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Photo-Enhanced-Coordination Triggered Unprecedented Bistable AIE for Long-Term Optical Memories

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Photo-triggered chromism has emerged as critically important in materials for advanced soft photonic devices. The conventional photochromic units with reversible color change between two isomers are unstable either thermally or photochemically, which is an important challenge for long-standing optical devices. Here, a novel photo-enhanced coordination mechanism leading to stable chromism is reported. Upon tethering the aggregation-induced emission (AIE) moiety diphenyldibenzofulvene (PBF) to a dicarboxylic pyridine group, photo-irradiation triggers the coordination transition between the carbonate groups and Mg^{2+} from bidentate to the more stable bridging mode, which further influences the conformation of the remote PBF group, leading to transition of the emission color from cyan to yellow. Under ambient conditions, both coordinating isomers display excellent thermal and photochemical stability. As a result, the photo writings on the films based on the coordinating AIE materials exhibit the long-term stability, which barely fades even upon heating, vapor fuming, or day-light exposure. This photo-enhanced-coordination enabled bistable chromism is expected to open a new vista in the study of chromism and high durable optical memories.

1. Introduction

Photo-triggered chromism is very promising owing to its diversified applications in fields such as optical writing, memories, switches, and security technologies.[1–6] The general chemistry behind the reversible photochromism is the irradiation triggered transition between the isomer A and B (**Scheme 1**).[7–9] The significantly different absorption or emission between the two isomers endows the photochromic compounds genetic advantages in optical memories.[10–14] However, the practical application has been drastically restricted by the lack of sufficient photochemical stability of the isomer B, since it will relax to the isomer A either thermally or photochemically within a period ranging from seconds to hours (Scheme 1).[15–20]

The ideal photochromic units with long-standing device performance are supposed to be durable, thermal irreversible, and photostable.[14] Among all the photochromic molecules, the most widely studied are azobenzenes, diarylethenes, and spiropyrans-oxazines.[7,21–24] Specially, the dithienylethenes have been proved promising owing to their excellent thermal stability.[14–16,25–28] However, they display poor photostability and must be stored in dark. As a fact, the recorded data fade quickly under visible light, which severely hindered them from practical applications. Recently, some aggregation-induced emission (AIE) molecules were reported to show photochromism through formation of photocyclization intermediates.[6,29–32] Unfortunately, similar to traditional photochromic molecules, they can hardly display long-standing photo memories since they would fade to its original state within a few minutes. So far, it still remains challenging to achieve bistable chromism through molecular design.

Herein, we report an unprecedent photo-enhanced coordination pathway to achieve bistable chromism suitable for long-term photo memory. By tethering a coordinating head via butyl chain to an AIE luminescent group diphenyldibenzofulvene (PBF),[33–38] coordination with Mg^{2+} leads to AIE materials displaying remarkable emission response to UV irradiation (**Figure 1**a). Mechanism study suggests that photo irradiation have triggered the coordination between Mg^{2+} and the COO^- group changes from the less stable bidentate to the thermal stable bridging mode, while the latter locks the more planar conformation of the PBF group. This allows creation of both positive and negative photo writings that do not fade upon heating, vapor fuming, or daylight exposure. The optical memory remained unchanged under ambient conditions over 300 days. We expect that the combination of AIE and coordination chemistry may open a new vista in creating optical materials with long-period memories.

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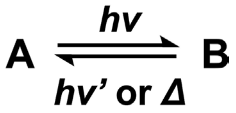

$$A \underset{hv' \text{ or } \Delta}{\overset{hv}{\rightleftharpoons}} B$$

Scheme 1. Reversible transformation between two isomers of conventional photochromic organics.

2. Results and Discussion

The hydrophobic PBF moiety is an AIE fluorophore that is well known to display emission color change from cyan to yellow as it becomes more planar.[35–37] Here, the PBF group is tethered via an oxy-butyl group to the pyridine-2, 6-dicarboxylate, a hydrophilic coordinating head capable to coordinate with a vast number of metal ions.[39–46] We have reported in our previous work that upon coordination with metal ions, the resultant PBFM complex (M denotes metal ions coordinating to this PBF derivative) shows both thermochromism and mechanochromism due to dehydration on the metal ions that further results in changes in the molecular conformation and fluorescence.[46] However, it is never expected that the emission color of PBF or PBFM series compounds can be changed under photo-irradiation.

