

Emission Color

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Hydration-Facilitated Fine-Tuning of the AIE Amphiphile Color and Application as Erasable Materials with Hot/Cold Dual Writing Modes

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Abstract: Hydration water greatly impacts the color of inorganic crystals, but it is still unknown whether hydration water can be utilized to systematically manipulate the emission color of organic luminescent groups. Now, metal ions with different hydration ability allow fine-tuning the emission color of a fluorescent group displaying aggregation induced emission (AIE). Because the hydration water can be removed easily by gentle heating or mechanical grinding and re-gained by solvent fuming, rewritable materials can be fabricated both in the hot-writing and cold-writing modes. This hydration-facilitated strategy will open up a new vista in fine-tuning the emission color of AIE molecules based on one synthesis and in the design of smart luminescent devices.

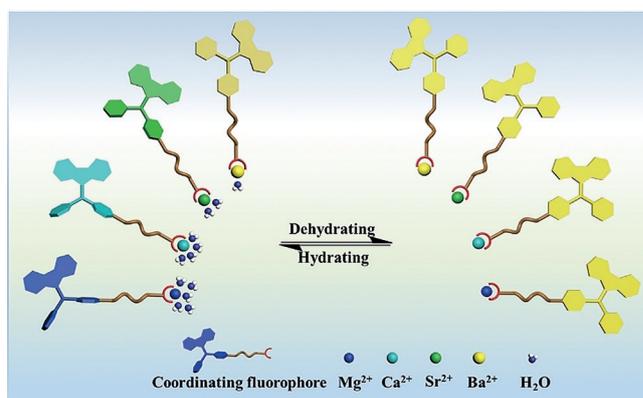
Introduction

Many inorganic crystals in nature contain a certain amount of coordinating water, which induces energy level splitting of the central metal ions. This results in absorption of visible light of certain wavelength, so that the crystal displays the complementary color.^[1] Well-known examples are $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$. They are blue and pink, but become white and blue, respectively, as the coordinating water is lost upon heating. Recently, with the extensive research on metal–organic framework (MOF),^[2–8] it is found that hydration water shows a miraculous impact on the fluorescent color of the organic ligands in MOF materials.^[9,10] However, so far hydration water has not been utilized to manipulate the emission color of various luminescent groups.

Fine-tuning of luminescent colors of an organic material is important to achieve multi-color displays and to meet the need of next generation light-emitting materials.^[11–15] However, obtaining light emission of an appropriate wavelength remains a challenge.^[16,17] Usually, the luminescence of an organic compound is manipulated by changing the chemical structure of the luminescent or substituting groups,^[18–20] which can be achieved through complicated organic synthesis. Compared to the organic synthesis strategy, the approach of hydration and dehydration of a coordinating compound only involves one step physical treatment. Therefore, it would be very promising if the fluorescence can be manipulated via the

hydration/dehydration process. Furthermore, variation of the coordinating metal ions may add another tunable parameter toward the luminescence. However, so far, this facile strategy has not been adopted in the design of luminescent materials.

In this work we show that by attaching a coordinating head to a luminescent group displaying aggregation-induced emission (AIE),^[21–24] the emission color of the fluorophore can be fine-tuned between blue and yellowish green simply by coordinating to metal ions with different hydration ability. Further study reveals that all the coordinating complexes, regardless of the used metal ions, end in yellow as the hydration water is removed by mild heating or mechanical grinding (Scheme 1). Thus we are able to create the maximum



Scheme 1. Illustration of hydration-facilitated reversible fine-tuning the emission color by coordinating of metal ions with different hydration ability.

