Reversible Photochromic System Based on Rhodamine B Salicylaldehyde Hydrazone Metal Complex

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S *Supporting Information*

ABSTRACT: Photochromic molecules are widely applied in chemistry, physics, biology, and materials science. Although a few photochromic systems have been developed before, their applications are still limited by complicated synthesis, low fatigue resistance, or incomplete light conversion. Rhodamine is a class of dyes with excellent optical properties including long-wavelength absorption, large absorption coefficient, and high photostability in its ring-open form. It is an ideal chromophore for the development of new photochromic systems. However, known photochromic rhodamine derivatives, such as amides, exhibit only millisecond lifetimes in their colored ring-open forms, making their application very limited and difficult. In this work, rhodamine B salicylaldehyde hydrazone metal complex was found to undergo intramolecular ring-open reactions upon UV irradiation, which led to a distinct color and fluorescence change both in solution and in solid matrix. The complex showed good fatigue resistance for the reversible photochromism and long lifetime for the ring-open state. Interestingly, the thermal bleaching rate was tunable by using different metal ions, temperatures, solvents, and chemical substitutions. It was proposed that UV light promoted isomerization of the rhodamine B derivative from enol-form to keto-form, which induced ring-opening of the rhodamine spirolactam in the complex to generate color. The photochromic system was successfully applied for photoprinting and UV strength measurement in the solid state. As compared to other reported photochromic molecules, the system in this study has its advantages of facile synthesis and tunable thermal bleaching rate, and also provides new insights into the development of photochromic materials based on metal complex and spirolactam-containing dyes.
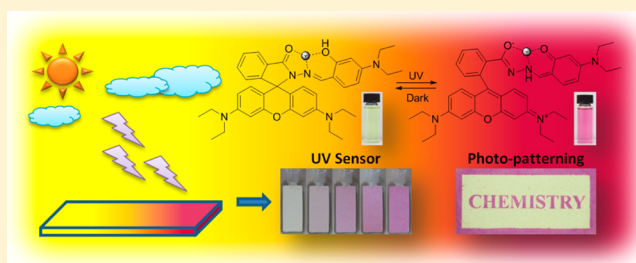
INTRODUCTION

Photochromic materials have attracted increasing interest because of their potential application in developing molecular switches,[1,2] molecular logic gates,[3] optical data storage,[4] optoelectronic devices,[4–8] photoresponsive supramolecular self-assembly,[9–11] photocontrollable drug or ion delivery,[12–15] photocontrollable biological processes[16,17] and molecular machines.[18–20] Among them, organic photochromic molecules, including azobenzene, spiropyran, dithienylethene, spirooxazine, fulgide, anil, viologen, etc., undergo color changes upon photo irradiation, and have shown good performance in their chemical, biological, physical, and nanotechnology applications.[13,21] Azobenzene is one classic photochromic material with its trans and cis isomers interchanged by light irradiation and heat,[22,23] making it a very useful platform for photo-triggered biological systems.[17,23,24] However, the incomplete reverse between trans and cis isomers and moderate fatigue resistance limit its scope of practical application.[25] Spiropyran is another well-known photochromic compound, which has a dipole moment enhancement and a large absorption change upon UV irradiation.[26] The phenol group in the ring-open form of spiropyran can chelate metal ions, which enables its

application in the development of electrochemical devices.[27–30] Unfortunately, the fatigue resistance of spiropyran is still moderate, especially under strong irradiation.[14,31] On the other hand, dithienylethene derivatives have attracted much attention because of their excellent fatigue resistance and thermally irreversible photochromic properties. The response of dithienylethene to UV irradiation is fast both in solution and in the solid state.[32–34] Nevertheless, the unique structure of dithienylethene usually makes the synthesis of its derivatives multiple-step and high-cost.[35–37] Therefore, the development of a facilely synthesized photochromic system with good photochromic properties is still highly demanded and challenging.[38–41] Moreover, for most of the known photochromic molecules, the available methods to modulate thermal bleaching rate are still limited. Besides environmental factors such as temperature and solvent, changing substitution groups is a common strategy, but it usually requires intense synthesis works.[42,43] Thus, simpler methods to tune thermal bleaching rate are also needed.

Rhodamine is a class of dyes with long-wavelength absorption and emission, high absorption coefficient and quantum efficiency, and good photostability. It is widely available and used in industrial coloration, biomarkers, and fluorometric probes.[44−46] However, the report of using rhodamine derivatives as long-lifetime photochromic molecules is still very scarce. As shown in Scheme 1, rhodamine amide

**Scheme 1. Short-Lifetime Photochromism of a Rhodamine Amide**
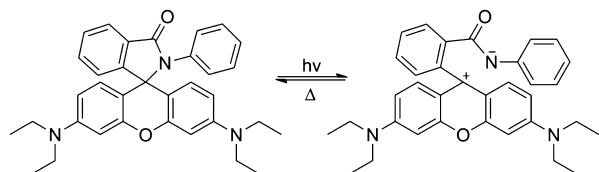
was reported to exhibit photochromic features in 1977.[47] Unfortunately, the lifetime of the ring-open state is very short, with only a few milliseconds in polar solvents.[48] Because of the short lifetime and low quantum efficiency of the photoinduced reaction, the photochromic properties of rhodamine amides were almost disregarded in the next 30 years.[49−52] New photochromic molecules can be developed by taking advantages of rhodamine's excellent optical properties if the lifetime of the ring-open state is dramatically improved.

