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

Hongjun Jin, Hongpeng Li, Zhiyang Zhu, Jianbin Huang, Yunlong Xiao, Yun Yan*

This paper it to dedicated to the 20 Anniversary of Aggregation Induced Emission (AIE)

Abstract: It has long been recognized that 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. Herein, we report that 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 facilely 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 complementary color.^[1] Well-known examples are CuSO₄•5H₂O and CoCl₂•6H₂O. 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 hasn't 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] To obtain lightemission of an appropriate wavelength remains, however, 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. In addition, variation of the coordinating metal ions may add another tunable parameter toward the luminescence. However, so far, this facile strategy hasn't 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 finetuned 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 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.



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

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Scheme 2. Synthesis of PBFL.

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, and SI for synthesis details). PBF has been found to show unusual aggregation-induced emission (AIE),^[25,26] perfectly

solving the notorious fluorescent quenching in organic solidstate materials. Up to now, literatures 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.



Figure 1. (a) Normalized fluorescent emission spectra of 0.5mM PBFL-M²⁺ dispersed in acetonitrile-water mixed solvent (1:1, v/v) and PBFL-2K⁺ in acetonitrile excited at 350nm. The inset picture is the fluorescent photo of PBFL-M²⁺ under 365nm UV lamp. 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-Ca²⁺, and PBFL-Ba²⁺.

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 Mg²⁺, Ca²⁺, Ba²⁺, at the molar ratio of PBFL/M²⁺=1:1, the solution immediately turns turbid and produces precipitates with different fluorescence (Figure 1a). 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 M²⁺ is 1:1 in all the precipitates (Table S1). SEM images in Figure 1b-d show the formation of different self-assembled structures (more images in Figure S1). All these structures display typical lamellar Bragg diffractions (Figure 1f and Figure S2). High-resolution TEM (HRTEM) images for PBFL-Mg²⁺, K⁺, and Ca²⁺ (Figure 1e and 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 2 times of the extending length of PBFL (2.18 nm), indicating that the lamellae are stacked from the bilayers of PBFL-M²⁺, just as those in other amphiphilic systems.^[32-37]

It is noticed that 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 alkalineearth metal series, the hydration enthalpies are -1920, -1620, -1480 and -1360 kJ•mol-1, for Mg2+, Ca2+, Sr2+, Ba2+ respectively.^[38] In line with this decreasing tendency, the number of hydration water, which is obtained from the thermogravimetric analysis (TGA) (Figure 2a), for each PBFL-M²⁺ 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-M2+ complexes were heated to remove the hydration water. Strikingly, all the dehydrated PBFL-M²⁺ complexes displayed the same yellow fluorescence (Figure 2b), 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-M²⁺ became almost the same(Table 1 and Figure 2c).

It is notable that hydration triggered emission change is completely reversible at room temperature. If we use N_2 flow instead of heating, removal of the hydration water occurred as well(Figure 2d), which also leads to the dehydrated yellow emissive PBFL- M^{2+} complexes(inset in Figure 2d). All the yellow emissive powders, no matter 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(Figure S4), and the X-ray diffraction

peaks recovered to their original position. This clearly verified that the hydration water may trigger conformation 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 emission of the PBF group in the hydrated precipitates systematically changes with increasing the hydrated 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 Ba^{2+} , Sr^{2+} , Ca^{2+} and Mg^{2+} (Figure 1a).

 Table 1. d values obtained from Bragg diffractions for the complexes formed

 with PBFL and alkaline-earth metal ions before and after dehydration.

Sample ^[a]	d/nm, before heating	d/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



Figure 2. (a) TGA curves of PBFL-M²⁺ powder. (b) Normalized fluorescent emission spectra of the heated PBFL-M²⁺ dispersing in acetonitrile excited at 350nm. The inset is the photograph of PBFL-M²⁺ powder after heating under a 365nm 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. The inset is photograph of the PBFL-Mg²⁺ powder after N₂ blowing under a 365nm UV lamp.

It is amazing 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 high analogy to the allosteric effect occurs in nature.^[36,39,40] Usually, variation of

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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.



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



Figure 3. (a) Normalized fluorescent emission spectra of PBFL-Mg²⁺ before heating, after heating, and rehydrated by fuming with ethanol/ water, respectively. Insets are the corresponding photos under 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 hours to obtain a transparent blue emissive film. Yellow images could be obtained on the blue fluorescent film when written with a soldering pen around 250 °C. The image can be erased by wetting or fuming with water/ ethanol mixed solvent 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.

