Photoresponsive luminescence switching of metal-free organic phosphors-doped polymer matrices

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Abstract: A new type of luminescence switching behavior based on phosphorescence enhancement from a series of metal-free organic phosphors doped polymers by UV-irradiation was investigated. This phenomenon is observed only from pairs of organic phosphors and polymer matrices having a combination of appropriate triplet exciton lifetime and oxygen permeability. Systematic investigation revealed that the luminescence switching behavior of organic phosphors embedded in a specific polymeric matrix stems from the conversion of triplet oxygens to singlet oxygens by UV-irradiation, leading to the unique phosphorescence enhancement of organic phosphors. Visualization of latent information by UV-irradiation was demonstrated toward novel secure information communication applications.



## 1. INTRODUCTION (477 words)

Switching of optical properties of materials in response to light has been an intriguing topic owing to its importance in the application of molecular switches, imaging devices, transmission glasses, and smart windows.[1] Photoresponsive switching in materials' optical properties is devised most commonly from reversible transformation between two chemical isomers (i.e. photoisomerism) having different absorption characteristics by photoirradiation.[2] Photo-induced reversible ring opening and closing reactions and cis/trans isomerizations observed in diarylethenes, azobenzenes, and spiropyrans[2,3] can alter the effective conjugation length of the photochromic molecules which can also turn on and off intramolecular and intermolecular energy transfers,

leading to chromatic transition.[4] Photoresponsive luminescence switching can be commonly achieved by either reversible conversion between the non-emissive and emissive states of photochromic compounds, or by the control of energy transfer between a photochromic donor molecule and an emitting acceptor. While luminescence switching responding to light has been developed mostly from fluorophores,[4] phosphorescence switching have some unique advantages such as freedom from the interference of background emission due to their much longer emission lifetime.[5]

Most phosphors are organometallic by nature and accordingly, photoresponsive phosphorescence switching has also been limited to organometallic complexes having a photochromic moiety as a ligand.[6,7] Even though, metal-free purely organic phosphors (POP) have a much longer triplet lifetime[8,9] than their organometallic counterparts due to the absence of heavy metal atoms promoting spin-orbit coupling (SOC), photoinduced phosphorescence switching has rarely been reported from POP.[10-12]

To design photoresponsive phosphorescence switching from POP, we first consider the oxygen sensitivity of POP as phosphorescence is originated from triplet states and the phosphorescence lifetime of POP is in a millisecond or longer regime.[13,14] In fact, oxygen-induced phosphorescence quenching is the major non-radiative decay process of POP. On the other hand, the energy transfer from the lowest triplet state ($T_1$) of phosphorescence emitters to triplet oxygens can generate singlet oxygens that are highly reactive and often result in chemical reactions (e.g. photodynamic therapy of triplet photosensitizers).[15] Considering this fact, we envisioned that the conversion of triplet oxygens to singlet oxygens by photo-irradiation would result in triplet oxygen

consumption and thereby potentially enhance phosphorescence of POP, rendering a new type of phosphorescence switching behavior.

Here, we report UV-induced phosphorescence enhancement of POP-doped polymers. To investigate the underlying mechanism of this phenomenon, fluorophores and organometallic phosphors having a shorter emission lifetime are compared with POP. We also studied the effect of oxygen permeability of matrix polymers by using a series of polymer matrices having different oxygen diffusion rates. We found that distinctive light-responsive luminescence switching is observed only in the combination of POP with a long phosphorescence lifetime and atactic poly(methyl methacrylate) (*a*-PMMA). Our studies revealed that the phosphorescence switching behavior of POP-doped *a*-PMMA films is originated from the conversion of triplet to singlet oxygen mediated by photoexcitation of POP, which leads to the phosphorescence enhancement. Visualization of latent information by UV-irradiation was demonstrated toward novel secure communication applications.

