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Achieving multi-stimuli-responsive and color-tunable luminescence from ultralong organic phosphorescent materials[†]

Lu Zhou, \ddagger^{ab} Yu Yan, \ddagger^{b} Jianzhong Fan, \textcircled{D}^{c} Qingfang Mu,^c Xiangchun Li^b and Wen-Yong Lai $\textcircled{D} *^{b}$

Stimuli-responsive ultralong organic phosphorescence (UOP) materials have drawn widespread attention owing to their potential in intelligent optoelectronics. However, their tunable emission characteristics are typically observed only after the removal of irradiation sources, which makes their applications heavily reliant on time-resolved technology. Herein, we propose a facile approach to achieve multi-stimuli-responsive and steady-state color-tunable luminescence for direct visualization-based applications by regulating multimode emissions in UOP materials. The steady-state emission color of the UOP material (PhP-B) can be regulated by multiple stimuli, including excitation wavelength, temperature, oxygen environment, mechanical force, and decay time. This work provides not only a new platform for developing multi-stimuli-responsive UOP materials, but also extends the direct visualization-based applications in multicolor patterns and visual monitoring.

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Introduction

Organic luminescent materials^{1–4} have attracted great interest due to their considerable potential in optoelectronic fields,^{5,6} including organic light-emitting transistors,^{7,8} organic light-emitting diodes,^{9–11} and organic lasers.^{12,13} In particular, stimuli-responsive organic luminescent materials^{14–17} that can exhibit tunable emission properties in response to external stimuli, such as excitation wavelength,^{18–21} external force,^{22–25} and temperature,^{26–28} have witnessed remarkable advances in recent years. Owing to the long-lived emissive characteristics and high sensitivities of excited triplet states to external stimuli, ultralong organic phosphorescence (UOP) materials^{29–32} can provide an ideal platform for achieving stimuli-responsive luminescence.^{33–35} Generally, the stimuliresponsive UOP materials exhibit tunable afterglow characteristics after removing the irradiation source,^{36–40} making their applications heavily reliant on time-resolved technology.^{41,42} As a comparison, the variations of steady-state emissive colors in UOP materials can be utilized for direct visualization-based applications, which are more easily observed by the naked eye and detected using conventional photoluminescence (PL) measurements. Therefore, it is highly desired to develop UOP materials that exhibit steady-state color-tunable emission in response to external stimuli.

To address the aforementioned issue, a small set of efficient fluorescence-phosphorescence dual emissions43 have been constructed in UOP materials. For example, Cai et al. reported a type of host-guest UOP material with dual emissions of fluorescence and phosphorescence, whose steady-state emission color can respond to changes in temperature and mechanical force.⁴⁴ Cao et al. reported two UOP materials with fluorescence-phosphorescence dual-emission properties, demonstrating steady-state color-tunable emission in response to multiple stimuli, including temperature, external force and excitation intensity.⁴⁵ It can be envisioned that by constructing and regulating a greater number of emission modes originating from both excited singlet and triplet states in UOP materials, the distinct sensitivities of these multimode emissions²⁶ to external stimuli can be fully utilized. This would allow for precise control of emission color and wide responsive abilities to multiple stimuli. However, it remains a formidable task due to the competitive relationships among the multiple emission modes.

Herein, we design a kind of UOP material (PhP-B) utilizing a phenothiazine 5,5-dioxide (PTZO) unit as the triplet

^a Jiangsu Key Laboratory of Industrial Online Detection and Intelligent Perception & Institute of Electrical Engineering, Nanjing Vocational University of Industry Technology, 1 Yangshan Road, Nanjing 210023, China

^b State Key Laboratory of Flexible Electronics (LoFE), Institute of Advanced Materials (IAM), School of Chemistry and Life Sciences, Nanjing University of Posts & Telecommunications, 9 Wenyuan Road, Nanjing 210023, China. E-mail: iamwylai@njupt.edu.cn

^c Shandong Province Key Laboratory of Medical Physics and Image Processing Technology, School of Physics and Electronics, Shandong Normal University, Jinan 250358, China

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 $[\]ddagger$ L. Z. and Y. Y. are co-first authors with equal contribution to this work.



