

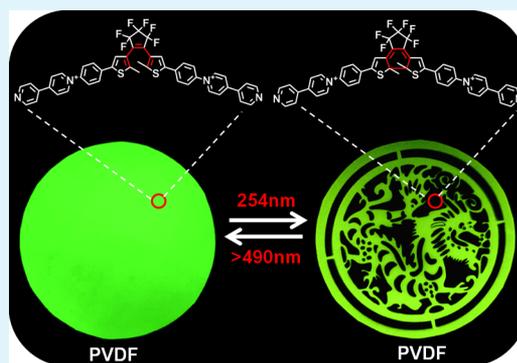
Controlled Photoerasable Fluorescent Behaviors with Dithienylethene-Based Molecular Turnstile

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Supporting Information

ABSTRACT: The precise control of molecular interaction and motion is a powerful strategy in the creation and development of intelligent materials. We demonstrate here a simple concept and approach to integrate intramolecular photochromic property with intermolecular aggregation-induced emission behaviors, with the aim to construct a new type of photoswitchable luminescent materials. This strategy is realized by the dithienylethene-bridged bispyridinium salt as photochromic molecular turnstile, and their subsequent fabrication into optically functional materials is reported. By restricting the rotation of central chemical bonds, the obtained molecular turnstile not only exhibits photocontrolled fluorescence emission through solvent exchange but is also capable of transforming into photowritable and photoerasable films in polymeric matrix with good recyclability. This functional molecular turnstile provides convenient routes to construct photochromic nanomaterials with controlled photophysical behaviors.

KEYWORDS: photoerasing, solid-state fluorescence, photochromism, aggregation-induced emission, molecular turnstile



INTRODUCTION

To build practical optoelectronic materials, the efficient regulation of molecular conformation and intermolecular arrangements is a prerequisite to achieve high optical performance in both solution and the solid state.¹ As a consequence, in recent years, the controlled photoluminescence behaviors with unique physiochemical properties have stimulated an upsurge of interest, and most of intelligent luminescent materials exhibit desirable photophysical behaviors in response to various external stimuli, such as mechanical forces,^{2–5} vapor,^{6–8} temperature,^{9–12} and light input.^{13–17} However, the development of highly tunable luminescent materials is always subjected to the unstable photostationary state and inherent quenching in aggregate mode, which severely hampers their application in practical fields.^{18–24} Thus, it is absolutely imperative to explore photostable optoelectronic materials in a controlled manner.

To circumvent these obstacles, the rational design of a dithienylethene-bridged bispyridinium salt (DTE-BP) as photochromic molecular turnstile (similar to the type of molecular rotors) was presented in our previous work, which could be used as the photoswitchable luminescent hydrogels.²⁵ In this work, we further investigated the aggregation-induced emission (AIE) and photoswitchable fluorescence behaviors of DTE-BP. More interestingly, the resultant DTE-BP can be well-implanted into the polymeric matrix to obtain photowritable and photoerasable films with good recyclability. There is a cooperative communication in the photochromic molecular turnstile of DTE-BP; that is, on one hand, the introduction of

dithienylethene can endow the whole molecule with reversible photochromic behaviors by the ring-closing and ring-opening reactions, thus providing regulatory sites for the fluorescence photoswitching mode; on the other hand, the molecular conformation of molecular turnstile located at both sides of dithienylethene core is sensitive to the restricted environment, thus giving rise to the strong fluorescence emission in the high-viscosity solvent and the solid state (Scheme 1). Thus, we can anticipate that this photowritable/erasable system constructed by the dual-functional photochromic molecular turnstile can be considered as a promising candidate for attaining truly operational solid-state luminescent materials.

