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# Molecular Engineering *via* Controlling Structural Deformation for Highly Efficient Ultralong Organic Phosphorescence

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**Abstract:** It is an enormous challenge to achieve the highly efficient organic room-temperature phosphorescence (RTP) with long lifetime. Here we demonstrated that by bridging the carbazole and halogenated phenyl ring with methylene linker, a type of RTP phosphors CzBX (X = Cl, Br) shows high phosphorescence efficiency ( $\Phi_{Ph}$ ), up to 38% for CzBBr with a lifetime of 220 ms, which is much higher than that of compounds CzPX (X = Cl, Br) with C-N bond as a linker ( $\Phi_{Ph} < 1\%$ ). Single crystal analysis and theoretical calculations revealed that, in the crystal phase, the intermolecular  $\pi$ -Br interaction accelerates the intersystem crossing process, while tetrahedron-like structure induced by *sp*<sup>3</sup> methylene linker restrains the nonradiative decay channel, leading to the high phosphorescence efficiency in CzBBr. This research not only paves a new road for achieving highly efficient and long-lived RTP materials but also expands the applications in anti-counterfeiting or data encryption.

Room temperature phosphorescence (RTP) materials have been pursued by academics owing to their full utilization of excited state energy and long lifetimes, which show potential applications in displays, encryption, anti-counterfeiting, sensors and bioimaging.<sup>[1]</sup> However, it is an enormous challenge to realize efficient RTP in pure organic molecules due to the inefficient intersystem crossing (ISC) caused by weak spin-orbit coupling (SOC) and the fast deactivation pathways of triplet excitons.<sup>[2]</sup> Recently, numerous strategies have been proposed to overcome this issue. The common way to promote ISC process is incorporating the n-electron groups (e.g, aldehyde and carbonyl) into π-conjugated organic molecules.<sup>[3]</sup> These compounds have donor-acceptor skeleton featuring with strong electronic coupling, which are inclined to forming distinct structural deformation in excited-state transition process, leading to limited suppression of molecular motions even restrained by rigid environments, such as polymer aggregation,<sup>[4]</sup> host-guest systems,<sup>[5]</sup> self-assembly,<sup>[6]</sup> crystallization,<sup>[7]</sup> H-aggregation,<sup>[8]</sup> etc. Consequently, long-lived

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Supporting information for this article is given via a link at the end of the document. organic RTP molecules with high phosphorescence efficiency ( $\Phi_{Ph} > 20\%$ ) were seldom reported.<sup>[9]</sup> On the other hand, heavy atoms, like bromine, can largely promote phosphorescence efficiency but shorten phosphorescence lifetime, thus it is hard to trigger long-lived RTP.<sup>[3e-g,10]</sup> Therefore, how to achieve organic RTP with both high efficiency and ultralong lifetime is an extremely intriguing topic to explore.



Figure 1. a) The schematic illustration of design concept. b) Molecular structures of CzPX and CzBX (X=Cl, Br).

To address the above issue, we proposed to introduce methylene linker into the donor-acceptor RTP molecules based on two rationales: the *sp*<sup>3</sup> methylene 1) makes tetrahedron-like molecular geometry, favoring formation of strong intermolecular interaction in crystal<sup>[11]</sup>; 2) breaks the electron delocalization between donor and acceptor units, hampering the structural deformation in excited-state transition. Both features will suppress the non-radiative decay pathways in the solid state. Besides, halogennated acceptor could form intermolecular  $\pi$  -halogen interation in crystal, which only accelerates ISC channel, but not shortens RTP lifetime.<sup>[12]</sup>

With these in mind, we designed and synthesized CzBX (X = Cl, Br) compounds (Figure 1), i.e., the *sp*<sup>3</sup> methylene linker was used to bridge carbazole and halogenated phenyl ring. As expected, CzBX show a huge promotion of RTP efficiency, compared to the donor-acceptor molecules CzPX (X = Cl, Br, Figure 1) with low RTP efficiency. Intriguingly, CzBBr crystal exhibited a high phosphorescence efficiency ( $\Phi_{Ph}$ ) of 37.96%, along with a long-lived lifetime of 220.24 ms. Experiments and theoretical simulations demonstrated that this improvement on RTP can be ascribed to the largely restricted nonradiative decay and enhanced ISC channel by both methylene linker and  $\pi$  - halogen interaction in crystal, respectively. Given the high efficiency and ultralong lifetime of RTP, these compounds were finely applied in multiple data encryption technique by utilizing the time resolution technique.

