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Reversible Switching Emissions of Tetraphenylethene Derivatives among Multiple Colors with Solvent Vapor, Mechanical, and Thermal Stimuli

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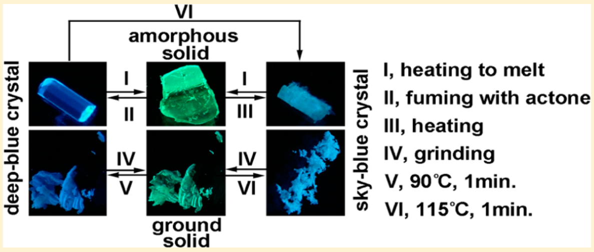
Supporting Information

ABSTRACT: Luminogens exhibiting reversible multicolored emission switching in the solid state have been seldom reported, though they are of theoretical and practical importance. Through introduction of weak interaction to the propeller-like molecules, we obtained two tetraphenylethene derivatives exhibiting morphology dependent multicolored emissions. The emissions of the two compounds could be switched reversibly among three colors in the solid state by reversible transformation among three different aggregation states of the luminogens when treated with different stimuli. Hence a possible strategy to construct luminogen exhibiting reversible multicolored emission swithching is disclosed.



INTRODUCTION

Stimulus responsive luminescent materials have drawn much attention because of their fundamental importance and potential applications in sensors,[1−6] memory,[7] and security inks[8] fields. Dynamical and reversible switching of molecule emission in the solid state is particularly attractive. Some luminogens exhibit morphology dependent fluorescence; thus, the emission of solid materials can be modulated by simply altering the packing pattern instead of changing molecule structures.[9−14] Some pyrene, anthracene, and *p*-phenylenevinylene based liquid crystals (LC) show mechanochromic and thermochromic luminescence in LC states.[15−22] Some luminogens switch their emissions by reversibly changing their aggregates between amorphous and crystalline or between two different crystalline states when treated with solvent vapor, thermal or mechanical stimuli.[23−39] Several luminogen-containing polymer blends have also been reported to exhibit mechanochromic fluorescence.[40−47] However, most of the reported luminescent materials contain only one luminophore and form merely two luminescent states; thus their emissions can be switched between only two states. Though several luminogens do emit multicolor lights in various states,[14,48−51] luminescence switching among multiple colors has rarely been achieved.

Kato and Sagara have successfully developed a LC mixture (containing one dumbbell-shaped luminophore) that can emit reddish-orange, yellow, and green lights respectively at different LC states. The emission colors are easily distinguished by the naked eye. The luminescence can be switched among multiple colors by changing the molecularly assembled structures with mechanical and thermal stimuli.[52] Jia and co-workers have also obtained mechanochromic material exhibiting multicolored emission through mixing of two types of peptides bearing a pyrene group and rhodamine B moieties, respectively.[53]

We still cannot find any report on a single compound whose emission could be switched among three different colors by external stimuli, though it may lead to multiresponsive sensors and may greatly increase the optical data storage density.

In 2001, we observed a novel phenomenon of aggregation-induced emission (AIE): a series of propeller-like molecules, such as hexaphenylsilole and tetraphenylethene (TPE), are nonemissive when dissolved in solution but are induced to emit intensely by aggregate formation. The restriction of intramolecular rotation (IMR) was identified as the main cause for the AIE effect.[54−60]

Introduction of weak interaction to AIE molecules may yield polymorphic compounds due to the varied balance of the weak interactions between molecules in the solid state. The twisted

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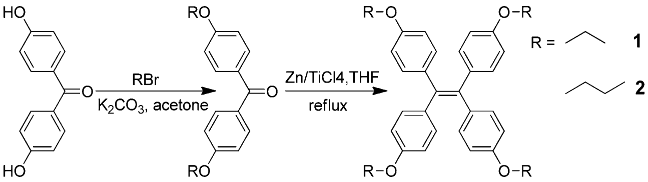
conformations of AIE molecules afford loose packing patterns in the solid state, which may facilitate the transforming between different aggregate states.

