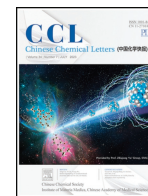




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# Intrinsic persistent room temperature phosphorescence derived from 1*H*-benzo[*f*]indole itself as a guest

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## ABSTRACT

The influence of 1*H*-benzo[*f*]indole (Bd) and its derivatives on room temperature phosphorescence (RTP) has raised great concern since they were found to significantly affect RTP of the extensively studied carbazole (Cz) derivatives. However, the role of Bd itself existing in Cz-based or other doping systems was still unclear. In order to clarify its intrinsic phosphorescent property, Bd was introduced as a guest into different organic matrixes including substituted Cz derivatives and polymers. The phosphorescence located in 560–620 nm was confirmed to be derived from Bd itself, which can be detected whatever Bd was doped in the crystal or amorphous state of Cz derivatives. The suitable energy gap between Cz derivatives and Bd is the key to achieve ultralong RTP of Bd. Additionally, when doped in polymers with plenty of hydrogen bonds, RTP of Bd with lifetime over 280 ms was easily obtained. Among them, Bd@PHEMA (poly(hydroxyethyl methacrylate)) exhibited superior phosphorescence, with yellow afterglow lasting for over 2.5 s. Therefore, this work demonstrated that a new organic RTP phosphor, Bd, is discovered, and ultralong RTP of Bd can be achieved not only doped in Cz derivatives but also in polymers as the hosts.

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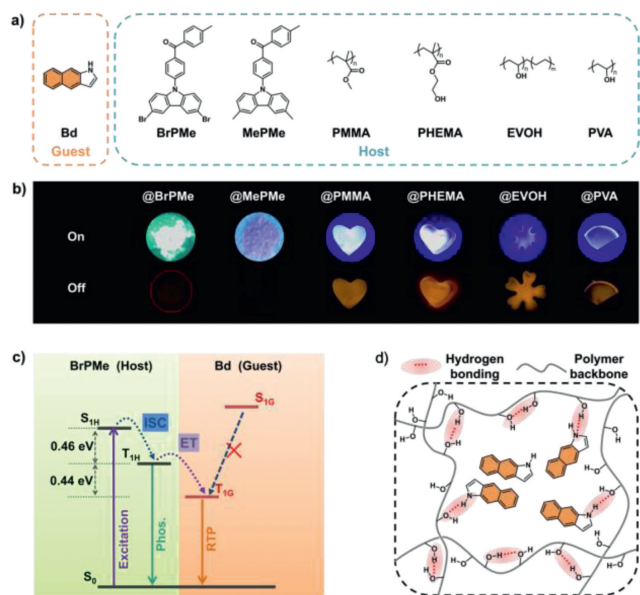
Pure organic materials with room temperature phosphorescence (RTP) have attracted increasing attentions, owing to not only the fundamental research interest, but also promising application potentials in optics, sensors and biological areas [1–5]. Moreover, compared with metal-containing inorganic and organometallic RTP analogues, pure organic RTP luminophores have the advantages of lightweight, biocompatibility, facile functionality, and good processability [6–8]. However, developing organic RTP materials, especially those with persistent emission, is a challenging issue, because of inefficient intersystem crossing (ISC) caused by their weak spin-orbit coupling, plus the excited triplet excitons being sensitive to oxygen and their ultrafast nonradiative relaxations [9–11].

In recent decade, with the exploitation of various methodologies including crystallization [12–14], halogen bond [15,16], *n*- $\pi$  stacking [17], H-aggregation [18], host-guest doping [19–21], and polymer-matrix assistance [22,23], several efficient organic ultralong RTP systems with lifetime of over 100 ms such as car-

