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# Pure Organic Persistent Room Temperature Phosphorescence at both Crystalline and Amorphous States

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Abstract: Persistent room temperature phosphorescence (p-RTP) of pure organic materials is attracting increasing attention. The design of efficient phosphors and understanding on the origin of p-RTP, however, remain challenging. Herein, to gain further insights into pure organic p-RTP, we prepared a group of carbazole (CZ) and methyl benzoate (MBA) conjugates with methyl ester unit at para (4-MBACZ), meta (3-MBACZ), and ortho (2-MBACZ) sites. These isomers merely produce prompt fluorescence in solutions, but generate blue prompt/delayed fluorescence (DF) and orange p-RTP with lifetimes up to 865.2 ms in the crystalline state. Lifetimes of p-RTP are in the turn of 2-MBACZ>3-MBACZ>4-MBACZ, which might be mainly ascribed to the combined effect of packing density, intermolecular interactions and steric hindrance. Meanwhile, upon mechanical grinding, while the emission color and profile of the luminogens do not significantly change, no (4-MBACZ) or shortened (3-MBACZ, 2-MBACZ) p-RTP is observed, accompanying the change from crystalline to amorphous states. Such p-RTP at amorphous states without external hosts is rarely reported, which demonstrates important implications for the molecular design and mechanism understanding towards p-RTP. Furthermore, their p-RTP attribute and different emission colors before and after ceasing the UV irradiation endow them promising in encryption and anticounterfeiting applications.

#### Introduction

Recently, room temperature phosphorescence (RTP) from pure organic compounds has attracted increasing attention as for its fundamental importance and such applications in bioimaging, anticounterfeiting, and optoelectronic devices.<sup>[1-29]</sup> However,

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unlike inorganic and organometallic phosphors, [30-34] the fabrication of efficient pure organic RTP luminogens remains challenging, owing to the spin-forbidden intersystem crossing (ISC) process and the high susceptibility of phosphorescence to molecular motions and external quenchers.[3-5,7-13] Even though great advances have been achieved for the molecular design of pure organic RTP through incorporation of halogens, aromatic carbonyls, and heteroatoms,<sup>[7-13]</sup> as well as effective suppression of nonradiative processes by supramolecular interactions,[35,36] stabilization,<sup>[37]</sup> absorption on solid substrate,<sup>[38]</sup> micelle crystallization,<sup>[3,4,7,15-17]</sup> embedding into rigid matrices,<sup>[5,23,39]</sup> chemical bonding to polymer chains,<sup>[14]</sup> etc., the development of pure organic RTP remains in its infant stage. Furthermore, persistent RTP (p-RTP) with naked eye visible emission after ceasing the excitation is even difficult to achieve, despite it has diverse promising applications in advanced OLEDs, bioimaging, encryption and anticounterfeiting.[5-12,40-46] So far, increasing examples have been explored in host-guest systems,[5,40] Haggregates,<sup>[6,41,42]</sup> crystals<sup>[43-50]</sup> and even nonconventional luminogens free of aromatics,<sup>[51,52]</sup> the mechanism and rational design strategy, however, remain open questions.

It is known that phosphorescence lifetime  $(\langle \tau \rangle_p)$  could be expressed by equation (1):

(1)

 $<\tau >_{\rm p} = 1/(k_{\rm r}^{\rm p} + k_{\rm nr}^{\rm p} + k_{\rm q}^{\rm p})$ 

