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An ensemble of Zn^{2+} with a rhodamine B-3-allylsalicylaldehyde hydrazone as novel photosensitive material: Photochromism, photopatterning, photoprinting and molecular logic gates



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ABSTRACT

An ensemble of Zn^{2+} with Rhodamine B-3-allylsalicylaldehyde hydrazone ($1-Zn^{2+}$), has been synthesized and fully characterized using spectroscopic techniques. A solution of 1-Zn²⁺ in THF, displays color changes from light yellow to pink color in the presence UV light (λ , 405 nm). The process is reversible and owes to keto-enol tautomerism which allows the opening of spirolactam ring of rhodamine in the presence of UV light. It is corroborated by the appearance of a new peak at $\lambda_{max} = 554$ nm. The ensemble, 1-2n²⁺ embedded in the matrix of silica gel, displays photo patterning phenomena initiated by the conventional light sources including sunlight. It also displays photoprinting property with a laser pen (λ 405 nm) and has been displayed by a videography. The module $1-Zn^{2+}$ meets real challenges through a simple synthetic route, fast response, and as a binary data storage system with non-destructive optical identity.

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1. Introduction

Photochromism can be defined as a reversible transformation between two isomers with different characteristics induced by alternating illumination with UV or visible light. Photochromic materials are of immense interest owing to their potential applications in photonic devices and optical memory media [1], switches [2], logic gates [3], optical data storage [4], photoresponsive, supramolecular self-assembly [5] and sensors [6]. In this context, Fulgide, spiropyran, spirooxazine, dithienylethene and diarylethene derivatives were reported as photochromic materials based on photoinduced isomerization involving ring-opening/closing reactions [7]. In some cases, it resulted out of enol-keto tautomerism [8]. Their applications as drug carrier and in molecular imaging processes are quite significant [9]. There are several classes of organic or inorganic materials which exhibited photochromic properties [10]. Tong et al reported Crystal violet lactone, a classic halochromic dye whose zinc complex acted as reversible photochromic material [11]. Zeng

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et al. reported a phenanthrene-bridged photochromic diarylethene recognizing Cu^{2+} and Hg^{2+} ions [12]. It had been reported earlier [13] that diarylethene could be utilized as a multi-addressable fluorescence switch in the presence of light, acids and bases. In this context, diarylethene derivatives had also been reported as colorimetric sensor for CN⁻ ions and fluorescent relay-sensor for Al³⁺/Cr³⁺ ions [14]. The MOF constructed on azobenzene and diarylethene ligands displayed light modulating absorption behavior of guests (CO₂, C_2H_2 , C_2H_4) [15]. The temperature and light dependent separation of C₂H₂/C₂H₄ mixture had also been accomplished by diarylethene based MOF [16]. Shouzhi Pu et al. reported a diarylethene derivative as a turn-on fluorescence sensor for the detection of Zn^{2+} ions at nano molar level [17]. Qianfu Luo et al. reported porous polymers based on diarylethenes modified triptycene as reversible photochromic material in solid and solution in THF. It also demonstrated characteristic solvent-dependent photochromism [18].

Rhodamine B and its several derivatives are considered most promising candidates for the construction of fluorescent switches and design of photochromic materials [19]. They reside in the home of dyes with long-wavelength absorption and emission, high absorption coefficient and excellent photostability [20]. Thus, their optical properties can be exploited for the development of novel photochromic materials. Unlike dithienylethene, rhodamine derivatives are less expensive and do not involve multi step synthesis [21]. The presence of phenolic group is imperative for enol-to-keto

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Scheme 1. Synthesis of 1-Zn²⁺.

conversion on exposure to UV radiation resulting into visual eye color changes. Thus, modification on the skeleton of the reactants by tuning of substituents may be considered an easy approach of preparation of a novel synthetic material. Rhodamine derivatives dispersed in a matrix, incorporated into the main chain of silica gel, or connected to the polymer chain, are useful in the display devices as they can be directly coated on a paper or any other solid surface [22].

