Intermolecular Electronic Coupling of Organic Units for Efficient Persistent Room-Temperature Phosphorescence **

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Abstract: Although persistent room-temperature phosphorescence (RTP) emissions have been observed for a few pure crystalline organic molecules, there is no consistent mechanism and no universal design strategy for such organic persistent RTP (pRTP) materials. Here, a new mechanism for pRTP is presented, based on combining the advantages of their different excited state configurations in the coupled intermolecular units, which may be applicable for a wide range of organic molecules. Following this mechanism, we describe a successful design strategy to obtain bright pRTP, utilizing a heavy halogen atom to further increase the intersystem crossing rate of the coupled units. RTP with a remarkably long lifetime of 0.28 s and a very high quantum efficiency of 5% was thus obtained under ambient conditions. This strategy provides an important step forward in the understanding of organic pRTP emission.

Room-temperature phosphorescence (RTP) in organic materials is important in optoelectronic technologies, such as electroluminescence, molecular sensing and time-resolved bioimaging.[1] However, unlike inorganic materials which can possess afterglow or persistent room-temperature luminescence with lifetimes from seconds to days,[2] organic materials have a relatively short RTP lifetime (typically <10 ms).[3] To date, only a few examples of organic materials with persistent RTP (pRTP) in air with a long lifetime (>10 ms) have been described.[4] Morantz *et al*.[4a] reported the first observation of weak RTP with lifetimes of several seconds in planar crystalline organic compounds, which was proposed to be related to dimer emission. In 2013, Adachi *et al*.[4b,5] reported a complex host–guest system to achieve pRTP in deuterated organic compounds. The inevitable phase separation in such a system, which results in unstable luminescence, limits its practical applications. Recently, a few groups and our group have observed pRTP in crystals of different types of organic molecules, including 1,3,5-triazines,[4d] phenylphosphines,[4d] ketones,[4e,4g] aldehydes[4f] and sulfones.[4c] Various explanations for the rare phenomenon have been proposed including: the essential role of solvent molecules in the crystals,[4e] the chemical structure itself,[4f] strong coupling in H-aggregated near-planar molecules,[4d] and crystallization-induced phosphorescence.[4g] There is currently no universal design strategy for new organic pRTP molecules. In addition, the limitation of low RTP quantum efficiency impedes their practical applications. Based on new results, we now propose a new mechanism for pRTP, which may also be applicable for the different molecules reported previously. We identify the key role of intermolecular coupling within the crystal structure of different sub-units which possess different excited state configurations (*i.e.*, nπ* and ππ* states). Based on this proposed mechanism, we have designed two new organic molecules which achieve bright pRTP with the highest reported quantum efficiency. This may be a simple strategy to obtain efficient and pRTP, which could be readily applied to diverse families of organic molecules.

As shown in Figure 1, in organic molecules the lowest triplet state (T_1) excitons are generated via spin-forbidden intersystem crossing (ISC) from the lowest singlet state (S_1) excitons. Thus, heavy atoms and organic moieties with lone pair electrons can increase the ISC rate (k_{ST}) through strong spin–orbit coupling, resulting in efficient phosphorescence.[6] The heavy atoms possess strong spin–orbit coupling capabilities and are generally metallic ions and heavy halogen atoms. The organic moieties are usually aromatic aldehydes and ketones; thus, the lone-pair electrons contribute to an increase in k_{ST} through an allowed transition between nπ* and ππ* states (Figure 1a, generally with a small energy gap). However, the radiative rate (k_r) from the T_1 state to the ground state (S_0) also increases when the spin–orbit coupling is enhanced, thereby resulting in the short lifetime of phosphorescence (<10 ms, typically in the ms range, Table S1). By contrast, the spin–orbit coupling in typical hydrocarbon molecules is through a forbidden transition between two different ππ* states (generally with a large energy gap) and this transition is usually weak. Hence, they generally exhibit phosphorescence with long lifetimes because of the low k_r rate of the forbidden radiative process from T_1 to S_0 (Figure 1b). Similarly, their phosphorescence quantum efficiencies are low, leading to weak emissions (Table S1).