Both the hydrated and the dehydrated PBFL- M^{2+} powder can be stable for months in ambient environment. Only strong desiccant, such as P₂O₅, can remove the hydration water within 12 hours in vacuum (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 the blue PBFL-Mg²⁺ powder becomes yellow after grinding, and it recovers blue 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 (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 (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 PFB group.



Figure 4. (a) Photograph of PBFL-Mg²⁺ powder after grinding and its rehydrated one under 365nm 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), respectively. The inset is the procedures of repeating writing and erasing process of the PBFL-Mg²⁺ casted on a filter paper: writing with a glass rod gently, and erasing by fuming with water/ ethanol mixed solvent. Photos were taken under 365 nm UV lamp.

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 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 possible, (Inset in Figure 4b), too

Conclusion

In summary, we demonstrated a new strategy of hydration facilitated fine-tune of fluorescent color using the amphiphilic coordinating PBFL. Upon coordinating to metal ions with different hydration ability, PBFL-M2+ exhibited almost continuous fluorescent color change from blue to yellowish green. When the coordinating water was removed by heating, desiccation, or grinding, all 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. Within the help of this hydrationfacilitated fluorescent color-tuning strategy, it's very easy to get the largest emission change for a potential application as high performance optical recording material.

Experimental Section

PBFL is synthesized in our lab (See details in Supporting information). Sample Preparation. 2.5 mM PBFL in the water/ acetonitrile (1:1, v/v) mixed solvent were prepared as stock solution. The PBFL-M2+ complexes can be obtained by directly vortex mixing PBFL solution and the metal nitrate solution in water/ acetonitrile (1:1, v/v). The final concentration of PBFL was 0.5 mM. The mole ratio of PBFL/ M^{2+} and the volume ratio of water/ acetonitrile solvent were both 1:1. The resulting suspensions were then equilibrated at 25 °C for one day before further analysis.

PBFL-Mg²⁺ doped PDMS film was prepared by weighting 2 mg PBFL-Mg²⁺ powder into 1g liquid PDMS monomer(contains 0.1g initiator). The mixture was then casted on a glass slide, heated at 60 °C for 4 hr to get a solid film.

The fluorescence spectra of the PBFL-M²⁺ suspensions were recorded on a Hitachi F-7000 fluorescence spectrometer. The excitation wavelength was 350 nm. The slit for excitation was 5.0 nm and for emission was 5.0 nm. The scanning rate was 1200 nm· min-1. The scanning voltage of the Xe lamp was set at 750 V.

Powder X-ray Diffraction (XRD) measurements were performed using a Rigaku Dmax-2400 diffractometer with Cu Ka radiation. The powder samples were placed on clean glass slides for tests. The lamellar period d in each sample was calculated using Bragg's Law, where d = $\lambda / 2 \sin \theta$.

Scanning Electron Microscopy (SEM) measurements were performed using a Hitachi S4800 microscope at an acceleration voltage of 5.0 kV. A drop of the PBFL-M2+ suspension was placed on a clean silicon wafer and then dried in ambient condition for SEM observations.

The clear strips of PBFL-M2+ were recorded on high-resolution transmission electron microscope (FEI Tecnai F20). Drops of the PBFL-M²⁺ suspensions were put onto 200 mesh copper grids coated with ultrathin carbon film. Excess solvent was removed by filter paper and dried in ambient condition.

Thermogravimetric analysis (TGA) was carried out on TA Instrument Q600 SDT at a heating rate of 10 °C•min⁻¹ under nitrogen flow of 100 mL•min⁻¹ from room temperature to 800°C.

Differential scanning calormetry (DSC) wad carried on TA Instrument Q100 DSC at a heating rate of 5 °C•min⁻¹ under nitrogen flow of 50 mL•min⁻¹ from room temperature to 300°C.

Elemental Analysis (EA) of the PBFL-M²⁺ powders were carried out on Vario EL elemental analyzer with 0.1% accuracy for C, H and N.

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RESEARCH ARTICLE

Hydration water on metal ions can be utilized to reversibly fine-tune the emission colour of organic luminescent groups.

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