**2. RESULTS & DISCUSSIONS**

2,5-dihexyloxy-4-bromobenzaldehyde (Br6A) is a metal-free purely organic phosphor having its triplet lifetime in a millisecond regime.[16-19] The bromo-benzaldehyde moiety of Br6A greatly enhances intersystem crossing (ISC) via the El-Sayed rule-satisfying aromatic aldehyde combined with the heavy atom effect of bromine.[16] As we previously reported, Br6A-doped *a*-PMMA film showed negligible phosphorescence because *a*-PMMA has substantial oxygen permeability and *β*-relaxation, and thus phosphorescence is quenched by oxygen.[20,21] Based on that, we recently

devised oxygen-sniffing core-shell nanoparticles by incorporating a covalently crosslinked Br6A derivative into an oxygen permeable polystyrene core.[13]

Figure 1 illustrates the photoresponsive phosphorescence switching of a Br6A doped *α*-PMMA film. Interestingly, the emission of Br6A is significantly enhanced upon continuous 365 nm UV-irradiation as shown in Figure 1b. To better visualize this phenomenon, a M-shaped card was placed on and later removed from the film surface to enable comparison between the emission intensities of the covered and uncovered areas during the UV-irradiation. When the M-shaped card was removed after 95s of the UV irradiation, the uncovered region appeared much brighter than the covered region, clearly demonstrating the emission enhancement. Further irradiation of the film after removing the M-shaped card showed that the formerly dark character M region was brightened. Notable phosphorescence enhancement was observed in this process from almost no emission to bright green emission. To quantitatively investigate this phenomenon, the photoluminescence spectra and decay curves of the 1 wt% Br6A doped *α*-PMMA film before and after the exposure to UV light were recorded (Figure S2). Figure 1c shows the gated emission spectra of the film before and after 30 s irradiation by LED (28.21 mW/cm$^2$), revealing a ca. 6.5-fold intensity enhancement.

It is well known that oxygen level can greatly affect the phosphorescence intensity of POP. Thus, to examine the effect of oxygen on the UV-induced phosphorescence enhancement behavior of POP, we first carried out the same UV-irradiation experiment in a glove box in which the oxygen level is maintained below 3 ppm. As shown in Figure S3, no emission enhancement is observed even after 30 s continuous UV-irradiation, and thus the covered and uncovered regions are indistinguishable, implying that the luminescence switching behavior is closely related to the

existence of oxygen. To further confirm that phosphorescence enhancement is related to the oxygen level in the polymer matrix, the phosphorescence spectra, decay curves, and phosphorescence quantum yield ($\Phi_p$) of an epoxy-sealed 1 wt% Br6A doped *a*-PMMA film (sealed in the glove box to exclude oxygen entrapping) were obtained (Figure 2 and Figure S4). As shown in Figure 2a, the emission of the sealed sample ($\Phi_p$ = 19%) is 20-fold brighter than that of the unsealed sample, clearly indicating that the phosphorescence enhancement is related to oxygen level in the polymer.

We next investigated the reversibility of the observed photoswitching behavior. Because the depleted triplet oxygen level can be replenished as oxygen penetrates through the polymer matrix when the UV-irradiation is halted, the enhanced phosphorescence intensity should drop down. As we expected, the photoswitching behavior is reversible through repeated cycles of turn-on and -off the UV-irradiation as demonstrated in Video S1. However, a certain level of photobleaching is inevitable when Br6A is used as the chromophore, especially at higher light intensity (Section 2.8 in SI and Figure S12) since it is well known that aromatic aldehyde is prone to photo-oxidation.[22] In fact, photobleaching was substantially reduced when the aldehyde was replaced by trifluoroacetyl group, as demonstrated by our recently developed metal-free organic phosphor, BrPFL-TFK (Figure S12).[23]

To verify the suggested triplet oxygen consumption-based phosphorescence enhancement mechanism, we prepared methanol solutions of Br6A and BrPFL-TFK at various concentrations and studied singlet oxygen generation upon 365 nm and 345 nm UV irradiation, respectively. As shown in Figure S13 the singlet oxygen emission spectra at 1270 nm were observed. To further investigated the phosphorescence enhancement mechanism by preparing a camphorquinone-doped Br6A/a-PMMA film. Camphorquinone is known to generate triplet excitons upon photoexcitation at around

