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Switching the emission of di(4-ethoxyphenyl)dibenzofulvene among multiple colors in the solid state

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Luminescent materials exhibiting emission switching in the solid state have drawn much attention though there is still no clear design strategy for such materials. In this letter, we reported the crystallization induced emission enhancement (CIEE) of di(4-ethoxyphenyl)dibenzofulvene (1), and achieved switching its emission among four different colors through modulation of its molecular packing patterns. We have investigated its potential application as optical recording materials. The twisted conformations of CIEE compounds afford morphology dependent emission and facilitate tuning their emission through modulation of molecular packing patterns. Thus we provide a possible design strategy for solid stimulus responsive luminescent materials.

fulvene, crystallization induced emission enhancement, stimulus responsive luminescent materials, packing pattern

1 Introduction

Stimulus responsive luminescent materials have drawn much attention due to their potential application in fluorescent sensors, optical high density data storage, and security inks [1–4]. Of particular interest are those luminogens whose emission could be tuned reversibly in the solid state as many luminogens are used in the solid state in practical application [5, 6]. Modification of molecular structure is an effective way to modulate emission of luminogens in solutions; however, limit success has been made in switching the emission of solid materials due to the insufficient conversion or irreversible reactions in the solid state. Instead of chemical modification of molecular structure, emissions of some luminogens could be tuned through altering the molecular packing [7–10]. Though some luminescent materials exhibit obvious morphology dependent emissions, examples that show controllable and reversible luminescence switching are still rare, and there is still no clear design strategy for such materials. Moreover, most of the reported luminogens contain only one luminophore and form merely two luminescent states; thus their emissions can be switched between only two states and multi-colored emission switching has rarely been achieved [11–13].

Many panel-like organic luminescent materials suffer from the notorious aggregation-caused quenching (ACQ) due to the formation of such detrimental species as excimers in the aggregate state [14, 15]. Closely related to the ACQ effect is the crystallization of luminogens in the solid state, which normally red-shifts the luminescence spectra and weakens or even quenches their emissions [14, 16]. Although various approaches have been taken to interfere with luminogens aggregation and prevent the crystallization of luminogens, however, only limited success has been made due to the fact that aggregate formation and crystallization

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are intrinsic processes when luminogenic molecules are located in close vicinity in the condensed phase.

Tang reported a phenomenon which is exactly opposite to the ACQ effect: a group of non-planer molecules are nonemissive when molecularly dissolved in solution, however, intense emissions are turned on when they form aggregates [17–19]. As the emission are induced by aggregation, thus Tang coined it as aggregation-induced emission (AIE). Restriction of intramolecular rotation (RIR) in the aggregates have been identified as a main cause for the AIE phenomenon, and many new AIE luminogens have been developed based on the RIR mechanism, and used as chemosensors, bioprobes and solid-state emitters [20–27].

During development of the AIE active compounds, Tang and Dong [28, 29] first observed that some of them exhibit higher PL intensity and bluer emission in the crystalline state than in the amorphous phase, which is termed as crystallization induced emission enhancement (CIEE).

The propeller-like conformations of AIE molecules afford loose packing patterns and rule out any strong interaction between molecules, which facilitates transforming luminogens aggregates between amorphous and crystalline states through thermal, vapor and mechanical stimuli. Thus, emissions of those CIEE luminogens could be switched between two different colors accompanied with varied brightness through tuning the molecular packing patterns. Through introduction of weak interactions, we even obtained CIEE luminogens exhibiting multiple colored emission switching. Hence we provide a possible design strategy for the stimuli responsive solid luminescent materials [30, 31].

Dibenzodiphenylfulvenes exhibit CIEE effect and some of them even display three different emission colors depending on their morphology [29, 32]. Zhang and coworkers [33, 34] have also observed that di(4-ethoxyphenyl)dibenzo-fulvene (1) exhibit three different morphology dependent emission colors. However, no further effort has been paid on switching the emission of luminogen 1 in the solid state. In this letter, we reported the CIEE effect and four-colored morphology dependent emissions of 1 and tried to switch its emission through modulation of its molecular packing patterns. Luminogen 1 also exhibits solvent vapor, thermal, and mechanical stimulus responsive emission. And we try to provide a possible design strategy for stimulus responsive luminescent materials.



