Modulation of a solid-state reversible fluorescent photoswitching based on a controllable photochromic pyrazolones

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Abstract

A novel solid-state reversible fluorescence photoswitching system (FPS) based on photochromism of photochromic pyrazolones has been developed by employing phosphor \( \text{Sr}_2\text{P}_2\text{O}_7 \) co-doped with europium ion and chlorine ion \((\text{Sr}_2\text{P}_2\text{O}_7-\text{EC}) \) and 1,3-diphenyl-4-(3-chlorobenzal)-5-hydroxypyrazole-4-phenylsemicarbazone \((\text{1a}) \) as the fluorescence dye and the photochromic compound, respectively. With carefully selected components, the absorption band of the keto-form photochromic pyrazolones well overlaps with the emission peak of \( \text{Sr}_2\text{P}_2\text{O}_7-\text{EC} \). The fluorescence emission intensity of \( \text{Sr}_2\text{P}_2\text{O}_7-\text{EC} \) is efficiently modulated by the photoisomerization of \( \text{1a} \) with controlling the exposure time in the solid state. The fluorescence photoswitching system displayed high fluorescence quenching efficiency and remarkable fatigue resistance. It can be repeated 7 cycles without observable the changes of emission intensity. A fluorescence quenching efficiency can be achieved with a reversible colour change from white to yellow.

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1. Introduction

Photochromic compounds have drawn an increasing attention in fundamental academic research as well as practical applications such as optoelectronic materials and devices [1–9]. In recent years, the potential application of photochromic compounds as reversible optical data storage and photoswitching devices leads to extensive studies on the control of their chemical and physical properties upon irradiation [10,11]. Among various types of photochromic compounds, photochromic pyrazolones is the most promising candidates because of their excellent properties such as excellent fatigue resistance, good thermal stability, etc [12–15]. Generally, photochromic pyrazolones material undergoes a reversible transformation from the enol-form isomer to the keto-form isomer upon irradiation with UV light in the solid state. The photoinduced interconversion of two states of photochromic pyrazolones is generally accompanied with changing of emission intensity. However, the reverse process is followed an incompletely recovering the initial emission intensity with visible light wavelength or heating [16,17]. Although the photoinduced and reversible fluorescence switching property between the two states of photochromic compounds has been improved. During the process of photochromic photoisomerization, the fluorescence switching property of photochromic pyrazolones itself can’t meet the requirement for actual application in photoswitching area.

A conventional approach of modulating fluorescence emission intensity relies on integrating fluorescent dye and photochromic compound into one molecular skeleton, in which the photochromic compound component is attached covalently to the fluorescent partner [18–21]. As for this type of fluorescence photoswitching molecule, the modulating behavior of fluorescence emission intensity may be attributed to the electron transfer [22–24] or energy transfer [25–27] during its photoinduced interconversion process. Another strategy of modulating fluorescence emission intensity is the intermolecular level, i.e. the photochromic unit and the fluorescent dye are dispersed uniformly together a solution or polymer medium [28]. In the solid state, compared to the previous approach, the non-covalent approach based on intermolecular interaction is very simple, effective and economical for designing novel optoelectronic materials and devices. However, it is crucial for a FPS to lie in the spectrum overlap between the absorption band of photochromic compounds and the emission peak of fluorescent dye in the solid state [29–31]. Recently, modulation FPS has been achieved by doping photochromic compounds into fluorescent dyes. For instance, Corredor et al. used phenylbenzo-thiazole (fluorine-derivative) as the donor and a photochromic...
2. Experimental

2.1. Synthesis

\( \text{Sr}_2\text{P}_2\text{O}_7 \)-EC was synthesized based on the literature [33], 4-phenylthiosemicarbazide (PSC) and 3-chlorobenzoyl chloride were purchased from J&K Company. The other materials were of analytical grade and used without further purification. The intermediate 1,3-diphenyl-4-(3-chlorobenzal)-5-pyrazolone (DP3ClBP) was synthesized according to literature [34]. 1,3-Diphenyl-4-(3-chlorobenzal)-5-hydroxypyrazole-4-phenylsemicarbazone (1a) was synthesized with similar method of the literature [26]. 1,3-diphenyl-4-(3-chlorobenzal)-5-keto-pyrazole-4-phenyl-semicarbazone (1b) is the photoisomerization product of 1a with 365 nm light irradiation (Fig. S1).

