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Photochromic Switching of Excited-State Intramolecular Proton-Transfer (ESIPT) Fluorescence: A Unique Route to High-Contrast Memory Switching and Nondestructive Readout

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Abstract: Aiming at the high-contrast photochromic switching of fluorescence emission and its perfect nondestructive readout, a polymer film highly loaded with a specific photochromic compound, 1,2-bis(2′-methyl-5′-phenyl-3′-thienyl)perfluorocyclopentene (BP-BTE), and an excited-state intramolecular proton-transfer (ESIPT)-active compound, 2,5-bis(5′-*tert*-butyl-benzooxazol-2′-yl)hydroquinone (DHBO), was employed in this work. The special class of photochrome, BP-BTE, has negligible absorbance at 415 nm both in the open form and in the 365 nm photostationary state (PSS), and the ESIPT fluorophore, DHBO, emits large Stokes' shifted (175 nm; $\lambda_{max}^{abs} = 415$ nm, $\lambda_{max}^{em} = 590$ nm) and enhanced fluorescence ($\Phi_F^{powder} = 10\%$, $\Phi_F^{soln} = 2\%$). Bistability, high-contrast switching (on/off fluorescence switching ratio >290), nondestructive readout (over 125000 shots), and erasability were all together accomplished in this novel recording medium.

Introduction

Photoswitchable organic molecules are drawing great attention for their viable application to the ultrahigh-density erasable optical memory.[1] Among the various photon-mode molecular memory systems, bistable photoswitching of fluorescence emission has been considered to be a promising signaling mode because the fluorescence signals can be readily and sensitively recognized while the weak and color-tuned excitation light scarcely ever erases the recorded signal during the fluorescence readout process.[2−14] Aiming at the bistable photochromic switching of the fluorescence emission, highly efficient gated energy transfer from the fluorophore to the photochromic 1,2-bis(thienyl)ethene derivatives (BTEs) has been extensively investigated owing to the high thermal stability, excellent photofatigue resistance, and characteristic bistability of the BTEs.[2−12,15−19] Despite these encouraging principles and material properties of the BTEs, however, practical applications of these BTE switches to the fluorescence-based erasable optical memory are still limited by the insufficient performances of high-contrast fluorescence recording and complete nondestructive readout of the recorded signals.

As for the former issue of high-contrast fluorescence recording, many different classes of "fluorescent BTEs" (i.e., fluorescent molecules with BTE switch), such as a tungsten complex,[2] anthracene derivatives,[3,6] 2,4,5-triphenylimidazole,[4] diporphyrins,[5] *p*-phenylenevinylene moieties,[7] and a 3a,4a-diaza-*s*-indacene derivative,[8] have been developed to demonstrate the higher on/off fluorescence signaling ratio (mostly in solution) by enhancing the value of fluorescence quantum yield (Φ_F) in the open-form BTE state. Bistable photochromic switching in these fluorescent BTEs are well implemented by the efficient intramolecular energy transfer from the fluorophores to the BTE units in an isolated molecular state either in solutions or in polymer matrices. On the other hand, switching performances in the highly loaded polymer films, which are inevitably needed for their practical application to the ultrahigh-density erasable optical memory, are more complicated and less investigated because of the additional challenging problems, such as "concentration quenching" of the fluorescence emission,[20] irreversible photochromism of the BTE moieties, and segregation (phase separation) of the molecules in the highly loaded polymer films. For the realization of high-performance polymer films with the