Given the coupling structure of the exciplex state,[7] we hypothesized that the intermolecular coupling of units with different excited state configurations (*i.e.*, nπ* and ππ*) involves both units in the photophysical processes, when their orbitals are partially overlapped (Figure 1c). This coupling thus has hybrid ISC transitions with the advantages of improved k_{ST} and low k_r rates to promote bright pRTP. In addition, except for inert atmospheres and deuterated organic compounds, a rigid crystalline state is chosen to decrease the

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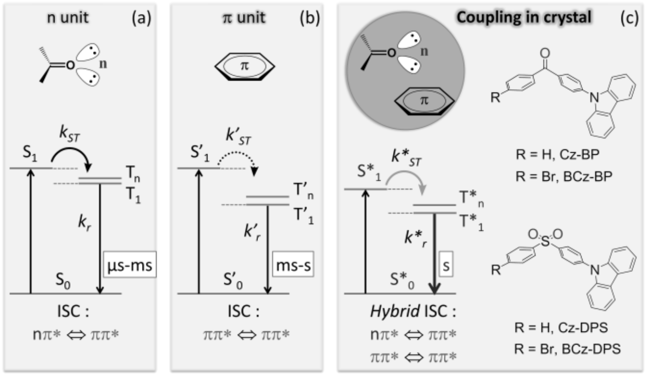

Figure 1. Energy level diagram of the relevant photophysical processes for the phosphorescence of organic molecules with (a) nπ* excited state configuration (i.e., containing n unit) and (b) ππ* excited state configuration (i.e., containing π unit). (c) Proposed energy level diagram of the relevant photophysical processes for pRTP of coupled intermolecular n and π units in organic crystals, and examples of rationally designed molecular structures for pRTP utilizing the proposed mechanism. S_0, the ground state; S_1, the lowest singlet excited state; T_1, the lowest triplet excited state; T_n, the high-level triplet excited state; ISC, intersystem crossing; k_{ST}, the ISC state; and k_r, the radiative rate. The superscript indicates the excited state with different configurations.

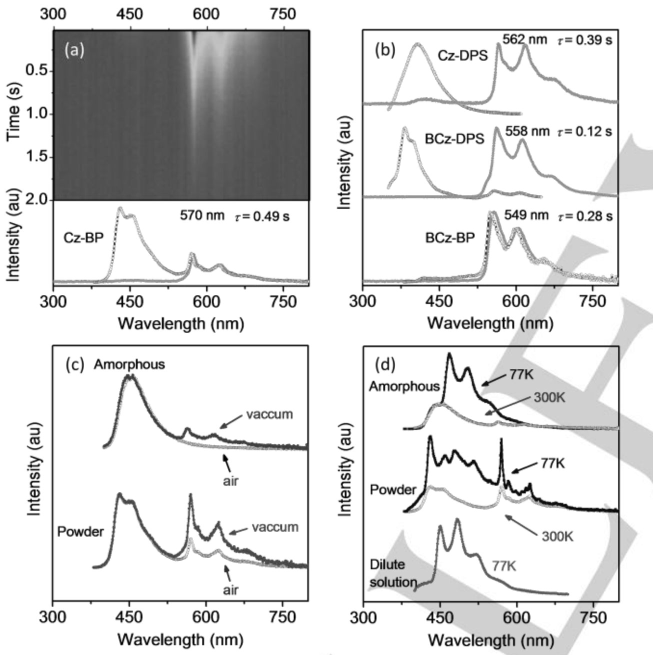

Figure 2. (a) The transient photoluminescence (PL) decay image (delay 25 ms) of the Cz-BP crystal powder sample, the color change from red to green indicates the decrease in emission intensity. Steady-state PL spectra (circle) and persistent phosphorescence spectra (delay 25 ms, ball) of different crystal powder samples: (a) Cz-BP and (b) Cz-DPS, BCz-DPS, and BCz-BP. Steady-state PL spectra of the Cz-BP samples under different conditions: (c) in air or in vacuum and (d) crystal powder, amorphous and dilute solution in vacuum. The spectra and images were recorded in air at 300 K unless otherwise stated.