bazole [2,17,24,25], benzophenone [26] and dibenzothiophene [27–29] have been successfully developed. Among them, carbazole (Cz) is the most popular used phosphorescence unit to construct organic ultralong RTP compounds. This is because its triplet state with high energy level and its lone-pairs of electrons in nitrogen atom are both in favor to promote ISC for the generation of efficient triplet excitons. On the other hands, its delocalized  $\pi$  bond in the fused rings and rigid conformation with less nonradiative decay process are of benefit to stabilize the triplet excitons. So, a variety of Cz-based ultralong RTP systems have been designed and synthesized [30,31], and their persistent phosphorescence was generally attributed to crystallization-induced phosphorescence [24] or intermolecular electronic coupling (or *n*- $\pi$  stacking) mechanism [17]. However, we and our collaborators discovered that in Cz derivatives, trace isomer of commercial Cz, 1*H*-benzo[*f*]indole (Bd), could be synchronously functionalized into trace isomers of Cz derivatives, which played a crucial factor to enhance phosphorescent intensity and prolong the lifetime of Cz derivative crystals [32]. After that, some Bd derivatives have been synthesized and doped in their Cz isomer crystals for exploring ultralong RTP systems [33]. Recently, Ma's group reported some Bd derivatives ex-

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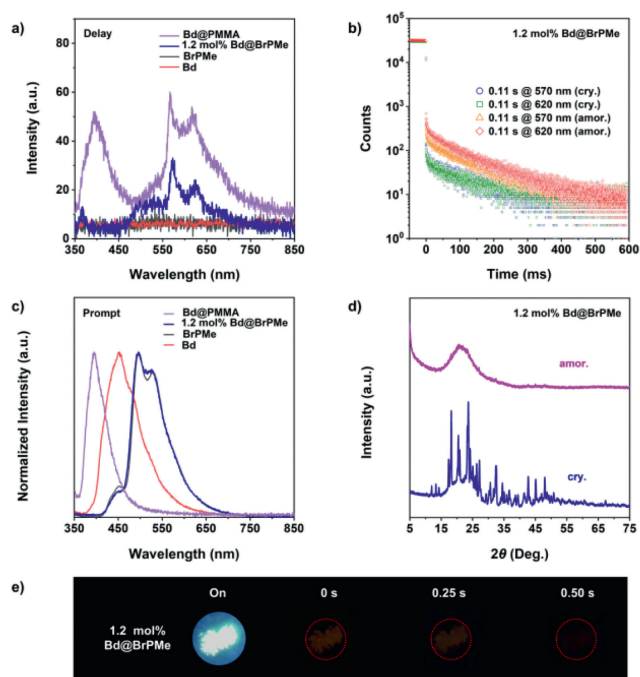


**Fig. 1.** (a) The molecular structures of Bd guest and organic hosts including BrPMe, MePMe, PMMA, PHEMA, EVOH and PVA. (b) Luminescent photographs of 1.2 mol% Bd@BrPMe, 1.5 mol% Bd@MePMe, Bd@PMMA, Bd@PHEMA, Bd@EVOH and Bd@PVA captured using Apple 12 Camera before and after turning off the excited UV light (298 K,  $\lambda_{\text{ex}} = 365$  nm, the Bd content doped in polymers was 1.0 wt%). (c) The energy level distribution diagram of BrPMe and Bd. The energy level of BrPMe was calculated from the spectra of its powder, while the energy level of Bd was calculated from the spectra of 1.0 wt% Bd@PMMA system. ISC: intersystem crossing; ET: energy transfer. (d) Schematic diagram of intermolecular hydrogen bonding interaction between Bd and polymers, and hydrogen bonding interaction among the polymers themselves.

hibited photo-activated ultralong RTP in the doped PMMA film as well [34]. Nevertheless, up to now, the role of Bd itself existing in Cz-based systems still remained unclear. Meanwhile, the study on the intrinsic phosphorescent property of Bd was scarce [32–34]. These questions are actually necessary to be investigated, which are helpful to gain a full and deep knowledge of the nature of RTP for Cz-based systems and other organic phosphorescent materials.

Herein, we report that Bd alone can be used as a universally phosphorescent guest and its persistent RTP emission at ambient condition can be achieved when doped either in a small molecule (derivatives with substituted Cz, named BrPMe) host or in various polymer matrixes as shown in Fig. 1. It has to be noted that no RTP emission of the hosts could be recorded while yellow afterglow lasting for even over 2.5 s observed by the naked eyes was derived from Bd itself in these doped systems. Regarding small molecules as the hosts in crystalline or amorphous state, the suitable energy gap between the substituted Cz host and Bd guest is the key for the achievement of ultralong RTP of Bd. For the polymer hosts, the strong intermolecular hydrogen bonding interaction between the host and Bd guest and the intramolecular hydrogen bonding interaction among the host itself are the main reason for minimizing the nonradiative relaxation of Bd molecule, thus enabling persistent RTP emission of Bd.