Figure 1b shows the amazing UV-triggered emission change of the PBFMg powder (where the coordinating metal ion is Mg^{2+}) from intense cyan to dark yellow after exposing it to a 45 W handheld 365 nm ultraviolet LED flashlight for 10 min. On the meanwhile, the color of the PBFMg powder under daylight has turned from white into yellow. This process occurs facilely regardless the sources of the 365 nm UV light. As presented in Figure 1c, under a total internal reflection fluorescent microscope (TIRFM) equipped with 5 mW mercury lamp, the initial cyan emission of the needle-like microrods, which is the basic particles in the PBFMg powder, turns quickly into yellow within 2 min. Figure 1d shows the fluorescent spectra of PBFMg powder at different UV irradiation time. The fluorescence intensity dramatically decreases and red shifts. The corresponding fluorescent quantum yield (FQY) decreased from 6.86% to 0.71%

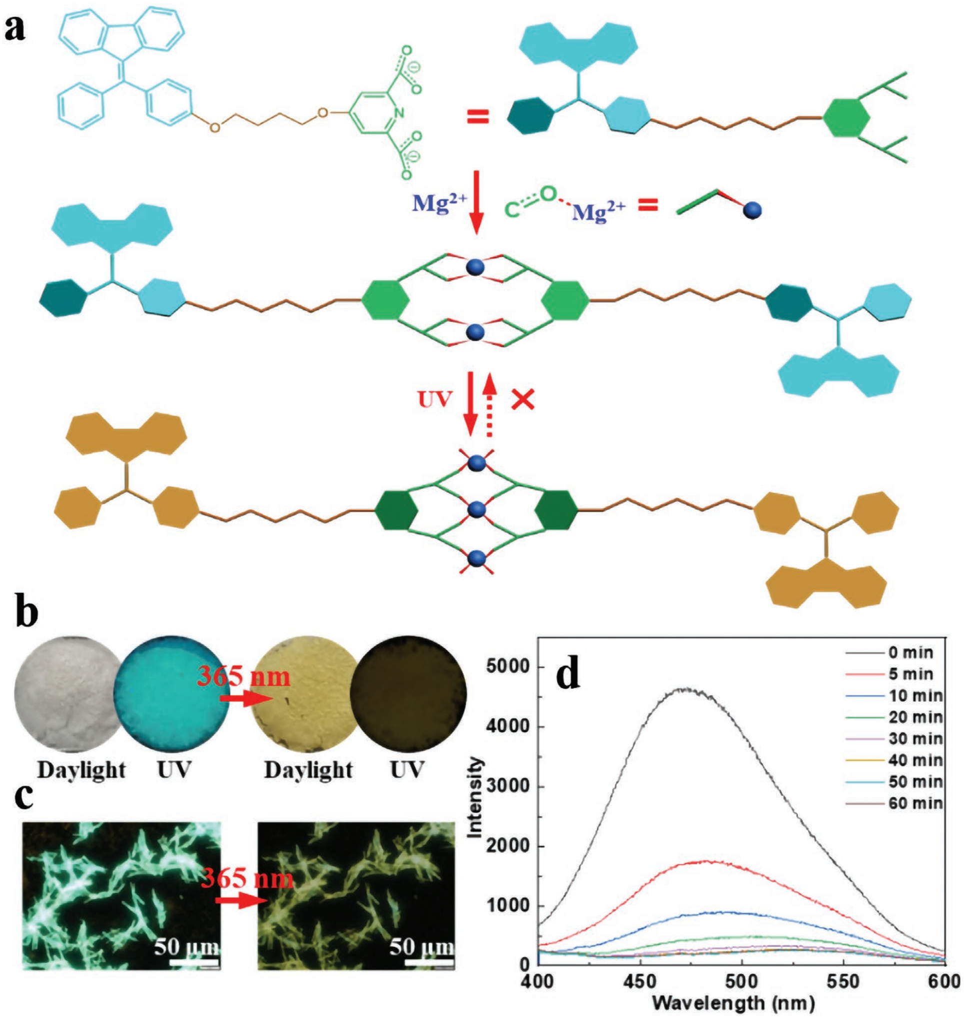

Figure 1. a) Illustration of the photo-enhanced-coordination triggered chromism in the diphenyldibenzofulvene (PBF)-Mg coordinating complex. b) Photographs of PBFMg and irradiated PBFMg (iPBFMg) powder under daylight and 365 nm UV lamp, respectively. c) The image of the PBFMg aggregates under total internal reflection fluorescent microscope (TIRFM). The 365 nm UV light source is from mercury lamp. d) Fluorescent spectra of the PBFMg powder under different UV irradiation time excited by 45 W handheld 365 nm ultraviolet LED flashlight.