RESULT AND DISCUSSION

The intermediates **1**²⁶ and **2**²⁷ were refluxed in anhydrous ethanol and then underwent ion exchange to obtain the target molecule DTE-BP as tetrafluoroborate in 82% yield, which was characterized by ¹H NMR, ¹³C NMR, and high-resolution mass spectrometry (HR-MS; Scheme S1 and Figures S1–S3, Supporting Information). As expected, the photoswitchable molecule DTE-BP exhibited good reversible photochromic behaviors. As shown in Figure S4, the absorption maxima of the open-ring form (OF) were observed at 275 nm ($\epsilon = 7.1 \times 10^4$

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Scheme 1. Schematic Illustration of the Formation of DTE-BP-Embedded PVDF (or PMMA) Film and Their Photoswitching Fluorescence Behaviors

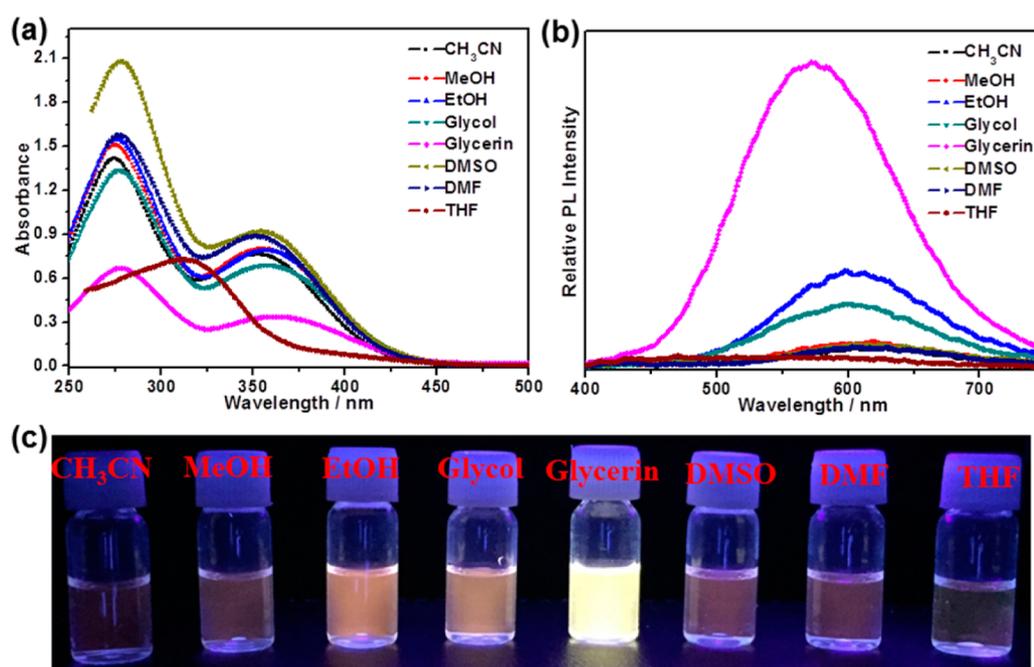
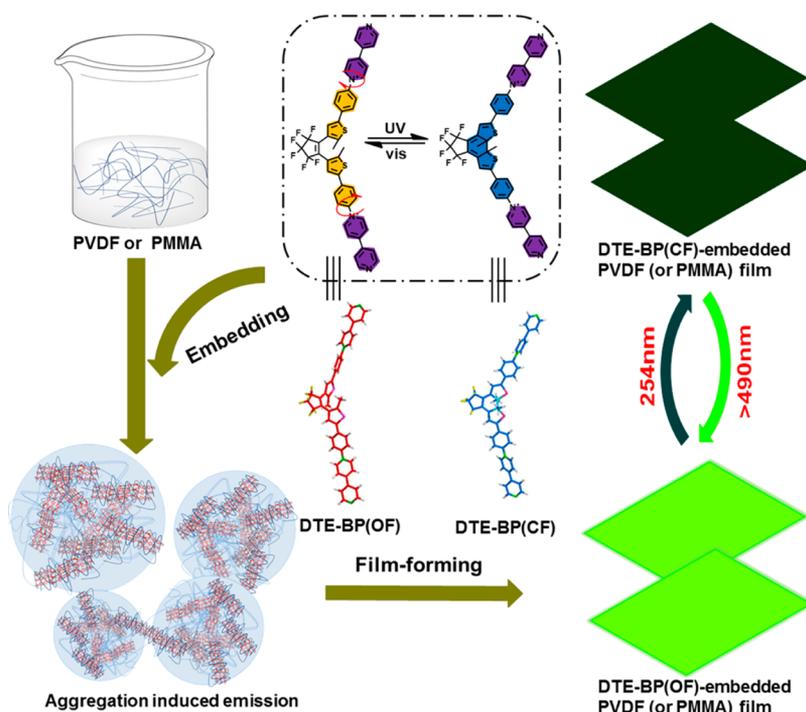