460 nm where Br6A is barely excited.[24] As demonstrated in Video S2 and Figure 3, strong phosphorescence was observed from the camphorquinone-doped Br6A/*a*-PMMA film after 1 min of 455 nm LED irradiation due to the conversion of triplet oxygen to singlet oxygen by the triplet excitons of camphorquione, which is commonly used for photopolymerization of dental resins. Further phosphorescence enhancement was negligible when 365 nm lamp was turned on. On the contrary, without camphorquinone, phosphorescence from Br6A/*a*-PMMA film was not brightened by 455 nm irradiation but sharp emission enhancement was clearly observed by 365 nm irradiation. These results strongly support that the observed phosphorescence enhancement originates from the triplet oxygen conversion to singlet oxygen by photoexcited POP.

Based on these results, a phosphorescence emission enhancement mechanism through triplet oxygen consumption is proposed as follows (Figure 2b). Upon excitation, Br6A is excited from its ground state to the singlet excited state, and quickly undergoes ISC to the triplet state. Then the triplet energy is transferred to surrounding oxygen molecules in the ground state (i.e. $^{3}\sum_{g}^{-}$).[25] This process might be efficient due to the sufficiently long triplet exciton lifetime of Br6A (0.21 ms). As a result, highly reactive singlet oxygen is generated[26] and, subsequently, consumed through reactions with chemical species around the polymer matrices (e.g. oxidation of PMMA).[27] However, considering the reversible feature of the observed photoswitching, oxidation of PMMA is reasonably ruled out as the origin of the photoresponsive phenomenon. Moreover, PMMA does not absorb 365 nm. Therefore, the energy transfer of transient PMMA radical species cannot be the origin of the photoswitching either.[28-29] The rate of oxygen consumption inside the *a*-PMMA matrix should be faster than the oxygen permeation rate into the polymer matrix. Consequently, the triplet oxygen

consumption by UV-irradiation leads to the phosphorescence enhancement of Br6A in the *a*-PMMA matrix.

It is worth noting that the emission intensity difference between the sealed and unsealed samples (i.e. 20-fold) is much larger than the enhancement produced by UV-irradiation (6.5 fold). This is likely because even though oxygens are consumed inside the polymer matrix, due to the oxygen permeation into the polymer matrix, in steady-state, oxygen concentration in the *a*-PMMA matrix cannot be as low as in the sealed sample.[20] Another possible reason is that oxygen in the deep bottom of the polymer film close to the glass substrate cannot be fully consumed because of the limited UV penetration depth. In fact, it is well-known that light has a certain penetration depth depending on its wavelength: e.g., blue photons can only penetrate less than 1 mm.[30] To further investigate the penetration limit issue, the effect of film thickness on the phosphorescence enhancement was studied. Figure 2c shows the normalized PL enhancement of the Br6A/*a*-PMMA films having different thicknesses along the UV irradiation by a xenoflash lamp integrated in a fluorimeter. The phosphorescence intensity increased gradually with the irradiation time, except for the sealed sample, consistent with the visual observation by using the LED lamp shown in Figure 1. However, one can see in Figure 2c, the achievable maximum emission enhancement was reduced upon increasing the film thickness, denoting the limit of UV penetration depth. Hence, oxygens cannot be completely consumed by UV irradiation and consequently the enhancement by UV irradiation is not as significant as the sealed sample.

We observed the same emission enhancement from several other POPs including 4-chloro-2,5-dihexyloxybenzaldehyde (Cl6A), 2,5-dihexyloxy-4-iodobenzaldehyde (I6A), and 7-Bromo-9,9-diphenyl-9H-fluorene-2-carbaldehyde (BrPhFlA), which clearly supports the suggested mechanism.