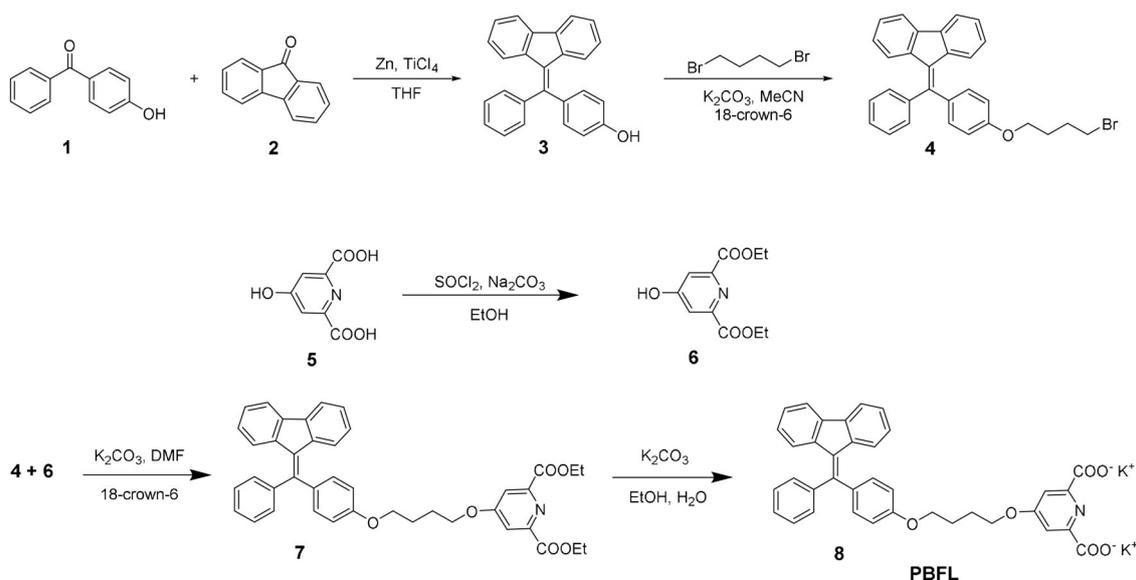
color change in the process of hydration/dehydration simply by using appropriate coordinating metal ions. Finally, we show that color change from blue to yellow can be employed in erasable materials both in the mode of hot-writing and cold-writing, corresponding to heating and grinding triggered water loss, respectively. We expect the present strategy opens a new paradigm in fine-tuning the emission colors of AIE molecules based on one synthesis and in the design of smart luminescent devices.

Results and Discussion

The hydrophobic diphenyldibenzofulvene (PBF) was chosen as the fluorophore in this study, which was tethered to a hydrophilic coordinating head (L) with three coordinating sites (Scheme 2; see the Supporting Information for

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Scheme 2. Synthesis of PBFL.

synthesis details). PBF has been found to show unusual aggregation-induced emission (AIE),^[25,26] perfectly solving the notorious fluorescent quenching in organic solid-state materials. Previous reports have shown that PBF has three fluorescent colors (blue, green, and yellow), which are related to the aggregation states and can be switched by grinding, heating, and solvent fuming.^[27–30] The coordinating head L is reported to interact with most metal ions except the alkaline family,^[31] thus rendering judicious choice on the metal ions with different hydration ability.

The obtained PBFL is a coordinating amphiphilic AIE molecule. The fresh solution of PBFL in acetonitrile–water mixed solvent (1:1, v/v) is clear with almost no fluorescent emission. However, upon addition of metal ions with different hydration ability, such as Mg^{2+} , Ca^{2+} , Ba^{2+} , at the molar ratio of $\text{PBFL}/\text{M}^{2+} = 1:1$, the solution immediately turns turbid and produces precipitates with different fluorescence (Figure 1 a). It is interesting to find the emissions can be fine-tuned continuously from blue to yellowish green simply by varying metal ions. Elemental analysis confirmed that the molar ratio between PBFL and M^{2+} is 1:1 in all the precipitates (Supporting Information, Table S1). SEM images in Figure 1b–d show the formation of different self-assembled structures (more images in the Supporting Information, Figure S1). All these structures display typical lamellar Bragg diffractions (Figure 1 f; Supporting Information, Figure S2). High-resolution TEM (HRTEM) images for PBFL-Mg^{2+} , K^+ , and Ca^{2+} (Figure 1 e; Supporting Information, Figure S3) shows clear strips, confirming the formation of lamellar structures. The lamellar thickness d , obtained from the Bragg diffractions, is in perfect agreement with the interlamellar distance obtained from HRTEM. These d values (Table 1) are all close to twice the extending length of PBFL (2.18 nm), indicating that the lamellae are stacked from the bilayers of PBFL-M^{2+} , just as those in other amphiphilic systems.^[32–37]