the nonradiative decay (k_{nr}) rates of the deactivation process by oxygen and heat, which can efficiently promote the RTP emissions.[6b,8,9] Therefore, the intermolecular coupling of sub-units within a crystal may be a key factor for pRTP emission. A study of the single-crystal structures of reported organic pRTP molecules, reveals the presence of close intermolecular interactions of the n–π* unit (n unit, excited state with nπ* configuration) and π–π* unit (π unit, excited state with ππ* configuration) in most systems (for examples see Figure S1). We therefore propose a new explanation for organic pRTP: the intermolecular coupled units (n and π units) combine their advantages, including high ISC and low radiative rates, in the photophysical processes of the crystal, which produces hybrid ISC transitions and leads to bright long-lived RTP. With this idea in mind, we designed two kinds of twisted organic molecules containing a carbonyl or sulfonyl group as the n unit and a carbazolyl (Cz) group as the π unit (Figure 1c).[10,11] The π unit also functions as an electron donor (D) and the n unit as an electron acceptor (A). Thus, similar to thermally activated delayed fluorescence (TADF) materials,[12] the spatial overlap between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) is decreased in D−A type twisted molecular structures. A small energy gap (ΔE_{ST}) between the S_1 and T_1 excited states was thus obtained, which should increase the k_{ST} rate for phosphorescence. On the other hand, the n and π units have a tendency to form close intermolecular stacking in the crystals due to the electrostatic interactions between them. All the designed compounds show obvious pRTP emissions, as expected. To confirm our hypothesis, the pRTP property of 4-(9*H*-carbazol-9-yl)benzophone (Cz-BP, Figure 1c) was systematically investigated because of its simple ketone structure. When irradiated at 350 nm, the Cz-BP crystal powder exhibited dual emission, both fluorescence and phosphorescence (Figure 2a). The fluorescence peak at 431 nm with a shoulder at 453 nm showed a typical emission lifetime of 2.5 ns (Figure S2a). Two RTP peaks were observed at 570 and 624 nm.. After the excitation lamp was turned off, the orange pRTP emission can be directly observed by the naked eyes because of its ultralong luminescence lifetime of 0.49 s with a single-exponential decay (Figures 2a, S2b and S15).

As expected, the ultralong-lived RTP is due to the coupling of intermolecular units in the Cz-BP crystal (Figure 2 and Table S2). First, the crystalline state is one of the essential factors to ensure the occurrence of pRTP emission, by providing a rigid state insulated from oxygen in the air.[4] This pRTP faded when the crystal powder was ground into an amorphous state or isolated in solutions, in which the increased intramolecular motion will quench the excitons. (Figures 2c, S3 and S4). The lack of RTP in the amorphous film in Fig. 2c is due to the presence of oxygen. Nevertheless, in vacuum, pRTP is still observed in the amorphous sample because the intermolecular coupling between different Cz-BP molecules can exist even in an amorphous sample (Figure 2c). The intensity of RTP in the crystal powder also increased in vacuum because the crystalline sample still contained some amorphous parts. The pRTP was attributed to the intermolecular coupling, which was further confirmed by comparing these results with the phosphorescence of a dilute solution of Cz-BP at 77 K (Figure 2d). The phosphorescence of a single Cz-BP molecule was much bluer than the pRTP of the coupled structure, with peaks at 450, 484 and 521 nm. The luminescence lifetime was shorter at ~90 ms and also exhibited a single exponential decay. Such peaks were also observed in a similar range in the crystalline or amorphous samples at 77 K (Figures 2d, S2c and Table S2). The intensity of such peaks, attributed to a single molecule, was lower than the emission of coupled molecules in the crystalline sample but much higher in the amorphous sample. These results indicated that most Cz-BP molecules coupled and exhibit persistent phosphorescence in the crystalline state.

