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Readily accessible rhodamine B-based photoresponsive material

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A photochromic rhodamine B-based material containing Cd(II) as bridge was facilely prepared. The 4-methoxylsalicylaldehyde rhodamine B hydrazone Cd(II) complex displayed unusual ring-open response upon 365 nm UV irradiation, exhibiting long photochromic lifetime and good fatigue resistance. The UV-induced ring-open of the complex led to a distinct color and fluorescence change in acetonitrile. A new mechanism was put forward: salicylaldehyde part in the complex underwent UV-promoted isomerization from enol-form to keto-form, enhancing the chelation of Cd(II) and yielding the ring-opening rhodamine B part. Compared to other reported photochromic systems, this new photochromic material offered attractive new insights into the development of low cost photochromic materials with good performance.

photochromism, coordination compound, rhodamine B, salicylaldehyde hydrazone, cadmium, UV-light

1 Introduction

Photoresponsive materials have been widely used in molecular machines [1, 2], molecular logic gates [3], photoelectronic devices [4], photoresponsive liquid crystals [5, 6] and photoinduced nanoparticle devices [7]. The classic photoresponsive materials include diarylethene, azobenzene, spiropyran, spirooxazine, anil, fulgide, polycyclic quinone, and so on. Although they have demonstrated excellent photochromic properties [8, 9], these materials still possess some limitations. For example, diarylethene has excellent fatigue resistance and thermally irreversible properties, but the production of this material requires complicated multiple-step synthesis, resulting in high cost [10]. On the other hand, azobenzene and spiropyran are easy to prepare, but their fatigue resistance is moderate, which limits their practical applications [11, 12]. Therefore, the design and development of photochromic systems with convenient synthesis and good properties are of great interest and challenge [8, 13–16].

Rhodamine B is a classic fluorescent dye with long wavelength absorption/emission, high absorption coefficient/quantum efficiency, and excellent photostability [17]. Its derivatives have been widely applied in analytical applications. Recently, rhodamine-based fluorescent chemosensors were developed in our group for the detection of a series of analytes [18–21]. Taking advantage of rhodamine B's photophysical properties, new photochromic molecules could be developed to overcome the challenges.

In this work, 4-methoxylsalicylaldehyde rhodamine B hydrazone (**1**) and its Cd(II) complex (**1**+Cd(II)) were synthesized. The complex could be facilely prepared with low cost, and showed excellent photochromic properties in acetonitrile, as well as good fatigue resistance and long photochromic lifetime. Its photochromic properties, including absorption/fluorescence spectral changes upon 365 nm UV irradiation and photochromic kinetics were investigated in details.

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2 Experimental

2.1 Materials and methods

Absorption spectra were performed on JASCO V-550 UV-Vis spectrophotometer. Fluorescence spectra were recorded on JASCO FP-6500 spectrofluorimeter. The photos were carried by Canon EOS 600D camera. NMR spectra were recorded using a Joel JNM-ECA300 spectrometer operated at 300 MHz. ESI mass spectra were obtained on HP 1100 LC-MS spectrometer. Rhodamine B, hydrazine hydrate, 4-methoxylsalicylaldehyde and cadmium nitratetetrahydrate were purchased from Alfa Aesar Co., Tianjin, China. All the other materials were purchased from Sinopharm Chemical Reagent Beijing Co., Beijing, China.

2.2 Synthesis of 4-methoxylsalicylaldehyde rhodamine B hydrazone (1)

The synthesis of 4-methoxylsalicylaldehyde rhodamine B hydrazone was shown in Scheme 1. Rhodamine B hydrazide was prepared through an early procedure [19]. 0.91 g rhodamine B hydrazide (2 mmol) was dissolved in 40 mL absolute ethanol. 0.47 g 4-methoxylsalicylaldehyde (3 mmol) was added, the mixture was refluxed overnight. The reaction mixture was concentrated to about 15 mL and allowed to stand at 4 °C overnight. The precipitate formed was filtered and washed with 50 mL ethanol for 3 times. After drying under reduced pressure, 0.66 g **1** was obtained as a red-brown solid (61%). ESI mass spectrometry: *m/z* 591.3 (48% $[M + H]^+$), 613.3 (52% $[M + Na]^+$), M^+ calculated 590.3. ^1H NMR (300 MHz, DMSO-d_6) δ (ppm): 1.06 (t, 12H), 3.29 (m, 8H), 3.70 (s, 3H), 6.39 (m, 8H), 7.10(d, 1H), 7.20 (d, 1H), 7.59 (m, 2H), 7.92 (d, 1H), 9.08 (s, 1H), 10.79 (s, 1H). ^{13}C NMR (DMSO-d_6) δ (ppm): 12.92, 44.19, 55.80, 66.05, 97.83, 101.69, 105.43, 107.01, 108.66, 112.49, 123.46, 124.37, 128.26, 129.38, 129.54, 131.67, 134.27, 149.04, 151.38, 151.90, 153.32, 159.85, 162.82, 163.76.