In this work, rhodamine B salicylaldehyde hydrazone, which contains a rhodamine amide moiety and a photosensitive salicylaldehyde Schiff bases part,[53,54] was found to exhibit photochromic properties with a long lifetime when forming metal complex. This photochromic system exhibited good fatigue resistance, and the thermal bleaching rate was tunable by using different metal ions to form the complex. Moreover, the photochromic system was successfully applied for photoprinting and UV strength measurement in the solid state.

■ RESULTS AND DISCUSSION

Compound **1** was prepared by a simple reaction between 4-N,N-diethylaminosalicylaldehyde and rhodamine B hydrazide in high yield according to a reported procedure.[55] As shown in Scheme 2, **1-Zn** complex was prepared by the addition of 10-

Scheme 2. Synthesis of 1-Zn
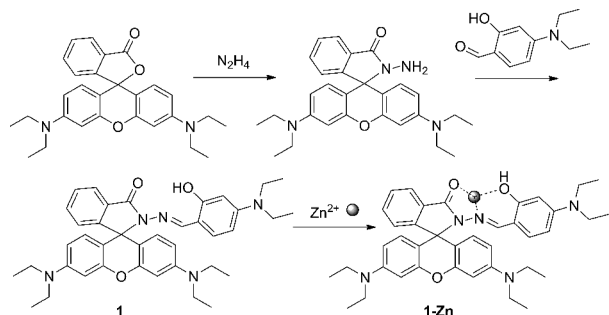
fold Zn(II) to **1** in THF to ensure efficient formation of the complex. The absorption and fluorescence characteristics of the complex (Supporting Information Figure S1) were in accordance with a previous study.[55]

Interestingly, complex **1-Zn**, not **1** alone, was found to display reversible photochromism in THF. As shown in Figure 1a, upon irradiation at 365 nm, the light yellow solution
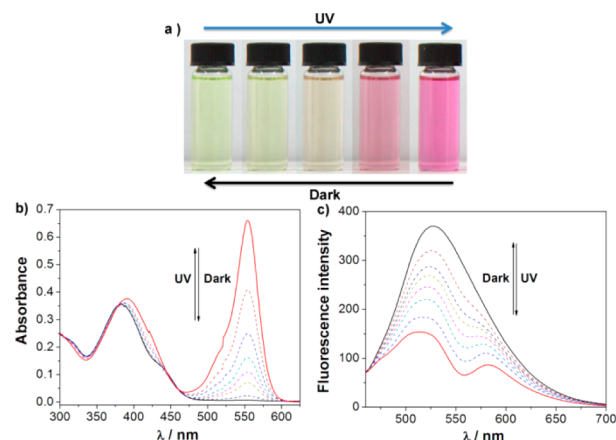

Figure 1. (a) Photographic images of **1-Zn** in THF upon irradiation, and the recovery in dark at 25 °C. (b) Absorption and (c) fluorescence spectra of **1-Zn** in THF before and after UV irradiation. $[1] = 10$ μmol/L, $[Zn(II)] = 100$ μmol/L.

gradually turned purple. When the UV light was removed, the solution restored to its original state in 10 min, suggesting a long lifetime of the purple form under ambient condition (Supporting Information video 1). Before UV irradiation, no absorption band above 500 nm was observed for **1-Zn**. However, upon irradiation at 365 nm, a strong band centered at 554 nm emerged (Figure 1b). The molar absorption coefficient at 554 nm was as high as 6.7×10^4 cm^{-1} mol^{-1} L for **1-Zn** after UV irradiation, which was higher than most reported photochromic systems with similar absorption ranges.[6,10,35−39] In contrast, the fluorescence emission of **1-Zn** at 527 nm was intense before UV irradiation, while it decreased and transformed into two weaker peaks at 513 and 582 nm upon UV irradiation (Figure 1c). When in the dark, the fluorescence of UV-irradiated **1-Zn** also gradually recovered.

Because of the presence of both rhodamine B and salicylaldehyde hydrazone moieties in **1-Zn** and the indispensable role of Zn(II) chelation in the photochromism, we propose the mechanism for the color change of **1-Zn** upon UV irradiation is as shown in Scheme 3. To support the hypothesis, the control compounds of rhodamine B (**Rd**) and **2-Zn** (Scheme 3) were investigated. **Rd** in its ring-open form of **Rd-Open** was photostable and constantly showed strong