Scheme 1 The synthetic route of luminogen 1.

2 Results and discussion

Compound **1** was prepared according to the synthetic route given in Scheme **1** with ethoxyl groups introduced to the DPDBF molecules [32].

Similar to other diphenyldibenzofulvenes, 1 is nonemissive when molecularly dissolved in solution indicated by photos and PL spectrum in Figure 1 [29, 32]. However, the emission of 1 is turned on, when large amount of water is added to the solution due to the formation of aggregates in the mixtures with high water contents. That is, luminogen 1is AIE active.

Careful inspection of the PL spectra of dye 1 in the aqueous mixtures reveals that the aggregates of 1 in suspensions with varied water fraction (f_w) emit lights with different colors and different intensity. The emission is switched on when f_w is increased to 60%. The intensity reaches a maximum at the 70% water content, and then decreases with further increase of f_w . The emission color also changes from green ($f_w = 60\%$, 485 nm) via blue ($f_w = 70\%$, 455 nm) to orange ($f_w = 80\%$ and 90%, 583 nm). Evidently, the emission of 1 in the acetonitrile/water mixture can be tuned easily among three different colors at various efficiencies (cf., Figure 1) by simply adjusting the volume ratio of the two solvents, which is seldom reported. Why does the emission of aggregate of 1 depend on the water content in solvent mixtures? As mixing of solvent cannot change the chemical structure of 1, which is confirmed by the TLC plates checking, thus, similar to one reported diphenyldibenzofulvene derivatives, the varied emissions of 1 should be caused by the formation of different packing patterns in mixtures with varied f_w . In mixtures with the "lower" $f_{\rm w}$, the luminogen molecules may assemble steadily in an ordered fashion to form more emissive, bluer crystalline aggregates. In the mixture with the "higher" f_w , however, the luminogen molecules may agglomerate quickly in a random way to form less emissive, redder amorphous particles [29, 32].

In addition to the photophysical properties of the luminogen suspensions, the morphology dependent emission and multiple colored emissions switching in the solid state are more attractive. Similar to di(4-propoxyphenyl)dibenzofulven, luminogen 1 was also reported to exhibit three different emission colors (blue, green and orange) with varied efficiency. However, emission modulation of luminogen 1 in the solid state have not been tried which may enable its potential application in high density data storage.

The green emissive single crystal of **1** (**1GSC**, Figure 2(A)) was obtained through slow evaporation of chloroform-petroleum ether mixture. As is shown in Figure 2(B), the emission of **1GSC** was turned to sky blue upon heating at 120 °C for 30 minutes, and the PL spectrum of the annealed **1GSC** fitted well with that of the crystals grown from methanol. The emission change should be caused by



Figure 1 (a) PL spectra of luminogen **1** in acetonitrile/water mixtures with varied water fraction (f_w). Excitation wavelength: 350 nm; (b) plot of PL peak intensity *vs.* f_w of the aqueous mixture. Concentration: 50 μ M; excitation wavelength: 350 nm. Photos of **1** in acetonitrile/water mixtures with f_w of 0, 60%, 70%, 90% were taken under 365 nm UV illumination.

the transformation of 1 from one crystalline phase to another during heating. However the blue-crystal cannot return back to green crystal indicating an irreversible phase transition.

Amorphous solid of organic compounds will crystallize when they are fumed by organic solvents or heated, thus we try to switch the emission of luminogen 1 through modulation of its morphology. The amorphous solid of 1 (1Am, Figure 2(E)) which was prepared through quenching its melt with liquid nitrogen emits weak orange light under UV light. However, the emission of 1Am is intensified and PL spectrum is blue-shifted to 495nm when fumed with chloroform, while 1Am transfers to bright yellow emissive solid when heated at 105 °C for 10 min. The powder X-ray diffraction (XRD) of the fumed and annealed solid of 1 indicated that 1Am transform to varied crystalline solids which exhibit varied emission colors (Figure S1). 1Am could be obtained again through quenching of its melt. Thus it is clear that