Fig. 1 (a) Molecular structure and molecular stacking of PhP-B. (b) Multimode emissions of fluorescence, delayed fluorescence, and ultralong organic phosphorescence in PhP-B. (c) Multi-stimuli-responsive and color-tunable emissive characteristics of PhP-B.

chromophore, coupled with a boronic acid pinacol ester (Bpin) group as the modifying unit (Fig. 1a). The chemical structures of the reported phenothiazine 5,5-dioxide UOP derivatives based on PTZO units are shown in Fig. S1 (ESI⁺). It has been discovered that these UOP molecules with a PTZO unit as the triplet chromophore exhibit good UOP performances.⁴⁶⁻⁴⁸ The molecular structures of the observed Bpin UOP derivatives are displayed in Fig. S2 (ESI⁺). The ability of the Bpin group to enhance spin-orbit coupling as the modifying unit has been demonstrated.^{49,50} Thus, the PhP-B is constructed by combining a Bpin group as the modifying unit with a PTZO unit as the triplet chromophore. This modification has been found to enhance spin-orbit coupling (SOC), generate hybridized local and charge-transfer (HLCT) states, and form tight stacking of triplet chromophores via robust intermolecular interactions. As expected, PhP-B generates multimode emissions of fluorescence, delayed fluorescence (DF), and UOP (Fig. 1b). This enables the material to exhibit steady-state color-tunable emission in response to multiple stimuli of excitation wavelength, temperature, oxygen environment, mechanical force, and decay time by regulating multimode emissions (Fig. 1c). Given the multi-stimuliresponsive emission features, direct visualization-based smart applications have been exploited including multicolor patterns, as well as the visual monitoring of aggregation state, temperature and oxygen environment.51

Results and discussion

Material synthesis and characterization

The targeted molecule PhP-B is designed with a phenothiazine PTZO triplet chromophore as the skeleton, which is further modified by a boronic acid pinacol ester (Bpin) group (Scheme S1, ESI†). The PTZO group can promote $n-\pi^*$ transitions to populate triplet excitons due to the existence of O and N atoms with lone pair electrons.^{52–54} Additionally, the Bpin

group can not only facilitate the intersystem crossing (ISC) due to the enhanced SOC,⁴⁹ but also tend to form intermolecular interactions with neighbor molecules for suppressing nonradiative transitions. An isomer B-PhP (Scheme S1, ESI⁺) is synthesized for comparison, where the modification position of the Bpin group is not connected with the PTZO chromophore. The synthetic routes for PhP-B and B-PhP are presented in Scheme S2 (ESI⁺). The targeted compounds were synthesized via three-step reactions with satisfactory yields, and then purified by column chromatography and recrystallization to obtain crystalline powders, respectively. A nuclear magnetic resonance spectrum for ¹H and ¹³C and a high-resolution mass spectrum were conducted on the two compounds (Fig. S3-S5 and S6-S8, ESI[†]). The green transparent needle-like single crystals of PhP-B were cultivated by the method of solvent evaporation at room temperature. Single-crystal X-ray diffraction was employed to figure out the molecular geometry and packing modes.

Photophysical properties

Firstly, the absorption and PL spectra of the two isomers were investigated in dilute solution. In dilute tetrahydrofuran (THF) solution (10^{-5} M) , PhP-B exhibited two absorption peaks at around 278 nm and 340 nm, and the absorption peaks of B-PhP were located at around 273 nm, 300 nm, and 340 nm (Fig. S9, ESI†). As shown in Fig. S10 (ESI†), PhP-B presented emission peaks at around 383 nm and 395 nm in dilute toluene (TOL) solution, and exhibited a weak solvatochromic effect in dilute solutions of different polarity. As for B-PhP, its fluorescence peaks mainly located at around 365 nm and 395 nm in dilute TOL solution, and the emission peaks were influenced by the polarity of the solvents (Fig. S8, ESI†), demonstrating an intramolecular charge transfer (ICT) feature.