Scheme 3. Proposed Mechanism for Color Change of 1-Zn upon UV Irradiation and the Known Tautomerism of the Control Compounds
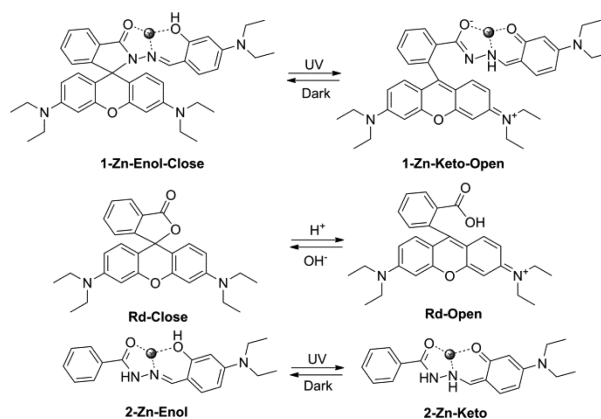
absorption at 554 nm and fluorescence at 595 nm regardless of UV irradiation (Figure 2b and d), unless excess base such as
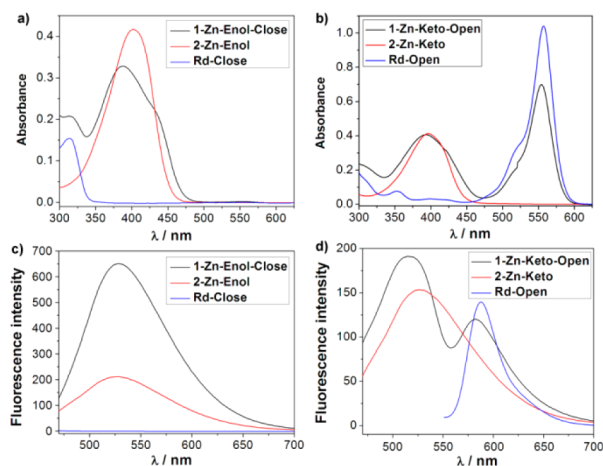

Figure 2. Absorption (a and b) and fluorescence spectra (c and d) of different states of **1-Zn** and its control compounds in THF. [**1**] = 10 μmol/L, [**2**] = 10 μmol/L, [**Rd**] = 10 μmol/L, [Zn(II)] = 100 μmol/L; ring-open and closed forms of **Rd** were controlled by the addition of HCl and NaOH.

NaOH was added to form the colorless and nonfluorescent spirolactone of **Rd-Close** (Figure 2a and c). On the other hand, **2-Zn** was sensitive to UV irradiation. UV light promoted the isomerization of its salicylaldehyde hydrazone from the enol-form to the keto-form.[53,54] As shown in Supporting Information Figure S2, **2-Zn-Enol** (before UV irradiation) and **2-Zn-Keto** (after UV irradiation) had similar but indeed different absorption and fluorescence spectra. It was found that **1-Zn-Keto-Open** had two absorbance bands around 400 and 554 nm, and emission bands around 513 and 582 nm, which were similar to an overlay of **2-Zn-Keto** and **Rd-Open** (Figure 2b and d). In addition, **1-Zn-Enol-Close** had two absorbance band around 325 and 400 nm, and an emission band at 527 nm, which were similar to an overlay of **2-Zn-Enol** and **Rd-Close** (Figure 2a and c). On the basis of these results, **1-Zn** could be considered as the combination of **Rd** and **2-Zn**. The **1-Zn** complex took advantages of both the excellent optical properties of rhodamine B and the fast photoresponse and long-lifetime photochromic characteristics of salicylaldehyde hydrazone.[53,54] UV light promoted isomerization of the salicylaldehyde moiety in **1-Zn** from the enol-form (**1-Zn-Enol-Close**) to the keto-form (**1-Zn-Keto-Open**), and this change that induced ring-opening of the rhodamine B spirolactam due to the charge separation was preferred in the excited state, generating the purple-colored **1-Zn-Keto-Open** (Scheme 3).

According to the proposed mechanism, the phenol group should be an indispensable factor for the photochromism during the enol-to-keto transformation. To testify it, a control compound **3** containing a pyridine group for metal ion chelation but lack of the phenolic hydroxyl group as compared to **1** was prepared. We found that **3** was able to chelate zinc ions to form **3-Zn**, but the complex had no photochromic property upon UV irradiation (Figure 3).

The role of metal ion chelation on the photochromism of complex **1-Zn** was also investigated. Without Zn(II), the five-membered spirolactam ring in **1** was photostable upon UV irradiation. Only very slight changes of absorption and
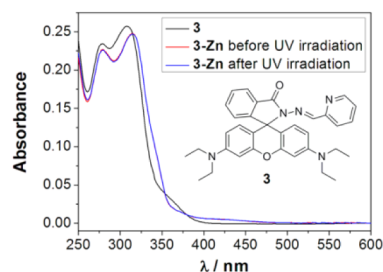

Figure 3. Absorption spectra of **3** and **3-Zn** in THF before and after UV irradiation. [**3**] = 10 μmol/L, [Zn(II)] = 100 μmol/L.

fluorescence were observed for **1** after exposure to UV irradiation (Supporting Information Figure S3), which was due to the isomerization of the salicylaldehyde hydrazone moiety. This result suggested the essential role of Zn(II) chelation for the photochromism. In addition to Zn(II), other metal ions were also used to form complex with **1** to study their effects on the photochromism. As shown in Supporting Information Figure S4, different metal ions were added to the solution of **1** in THF, and the solutions with Cu(II), Ni(II), Zn(II), and Cd(II) showed strong color change after UV irradiation. Interestingly, the thermal bleaching rate of **1** in dark in the presence of these four metal ions was dependent on the type of metal ions (Figure 4), with **1-Cu** and **1-Cd** as the

Figure 4. Photographic images of thermal bleaching of **1** in the presence of different metal ions in THF in dark at room temperature.

slowest and the fastest, respectively. We chose **1-Zn** as the example for the subsequent studies in this work, because it had a suitable thermal bleaching rate that is not too slow or too fast for measurement. In contrast to metal ions, the photochromism of **1-Zn** was not affected by anions such as F^-, Cl^-, Br^-, I^-, SCN^-, Ac^-, and SO_4^{2-}, unless strong ligands such as $EDTA^{2-}$ were used to compete with **1** in Zn(II) binding (Supporting Information Figure S5).