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Figure 2. Photophysical properties of compounds CzPX and CzBX in crystals under ambient conditions. a) Normalized steady-state photoluminescence (blue line) and ultralong phosphorescence (red line) spectra of CzPX and CzBX crystals. Insets: the photographs of CzPX and CzBX crystals under 365 nm UV light on (left) and off (right). b) Lifetime decay profiles of the phosphorescence emission peaks measured under ambient conditions. c) CIE 1931 coordinates of steady-state photoluminescence of CzBBr crystal excited by 370 nm. d) Excitation-phosphorescence emission mapping of CzBBr crystal. e) Bar charts of phosphorescence quantum yields of CzPX and CzBX crystals.

In this work, a series of aromatic amide derivatives with halogen substituents, namely, 9-(4-chlorophenyl)-9H-carbazole(CzPCI), 9-(4-bromophenyl)-9H-carbazole (CzPBr), 9-(4-chlorobenzyl)-9H-carbazole (CzBBr), were facilely prepared through one-step nucleophilic substitution reaction (Scheme S2). All target compounds were thoroughly characterized by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy (Figure S1-S8), elemental analyses and X-ray single-crystal diffraction. HPLC was carried out to further confirm the purity (Figure S9-S12).

Firstly, the photophysical properties of these compounds both in solution and crystal were systematically explored by absorption spectra, steady-state photoluminescence (PL) spectra and timeresolved emission spectra (TRES). The absorption bands of compound CzPX in 2-methyltetrahydrofuran (2-MeTHF) solution are located at ca. 240, 291, 325 and 338 nm, and those for CzBX red-shifted to 240, 292, 328 and 341 nm (Figure S13a and Table S1) under ambient condition. While these four compounds show similar steady-state PL emission peaks at 350 and 365 nm in 2-MeTHF solution, but display a small difference to the structured emission profiles (Figure S13b and Table S1), which can be attributed to the variation of singlet excited states caused by methylene linker. At 77 K, the fluorescent spectra present dual emissions in the solution, in which the high-energy regions are attributed to the fluorescence, while the low-energy region is regarded as the phosphorescence. It is worthy noting that the CzPBr has the largest phosphoresce ratio, which can be ascribed to the efficient intramolecular heavy-atom effect. One the other hand, these compounds show almost identical phosphorescence profile (Figure S14), indicating the methylene and halogens have little influence on the T<sub>1</sub> states. Whereas the phosphoresce ratios in CzBX molecules are similar to CzPCI, it speculated that the methylene linker may weaken the impact of heavy atom effect, providing a possibility to achieve long-lived RTP in halogenated organic materials.

In crystals, all compounds exhibited bright blue or bluish white emissions upon irradiated by a 365 nm ultraviolet (UV) lamp. As shown in Figure 2a, CzPX and CzBX crystals showed a strong fluorescence emission ranging from 350 to 450 nm with a short lifetime of ns-scale (Figure S16, Table S2). After removing the excitation light source, yellowish afterglow was observed by the naked eye, lasting for several seconds (Video SV1-SV4). With a delay time of 8 ms, CzPBr displayed a maximal RTP peak around 524 nm with a lifetime of 299.42 ms, along with a shoulder peak at 560 nm. While CzPCI, CzBCI and CzBBr showed a red-shifted RTP bands at 550 nm with lifetimes of 224.07, 777.37 and 220.24 ms, respectively, accompanied by shoulders at 600 nm (Figure 2a, 2b). On the other hand, very weak emissions from the region of 400-520 nm are observed for these compounds, which could be ascribed to the triplet-triplet annihilation.[10e] Excitationphosphorescence emission mappings demonstrated that CzBX and CzPX crystals all remained their RTP emission positions when the excitation wavelength changed from 250 to 420 nm (Figure 2d, Figure S15). Impressively, CzBBr has an intense RTP, which can be comparable to its fluorescence emission, resulting in a distinct white luminescence with a CIE (Commission International de l'Eclairage) of (0.34, 0.30) under UV irradiation (Figure 2c). This is different to blue luminescence in other three compounds owing to the faint RTP emission. Unsurprisingly, CzBBr exhibits a high RTP efficiency, up to 37.96%, and this