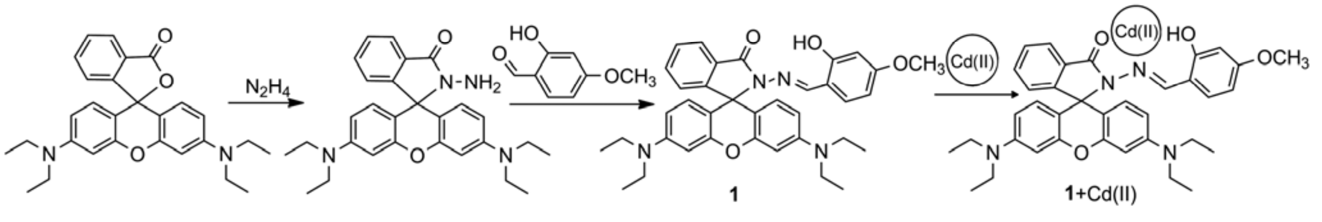
2.3 Preparation of 4-methoxylsalicylaldehyde rhodamine B hydrazone Cd(II) complex (1+Cd(II))

1+Cd(II) were prepared by the addition of 10 μmol/L Cd(II) to 10 μmol/L of **1** in acetonitrile at room temperature. ESI mass spectrometry: *m/z* 703.2 ($[M - H + Cd]^+$), calculated 703.2 (Figure S1).

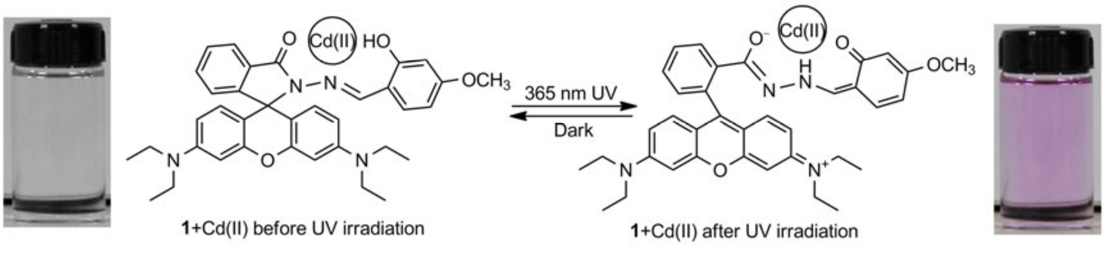
3 Results and discussion

The complex **1**+Cd(II) exhibited reversible photochromism in acetonitrile between UV irradiation and dark. As shown in Scheme 2, upon irradiation at 365 nm, the colorless solution gradually turned purple. When the UV light was removed, the solution restored colorless in ten minutes. The absorption spectra of 10 μmol/L **1**+Cd(II) before UV irradiation displayed no band above 450 nm. However, upon irradiation at 365 nm, the solution became purple along with an absorption enhancement of a new peak located at 555 nm (Figure 1(a)). This photochromic process was also studied by fluorescence spectra. When excited at 412 nm, fluorescence emission of **1**+Cd(II) was observed at 522 nm before UV irradiation. Subsequently, upon irradiation, the emission band at 522 nm gradually decreased, with two new emission bands at 517 and 579 nm emerged simultaneously (Figure 1(b)). The recovery reaction in dark was also investigated. At room temperature, the time for 99.9% recovery was about ten minutes (Figure 2).

To get insight into the mechanism of the unique photochromic property of **1**+Cd(II), rhodamine B was used as a control molecule. It is well known that rhodamine B is



Scheme 1 Preparation of **1**+Cd(II).