In addition to metal ion, other factors for thermal bleaching rate were also studied. Initially, **1-Zn-Enol-Close** had no absorption band above 500 nm, so the absorbance at 554 nm should be proportional to the concentration of **1-Zn-Keto-Open** formed upon UV irradiation. Thus, the recovery kinetics from **1-Zn-Keto-Open** to **1-Zn-Enol-Close** could be moni-

tored by measuring the absorbance at 554 nm over time. As shown in Figure 5a, elevated temperature could accelerate the
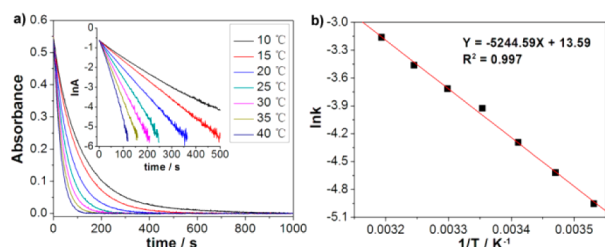

Figure 5. (a) The thermal fading kinetics of **1-Zn** in THF at different temperature. Inset: The curves fitted with one-order reaction dynamics $\ln A = -kt$ to calculate the thermal bleaching speed constant: $k = 7.39 \times 10^{-3}$ s^{-1} ($T = 10$ °C), $k = 9.85 \times 10^{-3}$ s^{-1} ($T = 15$ °C), $k = 1.39 \times 10^{-2}$ s^{-1} ($T = 20$ °C), $k = 1.84 \times 10^{-2}$ s^{-1} ($T = 25$ °C), $k = 2.38 \times 10^{-2}$ s^{-1} ($T = 30$ °C), $k = 3.03 \times 10^{-2}$ s^{-1} ($T = 35$ °C), $k = 3.73 \times 10^{-2}$ s^{-1} ($T = 40$ °C). [**1**] = 10 μmol/L, [Zn(II)] = 100 μmol/L, $\lambda = 554$ nm. (b) The data were fitted with Arrhenius expressions.

conversion of **1-Zn-Keto-Open** to **1-Zn-Enol-Close**. All seven curves obtained at different temperatures were fitted well with first-order reaction kinetics (Figure 5a, inset). Thus, the rate constants (k) could be calculated to evaluate the activation energy (E_a) according to the Arrhenius expression ($\ln k = -E_a/RT +$ constant). The E_a for the recovery reaction of **1-Zn-Keto-Open** to **1-Zn-Enol-Close** was calculated as 43.58 kJ/mol. This result suggested the lifetime of **1-Zn-Keto-Open** could be increased by lowering temperature.

To study the effects of different solvents on the photochromic reaction of **1-Zn**, 13 types of common solvents were chosen in which **1-Zn** could easily dissolve. According to previous reports,[56] we thought the solvent polarity might be a determinant factor for the photochromic properties of **1-Zn**. However, as shown in Supporting Information Table S1, the solvent polarity did not seem to be the only determinant factor. Although the photochromism was valid in most solvents with low polarity (less than 2.0), it was still so in some of the solvents with dipole moment more than 2.0 (such as acetonitrile). It seemed that the chemical structure of the solvent molecule was also important. In protic solvents such as alcohols, and some aprotic but high-polar solvents such as pyridine, DMF, and DMSO, **1-Zn** exhibited no photochromic property. In other solvents investigated, **1-Zn** exhibited photochromic properties with different kinetics. Excellent reversible photochromic property of **1-Zn** was observed in ethers including THF, 1,4-dioxane, and diethyl ether. On the basis of these results, solvent effect was also used to control the dynamics of the recovery reaction. For this purpose, THF–DCM solvent mixtures were utilized because the recovery was fast in THF but slow in DCM. As illustrated in Figure 6, the reaction rate increased with increasing THF fraction in the solvent mixture, and the rate constants could be tuned from 10^{-2} to 10^{-5} s^{-1} at 25 °C, which suggested the half-life of thermal recovery reaction from **1-Zn-Keto-Open** to **1-Zn-Enol-Close** could be as short as several minutes or as long as several hours at 25 °C.

Chemical substitutions on **1** could also influence the kinetics of the recovery reaction in the dark. Control compound **4** was synthesized in lack of a diethylamino group as compared to **1** (Figure 7a). The complex **4-Zn** exhibited reversible photochromism similar to that of **1-Zn** (Figure 7b and c), but its rate
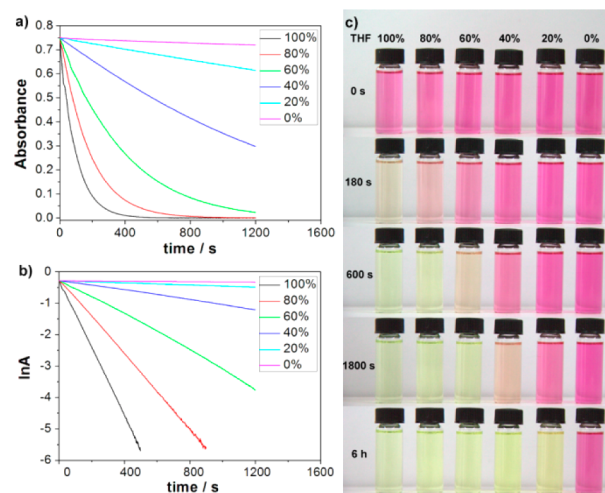