Chemical structures of Cl6A, I6A, and BrPhFlA are provided in the SI. Photos showing the enhancement properties of Cl6A, I6A, and BrPhFlA can be found in the SI (Figure S5, S6, and S7). However, we were unable to observe any notable UV-induced luminescence switching from Rhodamine 6G (R6G)- and $Ir(ppy)_3$-doped *a*-PMMA films (Figure S8a and S8b). We reasoned that the negligible emission enhancement in the R6G- and $Ir(ppy)_3$-doped *a*-PMMA films is because the emitting state of R6G is a singlet state and $Ir(ppy)_3$ has a rather short phosphorescence lifetime (i.e. 3 μs) and thus it is much less sensitive to oxygen compared to POP. In fact, singlet excitons are usually not quenched by triplet oxygen and the short triplet lifetimes of organometallic phosphors do not allow enough time for efficient energy migration to triplet oxygen.[31] According to Stern-Volmer equation ($I_0/I_P = 1 + K_{SV}[O_2] = 1+k_q\tau_0[O_2]$, here, $I_0$ and $I_p$ are the emission intensity without oxygen and at a given oxygen concentration ($[O_2]$), respectively; $K_{sv}$ is the Stern-Volmer rate constant; $k_q$ is the bimolecular quenching rate constant, and $\tau_0$ is the emission lifetime without oxygen),[31] the sensitivity of phosphorescence to oxygen depends on $\tau_0$. Thus, the sensitivity of organometallic phosphors to oxygen is much lower because their $\tau_0$ is approximately three orders of magnitude shorter than that of POPs. These results indicate that the observed UV-induced luminescence switching is a unique property of POP.

We further examined the phosphorescence switching of Br6A in isotactic PMMA (*i*-PMMA). Figure S8c shows the photos of Br6A in *i*-PMMA before and after the UV irradiation. Luminescence switching is weak because the initial phosphorescence intensity is already high due to both the poor oxygen permeability and the absence of *β*-transition of i-PMMA. It has been reported that $\Phi_p$ of Br6A in *i*-PMMA (7.5%) is much higher than that in *a*-PMMA (0.7%) at ambient conditions.[21] Table 1 summarizes the behaviors of several POPs, the organometallic phosphor $Ir(ppy)_3$, and a fluorophore

R6G in a-PMMA, as well as Br6A in *i*-PMMA, and their emission lifetime values.[32,33] The decay curves of Cl6A, I6A, BrPhFlA, and $Ir(ppy)_3$ in *a*-PMMA, as well as Br6A in *i*-PMMA are provided in Figure S9-S11.

Effect of the UV-power on the enhancement was also investigated.[26] The emission enhancements at different excitation power densities (*P*) for the same samples were recorded. The time required to reach the saturation was defined as the saturation time ($t_s$), and could be obtained from the video recordings. Figure 4 shows the relationship between $t_s$ and *P*. The $t_s$ decreases as *P* increases. Considering the reaction kinetics between singlet oxygens and the substance in the polymer that are oxidized by singlet oxygen[34] and the Stern-Volmer equation,[35] we deduce an inverse linear correlation between $t_s$ and *P* (shown in the inset of Figure 4 and the detailed derivations are provided in the SI). As predicted, the obtained data show a linear inverse proportionality between $t_s$ and P, supporting that the observed enhancement is related to the triplet oxygen consumption by UV.

We applied the UV-induced phosphorescence enhancement to a secure information communication. Figure 5 shows photographs (captured from the video in the SI) of a sample excited by the 365 nm LED having a power density of 57.53 $mW/cm^2$ for (a) 1 s and (b) after 10 s of irradiation. In the square patterns, only the sections for “UM1817” are printed with Br6A/a-PMMA dissolved in chloroform as the ink, and the remaining characters are printed with a secondary ink containing a “non-phosphorescent” derivative of Br6A, 2,5-Dihexyloxybenzaldehyde (6A, chemical structure in Figure S1) with similar fluorescence characteristics as Br6A. Upon excitation at 365 nm, the latent information UM1817 is indistinguishable because there is essentially no phosphorescence emission from Br6A in the presence of oxygen and its fluorescence intensity is similar to that of 6A.

