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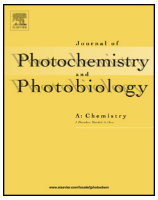

Aggregation-induced emission, photochromism and self-assembly of pyrazolone phenlysemicarbazones

Tianzhen Ning[a], Lang Liu[a,*], Dianzeng Jia[a,*], Xiaolin Xie[b], Dongling Wu[a]

[a] *Key Laboratory of Advanced Functional Materials, Autonomous Region, Institute of Applied Chemistry, Xinjiang University, Urumqi 830046, Xinjiang, China*

[b] *Key Laboratory for Large-Format Battery Materials and Systems, Ministry of Education, School of Chemistry and Chemical Engineering, Huazhong University of Science and Technology, Wuhan 430074, China*

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ABSTRACT

Four pyrazolone phenylsemicarbazone derivatives, 1,3-diphenyl-4-(3-substituent)-5-hydroxypyrazole 4-phenylsemicarbazone [substituent = chlorolbenzal (**1**), fluorobenzal (**2**), bromobenzal (**3**) and benzal (**4**)], were synthesized. On the one hand, the four compounds exhibit good solid-state photochromic behaviors upon the irradiation of UV light and heat, and high fatigue resistance. On the other hand, they have aggregation-induced emission (AIE) characteristics. The emission could also be greatly enhanced by cooling solutions, suggesting that the aggregation-induced emission is caused by the restricted intramolecular rotations of the peripheral aromatic rings or other substituents around the central pyrazole ring. In addition, with the increase of the aging time, aggregates of these compounds can self-assemble into 1D nanostructures from 0D nanoballs by the reprecipitation, leading to the red-shift of emission spectra. Thus, it paves the way for preparing multifunctional materials with photochromic and AIE behaviors.

1. Introduction

Since Tang and co-workers found some propeller-shaped molecules with aggregation-induced emission (AIE) phenomenon in 2001 [1,2], the design and synthesis of the organic compounds with excellent emission properties in solid state or aggregate state [3,4] have gained tremendous interest owing to their intriguing photophysical properties and widely potential applications, such as organic light-emitting diodes (OLEDs) and fluorescent biosensors [5–9], and a variety of AIE systems have been developed in the past decade [3,10]. Many efforts were focused on silole derivatives, substituted ethenes, CN-substituted phenylene vinylene, pyrene, anthracene derivatives and polymers, *etc*. For example, by means of the above AIE effect, silole derivatives were reported to use as biolabels for immunoassays [11], substituted ethenes were used to fabricate chemosensors, bioprobes and latent fingerprints [12–14], CN-substituted phenylene vinylenes were applied in on/off fluorescence switches for organic vapor [15], the pyrene and anthracene derivatives were widely used in fluorescence (FL) sensors [16], some polymers were also reported to show an unusual AIE characteristic, and have a great potential for optoelectronic applications [17]. Till now, the following mechanisms, such as the restriction of intramolecular rotation (RIR) [1,10,18], non-activation by avoiding non-radiative decay, preventability of excimers by twisted conformation [19], *J*-aggregate state [15] and intermolecular C—H/π interaction [20] are usually used to theoretically explain the AIE phenomenon. It is well known that the photophysical properties of photochromic materials depend on the intrinsic natures and AIE behaviors of photochromic compounds. Although there are some progresses in AIE families, it is still very important to develop new compounds with AIE behaviors for enriching the AIE system and exploring their potential applications.

Recently, we found that pyrazolone derivatives exhibit reversible photochromic, high fatigue resistance, and fast response in the solid state [21–23]. And their synthesis method is very simple compared with other photochromic compounds such as spiropyrans, spiroxazines, dithienylethenes and fulgides, *etc*. Furthermore, photochromic mechanism of pyrazolones in solid state is related to the transformation between the enol form and the keto form through proton transfers upon the irradiation of light and by heating [24–26]. However, little attention is paid on their AIE behaviors. The combination of solid-state photochromism and light-emitting ability within a simple compound is of fundamental interest for such applications as molecular electronics, fluorescent switches,

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* Corresponding authors. Tel.: +86 991 8588883; fax: +86 991 8588883.
E-mail addresses: liulang@xju.edu.cn, llyhs1973@sina.com (L. Liu).

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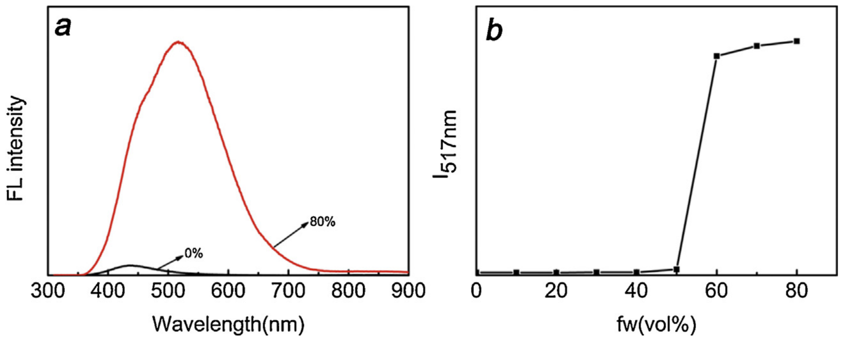


Fig. 1. (a) Emission spectra of **1** in ethanol and ethanol–water mixtures. (b) Plot of emission intensity at 517 nm versus f_W for **1** in ethanol and ethanol–water mixtures. Concentration = 2 mM; excitation wavelength = 290 nm.

and optical memory devices [27–30], and exploiting some novel AIE-active compounds with solid-state photochromic properties is a possible way to develop new photochromic materials. Herein, pyrazolone phenylsemicarbazones with different substitutes, such as 3-chlorolbenzal, 3-fluorobenzal, 3-bromobenzal or benzal at the 4-position of the pyrazole ring, are designed and synthesized. And their aggregation-induced emission (AIE) characteristics and self-organization are investigated for the first time.