Scheme 2 Proposed mechanism for photochromism of **1**+Cd(II) upon 365 nm UV irradiation.

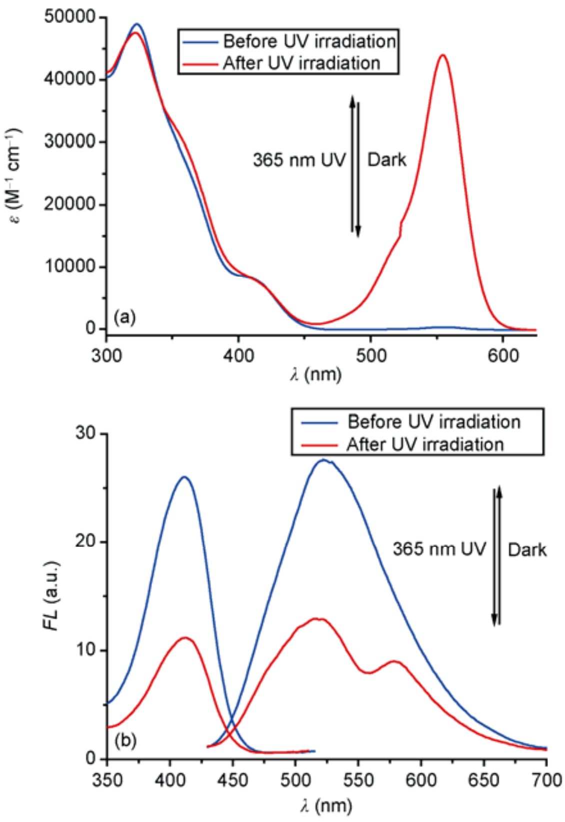


Figure 1 Absorption (a), fluorescence excitation (b, left) and emission spectra (b, right) of 10 μmol/L **1**+Cd(II) in acetonitrile upon 365 nm UV irradiation.

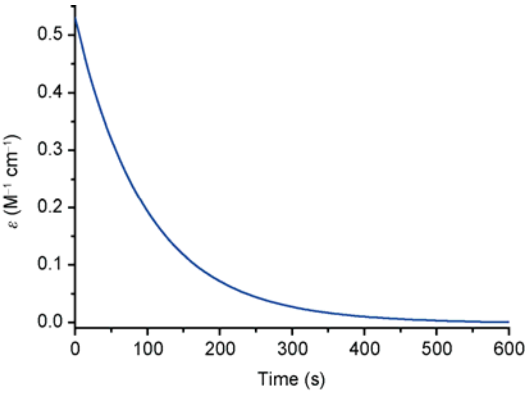


Figure 2 The thermal fading kinetics of 10 μmol/L **1**+Cd(II) in acetonitrile at room temperature. λ = 555 nm.

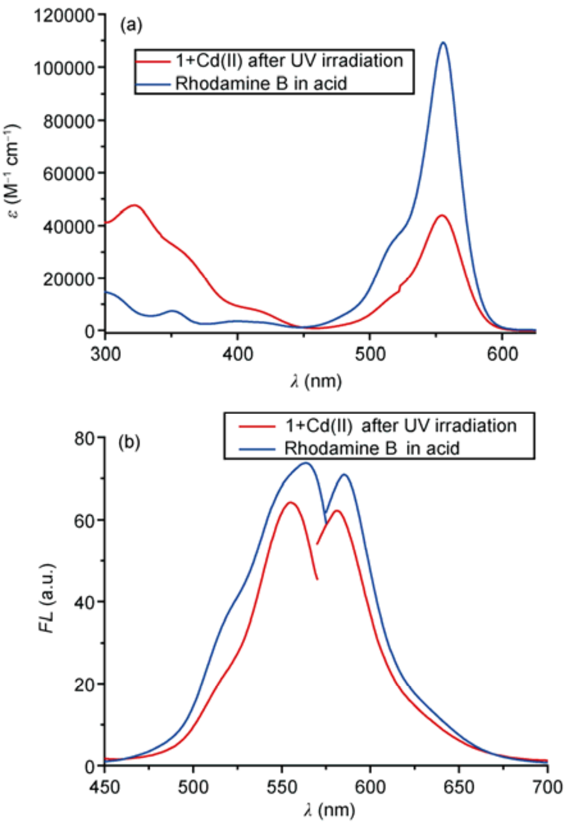


Figure 3 Absorption (a), fluorescence excitation (b, left) and emission spectra (b, right) of 10 μmol/L **1**+Cd(II) in acetonitrile after 365 nm UV irradiation and 10 μmol/L rhodamine B in acetonitrile with 100 μmol/L HCl.