The encrypted "UM1817" is clearly revealed after 10s of UV irradiation owing to the triplet oxygen consumption by UV light and the consequent phosphorescence enhancement. This unique photoresponsive luminescence switching from a specific combination of organic phosphors and a proper polymer matrix can also render their potential use in detecting harmful UV-light or monitoring oxygen levels in various processes.

In summary, a new type of light-induced luminescence switching was devised based on the triplet oxygen consumption by UV-light and consequent phosphorescence enhancement of metal-free organic phosphors embedded in a-PMMA. The phosphorescence intensity is greatly enhanced by the UV-light exposure in the presence of oxygen but this enhancement could not be observed in an oxygen-free environment. The photoresponsive luminescence switching was not observed in fluorescent dyes or organometallic phosphors having a fast emission lifetime. *i*-PMMA having a better oxygen barrier property than *a*-PMMA cannot induce the notable luminescence change either. Conversion ground-state triplet oxygen to singlet oxygen mediated by UV-excited POP was proposed as the origin of the photoresponsive luminescence switching of the organic phosphor. Therefore, the observed light-responsive phosphorescence enhancement is a unique phenomenon pertinent to purely organic phosphors having a long emission lifetime when they are embedded in a polymer matrix having proper oxygen permeability. Visualization of concealed information on such organic phosphor films by UV-irradiation was demonstrated toward novel secure information communication applications.

**Experimental Section**

All experimental details are described in supporting information.

**Supporting Information**

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

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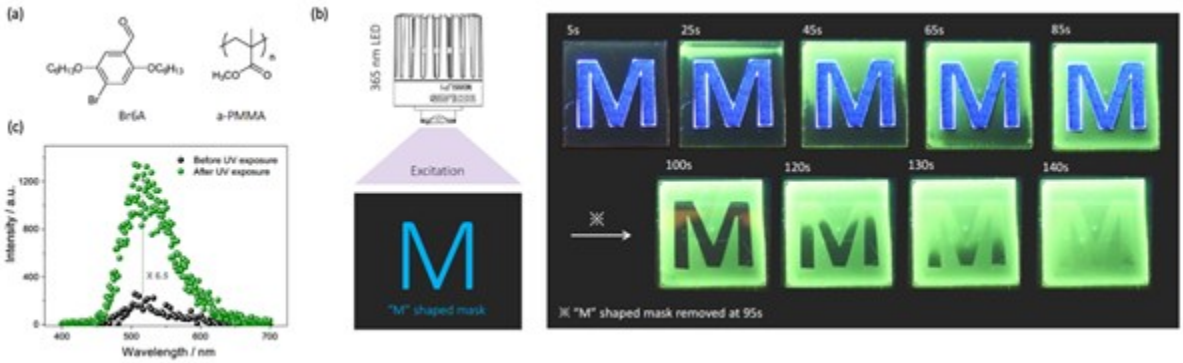


**Figure 1.** (a) Chemical structures of Br6A, a metal-free organic phosphor, and a-PMMA (b) Images taken from the video recording 1 wt% Br6A doped a-PMMA (Br6A/a-PMMA) irradiated by a UV lamp (1.06 mW/cm$^2$) (c) Gated PL spectra of the Br6A/a-PMMA before and after the UV exposure.

**Table 1.** Emission enhancement of several POPs, $Ir(ppy)_3$, an organometallic, and R6G a fluorophore in a-PMMA, as well as Br6A in i-PMMA, and their emission lifetime values in air (before long-term irradiation).

| Emitter | Polymer | Photochromism | Type | Lifetime |
|---|---|---|---|---|
| Cl6A | *a*-PMMA | Yes | POP | 540 µs |
| Br6A | *a*-PMMA | Yes | POP | 210 µs |
| Br6A | *i*-PMMA | Yes | POP | 310 µs |
| I6A | *a*-PMMA | Yes | POP | 285 µs |
| BrPhFLA | *a*-PMMA | Yes | POP | 2006 µs |
| $Ir(ppy)_3$ | *a*-PMMA | No | Organometallic | 3 µs |
| R6G | *a*-PMMA | No | Fluorophore | 4 ns [25,26] |