where  $k_r^p$  and  $k_{nr}^p$  correspond to the rate constants of radiative and nonradiative transitions from lowest excited triplet state (T<sub>1</sub>) to the ground state (S<sub>0</sub>), while  $k_q^p$  is the rate constant based on quenching of the triplet excitons by interaction with the surroundings like humidity and oxygen. To realize long  $\langle \tau \rangle_p$ , it is important to lower  $k_r^p$ ,  $k_{nr}^p$ , and  $k_q^p$  as more as possible. According to the El-Sayed's rule,<sup>[53,54]</sup> the ISC transitions of  ${}^1(\pi,\pi^*) \rightarrow {}^3(\pi,\pi^*)$ and  ${}^1(\pi,\pi^*) \rightarrow {}^3(n,\pi^*)$  are spin-forbidden, while  ${}^1(n,\pi^*) \rightarrow {}^3(\pi,\pi^*)$  and  ${}^1(\pi,\pi^*) \rightarrow {}^3(n,\pi^*)$  processes are spin-allowed. For the deactivation T<sub>1</sub> $\rightarrow$ S<sub>0</sub> process,  ${}^3(n,\pi^*) \rightarrow \pi^2$  is allowed and relatively fast, while  ${}^3(\pi,\pi^*) \rightarrow \pi^2$  is spin-prohibited and relatively slow. Therefore, to gain *p*-RTP, it is crucial to realize  ${}^3(\pi,\pi^*)$  configurations to ensure enough low  $k_r^{p}$ .<sup>[16,55]</sup>

Previously, we reported *p*-RTP from the carbazole (CZ)benzophenone conjugate with dense molecular packing and effective intermolecular interactions.<sup>[43]</sup> Other luminogens based on CZ and phenylphosphines,<sup>[6]</sup> triazines,<sup>[6]</sup> aldehydes,<sup>[49]</sup> and sulfones<sup>[47]</sup> also demonstrate *p*-RTP characteristics. Theoretical calculations indicate that their T<sub>1</sub> states possess <sup>3</sup>( $\pi$ , $\pi^*$ ) fractions. That's to say, the combination of CZ with other units bearing lone pairs is highly possible to generate pure organic phosphors with the T<sub>1</sub> <sup>3</sup>( $\pi$ , $\pi^*$ ) configuration, thus offering *p*-RTP under suitable conditions. Herein, in order to construct new *p*-RTP phosphors and moreover to gain further insights into the mechanism, we fabricated a group of CZ-methyl benzoate (MBA) isomers, namely 4-MBACZ, 3-MBACZ, and 2-MBACZ with varied methyl ester positions (Chart 1). All luminogens demonstrate both

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fluorescence and *p*-RTP dual emission in the crystalline state with  $\langle \tau \rangle_p$  up to 865.2 ms. Moreover, 3-MBACZ and 2-MBACZ even demonstrate *p*-RTP in their amorphous powders, which is rarely found in pure organics. Their detailed photophysical properties and potential applications as smart mechanochromic candidates, as well as encryption and anticounterfeiting materials were studied.



Chart 1. Structure of 4-MBACZ, 3-MBACZ, and 2-MBACZ studied herein.

#### **Results and Discussion**

The target compounds were facilely prepared by the C–N coupling between CZ and corresponding esters (Scheme S1). They were spectroscopically characterized by high resolution mass spectrometry (HRMS) together with <sup>1</sup>H and <sup>13</sup>C NMR spectra (Figure S1–S7), which are consistent with their expected structures. Furthermore, their single crystals were cultured,

whose structure data definitely indicate the successfully preparation of the target compounds (CCDC 1820457-1820459).

Their absorption in different solvents slightly varies, with approaching maxima at ~292, 325, and 338 nm (Figure 1A-1C, Table S1). While the first peak should be ascribed to the  $\pi$ - $\pi$ \* transitions, the clear vibronic progressions of the latter two still indicate the locally excited character. To gain further insights, natural transition orbitals (NTOs) of S1 for 4-MBACZ, 3-MBACZ, and 2-MBACZ were evaluated using the time-dependent density functional theory (TDDFT) method. As can be seen in Figure S8, for the hole and particle NTOs of S1 states, separation and overlap are found to be well balanced, implying the simultaneously existed local excited (LE) and charge transfer (CT) states. Therefore, the absorption spectra at much longer wavelength band should also be ascribed to the  $\pi$ - $\pi$ <sup>\*</sup> transitions with hybrid LE and CT states. Their emission spectra, however, demonstrate typical bathochromic-shifts with increasing solvent polarity (Figure 1D-1F, Table S1), which is normally observed in typical D-A structured luminogens. In the same solvent, for example in tetrahydrofuran (THF), obviously red-shifted emission maxima  $(\lambda_{em})$  are found in the turn of 4-MBACZ, 3-MBACZ, and 2-MBACZ, which implies their increased intramolecular charge transfer (ICT) strength. Under 312 nm UV irradiation, these solutions exhibit blue emissions in varying solvents (Figure 1G) with emission efficiencies ( $\Phi_s$ ) up to 89.5% (Table S1).