Figure 6. The thermal fading kinetics of **1-Zn** at different volume fractions of THF in DCM at 25 °C. [**1**] = 10 μmol/L, [Zn(II)] = 100 μmol/L, $\lambda = 554$ nm. (a) Absorbance change. (b) The curves fitted with one-order reaction dynamics $\ln A = -kt$ to calculate the thermal bleaching speed constant: $k = 1.80 \times 10^{-2}$ s^{-1} (100%), $k = 6.00 \times 10^{-3}$ s^{-1} (80%), $k = 2.88 \times 10^{-3}$ s^{-1} (60%), $k = 7.74 \times 10^{-4}$ s^{-1} (40%), $k = 1.65 \times 10^{-4}$ s^{-1} (20%), $k = 3.31 \times 10^{-5}$ s^{-1} (0%).
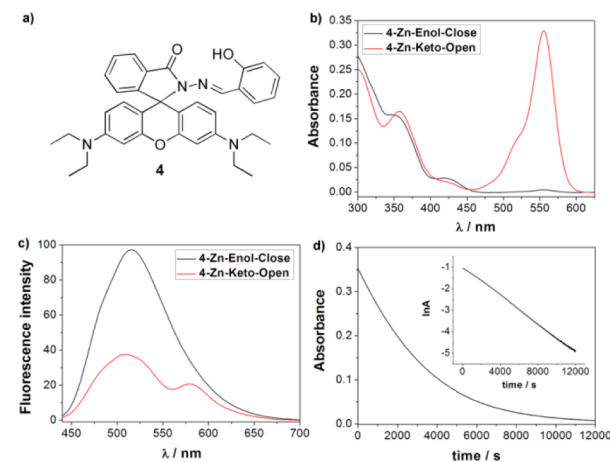

Figure 7. (a) Structure of **4**. (b) Absorption and (c) fluorescence spectra of **4-Zn** in THF before and after UV irradiation. (d) The thermal fading kinetics of **4-Zn** in THF at 25 °C, $\lambda = 554$ nm. Inset: The curves fitted with one-order reaction dynamics. [**4**] = 10 μmol/L, [Zn(II)] = 100 μmol/L.

of recovery in the dark from **4-Zn-Keto-Open** to **4-Zn-Enol-Close** was much slower than that of **1-Zn** under the same condition (Figure 7d). The recovery rate constant was calculated as 3.33×10^{-4} s^{-1} for **4-Zn**, which is only 2% of that of **1-Zn** at 25 °C.

Besides the tunable thermal bleaching rate, the fatigue resistance of **1-Zn** was investigated to evaluate its performance as a reversible photochromic complex. As shown in Figure 8a, **1-Zn** was toggled repeatedly between the two states of **1-Zn-Keto-Open** and **1-Zn-Enol-Close** 10 times, and the absorbance at 554 nm stayed almost constant without any apparent degradation.

To gain further insight into the photochromic properties, the calculations were performed on **1-Zn-Keto-Open** and **1-Zn-Enol-Close** with the Gaussian 09 program. The geometries were optimized with B3LYP hybrid density function and the 6-
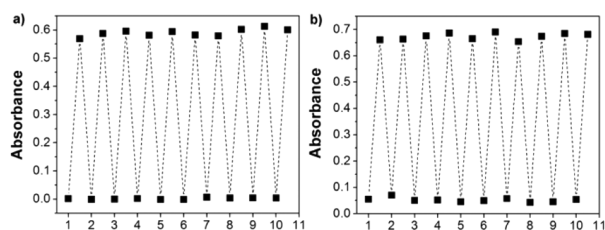
Figure 8. Fatigue resistance of **1-Zn** upon irradiation with 365 nm and standing in dark alternatively. (a) In THF, [**1**] = 10 μmol/L, [Zn(II)] = 100 μmol/L, λ = 554 nm. (b) In poloxamer 407, [**1**] = 1 μmol/g, [Zn(II)] = 10 μmol/g, λ = 560 nm.

31G (d,p) basis set. For both **1-Zn-Keto-Open** and **1-Zn-Enol-Close**, HOMO and LUMO are localized at the rhodamine B part and the salicylaldehyde hydrazone part, respectively (Figure 9), suggesting their roles in the photochromic property.
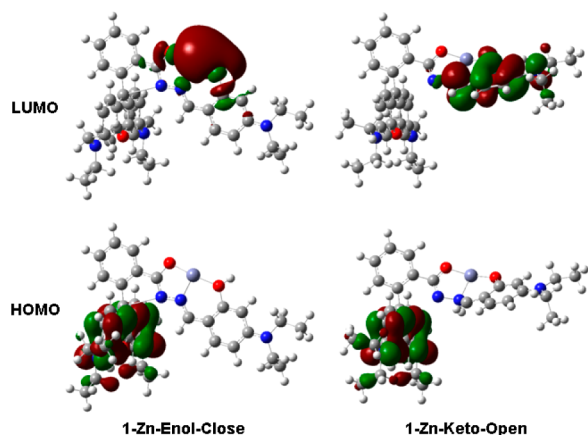

Figure 9. Frontier canonical Kohn−Sham valence MO envelopes of **1-Zn-Enol-Close** and **1-Zn-Keto-Open**, with dominant AO contributions. Value of contour envelopes is 0.025 au.