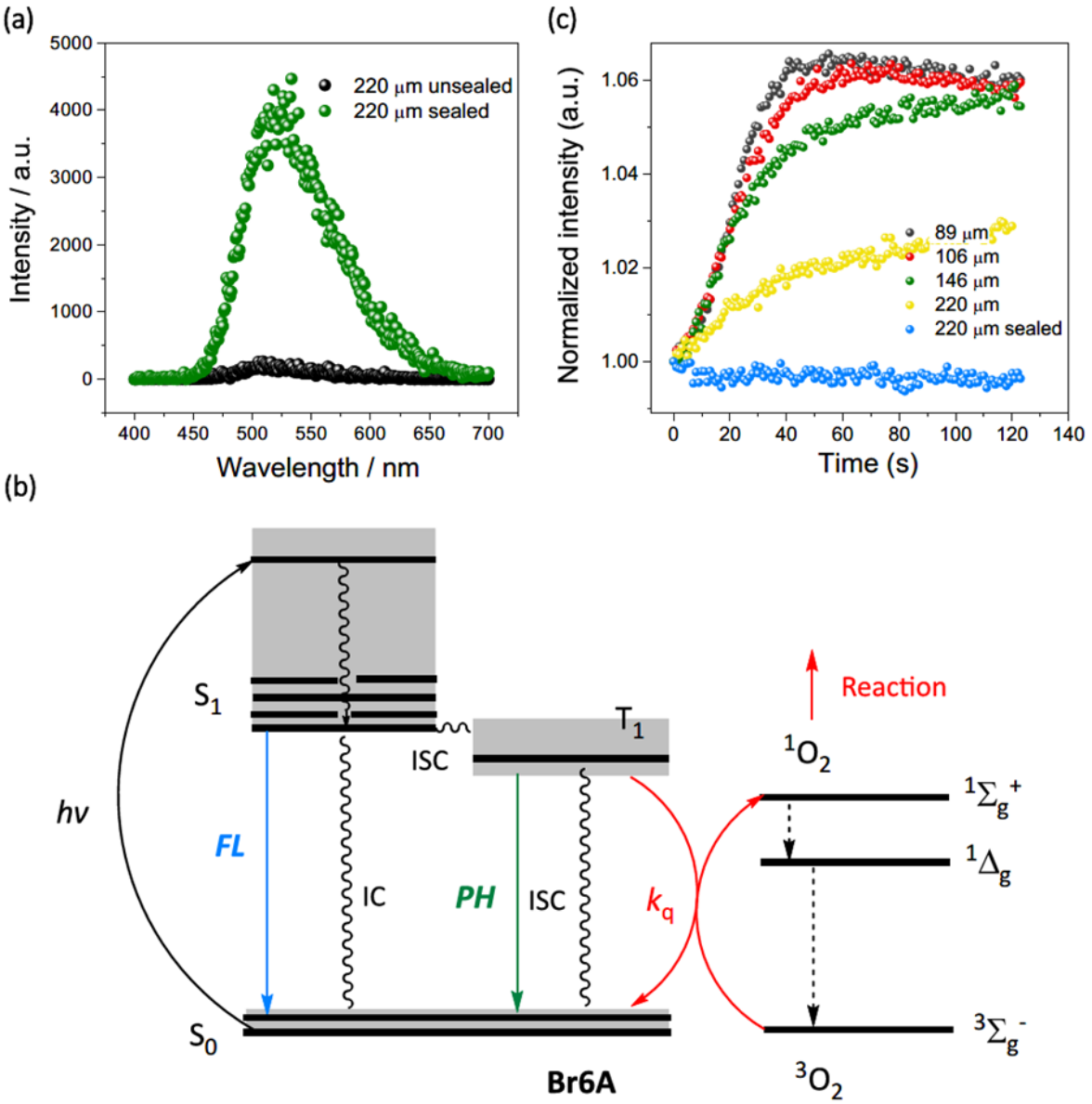


**Figure 2.** (a) The emission spectra of 1 wt% Br6A doped a-PMMA films under unsealed and sealed conditions; (b) The energy diagram of a possible enhancement mechanism; (c) The relative phosphorescence intensity of 1 wt% Br6A doped a-PMMA films with different thicknesses compared to the initial value upon UV irradiation. As one can see, the enhancement in Fig. 2c is not as significant as Fig. 1c because the light source used for Fig. 2c is a xenoflash lamp integrated in a