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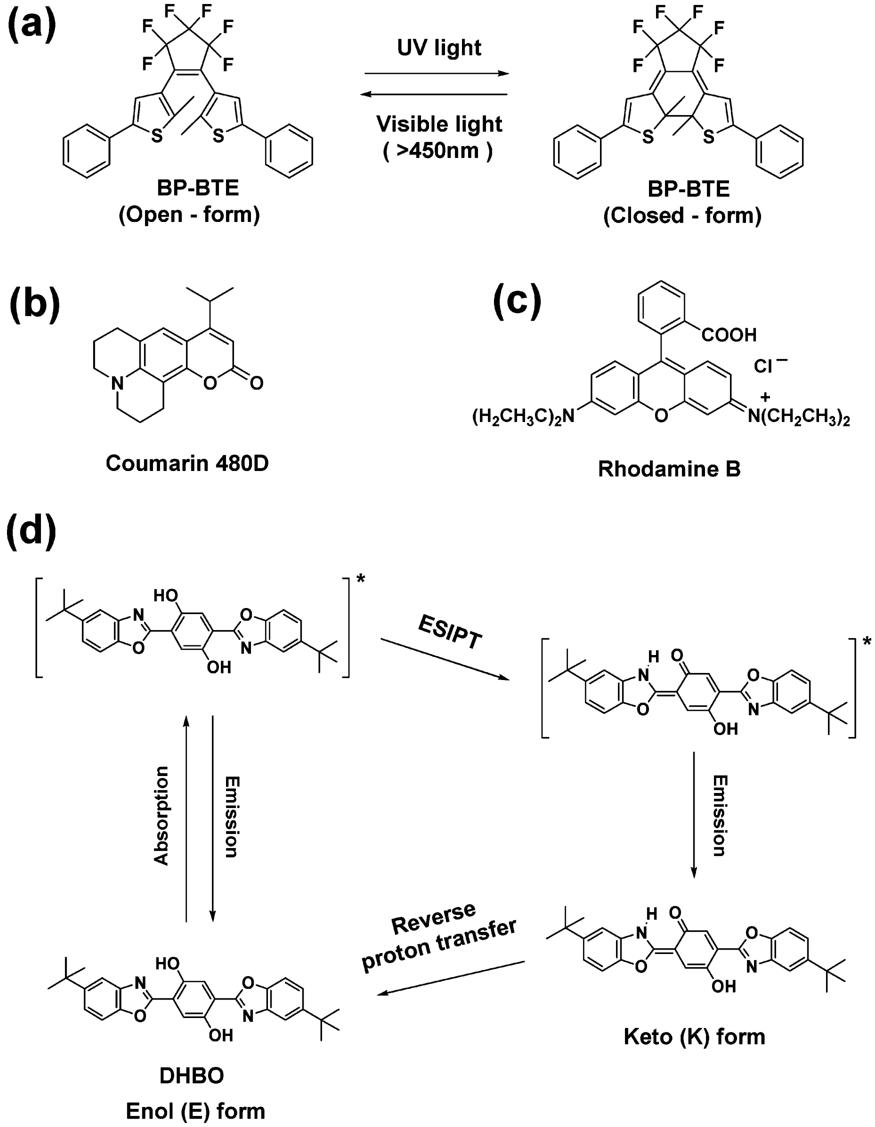

Figure 1. (a) Chemical structure and photochromic reaction of BP-BTE; (b, c) Chemical structures of the model fluorophores, coumarin 480D and rhodamine B, respectively; (d) four-level photochemical and photophysical excited-state intramolecular proton-transfer (ESIPT) process of DHBO.

high-contrast on/off fluorescence recording capability, consequently, these problems should be answered all together.[9−14] Very recently, one encouraging achievement was made by using a special class of fluorophores showing a gradually enhanced fluorescence emission with increasing concentration, a so-called “aggregation-induced enhanced emission (AIEE)”.[10,11]

As for the latter issue of nondestructive readout of the fluorescence signal, it is demanded that the readout light for the fluorescence excitation should not induce any photoisomerization reactions during the fluorescence readout cycles. This means that the photochromic units or the BTEs (both open-form and closed-form) in the highly loaded polymer films should have zero absorbance at the fluorescence excitation wavelength ideally to generate no photochromic reactions during the fluorescence readout process for their practical applications.[9,11] Despite these simple strategic principles for the nondestructive readout, no suitable material systems have been found so far due to the inherent limitation of the Stokes’ shift in conventional fluorescent molecules (vide infra).

In this work, we demonstrate a high-contrast photochromic switching of fluorescence emission and its perfect nondestructive readout capability by employing a polymer film highly loaded with a special class of fluorescent BTE incorporating a large Stokes’ shifted excited-state intramolecular proton-transfer (ESIPT) fluorescence.

Results and Discussion

A special class of BTE compound, 1,2-bis(2′-methyl-5′-phenyl-3′-thienyl)perfluorocyclopentene (BP-BTE),[21] was adopted as a photochromic switch in this work not only because the BP-BTE shows a highly efficient bistable photochromism (see Figure 1a for its chemical structure and photochromic reaction) but also because it has negligible absorbance at around 415 nm both in the open form and in the 365 nm (hand-held lamp, 1.2 mW cm^{-2}) photostationary state (PSS).[15−19] The extinction coefficient (ϵ) at 415 nm of the closed-form BP-BTE dissolved in hexane was estimated to be only 450 (M^{-1} cm^{-1}) while that in the poly(methyl methacrylate) (PMMA; $M_w \approx 120\,000$) matrix was noted to be even less as shown in Figure 2a and c.

