10 and $Cu^{2+}(A)$, and ESI-MS spectrum changes of



Scheme 5. Proposed mechanism of the absorption and emission intensity changes for 10 in the presence of Cu^{2+} by photo-irradiation.

4. Conclusions

In summary, a novel asymmetrical photochromic diarylethene containing a 2-(2'-hydroxyphenyl)benzothiazole unit was synthesized, and its multi-responsive behaviors to light, acid/base, and Cu²⁺ were systematically investigated. The results demonstrated that different energy UV light could regulate its conformational transition between enol form and ketone form. Induced by the stimulation of base, the maximum absorption of the closed-ring isomer exhibited remarkable

bathochromic shift of 121 nm. However, the fluorescence intensity of the diarylethene remarkably increased by 5.5 fold when it was protonated with acid. Moreover, the diarylethene exhibited dramatic changes in its absorption spectra and color upon addition of Cu^{2+} , indicating it could be potentially applied as highly selective 'naked-eye' colorimetric sensors for Cu^{2+} . Our experimental results demonstrated that multi-responsive signal transmission at the unimolecular platform could be realized by using a photochromic diarylethene with a HBT functional group.

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