Fast Photo Stimulus Responsive Ultralong Room-temperature Phosphorescence Behaviour of Benzoic Acid Derivatives @ Boric acid

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Abstract

Ultralong room-temperature phosphorescence (URTP) materials with photo stimulus responsive (named URTP-PSR) behavior are amazing but still rarely reported due to their great requirements on the crystal structure, complicated synthesis process, long photo-activation and deactivation time. Herein, a series of URTP-PSR materials were prepared by a facile doping process, which involved one-pot heating treatment of benzoic acid derivatives and boric acid to form an amorphous phase. The URTP-PSR materials displayed gradually enhanced ultra-long phosphorescence upon prolonged deep UV light illumination under ambient conditions to restricts the vibration and rotation of molecular. Impressively, both of the photo-activation and deactivation process can be finished within several seconds, which was much fast than previously reported URTP-PSR materials. The optical properties can be repeated many times without obvious losing performance, suggesting excellent fatigue resistance behaviors of the URTP-PSR materials. Simultaneously, the URTP-PSR materials also displayed excellent atmosphere stability, which still maintained good optical properties even under oxygen atmosphere. Furthermore, owing to the high processability and light-stimulus emission, the URTP-PSR materials have been utilized as security ink for anti-counterfeiting pattern application. It's worth mentioning that all the raw materials are commercialized and low-cost, which could be purchased directly and benefit for the practical application. These findings break through many limitations of existing dynamic RTP materials, such as complicated preparation process, fine crystal structure, long photo-activation and deactivation time, and furthermore expand the scope of dynamic smart-response materials for great potential in many fields.

Introduction

Ultralong room-temperature phosphorescence (with long lifetimes >100 ms) has attracted extensive attention due to its long lifetime, low background, and large Stokes shift.¹ Owing to these charming features, it has been widely used in various fields such as molecular sensing,² photocatalytic reaction,³ optical sensors,⁴ bioimaging,⁵ encryption and decryption.⁶ For example, on the basis of the mechanochromic and vapochromic phosphorescence of the complexes, Huang et al. construct a data-recording device and demonstrate data encryption and decryption via fluorescence lifetime imaging and time-gated luminescence imaging techniques.⁶ Nowadays, most RTP materials usually contain heavy metal elements, high biological toxicity and high cost, which block their further applications.⁷ In view of the fact that the energy of excited triplet states of organic molecules could be easily de-activated by thermodynamic vibration and collision processes or exposure to quenching factors such as oxygen, it is difficult for these pure organic materials to generate efficient room temperature phosphorescence emission. To solve the inherent obstacle of pure organic molecules, many strategies such as host-guest doping,⁸ halogen bonding,⁹ π - π stacking,¹⁰ crystallization¹¹ and H-aggregation¹² are applied for achieving organic RTP emission. These strategies focused on the enhancement of intersystem crossing (ISC) process and reduced the non-radiative transition.¹³ However, the preparation of organic URTP materials has many limitations currently. For example, most materials require good crystal structure for generating URTP emission and the preparation steps of organic molecular are tedious.

Stimulus responsive materials play a more and more important role in various application fields such as information storage and security,¹⁴ biomedicine,¹⁵ gas storage and separation.^{16,17} These materials could tune their properties and respond to external stimuli, including light,¹⁸ temperature,¹⁹ pressure,²⁰ magnetic and electric fields^{21,22} and so forth.^{23,24} Among these stimuluses, light is a most attractive external stimulus as it offers clean and noninvasive control of the operation with high accuracy, showing greater convenience in activating or erasing the secret encoded information with high level of spatiotemporal resolution as compared to other chemical stimuli.²⁵ For instance, photo-switchable molecules can transfer from one isomeric form to another through reversible photochemical reactions with various optical properties.^{26,27} Light stimulus driven reversible dynamic property in such functional materials was of paramount importance in the field of opto-electronics, drug delivery and photo actuators. Therefore, for reversible information encryption and decryption, it is desirable to develop photo-stimulus luminescent materials which are capable of being easily operated in a noninvasive manner. In recent research, a few of URTP-PSR materials showed an enhanced ultralong phosphorescence emission upon photo stimulation, which was due to the restriction of the nonradiative transition caused by decreasing adjacent molecular distance and vibrations in these crystals after light illumination.²⁸ The emerge of URTP-PSR materials presents a breakthrough strategy in applying URTP materials for information storage and security as the additional affect for controlling the optical behavior by light illumination. Nevertheless, these URTP-PSR materials always have a long photo-activation and deactivation time, which need a very fine crystal structure, expensive price, and complicated preparation process. With the current rapid development of stimulus responsive materials, it is urgent to desire for URTP-PSR materials that can act as effective respond units.