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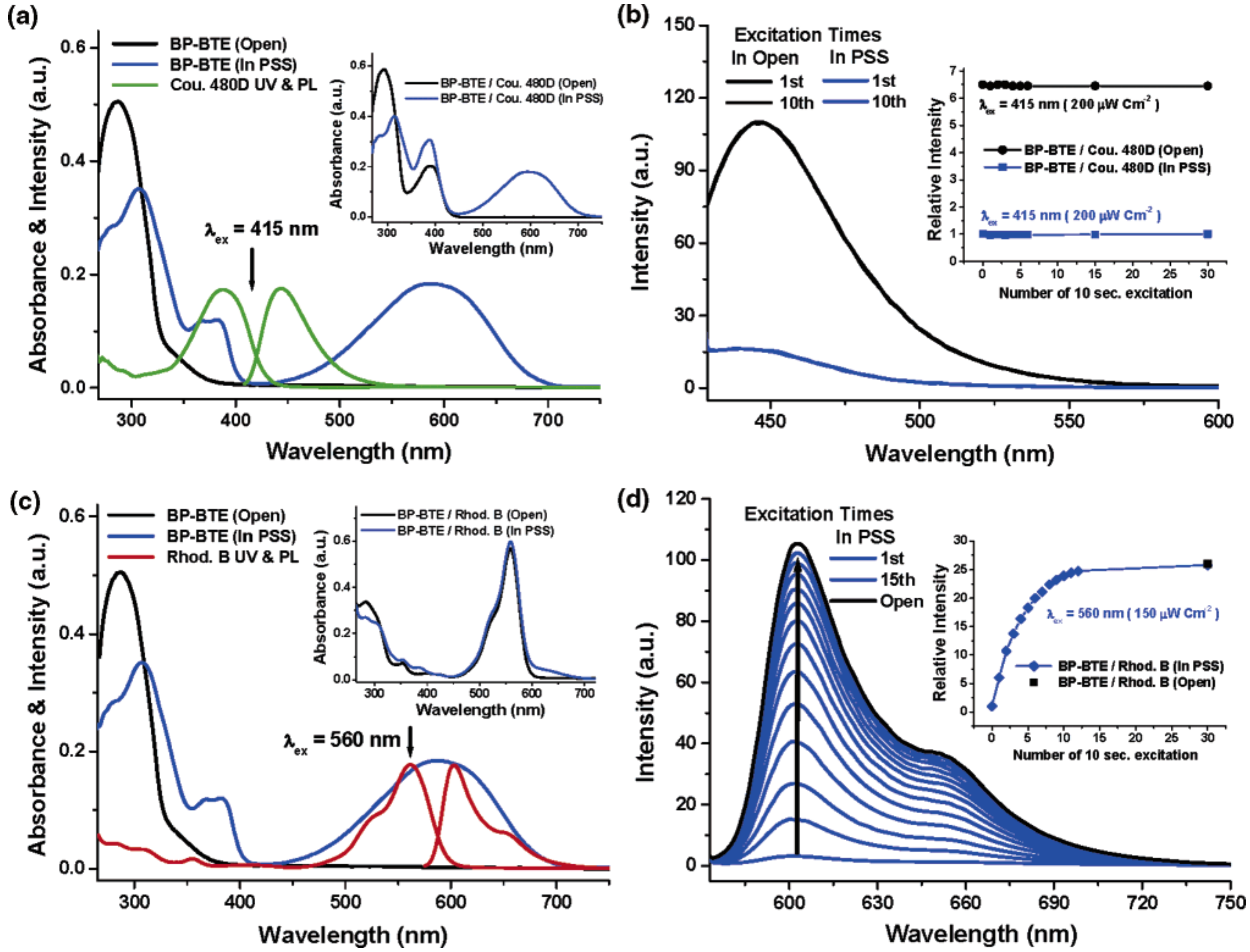