Thus, in view of excellent precedence of rhodamine B, salicylaldehyde and allyl groups, judicious design and synthesis of rhodamine B allyl salicylaldehyde hydrazone **1** has been carried out in view of earlier report [23]. The incorporation of allyl group to **1** enhance overall optical properties of the system. Its ensemble with Zn^{2+} ions (Scheme 1) exhibited photochromic properties in THF solution. It exhibited good fatigue resistance, thermal bleaching rate, tunable detection of metal ions and photo printing.

2. Experimental

2.1. Materials and methods

The reagents and solvents were obtained from commercial sources. Solvents were dried and distilled prior to their use. Infrared and absorption spectra were recorded using Varian 3300 FT-IR and Shimadzu UV-1601 spectrophotometers, respectively. ¹H and ¹³C NMR spectra were recorded on a JEOL AL500 FT-NMR spectrometer using tetramethylsilane (TMS) as an internal reference. Fluorescence was measured on a Perkin Elmer fluorescence spectrophotometer in THF at room temperature. Electrospray ionization mass spectrometry (ESI-MS) was carried out in THF using an AMAZONSL Max ion trap mass spectrometer. The photochromic experiment was carried out using different light sources, including sunlight, UV lamp ($\lambda = 365$ nm, VL-6.LC) and UV torch ($\lambda = 405$ nm).



Fig. 1. (a) Images of 1- Zn^{2+} in THF upon irradiation ($\lambda = 365$ nm), and the recovery in dark at 25 °C. (b) Absorption and (c) fluorescence spectra of 1- Zn^{2+} in THF before and after UV irradiation. [1] = 10 μ mol/L, [Zn(II)] = 100 μ mol/L.



Fig. 2. (a) Color changes of 1-Zn²⁺ at different volume % of THF in DCM at 25 °C. [1] = 10 μ mol/L, [Zn(II)] = 1000 μ mol/L, 1 = 100, 2 = 80, 3 = 60, 4 = 40, 5 = 20, 6 = 0. corresponding absorbance changes at different time interval (b).

2.2. Synthesis of 1

Rhodamine hydrazone **1** was prepared by one-step condensation of rhodamine B hydrazide with 3-allyl salicylaldehyde in absolute ethanol at room temperature as reported earlier by us [23].

2.3. Synthesis of 1- Zn^{2+} ensemble

1-Zn²⁺ ensemble was prepared by the addition of $Zn(NO_3)_2$ (1.1 eq., H_2O) to the solutions of 1 (1.0 eq, THF). The reaction mixture was stirred for 2 h at room temperature; a dark yellow colored solution was allowed for its slow evaporation for getting its single crystals. But it turned out to be a light yellow powder. The solid was obtained in 40%, Yield and it was analyzed as: FT-IR (KBr, cm⁻¹): 3436, 2967–2869, 1713, 1612, 1545, 1515, 1449, 1384, 1356, 1307, 1270, 1233, 1180, 1153, 1117, 1076, 998, 975, 915, 869, 823, 787, 753, 710, 684, 620, 577, 528, 450; ¹H NMR (500 MHz, CDCl₃): δ 10.899 (s, 1H, --OH), 9.014 (s, 1H, --CH==N), 7.994 (d, *J* = 7.0 Hz, 1H, Ph—Ph), 7.529 (t, *J* = 6.75 Hz, 2H, —Ph), 7.157 (d, J = 7.5 Hz, 1H, --Ph), 7.062 (d, J = 7.0 Hz, 1H, --Ph), 6.959 (d, J = 7.5Hz, 1H, —Ph), 6.733 (t, J = 7.5 Hz, 1H, —Ph), 6.569 (d, J = 7.0 Hz, 4H, --Ph), 6.384 (s, 2H, --Ph), 5.950-5.936 (m, 1H), 5.056-4.981 (m, 1H), 3.359 (d, J = 8.0Hz, 10H, -CH₂), 1.164 (t, J = 6.75 Hz, 12H, CH₃); ¹³CNMR (125 MHz, CDCl₃): δ164.195, 156.343, 153.137, 136.627, 133.594, 131.636, 129.716, 129.457, 128.718, 128.334, 127.959, 123.976, 123.486, 118.582, 117.862, 115.462, 67.948, 65.942, 33.547, 25.580, 12.228; ESI-MS calcd for $[1-Zn^{2+} \cdot H_2O]^+$ (m/z): 683.1465; found: 683.1910.