The molecular conformational change was small before and after UV irradiation (Supporting Information Figure S6), supporting the good fatigue resistance of **1-Zn**.

For applications as photochromic materials, the compound is more preferred to be embedded in solid state than in solution. Therefore, the photochromic properties of **1-Zn** in solid matrix were also studied. Complex **1-Zn** in poloxamer 407 (poly-(ethyleneglycol)-*block*-poly(propyleneglycol)-*block*-poly-(ethyleneglycol) with average molecular weight of 14 600, which is an ether polymer) solid was prepared by slow evaporation of solvent from **1-Zn** and poloxamer 407 in THF (see the Supporting Information). Similar to that of **1-Zn** in THF, the absorbance of **1-Zn** in poloxamer 407 solid at 554 nm enhanced dramatically, while the fluorescence at 595 nm decreased upon UV irradiation, displaying as the color change of the powder from light yellow to purple (Figure 10, Supporting Information video 2). Surprisingly, the fluorescence quenching of **1-Zn** upon UV irradiation was much more efficient in poloxamer 407 than that in THF, and the quantum yield of the solid fluorescence changed from 23% to 1.3% (Supporting Information Figure S7).

Interestingly, **1-Zn** in poloxamer 407 was capable of serving as material for photoprinting. Letters were preorganized and recorded on **1-Zn** in poloxamer 407 (Figure 11, Supporting Information video 3). Upon UV irradiation, letters were successfully visualized, and they gradually disappeared until
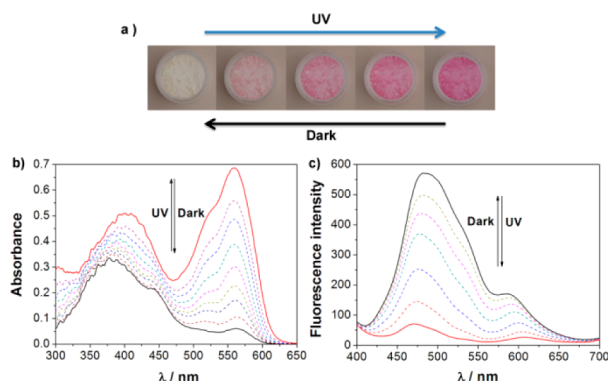

Figure 10. (a) Photographic images of **1-Zn** in poloxamer 407 upon irradiation at 365 nm, and the thermal bleaching in dark at 25 °C. (b) Absorption and (c) fluorescence spectra of **1-Zn** in poloxamer 407 before and after UV irradiation. [**1**] = 1 μmol/g, [Zn(II)] = 10 μmol/g.

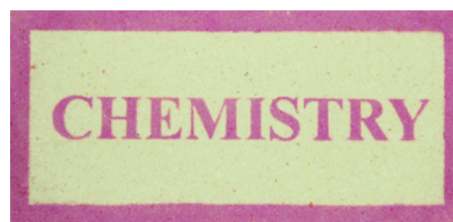**Figure 11.** Generating letters on **1-Zn** in poloxamer 407 upon UV irradiation. [**1**] = 1 μmol/g, [Zn(II)] = 10 μmol/g. Size: 4.2 cm × 2 cm.

the next round of irradiation. As shown in Supporting Information Figure S8, the thickness of the polymer layer that UV light could penetrate is less than 1 mm, because the polymer was not transparent. The fatigue resistance of **1-Zn** in poloxamer 407 was found as good as that in THF (Figure 8b).

As the ozone layer becomes thinner, UV radiation pollution is increasingly serious. Excessive UV radiation will cause an additional risk of skin cancers and cataracts, so the detection of UV radiation becomes significant.[57−59] According to the definition of UV index by the world health organization (WHO), the UV radiation reaching the earth's surface is largely composed of UVA (315−400 nm), with only a small fraction of UVB (280−315 nm) component.[60] We found that both of 325 and 405 nm UV light could lead to the photochromism of **1-Zn** in poloxamer 407, and the wavelength range fitted well with the UVA range. Therefore, a test bar for UV radiation pollution was developed on the basis of **1-Zn** in poloxamer 407 sealed in a colorimetric cell. Under different UV radiant intensities as monitored by a commercial UV meter, the cell showed different intensities of color changes (Figure 12), which could be used as a UV strength sensor suitable for naked eye detection.

In summary, we have developed a new photochromic system based on rhodamine B salicylaldehyde hydrazone metal complex. The molecules showed absorption "turn-on" and fluorescence "turn-off" response upon UV irradiation both in solution and in solid matrix. UV light promoted the isomerization of the salicylaldehyde hydrazone moiety from the enol-form to the keto-form, and subsequently induced the spirolactam ring-opening in the rhodamine B part and caused the photochromic reaction. The system exhibited good fatigue resistance, and the lifetime of the ring-open state could be tuned by metal ions, temperatures, solvents, and chemical

Figure 12. Complex **1-Zn** in poloxamer 407 was exposed under different radiant intensity of UV. From left to right: 0, 25, 50, 75, 100 μW/cm^2. Exposure time was 2 min.