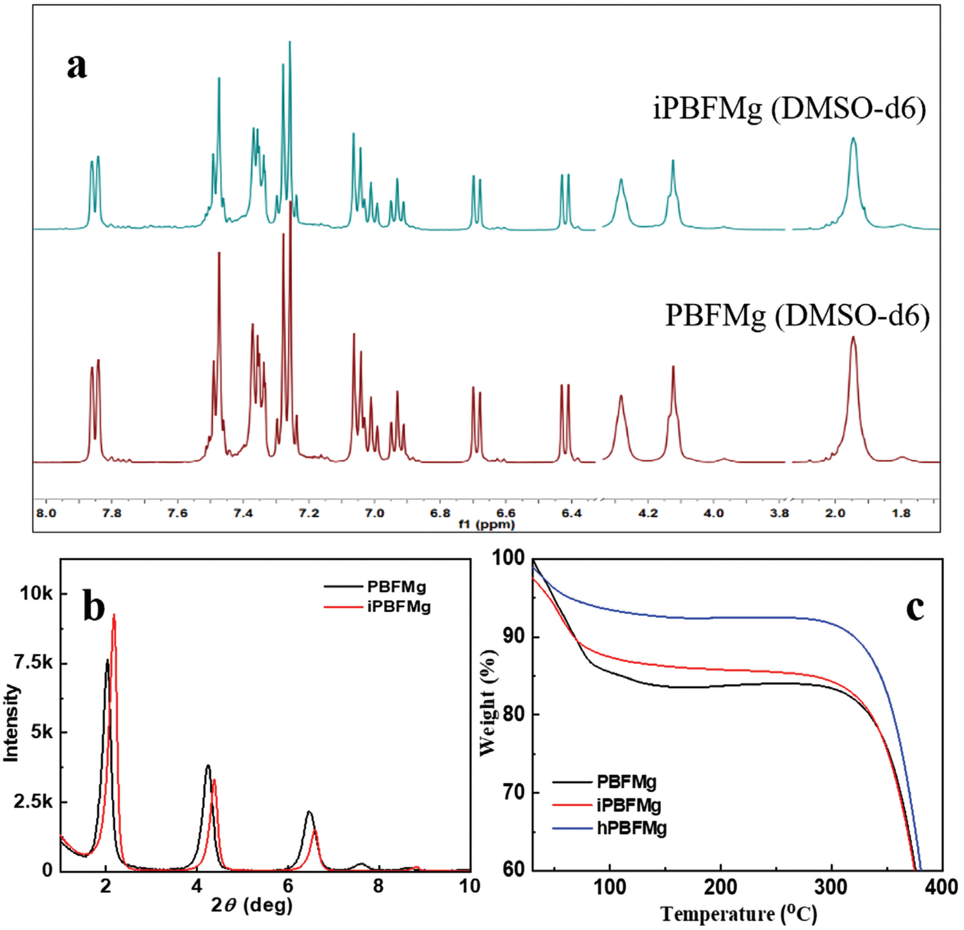

Figure 2. a) ^{1}H NMR (600 MHz, DMSO-d_6) spectra of PBFMg (red) and iPBFMg (cyan). b) XRD patterns of the PBFMg and iPBFMg powder. c) TGA curves of the PBFMg powders after different treating process: pristine (black line), UV irradiated (red line) and heated (blue line).

Different from the reversible photocyclization of AIEgens[6,29–32] and other photo-isomerizable dyes[7,21–24] reported in literature, UV-irradiation does not change the structure of PBFMg at molecular level, which is evidenced by ^{1}H NMR (^{1}H NMR, **Figure 2**a), 2D nuclear overhauser effect spectroscopy (2D NOESY; Figure S1, Supporting Information) and mass spectra (MS; Figures S2 and S3, Supporting Information). The formation of stable radicals and aggregates are also excluded by electron paramagnetic resonance (EPR; Figure S4, Supporting Information) and self-diffusion ^{1}H NMR measurement (Table S1, Supporting Information). Thus, the current chromism can be ascribed to the photo-irradiation triggered conformational change of the PBF group. According to crystal structure analysis, the transition from cyan to yellow emission is a result of reduction of the torsion angles between the two phenyl rings in the PBF group.[35–37] In line with this, the UV–vis absorbance red shifts from 327 to 330 nm after UV irradiation (Figure S5, Supporting Information), indicating the alteration of molecular conformation to higher conjugation.[33] X-ray diffraction (XRD) measurements reveal that both PBFMg and iPBFMg powder display typical lamellar Bragg diffractions (Figure 2b). However, UV-irradiation has shifted the diffraction to higher angles. The lamellar thickness d obtained from the 001 diffraction for the iPBFMg system is 4.1 nm, which is shortened by 0.2 nm than the 4.3 nm thickness for the original PBFMg. Since both d values are close to twice the extending length of PBFMg unit (2.18 nm, Figure S6, Supporting Information), this means the photo-irradiation did not change the bilayer stacking status of the PBFMg unit.[46]