Upon crystallization, all luminogens exhibit bright blue or bluishwhite emissions under 365 nm UV light. Furthermore, after ceasing the irradiation, orange afterglows lasting for several seconds are observed (Figure 2, Video S1). Photoluminescence



Figure 1. (A–C) Absorption and (D–F) emission spectra of (A,D) 4-MBACZ, (B,E) 3-MBACZ, and (C,F) 2-MBACZ in different solvents. (G) Photographs of the luminogens in toluene, THF, dichloromethane (DCM), and dimethylformamide (DMF) (from left to right) taken under 312 nm UV light.

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(PL) measurements show the  $\lambda_{em}$  at 372/403/427/453, 382/403/425/450/483, and 413/430 nm for 4-MBACZ, 3-MBACZ, and 2-MBACZ crystals (Figure 3), respectively. With a delay time ( $t_d$ ) of 0.1 ms, besides above peaks, emerging  $\lambda_{em}$ s at 553/600, 544/562/588, and 553/598 nm are observed (Figure 3). While those approaching prompt emissions can be readily assigned to the delayed fluorescence (DF), the new peaks should be attributed to *p*-RTP. That's to say, all luminogens exhibit prompt fluorescence, DF, and *p*-RTP emissions. To probe the origin of DF, we calculated the energy gaps ( $\Delta E_{ST}$ ) between the S<sub>1</sub> and T<sub>1</sub> based on the delayed emission spectra, which are 0.84, 0.80, and 0.76 eV for 4-MBACZ, 3-MBACZ, and 2-MBACZ (Table S2), respectively. It is known that if the  $\Delta E_{ST}$  value is larger than 0.37 eV, a thermal population of S<sub>1</sub> is not effective,<sup>[56]</sup> namely, thermally

measurement gives the PL lifetimes of 8.6, 16.7, and 12.4 ns for 4-MBACZ, 3-MBACZ, and 2-MBACZ in THF (Figure S9), respectively, indicating their fluorescence nature. Therefore, crystallization has induced both DF and RTP emissions for these isomers, which is similar to our previous observation in aromatic acids and esters.<sup>[45]</sup> The activation of such longlived tripletinvolved emissions, on one hand, is associated to the conformation rigidification and quencher isolation in the crystalline state; on the other hand, ISC processes might also be promoted upon crystallization.<sup>[45,59]</sup>

Though no apparent difference in the emission profile is noticed (Figure S10), prolonged orange afterglows are observed from para-, meta- to ortho-substituted isomers in turn (Figure 2, Video S1). Further time-resolved tests show the lifetimes of prompt



Figure 2. Photographs of 4-MBACZ, 3-MBACZ and 2-MBACZ crystals taken under 365 nm UV light and after ceasing the UV irradiation.60



Figure 3. Normalized emission spectra of (A) 4-MBACZ, (B) 3-MBACZ, and (C) 2-MBACZ crystals with to of 0 (purple) and 0.1 ms (orange). Excitation wavelength = 350 nm.