substitutions. The system was applied in photoprinting, as well as in UV strength sensors for direct eye detection of UV radiation pollution. Rhodamine B salicylaldehyde hydrazone metal complex is a new member of the photochromic family with advantages such as long-wavelength absorption, high molar absorption coefficient, facile synthesis, fast photoresponse, and good fatigue resistance. This work also provided a new strategy for designing photochromic systems based on coordination compounds and spirolactam-containing dyes. Currently, efforts toward developing more multifunctional molecules of this kind are under investigation in our laboratories.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Details on experimental procedures. Additional experimental data, including photos, videos, absorption spectra, fluorescence spectra, etc. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

■ REFERENCES

(1) Raymo, F. M.; Tomasulo, M. *Chem. Soc. Rev.* **2005**, *34*, 327.
(2) Yildiz, I.; Deniz, E.; Raymo, F. M. *Chem. Soc. Rev.* **2009**, *38*, 1859.
(3) Liu, D.; Chen, W.; Sun, K.; Deng, K.; Zhang, W.; Wang, Z.; Jiang, X. *Angew. Chem., Int. Ed.* **2011**, *50*, 4103.
(4) Dong, H.; Zhu, H.; Meng, Q.; Gong, X.; Hu, W. *Chem. Soc. Rev.* **2012**, *41*, 1754.
(5) Tsujioka, T.; Irie, M. *J. Photochem. Photobiol., C* **2010**, *11*, 1.
(6) Herder, M.; Utecht, M.; Manicke, N.; Grubert, L.; Pätzel, M.; Saalfrank, P.; Hecht, S. *Chem. Sci.* **2013**, *4*, 1028.
(7) Roldan, D.; Kaliginedi, V.; Cobo, S.; Kolivoska, V.; Bucher, C.; Hong, W.; Royal, G.; Wandlowski, T. *J. Am. Chem. Soc.* **2013**, *135*, 5974.
(8) Wang, F.; Liu, X.; Willner, I. *Adv. Mater.* **2013**, *25*, 349.
(9) Yagai, S.; Kitamura, A. *Chem. Soc. Rev.* **2008**, *37*, 1520.
(10) Chen, S.; Chen, L.-J.; Yang, H.-B.; Tian, H.; Zhu, W. *J. Am. Chem. Soc.* **2012**, *134*, 13596.

(11) Gopal, A.; Hifsudheen, M.; Furumi, S.; Takeuchi, M.; Ajayaghosh, A. *Angew. Chem., Int. Ed.* **2012**, *124*, 10657.
(12) Cui, J.; Gropeanu, R. A.; Stevens, D. R.; Rettig, J.; Campo, A. *J. Am. Chem. Soc.* **2012**, *134*, 7733.
(13) Natali, M.; Giordani, S. *Chem. Soc. Rev.* **2012**, *41*, 4010.
(14) Tong, R.; Hemmati, H. D.; Langer, R.; Kohane, D. S. *J. Am. Chem. Soc.* **2012**, *134*, 8848.
(15) Vantomme, G.; Lehn, J. M. *Angew. Chem., Int. Ed.* **2013**, *125*, 4032.
(16) Blanco-Lomas, M.; Samanta, S.; Campos, P. J.; Woolley, G. A.; Sampedro, D. *J. Am. Chem. Soc.* **2012**, *134*, 6960.
(17) Szymanski, W.; Beierle, J. M.; Kistemaker, H. A.; Velema, W. A.; Feringa, B. L. *Chem. Rev.* **2013**, *113*, 6114.
(18) Carroll, G. T.; Pollard, M. M.; van Delden, R.; Feringa, B. L. *Chem. Sci.* **2010**, *1*, 97.
(19) Marchi, E.; Baroncini, M.; Bergamini, G.; Van Heyst, J.; Vögtle, F.; Ceroni, P. *J. Am. Chem. Soc.* **2012**, *134*, 15277.
(20) Han, M.; Michel, R.; He, B.; Chen, Y. S.; Stalke, D.; John, M.; Clever, G. H. *Angew. Chem., Int. Ed.* **2013**, *52*, 1319.
(21) Zhang, J.; Zou, Q.; Tian, H. *Adv. Mater.* **2013**, *25*, 378.
(22) Wang, Z. Y.; Todd, E. K.; Meng, X. S.; Gao, J. P. *J. Am. Chem. Soc.* **2005**, *127*, 11552.
(23) Beharry, A. A.; Woolley, G. A. *Chem. Soc. Rev.* **2011**, *40*, 4422.
(24) Stein, M.; Middendorp, S. J.; Carta, V.; Pejo, E.; Raines, D. E.; Forman, S. A.; Sigel, E.; Trauner, D. *Angew. Chem., Int. Ed.* **2012**, *51*, 10500.
(25) Bleger, D.; Schwarz, J.; Brouwer, A. M.; Hecht, S. *J. Am. Chem. Soc.* **2012**, *134*, 20597.
(26) Minkin, V. I. *Chem. Rev.* **2004**, *104*, 2751.
(27) Wen, G.; Yan, J.; Zhou, Y.; Zhang, D.; Mao, L.; Zhu, D. *Chem. Commun.* **2006**, *28*, 3016.
(28) Niazov, T.; Shlyahovsky, B.; Willner, I. *J. Am. Chem. Soc.* **2007**, *129*, 6374.
(29) Balogh, D.; Tel-Vered, R.; Freeman, R.; Willner, I. *J. Am. Chem. Soc.* **2011**, *133*, 6533.
(30) Leung, D.; Kang, S. O.; Anslyn, E. V. *Chem. Soc. Rev.* **2012**, *41*, 448.
(31) Xie, X.; Mistlberger, G. N.; Bakker, E. *J. Am. Chem. Soc.* **2012**, *134*, 16929.
(32) Tian, H.; Yang, S. *Chem. Soc. Rev.* **2004**, *33*, 85.
(33) Zhu, W.; Yang, Y.; Métivier, R.; Zhang, Q.; Guillot, R.; Xie, Y.; Tian, H.; Nakatani, K. *Angew. Chem., Int. Ed.* **2011**, *50*, 10986.
(34) Perrier, A. l.; Maurel, F. O.; Jacquemin, D. *Acc. Chem. Res.* **2012**, *45*, 1173.
(35) Fukaminato, T.; Doi, T.; Tamaoki, N.; Okuno, K.; Ishibashi, Y.; Miyasaka, H.; Irie, M. *J. Am. Chem. Soc.* **2011**, *133*, 4984.
(36) Berberich, M.; Natali, M.; Spenst, P.; Chiorboli, C.; Scandola, F.; Würthner, F. *Chem.—Eur. J.* **2012**, *18*, 13651.
(37) Cheng, H.-B.; Zhang, H.-Y.; Liu, Y. *J. Am. Chem. Soc.* **2013**, *135*, 10190.
(38) Yang, Y.; Hughes, R. P.; Aprahamian, I. *J. Am. Chem. Soc.* **2012**, *134*, 15221.
(39) Iida, A.; Saito, S.; Sasamori, T.; Yamaguchi, S. *Angew. Chem., Int. Ed.* **2013**, *52*, 3760.
(40) Moorthy, J. N.; Mandal, S.; Mukhopadhyay, A.; Samanta, S. *J. Am. Chem. Soc.* **2013**, *135*, 6872.
(41) Nakai, H.; Kitagawa, K.; Nakamori, H.; Tokunaga, T.; Matsumoto, T.; Nozaki, K.; Ogo, S. *Angew. Chem., Int. Ed.* **2013**, *52*, 1.
(42) Song, L.; Yang, Y.; Zhang, Q.; Tian, H.; Zhu, W. *J. Phys. Chem. B* **2011**, *115*, 14648.
(43) Yang, Y.; Xie, Y.; Zhang, Q.; Nakatani, K.; Tian, H.; Zhu, W. *Chem.—Eur. J.* **2012**, *18*, 11685.
(44) Shi, W.; Ma, H. *Chem. Commun.* **2012**, *48*, 8732.
(45) Yang, Y.; Zhao, Q.; Feng, W.; Li, F. *Chem. Rev.* **2013**, *113*, 192.
(46) Yang, Y.; Seidlits, S. K.; Adams, M. M.; Lynch, V. M.; Schmidt, C. E.; Anslyn, E. V.; Shear, J. B. *J. Am. Chem. Soc.* **2010**, *132*, 13114.
(47) Knauer, K. H.; Gleiter, R. *Angew. Chem.* **1977**, *89*, 116.
(48) Willwohl, H.; Wolfrum, J.; Gleiter, R. *Laser Chem.* **1989**, *10*, 63.