3. Results and discussion

The compound **1** was prepared in good yield (75%) by a simple reaction between rhodamine B hydrazide and 3-allylsalicylaldehyde. Its ensemble with Zn^{2+} was obtained by the reaction of 1.0 eq of aqueous Zn^{2+} ions solution to **1** in THF (Scheme 1). It was well characterized by IR, NMR (¹H, ¹³C) and ESI-MS spectra (Figs, S1–S4[†], ESI). The FTIR spectrum of **1** displayed peaks at 1647 and 1763 cm⁻¹ assigned to v(>C=N) and ν (>C=O) vibrations respectively. These peaks shifted to 1612 and 1713 cm⁻¹ respectively in the spectrum of **1**-Zn²⁺. It supported the coordination of Zn^{2+} ion with **1**. A peak observed at 3436 cm⁻¹ supported the presence of the coordinated water molecule in $1-Zn^{2+}$. The presence of counter anions (nitrate) was supported by a peak observed at 1384 cm⁻¹. Further, ¹H NMR spectrum of **1**-Zn²⁺ showed peak at δ 10.899 and 9.014 assigned to -OH and -CH=N groups, respectively. They were shifted as compared to the peaks observed in the spectrum of free **1** at δ 11.132 and 8.851 respectively. ¹³C NMR spectrum of 1-Zn²⁺, displayed a peak at δ 65.942 ppm, assigned to tertiary carbon (sp³ hybridized) of closed spirolactam ring in consistence with the earlier report [24]. ESI-mass data of the ensemble displayed a peak at m/z 683.1910 and corroborates to $[1-Zn^{2+} \cdot H_2O]^+$ found very close to calcd., m/z: 683.1465. To investigate the stoichiometry of ensemble, a solution of 1 (10 µM, THF) was titrated with the incremental addition of an aqueous solution of Zn^{2+} ions. The absorption bands of 1 were observed at λ_{max} 276, 308, 346 nm. Its latter band was red-shifted by ~72 nm on the addition of Zn^{2+} ions (1.1 eq) and was observed at λ_{max} 418 nm with an isosbestic points at 330 and 372 nm (Fig. S5[†], ESI). The maximum absorbance was observed at 0.5 mol fractions, indicating a 1: 1 stoichiometry between **1** and Zn^{2+} ions (Fig. S6⁺, ESI). The binding constant was calculated (Fig. S7[†], ESI) using Benesi–Hildebrand method [25] and was found to be $1.8 \times 10^4 \text{ M}^{-1}$.

3.1. Photochromism of $1-Zn^{2+}$ in solution

As depicted in Fig. 1a, on the exposure of UV light to ensemble 1-Zn² $^+$ in THF solution, its color changed from light yellow to pink. Its original



Fig. 3. Colors of (a) silica gel + 1-Zn²⁺ (b) silica gel + 1-Zn²⁺ (daylight) (c) silica gel + 1-Zn²⁺ (UV light).