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Figure 3. The intermolecular interactions around one molecule in CzPX (a, b) and CzBX (c, d). e) The calculated free volume region in the single crystal cells of CzPX and CzBX. Intermolecular heavy-atom interactions of CzPBr (f) and CzBBr (g).

value is less than 1% for CzPBr, CzBCl and CzPCl (Figure 2e, Table S3). To the best of our knowledge, this is one of the highest RTP efficiency among the reported single component organic RTP molecules with long afterglow (Figure S18). Notably, the phosphorescence is highly sensitive to oxygen. Therefore, the control experiments on the steady-state photoluminescence spectra of model CzBCl phosphor were conducted in vacuum and oxygen (Figure S19). We found that no phosphorescence band appeared in vacuum, indicating the ambient conditions have little influence on the phosphorescence efficiency. Because the phosphorescence can be largely preserved by the rigid molecular stacking in crystal state.

Single crystal analysis was then carried out to elucidate the intrinsic RTP mechanism. As shown in Figure 3 and S20, CzBX adopts tetrahedron-like conformations with amounts of intermolecular interactions, such as C-H… $\pi$  (2.854, 2.866, 2.891, 2.893 Å) and C-H…H-C (2.388 Å) in CzBBr crystals, whereas CzPX possesses less intermolecular interactions, such as C-H…Br-C (2.986 Å) and edge to face  $\pi$ … $\pi$  (3.338 Å) contacts in

CzPBr. On the other hand, the molecules in a crystal lattice usually occupy most of the space of a unit cell. However, there are plenty of unoccupied spaces, i.e., the free volume, which can afford the molecular motions with nonradiative decay process.[13] As shown in Figure 3e, we calculated the free volume distribution of the compounds CzPX and CzBX. Intriguingly, by introducing the methylene linker, the fractional free volumes are decreased from CzPX (~7%) to CzBX (~4%) (Figure S21). The tendency is consistent with the reduced nonradiative decay rates of T1 states (Table S4), which can be ascribed to the restricted twisted vibrations in the low-frequency regions (Figure S22). These results showed that CzBX crystals afford more rigid environment with aid of the methylene linker, which can prevent molecular motions and stabilize triplet excitons, facilitating the generation of efficient RTP. More importantly, Figure 3f, 3g displayed that the angle between bromine atom and carbazole plane ( $\alpha_{Br \cdots \pi}$ =138.16°, 138.26°) in CzBBr is largely smaller than that in CzPBr ( $\alpha_{Br\cdots\pi}$ =177.86°). It speculated that CzBBr has efficient C-Br $\cdots\pi$ interaction, which can promote ISC process significantly, leading to high RTP efficiency (37.96%) in CzBBr.<sup>[11]</sup> Similar halogen-π

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Figure 4. Electronic structure natures for CzPBr and CzBBr. a) Natural transition orbitals (NTOs) of S<sub>1</sub> states. b) The dihedral angles tween carbazole and phenyl ring ( $\phi$ ) of S<sub>0</sub>, S<sub>1</sub> and T<sub>1</sub> states. c) Calculated energy diagram, oscillator strength (*f*) and spin-orbit coupling (SOC) matrix elements ( $\xi$ ). (d) Proposed RTP mechanism.

interaction was also found in CzBCI (Figure 3c), but there existed low RTP efficiency (0.57%), which might be attributed to the negligible heavy atom effect due to the light Cl atom.