Figure 1. (a) UV/vis absorption and (b) fluorescence emission spectra, and (c) fluorescence photographic images of DTE-BP in different solvents ($[DTE-BP] = 2 \times 10^{-5} M$ and $\lambda_{ex} = 385 nm$).

$L \cdot mol^{-1} \cdot cm^{-1}$) and 352 nm ($\epsilon = 3.8 \times 10^4 L \cdot mol^{-1} \cdot cm^{-1}$), respectively. Upon irradiation with 254 nm UV light, these absorption maxima gradually declined, and a new absorption band at 606 nm appeared and augmented to the photostationary state ($\epsilon = 2.2 \times 10^4 L \cdot mol^{-1} \cdot cm^{-1}$), accompanied by three clear isosbestic points at 291, 340, and 413 nm, corresponding to the generation of the photocyclized product as the closed-ring form (CF). Accordingly, the color of the solution gradually turned from colorless to blue (Figure S4,

inset). The ring-closing conversion rate was measured as 78% by 1H NMR spectroscopic examination on the irradiated sample (Figure S5). Subsequently, the UV/vis absorption, NMR signals, and solution color could be thoroughly restored to the original states under greater than 490 nm visible light irradiation, indicative of the complete conversion between CF and OF in DTE-BP (Figures S4–S6, Supporting Information). The photocyclization and cycloreversion quantum yields were determined as 0.14 and 0.0013 in acetonitrile, respectively.^{28,29}