Figure 2. (a) UV−visible absorption spectra of the poly(methyl methacrylate) (PMMA) films loaded with BP-BTE and BP-BTE/coumarin 480D in the open-form state (black lines) and in the 365 nm photostationary state (PSS) (blue lines). UV−visible absorption and photoluminescence (PL) spectra of the PMMA film loaded with coumarin 480D (green lines); (b) nondestructive readout capabilities of the BP-BTE/coumarin 480D-loaded PMMA film in the open-form state (black lines, $\lambda_{ex} = 415$ nm, 200 μW cm^{-2}) and in the 365 nm PSS (blue lines, $\lambda_{ex} = 415$ nm, 200 μW cm^{-2}); (c) UV−visible absorption spectra of the PMMA films containing BP-BTE and BP-BTE/rhodamine B in the open-form state (black lines) and in the 365 nm PSS (blue lines). UV−visible absorption and PL spectra of the PMMA film containing rhodamine B (red lines); (d) PL spectra showing destructive readout trails of the BP−BTE/rhodamine B-loaded PMMA film in the 365 nm PSS (blue lines, $\lambda_{ex} = 560$ nm, 150 μW cm^{-2}) and PL spectrum of the film in the open-form state (black line, $\lambda_{ex} = 560$ nm, 150 μW cm^{-2}).

Considering that the ring-opening quantum yield of the closed-form BP-BTE was rather low ($\Phi_{PC}{}^{C\rightarrow O} = 0.013$ in hexane), it was readily expected that the relatively weak and narrow range of fluorescence emission in the visible region of the fluorophore might induce no ring-opening reaction of the closed-form BP-BTE during the fluorescence readout cycles. In addition, photochromic conversion of the BP-BTE was significant to be employed as a switch unit; by a simple calculation from the ϵ value at 280 nm of the open-form BP-BTE (35 600 M^{-1} cm^{-1} in hexane) and that at 575 nm of the closed-form BP-BTE (15 600 M^{-1} cm^{-1} in hexane) as well as from the UV−visible absorption spectra in the open form and in the 365 nm PSS, it was readily estimated that at least 76% of the open-form BP-BTE was converted into the closed form ($\Phi_{PC}{}^{O\rightarrow C} = 0.59$ in hexane) under the 365 nm PSS.

To understand the fundamental principles and limitations of high-contrast fluorescence recording and nondestructive readout, spin-coated PMMA films containing a high level of conventional fluorophores and BP-BTE photochrome were prepared. Commercially available coumarin 480D (Aldrich Chemical Co.) and rhodamine B (Aldrich Chemical Co.) (see Figure 1b and c for their chemical structures) were used as the model fluorophores. First, PMMA film containing a high level (17 wt %) of BP-BTE/coumarin 480D was prepared at the molar ratio of 1.6 to examine the nondestructive readout capability of the fluorescent BP-BTE mixture. Inset in Figure 2a shows the UV−visible absorption spectra of the BP-BTE/coumarin 480D-loaded PMMA film in the open form and in the 365 nm PSS, in which the new absorption band in the visible region ($\lambda_{max} \approx 590$ nm) went up and down repeatedly with alternate UV and visible light irradiation, respectively. When the film was irradiated with the relatively high-intensity 415 nm light (200 μW cm^{-2}) for the fluorescence excitation, the initial "on" state was continuously preserved regardless of the excitation numbers as shown in Figure 2b. It is considered that such a nondestructive readout capability with the 415 nm light is attributed to the absolutely negligible absorbance of the open-form BP-BTE at 415 nm. Furthermore, the quenched "off" state by the closed-form BP-BTE in the 365 nm PSS did not increase with the irradiation of the 415 nm light as well, as shown in Figure 2b again due to the totally small absorbance of the closed-form BP-BTE at 415 nm. Despite these encouraging nondestructive readout capabilities in the BP-BTE/coumarin 480D-loaded PMMA film, the integrated fluorescence intensity of the film in the 365 nm PSS was reduced down to only a 15% level of the initial open-form state (on/off fluorescence switching ratio < 7). It was considered that such a rather low on/off contrast ratio resulted from the inefficient intermolecular energy transfer between the coumarin 480D and the closed-form BP-BTE in the 365 nm PSS (i.e. only partial overlap between the emission band of the coumarin 480D and the absorption band of the closed-form BP−BTE, see Figure 2a).[12] It was also noted that the fluorescence intensity of the coumarin 480D in the open-form BP-BTE state ("on" state) itself was pretty low owing to the "concentration quenching" effect in such a highly loaded polymer film.[10,20]