In this paper, we introduce weak interaction (such as C−H⋯π and C−H⋯O interaction) to TPE molecule through attachment of alkoxy groups to TPE molecules, and successfully obtained two luminogens exhibiting vapo-, thermo-, and mechanochromic fluorescence. And the emissions of both luminogens can be switched among three colors by external stimuli in the solid state.

■ RESULTS AND DISCUSSION

Luminogen **1** and **2** were prepared conveniently by McMurry coupling of alkoxy-substituted benzophenone, and their structures are shown in Scheme 1. Detailed synthetic routes and characterization of the product are described in the Supporting Information.

Scheme 1. Synthetic Route of Compounds 1 and 2



Both **1** and **2** are nonemissive when molecularly dissolved in acetonitrile. However, when a large amount of water is added to the solution, the emissions of **1** and **2** are turned on. When the volume fraction of water (f_w) is 90%, the corresponding PL intensities of luminogen **1** and **2** are increased by up to 330 and 310 times in comparison with those at f_w = 0% (Figure 1).

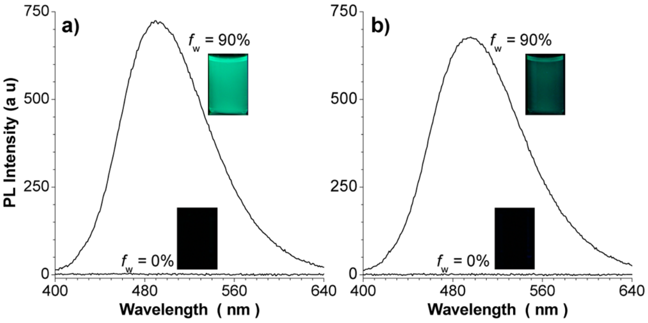


Figure 1. PL spectra of luminogens (a) **1** and (b) **2** in acetonitrile and acetonitrile/water mixtures. Luminogen concentration: 5 × 10^{-5} M. Inset: Photographs of luminogen (a) **1** and (b) **2** in acetonitrile/water mixtures with the volume fraction of water (f_w) is 0% and 90% taken under illumination of a UV light.

Water is a nonsolvent of both luminogens; thus aggregation will form with the f_w increased. Then the emissions of both the luminogens are caused by aggregation; that is, they exhibit AIE activity as many other TPE derivatives.[10] Rotations and vibrations of phenyl rings may serve as effective energy dissipation pathways of the whole excited luminogens and result in their fluorescence quenching in dilute solutions. While in aggregates, the phenyl rings are solidified by interaction between molecules, thus preventing the molecules from nonradiative pathways caused by rotations and vibrations of phenyl rings. The twisted conformations (evidenced by the crystal structures in Figure S2 (Supporting Information) and their cif files (Supporting Information)) rule out specific strong intermolecular interactions (such as π−π stacking or H/J-aggregates), which may quench the emission of traditional panel-like luminogens.

The photophysical properties of luminogens in the solid state deserve more attention as most of luminogens are used in solid states. Deep-blue emissive crystals of luminogen **1** (**1CA**, Figure 2a, emitting at 448 nm) are obtained from its solution by slow evaporation of solvent. Because many AIE luminogens show morphology dependent luminescence,[61,62] we prepared the pure amorphous solid of luminogen **1** (**1Am**, Figure 2c) by quenching of its melt. **1Am** emits green light peaked at 491 nm, which is about 43 nm red-shifted compared with that of **1CA**. However, **1Am** cannot return to **1CA** upon heating but affords another crystal (**1CB**) of luminogen **1**, which emits a sky-blue light peaked at 462 nm. The exothermic peak at 66 °C in the differential scanning calorimetry (DSC) thermogram of **1Am** (Figure 2h, line c) indicates this solid−solid phase transition (from **1Am** to **1CB**). The DSC thermogram and powder X-ray diffraction (XRD) patterns of **1CB** also reveal that **1CB** is a new crystalline phase different from **1CA**. Thus, it is clear that luminogen **1** exhibits tricolored luminescence depending on the molecule packing patterns in solid states.