Fig. 4. (a) Pattern of a flower created on a powder sample prepared by mixing the solid 1-Zn²⁺ with-silica gel and supported on a plate and (b) colored pattern of the flower after exposure to sunlight/day light for 5.0 min.

light vellow color was again obtained in 10 min after the removal of UV light source (ESI, Video 1). The photochromic behavior of $1-Zn^{2+}$ was also monitored by UV-visible titrations as depicted in Fig. 1b. Upon exposure to light, closed-ring (enolic form) of 1-Zn²⁺ progressively photoisomerized to open keto form of $1-Zn^{2+}$ with concomitant appearance of a new band at $\lambda_{max} = 554$ nm. This band had been reported as a characteristic band of open ring formation. The pink colored solution appeared in the presence of light was bleached completely in the dark and the changes were found reversible as shown in Fig. 1a. The changes have also been demonstrated by their emission spectra as shown in Fig. 1(c). The keto-form was found as a typical fluorescence quencher owing to its strong electron-withdrawing nature. Therefore upon exposure of UV light, emission intensity gradually decreases with the appearance of two weaker peaks at $\lambda_{emission}$ 516 and 580 nm as shown in Fig. 1(c). However, in dark fluorescence emission from 1- Zn^{2+} observed at $\lambda_{emission} = 527$ nm was found intense.

Among other tested metal ions, Cu^{2+} and Ni^{2+} ions were also able to induce a keto-enol tautomerism. But their rates of conversion were either too fast or too slow and they lack the essential property of reversibility as observed in **1**-Zn²⁺ ensemble (Fig. S8†, ESI).

The polarity of the solvents significantly affects the dynamics of photochromism. In our present system, photochromic recovery was found moderate in THF: DCM mixture (60:40, v/v) with respect to time as depicted in Fig. 2(a). It was found fast in THF alone and slow in DCM. This was further corroborated by corresponding changes in their absorbance as shown in Fig. 2(b). In contrast to metal ions under consideration, anions such as F⁻, Cl⁻, Br⁻, l⁻, CN⁻, PO₄³⁻, were not able to perturb the photochromic property of **1**-Zn²⁺ system, (Fig. S9†, ESI) except EDTA²⁻ owing to its strong chelating ability with Zn²⁺ ions.

3.2. Photochromism of $1-Zn^{2+}$ in the matrix of silica gel

The photochromic property of $1-Zn^{2+}$ was also studied in a solid matrix of silica gel. The photochromic system on silica gel was prepared by mixing silica gel (10 g, 200–300 mesh), 0.5 g $Zn(NO_3)_2$ and 1 (0.2g) together with few drops of THF. After complete mixing, THF was evaporated at room temperature which provided a light yellow powder (Fig. 3(a)). After exposure to normal light for few minutes, the color changes to pink color as shown in Fig. 3 (b). However, color deepens on the exposure to UV light (Fig. 3 (c)). The color changes were not reversible as it was observed in the solution phase. It could be probably attributed to the acidic nature of silica gel which may bring out some side reactions. Furthermore, all the conformist light sources even sunlight could induce photochromism and prove the worth of the material as an added advantage.

It was further interesting to observe that a template of flower created on the surface of this material (Fig. 4a), turned to colored template of the flower on exposure of UV light as depicted in Fig. 4b. The novelty of this material in photo printing has also been displayed in Video 2 attached in the supplementary informations.

Evaluation of the fatigue resistance of 1-Zn²⁺ is an essential criterion to be investigated to evaluate its performance as a reversible photochromic material. As shown in Fig. 5, reversible transformation between two states of Keto (open) and Enol (close) for 5 times, and the absorbance at $\lambda_{max} = 554$ nm stayed almost constant without any apparent degradation.



Fig 5. Fatigue resistance of 1-Zn²⁺ upon irradiation with a light source of $\lambda = 365$ nm as well as keeping in dark alternatively in THF, [1] = 10 µmol/L, [Zn(II)] = 1000 µmol/L, and corresponding absorbance are recorded at $\lambda_{max} = 554$ nm.



Scheme 2. Proposed mechanism for color change of 1-Zn²⁺ upon UV irradiation.