photo stable upon UV irradiation, and fluorescent in acidic solutions rather than basic ones. The absorption and fluorescence spectra of **1**+Cd(II), after 365 nm UV irradiation, were compared with those of rhodamine B in acidic acetonitrile. As shown in Figure 3, the position and shape of the peaks in **1**+Cd(II)'s spectra after 365 nm UV irradiation were similar to those of rhodamine B, indicating that **1**+Cd(II) underwent a ring-open reaction to yield a ring-open product with color. In addition, according to the previous reports, salicylaldehyde hydrazones are sensitive to UV irradiation [11, 22]. UV light can promote the isomerization of salicylaldehyde hydrazone from enol-form to keto-form. Based on the known facts, we proposed a mechanism for the color change of **1**+Cd(II) upon the 365 nm UV irradiation. UV light promoted an isomerization of salicylaldehyde part in **1** from enol-form to keto-form, and such change of chelating group to Cd(II) induced the ring opening of rhodamine B part, yielding a purple product (as shown in Scheme 2). Although the product has a larger π-conjugation, which is supposed to produce stronger fluorescence [23, 24], the product (**1**+Cd(II) after UV irradiation) shows a weaker fluorescence than its precursor (Figure 1(b)). The fluorescence decrease might be due to the formation of the keto-form that can serve as a strong fluorescence quenching unit. Interestingly, the bare compound **1** without coordination with Cd(II) displayed no photochromic properties (Figure 4), suggesting Cd(II) chelation was essential for the photochromism.

The fatigue resistance of **1**+Cd(II) in acetonitrile was investigated to evaluate its advantage as a potential photochromic material. As shown in Figure 5, **1**+Cd(II) in acetonitrile was toggled repeatedly between the purple state (UV irradiation) and colorless state (dark) for 10 times.

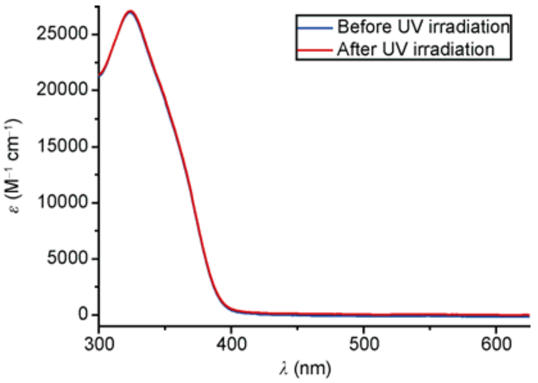


Figure 4 Absorption spectra of 10 μmol/L **1** in acetonitrile upon 365 nm UV irradiation.

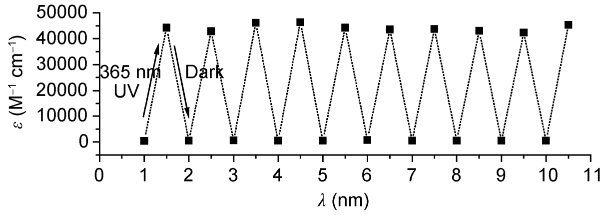


Figure 5 Fatigue resistance of **1**+Cd(II) in acetonitrile upon irradiation with 365 nm and stand in dark alternatively.

The absorbance at 555 nm was stable without apparent degradation.

4 Conclusions

In summary, we have designed and synthesized a new photoresponsive material based on salicylaldehyde rhodamine B hydrazone Cd(II) complex. The system showed absorption "turn-on" and fluorescence "turn-off" response upon 365 nm UV irradiation in acetonitrile. The photochromism was suggested as the result of UV light-promoted isomerization of salicylaldehyde part from the enol-form to the keto-form, which changed the chelation with Cd(II) and induced the ring opening of rhodamine B part. The photochromic system exhibited good fatigue resistance and long photochromic lifetime at room temperature. This study provided a new approach to design photoresponsive system based on coordination compounds. Currently, more photoresponsive molecules derived from such a rhodamine metal complex are under further investigation in our laboratory.

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