In order to probe the origin of the 0.2 nm smaller interlayer distance in the iPBFMg system, the possibility of hydration water loss from Mg^{2+} was first examined. The TGA curves in Figure 2c reveal that the water contents in the pristine PBFMg, iPBFMg, and heated PBFMg (hPBFMg) are 16.3%, 14.2%, and 7.5%, respectively. It is noticed that UV irradiation has caused only a slight water loss of 2.1%, which is far less than the drastic water reduction of 8.8% triggered by heating, indicating the shortened interlayer distance is not originated from the loss of hydration water.

Considering photo-irradiation often causes enhanced vibration of the coordinating bond,[47] we wonder if this could impact the coordination between $-COO^-$ and Mg^{2+}. The Fourier transform infrared (FT-IR) spectra in **Figure 3**a show that before UV irradiation, the symmetric and asymmetric vibration of the $-COO^-$ group in PBFMg occurs at 1440 cm^{-1} and 1597 cm^{-1}, respectively. The frequency separation of 1597–1440 cm^{-1} = 157 cm^{-1} is much smaller than 200 cm^{-1}, indicating the carboxylate group and Mg^{2+} forms bidentate binding.[48–52] However, after

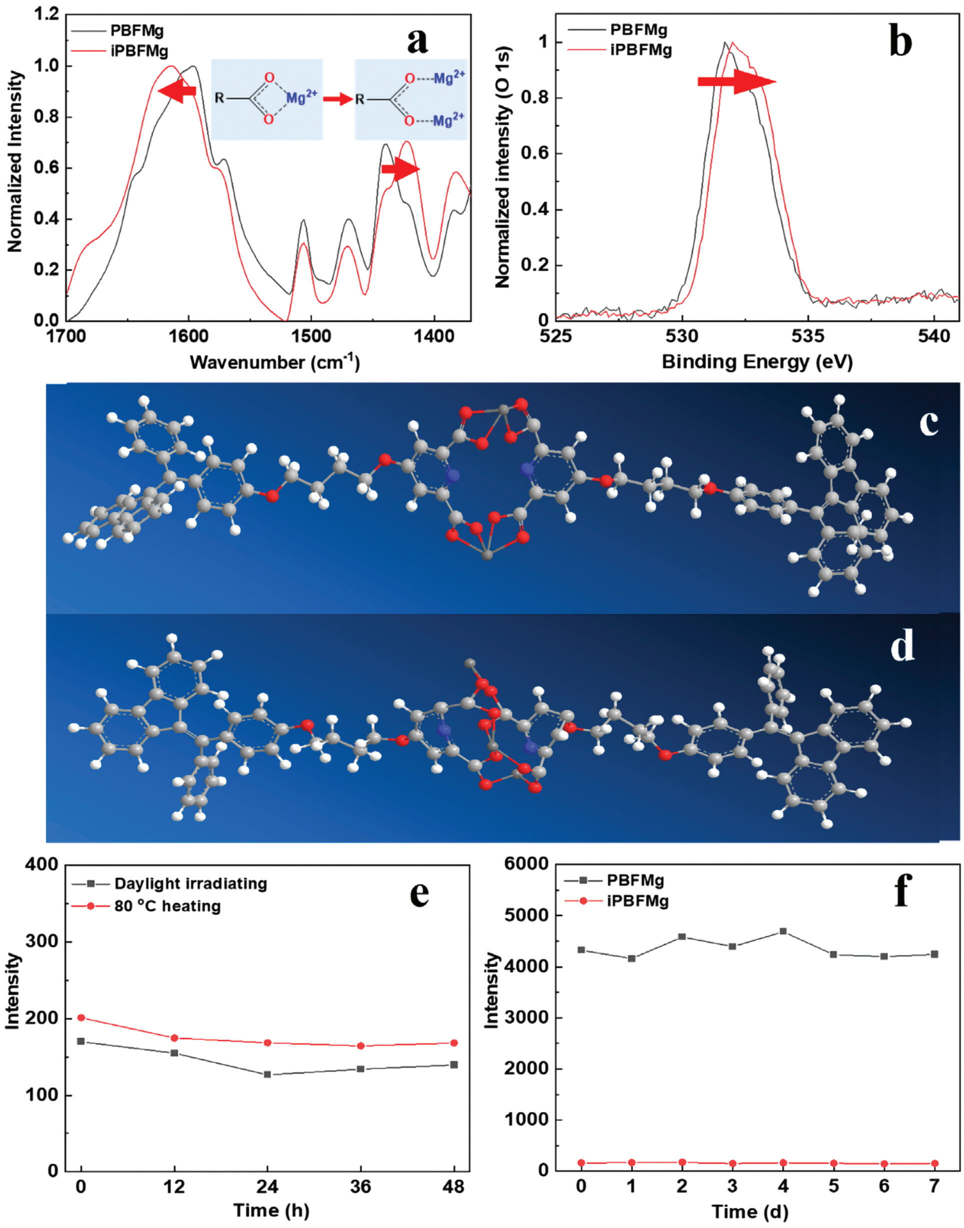

Figure 3. a) FT-IR spectra of PBFMg and iPBFMg powder, respectively. The inset shows the coordinating mode between the carboxylate group and Mg^{2+} changes from bidentate to bridging. b) XPS spectra of binding energy for O 1s of PBFMg and iPBFMg powder. c) The bilayer thickness of the bidentate coordination PBFMg and d) the bilayer thickness of the bridging coordination PBFMg. e) The emission intensity at 470 