Furthermore, steady PL and delayed PL spectra of PhP-B and B-PhP crystals were measured at room temperature. As



Fig. 2 Photophysical properties of PhP-B crystals. (a) Normalized PL and delayed PL spectra (delayed time: 0.1 s) when excited at 340 nm. (b) Afterglow spectra. (c) Delayed PL spectra with delayed time of 10 μ s. (d) Decay profiles of the 490 nm and 520 nm emission bands when excited at 340 nm at room temperature.

illustrated in Fig. 2a, PhP-B presented a main emission peak at around 390 nm with two shoulder peaks at around 490 nm and 520 nm, which corresponded to the peaks of the delayed PL spectra. There was a remarkable overlap from 450 nm to 650 nm between PL and delayed PL spectra. It was observed that PhP-B exhibited obvious green afterglow lasting for nearly 8 s after removing the ultraviolet (UV) source. Meanwhile, the emission intensities of the two emission peaks at 490 nm and 520 nm in the delayed PL spectra were enhanced at low temperatures (Fig. S11, ESI⁺), further indicating their phosphorescence natures. Because triplet excitons are sensitive to oxygen, DF can be easily inhibited in an oxygen environment at ambient temperature. As a result, the PL spectra of PhP-B crystals in Fig. 2a do not show obvious DF emission. As a comparison, B-PhP exhibited a fluorescence band at around 360 nm and a weak emission band that corresponded to its delayed PL band (Fig. S12, ESI⁺). Furthermore, phosphorescence spectra of isolated molecules were measured at low temperature in the dilute 2-methyltetrahydrofuran solution $(5.0 \times 10^{-5} \text{ M}, \text{ Fig. S13}, \text{ESI}^{+})$, which differed from the delayed PL spectra of the crystals. Given that excimer complex formation was difficult in solutions at this concentration, the possibility of excimer emission was likewise small. This indicated that the UOP of the crystals stemmed from crystalline aggregates rather than isolated molecules.

As shown in Fig. 2b, PhP-B showed a remarkable afterglow band centered at 490 nm and 520 nm. Meanwhile, another delayed PL band centered at around 400 nm was observed within the delayed time of 10 µs (Fig. S14, ESI[†]). Moreover, the emission intensity of 400 nm was enhanced as the temperature increased, demonstrating its DF attribute (Fig. S11, ESI[†]). The decay profiles of different emission peaks were measured (Fig. 2d and Fig. S15, ESI⁺), and the UOP lifetimes are listed in Table S1 (ESI[†]). For the targeted material PhP-B, the average UOP lifetimes of 490 nm and 520 nm were 589.29 ms and 583.03 ms, respectively (Fig. 2d and Table S1, ESI⁺), and the average lifetime of DF emission of 400 nm was 16.59 µs (Fig. S15, ESI[†]). According to the above results, it can be concluded that PhP-B exhibited multimode emissions consisting of fluorescence, DF, and UOP. As a comparison, the UOP lifetimes of B-PhP were obviously smaller than PhP-B (Fig. S16 and Table S1, ESI[†]).



Fig. 3 Multi-stimuli responsive emission properties of PhP-B crystals. (a) Excitation-dependent PL spectra excited at varied UV excitation wavelengths. (b) Temperature-dependent PL spectra at different temperatures. (c) Steady PL spectra in vacuum and atmosphere environments. (d) Steady PL spectra before and after grinding. (e) Delayed PL spectra with varied delayed time.

Comparative analysis with previously reported UOP materials (Fig. S1, ESI[†]) revealed that PhP-B demonstrates exceptional average UOP lifetime performance.^{46–48} Notably, this study presents the first observation of multi-stimuli-responsive emission characteristics in UOP materials, simultaneously exhibiting fluorescence, DF, and UOP, a combination of photophysical phenomena previously unreported for this class of materials.