As we know, there was no report about the ultralong RTP properties of compounds with substituted Cz unit [35,36], not to mention how Bd influenced on the luminescence properties of these Cz derivatives. Two substituted Cz units, 3,6-dimethylcarbazole (MeCz) and 3,6-dibromocarbazole (BrCz) were chosen to prepare MePMe and BrPMe host molecules, respectively (Fig. 1a). BrPMe and MePMe were synthesized by our lab through a typical substitution reaction between 4-fluoro-4'-methylbenzophenone and commercially available BrCz and MeCz, respectively. Bd was synthesized by using 2-naphthylamine as raw material. The chemical



**Fig. 2.** (a) Delayed luminescence spectra of 1 wt% Bd@PMMA (purple), 1.2 mol% Bd@BrPMe (blue), BrPMe (black), Bd (red) (298 K,  $\lambda_{\text{ex}} = 365$  nm, delay time: 8 ms). (b) Photoluminescence (PL) decay profiles of 1.2 mol% Bd@BrPMe (cry. or amor.) at peaks of 567 nm and 620 nm in air (298 K,  $\lambda_{\text{ex}} = 340$  nm). (c) Prompt luminescence spectra of 1 wt% Bd@PMMA (purple), 1.2 mol% Bd@BrPMe (blue), BrPMe (black), Bd (red) (298 K,  $\lambda_{\text{ex}} = 310$  nm). (d) The X-ray diffraction (XRD) of 1.2 mol% Bd@BrPMe (cry., blue) and 1.2 mol% Bd@BrPMe (amor., pink) doped powder measured at 298 K. (e) Luminescent photographs of 1.2 mol% Bd@BrPMe (cry.) captured using Apple 12 Camera before and after turning off the excited UV light (298 K,  $\lambda_{\text{ex}} = 365$  nm). Cry.: crystalline; amor.: amorphous.

structures of Bd, BrPMe and MePMe were confirmed by proton nuclear magnetic resonance ( $^1\text{H}$  NMR),  $^{13}\text{C}$  NMR, and mass spectrometry (MS). Their detailed synthetic procedures and molecular characterization are offered in Supporting information (Scheme S1 and Figs. S1–S12 in Supporting information).

As shown in Fig. 2a and Fig. S16 (Supporting information), after delayed 8 ms, no afterglow emission was detected at room temperature for either two substituted Cz derivatives (BrPMe and MePMe) or Bd crystal. It is surprised that BrPMe and MePMe did not exhibit persistent RTP, in spite of they were synthesized from commercial substituted Cz units. This probably because trace Bd in Cz cannot be substituted similar to Cz and subsequently no relative substituted Bd isomer struggled in substituted Cz. At 77 K in diluted solution or solid states, BrPMe however exhibited strong phosphorescent emission at 495 and 530 nm, while Bd alone did not show any emission, after turning off the excited UV light (Figs. S17 and S18 in Supporting information). Nevertheless, relatively weak yellow afterglow lasting for about 0.5 s was observed by the naked eyes for the Bd@BrPMe doped crystalline system at room temperature. Moreover, except the minor emission peaks from 470 nm to 530 nm belonging to BrPMe, two additional emission peaks at 567 and 620 nm were clearly detected in the phosphorescence spectra of two Bd@BrPMe samples in which Bd contents were 0.5 and 1.2 mol%, respectively. To make it clear where the phosphorescence peaks at 567 and 620 nm derived from, the luminescence of Bd dispersed in poly(methyl methacrylate) (PMMA) film was studied. As shown in Fig. S18a, the fluorescence spectra of Bd were similar in diluted solution ( $5 \times 10^{-5}$  mol/L) or doped in PMMA film with 1 wt% content, revealing that Bd was dispersed well in PMMA. Obviously, this Bd@PMMA doped film exhibited two same phosphorescent peaks at 567 and 620 nm after removed