Previously, some crystalline benzoic acid derivatives have been reported to show visible afterglows persisting for more than one second at room temperature upon irradiating with a UV light, which is due to the suppressed vibronic couplings of the crystal structure retard the non-radiative relaxation of the triplet state (T_1).²⁹ However, benzoic acid based RTP-PSR materials with fast light stimulus responsive behavior are underexplored. Herein, we designed a general method to obtain photoexcitation-controlled URTP materials by one-pot heating treatment of commercial benzoic acid derivatives, including phthalic acid (PA), isophthalic acid (IPA), terephthalic acid (TPA), and trimesic acid (TA) with boric acid (BA). BA was chosen to form a matrix for restricting the vibration and rotation of molecular. The product (named BADs@BA) exhibits blue RTP with a lifetime longer than 1.0 s and shows extremely sensitive photoexcitation- RTP under the 254 nm light irradiation from a handy UV lamp. The photo-activation, deactivation behavior is astonishingly rapid, and both processes could be completed in seconds. Further, move by the light of the high processability and light-stimulus emission, the URTP-PSR materials have been utilized as security ink for anti-counterfeiting pattern.

Results And Discussion

The BADs@BA preparation procedure was described in the Figure 1A. Typically, 3 g (48.5 mmol) BA were firstly diluted with 40 mL doubly distilled water in a beaker and mixed with BADs, then the beaker was

covered with foil to prevent water evaporating too fast. And the beaker was put in an oven at 180 °C for 5 h and cooled down to room temperature. After one-pot heating treatment of benzoic acid derivatives with boric acid, the product was white glassy solid, which displayed blue phosphorescence under 254 nm light irradiation (Figure 1B). Blue phosphorescence can be observed lasting 10 seconds after turn off the UV light by naked-eye, indicating that the product possesses URTP behavior. To investigate the composition of the glassy solid, the powder X-ray diffraction (PXRD), Fourier transform-infrared spectroscopy (FT-IR) and Raman spectra measurements of these samples were carried out. As shown in PXRD pattern, BADs@BA displays the characteristic peaks of benzoic acid derivatives and boron oxide within glassy state (Figure 2A and S2), indicating the presence of both in the product. Then, FT-IR spectra show that the IPA@BA displays similar characteristic absorption peaks with BA, and two new weak peaks at 1694 cm⁻¹ and 1282 cm⁻¹ are assigned to C=O and O-H of benzoic acid derivatives' telescopic vibration (Figure 2B). In addition, in Raman spectra (Figure 2C), three characteristic peaks of BA at 207 cm⁻¹, 497 cm⁻¹ and 878 cm⁻¹ in all IPA@BA can be found, and IPA characteristic peaks at 195 cm⁻¹, 650 cm⁻¹, 758 cm⁻¹ and 999 cm⁻¹ could be found in the spectra simultaneously. The same phenomenon of FT-IR spectra and Raman spectra can also be found in other BADs@BA (Figure S3-4). Therefore, we have a point of view that benzoic acid derivatives are successfully doped in boric matrix upon the heat treatment.