Multi-stimuli-responsive emission properties

According to the steady-state PL spectra in Fig. 3a, the UOP proportion of the PhP-B crystals decreased as the excitation wavelength increased from 240 nm to 360 nm, indicating that the emission color of PhP-B can be tuned in response to excitation wavelengths. The excitation-emission mapping of steady PL emission and UOP emission of PhP-B crystals is shown in Fig. S17 and S18 (ESI[†]). The optimal excitation wavelengths for steady PL and UOP emissions were 330 nm and 360 nm, respectively. The optimal excitation wavelengths for the two were different, leading to a dynamic change of intensity ratio of the two primary emission peaks at room temperature under different excitation wavelengths. Since PhP-B exhibited multimode emissions containing DF and UOP with different sensitivities to temperature, the varied temperatures can arouse color-tunable emission. According to the variable temperature PL spectra in Fig. 3b, as the temperature increased from 200 K to 300 K, the DF proportion gradually increased, while the UOP proportion showed a downward trend. Moreover, the oxygen in the environment can influence DF and UOP emissions due to the susceptibility of triplet excitons to oxygen. Fig. 3c demonstrates that the DF emission of PhP-B became more pronounced, and the proportion of UOP significantly increased in an oxygen-free environment. The temperature- and oxygen-dependent luminescence behaviors observed in Fig. 3b and c aligned closely with characteristic phosphorescent responses. This correlation strongly supports the conclusion that the green photoluminescence (PL) in PhP-B originates from phosphorescent processes rather than excimer emission, thereby excluding alternative mechanistic pathways. PhP-B exhibited grinding-induced color-tunable emission from cyan to blue, which resulted from the reduced proportion of UOP emission (Fig. 3d). Meanwhile, the UOP lifetimes also decreased after mechanical grinding (Fig. S20, ESI⁺). Such tunable emission behaviors were related to the reduced crystallinity and increased surface area exposed to oxygen in the ambient conditions after grinding, which can be confirmed by the weakened powder X-ray diffraction diffraction peaks (Fig. S21, ESI⁺). Besides, PhP-B also exhibited time-dependent emission features (Fig. 3e), because the excitedstate lifetimes of DF and UOP possessed different time scales.

Crystallography analyses and theoretical investigations

For an in-depth understanding of the relationship between molecular packing and fluorescence-DF-UOP multimode emission behaviors, PhP-B single crystals were cultivated and analyzed (Table S3, ESI†). As shown in Fig. 4a and Fig. S22 (ESI†), PhP-B presented a twisted molecular conformation, and each PhP-B molecule was closely interacted with adjacent molecules through effective intermolecular interactions, including $C-H\cdots\pi$



Fig. 4 (a) Single-crystal structure of PhP-B. (b) Frontier molecular orbital distributions for the monomer and the selected dimer. (c) The calculated energy levels based on the selected dimer. (d) The emission mechanism insights of PhP-B.

(2.876 Å) and C–H···O interactions (2.638 Å, 2.684 Å). These interactions can restrict molecular motions and inhibit nonradiative relaxation. It can be observed that a dimer structure was composed of two almost antiparallel molecules in each unit cell *via* robust C-H··· π intermolecular interactions. Meanwhile, the triplet chromophores PTZO exhibited tight stacking in the dimer, which is vital for efficient UOP generation.55 Furthermore, an independent gradient model analysis of PhP-B was also conducted to demonstrate intermolecular interactions in the coupling units of two adjacent molecules (Fig. S23, ESI⁺). Notably, distinct isosurfaces were observed within each coupling unit, providing further evidence of intermolecular interactions within PhP-B. In particular, dimer 1 exhibited the largest isosurface between two PhP-B molecules, which indicated the robust intermolecular interactions in dimer 1. Thus, dimer 1 was selected as the model for further theoretical investigation.

The PhP-B emission mechanism was further explored using time-dependent density functional theory (TD-DFT) calculations. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) distributions for the monomer and the coupled dimer (dimer 1) were calculated. As shown in Fig. 4b, the PhP-B monomer showed a large overlap for its HOMO and LUMO, and the HOMO and LUMO of dimer 1 were separated much better than the monomer. The nature transition orbitals (NTO) analysis further revealed that PhP-B produced LEdominated HLCT excited states (Fig. S24 and S25, ESI†). The LEdominated HLCT excited states could indicate the coexistence of the LE state and CT state for PhP-B, corresponding to the fluorescence and DF emissions, respectively. In addition, the NTOs of the lowest triplet state (T1) of PhP-B were mainly distributed on the PTZO unit, further indicating that PTZO acted as the triplet chromophore for UOP emission. Furthermore, the energy levels and SOC constants (ξ) were calculated for both the monomer and dimer 1 of PhP-B (Fig. S26, ESI[†] and Fig. 4c). The triplet energy levels were increased in dimer 1 owing to energy splitting in the aggregation state. The calculated energy gap between the singlet excited state (S_1) and its closest triplet excited states for the monomer and dimer 1 was 0.240 eV and 0.209 eV, respectively.