**Table 1**  
Lifetimes of Bd doped systems at their corresponding peaks.<sup>a</sup>

Compound	495 nm	530 nm	570/567 nm <sup>d</sup>	620 nm
	$\tau_{\text{air}}/\tau_{\text{vac.}}(\text{ms})$	$\tau_{\text{air}}/\tau_{\text{vac.}}(\text{ms})$	$\tau_{\text{air}}/\tau_{\text{vac.}}(\text{s})$	$\tau_{\text{air}}/\tau_{\text{vac.}}(\text{ms})$
Bd@BrPMe <sup>b</sup>	0.48/90.2	0.47/80.3	0.11/0.12	0.11/0.12
Bd@BrPMe <sup>c</sup>	0.77/72.8	0.76/96.4	0.11/0.10	0.11/0.12
Bd@EVOH	–	–	0.43/0.45	0.41/0.44
Bd@PHEMA	–	–	0.46/0.46	0.41/0.45
Bd@PMMA	–	–	0.29/0.24	0.30/0.29
Bd@PVA	–	–	0.34/0.42	0.33/0.40

<sup>a</sup>  $\lambda_{\text{ex}} = 340$  nm, room temperature.

<sup>b</sup> BrPMe in crystalline state.

<sup>c</sup> BrPMe in amorphous state.

<sup>d</sup> 570 nm for phosphorescent peak of Bd@BrPMe system, 567 nm for phosphorescent peaks of doped polymer systems.

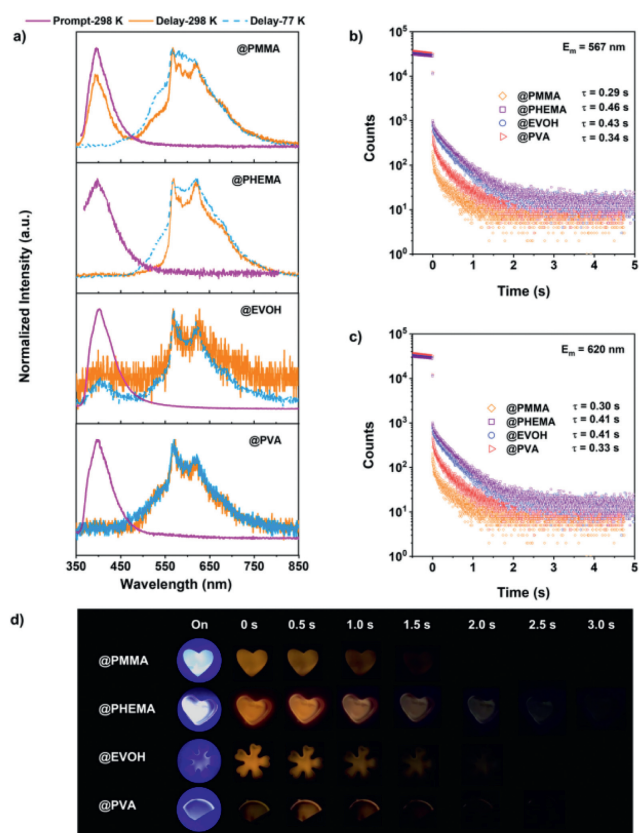
the UV light. Moreover, along with the decrease of temperature, the intensities of both peaks at 567 and 620 nm significantly increased for Bd@BrPMe crystalline system and Bd@PMMA doped film (Figs. S19 and S20 in Supporting information), clearly indicating that two phosphorescence peaks can be attributed to the dispersion state of Bd molecule. At the same time, in Bd@BrPMe systems, the phosphorescent peaks between 470 and 530 nm belonging to host molecule also increased sharply at 77 K (Figs. 2a–c and Fig. S19). Thus, for Bd@BrPMe crystalline system, both of BrPMe host and Bd guest show their respective RTP emission. What is more, from the time-resolved emission decay curves at room temperature (Fig. 2b), the lifetimes of Bd dispersion state monitoring at 567 and 620 nm were 110 ms, indicating the achievement of persistent RTP of Bd. Moreover, the lifetimes of Bd did not be prolonged in vacuum (Table 1). These results reflect that BrPMe crystals not only can restrict the molecular motion of Bd and decrease the non-radiation transitions, but also effectively avoid the quenching of the triplet excitons of Bd by oxygen. It is worth mentioning that the lifetime of BrPMe host is only about 0.40 ms at ambient condition and it can be prolonged up to 90 ms at 495 nm in vacuum (Figs. S21 and S22 in Supporting information), indicating that oxygen in the atmosphere obviously quenched the phosphorescent emission of the host.