(49) Fölling, J.; Belov, V.; Kunetsky, R.; Medda, R.; Schönle, A.; Egner, A.; Eggeling, C.; Bossi, M.; Hell, S. E. W. *Angew. Chem., Int. Ed.* **2007**, *46*, 6266.

(50) Belov, V. N.; Bossi, M. L.; Fölling, J.; Boyarskiy, V. P.; Hell, S. W. *Chem.—Eur. J.* **2009**, *15*, 10762.

(51) Wu, L.; Dai, Y.; Marriott, G. *Org. Lett.* **2011**, *13*, 2018.

(52) Schäfer, C. G.; Gallei, M.; Zahn, J.; Engelhardt, J.; Hellmann, G. P.; Rehahn, M. *Chem. Mater.* **2013**, *25*, 2309.

(53) Dürr, H.; Bouas-Laurent, H. *Photochromism: Molecules and Systems*; Elsevier: Amsterdam, 1990.

(54) Hadjoudis, E.; Mavridis, I. M. *Chem. Soc. Rev.* **2004**, *33*, 579.

(55) Li, N.; Tang, W.; Xiang, Y.; Tong, A.; Jin, P.; Ju, Y. *Luminescence* **2010**, *25*, 445.

(56) Meriwether, L.; Breitner, E.; Sloan, C. *J. Am. Chem. Soc.* **1965**, *87*, 4441.

(57) Fang, X.; Bando, Y.; Gautam, U. K.; Zhai, T.; Zeng, H.; Xu, X.; Liao, M.; Golberg, D. *Crit. Rev. Solid State Mater. Sci.* **2009**, *34*, 190.

(58) Fang, X.; Bando, Y.; Liao, M.; Gautam, U. K.; Zhi, C.; Dierre, B.; Liu, B.; Zhai, T.; Sekiguchi, T.; Koide, Y. *Adv. Mater.* **2009**, *21*, 2034.

(59) Fang, X.; Bando, Y.; Liao, M.; Zhai, T.; Gautam, U. K.; Li, L.; Koide, Y.; Golberg, D. *Adv. Funct. Mater.* **2010**, *20*, 500.

(60) World Health Organization. Ultraviolet radiation and the INTERSUN Programme. 2010. Available at http://www.who.int/uv/en/.

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