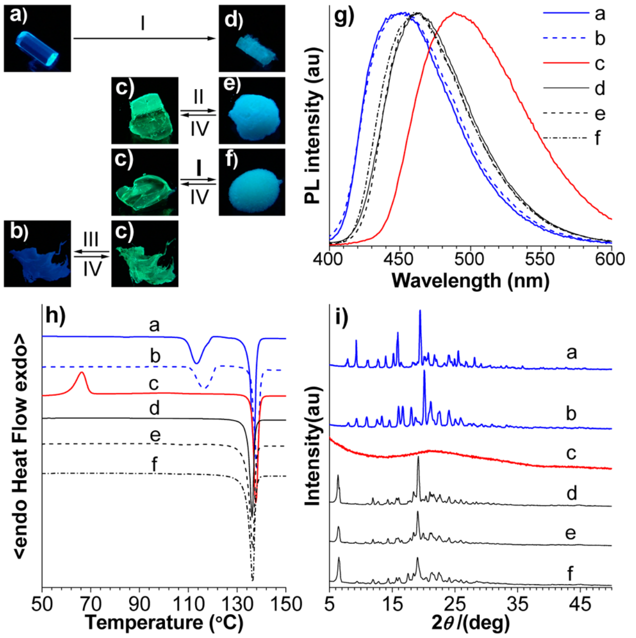


Figure 2. Photos of (a) **1CA**, (b) **1Am** fumed by acetone, (c) **1Am**, (d) **1CB**, and (e, f) **1Am** annealed at (e) 90 °C and (f) 115 °C. (g) PL spectra (Excitation wavelength: 370 nm), (h) DSC thermograms, and (i) powder XRD patterns of samples (a)−(g) in the images. Photos were taken under UV illumination. Conditions: I, 115 °C, 1 min; II, 90 °C, 1 min; III, fuming with acetone vapor, 5 min; iv, heating to melt and quickly cooling.

Similar to luminogen **1**, luminogen **2** can also emit three different color lights at different aggregation states. Deep-blue emissive crystals of luminogen **2** (**2CA**) were obtained by recystallization from its solution, and the sky-blue emissive crystals (**2CB**) were obtained through annealing of its amorphous solid (**2Am**) (Figure 3).

Luminogens **1** and **2** exhibit about 44−56% quantum yield in crystal and amorphous states, which coincides with the reported value of other TPE derivatives.[63] Close inspection of

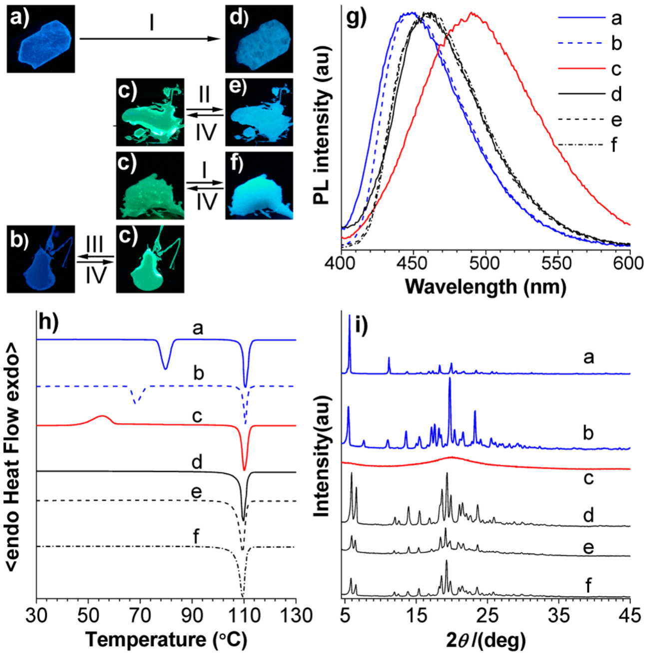


Figure 3. Digital images of (a) **2CA**, (b) **2Am** fumed by acetone, (c) **2Am**, (d) **2CB**, and **2AM** annealed at (e) 70 °C and (f) 100 °C for different time intervals. (g) PL spectra, (h) DSC thermograms, and (i) powder X-ray diffraction patterns of samples (a)−(e) in the images. Excitation wavelength: 370 nm. Photographs were taken under UV illumination. Conditions: I, 100 °C, 3 min; II, 70 °C, 5 min; III, fume by acetone for 5 min; IV, heating to melt and quickly cooling.