activated delayed fluorescence (TADF) is less likely to happen. Therefore, DF of the isomers should stem from the triplet-triplet annihilation (TTA) processes. Such pure organic luminogens with simultaneous and intrinsic fluorescence-phosphorescence dual emission at room temperature remain rare, which hold great promises to study dynamic processes and the underlying spin correlations of organic semiconductors.<sup>[57,58]</sup> Time-resolved

fluorescence (< $\tau$ ><sub>pf</sub>), DF (< $\tau$ ><sub>df</sub>), and < $\tau$ ><sub>p</sub> for 4-MBACZ/3-MBACZ/2-MBACZ being 11.4/12.3/15.3 ns, 46.2/130.3/48.7 ms, and 222.1/513.9/865.2 ms (Table S3), respectively. To gain more insights into the crystal emissions, their efficiencies ( $\Phi_c$ ) were further determined, which are 32.2%, 36.9%, and 6.4% for 4-MBACZ, 3-MBACZ, and 2-MBACZ, respectively. The triplet-involved emissions are activated upon crystallization, and the *p*-

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Figure 4. Emission decay profiles of (A) prompt fluorescence, (B) DF and RTP for 4-MBACZ, 3-MBACZ, and 2-MBACZ crystals.

RTP efficiencies ( $\phi_p$ ) are calculated to be 2.6%, 0.7%, and 0.1% for 4-MBACZ, 3-MBACZ, and 2-MBACZ crystals (Table 1), respectively. Derived from  $<\tau >_p$  and  $\Phi_p$  values, the  $k_r^p$  and  $(k_{nr}^p +$  $k_{q^{p}}$ ) values were estimated and summarized in Table 1. The  $k_{r^{p}}$ values are in the range of 9.1×10-4~1.2×10-1 s-1, which are comparable to or even lower than those of reported phosphors  $(2.7 \times 10^{-2} \sim 4.5 \times 10^{-2} \text{ s}^{-1})$ .<sup>[6,43]</sup> Moreover, the  $(k_{nr}^{p} + k_{q}^{p})$  ranges from 1.2 to 4.4 s<sup>-1</sup>, which are one to three orders higher than their corresponding  $k_{r^{p}}$  values, thus predominantly controlling the RTP durations. The relatively small  $k_r^p$  values and highly impeded nonradiative process impart the compounds with unique *p*-RTP. Obviously, both  $k_r^p$  (1.2×10<sup>-1</sup>) and  $(k_{nr}^p + k_q^p)$  (4.4 s<sup>-1</sup>) for 4-MBACZ are considerably higher than those of the other two isomers, which should be accountable for its shortest  $<\tau>_p$ . Meanwhile, those for 2-MBACZ (9.1×10<sup>-4</sup> and 1.2 s<sup>-1</sup>) are the lowest, which are consistent with its longest  $<\tau>_p$ .

Table 1. Photophysical parameters of varying compounds in crystals.[a]

Sample	<7>pf	<7>df	< <b>t&gt;</b> p	Φŕ	${\pmb \phi}_{p}$	<i>k</i> r <sup>p</sup> (s <sup>-1</sup> )	knr <sup>p</sup> +
Campio	(ns)	(ms)	(ms)	(%)	(%)		<i>k</i> q <sup>p</sup> (s <sup>-1</sup> )
4-MBACZ	11.4	46.2	222.1	32.2	2.6	1.2×10 <sup>-1</sup>	4.4
3-MBACZ	12.3	130.3	513.9	36.9	0.7	1.4×10 <sup>-2</sup>	1.9
2-MBACZ	15.3	48.7	865.2	6.4	0.1	9.1×10 <sup>-4</sup>	1.2

<sup>[a]</sup>  $k_{f^p} = \Phi_p/\langle \tau >_p$ ;  $k_{fn}r^p + k_q^p = (1-\Phi_p)/\langle \tau >_p$ ;  $\Phi_p$  was estimated according to the ratio of *p*-RTP to the whole emission without consideration on the efficiency of ISC.