To gain deep insight into the high RTP efficiency in CzBBr caused by methylene linker, we evaluated the electronic structure natures of CzPBr and CzBBr at the level of (TD)B3LYP/cc-pVDZ, including excitation energy, natural transition orbitals (NTOs) and spin-orbit coupling (SOC) matrix elements ( $\xi$ ), as well as reorganization energy ( $\lambda$ ) shown in Figure 4. When going from CzPBr to CzBBr, the methylene linker makes the singlet excited state S<sub>1</sub> changed from delocalization transition on the whole molecule to local carbazole transition. This means that the structure deformation in the excited states decay process of CzPBr is much larger than that of CzBBr, which was further verified by the fact that the dihedral angle ( $\varphi$ ) between carbazole and phenyl ring is changed from 38.77 °in S1 to 42.06 °in S0 states for CzPBr, and such variation is hugely reduced from 56.92 °in S1 to 56.19 ° in S<sub>0</sub> states for CzBBr. Consequently, the  $\lambda$  of S<sub>1</sub> state is decreased from 0.162 eV in CzPBr to 0.104 eV in CzBX (Table S6), which is responsible for the sharply decreased nonradiative decay rates of S<sub>1</sub> state from  $8.05 \times 10^8 \text{ s}^{-1}$  in CzPBr to  $3.14 \times 10^7$ s<sup>-1</sup> in CzBBr (Table S4), resulting in a hugely increase of PL quantum yields from 6.60% in CzPBr to 68.60% in CzBBr (Table S3), combining with a little increased radiative decay rates due to the small change of oscillator strength (Figure 4c, Table S3). On the other hand, from CzPBr to CzBBr, the energy gaps ( $\Delta E_{ST}$ ) of  $S_1 \rightarrow T_4$  and  $S_1 \rightarrow T_3$  are reduced from 0.25 eV, 0.50 eV to 0.003 eV, 0.26 eV, respectively, which facilitates the promotion of ISC channel. However, the SOC value of  $S_1{\rightarrow}T_3$  is decreased from

1.416 to 0.216 cm<sup>-1</sup>, implying that the methylene linker reduces the internal heavy atom effect. It results in a limited acceleration of ISC channel for CzBBr. We then turn into probe the intermolecular π-halogen interaction. A model system of CzPBr surrounding a BrH moleclue, named as CzPBr-Ext, was firstly built based on molecular packing in single crystal. Impressively, the SOC value of  $S_1 \rightarrow T_4$  is increased from 0.331 cm<sup>-1</sup> in CzPBr to 2.060 cm<sup>-1</sup> in CzPBr-Ext, along with the unchanged  $\Delta E_{ST}$ . Whereas this π-halogen interaction cannot increased the SOC values in CzBCI (Figure S25). Thus, the  $\pi$ -halogen interaction can be responsible for the large ISC rate  $(3.80 \times 10^7 \text{ s}^{-1})$  in CzBBr, which is larger two orders of magnitude than that in other three compounds (Table S4). Subsequently, this large SOC also makes a huge increase of oscillator strength (1.57×10<sup>-6</sup>) of  $T_1 \rightarrow S_0$  for CzBBr-Ext, in comparison to 5.67×10<sup>-8</sup> for CzPBr and for 1.38 ×10<sup>-7</sup> for CzBBr. Such tendency can be reponsible for the decreased radiative decay rate of  $T_1 \rightarrow S_0$  from CzBBr (1.73 s<sup>-1</sup>) to CzPBr (0.70×10<sup>-2</sup> s<sup>-1</sup>) (Table S3), in combination with the almost unchanged SOC values of  $\xi$  (T<sub>1</sub>,S<sub>0</sub>). Whereas the nonradiative decay rate of  $T_1 \rightarrow S_0$  has a small change for these compounds, owing to the almost unchanged T1 states with a local transition on carbazole units (Figure S23). Therefore, the increased ISC and radiative decay process make the high RTP efficiency in CzBBr.