The bilayer thickness in Table 1 decreases regularly from 4.3 nm to 3.8 nm as the radii of the alkaline-earth metal ions

increase. This order is in line with the decreased hydration ability of the alkaline-earth metals. For the alkaline-earth metal series, the hydration enthalpies are -1920 , -1620 , -1480 , and $-1360 \text{ kJ mol}^{-1}$, for Mg^{2+} , Ca^{2+} , Sr^{2+} , Ba^{2+} , respectively.^[38] In line with this decreasing tendency, the number of hydration water, which is obtained from the thermogravimetric analysis (TGA; Figure 2 a), for each PBFL-M^{2+} pair also decreases, are 5.0, 4.0, 2.4, and 1.6, respectively. We therefore speculate that the bilayer thickness is mainly affected by the different number of hydration water binding to the metal ions. To test this hypothesis, the PBFL-M^{2+} complexes were heated to remove the hydration water. Strikingly, all the dehydrated PBFL-M^{2+} complexes displayed the same yellow fluorescence (Figure 2 b), indicating that the emission change is solely triggered by the extent of hydration, rather than the difference in the electronic structure of metal ions. The same yellow emission also suggests that the PBF groups have adopted the same molecular conformation in all the dehydrated systems.^[26–30] In line with this, the bilayer thickness of the all the dehydrated PBFL-M^{2+} became almost the same (Table 1 and Figure 2 c).

It is notable that hydration triggered emission change is completely reversible at room temperature. If N_2 flow is used instead of heating, removal of the hydration water occurred as well (Figure 2 d), which also leads to the dehydrated yellow emissive PBFL-M^{2+} complexes (inset in Figure 2 d). All of the yellow emissive powders, no matter whether obtained by heating or by N_2 blowing, recovered their original emission after rehydrating the PBFL-M^{2+} complexes by fuming with ethanol/water mixed solvent for 30 minutes (Supporting Information, Figure S4), and the X-ray diffraction peaks recovered to their original position. This clearly verified that the hydration water may trigger a conformational change of the PBF group, and the extent of the conformational change depends on the hydration ability of the metal ions binding to the head of the PBFL molecule. This conclusion is further consolidated by the fact that the maximum fluorescent