Table 1. Optical Properties of Luminogens 1 and 2 in Varied Aggregate States

			fluorescence decay			
samples	$\lambda_{em}{}^a$ (nm)	$\Phi_F{}^b$ (%)	$A_1/A_2{}^c$	τ_1 (ns)	τ_2 (ns)	$\langle\tau\rangle^d$ (ns)
1CA	448	56	100/0	3.24		3.24
1CB	462	51	100/0	3.38		3.38
1Am	491	47	43/57	1.60	5.53	3.8
2CA	446	54	100/0	3.09		3.09
2CB	460	48	100/0	3.33		3.33
2Am	490	44	41/59	1.73	5.38	3.88

$^a\lambda_{em}$ = emission maximum. $^b\Phi_F$ = fluorescence quantum yield determined using a calibrated integrating sphere, excited at 350 nm. ^{c}Fraction (A, %) and lifetime (τ, ns) of shorter (1) or longer lived species (2). ^{d}The mean lifetime $\langle\tau\rangle$ was calculated according to $\langle\tau\rangle = (A_1\tau_1 + A_2\tau_2)/(A_1 + A_2)$.

the photophysical properties disclosed that emissions of luminogen **1** and **2** are blue-shifted with increased quantum yield upon crystallization. Crystallization usually red-shifts the emission and decreases the emission efficiency; however, why do the two compounds behave oppositely? The twisted conformation of luminogens **1** and **2** may rule out any specific strong intermolecular interactions (such as $\pi-\pi$ stacking or H/J-aggregates) in its aggregates due to the steric hindrance. Thus the various emission colors may be ascribed to the conformation difference of the independent molecule in different aggregates. That is, molecules in the crystals may take a more twisted conformation than those in amorphous solid, which is responsible for the blue-shifted PL spectra upon crystallization. The increased quantum yield may be ascribed to the C−H···π and C−H···O interaction, which will further hinder the rotation of phenyl rings and block the nonradiative pathway (Figure S2, Supporting Information).

In addition to the steady-state spectra measurements, time-resolved PL spectra can provide information on the excited states of luminogens. The time-resolved PL spectra of the solution and aggregate states of the two luminogens were measured at room temperature and dynamic parameters were summarized in Table 1. The excited states of the two luminogens in solutions deactivated too fast to be measured with our equipment (the limit is 0.1 ns) which coincides with some reported TPE derivatives.[55] The PL lifetimes of all aggregated samples of the two luminogens were lengthened to more than 3 ns, indicating that the nonradiative pathway may be blocked in aggregate states. In their crystalline forms, the excited states of the two luminogens relax single-exponentially, indicating one relaxation pathways in their fluorescence decays. The amorphous solids of the two luminogens deactivated double-exponentially, hinting of two relaxation pathways in their fluorescence decays.