In addition, when Bd was doped in another Cz derivative with methyl substituents, named MePMe, only a weak and broad phosphorescence peak in the range of 470–630 nm was detected in the delayed spectrum of Bd@MePMe containing 1.5 mol% Bd (Fig. S23 in Supporting information). And the lifetime at 580 nm was less than 50 ms (Fig. S24 in Supporting information). It indicates that the substituent groups of Cz unit have a significant influence on the phosphorescence of Bd molecule. Density functional theory (DFT) calculations were carried out to gain deep insight into these Cz-based host. Both BrPMe and MePMe exhibited obviously intramolecular charge transfer (ICT) properties and small overlap between their highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), which would facilitate the ISC transition (Tables S3 and S4 in Supporting information). The calculated energy arrangements of the excited states in BrPMe and MePMe are similar. However, the energy gaps between higher triplet states ( $T_2$  and  $T_3$ ) and the lowest singlet state ( $S_1$ ) are almost equal to zero in BrPMe, which are much smaller than those in MePMe (Fig. S25 and Table S5 in Supporting information). This offers more efficient transition channels for ISC from  $S_1$  to the lowest triplet state ( $T_1$ ) of BrPMe through  $T_2$  or  $T_3$ , resulting in more population of triplet exciton in BrPMe. It is known that the large energy gap between  $S_1$  and  $T_1$  in organic molecules does not facilitate to the occurrence of ISC process. As calculated from their luminescent spectra and summarized in Table S2 (Supporting information), the energy gap between the  $S_1$  and  $T_1$  of Bd is very large (1.19 eV), so the ISC is difficult to occur among Bd itself. For-

unately, we found that the energy gap between the  $T_1$  of Bd and  $T_1$  of BrPMe is small (0.45 eV). As shown in Fig. 1c, it is reasonable that under the UV light, the exciton from the  $T_1$  of BrPMe can easily transfer to the  $T_1$  state of Bd, thus enabling promotion of more  $T_1$  exciton of Bd. So, the RTP of BrPMe and Bd can be obtained simultaneously. For Bd@BrPMe crystalline system, except their suitable energy gap, the presence of bromine units also offers external heavy atom effect to Bd molecule, further promoting its ISC transition for triplet excitons generation. However, because of the large energy gap between the  $T_1$  of Bd and  $T_1$  of MePMe aggregate state (0.54 eV, Fig. S26 in Supporting information), plus the absence of heavy atom in MePMe host, RTP emission from either Bd or MePMe did not be clearly detected in the Bd@MePMe system. In order to obtain deep insights about energy transfer (ET) process inside these doped systems, their delayed spectra excited at 365, 385 and 405 nm, respectively, have been checked (Figs. S27a and b in Supporting information). When excitation wavelength redshifted, it was found that persistent RTP intensity of Bd doped in polymers such as PMMA gradually decreased. However, RTP intensity of Bd doped in substituted Cz derivatives such as BrPMe showed no reduction but a little increase. Especially for Bd@BrPMe excitation at 405 nm, additional RTP peak from host BrPMe in the range of 450–550 nm also occurred in the delayed spectrum. As shown in Fig. S27c (Supporting information), Bd possessed weak absorption beyond 400 nm but BrPMe has strong absorption around 400 nm. Therefore, using excitation wavelength of 405 nm, it was BrPMe but not Bd can excited. These results confirmed that ET process from BrPMe to Bd existed in Bd@BrPMe system. This also further proved that RTP peak at around 450–550 nm came from the host BrPMe.

In general, the crystalline state is essential to achieve persistent RTP for small molecular host-guest systems. Amazingly, the minor yet clear emission peaks in the range of 470–630 nm are observed in the delayed spectrum of Bd@BrPMe amorphous system (Fig. S28a in Supporting information). Moreover, the lifetimes at 570 and 620 nm belonging to Bd itself were also about 110 ms (Table 1 and Fig. S21), which are the same as those in doped crystalline matrix. This Bd@BrPMe amorphous system was prepared through heating to molten state and subsequently quenching with liquid nitrogen. The amorphous structure of host molecule was confirmed by X-ray diffractometer (XRD), as there are no sharp scattering signals and only a broad peak in the spectra (Fig. 2d). The cool crystallization peaks are detected in the first heating curve of differential scanning calorimetry (DSC) (Fig. S28b in Supporting information), further supporting the formation of the amorphous BrPMe. These results indicate that the BrPMe amorphous matrix also can offer enough rigid environment for restraining the molecular motion of Bd and minimize the quenching of the triplet exciton by oxygen, which is the first example of Cz-based amorphous system with persistent RTP character. In addition, for BrPMe host molecule, their lifetimes at 495 and 530 nm of whatever its crystalline or not were very short (less than 1 ms) at ambient condition.