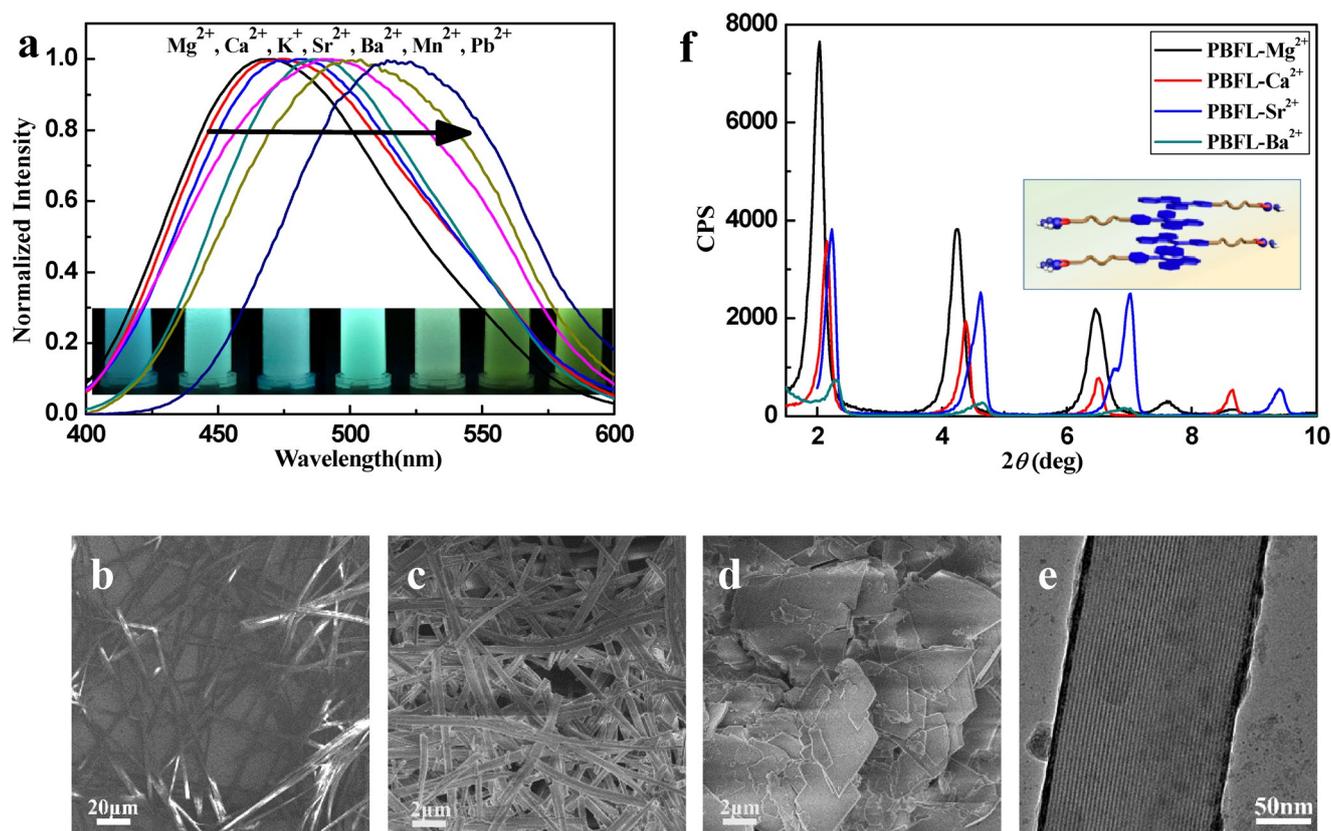


Figure 1. a) Normalized fluorescent emission spectra of 0.5 mm PBFL-M²⁺ dispersed in acetonitrile–water mixed solvent (1:1, v/v) and PBFL-2K⁺ in acetonitrile excited at 350 nm. Inset: fluorescent photo of PBFL-M²⁺ under 365 nm UV lamp. b)–d) SEM images of the precipitate of b) PBFL-Mg²⁺, c) PBFL-Ca²⁺, and d) PBFL-Ba²⁺. e) HRTEM image of PBFL-Mg²⁺. f) XRD patterns for PBFL-Mg²⁺, PBFL-Ca²⁺, PBFL-Sr²⁺, and PBFL-Ba²⁺.

Table 1: The *d* values obtained from Bragg diffractions for the complexes formed with PBFL and alkaline-earth metal ions before and after dehydration.

Sample	<i>d</i> [nm] before heating	<i>d</i> [nm] after heating
PBFL-Mg ²⁺	4.3	3.9
PBFL-Ca ²⁺	4.1	4.0
PBFL-Sr ²⁺	4.0	4.0
PBFL-Ba ²⁺	3.8	4.0

emission of the PBF group in the hydrated precipitates systematically changes with increasing the hydration ability of the metal ions. The emission for all the dehydrated sample centered at 540 nm (Figure 2c), whereas this value blue-shifted to 494 nm, 488 nm, 473 nm, and 468 nm, respectively, as the hydration ability is increased by varying metal ions in the sequence of Ba²⁺, Sr²⁺, Ca²⁺, and Mg²⁺ (Figure 1a).