Switching the emission of a single luminogen in the solid state between two colors has been reported several times. However, examples of multicolored luminescence switching are still rare. If we can modulate the molecular aggregation patterns of **1** and **2** reversibly, then we may switch their emissions in the solid state among multiple colors. Normally an amorphous solid will crystallize upon heating or fuming by solvent vapor. Thus, we try to anneal **1Am** at different temperatures and expect that it will transform to **1CA** or **1CB**, respectively. However, **1Am** transformed to **1CB** when annealed at both 90 and 115 °C, which is verified by photos (Figure 2e,f), overlapping of PL spectra of samples (e, f) in Figure 2g, DSC curves (Figure 2h), and powder XRD patterns (Figure 2i). As **1CA** was obtained by recrystallization from solution, we try to fume **1Am** by acetone vapor. **1CA** was obtained again, which is verified by the photo (Figure 2b), PL spectra, DSC curves, and powder XRD patterns (line b in Figure 2g−i). Thus, the green emissive **1Am** can be tuned to emit sky-blue light (**1CB**) by heating or deep-blue light (**1CA**) by fuming with acetone vapor, and **1Am** can be obtained again by quenching the melt of **1** with liquid nitrogen. Thus, we can switch the emission of **1** reversibly between deep blue and green, or between sky blue and green. Then we wonder if we can realize the reversible transforming between **1CA** and **1CB**. The sky-blue emissive **1CB** (Figure 2d) can be obtained by annealing of **1CA** before melting, which are easily distinguished by the naked eye. The endothermic peak at around 110 °C in the DSC curve of **1CA** (Figure 2h, line a) indicates this crystal−crystal phase transition (from **1CA** to **1CB**), which is further verified by the PL spectrum and powder XRD pattern. However, no peak is found in the DSC curve of **1CB** before melting; therefore, **1CB** cannot transfer back to **1CA** before melting by thermal treatment. It is a pity that **1CB** cannot be transformed back to **1CA** directly, even though we have tried to fume **1CB** with many kinds of solvent; however, the process can be achieved via **1CB** to **1Am** and then to **1CA**. Thus, we can switch the emission of a single compound among three colors in solid states.

Luminogen **2** behaves similarly to **1** (Figure 3). Deep-blue emissive crystals (**2CA**, Figure 3a) obtained from recrystallization can transfer to sky-blue crystals (**2CB**) before melting when heated at 100 °C, but the reverse process (**2CB** to **2CA**) cannot be achieved directly. The green emissive amorphous solid of luminogen **2** (**2Am**) can transform to **2CA** when fumed with acetone vapor, and to **2CB** upon annealing. Thus, similar to that for luminogen **1**, the emission of **2** can also be switched reversibly by reversible changing of the molecule packing pattern. The transferring processes happened more quickly or at lower temperature than luminogen **1** due to the higher flexibility provided by the longer aryl chain.

Some AIE luminogens exhibiting morphology dependent emission also show mechanochromic fluorescence. Mechanical stimulus normally amorphizes crystals of luminogens, and the amorphized solid of luminogens will crystallize again upon heating, thus the emission of the AIE luminogens can be reversibly transferred between two different colors by the mechanical and thermal stimuli.

Both **1** and **2** exhibit three emission colors depending on the packing patterns of their molecules; thus we may switch their emissions among three colors with mechanical and thermal stimulus. The deep-blue emissive **1CA** turns to green upon grinding (Figure 4a,d). The PL spectrum of the ground powder overlaps with that of **1Am**, indicating that grinding has amorphized **1CA** (Figure S3, Supporting Information). As we described above, **1Am** can transform to **1CB** with the emission color changing from green to sky blue when heated; thus we expect that the ground powder of **1** will transform to **1CB** upon annealing. However, the emission of the ground powder turns to deep blue when heated at 90 °C for 1 min (Figure 4a,b), and the PL spectrum of the annealed powder overlaps with that of **1CA**, suggesting that the ground powder transferred to **1CA** when heated at a lower temperature, not to **1CB** as **1Am** did. Thus, the emission of **1** can be reversibly switched between green and deep blue by repeated grinding and heating (Figure S3, Supporting Information).

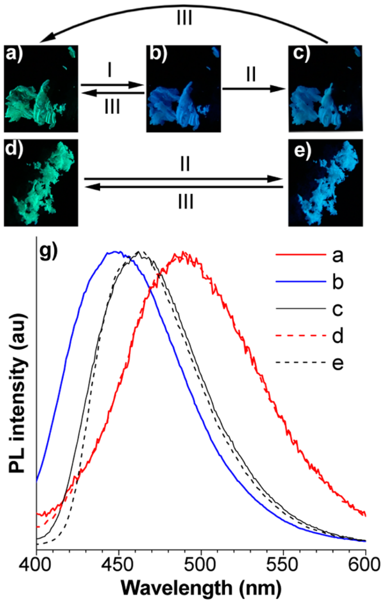


Figure 4. Photos of ground solid from **1CA** (a, d) before and (b, c, e) after annealing at (b) 90 and (c, e) 115 °C. (g) PL spectra (excitation wavelength: 370 nm) of samples (a)−(e) in the images. Photos were taken under UV illumination. Conditions: I, 90 °C, 1 min; II, 115 °C, 1 min; III, grinding.