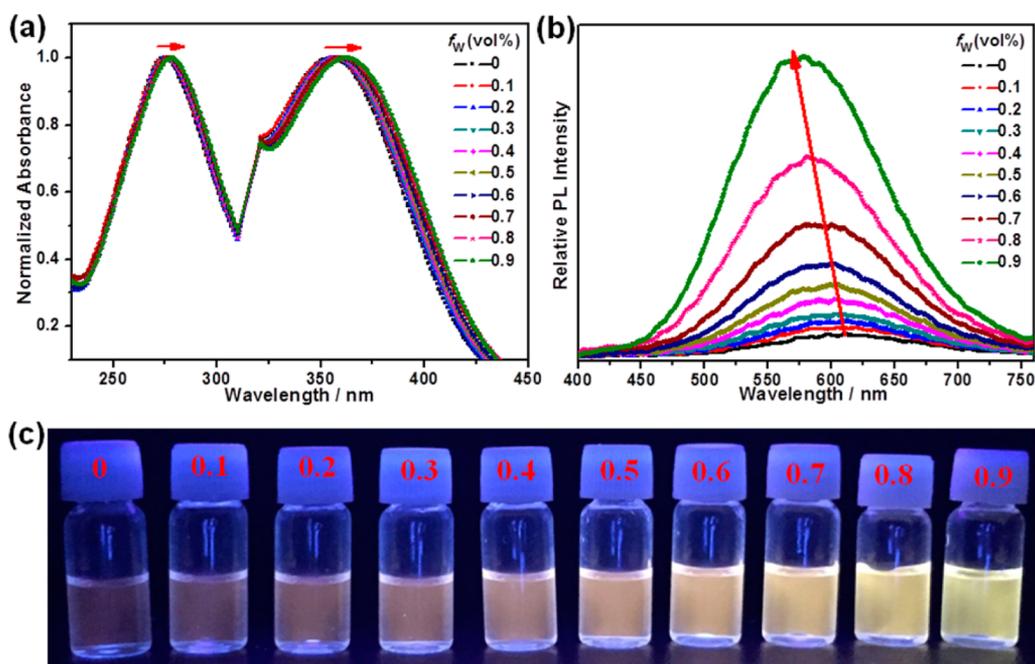


Figure 2. (a) UV/vis absorption and (b) fluorescence emission spectra, and (c) fluorescence emission images of DTE-BP in different fraction of methanol–glycerin mixed solvents ($V_{\text{glycerin}}/(V_{\text{methanol}} + V_{\text{glycerin}}) = 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9$, $[\text{DTE-BP}] = 2 \times 10^{-5}$ M and $\lambda_{\text{ex}} = 385$ nm).

Notably, the CF–OF cycle could be repeated at least seven times without any apparent recession (Figure S7, Supporting Information).

From the perspective of twisted donor–acceptor molecular structure, the photoswitchable molecule DTE-BP may be defined as a fluorescent molecular turnstile, which may exhibit AIE behaviors.^{30–33} With this in mind, the UV/vis absorption and fluorescence spectra of DTE-BP were recorded in different solvents. As shown in Figure 1a, among all the examined solvents, the absorption maxima of DTE-BP at 277 and 366 nm in glycerin displayed obvious bathochromic shift, indicative of the formation of nanoaggregates of DTE-BP in high-viscosity media. Moreover, DTE-BP also showed the strongest fluorescent emission in glycerin, accompanied by the obvious hypochromic shift of 47 nm, which was the characteristic AIE photophysical property originating from the restriction of intermolecular rotation (Figure 1b). Moreover, as shown in Figures S13a and S13b, the fluorescence quantum yield was measured by 0.069 in glycerin, which was much higher than that in acetonitrile (0.006). Intuitively, the nanoaggregation of DTE-BP could be further observed by naked eyes; that is, strongest yellow fluorescence was shown only in glycerin, which was contributed to both the inferior solubility of DTE-BP and higher viscosity of glycerin (Figure 1c).

To further verify the AIE characteristics of the molecular turnstile, the corresponding UV/vis absorption and emission spectra were recorded in different proportion of glycerin–methanol mixed solution. The absorption maxima of DTE-BP showed obvious bathochromic shift, and inversely, the emission bands showed hypochromic shift, and the fluorescence intensity was enhanced with the increasing fraction of glycerin (Figure 2a,b). Meanwhile, the fluorescent emission changed from light red to strong yellow in diverse proportional DTE-BP-containing solution (Figure 2c). Therefore, these spectroscopic phenomena jointly demonstrated that the molecular turnstile DTE-BP possessed good AIE property.

Benefiting from the diarylethene-derived photoisomerization of the molecular turnstile, DTE-BP could act as a fluorescent photoswitch in high-viscosity medium. Indeed, the fluorescence of DTE-BP was greatly quenched by 93% in glycerin upon 254 nm light irradiation for 7 min, due to the photocyclization of diarylethene core from emissive OF to nonluminescent CF. Accordingly, the fluorescence on/off quenching ratio ($R_{\text{on/off}}$) was calculated by a factor of 14 by comparing the intensity at maximum emission wavelength before and after UV irradiation at 254 nm. On the contrary, visible light (>490 nm) irradiation could lead to the complete recovery of the fluorescent intensity and emission color (Figure 3).