Figure 2 Digital images of **1**. (A) **1GSC**; (B) annealed **1GSC**; (C) blue crystals grown from solutions; (D) **1Am** fumed with chloroform; (E) **1Am**; (F) annealed **1Am**; (G) PL spectra of samples from a to f in the images. Excitation wavelength: 400 nm for **1Am** and 350 nm for others. Photos were taken under UV illumination. I, 120 °C, 30 min; II, fuming with chloroform vapor, 15min; III, 105 °C, 10 min, under ambient condition; IV, heating to melt and quickly cooling.

luminogens 1 exhibit four different emission colors and the emission of 1 could be tuned between blue, green, yellow and orange color with varied efficiency, which is seldom reported.

Grinding normally transforms organic luminogens from crystals to amorphous solid [35–38], and the amorphized solid of luminogens will crystallize again upon heating or fuming with organic solvent, thus the emission of the AIE luminogens can be reversibly tuned between varied colors by the mechanical and thermal stimuli or solvent fuming. As we expected, luminogen 1 exhibits mechanochromic fluorescence. The ground solid was prepared through grinding the crystals of 1 in a mortar and was transfer to quartz plates for investigation of emission switching. As is shown in Figure 3, emissions of all the three colored crystals (Figure 2) are turned dark and red-shifted (Figure 3(A1-A4)) due to the transformation from crystal to amorphous solid upon grinding.

The weak orange emissive ground solid piled in a heap on the quartz plate transferred to green emissive solid upon heating and the PL of annealed sample fit well with that of **1GSC** (Figure 3(A1-B)). However, we noticed that when the ground powder of **1** are dispersed on the quartz plate, its emission turned to sky blue upon heating. Why does the macroscopic scale piling patterns affect phase transformation in the molecular scale? As the ground powder in dispersed state will be heated quickly when put into the oven, and samples in a heap may be heated slowly compared with those dispersed powder. Thus the emission of luminogen **1** could be tuned reversibly among three different colors through repeating grinding and heating. The emission of ground powder can also be tuned reversibly between bright green and dark orange through repeating grinding and solvent fuming, and this process is independent of the macroscopic scale aggregate pattern. (Figure 3(A3), 3(A4), 3(D), 3(E))

The mechanochromic fluorescence of luminogen **1** prompts us to investigate its potential application as optical recording materials. We ground luminogen **1** on a piece of weighing paper and obtained a dark orange emissive paper. The paper turned to intensively blue-green emissive when annealed at 120 °C. Then we wrote "BNU" (the abbreviation of Beijing Normal University) on the paper, and faint



Figure 3 Photos of ground solid of luminogen **1** in (A1 and A3) pile or dispersed powder on quartz plate (A2 and A4); (B–E) photos of ground solid after treating are placed in corresponding places; (F) PL spectra of samples in the photos. Excitation wavelength: 400 nm for A, and 350 nm for others. Photos were taken under UV illumination. I, heating at 120 $^{\circ}$ C, 10 min, under ambient condition; II, grinding; III, fuming with chloroform, 5 min.



Figure 4 Procedures of repeating writing and erasing process using luminogen **1** as the emissive materials. Photoluminescent images were taken on a weighing paper under UV irradiation at 365 nm. All the experiments were carried out under ambient condition.

orange letters appeared on the blue-green background due to the amorphization of 1 in the written "BNU" area. However, after heated at 120 °C, the "BNU" nearly merged in the background due to the crystallization of 1 in area of "BNU". The writing and erasing process can be repeated many times due to the physical essence of the transformation.

3 Conclusions

In this letter, multi-colored emission switching of luminogen 1 in the solid state is achieved and potential application of luminogen 1 has also been investigated. Many AIE and CIEE active compounds take propeller-like conformations. Introduction of weak interactions into those AIE and CIEE compounds may lead to polymorph of those compounds. The non-planar conformations of those molecules induce loose packing patterns, thus facilitate their transforming between varied morphology through thermal, vapor and mechanical stimuli. Thus we provided a possible design strategy for solid stimulus responsive luminescent materials.

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