The annealed ground powder, as **1CA** behaves, can transfer to sky-blue emissive **1CB** (Figure 4c) when heated at 115 °C and **1CB** can transfer to green emissive solid again upon grinding. Then we wonder if the ground solid of luminogen **1** could transform directly to the sky-blue emissive **1CB**. When we tried to heat the ground powder directly at 115 °C, as we have expected, the emission of the ground solid turned to sky blue directly. The green emissive solid can be obtained again by grinding.

Thus emission of luminogen **1** could be reversibly switched between green and deep blue (**1CA**) by repeating the grinding at room temperature and annealing at 90 °C, or between green and sky blue (**1CB**) by repeating the grinding at room temperature and annealing at 115 °C (Figure S3, Supporting Information). Both the transforming processes can be repeated many times due to their physical nature, thus making **1** a promising candidate for optical recording and temperature or mechanical sensing systems.

Grinding normally transfers the organic crystals to amorphous powder, and the PL spectra of the ground powder from **1CA** do overlap with that of **1Am**. However, **1Am** returns to **1CB** when heated or even annealed at room temperature with longer time, whereas the ground powder of **1** transfers to **1CA** (deep blue) and **1CB** (sky blue) when annealed at 90 and 115 °C, respectively, which have seldom been reported.

To further understand the mechanochromic fluorescence and the difference between **1Am** and the ground powder, DSC and powder XRD measurements were carried out. The DSC thermograms of ground powder before and after annealing at 90 °C (line A and line C in Figure S4, Supporting Information) show an endothermic peak at around 110 °C corresponding to the transformation from **1CA** to **1CB**, which is absent in the DSC curves of **1Am**. Thus the exothermic peak at around 43 °C in the DSC curve of ground powder indicates the crystallization process to **1CA**, which is absent in the annealed ground powder, as the ground power has already transferred to **1CA** upon heating.

Diffraction of the ground powder exhibits some weak reflections that agree with those of **1CA** but does not have as many or as sharp peaks, hinting of a not absolutely amorphous phase (Figure S4b, Supporting Information) due to the spontaneous crystallization during the sample preparation. The diffraction curve (line C in Figure S4b, Supporting Information) of the ground powder annealed at 90 °C displays many sharp and intense reflection peaks that coincide with that of **1CA**, further verifying their same crystalline orders. However, the diffraction of ground powder annealed at 115 °C fits well with that of **1CB**, suggesting their same packing orders. Thus the mechanochromic fluorescence of luminogen **1** can be ascribed to the transformation from a crystalline to an amorphous phase upon grinding, and through repeated grinding−heating cycles, we can switch the emission color between deep blue, green, and sky blue.

Because the ground powder described above is from **1CA**, and the crystal may not be absolutely amorphized by grinding, the ground powder may return to **1CA** when heated at low temperatures due to the residual small crystals acting as the nucleus. Then we wonder if the ground powder from **1Am** and **1CB** will return to **1CA** when heated at a lower temperature. The ground powders from both **1Am** and **1CB** are green emissive, with their PL spectra overlapping with that of **1Am** (Figure S5−8, Supporting Information), whereas after annealing at 90 °C for 1 min, both their emissions turn to deep blue with their PL spectra fitting well with that of **1CA** (Figure S5a and S7a, Supporting Information). In addition to the PL spectra, the DSC curves of the ground powder from both **1Am** and **1CB** (line A in Figure S5b and S7b, Supporting

Information) show an endothermic peak at around 110 °C corresponding to the transformation from **1CA** to **1CB** (thus the exothermic peak at around 45 °C in both of the DSC curves may correspond to transforming to **1CA**), whereas the DSC curves of both annealed ground powders (from **1Am** and **1CB**) fit well with that of **1CA**, further verifying that the ground powder can transform to **1CA** upon heating at 90 °C.