nm of iPBFMg powder after different heating time at 80 °C and different daylight lamp irradiating time. f) The emission intensity at 470 nm of the fluorescent spectra of PBFMg and iPBFMg powder within 7 days under ambient conditions at room temperature with daylight exposure.

UV irradiation, the symmetric and asymmetric vibration of the $-COO^{-}$ group shifts to 1423 and 1614 cm^{-1}, respectively. The frequency separation increases to 1614–1423 cm^{-1} = 191 cm^{-1}, which is close to 200 cm^{-1} thus featuring the bridging mode of coordination[48–52] (Figure 3a inset; Figure S7, Supporting Information). In line with this, the O 1s binding energy increases from 531.7 to 532.0 eV, whereas the N 1s binder energy remains unchanged after UV irradiation (Figure 3b; Figure S8, Supporting Information). This means that photo-irradiation has triggered coordinating mode transition between Mg^{2+} and the $-COO^{-}$. Molecular modeling analysis confirms that the bilayer thickness generated from the bidentate and bridging coordination between PBF and Mg^{2+} is 4.26 and 4.06 nm (Figure 3c,d), respectively, in perfect agreement with the results obtained in the XRD measurements.

It is noticed that the UV-irradiation triggered coordinating mode transition from bidentate to bridging is very crucial for the chromism. As the -COO^{-} groups are in the form of ester, photo-irradiation would not generate any color change (Figure S9a, Supporting Information). In contrast, irradiation triggered color change would occur in all the carbonate systems, including PBFK, PBFCo, and PBFPb (Figure S9b-d, Supporting