It is known that molecular conformation and packing exert remarkable impact on the photophysical properties, particularly for the RTP of pure organic luminogens. To acquire further insights, single crystal structures of the isomers were determined. As shown in Figure 5, these molecules adopt twisted conformations with large amounts of intermolecular interactions like C=O···H-C, C-H··· $\pi$ , C=O··· $\pi$ , C-H···O-C, and even edge to face  $\pi \cdots \pi$  short contacts. The densities ( $\rho$ ) of crystals are 1.255, 1.292, and 1.278 g cm<sup>-3</sup> for 4-MBACZ, 3-MBACZ, and 2-MBACZ, respectively. Considering their identical compositions, much higher density implies much closer molecular packing. Meanwhile, the mean torsion angles between MBA and CZ moieties are 52.0°, 47.9°, and 62.0°/63.1°/79.8°/81.0° for 4-MBACZ, 3-MBACZ, and 2-MBACZ molecules (Figure 6), respectively. While the torsion angles of 4-MBACZ and 3-MBACZ are mainly caused by the repulsion of neighboring hydrogens, those for the four conformers in 2-MBACZ with obviously higher values should be associated with the considerable steric hindrance brought about by the presence of the ortho methyl ester.

In view of all preceding facts, and taken the effective isolation from quenchers by the crystal lattices into consideration, the trend of the  $\langle \tau \rangle_p$  values for the isomers can be rationalized as below: (1) 4-MBACZ owns the most loosest molecular packing ( $\rho = 1.255$ g cm<sup>-3</sup>) and least intermolecular short contacts (Figure 5A), which corporately make it undergo relatively active molecular motions, thus resulting in highest  $k_{nr}$  and shortest  $\langle \tau \rangle_p$ ; (2) 3-MBACZ takes

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Figure 5. Crystal structure and fragmental packing of (A) 4-MBACZ (CCDC 1820457), (B) 3-MBACZ (CCDC 1820458), and (C) 2-MBACZ (CCDC 1820459) with denoted intermolecular interactions.



Figure 6. Torsion angles between MBA and CZ moieties in the crystals of (A) 4-MBACZ, (B) 3-MBACZ, and (C) 2-MBACZ.

the most densest packing ( $\rho = 1.292$  g cm<sup>-3</sup>) and moderate intermolecular interactions including  $\pi \cdots \pi$  contacts (Figure 5B),

the balanced effect endows it with moderate  $\langle \tau > p$ ; (3) Despite 2-MBACZ crystals shows much looser molecular packing ( $\rho = 1.278$  g cm<sup>-3</sup>) than 3-MBACZ, it possesses more short intermolecular contacts and the highest steric hindrances (Figure 5C and 6), which collectively contribute to the conformation rigidification in crystals, thereby greatly depressing the  $k_{nr}^{p}$  value and subsequently affording the longest  $\langle \tau > p$ . These results clearly show the isomeric effect on the molecular packing, intermolecular interaction, steric hindrance, conformation rigidity, and thus RTP emissions in pure organic crystals.

The long afterglow of these luminogens and high sensitivity to molecular motions and quenchers of RTP make the isomers highly promising as smart mechanochromic materials.<sup>[43,49]</sup> Upon grinding with a pestle in a mortar, the blue emission of 4-MBACZ crystals demonstrates no obvious change under UV light (Figure 3A, 7A, Video S2). After the stop of irradiation, however, the orange *p*-RTP is no longer observed (Figure 7A). While the prompt and delayed emission profiles of the ground solids also resemble to those of pristine 4-MBACZ crystals, the intensities are significantly decreased (Figure 3A, 7B). XRD measurement indicates the ordered crystalline lattices have been transformed into disordered amorphous packings upon manual grinding, as evidenced by the broad diffusion halo with extremely low intensity of the ground solids (Figure 7C). Therefore, the disappearance of

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UV on UV off 0 s UV on UV off 0 s 0.1 s A) 4-MBACZ 3-MBACZ UV on UV off 0 s 0.4 s 0.8 s 1.2 s 2-MBACZ B) 4-MBACZ 3-MBACZ 2-MBACZ t (ms) t (ms t, (ms) 0.1 480 420 480 600 660 360 420 540 660 370 430 490 550 610 360 540 600 670 Wavelength (nm) Wavelength (nm) Wavelength (nm) C) 4-MBACZ 3-MBACZ 2-MBACZ recrystallized recrystallized recrystallized ground ground ground 35 45 5 15 25 5 15 25 35 45 55 15 25 35 45  $2\theta$ (degree) 20(degree) 20(degree)

*p*-RTP should be ascribed to the destruction of the ordered molecular packing and intermolecular interactions, which triggers

activation of nonradiative transitions and consequently decreased RTP emission with shortened lifetime.