To further investigate the doping system, thermogravimetric analysis (TGA), ultraviolet-visible (UV-Vis) spectra and X-ray photoelectron spectroscopy (XPS) of these samples were measured. As shown in TGA spectra (Figure S5), all of these benzoic acid derivatives displayed well thermal stability between 25 °C and 200 °C, which indicated that they had an enough thermal stability without decomposing during the heating treatment. Next, UV-Vis spectra were applied for exploring the amount of benzoic acid derivatives in BADs@BA. The BADs@BA were grinded by ball milling, then PA@BA IPA@BA, TPA@BA and TA@BA were dissolved in water and methanol, respectively, and the standard curve was used to quantity their amount (Figure S6). These results indicated that the content of IPA, TPA and TA showed no mass loss during the heating treatment (Table S1). Since PA is easy to sublime under heating treatment, it has been chosen as an example and a system has been built to collect the sublimated PA and determine its amount (Figure S7). As shown in Table S1, the sum of the after-heating PA amount and sublimated amount are the same as the one of original amount, which confirms that PA has also no mass loss during heating treatment. In addition, the PA@BA powder was heated and collected the sublimation to carried out NMR spectroscopy measurement. The ¹H NMR and ¹³C NMR spectra of PA@BA sublimation was shown in Figure S8, which certificated the sublimation was PA definitely. Simultaneously, we carried out the mass spectrum of the sublimation and displayed in Figure S9, also proved the sublimation was PA. These results further support that PA in PA@BA sample was in the original one. Considering the thermal stability of IPA, TPA, TA are higher than PA, therefore, it indicated that all benzoic acid derivatives had no chemical changed after the heating treatment. In XPS spectra, the C 1s spectrum of IPA@BA exhibits three peaks at 284.81 eV, 286.38 eV and 289.51 eV for sp² C, C-O and O-C=O, respectively (Figure S10G). IPA@BA peak area of O-C=O is higher than the one of pure BA (Figure S10A), which is due to the doped IPA. The O 1s spectrum of IPA@BA shows the same peaks as BA and the B 1s spectrum of IPA@BA exhibits two peaks at 193.35 eV and 194.36 eV, which belongs to B-O and B₂O₃ (Figure S10I).

The XPS spectra of BA and other BADs@BA convinced that the embed BADs were original state in BA matrix. All of these above characterized results confirmed that benzoic acid derivatives were successfully doped into BA rigid matrix.

The steady-state spectra of IPA@BA are shown as in Figure 2D, the fluorescence and phosphorescence emission peaks of IPA@BA are at 328 nm and 404 nm, respectively. Comparatively, pure BA shows neglectable emission at 431 nm with weak signals. BADs@BA exhibited gradually increasing bright blue fluorescence under the handy UV lamp irradiation with 254 nm wavelength, while bluish violet ultralong phosphorescence appeared for several seconds after switching off the lamp (Figure 3A). Surprisingly, the intensity of phosphorescence also gradually increased with the prolonged irradiation time (Figure 3C), which was called “photo-activation” phosphorescence.²⁸ Actually, all of the BADs@BA show very sensitive and rapid photo-activation, deactivation behavior. The maximum phosphorescence excitation and emission peaks of IPA@BA were mainly at 248 nm and 404 nm, respectively (Figure S11B). The maximum absorbance peak of IPA@BA was at 250 nm (Figure S12B), which was consistent with the excitation spectrum.

In order to study the characteristic of BADs@BA in detail, the effect of preparation condition including the doping ratio between BADs and BA, heating treatment temperature on their optical properties were investigated. With increasing the mounts of IPA, TPA and TA, the phosphorescence intensity was increased at first, and gradually decreased when the molar ratio was above $1 : 1000$ ($n_{BADs} : n_{BA}$), which could be assigned to too much BADs could disturb the formation of the rigid BA matrix. Thus, the optimal molar ratio of IPA@BA, TPA@BA and TA@BA is $n_{BADs} : n_{BA} = 1 : 1000$ (Figure S13). Because of the easy sublimation property of PA, the best molar ratio of PA@BA is higher than the ones of others (around $1 : 200$, Figure S13A-C). As presented in Figure S14, the IPA and BA mixture was still liquid even after heating 10 h at the 100 °C, and even increasing the heating temperature up to 140 °C, the mixture could not form glassy IPA@BA and they showed very faint yellow-green phosphorescence, which was ascribed to IPA phosphorescence. When the temperature reached 160 °C, the glassy state of IPA@BA gradually appeared and showed bright blue RTP, but there were still some raw materials had not formed the glassy state. Finally, the heating temperature increased up to 180 °C, the completely glassy state of IPA@BA had formed and showed the best phosphorescence phenomenon. Thus, the best heating temperature of one-pot heating treatment was 180 °C, which could entirely form glassy IPA@BA with the best RTP performance.