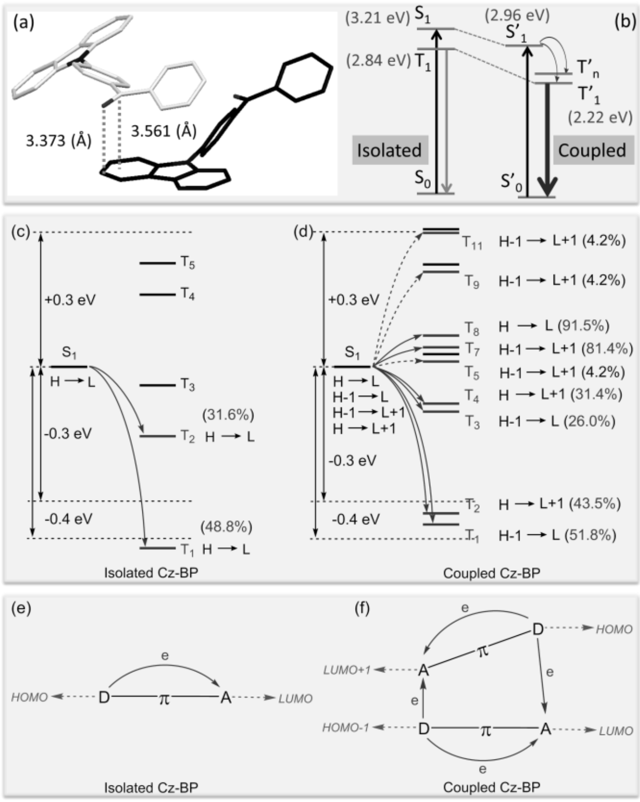

Figure 3. (a) Intermolecular coupling of the carbonyl and Cz groups in two Cz-BP molecules that are in close proximity in a single crystal. (b) Energy level diagram of the isolated and coupled Cz-BP molecule(s). Schematic representations of the TD-DFT calculated energy levels, main orbital configurations and possible ISC channels of (c) isolated Cz-BP and (d) coupled Cz-BP at the singlet (S_1) and triplet (T_n) states. H and L refer to HOMO and LUMO, respectively. Schematic representations of the possible intramolecular and intermolecular ISC channels in (e) isolated Cz-BP and (f) coupled Cz-BP molecules. The carbonyl (electron acceptor) and the Cz (electron donor) units are labeled as A and D, respectively. The plain and dashed arrows refer to the major and minor ISC channels in (c), (d), (e), and (f), respectively.

To gain further insight into the intermolecular coupling mechanism, the single crystals of these compounds were studied by X-ray structural analysis. The intermolecular coupling between the carbonyl (n) and Cz (π) units was observed in the crystals of Cz-BP (Figures 3a and S5). The carbonyl group of the Cz-BP molecule is stacked approximately parallel to the Cz group of a neighboring molecule. The distance between the two units is short (*i.e.*, 3.373 Å for the oxygen atom and 3.561 Å for the carbon atom to the Cz plane), which results in significant intermolecular interactions between their orbitals. Thus, the coupling of typical n and π units in the crystal state could integrate the excellent photophysical properties of both units, thereby resulting in intensive pRTP, as described in Figure 1c. An energy level diagram (Figure 3b) uses data estimated from the emission spectra of Cz-BP (Figure S3). Both the energy levels of the singlet and triplet excited states of the coupled molecules (*i.e.*, S'_1 and T'_1, respectively) decreased. Thus, the T'_1 state becomes the lowest energy state in the system, making the phosphorescence from the T'_1 state possible and efficient.[10b] The coupled n and π units play critical roles in the processes of pRTP emission. These roles are supported by theoretical time-dependent density functional theory (TD-DFT) calculations on single molecules and coupled structures derived from single-crystal structures (Figures 3, S9 and S11). For an isolated Cz-BP molecule, there are only two main channels for ISC transition. However, the increased number of ISC channels (nine channels) enhances the ISC transition in coupled Cz-BP molecules (Figures 3c-d).[13] Furthermore, significant intermolecular ISC channels are present in coupled Cz-BP (such as, $S_1 \rightarrow T_7$ and T_8, Figure 3f).[14]