For 1a. Yield: 75%. Mp. 196.1–197.3°C. MS: \( m/z \) 507.1. Elemental analysis: (C\(_{29}\)H\(_{22}\)N\(_5\)O\(_2\)Cl): calcd. (%) C, 68.57; H, 4.37; N, 13.79. Found: (%) C, 68.43; H, 4.49; N, 13.79. \(^1\)H NMR (400 MHz, DMSO-\(d_6\)): 12.02–11.97 (1H, Pz–OH), 9.86 (1H, N5–H), 9.13 (1H, N4–H), 8.05–6.99 (19H, phenyl-ring). FT-IR (\(\nu\), FPS\(^{-1}\)): 3399 \(\nu\)(N2–H), 3362, 3259 \(\nu\)(N–H), 1646 \(\nu\)(C=O), 1599 \(\nu\)(C=N), 1550, 1507 \(\nu\)(phenyl), 1521, 1453 \(\nu\)(pyrazole-ring).

The FPS was synthesized by refluxing DP3ClBP (1 mmol), \( \text{Sr}_2\text{P}_2\text{O}_7 \)-EC (0.001 g) and 4-phenylthiosemicarbazide (1 mmol) in 3 mL of ethanol solution. Following three drops glacial acetic acid were added into the ethanol solution for 0.5 h under powerfully magnetic stirring at 80°C oil bath (Scheme 2). After cooling to room temperature, white powders were isolated from the solution and separated by filtration. Then, the FPS with different concentration \( \text{Sr}_2\text{P}_2\text{O}_7 \)-EC was prepared in the same way.

2.2. Characterization

\(^1\)H NMR spectra were performed on an INOVA-400 NMR spectrometer with DMSO-\(d_6\) as solvent. Melting point was measured with a TECHXT-5 melting point apparatus. The elemental analyses were made on FLASH EA 1112 Series NCHS-O analyser. Absorption spectra were measured on Hitachi UV-3010 spectrophotometer equipped with an integrating sphere accessory. Fluorescence spectra were studied using a Hitachi F-4500 fluorescence spectrophotometer. FT-IR spectra were recorded by using infrared diffuse reflectance spectroscopy in the range 400–4000 cm\(^{-1}\) on a BRUKER EQUINOX-55 spectrometer.

3. Results and discussion

3.1. Characteristic spectrum

The absorption spectra of 1a and \( \text{Sr}_2\text{P}_2\text{O}_7 \)-EC are measured in pure solid state. However, the intensity of absorption band (350–470 nm) of 1b is increasing by photoisomerization of 1a with 365 nm light continuous irradiation. The original absorption spectrum of 1a is recovered completely by heating at 120°C in a constant temperature oven (Fig. 1a). In addition, fluorescence emission peak of each compound was also measured in pure solid state, respectively. When 1a is irradiated by 365 nm light, 1a gradually transform into 1b, the emission intensity of 1a is decreasing to the emission intensity of 1b in the correspondingly time interval (Fig. 1b). So Fig. 1b shows both 1a and 1b exhibit weakly emission in pure solid state with the excitation wavelengths of 260 nm. The fluorescence emission spectra of \( \text{Sr}_2\text{P}_2\text{O}_7 \)-EC center at 415 nm by 300 nm excitation, and the fluorescence image of \( \text{Sr}_2\text{P}_2\text{O}_7 \)-EC (Fig. 1c) shows that the \( \text{Sr}_2\text{P}_2\text{O}_7 \)-EC exhibit strong blue fluorescence. No significant fluorescence spectral changes of \( \text{Sr}_2\text{P}_2\text{O}_7 \)-EC were detected with 365 nm light irradiation indicating that \( \text{Sr}_2\text{P}_2\text{O}_7 \)-EC is photostable under 365 nm light (Fig. 1d).