The photo-activation process of IPA@BA was extremely fast, which took only 15 s to reached the strongest emission intensity in ambient temperature (Figure 3C). Simultaneously, the deactivation process was also very fast so that we can cycle all the phenomenon three times in 120 s without obvious loss performance (Figure 3D). It is worth noting that the activation and deactivation process of BADs@BA was much fast than previous URTP-PSR materials.²⁸ The same URTP-PSR behavior was also observed from others BADs@BA (Figure S15-17); while, pure BA and BADs did not exhibit the same photo active RTP behavior in the same condition (Figure S18). The phosphorescence lifetime of IPA@BA was also studied according to the following equation 1:

$$\tau_{avg} = \frac{\sum A_i \tau_i^2}{\sum A_i \tau_i} \quad (1)$$

As shown in Figure S19B, the average phosphorescence lifetime of IPA@BA was calculated to be 1.88 s, which was much longer than the most of present RTP materials. Meanwhile, the phosphorescence lifetime of 434 nm emission showed a sharp increase from 1.38 to 1.84 s after IPA@BA was photo-activated for 15 s with a 254 nm UV lamp under ambient conditions (Figure S20). The absolute phosphorescence quantum yield (Φ_p) of BADs@BA after photo-activated were shown in Table S2. The absolute phosphorescence quantum yield of IPA@BA was 38.79%, and the highest absolute phosphorescence quantum yield of these BADs@BA was TPA@BA, which was as high as 66.98%. All BADs@BA exhibited outstanding phosphorescence quantum yield. In addition, the equilibration photo-activation time reduced from around 15 to 5 s with the increase of excitation power, and the intensity was increased, but they showed no effect on lifetime for BADs@BA (Figure S21 and S22).

To gain a further insight into the influence of temperature on photo-activation, the phosphorescence property in different testing temperature was also investigated. When the temperature was decreased to 77 K, the phosphorescence intensity was significant enhanced and the phosphorescence lifetime had reached saturated within astonishing 3.47 s (Figure 4A and 4B). As the temperature rises, the phosphorescence intensity and lifetime decreased. However, RTP could still be observed by the naked eye at 357 K and its phosphorescence lifetime still was up to 0.68 s, which was a rare performance for phosphorescence at high temperature. This amazing behavior stems from the BA matrix has a good rigid structure and temperature stability so that the vibration and rotation of intermolecular could be greatly reduced. The reversibility activity towards temperature of IPA@BA is also studied (Figure 4C), the IPA@BA exhibits outstanding temperature recyclability after several cycles of 77 K to 357 K, which also indicates IPA@BA has high temperature stability. The light stimulus phosphorescence behaviors can be observed at 77 K or 357 K, and the equilibration photo-activation time could decrease from 20 (357 K) to 10 s (77 K) (Figure S24B). Simultaneously, the similar performance has also found in other BADs@BA (Figure S23 and S24). These results revealed that BADs@BA could maintain light stimulus phosphorescence at a broad temperature range, which was benefit for their further application.

The atmosphere has always been considered as one of the important factors to phosphorescence emission, especially the oxygen atmosphere can greatly quench the phosphorescence emission. Thus, the phosphorescence behaviors of BADs@BA were investigated in different atmosphere. As shown in Figure 4A, the phosphorescence maximal wavelength and intensity of IPA@BA are almost the same under vacuum, air and nitrogen atmosphere. Even under oxygen atmosphere, the phosphorescence peak intensity of IPA@BA only decreases slightly. Analogously, the photo-activation process could also be observed under high vacuum, inert atmosphere, and oxygen atmosphere at room temperature (Figure S25E-H). Other BADs@BA also showed the similar characteristic, which indicated that BADs@BA was wonderful inertness to atmosphere (Figure S25). These results can be ascribed to the airtight behavior of

BA matrix, which can block the contact of oxygen inner BADs, resulting the unquenched phosphorescence.