Fig. 6. Truth table and sequential logic circuits displaying memory units with two inputs and two outputs in the presence of chemical inputs viz. I1 (UV light) and I2 (Dark).

3.3. Plausible mechanism

Because of the presence of both rhodamine B and salicylaldehyde moieties in $1-Zn^{2+}$ and the mandatory role of Zn(II) chelation in the photochromism, a tentative mechanism of the color changes of ensemble $1-Zn^{2+}$ upon exposure of UV light is shown in Scheme 2. The mechanism is based on the phenomenon of keto-enol tautomerization. The photo conversion from the closed-ring isomer to the open-ring isomer of **1** was also supported by the IR, ¹H and ¹³C NMR spectral analysis (Figs. **S10–S12**†, ESI) The IR spectrum showed shift in the carbonyl peak from 1713 to 1716 cm⁻¹ due to formation of keto form. The absence of —OH peak and significant changes in the peak of phenyl protons indicated the formation of keto-form. Furthermore, the absence of spiro carbon in ¹³C NMR supported the formation of open ring keto form.

3.4. Gated photochromism

Stimulated by the excellent selectivity, sensitivity, switchability, "turn-on" dual-optical signature, naked-eye readout, and rapid response of **1**-Zn²⁺ towards multi-stimuli in a large optical window (λ = 450–700 nm) (*vide supra*), two-input and two-output sequential logic circuits have been constructed [26]. Notably, the "turn-on" readout allows measurement of low-concentration of the analyte and decreases the probability of a false positive signal. In the set-reset of $1-Zn^{2+}$ by inputs UV light and dark, the logic circuit is planned in such a way that UV light works as I_1 whereas dark works as I_2 (sequence 1). The deviations in the absorbance at $\lambda_{max} = 556$ nm (OUT1) and the color change by the naked eye (OUT2) have been captured as the outputs. The threshold values have been fixed at 0.025 for OUT1 (Fig. S13⁺, ESI). The color changes from light yellow to pink are allocated as "0" and "1" respectively. When I_1 is high (considered as input signal "1–0") the absorbance arises at OUT1 and the color changes to pink at OUT2 (output signal "1–1"). Conversely, successive addition of I₂ (input signal "1–1") regains its initial absorbance and color with a signal pattern of "0–0" (Fig. 6). The reversible and reconfigurable sequences of set-reset logic functions



Fig. 7. Schematic representation of molecular keypad locks to access a secret code by monitoring the absorbance at 556 nm with different input sequences.

in a feedback loop exhibit the memory feature through OUT1 and OUT2 (Fig. 6).

The variation in the input sequences to generate varied outputs could also be realized to devise miniaturized information lock for locking information at molecular level (Fig. 7). The UV light and dark is coded as "B" and "H", respectively. The first addition sequence of "B" followed by "H" assumed as "ON" state. On the contrary, the inverted sequence order of "H" followed by "B" led to "OFF" state. Hence only the correct password "BH" could unlock the absorbance keypad at λ_{max} = 556 nm whereas the incorrect entry "HB" fails to do so. Thus, the cracking of the keypad lock becomes more difficult, thereby improving the security of the molecular devices remarkably.

4. Conclusions

In conclusion, an ensemble of Zn²⁺ with a rhodamineB 3-allyl salicylaldehyde hydrazone (1-Zn²⁺) displays photochromic property in THF solution upon light irradiation. The light irradiation promotes enol-keto tautomerism of the phenolic hydroxyl group present in the skeleton of in salicylaldehyde moiety. Ensemble 1-Zn²⁺ turned from light yellow to pink color on the exposure of UV light (λ = 365 nm). The photochromic reaction is reversible with good fatigue resistance. Remarkably, the system exhibits photochromic property in solution as well as in a solid matrix of silica gel which enable it promising for photo-patterning and photo printing and binary data storage applications.

Supplementary data to this article can be found online at https://doi. org/10.1016/j.saa.2019.03.003.

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