As discussed above, Bd alone can be used as a phosphorescent luminophore; moreover, it can emit for longer than 100 ms when it is doped in either BrPMe crystalline or amorphous matrix. In addition, when Bd is doped in PMMA amorphous polymeric system, RTP of Bd also can be achieved. So, different polymers are used as host matrices to further investigate phosphorescent property of Bd, as film-forming polymer materials with persistent RTP are highly attractive for processing and optical device fabrication. Four kinds of polymers including PMMA, poly(vinyl alcohol) (PVA), ethylene vinyl alcohol copolymer (EVOH) and poly(hydroxyethyl methacrylate) (PHEMA) were chosen as hosts. In recent research, molecular motions of small phosphors can be restrained through hydrogen bonding or electrostatic interactions between phosphors and polymeric matrixes, thus enabling persistent RTP of phosphors



**Fig. 3.** (a) Normalized prompt luminescent spectra (red, 298 K,  $\lambda_{ex} = 310$  nm) and delayed luminescent spectra (orange for 298 K, blue for 77 K,  $\lambda_{ex} = 365$  nm, delay time: 8 ms) of Bd@polymer doped films in air. (b, c) PL decay profiles of Bd@polymer doped films at peaks of 567 and 620 nm in air (298 K,  $\lambda_{ex} = 340$  nm). (d) From top to bottom are luminescent photographs of Bd@PMMA, Bd@PHEMA, Bd@EVOH, Bd@PVA captured using Apple 12 Camera before and after turning off the excited UV lights (298 K,  $\lambda_{ex} = 365$  nm). The Bd content doped in polymers was 1.0 wt%.

[37–39]. Except PMMA, PVA was often used as polymer host to offer a rigid environment through hydrogen bonding interactions, but it is highly prone to absorb moisture, which seriously influenced the stability of RTP in air [40]. Additionally, PVA only can dissolve in hot water, while water is not a good solvent for organic molecules. Thus, herein, PHEMA, which also has abundant hydroxyl units but it can dissolve in methanol, was synthesized by our lab *via* atom transfer radical polymerization (ATRP). The synthetic procedure and characterization of PHEMA were offered by Supporting information (Scheme S2 and Figs. S13–S15 in Supporting information). In order to compare with PHEMA and PVA, EVOH containing 68 mol% -OH unit was also used as the host, which was one of the most commonly used oxygen barrier materials in food packages and can dissolve in some organic solvents [41]. PVA, PMMA and EVOH were commercially available. The structures of all the polymers were confirmed by XRD and DSC in Figs. S29 and S30 (Supporting information).

Four Bd doped polymer films with Bd content of 1.0 wt% were prepared through the solution casting method. As shown in the steady-state photoluminescence spectra of all Bd doped films (Fig. 3a), there is a fluorescent emission band with maxima at 395 nm. When delayed 8 ms after the excitation UV lamp turned off, both of the phosphorescence emissions at 567 and 620 nm are clearly detected in all doped polymer films either at room temperature or 77 K (Fig. 3a), whose phosphorescence are located at the similar regions as those of the Bd@BrPMe system. It indicates that RTP of Bd can be achieved when doped in these polymers, owing to