The aforementioned investigation encouraged us to examine photomodulated fluorescence ability of DTE-BP in the solid

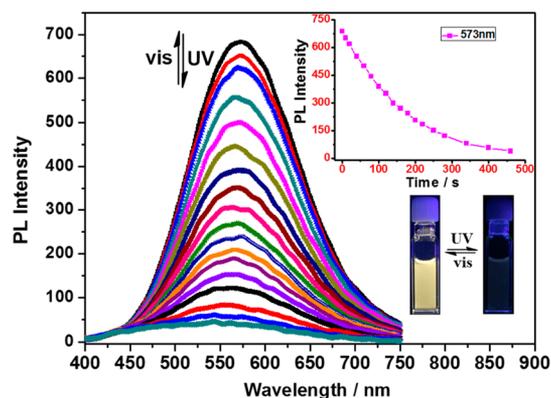


Figure 3. Fluorescence spectral changes of DTE-BP in glycerin upon alternating 254 nm and greater than 490 nm light irradiation. (inset) The variation curve of fluorescent intensity of DTE-BP in glycerin at 573 nm upon 254 nm light irradiation, and the fluorescent emission photographs of DTE-BP upon alternating UV and visible light irradiation ($[\text{DTE-BP}] = 2 \times 10^{-5}$ M, $\lambda_{\text{ex}} = 385$ nm, excitation and emission slit widths were 5 and 10 nm, respectively).

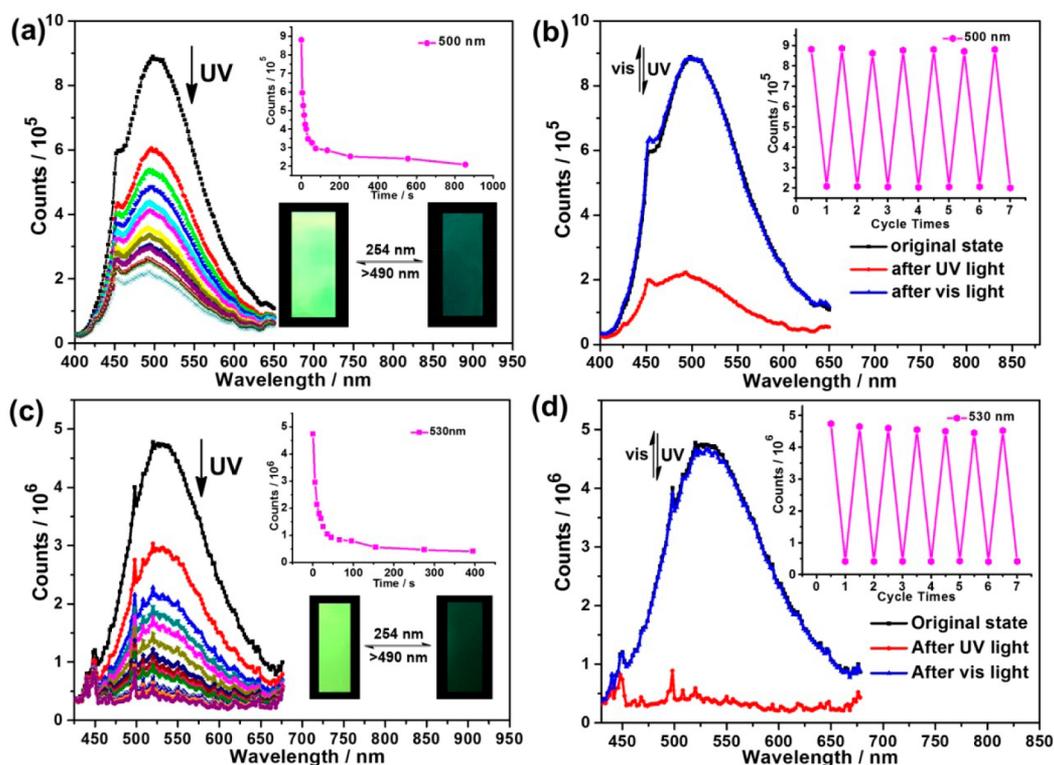


Figure 4. Solid-state fluorescence spectral variation of DTE-BP in (a) PMMA and (c) PVDF films (5 wt %) under 254 nm light irradiation. (inset) Fluorescence quenching curve of the films under UV light irradiation and the fluorescent photographic images of the films upon irradiation at 254 and greater than 490 nm. Solid-state fluorescence spectral variation of DTE-BP in (b) and (d) PVDF films (5 wt %) upon irradiation at 254 and greater than 490 nm. (inset) The reciprocation of photoswitching fluorescence in this process. The fluorescence intensity of DTE-BP was recorded at 500 nm for PMMA film and at 530 nm for PVDF film, respectively.

