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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 (**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 **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 phenylbenzothiazole (fluorine-derivative) as the donor and a photochromic

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diarylethene as the acceptor to modulate fluorescence in two-photon 3D optical-data-storage system [32]. Chen et al. designed a convenient FPS employing photochromic bis-(2,5-di-hydrogenthiényl)-ethane compound and 9,10-anthracenedinaphthalene dye, which fluorescence emission intensity could be effectively modulated in solution as well as in a polymer film [28].

Le et al. reported a luminescent material $\text{Sr}_2\text{P}_2\text{O}_7\text{-EC}$ with lower absorption coefficient and higher fluorescence emission intensity under UV light excitation in the solid state [33]. Given the advantages of $\text{Sr}_2\text{P}_2\text{O}_7\text{-EC}$ and photochromic pyrazolones, a FPS has been constructed successfully. There are also few reports of FPS based on fluorescence dye and photochromic pyrazolones. In this study, by using the pyrazolone derivative 1,3-diphenyl-4-(3-chlorobenzal)-5-hydroxypyrazole-4-phenylsemicarbazone (**1a**) as the photochromic unit and the $\text{Sr}_2\text{P}_2\text{O}_7\text{-EC}$ as the fluorescence dye, we have successfully synthesized a simple FPS with high fluorescence quenching efficiency and remarkable fatigue-resistance in the solid state. Schematic illustration of the FPS is shown in Scheme 1.

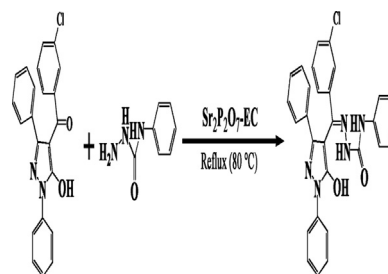
2. Experimental

2.1. Synthesis

$\text{Sr}_2\text{P}_2\text{O}_7\text{-EC}$ 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 (DP3CIBP) was synthesized according to literature [34]. 1,3-Diphenyl-4-(3-chlorobenzal)-5-hydroxypyrazole-4-phenyl-semicarbazone (**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: $m/zM+$: 507.1. Elemental analysis: ($\text{C}_{29}\text{H}_{22}\text{N}_5\text{O}_2\text{Cl}$): Calcd. (%) C, 68.57; H, 4.37; N, 13.79. Found: (%) C, 68.43; H, 4.49; N, 13.68. ^1H NMR (400 MHz, $\text{DMSO}-d_6$): 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 (ν , FPS^{-1}): 3399 ($\nu(\text{N}_2\text{-H})$), 3362, 3259 ($\nu(\text{N-H})$), 1646 ($\nu(\text{C=O})$), 1599 ($\nu(\text{C=N})$), 1550, 1507 ($\nu(\text{phenyl})$), 1521, 1453 ($\nu(\text{pyrazole-ring})$).

The FPS was synthesized by refluxing DP3CIBP (1 mmol), $\text{Sr}_2\text{P}_2\text{O}_7\text{-EC}$ (0.001 g) and 4-phenylthiosemicarbazide (1 mmol) in 3 mL of ethanol solution. Following three drops glacial acetic acid (0.1 mL) was dropwise 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



Scheme 2. Synthesis route of FPS.

solution and separated by filtration. And then, the FPS with different concentration $\text{Sr}_2\text{P}_2\text{O}_7\text{-EC}$ was prepared in the same way.

2.2. Characterization

^1H NMR spectra were performed on an INOVA-400 NMR spectrometer with $\text{DMSO}-d_6$ 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 spectrometer 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.

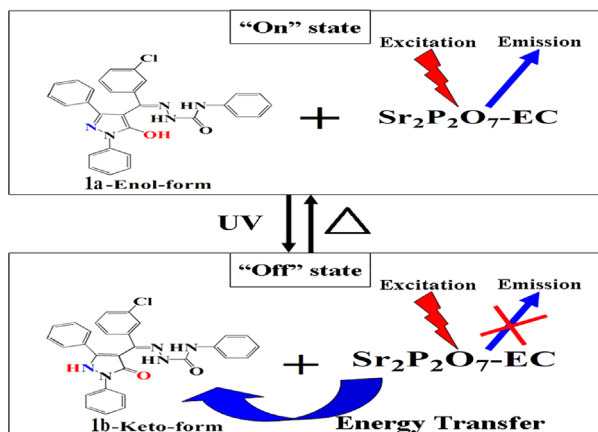
3. Results and discussion

3.1. Characteristic spectrum

The absorption spectra of **1a** and $\text{Sr}_2\text{P}_2\text{O}_7\text{-EC}$ 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 $\text{Sr}_2\text{P}_2\text{O}_7\text{-EC}$ center at 415 nm by 300 nm excitation, and the fluorescence image of $\text{Sr}_2\text{P}_2\text{O}_7\text{-EC}$ (Fig. 1c) shows that the $\text{Sr}_2\text{P}_2\text{O}_7\text{-EC}$ exhibit strong blue fluorescence. No significant fluorescence spectral changes of $\text{Sr}_2\text{P}_2\text{O}_7\text{-EC}$ were detected with 365 nm light irradiation indicating that $\text{Sr}_2\text{P}_2\text{O}_7\text{-EC}$ 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 $\text{Sr}_2\text{P}_2\text{O}_7\text{-EC}$ 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 $\text{Sr}_2\text{P}_2\text{O}_7\text{-EC}$ can be observed at 31.8° which is assigned to the (1 1 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 $\text{Sr}_2\text{P}_2\text{O}_7\text{-EC}$ in the FPS, an increasing intensity diffraction peak of $\text{Sr}_2\text{P}_2\text{O}_7\text{-EC}$ can be observed at 31.8°, which distinctly demonstrates that $\text{Sr}_2\text{P}_2\text{O}_7\text{-EC}$ is one of components of the FPS. So the FPS is composed of $\text{Sr}_2\text{P}_2\text{O}_7\text{-EC}$ and **1a**.



Scheme 1. Structures and photoswitching behavior of photochromic **1a** and fluorescent dye $\text{Sr}_2\text{P}_2\text{O}_7\text{-EC}$ by irradiation at 365 nm and heating, respectively.

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