It is remarkable that the hydration on the remote coordinating head has triggered conformational change of the PBF group at the chain end at ambient temperature, which is in analogy to the allosteric effect occurs in nature.^[36,39,40] Usually, variation of the conformation of PBF group may occur upon heating, which triggers irreversible phase transition from the green to yellow emissive crystal. Crystal structure analysis revealed that the torsion angles

between the two phenyl rings in the PBF group for the yellow emission and green emission state are different.^[27] Obviously, the current study suggests that hydration at a remote site away from the PBF group has triggered similar conformational change, as illustrated in Scheme 3.

Both the hydrated and the dehydrated PBFL-M²⁺ powder can be stable for months in ambient environment. Only strong desiccant, such as P₂O₅, can remove the hydration water within 12 h in vacuum (Supporting Information, Figure S5). Reversible transition between hydration and dehydration occurs only when heating/air blowing and mixed solvent fuming is applied alternatively. The sufficient stability and excellent reversibility of the two luminescent states allow us to create two-color photoluminescence switching materials. For instance, an erasable film capable of hot-writing can be made with the PBFL-Mg²⁺ system, since it offers the largest color change in the hydration/ dehydration process (Figure 3a). The film was prepared by mixing PBFL-Mg²⁺ powder with PDMS before solidification. After solidification, a transparent film displaying blue-green emission was obtained. Images could be thermally written using a soldering pen, and then be erased by simply wetting or fuming with water/ethanol mixed solvent for about 30 min. The writing and erasing could be conducted repeatedly (Figure 3b,c).

It is interesting to find that the coordinating water can also be removed under mechanical grinding. Figure 4a shows that

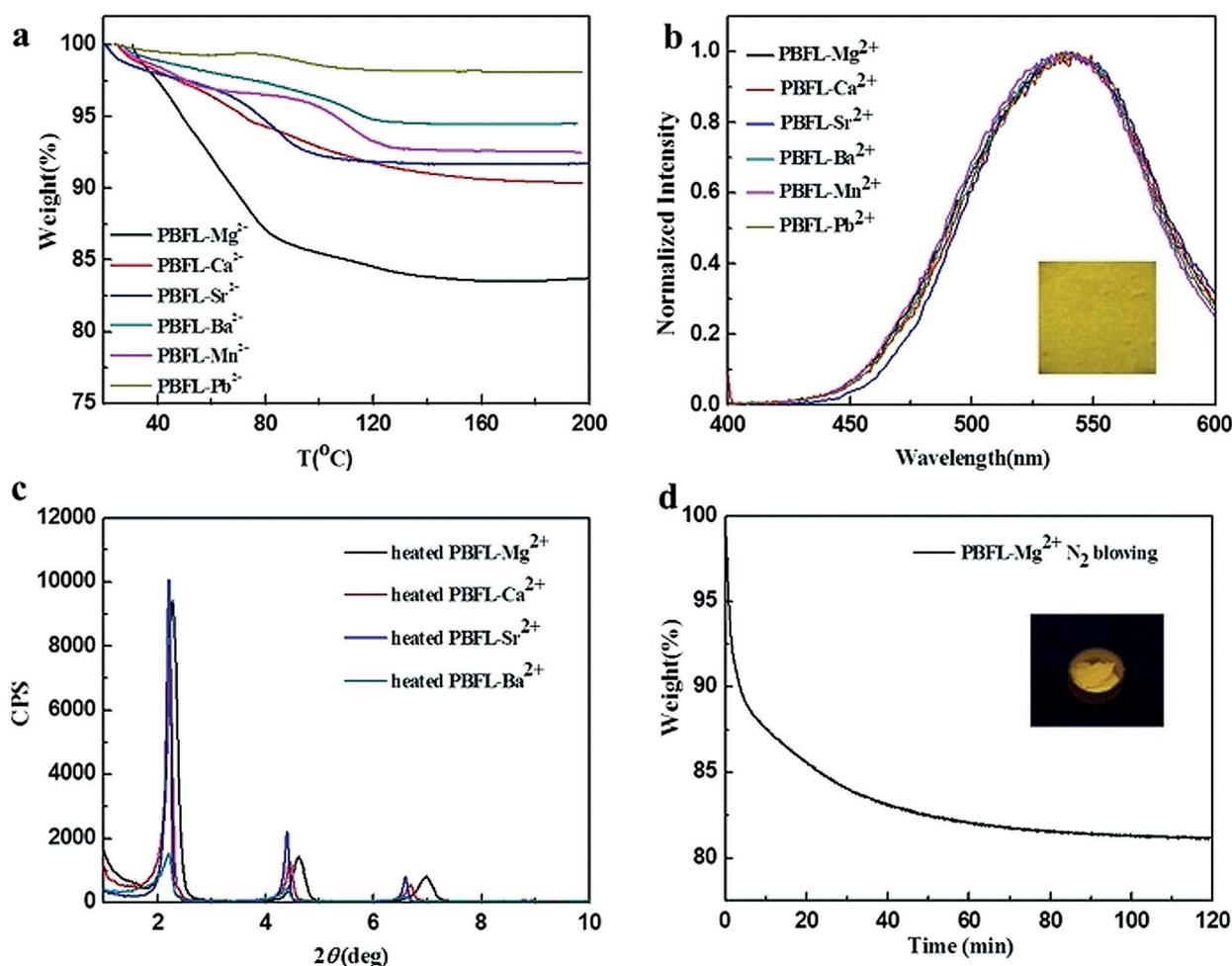
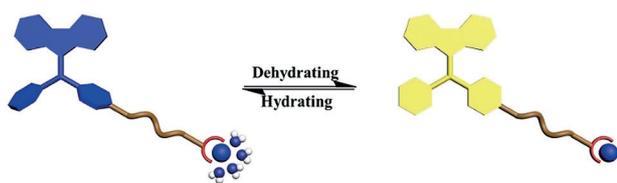