Figure 7. (A) Photographs of the ground solids of 4-MBACZ, 3-MBACZ, and 2-MBACZ taken under 365 nm UV light and after ceasing the UV irradiation. (B) Normalized emission spectra of ground solids of 4-MBACZ, 3-MBACZ, and 2-MBACZ with *t*<sub>d</sub> of 0 and 0.1 ms. (C) XRD patterns of recrystallized and ground solids of the luminogens.



**Figure 8.** Demonstration of the anticounterfeiting application of the isomers using 4-MBACZ microcrystals. Photographs were taken under 365 nm UV light (left) and after ceasing the UV irradiation (right).

active molecular motions and makes the powders exposed to the triplet quenchers like oxygen and moisture, thus resulting in the

3-MBACZ and 2-MBACZ depict similar mechanochromic behaviors to those of 4-MBACZ. They both exhibit blue emissions upon grinding, accompanying with slight changes in emission profiles but distinct variation from crystalline to amorphous states (Figure 7). Astonishingly, different to 4-MBACZ and other reported mechanochromic luminophores, their ground amorphous powders can still generate unprecedented p-RTP after ceasing the UV irradiation, despite with somewhat shortened durations (Figure 7, Video S3 and S4). Such p-RTP from amorphous solids is rarely found for pure organics without rigid hosts,[61,62] which might be ascribed to the self-restraint molecular motions and self-protection from oxygen<sup>[63]</sup> for 3-MBACZ and 2-MBACZ molecules. Meanwhile, these phosphors may also act as the rigid hosts for themselves.

It is also noted that the *p*-RTP feature together with the distinct emission colors with and without UV irradiation of the crystals makes the crystalline solids ready for promising applications like bioimaging, data security and anticounterfeiting. For example,

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when the microcrystals of 4-MBACZ are blended with aloe vera gel and stamped on a filter paper, a blue dolphin is clearly visualized under 365 nm UV light (Figure 8). After ceasing the UV irradiation, however, the emission color switches to orange and eventually disappears (Figure 8), thus affording double channels (luminescence and switchable emission color) to identify the truth from the fraud. These results highly suggest the potential applications for encryption and high-tech anticounterfeiting using these isomers.

#### Conclusions

In summary, a group of isomeric pure organic luminogens based on CZ and MBA with *p*-RTP up to 865.2 ms were prepared and investigated. They are merely fluorescent in solutions, while being fluorescence-phosphorescence dually emissive in crystals, owing to the activation of *p*-RTP emissions brought about by the quencher isolation and conformation rigidification. The isomeric effect matters in view of the RTP emissions, because of its influence on molecular parking, intermolecular interaction, steric hindrance, and conformation rigidity.

Upon mechanical stimuli, crystalline luminogens are readily transformed into amorphous powders; meanwhile, while p-RTP from 4-MBACZ crystals disappears, those from the other two isomers are maintained with shortened durations, which are scarcely found for nondoped pure organics. The vanishment of p-RTP in 4-MBACZ can be attributed to the activation of molecular motions and exposure to triplet quenchers, and the retaining in 3-MBACZ and 2-MBACZ might be ascribed to their self-restraint of molecular motions and self-protection from oxygen. Furthermore, the distinct emission color change before and after ceasing the UV irradiation and the p-RTP feature of the luminogens make them highly promising for encryption, anticounterfeiting, and bioimaging applications. In future, it is also believed that p-RTP from pure organics with much higher efficiencies from both crystalline and amorphous states can be achieved through molecular engineering to produce the molecules with balanced  $(\pi,\pi^*)$  and  $(n,\pi^*)$  characters of the T<sub>1</sub> state and impeded nonradiative processes.