fluorescence/phosphorescence spectrophotometer, whose power intensity is much lower than that of the UV lamp for the experiment shown in Fig. 1c.

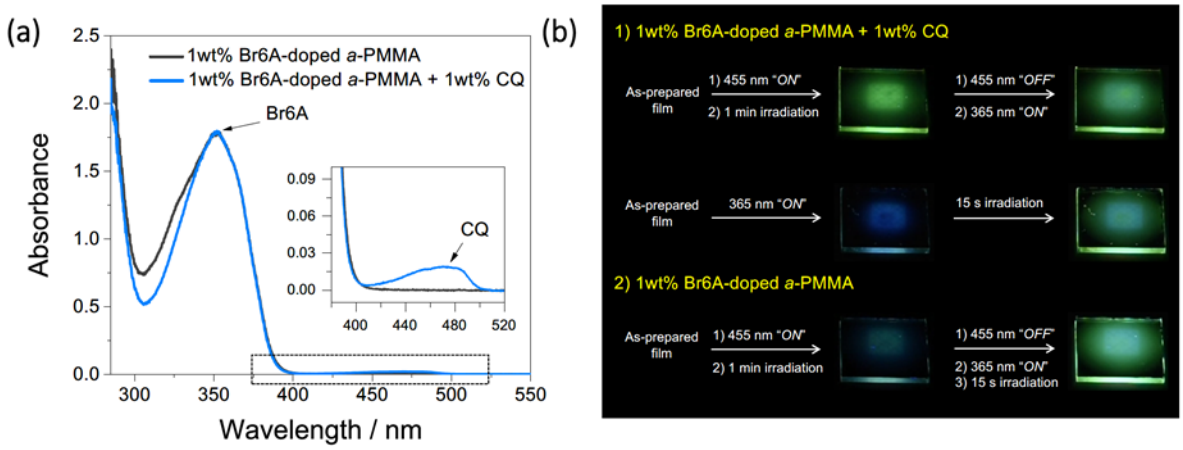


**Figure 3.** (a) UV-vis absorption spectra of 1 wt% Br6A in aPMMA and 1 wt% Br6A / 1wt% (±)camphorquinone (CQ) in aPMMA; (b) Photoresponsive luminescence switching study with and without CQ in the aPMMA: Br6A system (screenshots from Video S2).