Figure 2. a) TGA curves of PBFL-M²⁺ powder. b) Normalized fluorescent emission spectra of the heated PBFL-M²⁺ dispersing in acetonitrile excited at 350 nm. Inset: photograph of PBFL-M²⁺ powder after heating under a 365 nm UV lamp. c) XRD patterns of the heated PBFL-M²⁺ powders. d) TGA curve of the PBFL-Mg²⁺ powder at the room temperature of 22 ± 2 °C under 100 mL min⁻¹ N₂ flow. Inset: photograph of the PBFL-Mg²⁺ powder after N₂ blowing under a 365 nm UV lamp.



Scheme 3. Illustration of the hydration-facilitated reversible conformation change of the PBF group.

the blue PBFL-Mg²⁺ powder becomes yellow after grinding, and it recovers the blue color immediately when fumed with ethanol/water mixed solvent. XRD measurements (Figure 4b) reveal that the grinding has destroyed all the ordered lamellar structure, which is in clear contrast with the retained lamellar structures when treated with heating. However, TGA measurements (Supporting Information, Figure S6) reveal that the yellow powder has the same curve with the one obtained by heating, and elemental analysis suggests that

the two samples have exactly the same composition (Supporting Information, Table S1). This result indicates that the yellow emission is only related to the hydration state of PBFL-Mg²⁺ complex, rather than the lamellar packing. It is clear that the grinding process has removed the solvent coordinated to the metal ions, which results in conformation change of the PBF group.

Finally, we show that the grinding triggered color change enables direct cold-writing on the native film of PBFL-Mg²⁺. Such a PBFL-Mg²⁺ film was prepared by loading a thin layer of PBFL-Mg²⁺ powder onto a filter paper. The surface of the filter paper is coarse enough so that the PBFL-Mg²⁺ powder can be entrapped into the gaps between the paper fibers. Writing with a glass stick at room temperature on the PBFL-Mg²⁺ paper would lead to a yellow image on the bright blue emissive background. This image could be easily erased upon fuming with mixed water/ethanol vapor, and repeated writing and erasing is also possible (inset in Figure 4b).