2. Results and discussion

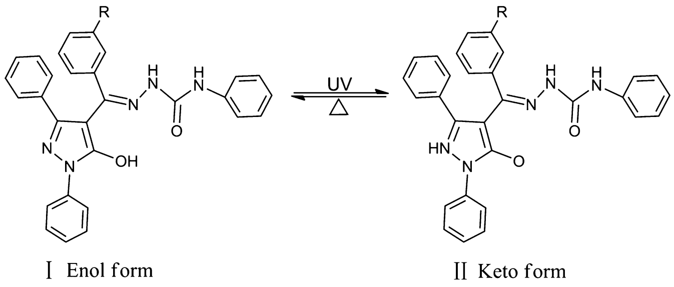
2.1. Aggregation-induced emission behaviors

The photoluminescence (PL) spectra for **1** in ethanol and ethanol–water mixtures and the emission peak intensities at varying water fractions are shown in Fig. 1. Since water is a non-solvent of **1**, and ethanol is a good solvent, the luminogen molecules must aggregate in the aqueous mixtures with high water fractions (f_W). From Fig. 1, it can be obviously seen that the dilute solution of **1** in ethanol gives a very weak emission peak at 437 nm. The weak PL signals are always recorded at $f_W \leq 50\%$ because the **1** molecules are still genuinely dissolved in these mixtures. The PL intensity starts to rise at $f_W > 50\%$, at which point slight increase in f_W gives abrupt promotion in emission intensity. When f_W is as high as 80%, the emission maximum is at 517 nm. Compared to the value in the ethanol solution, red-shift of 82 nm occurs in ethanol–water mixtures, suggesting that the luminogen molecules aggregate in such an aqueous media and conformational reorganization in geometry and form *J*-aggregation [31]. Furthermore, from the molecular solution in ethanol to the aggregate suspensions in 80% aqueous mixture, the emission intensity of **1** at 517 nm is increased by 24 times, which indicates that the compound **1** has AIE properties.

In order to understand the substituent effect at the 4-position of the pyrazolone ring, the other three compounds (**2**, **3** and **4** in Scheme 1) were synthesized. The emission spectra and the emission peak intensities at varying water fractions (f_W) for the three compounds in ethanol and ethanol–water mixtures are shown in Fig. S1 in Supporting Information. Similar AIE behaviors are also observed for **2**, **3** and **4**. The enhancement of the maximum emission peaks as adding 80% water is as high as 68 (**2**), 36 (**3**), and 65 (**4**) times in comparison with their corresponding values in ethanol solutions.

Furthermore, compared with PL spectrum of the compound **4** in 80% aqueous mixture, the wavelength of the maximum emission for compounds (**1**-Cl, **2**-F and **3**-Br) obviously blue-shifts to 17–67 nm due to the substituent effect of halogen atoms on the phenyl ring at the 4-position of the pyrazolone ring. Especially, F atom with the high electronegativity results in the maximum blue-shift for the emission wavelength of **2**. The results indicate that the intensity and wavelength of emission can be tuned by adjusting molecular structure with different substituent groups.

To validate the AIE activity of four compounds, the effect of temperature on their emission was further studied. PL spectra of **1** in ethanol at different temperatures are shown in Fig. 2. Generally, the spectral profile hardly changed with temperature, suggesting that the emission is still associated with the radiative decay of the singlet excitons [32,33]. However, when the dilute ethanol solution of **1** was cooled to below the melting point of ethanol (−114 °C) from room temperature, the liquid solution changed to a solid "glass". The intensity of the PL spectrum abruptly increased, which was 20 times higher than that at room temperature, indicating that the thermally activated intramolecular motions were obviously limited by freeze [1,20]. From Fig. S2 in Supporting Information, similar behaviors are observed for the other three compounds. Furthermore, we also found that the pyrazolone derivatives have similar structures for siloles (Fig. S3). In other words, substituents on the pyrazolone may rotate freely around the pyrazole ring in



1(R=Cl) **2**(R=F)
3(R=Br) **4**(R=H)

Scheme 1. Photochromic mechanism of the compounds.

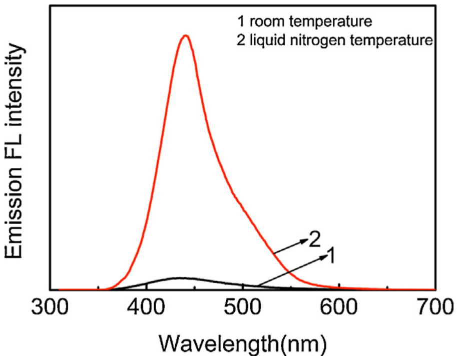


Fig. 2. Emission spectra of **1** in ethanol dilute solution at room temperature and liquid nitrogen temperature.