To probe the underlying mechanism of this unique dynamic photo-activation performance of these BADs@BA, confocal laser scanning microscope (CLSM) images and theoretical calculations were carried out. As shown in Figure 5A, there are many small and transparent crystals distribute in BA matrix. Before being irradiated by ultraviolet light, these small crystals were transparent and showed no emission. After photo-activated process, we could observe the bright emission signals and these emission signals were come from these small crystals (Figure 5B- C). These results revealed that BADs were doped into BA matrix with microcrystalline state, and the phosphorescence emission was come from BADs. Interestingly, pure BADs were found the similar photo-activation behavior in 77 K under inert atmosphere, as shown in Figure S26. According to these results, we propose a new mechanism: a glassy rigid matrix has been formed after heating boric acid with BADs, and BADs are doped into this rigid matrix with microcrystalline state. The vibration and rotation of BADs molecular are greatly restricted by BA matrix. Furthermore, the theoretical calculations via first-principle time-dependent density functional theory (TD-DFT) were conducted on BADs single crystal structures in triplet excited states (See the Supporting Information for details). The IPA single crystal³⁰ calculated results were shown in Figure 5E, the distance of interactions between two IPA molecules after photo-activation in the same plane indeed decreased as compared with those before photo-activation (Figure 5D), from 2.517 to 2.468 Å, 2.517 to 2.470 Å and 2.598 to 2.535 Å between carboxyl group and hydrogen on the benzene, respectively. The resulting in much stronger intermolecular interactions inhibited the vibration and rotation, which was beneficial for ultralong phosphorescence, by stabilizing the triplet excitons. Simultaneously, the hydrogen bond between adjacent IPA molecular also changed from 1.691 to 1.595 Å and 1.577 to 1.665 Å respectively with the changed twisting angles from 3.430° to 10.980° and 2.958° to 8.290° between carboxyl group and benzene ring respectively (Figure 5F and 5G). Additionally, molecular packing modes of IPA before and after photo-activation had also changed significantly (Figure S27). According to TD-DFT calculating, the distances of plane centroid to plane centroid and plane to plane were decreased from 3.760 to 3.664 Å and 3.397 to 3.191 Å respectively, and the slip angle at the same position had also changed from 64.518° to 79.134°. These changes could restrict the vibration and rotation causing by adjacent molecular. In the process of UV stimulation, enhanced π - π interactions might have been achieved, which led to the appearance of persistent RTP character. From these results, we reason that deep UV light plays a critical role in controlling molecular configuration and tuning intermolecular interactions in the microcrystal. It is worth mentioning that the TD-DFT-calculated excited-state energy levels showed the S_5 (5.2198 eV, 237.53 nm) had the best oscillator strength ($f = 0.2515$) with a high absolute contribution of HOMO $\rightarrow$ LUMO transitions (68.2%) and the S_1 (3.4951 eV, 354.74 nm) was the dark state ($f = 0.0001$). The energy of S_5 was close to the 254 nm handle deep UV light and the energy gap (ΔE_{ST}) between S_5 and T_7 was 0.55 eV, so we hold the view that the intersystem crossing (ISC) process occurred between S_5 and T_n . Correspondingly, the IPA dimer exhibits many possible ISC channels from S_5 to T_1 , T_3 , T_4 , T_7 , T_{20} due to intermolecular electronic coupling, and the T_1 had the highest absolute contribution of HOMO $\rightarrow$ LUMO transitions (92.0%) (Figure S31A). Furthermore, the BA matrix structure further restricts the

vibration and rotation of the IPA molecular in these microcrystals so that the triplet excitons could be more stable, and eventually bring about the photo-activation behavior, which was just like the low-temperature environment.

The PMMA material is usually used to suppress vibration in the small molecule phosphor and allows the long-living triplets of the organic compound to survive enough long lifetime to emission.³¹ We also prepared a series of BADs@PMMA with different doped molar amounts and investigated their optical properties. As shown in Figure S32, all BADs@PMMA showed no room temperature phosphorescence under ambient condition. However, the same photo-activation phosphorescence was displayed when the temperature decreased to 77 K. The emission and photo-activation cycle of BADs@PMMA were shown in Figure S33. These behaviors probably due to the PMMA matrix structure is not as rigid as BA matrix at room temperature, but increased rigidity after decreasing temperature to 77 K could generate photo-activation phosphorescence. These results further revealed the intrinsic photo-activation phosphorescence behaviors of BADs and the presence of special effect of BA matrix.