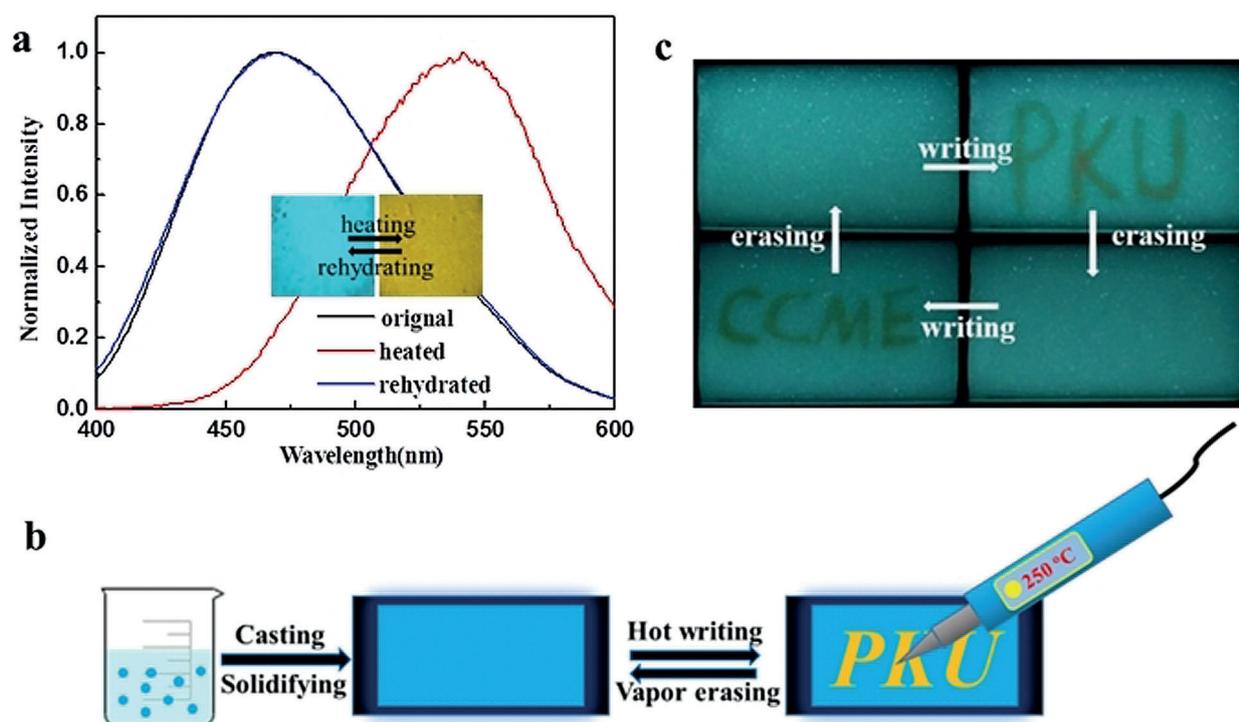


Figure 3. a) Normalized fluorescent emission spectra of PBFL-Mg²⁺ before heating, after heating, and rehydrated by fuming with ethanol–water, respectively. Insets: corresponding photos under a 365 nm UV lamp. b) Illustration of the hot writing process: PBFL-Mg²⁺ powder was dispersed into liquid PDMS monomer and casted on a glass slide, then heated at 60 °C for 4 h to obtain a transparent blue emissive film. Yellow images could be obtained on the blue fluorescent film when written with a soldering pen at about 250 °C. The image can be erased by wetting or fuming with water–ethanol mixed solvent for about 30 min. c) Experimental results of the repeated writing and erasing process on the PDMS film doped with PBFL-Mg²⁺. Photos were taken under 365 nm UV lamp.