state. The photoswitchable molecular turnstile DTE-BP was implanted into poly(methyl methacrylate) (PMMA) to fabricate a thin luminescent film (Scheme 1). Accordingly, the absorption maxima were observed at 278 and 362 nm, which gave bathochromic shifted by 3 and 10 nm, respectively, as compared to that in acetonitrile, due to the intermolecular aggregation of the OF-state of DTE-BP in the thin film (Figure S8a). The DTE-BP-embedded PMMA film manifested very strong fluorescence emission at 500 nm and large hypochromic shift (110 nm) resulting from the AIE effect in the solid state (Figure 4a). Furthermore, as shown in the scanning electron microscopic (SEM) and laser confocal images, the PMMA chains could intertwine each other and force DTE-BP aggregates to form nanoparticles, which may result in its AIE behaviors (Figures S14 and S15, Supporting Information). Meanwhile, the fluorescence lifetimes of DTE-BP in the PMMA film were elongated to 1.0 ns (41%) and 3.0 ns (59%), implying the more compact aggregation mode than that in glycerin (0.7 ns, Figure S9). The biexponential fluorescence lifetime was probably attributed to the formation of two aggregation forms with uneven structural distribution.³⁴ Next, the photoregulated photophysical behaviors of DTE-BP were further examined in PMMA film. The solid-state fluorescence was greatly quenched by 76% ($R_{\text{on/off}} = 4$) upon UV light irradiation at 254 nm for 4 min, which was much quicker than that in glycerin (7 min), indicating that the ring-closing reaction was accelerated in the solid state. The possible reason may be that the antiparallel conformation of the photochromic molecule was fixed in the solid state to some extent.³⁵ Crucially, the quenched fluorescence intensity could be largely

restored at greater than 490 nm light irradiation for 20 s, and this forward/backward process was repeatable for at least seven times without any apparent recession, indicative of the perfect reciprocation of photoswitching solid-state fluorescence (Figure 4b). In addition, the reversible variation of absorption spectra upon alternating 254 nm and greater than 490 nm light irradiation also suggested the reversible photocyclization/cycloreversion process of DTE-BP in the solid state (Figure S8a). Visually, the color of the film was changed between pale yellow and blue (Figure S8a, inset), and meanwhile, the corresponding fluorescence emission was altered between green and dark in this photoswitchable process (Figure 4a, inset). In addition, the DTE-BP-embedded polyvinylidene fluoride (PVDF) thin film was also fabricated to further validate the photoswitching solid-state fluorescence process. The solid-state fluorescence quantum yield was measured by 0.196, which was much higher than that in solution (Figure S13c, Supporting Information). As expected, a similar phenomenon was observed for DTE-BP in PVDF film but with notably higher fluorescence quenching efficiency up to 91% ($R_{\text{on/off}} = 11$), as shown in Figures 4c,d, S8b, and S9. Moreover, the fluorescence emission of DTE-BP-embedded PVDF film was centered at 530 nm, which was bathochromically shifted by 30 nm as compared to the case in PMMA film. These spectroscopic characteristics mainly contributed to the relatively looser intermolecular arrangement of DTE-BP in PVDF film (Figure 4c,d).

The photomodulated photophysical behaviors of DTE-BP in the solid state inspired us to further explore the application of such photochromic molecular turnstile. Owing to the reversible photoisomerization between the open form with AIE property

and the nonluminous closed form, the acetonitrile solution of DTE-BP could be utilized as a dual-functional fluorescence ink with photo- and vapor-erasable ability. As shown in Figure S10 and Figure 5a, when the English letters were written on the