To improve the on/off fluorescence contrast ratio, PMMA film containing the same content (17 wt %) of BP-BTE/rhodamine B which shows a larger spectral overlap was prepared at a molar ratio of 1.0. The inset in Figure 2c shows the UV−visible absorption spectra of the BP-BTE/rhodamine B-loaded PMMA film in the open form as well as in the 365 nm PSS. Absorbance change due to the closed-form BP-BTE is noted over the 600−750 nm region, while the larger absorption band at the 450−600 nm region is mostly due to the rhodamine B absorption. As expected from the favorable spectral overlap, it was observed that the integrated fluorescence intensity of the film in the 365 nm PSS was reduced down to the 4% level of the initial open-form BP-BTE state (on/off fluorescence switching ratio >25). It is obvious that this high-contrast fluorescence switching is attributed to the highly efficient intermolecular energy transfer between the rhodamine B and the closed-form BP-BTE (i.e., large spectral overlap between the emission band of the rhodamine B and the absorption band of the closed-form BP-BTE; see Figure 2c). When the film was irradiated with the 560 nm readout light (150 μW cm^{-2}) for the fluorescence excitation, however, the extinguished red fluorescence by the closed-form BP-BTE in the 365 nm PSS gradually increased up to reach the initial fluorescence intensity before the 365 nm UV light irradiation as shown in Figure 2d. This means that the 560 nm readout light for the fluorescence excitation induces the ring-opening reaction of the closed-form BP-BTE bringing about the destructive readout.[12]

Considering the BP-BTE/coumarin 480D and BP-BTE/rhodamine B systems together, it is deduced that the ideal fluorophore for the BP-BTE switch should have the maximum absorption wavelength at around 415 nm for the nondestructive readout capability as well as the maximum emission wavelength at around 590 nm (Stokes' shift = 175 nm) to maximize its energy transfer efficiency with the closed-form BP-BTE in the 365 nm PSS. Such a large Stokes' shift is very unusual in a conventional fluorophore but can be achieved with an ESIPT fluorophore. As an additional requirement, the ideal fluorophore should emit more enhanced fluorescence in the condensed solid state than in the isolated molecular state to overcome the "concentration quenching" problem in the highly loaded polymer films.[10,11]

Fluorescent molecules with the ESIPT process have a characteristic four-level photophysical scheme incorporating the ground and excited states of two different tautomers as shown in Figure 1d. Different absorbing ($E \rightarrow E^*$) and emitting ($K^* \rightarrow K$) molecular species in this ESIPT cycle normally result in the total exclusion of self-absorption and the large Stokes' shifted keto emission.[22−30] Because of these unique and beneficial photophysical properties, ESIPT fluorophores have been applied to the photostabilizers,[25] photopatterning media,[26] chemosensors,[27] white-light-emitting diodes,[28] and proton-transfer lasers.[29,30] Among various ESIPT fluorophores, 2,5-bis(5′-*tert*-butyl-benzooxazol-2′-yl)hydroquinone (DHBO) was selected as an ideal fluorophore in this work because it emits a large Stokes' shifted fluorescence ($\lambda_{\max}{}^{\mathrm{abs}} = 415$ nm, $\lambda_{\max}{}^{\mathrm{em}} = 590$ nm; see Figure 3a) as well as an enhanced fluorescence in the solid state than in the isolated molecular state ($\Phi_F{}^{\mathrm{powder}} = 10\%$, $\Phi_F{}^{\mathrm{soln}} = 2\%$ in chloroform; see the Experimental Section).[31] Aiming at the high-contrast on/off recording and nondestructive readout, a highly fluorescent and optically transparent PMMA film containing a very high level (20 wt %) of BP-BTE/DHBO was prepared at an optimized molar ratio of 1.3 (see the Experimental Section for details). UV−visible absorption spectra of the BP-BTE/DHBO-loaded PMMA film in the open form and in the 365 nm PSS are shown in Figure 3b. The new absorption band in the visible region ($\lambda_{\max} \approx 590$ nm) went up and down repeatedly with alternate UV and visible light irradiation indicating that the highly efficient bistable photochromism of the BP-BTE worked very well in this memory medium. When the film was irradiated with a 415 nm readout light (200 μW cm^{-2}) for the fluorescence excitation of the DHBO, strong orange fluorescence in the open-form BP-BTE state ($\Phi_F{}^{\mathrm{flm}} = 10\%$) as well as the remarkably quenched fluorescence by the closed-form BP-BTE in the 365 nm PSS ($\Phi_F{}^{\mathrm{film}} = 0.03\%$, or on/off switching ratio >290) could be bistably and nondestructively preserved under repeated excitation processes as shown in Figure 3c and d. Through a simple calculation from the Figure 3c and d results, it was estimated that the quenched fluorescence in the 365 nm PSS ($\Phi_F = 0.03\%$) would increase up to reach only the 0.05% Φ_F level after a 125 000 shots of excitation with the relatively high-intensity 415 nm readout light (200 μW cm^{-2}) (see the Experimental Section for details). This is a remarkable number considering that the clear fluorescence readout is possible with the 415 nm light whose intensity is as low as 10 μW cm^{-2}. It is considered that such a characteristically strong nondestructive readout capability in this BP-BTE/DHBO-loaded PMMA film in the 365 nm PSS is attributed to the very low ring-opening quantum yield of the closed-form BP-BTE ($\Phi_{PC}{}^{C\rightarrow O} = 0.013$) as well as the high ϵ value at 415 nm of the DHBO (31900 M^{-1} cm^{-1} in chloroform) in addition to the large Stokes' shift requirement described earlier. Although the relatively weak and narrow range of fluorescence emission of the DHBO may induce the excitation of the closed-form BP-BTE together with the fluorescence quenching, it is reasonably thought that the number of closed-form BP-BTEs for the fluorescence quenching can be suf-