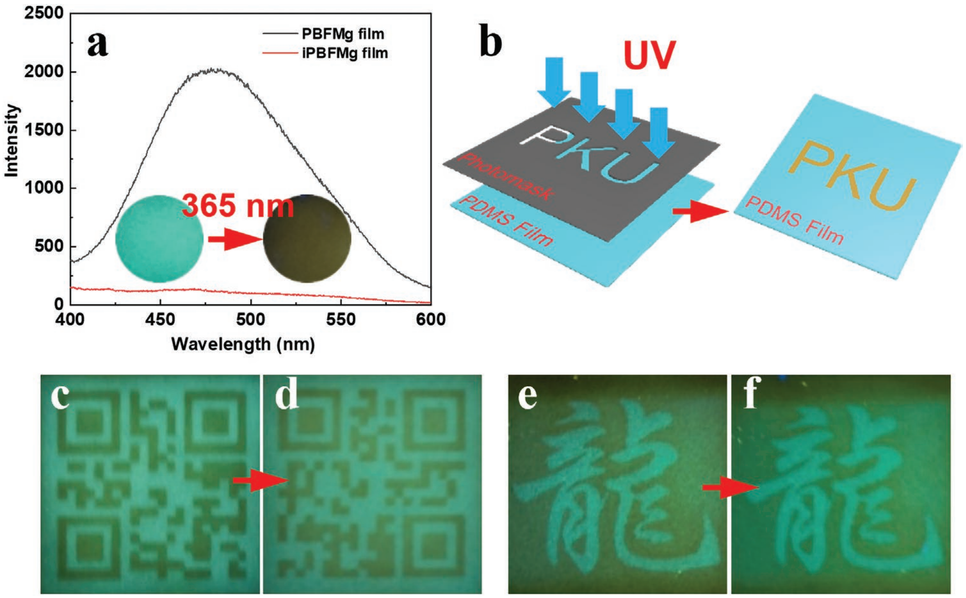

Figure 4. a) Fluorescent spectra of the PBFMg doped PDMS film before (PBFMg film) and after UV irradiation (iPBFMg film). b) Schematic representation of the data record process by masking method. c) Photographs of the QR code with the website information of “pku.edu.cn” made with a hollow out photomask and d) the film after 300 days under ambient conditions at room temperature with daylight exposure. e) Photographs of the Chinese character of “dragon” made with an invert hollow out photo mask and f) the film after 3 days immersed in water-ethanol mixed solvent.

Information, where the metal ions are K$^+$, Co^{2+}, and Pb^{2+}, respectively). Most importantly, when the UV light was switched off, the dark yellow emission of iPBFMg powder remains stable even under continuous daylight exposure (Figure S10, Supporting Information) or fuming with various vapors (Figure S11, Supporting Information), which is remarkably different from the conventional photochromic organics and the reported photochromic AIEgens.[6,29–32] Furthermore, the dark yellow emission of iPBFMg even remains stable after heating at 80 °C and exposure under an intense daylight lamp (45 W, 57 lm W^{-1}, 6500 K) for 48 h (Figure 3e; Figure S12, Supporting Information). As such, both PBFMg display unprecedented bistable photo-triggered chromism (Figure 3f).

The remarkable bistable photo-triggered chromism of PBFMg is very promising in photo writing with long-term stability. To make a demo, the PBFMg powders are doped in a polydimethylsiloxane (PDMS) film. The pristine PBFMg film shows intensive blue-green emission with an FQY of 4.77%. After exposing to 365 nm UV light for 10 min, the emission turns into dark yellow with an FQY of 0.8% (**Figure 4**a). Additional experiments indicate that the fluorescent emission of both states display similar stability to the pristine powders under ambient conditions (Figure S13, Supporting Information), validating that the bistable photo-triggered chromism of PBFMg remains in the PDMS film. Then positive photowriting is conducted with the assistance of hollow out photomasks (Figure 4b). Figure 4c shows a QR code of the website information of Peking University. The resolution of this photowriting image is high enough so that scanning of this code with a mobile phone will readily direct people to the website of Peking University. Furthermore, if an inverted photomask is applied, we are able to obtain negative photo-writings which are bright patterns with dark background (Figure 4e). Both the positive and negative photo-writings remain stable and barely fade over 300 days under ambient conditions (Figure 4d). Strikingly, the writings are even stable as they are immersed in various solvents, such as water, ethanol, and ethanol–water mixed solution (Figure 4f). This excellent stability implies that the current photo enhanced coordination triggered chromism is of distinct advantage in the practical applications of optical memories.

3. Conclusion

In summary, we demonstrated a novel photo-enhanced coordination mode switching triggered chromism of AIE that endows the AIE fluorophore PBF with unprecedented bistable emission state. Upon tethering a coordinating head to the PBF group, coordination with metal ions leading to self-assembled needle-like structures composed of the stacked bilayers of PBFMg. The coordinating states of the PBFMg will switch from bidentate to bridging, leading to enhanced coordination between the carbonate group and Mg^{2+}. As a result, the PBF group will be planarized, so that the emission turns from the original cyan to dark yellow. Since the photo-enhanced coordination is stable, the chromism is stable, too. As a result, the PBFMg displays unprecedented bistable thermal and photochemical stability. Photo writing on the PBFMg film shows long-term stability under ambient conditions. This high contrast of fluorescent emission change and excellent bistability endow the AIE coordinating complexes with promising advantages in long-standing optical record devices.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

aggregation-induced emission, bistable, coordination, optical memories, photo-triggered chromism

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