#### **Experimental Section**

Synthesis of 4-MBACZ and 3-MBACZ: The after adding CZ (650.8 mg, 3.9 mmol), methyl 4-bromobenzoate (922.7 mg, 4.3 mmol) and potassium carbonate (1300.7 mg, 9.4 mmol), toluene (5 mL) and xylene (3 mL) were added into a two necked flask. The flask was frozen, vacuumized, flushed with nitrogen and unfrozen three times. Afterwards, P(*t*-Bu)<sub>3</sub> (1.5 mL) and Pd(OAc)<sub>2</sub> (54.1 mg) in xylene (3 mL) were added. After adding 14 mL of toluene, the mixture was refluxed overnight. Then the solvent was evaporated, and the crude product was purified through column chromatography using DCM/petroleum ether (PE) (1/8~1/5) as eluent and recrystallized in PE. A colorless solid was obtained in 68.8% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 8.30 (s, 1H), 8.28 (s, 1H), 8.16 (s, 1H), 8.14 (s, 1H), 7.70 (s, 1H), 7.68 (s, 1H), 7.49-7.41(m, 4H), 7.34-7.30 (m, 2H), 4.00 (m, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 166.54, 142.17, 140.38, 131.50, 128.78, 126.53, 126.31, 123.92, 120.67, 120.57, 109.88, 52.49. 3-MBACZ (colorless solid, yield 41.5%) was synthesized through similar

approach to that of 4-MBACZ described above (Scheme S1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 8.27-8.26 (t, 1H), 8.17-8.14 (m, 3H), 7.80-7.77 (m, 1H), 7.72-7.68 (t, 1H), 7.45-7.38 (m, 4H), 7.33-7.29 (m, 2H), 3.96 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 166.45, 140.80, 138.19, 132.30, 131.65, 130.17, 128.64, 128.33, 126.24, 123.65, 120.54, 120.39, 109.71, 52.58.

Synthesis of 2-MBACZ: 2-MBACZ was synthesized according to the approach described in ref. [64]. Briefly, after adding potassium carbonate (2777.5 mg, 20.1 mmol), CZ (902.5 mg, 4.9 mmol) and copper powder (771.5 mg, 12.1 mmol), DMF (11 mL) was injected into a two necked flask. Then methyl 2-bromobenzoate (1 mL, 7.3 mmol) in DMF (9 mL) was added. After being refluxed for 23 h, large amount of deionized water was added. The solid was collected and further purified through column chromatography using DCM/PE (1/8~1/5) as eluent and recrystallized in ethanol. A colorless solid was obtained in 22.8% yield (332.7 mg). <sup>1</sup>H NMR (400 MHz, CDCIs,  $\delta$ , ppm): 8.15-8.11 (m, 3H), 7.78-7.74 (m, 1H), 7.62-7.58 (t, 2H), 7.40-7.36 (t, 2H), 7.29-7.27 (t, 2H), 7.15-7.13 (d, 2H), 3.20 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCIs,  $\delta$ , ppm): 166.58, 141.76, 137.11, 133.50, 132.14, 130.28, 130.25, 128.44, 126.09, 123.43, 120.41, 119.94, 109.45, 77.48, 77.16, 76.84, 52.24.

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**Keywords:** pure organic luminogens • persistent room temperature phosphorescence • delayed fluorescence • amorphous state

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# ARTICLE

#### **Entry for the Table of Contents**

# ARTICLE

# Persistent room temperature phosphorescence (*p*-RTP) is

observed in a group of isomeric metal-free luminogens based on carbazole and methyl benzoate units, not only at their crystalline states, but also at amorphous states for the meta- and ortho- isomers (see picture), thus illustrating the feasibility to realize pure organic *p*-RTP at both crystalline and amorphous states without doping or host-guest interactions.



Tingting Zhang, Xuan Wang, Zhongfu An, Zhiwei Fang, Yongming Zhang, Wang Zhang Yuan\*

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Pure Organic Persistent Room Temperature Phosphorescence at both Crystalline and Amorphous States