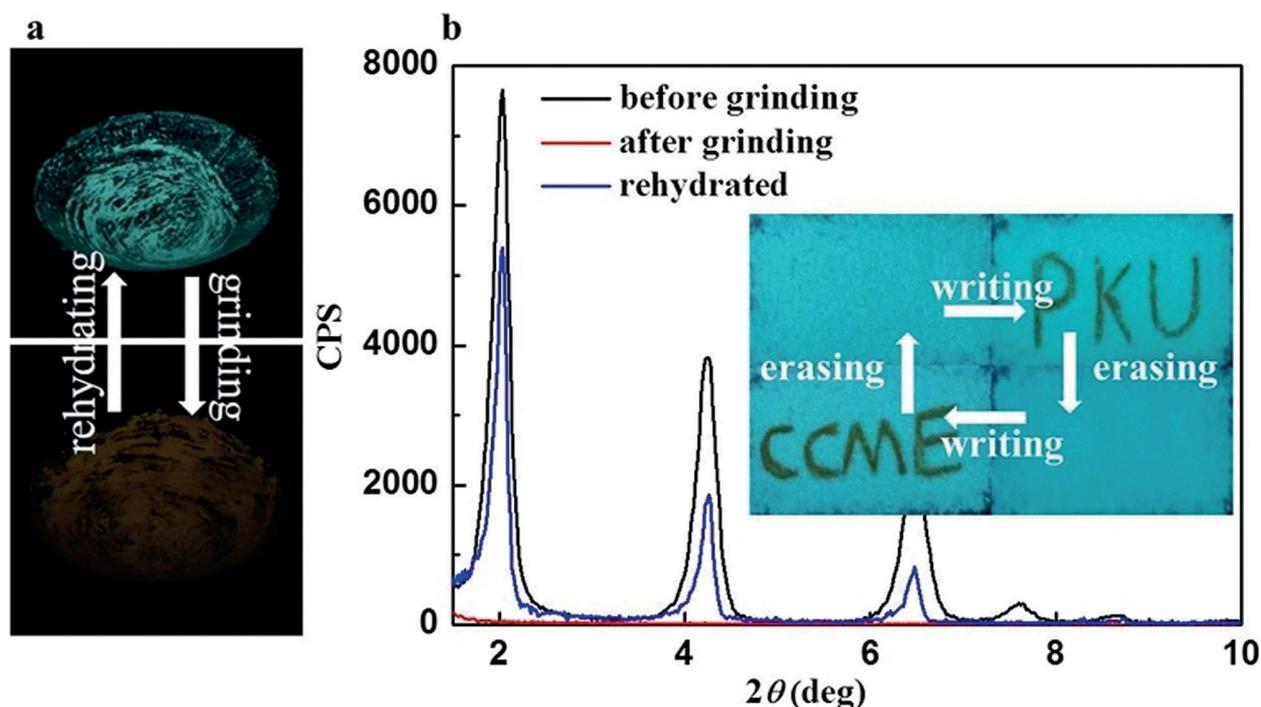


Figure 4. a) Photograph of PBFL-Mg²⁺ powder after grinding and its rehydrated one under a 365 nm UV lamp. b) XRD patterns of the original PBFL-Mg²⁺ powder before grinding (black line), the ground powder (red line), and the rehydrated powder (blue line). Inset: procedures of repeating writing and erasing process of the PBFL-Mg²⁺ cast on a filter paper: writing with a glass rod gently, and erasing by fuming with water/ethanol mixed solvent. Photos were taken under a 365 nm UV lamp.

Conclusion

We demonstrated a new strategy of hydration-facilitated fine-tuning of fluorescent color using the amphiphilic coordinating PBFL. Upon coordinating to metal ions with different hydration ability, PBFL-M²⁺ exhibited an almost continuous fluorescent color change from blue to yellowish green. When the coordinating water was removed by heating, desiccation, or grinding, all of the PBFL-M²⁺ complexes give out the same yellow emission, which can be reverted to their original state when rehydrated. The molecular conformation may simply be adjusted by coordinating water. The interconversion between the hydrated and dehydrated states results in a reversible two-color photoluminescence switching. With the help of this hydration-facilitated fluorescent color-tuning strategy, it is very easy to achieve the largest emission change for a potential application as high-performance optical recording material.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: aggregation induced emission · coordination · emission color · hydration water

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