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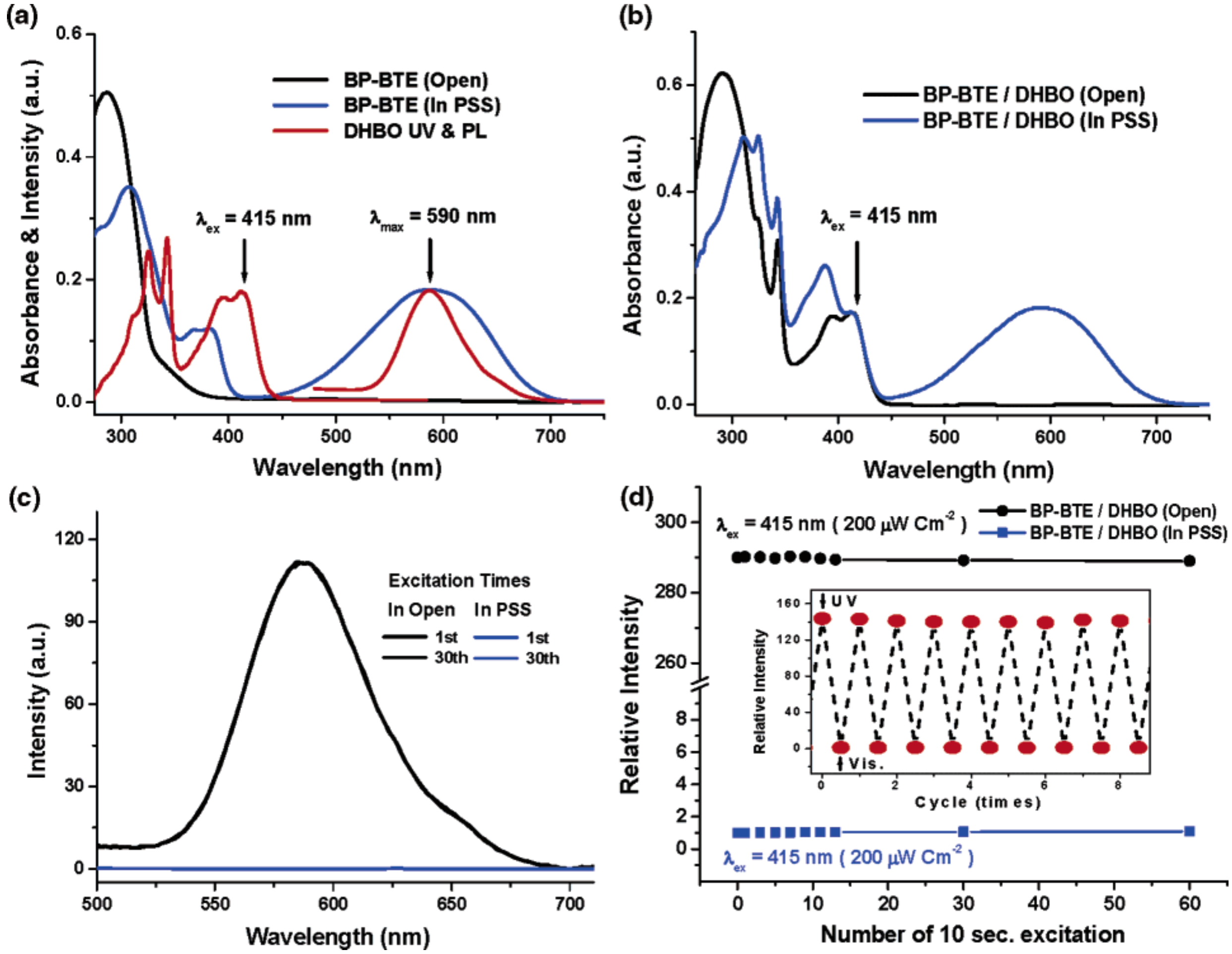