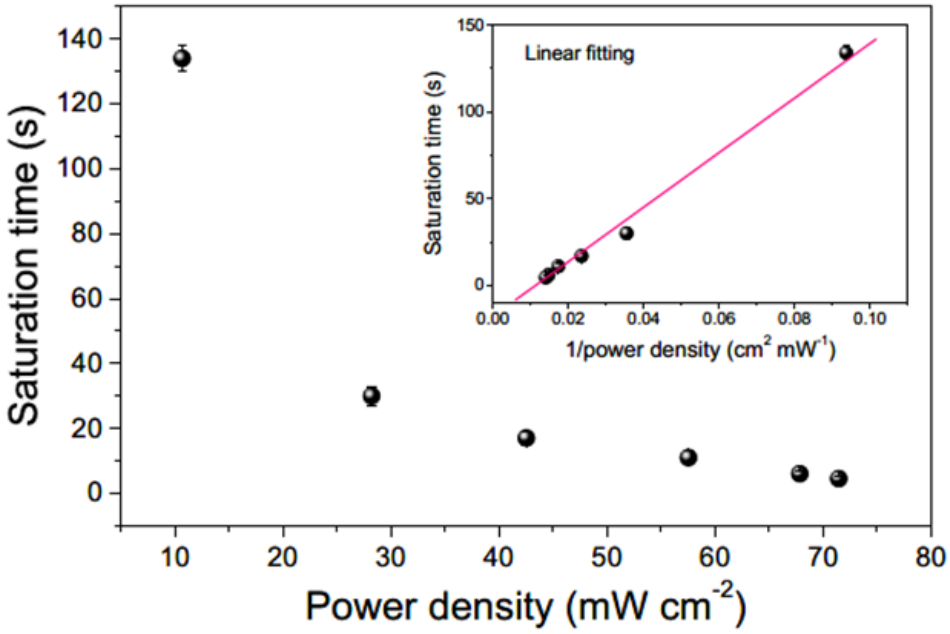


**Figure 4.** Relationship between the saturation time (ts) and the power density (P) of the excitation light (LED); inset, a linear correlation between the saturation time and (power density)$^{-1}$.

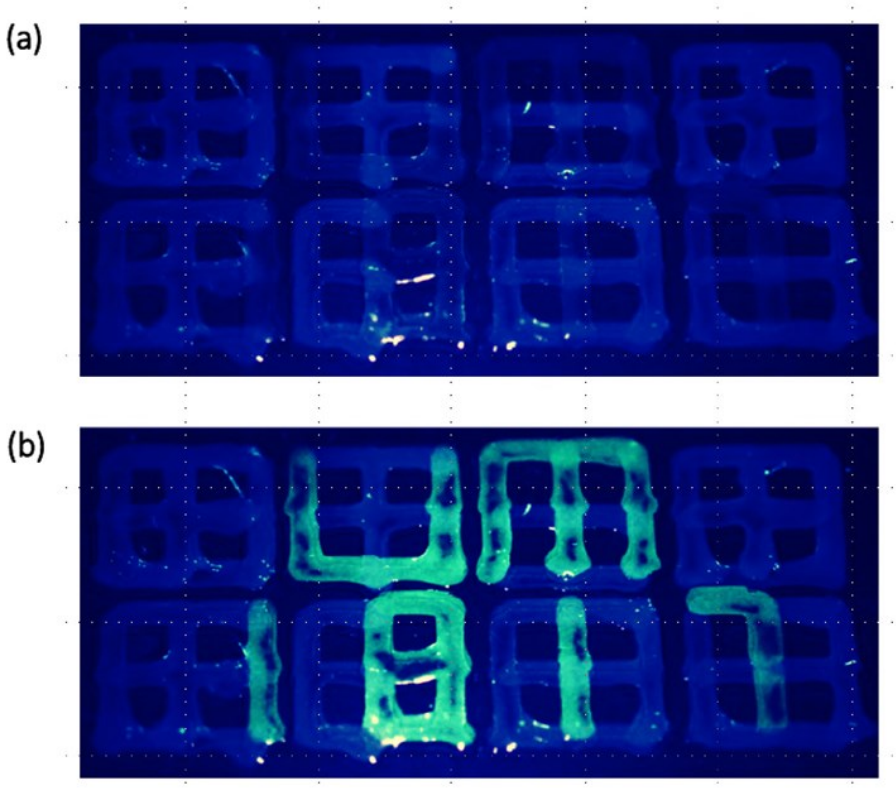


**Figure 5.** (a) Photograph of a sample excited for 1 s by a 365 nm LED having a power density of 57.53 mW/cm$^2$. (b) Photograph of the sample after 10 s of UV exposure.

A new type of luminescence switching behavior based on phosphorescence enhancement from a series of metal-free organic phosphors doped polymers by UV-irradiation was investigated, which stems from the conversion of triplet oxygens to singlet oxygens by UV-irradiation, leading to the unique phosphorescence enhancement of organic phosphors. Visualization of latent information by UV-irradiation was demonstrated toward novel secure information communication applications.

**Keyword:** photoresponsive luminescence switching

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**Photoresponsive luminescence switching of metal-free organic phosphors-doped polymer matrices**