3.2. XRD spectrum of FPS

The XRD spectroscopy is employed to confirm that the FPS is composed of \( \text{Sr}_2\text{P}_2\text{O}_7 \)-EC and 1a. As shown in Fig. 2, the strong characteristic diffraction peaks of 1a can be observed at 5.8° and 6.2°, and the characteristic diffraction peaks of \( \text{Sr}_2\text{P}_2\text{O}_7 \)-EC can be observed at 31.8° which is assigned to the (11 2) reflection of EuPO\(_4\) (JCPDS No. 25-1055) [33]. Obviously, the characteristic diffraction peaks of 1a were also observed in the FPS, the result confirms that 1a is one of components of the FPS. When increasing the concentration of \( \text{Sr}_2\text{P}_2\text{O}_7 \)-EC in the FPS, an increasing intensity diffraction peak of \( \text{Sr}_2\text{P}_2\text{O}_7 \)-EC can be observed at 31.8°, which distinctly demonstrates that \( \text{Sr}_2\text{P}_2\text{O}_7 \)-EC is one of components of the FPS. So the FPS is composed of \( \text{Sr}_2\text{P}_2\text{O}_7 \)-EC and 1a.
3.3. Photoswitching mechanism of FPS

To explain the photoswitching mechanism of FPS, the FPS was characterized by absorption spectrum and fluorescence spectrum in the solid state. The absorption spectrum and the emission spectra of FPS were recorded upon 365 nm light irradiation at room temperature. Before 365 nm light irradiation, the FPS exhibits weak absorption band around 350–470 nm and strong fluorescence emission at 415 nm, which correspond to the absorption spectrum of 1a and fluorescence spectrum of Sr$_2$P$_2$O$_7$–EC, respectively. Upon 365 nm light irradiation, the FPS can be observed that an increasing absorbing band intensity of 1b around 350–470 nm, which is assigned to the formation of keto-form isomer of photochromic pyrazolones (Fig. 3a–c).

With prolonging irradiation time, the emission intensity of 415 nm is gradually diminishing in Fig. 4a–c. The phenomenon convincingly testifies that the quenching of fluorescence occur via energy transfer between Sr$_2$P$_2$O$_7$–EC and the keto-form isomer of photochromic pyrazolones as expected, when the fluorescent emission peak of Sr$_2$P$_2$O$_7$–EC overlaps well with the absorption band of the keto-form isomer of the pyrazolone unit (Fig. 4d). Therefore, the fluorescence emission intensity of Sr$_2$P$_2$O$_7$–EC is modulated efficiently by photoisomerization of 1a with 365 nm light irradiation. The reverse reaction happens from keto-form to enol-form isomer and the absorption band around 350–470 nm is gradually diminishing and recovers completely to the original absorption band intensity when the FPS is heated, which is due to excellent fatigue resistance, thermally reversible properties and rapid response time of 1a in pure solid state. In agreement with the naked eye observation, these results evidently demonstrate that photochromic pyrazolones works as a modulator for photoswitchable Sr$_2$P$_2$O$_7$–EC. So we can confirm that the fluorescence emission intensity of Sr$_2$P$_2$O$_7$–EC is efficiently modulated by energy transfer between Sr$_2$P$_2$O$_7$–EC and the keto-form isomer of photochromic pyrazolones.

3.4. Fatigue resistance of FPS

Finally, the repeatability of the photoreaction of FPS was assessed. To test the reversibility of fluorescence photoswitching, the absorption
Fig. 3. (a), (b) and (c) Absorption spectra of FPS (the concentration of Sr2P2O7–EC: 5 wt%, 10 wt%, 15 wt%) under 365 nm light irradiation at room temperature, respectively.