improvement on ISC of Bd for phosphorescence by lone pair electrons in plenty of carbonyl or hydroxyl groups and the rigid environment offered by the polymers. Moreover, it was found that the phosphorescent intensity of Bd in the PHEMA system was obviously stronger than that in PVA or EVOH system. Additionally, new emission peak at 395 nm was detected in the delayed spectra of Bd@PMMA film at room temperature, which also appeared in Bd@EVOH system. As shown in Fig. S31 (Supporting information), the position of this new peak is exactly same as that of its fluorescence peak. Its lifetime of 4.5  $\mu$ s was much shorter than that of half of the associated phosphorescence lifetime, excluding the possibility of triplet-triplet annihilation (TTA). When the temperature increased from 178 K to 278 K, it is obvious the emission intensity of peak at 395 nm in the doped film increased gradually, which proved it is derived from thermally activated delayed fluorescence (TADF). This TADF peak might be induced by these plenty of hydroxyl groups in the polymer matrix of PMMA and EVOH. However, the clear mechanism about this TADF peak needs further investigation. Interestingly, from the time-resolved emission decay curves (Figs. 3b and c, Table 1), the lifetimes of the phosphorescent bands at 567 and 620 nm in PMMA doped films were as long as about 0.30 s. By comparison, the same bands in PHEMA and EVOH films exhibited the longest lifetime up to more than 0.40 s among all the Bd doped systems under ambient condition. The brown afterglow of the PHEMA doped films can be seen even for over 2.5 s, after the UV lamp turned off (Fig. 3d). These results clearly reflect that persistent RTP of Bd molecule can be achieved in those doped polymers, which is mainly ascribed to the intermolecular hydrogen bonding interaction between -NH unit of Bd and -OH of PHEMA (or EVOH). This is supported by fourier-transform infrared spectra (FTIR) where the characteristic absorptions of -OH groups at the region of 3000–3500  $\text{cm}^{-1}$  become broader after doping Bd molecule (Fig. S32 in Supporting information). In PMMA doped system, there is also the hydrogen bonding interaction between -NH of Bd and -C=O unit of PMMA. Of course, the strong intramolecular hydrogen bonding networks of PHEMA (or EVOH) offer a more rigid environment for effectively minimizing the vibrational dissipation of Bd molecule and promoting the ISC process from  $S_1$  to  $T_1$  as much as possible. Taken together, the PHEMA doped systems exhibited superior phosphorescence properties including the intensity and lifetime among these doped polymer films.

The factors on the phosphorescent property of Bd in doped polymer systems was further investigated. Firstly, the Bd content was studied. As shown in Figs. S33 and S34 (Supporting information), when the Bd content doped in PHEMA system was in the range of 0.5–2 wt%, the phosphorescent intensities remained almost no change. Nevertheless, as the Bd content further increased up to 5 wt% or more, the intensities significantly weakened, meanwhile the lifetimes become shorter, due to the quenching effect of  $\pi$ - $\pi$  interaction between Bd molecules (Table S6 in Supporting information). So, in our experiment, the content of 1 wt% Bd in doped systems was the optimized one. In addition, the lifetime of Bd@PVA at ambient condition was obviously shorter than that one in vacuum (Table 1 and Fig. S35 in Supporting information), which was also related to high hydrophilic property of PVA. However, the lifetimes of Bd doped in PHEMA and EVOH systems were almost constant at ambient condition or in vacuum (Figs. S36–S38 in Supporting information). These results reflect that in comparison with PVA, PHEMA film more effectively avoid the quenching of the triplet excitons of Bd by oxygen. Therefore, PHEMA material should be a kind of superior polymeric host for offering a rigid and stable environment to achieve persistent RTP of Bd molecule.

In summary, this work is focused on the study about the luminescence property of Bd itself, a key trace phosphorescence isomer inside Cz, as a doping guest in different matrixes, includ-

ing two substituted Cz derivatives and four kinds of polymers. Amazingly, it was found that the phosphorescence emission in the range of 560–620 nm was derived from Bd itself when doped in crystalline/amorphous BrPMe, or four hydrogen bond containing polymer matrixes. Moreover, the lifetime of Bd in all these doped systems was over 100 ms, even up to 0.46 s, with yellow afterglow lasting for over 2.5 s observed by the naked eyes. This is the first time to clearly demonstrate room temperature luminescent behavior of Bd alone as a guest. Moreover, its ultralong RTP emission can be achieved not only in Cz derivatives but also in polymer materials as the hosts, indicating Bd would be the key molecular structure in RTP systems with Bd or its derivatives. This work means that a new and universally organic RTP phosphor molecule, Bd, is discovered and its derivatives will be further explored and studied to develop novel organic room temperature phosphorescent materials.

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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#### Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.ccl.2022.107882.

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