Fig. 5 Applications of the multi-stimuli responsive and color-tunable PhP-B crystals. Color-tunable emissive patterns with (a) different excitation wavelengths and (b) varied excitation and decay time. (c) Mechanochromic luminescence with the corresponding CIE coordinates. (d) Visual detection for temperature with the corresponding CIE values. (e) Visual detection for the oxygen environment.

The value of the calculated energy gap was smaller than 0.37 eV, which demonstrated the possibility for the coexistence of DF and UOP.⁵⁶ Moreover, there were four transition channels with SOC constants (ξ) larger than 0.3 cm⁻¹ between excited singlet states and triplet states for both the monomer and dimer 1. The small energy gap and enhanced SOC can contribute together for promoting ISC and reverse ISC and thus realizing multimode emissions for PhP-B. Together with the results of the experiment and theoretical calculations, the internal mechanism of fluorescence-DF-UOP multimode emissions is proposed in Fig. 4d. The small energy gap between the excited singlet and triplet levels could further demonstrate the rationality of DF emission. Moreover, the sufficient ISC channels with the enhanced SOC were responsible for the obvious UOP emission. As a result, fluorescence-DF-UOP multimode emissions can be generated in the UOP material.

Applications

Considering the excitation-dependent and time-dependent color-tunable emission features, we fabricated multicolor emissive patterns of the UOP material PhP-B using a screen-printing technique. The inks for screen printing were prepared by dispersing the PhP-B crystalline powders into aloe vera gels. As illustrated in Fig. 5a, the pattern exhibited varied steadystate emission colors, ranging from blue to cyan, when the excitation wavelength was tuned from 365 nm to 254 nm. Furthermore, the pattern also demonstrated tunable emission colors in response to varied excitation time and decay time. As shown in Fig. 5b, the pattern exhibited a purple emission when exposed to a UV source. Subsequently, the emission color shifted to blue due to the continuous intensification of the UOP emission. Upon removal of the UV source, the emission color initially appeared cyan due to the coexistence of DF and UOP, and then transformed into a green afterglow from UOP emission. Fig. 5c illustrates that PhP-B displayed mechanochromic emission, as evidenced by a variation in Commission Internationale de l'Eclairage (CIE) coordinates from (0.22, 0.31) to (0.23, 0.22) after grinding for 2 minutes. Meanwhile, the decreased afterglow lifetimes were also observed and measured (Fig. S27, ESI†). The results indicated that the molecular aggregation state can be roughly monitored through directly observing the changes in steady-state emission colors and afterglow lifetimes. Additionally, due to its ability to exhibit tunable steady-state emission colors in response to changes in temperature and oxygen environment, PhP-B also showed potential for visual monitoring of variations in temperature and oxygen environment (Fig. 5d and e). Based on the material properties, PhP-B can be utilized to make anti-counterfeiting color-changing labels, environmental UV detectors, oxygen-free environment safety sensors and so on.

Conclusions

In conclusion, we have successfully achieved multi-stimuliresponsive and steady-state color-tunable luminescence in UOP materials by regulating the multimode emissions of fluorescence, DF, and UOP. Owing to the different sensitivities of these multimode emissions to external stimuli, the UOP material (PhP-B) exhibited tunable emission colors in response to various external factors, including excitation wavelength, temperature, oxygen, mechanical force, and decay time. The single-crystal data revealed the presence of strong C-H··· π and C-H···O intermolecular interactions, as well as tight stacking of triplet chromophores, which collectively contributed to the UOP emission. TD-DFT calculations further evidenced the presence of sufficient ISC channels in the PhP-B crystals because of the enhanced SOC. Meanwhile, the generation of HLCT excited states contributed to the construction of multimode emissions in PhP-B. In consideration of the multi-stimuli-responsive and color-tunable emissive properties of PhP-B, direct visualization-based potential applications have been exploited, including multicolor patterns and visual monitoring of external factors such as aggregation state, temperature, and oxygen environment.

Data availability

All data supporting the results are presented in the article and ESI.†

Conflicts of interest

There are no conflicts to declare.

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