Taken these results together, we proposed that the fast nonradiative decay rate of S<sub>1</sub> states was responsible for the low PL efficiency in CzPBr (Figure 4d), owing to the large structural deformation. When the methylene liner breaks the  $\pi$ -conjugation, the S<sub>1</sub> state in CzBBr becomes to a local carbazole transition, which largely reduced the nonradiative decay process, while the intermolecular  $\pi$ -halogen interaction hugely promotes the ISC of

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 $S_1 {\rightarrow} T_n$  and radiative decay rate of  $T_1 {\rightarrow} S_0$  (Figure 4e). However, it has little impact on the SOC of  $T_1 {\rightarrow} S_0$ . Consequently, both high RTP efficiency and long-lived RTP lifetime are achieved in CzBBr.

Given the unique RTP characteristic with ultralong RTP lifetime, these compounds can be finely applied in multiple anticounterfeiting or data encryption technique by utilizing the time resolution technique. In Figure 5a, the fitted lines of luminescence decay process of CzBBr, CzBCl and CzPBr are demonstrated in log 10 and linear modes. With the longest lifetime, the phosphorescence of CzBCI can last over 7 s. Moreover, with the highest phosphorescence efficiency, CzBBr can show the highest brightness in the same conditions, but its afterglow can only last for about 3 s for its shorter lifetime. With shorter lifetime and lower efficiency, CzPBr can hardly be observed. When they were fabricated in one pattern at the same time, different information can be observed under the different conditions. As illustrated in Figure 5d and 5e, under the irradiation of a 365 nm UV-lamp, the pattern only shows a white circular pattern fabricated by CzBBr (Info. 2). While the UV-lamp was switched off, the pattern can still keep an orange circular pattern (Info. 2) under the observation of naked eyes or a camera with low sensitivity and short exposure time. Only under the camera with high sensitivity and long exposure time, the hidden information can be found. Within 0 to 0.5 s after witching off the UV-lamp, eight stars fabricated by CzPBr can be observed (Info. 1), while within 2 to 3.5 s after witching off the UV-lamp, the crescent pattern fabricated by CzBCI can be observed (Info. 3).

In summary, a series of efficient pure organic phosphors, named CzPX and CzBX (X = Cl, Br) was developed bearing carbazole and halogen-substituent phenyl moieties. These molecules showed long-lived RTP lifetimes in the range of 200 to 900 ms. We found that compounds CzBX with tetrahedron-like geometries could largely suppress the molecular motions in excited stated decay process after introducing  $sp^3$  methylene linkers into the CzPX molecules. Moreover, the intermolecular  $\pi$ -halogen interaction has a large increase to the ISC and radiative decay channel, but it has a tiny influence on the nonradiation transition of T<sub>1</sub> $\rightarrow$ S<sub>0</sub>. Whereas it is invalid to CzBCI due to the light Cl atom. Consequently, CzBBr presented a long RTP lifetime and high RTP efficiency, up to 38%. This research paves a new road for achieving highly efficient pure organic phosphors.



Figure 5. The application of data encryption based on CzBBr, CzBCl and CzPBr. a) The fitted lines of luminescence decay process with log 10 and linear modes, respectively. b) The structure of pattern for security application using CzBBr, CzBCl and CzPBr. c) Three encrypted information patterns from the device. d) Photographs of the pattern under visible and UV light, respectively. e) Photographs of the pattern taken after tuning off the UV light with two different shooting modes under ambient conditions.

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## COMMUNICATION

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Molecular Engineering via Controlling Structural Deformation for Highly Efficient Ultralong Organic Phosphorescence

Through controlling the molecular motions by appending a  $sp^3$  methylene fragment and utilization of intermolecular Br- $\pi$  interaction, compound CzBBr shows excellent RTP with an ultrahigh  $\Phi_{Ph}$  up to 38% and an ultralong lifetime of 220 ms.

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