Fig. 4. (a), (b) and (c) Fluorescence emission spectra of FPS (the concentration of Sr2P2O7–EC: 5 wt%, 10 wt%, 15 wt%) under 365 nm light irradiation at room temperature (λex = 300 nm), respectively. (d) Normalized emission spectra of Sr2P2O7–EC (red line), absorption spectra of 1a before 365 nm light irradiation (blue line) and after 365 nm light irradiation (black line), respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
spectra of the different concentration of $\text{Sr}_2\text{P}_2\text{O}_7$–EC was checked upon 365 nm light irradiation and heating, respectively. Indeed, when the concentration of $\text{Sr}_2\text{P}_2\text{O}_7$–EC is 5 wt%, 10 wt% and 15 wt%, the absorption spectra of FPS is reversible and could go through more than 7 cycles without significant changes of absorbance spectra (Fig. 5a). The result indicates the photochromic reaction of pyrazolones is not affected by the presence of $\text{Sr}_2\text{P}_2\text{O}_7$–EC, which is crucial for fluorescence modulation. Whether reversible fluorescence on and off depended on the amount of doped $\text{Sr}_2\text{P}_2\text{O}_7$–EC into photochromic pyrazolones was further studied. However, when the concentration of $\text{Sr}_2\text{P}_2\text{O}_7$–EC is 5 wt%, 10 wt% and 15 wt%, the fluorescence emission intensity of the FPS increase correspondingly, and the fluorescence emission intensity of FPS was measured by alternating 365 nm light irradiation or heating. The fluorescence intensity of FPS returns fully to the initial state after heating at 120 °C, when the concentration of $\text{Sr}_2\text{P}_2\text{O}_7$–EC is 5 wt% and 10 wt% (Fig. 5b). It can be seen noteworthy that the reversible fluorescence “on” and “off” when the concentration of the $\text{Sr}_2\text{P}_2\text{O}_7$–EC is 5 wt% and 10 wt%. So fluorescence “on” and “off” efficiency can be improved remarkably by decreasing doping ratio, which also confirms that 1a regulate the fluorescence emission intensity of $\text{Sr}_2\text{P}_2\text{O}_7$–EC “on” and “off”. Although one might be concerned with the possibility of failing to photoswitching function of this system the overtime, the photoswitching property was not seen obvious degradation after a couple of months storage. The result indicates the fluorescence emission intensity of $\text{Sr}_2\text{P}_2\text{O}_7$–EC is modulated effectively and realized successfully by 365 nm light irradiation and heating at 120 °C based on the energy transfer between $\text{Sr}_2\text{P}_2\text{O}_7$–EC and the keto-form isomer of photochromic pyrazolones in the solid state. The highly optical sensitivity, excellent fatigue resistance and enhanced fluorescent contrast properties of FPS are promising for designing novel optoelectronic materials and devices in the solid state [35,36].

4. Conclusions

This work has demonstrated a novel approach of reversibly fluorescence photoswitching with the fluorescence responses driven by UV light and heating owing to the energy transfer between $\text{Sr}_2\text{P}_2\text{O}_7$–EC and the keto-form isomer of photochromic pyrazolones in the solid state. The FPS can work reversibly without apparent degradation in the solid state. The advantages of our binary organic–inorganic system are based on: (1) the optoelectronic devices are easily built for excellent photoresponse properties of FPS in the solid state. (2) the fluorescence photoswitching mechanism of FPS is unambiguously based on the photochromic reaction with the inherent properties of both photochromic pyrazolones and fluorescence dye integrality retained. Hence, the FPS is expected to broaden the applications of photochromic pyrazolones system in advanced optoelectronic materials and devices.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.jssc.2014.04.020.

References