Figure 3. (a) UV−visible absorption spectra of the PMMA film loaded with BP-BTE in the open-form state (black line) and in the 365 nm PSS (blue line). UV−visible absorption and PL spectra of the PMMA film loaded with DHBO (red lines); (b) UV−visible absorption spectra of the BP-BTE/DHBO-loaded PMMA film in the open-form state (black line) and in the 365 nm PSS (blue line); (c, d) nondestructive readout capabilities of the BP-BTE/DHBO-loaded PMMA film in the open-form state (black lines, $\lambda_{ex} = 415$ nm, 200 μW cm^{-2}) and in the 365 nm PSS (blue lines, $\lambda_{ex} = 415$ nm, 200 μW cm^{-2}). Inset graph in (d) shows the photochromic modulation of the ESIPT fluorescence in the BP-BTE/DHBO-loaded PMMA film.

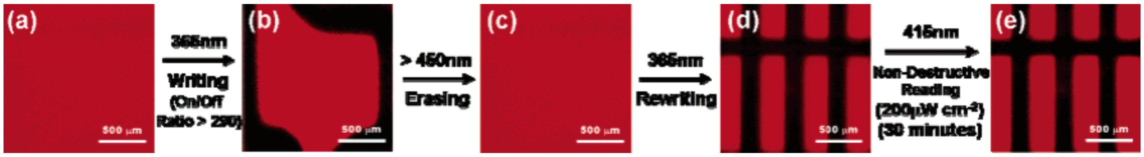

Figure 4. Microsized erasable ESIPT-fluorescence photoimaging on a spin-coated BP-BTE/DHBO-loaded PMMA film and its nondestructive readout capability; (a) initial open-form state; (b) writing; (c) erasing; (d) rewriting; and (e) continuous nondestructive reading under irradiation with the relatively high-intensity 415 nm light (200 μW cm^{-2}) for 30 min. The dark region represents the irradiated area with the 365 nm UV light.

ficiently preserved because the ring-opening quantum yield of the closed-form BP-BTE is low enough. It is also worth mentioning that most of the 415 nm readout photons interact favorably with the DHBO because the ϵ value (at 415 nm) of the DHBO is over 70 times larger than that of the closed-form BP-BTE.

When the BP-BTE/DHBO-loaded PMMA film stabilized in the "off" state was irradiated with visible light (>450 nm, xenon arc lamp, 300 W, 5 min), it was reversibly and completely recovered to the initial strongly fluorescent "on" state. The inset graph in Figure 3d shows the highly bistable photochromic modulation of the strong ESIPT fluorescence of the DHBO with alternate UV (i.e., 365 nm, 5 min) and visible light (i.e., >450 nm, 5 min) irradiation.

Such a strong ESIPT fluorescence emission coupled with the bistable and high-contrast photochromic switching and perfect nondestructive readout in the BP-BTE/DHBO-loaded PMMA film suggests its viable application to the practically available erasable optical memory medium. By employing the patterned illumination through the photomasks, we could successfully demonstrate that the different microsized images could be effectively recorded, erased, and read out on a polymer film as shown in Figure 4. Particularly, all the recorded images in Figure 4 could be nondestructively and repeatedly monitored even with the relatively high-intensity (200 μW cm^{-2}) readout light of a different wavelength (i.e., 415 nm) from the writing (i.e., 365 nm) and the erasing (i.e., >450 nm) wavelengths inducing the photochromic reaction of the BP-BTE. It must be noted that the recorded fluorescence images could be clearly read out even with the much lower intensity irradiation for the fluorescence excitation (e.g., 415 nm, 10 μW cm^{-2}).

Conclusion

In summary, we have demonstrated a novel and unique route to the highly efficient erasable optical memory that utilizes the photochromic switching of ESIPT fluorescence. Specific photochromic compound BP-BTE, which has negligible absorbance at 415 nm both in the open form and in the 365 nm PSS, and an ESIPT-active compound, DHBO, which emits large Stokes' shifted (175 nm) and enhanced fluorescence, were employed as the main components of an optical recording medium. Bistability, high-contrast switching (on/off fluorescence switching ratio >290), nondestructive readout (over 125000 shots), and erasability were all together demonstrated in these novel recording mediums.