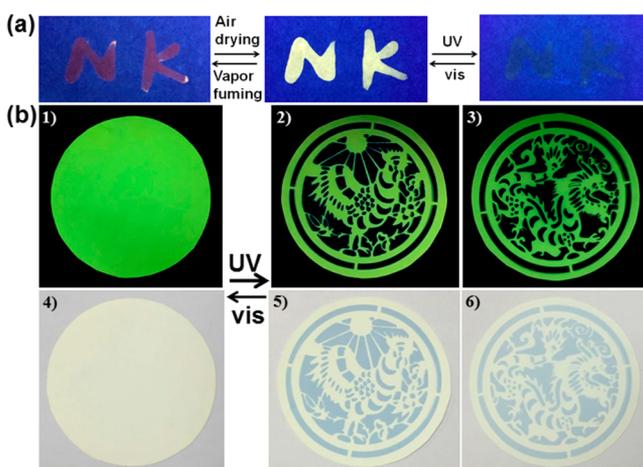


Figure 5. (a) Fluorescence photographic images of English letters written using the DTE-BP-containing acetonitrile solution in air-drying and acetonitrile-vaporizing process and the fluorescence photographic images of the air-dried pattern upon irradiation at 254 and greater than 490 nm. (b) Fluorescence photographic images of DTE-BP-embedded PVDF film before (images 1 and 4) and after (images 2, 3, 5, and 6) irradiation at 254 nm. Images (a) and b(1–3) were observed under 365 nm light.

filter paper using DTE-BP-containing solution, it initially showed very weak red fluorescence, but it gradually turned very strong yellow fluorescence after a few seconds, because the emission band gave hypochromatic shift as the solvent volatilization in the air-drying process (Figure 2). Reversibly, the strong yellow fluorescence could be recovered to the very weak red state after treatment of acetonitrile vapor. Obviously, the bathochromic shift and quenched fluorescence emission were originated from the evacuation of the self-aggregated DTE-BP molecules in acetonitrile. Furthermore, the fluorescent letters could be erased upon UV light irradiation, and subsequently, visible light irradiation could make the yellow letters reemerge. Importantly, the fluorescent characters could be repeatedly written and erased with visible and UV light many times.

Significantly, our obtained DTE-BP-containing PVDF and PMMA films could further serve as controlled luminescence photowritable and erasable materials originating from its reversible photoswitchable solid-state fluorescence. Indeed, various patterns could be light-written on the polymeric films with a simple hollowed-out mold in our case. As shown in Figure S11, when the mold was covered on the film, only the exposed parts could be irradiated by UV light and then converted to the closed form of DTE-BP with quenching, whereas the mold-protected parts maintained its original fluorescence in ring-open form. Therefore, beautiful and realistic patterns could be accurately printed on the DTE-BP films with fluorescence on/off contrast (Figure 5b-2, 5b-3, 5b-5, and 5b-6). Subsequently, when the resultant film was exposed under greater than 490 nm visible light, the printed pattern could be completely erased due to the restoration of the quenched fluorescence state. Crucially, the photowriting/erasing process could be repeatable many times, indicating

that the luminescent film was recyclable. Meanwhile, DTE-BP-embedded PMMA film also displayed similar function with controlled light-writable/erasable capability (Figure S12).

CONCLUSION

In summary, a photochromic molecular turnstile DTE-BP has been rationally designed and synthesized, exhibiting prominent AIE and photochromic characteristics in both organic solution and the solid state. Benefiting from these satisfactory photophysical properties, strong solid-state fluorescence was observed and could be reversibly regulated by distinct light input and solvent vapor. More remarkably, DTE-BP could be conveniently implanted into PVDF and PMMA polymeric matrix to fabricate photowritable and erasable fluorescent materials with good reproducibility and easier operability. We also envision that our obtained luminescent films may be written and erased by specific light resource with single and fixed wavelength, which will present more practical application in the future.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.7b12822.

Compound characterization, UV/vis absorption, and ^1H NMR spectra of DTE-BP upon light irradiation at 254 and greater than 490 nm, fluorescence quantum yield measurements, and additional images in the photo-printing experiments (PDF)

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Notes

The authors declare no competing financial interest.

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