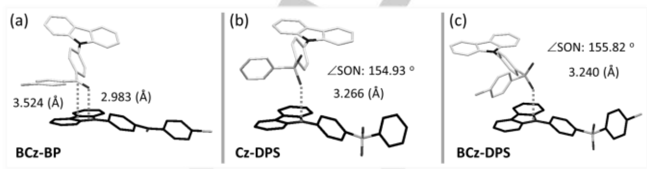

Figure 4. Intermolecular coupling of the n and π units in two neighboring molecules in single crystal structures: (a) Cz-DPS, (b) BCz-BP, and (c) BCz-DPS. The distance from the n group to the coupled π plane Cz plane) is indicated by green dashed lines: (a) 2.983 Å (O−Cz plane) and 3.524 Å (C−Cz plane), (b) 3.266 Å (O−Cz plane), and (c) 3.240 Å (O−Cz plane). The relative angle (∠SON) between the S=O bond and the N atom of the Cz plane in (b) and (c) is also indicated: (b) 154.93° and (c) 155.82°.

It is clear that the intermolecular coupling within the crystal structure of different n and π sub-units has a key role in pRTP. The RTP of Cz-BP exhibits a long lifetime; however, its absolute phosphorescence quantum efficiency (Φ_P, ~0.3%) is low.[4d] As heavy halogen atoms facilitate strong spin–orbit coupling, their presence in the molecules should further improve the ISC rate, thereby promoting bright RTP emission. A bromine atom was, therefore, attached onto Cz-BP *para* to the carbonyl group (BCz-BP, Figure 1c). Due to its conjugation to the carbonyl group, the bromine atom will be involved in the ISC process and should further enhance the k_{ST} rate of the n unit. The π units (Cz group) will keep its low radiative rates with little or no adverse effect from the bromine atom. Indeed, BCz-BP exhibits markedly enhanced RTP emission with a high absolute Φ_P of 5% and a slightly decreased long lifetime of 0.28 s (Figures 2b, S2b and S15). It is notable that this Φ_P is more than twice the highest value in the literature (2.1 %).[4d] On the contrary, no pRTP will be observed in the bromide of Cz-BP with bromine atom introduced into its π units.[4g]

Similar coupling of intermolecular units was observed in the single crystal of BCz-BP, where the distance between the n and π units of two neighboring molecules is even shorter (*i.e.*, 2.983 Å for the oxygen atom and 3.524 Å for the carbon atom to the Cz plane, Figures 4a and S6). Therefore, the interaction between two coupled units in BCz-BP crystals is stronger: this result is fully consistent with the fact that the pRTP emission is more intense for BCz-BP compared to Cz-BP. Interestingly, in the coupled BCz-BP molecules, only intermolecular ISC transition is found based on the calculated results (Figure S9 and S12). That is, the intermolecular ISC transition could be dramatically increased by the enhancement of the spin–orbit coupling ability of the n unit, after introduction of a bromine atom. Thus, conjugating a heavy halogen atom into the n unit is a simple and efficient way to enhance the ISC rate of the intermolecular coupling of n and π moieties, leading to bright pRTP.

When the n unit was changed to a sulfonyl group, our proposed mechanism was again supported by the experimental data. As shown in Figure 2b, S2d and S15, Cz-DPS and BCz-DPS, exhibit obvious pRTP. Similar coupling of intermolecular n and π units was also observed in their single crystals (Figures 4b-c and S7-8). All of these stackings facilitate the orbital overlap between the n and the π units. The TD-DFT calculations also show that newly generated intermolecular ISC channels in these coupled units promote RTP (Figures S10 and S13-14). Therefore, as shown schematically in Figure 1c, the coupling of n and π units in the crystals is the key factor for pRTP. This explanation should be applicable to different pRTP materials. The brominated sulfone derivative BCz-DPS, analogously exhibits much brighter RTP emission compared to Cz-DPS (Figures S15). The absolute Φ_P of BCz-DPS is as high as 6% (the highest reported one), and its lifetime is as long as 0.12 s.