The amorphous solid prepared by quenching the melt of **1** tends to form **1CB** upon heating. However, the ground powder can form deep-blue emissive **1CA** and sky-blue **1CB** by varying the annealing temperature. Thus we can see that grinding not only can amorphize organic solid but also can endow the ground powder tendency to special crystals, which have seldom been reported before.

The ground solid of **2** transfers to the deep-blue emissive crystals (**2CA**) very quickly. We can only observe the green emission of the ground during grinding; once the grinding stopped, the ground powder transfers to **2CA** in 30S at room temperature (about 30 °C, Figure S9, Supporting Information). Thus we cannot get the PL, DSC, and powder XRD information about the ground solid of **2**. **2CA** can transfer to **2CB** when treated at a higher temperature. Thus the emission of the ground solid of **2** can be transferred to deep blue when annealed at room temperature and to sky blue when heated at 100 °C for 1 min (Figure S10, Supporting Information).

The ground solid of **1** is more stable than **2**; the emission did not change in 10 min at 30 °C, but there was spontaneously transfer to **1CA** at longer periods (Figure S11, Supporting Information). The longer alkyl groups in luminogen **2** afford a looser packing, thus enabling the quicker transformation from ground solid to crystals at room temperature. Though emissions of some luminogens can be tuned reversibly, most of them must be heated or treated with solvent vapor to return to the original emission, and only a few of them can recover spontaneously.[8a,8c] Thus the spontaneous recovery of **1** and **2** makes them a promising self-healing optical material. The comparison of the two compounds also inform us that the self-recovery speed can be tuned by varying the substitute groups on the phenyl rings.

The multicolored mechanochromic fluorescence of **1** and **2** prompts us to find their potential application as an optical recording material. Luminogen **1** was ground on one piece of weighing paper, and then the green film turned to sky blue after annealing at 115 °C for 1 min (Figure 5). We wrote "B" on the "paper", a green "B" appeared on the sky-blue background due to the amorphization of **1CB** in the sheared "B" area. When the "paper" was heated at 90 °C, the "B" turned to deep blue (**1CA**) but was still visible to naked eye. However, after heating at 115 °C, the "B" nearly merged in the background due to the transformation of **1** in the area of "B" from **1CA** to **1CB**.

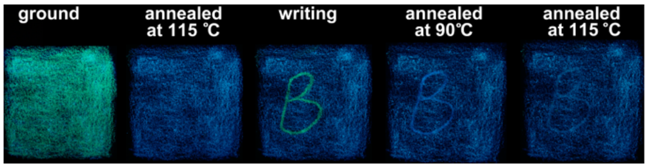


Figure 5. Procedures of the writing and erasing process of the tricolored image. Photoluminescent images were taken on a weighing paper under UV irradiation at 365 nm.

CONCLUSION

In summary, we have developed two AIE luminogens whose emissions can be reversibly switched among three colors by modulating their molecule packing patterns with mechanical, thermal, and solvent vapor stimuli. The green emissive amorphous solid of both luminogens can transform to sky-blue crystals upon heating, and to deep-blue crystals when fumed by the organic solvent vapor. The ground solid of both luminogens can transform to deep-blue crystals when heated at lower temperature (even at room temperature) and sky-blue crystals at higher temperature; thus we can see that grinding endows the luminogen the tendency to special crystals. Many AIE-active molecules take propeller-like conformations, thus affording loose packing patterns. Introduction of a weak interaction to such propeller-like molecules may yield materials showing morphology dependent multicolored emissions. The loose packing will make the transformation among different packing patterns easy, thus reversible switching the emission of luminogens among multiple colors could be achieved.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures, crystal structure data for **1** and **2** (CCDC 865201 and 865202) (CIF), characterization data and UV, PL, and mass spectra for **1** and **2**, structural diagrams, DSC thermograms and powder XRD patterns of **1** and **2** in different aggregation states, photographs under UV illumination, and ^{13}C and ^{1}H NMR spectra of **1** and **2**. This information is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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