According to the unique dynamic photo-activation behavior, an anti-counterfeiting pattern “8” was written by IPA@BA with other fluorescent material. In detail, the anti-counterfeiting pattern “8” was written with a brush on filter paper. The part of number “3” was written with salicylic acid solution, the part of number “1” was IPA@BA that had been ball milled and dispersed in dichloromethane. As illustrated in Figure 6, it showed bright blue luminescent number “3” under the handy UV lamp excitation at the beginning. As the increases of excitation time, the number “1” written with IPA@BA gradually appeared and the bright blue luminescent number “8” appeared finally. When handy UV lamp was switched off, the ultralong phosphorescence generated and the luminous number “1” arose; thus, we have successfully realized the transformation of the number “3 → 8 → 1” by switch on/off the handy UV lamp in darkness. Depending on the application, the URTP-PSR imaging technique can open up new possibilities for information storage and security.

Conclusion

In summary, a new series of URTP-PSR materials with excellent phosphorescence quantum yield and rapid photo stimulus responsive properties were obtained by one-pot heating treatment. Upon few seconds photoirradiation, the BADs microcrystal of BADs@BA could be activated and gradually generate bright blue phosphorescence under ambient conditions, which exhibited extremely fast photo-activation and deactivation activity, good stability in various atmosphere and temperature. Considering all raw materials are cheap and commercialized, the preparation process is also facile and convenient, which was benefit for the practical application. This study breakthrough the inherent disadvantages of the existing photo-activation materials, such as difficulty in preparation and the necessity of good crystallinity, shows great potential in the fields of information encryption, security and organic optoelectronics.

Methods

Chemical section: All benzoic acid derivatives and boric acid were purchased from Energy Chemical and without further purification unless otherwise noted. Dichloromethane and absolute ethanol were purchased from General-Reagent. Doubly distilled water was used throughout the experiments and was prepared using a Milli-Q water purification system.

Characterizations: Powder X-ray diffraction (RXRD) was performed by using a YRIII X-30 ray diffractometer (Rigaku, Japan) with CuK α radiation at 40 kV and 200 mA. Fourier transform-infrared spectroscopy (FT-IR) spectra were recorded in the range 4000-400 cm⁻¹ using a Thermo Nicolet spectrometer with KBr pellets. Ground-state stimulated Raman spectra were recorded in the range 1500-150 cm⁻¹ using HR evolution (Horiba Jobin Yvon, Japan) with 785 nm laser excitation. Photoluminescence spectra and afterglow decay curves were recorded with Horiba Jobin Yvon Fluorolog-3. Thermogravimetric analysis (TGA) was performed by using a NETZSCH STA 449F3 instrument with a heating rate of 10 °C min⁻¹ under a nitrogen atmosphere. UV-Vis spectroscopy was performed with a UV-2700 UV-Vis spectrophotometer (Shimadzu, Japan). XPS was performed using a K-Alpha X-ray photoelectron spectrometer. Temperature-dependent PL emission spectra, afterglow emission spectra, and afterglow decay curves were conducted by combining a heating apparatus (Oxford Instruments) with the same Horiba Jobin Yvon Fluorolog-3. ¹H, ¹³C NMR spectra were recorded on AVANCE DRX 400 spectrometer (Bruker, German). Electrospray ionization mass spectra were obtained with a High Performance 1100 Liquid Chromatography-Mass Spectrometer (Agilent Technologies, USA). Digital photos were taken with Redmi K20 pro smartphone.

Synthesis of four kinds of BADs@BA at different doped ratio: 3 g (48.5 mmol) BA were firstly diluted with 40 mL doubly distilled water in a beaker and mixed with different molar BADs: 0.97 mmol, 0.485 mmol, 0.2425 mmol, 97 μ mol, 48.5 μ mol, 24.25 μ mol, 12.125 μ mol, 6.0625 μ mol ($n_{BADs} : n_{BA} = 1 : 50, 1 : 100, 1 : 200, 1 : 500, 1 : 1000, 1 : 2000, 1 : 4000, 1 : 8000$). Then the beaker was covered with foil to prevent the water from evaporating too fast. And the beaker was put in an oven at 180 °C for 5h and cooled down to room temperature naturally. The final glassy state BADs@BA were ground into powder by ball milling.