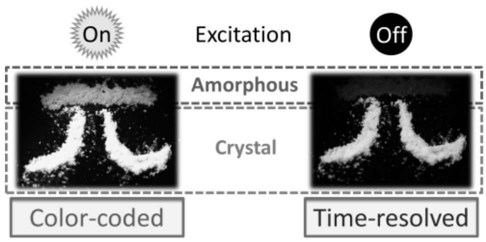

Figure 5. Two-dimensional security protection applications involving the use of BCz-BP for color-coded and time-resolved applications. When excited with 365 nm ultraviolet irradiation, the ground part (light blue) of security letter 'π' was clearly recognized from the crystal part (yellow). After the excitation is turned off, only the crystal part (orange) of the letter 'π' can be observed.

Given that the pRTP of these molecules is apparent only in their crystalline state in the air, they are also unique mechanoluminochromic materials and different from the inorganic analogues.[15] Aside from the fluorescent emission color, the visible RTP of these materials is also mechano-responsive, making them promising smart materials for use in two-dimensional security protection with color-coded and time-resolved features (Figures 5 and S16). As shown in Figure 5, the transient emission of security letter 'π' (BCz-BP) contain two parts: the light blue ground part and the yellow crystal part under 365 nm ultraviolet excitation. In terms of its time-resolved feature, only the crystal part of letter 'π' was clearly observed by the naked eyes with an orange pRTP emission after the excitation lamp was turned off. When Cz-BP is used, the ground part will gradually convert back to crystal state when the sample was stored at room temperature for about 1 week, due to its low glass transition temperature (T_g = 33 ^{o}C) (Figures S16-17). This reversible process at room temperature without any other external stimuli makes BCz-BP a promising simple two-dimensional security protection material.

In summary, we have presented a new reasonable explanation for pRTP in organic materials, based on a combined experimental and theoretical investigation. In such a mechanism, the n and π sub-units that possess different excited state configurations couple intermolecularly in the crystal, and thereby combine their individual advantages. Therefore, the crystals exhibit not only a high ISC rate inherited from the n unit, but also a low radiative rate originating from the π unit, resulting in a hybrid ISC process to produce pRTP at ambient conditions. *This mechanism is clearly distinct from those proposed recently, and it may also be applicable to these molecules reported previously*. Consistent with this mechanism, we further demonstrate a molecular design strategy to obtain bright pRTP by simply incorporating a bromine atom in the conjugation of the n sub-unit to further increase the spin–orbit coupling ability of that unit. Bright long-lived RTP with high phosphorescence quantum efficiency of 5% and emission lifetime around 0.3 s was achieved for a pure organic compound. These results should promote new work on the rational design of new organic persistent RTP materials including studies on transition dipole orientation and intermolecular coupling, This, in turn, may lead to the development of the next-generation organic luminescent materials with innovative applications in electronic and photonic technologies.

Keywords: room-temperature phosphorescence • persistent • coupling • mechanical • security

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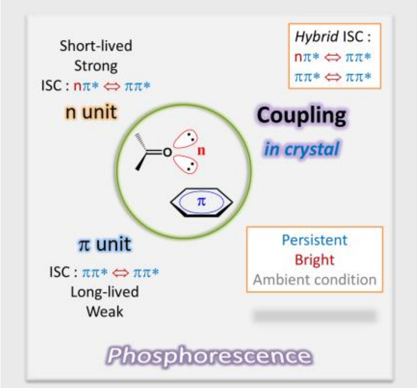
COMMUNICATION

Bright organic persistent room-temperature phosphorescence (RTP): Bright persistent RTP from pure organic molecules was achieved by coupling intermolecular units in crystals with intergated advantages of their different excited state configurations (i.e., nπ* state with a high intersystem crossing rate and ππ* state with a low radiative rate).



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