Experimental Section

Preparation and Structural Analytical Data of 1,2-Bis(2′-methyl-5′-phenyl-3′-thienyl)perfluorocyclopentene (BP-BTE): BP-BTE was synthesized according to the literature (see ref 21 for details). Analytical data of BP-BTE: white colored amorphous powder; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.6−7.2 (m, 10H), 7.28 (s, 2H), 1.97 (s, 6H); MS *m*/*z* 520 (M+); Elemental analysis, calculated for $C_{27}H_{18}F_6S_2$: C, 62.30; H, 3.49; S, 12.32%. Found: C, 62.56; H, 3.59; S, 12.35%.

Preparation and Structural Analytical Data of 2,5-Bis(5′-*tert*-butyl-benzooxazol-2′-yl)hydroquinone (DHBO): DHBO was synthesized according to the literature (see ref 32 for details). Analytical data of DHBO: yellow colored amorphous powder, ^{1}H NMR (300 MHz, $CDCl_3$) δ 11.10 (s, 2H), 7.77 (m, 4H), 7.56 (d, 2H, $J = 8.6$ Hz), 7.48 (d, 2H, $J = 8.6$ Hz), 1.41 (s, 18H); MS *m*/*z* 456 (M+); Elemental analysis, calculated for $C_{28}H_{28}N_2O_4$: C, 73.66; H, 6.18; N, 6.14%, Found: C, 73.76; H, 6.17; N, 6.00%.

Instrumentation: ^{1}H NMR spectra were obtained on a JEOL JNM-LA300 (300 MHz) using $CDCl_3$ as the solvent. Mass spectra were measured on a JMS AX505WA by EI mode, and elemental analysis was carried out on an EA1110 (CE Instrument). UV−visible absorption and fluorescence emission spectra were measured on a Shimadzu UV-1650PC and Shimadzu RF-500 spectrophotometer, respectively. A UV hand-held lamp (365 nm, 1.2 mW cm^{-2}) was used as a UV light source, and a xenon arc lamp (>450 nm, 300 W) was used as a visible light source through a color filter (Newport, FS-C). The fluorescence images were acquired on a photomicroscope (Axiophot, ZEISS).

Fluorescence Quantum Yields (Φ_F) Measurement: The fluorescence quantum yields (Φ_F) were determined using a 6 in. (15.24 cm) integrating sphere (Labsphere, 3P-GPS-060-SF) equipped with a 325 nm continuous wave (CW) HeCd laser (OmNichrome, Series 56) and a photomultiplier tube (PMT) detector (Hamamatsu, PD471) attached to a monochromator (Acton Research, Spectrapro-300i) (see ref 31 for more details).

Optimized Molar Ratio of BP-BTE/DHBO in PMMA: A highly fluorescent and optically transparent PMMA film containing a very high level (20 wt %) of BP-BTE/DHBO was prepared in this work at an optimized molar ratio of 1.3. On the other hand, when the molar ratio of BP-BTE/DHBO was lower than 1.3, the strong ESIPT fluorescence of the DHBO was not perfectly quenched in the 365 nm PSS. Besides, when the BP-BTE was more added to the optimized PMMA film containing 20 wt % of BP-BTE/DHBO (molar ratio of 1.3), some segregation (or phase-separation) of the active molecules in the highly loaded polymer films took place urging the amount of DHBO to be lowered in these PMMA films. In the case of these PMMA films containing higher than 20 wt % of BP-BTE/DHBO, considerable light scattering at the visible region was clearly observed in their UV−visible absorption spectra. Consequently, the high-density inclusion of the active fluorophore, DHBO, into the PMMA matrix and high-contrast fluorescence recording capability could be all together accomplished in this optimized PMMA film containing 20 wt % of BP-BTE/DHBO (molar ratio of 1.3).

Nondestructive Readout Time Calculation: The integrated fluorescence intensity of the BP-BTE/DHBO-loaded PMMA film in the 365 nm PSS increased up to reach $((1 + 3.2) \times 10^{-4})$ times of initial value ($\Phi_F = 0.03\%$) after 60 shots of excitation. If it were assumed that the ring-opening reaction of the closed-form BP-BTE occurred linearly for a simple calculation, although it actually happened logarithmically as shown in Figure 2d, the Φ_F of 0.03% would increase up to reach the 0.05% Φ_F level after 120 500 shots of excitation.

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