Synthesis of IPA@BA at different temperature: 3 g (48.5 mmol) BA were firstly diluted with 40 mL doubly distilled water in a beaker and mixed with the best molar ratio IPA Then the beaker was covered with foil to prevent the water from evaporating too fast. And the beaker was put in an oven at different temperature (100 °C, 120 °C, 140 °C, 160 °C, 180 °C) for 5h and cooled down to room temperature naturally.

Synthesis of four kinds of BADs@PMMA at different doped ratio: 3 g PMMA were firstly diluted with 80 mL dichloromethane in a beaker. BADs were dissolved in ethanol with different molar: 0.485 mmol, 0.2425 mmol, 97 μ mol, 48.5 μ mol, 24.25 μ mol, 12.125 μ mol, 6.0625 μ mol. Then mixed them and slow evaporated under 40 °C in a day, the solid BADs@PMMA were obtained.

Theoretical calculations: The computational model was built from the crystal structures.^{30,32} The distribution of frontier molecule orbitals and excited states were obtained from the Gaussian09 program

(version D.01).³³ The Becke's three-parameter exchange functional along with the M062X using 6-31G(d) basis sets were adopted throughout the calculation.³⁴ The excitation energies in the n-th singlet (S_n) and n-th triplet (T_n) states were obtained using the TD-DFT method based on optimized molecular structures at ground state (S_0). Intermolecular structure and stacking diagrams were drawn and measured by Olex2.³⁵

Declarations

Data availability

The data that support the findings of this paper are available in the paper and supplementary information files. Any further relevant data are available from the authors upon reasonable request.

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Author Contributions

Yi Cheng: conceptualization, data curation, formal analysis, theoretical calculations, writing – original draft. Wenwen Fan: data collection, conceptualization, supervision. Longjie Wang: theoretical calculations. Yanxiong Liu: data collection. Qiufeng Wang: data collection. Shaoxiong Yang: conceptualization, supervision. Yu Qin: conceptualization, supervision. Yonggang Shi: funding acquisition. Shixi Liu: funding acquisition, resources, project administration, supervision. Liyan Zheng: funding acquisition, resources, Writing – review & editing. Qiue Cao: funding acquisition, resources, project administration.

Competing interests

The authors declare no competing interests.

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Figures

Figure 1

A) Schematic representation of the preparation of BADs@BA. B) The ultralong phosphorescence images of BADs@BA.

Figure 2

A) XRD patterns, B) FT-IR spectra and C) Raman spectra of BA, IPA, and IPA@BA, respectively. D) Fluorescence and phosphorescence spectra of IPA@BA, and fluorescence spectra of BA.

Figure 3

A) The photo-activation phenomenon pictures of IPA@BA from 0 to 60 seconds under the ambient conditions. B) Fluorescence spectra and phosphorescence spectra of IPA@BA excited at different lasting times. D) The cycle of IPA@BA photo-activation and deactivation behavior during 120 seconds.

Figure 4

A) Phosphorescence intensity at optimal emission wavelength of BADs@BA at different temperatures (from 77 K to 357 K). B) Lifetime tendencies of BADs@BA at optimal emission wavelength at different temperatures (from 77 K to 357 K). C) The temperature cyclicity of IPA@BA between 77 K and 357 K. D) Fluorescence spectra of IPA@BA under different atmosphere.

Figure 5

. A) The IPA@BA CLSM image under white light. B) The IPA@BA CLSM image after photo-activation by ultraviolet light under dark condition. C) The overlapping of CLSM image under white light and CLSM image after photo-activation. D) and F) Intermolecular interactions and twisting angles of IPA before photo-activation by single crystal. E) and G) Intermolecular interactions and twisting angles of IPA after photo-activation by calculating.

Figure 6

A) Schematic representation of the designed pattern number “8” using different materials. B) Demonstration of anti-counterfeiting pattern “3” → “8” → “1”.

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