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Regulation of Thermally Activated Delayed Fluorescence to Room Temperature Phosphorescent Emission Channels by Controlling the Excited-States Dynamics via J- and H-Aggregation

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Abstract: Control of excited-state dynamics plays a central role in tuning room-temperature phosphorescence (RTP) and thermally activated delayed fluorescence (TADF) emissions, but remaining challenging in the exploration of organic luminescent materials (OLMs). Herein, we demonstrated the regulation of TADF and RTP emissions of a boron difluoride β-acetylnaphthalene chelate (βCBF₂) by controlling the excited-state dynamics via its J- and Haggregation states. Two crystalline polymorphs emitting green and red light have been controllably obtained. Although both belong to the monoclinic system, the green and red crystals are dominated by J- and H-aggregation, respectively, due to different molecular packing arrangements. Experimental and theoretical studies show that J-aggregation not only significantly reduces the energy gap between the lowest singlet and triplet excited states for the realization of ultra-fast reverse intersystem crossing (RISC) process. but also enhances the radiative decay of singlet, together leading to TADF. The H-aggregation accelerates the ISC and meanwhile suppresses the radiative decay of singlet, helping to stabilize the triplet exciton for RTP. These results deepen the understanding of the effect of aggregation on the luminescence mechanism of organic solids, and provide new strategy to tuning TADF and RTP OLMs.

Introduction

Organic luminescent materials (OLMs) have attracted extensive attention of researchers due to their unique electronic structures and optical properties.^[1] In particular, roomtemperature phosphorescence (RTP) and thermally activated delayed fluorescence (TADF) materials are of great importance for applications in organic light emitting diodes (OLEDs), sensors, bio-imaging and anti-counterfeiting agents.[2] Phosphorescence is generated through two consecutive intersystem crossing (ISC) steps, i.e., $S_1 \rightarrow T_1$ non-radiative ISC and $T_1 \rightarrow S_0$ radiative transition, which are both spin-forbidden processes. Differently, up-conversion from T_1 to S_1 through reverse intersystem crossing (RISC) gives rise to TADF. According to the perturbation theory, the rate of ISC (or RISC), $k_{\rm ISC(RISC)}$, is expressed by the equation (1),^[3]

$$k_{ISC(RISC)} \propto \zeta_{ST}^2 \exp\left(\frac{-\Delta E_{ST}}{k_B T}\right)$$
 (1)

where ξ_{ST} is the spin-orbit coupling (SOC) constant and ΔE_{ST} the energy gap between the involved singlet and triplet states, $k_{\rm B}$ is the Boltzmann constant, and T is temperature. In the past few years, several methods have been developed to achieve organic RTP: 1) introducing aromatic carbonyl groups, heteroatoms or heavy halogen atoms to improve the SOC constant ξ_{ST} thus to accelerate ISC:^[4] 2) using polymerization, metal-organic framework coordination, and formation of rigid crystals to effectively suppress the non-radiative decay of low-lying triplet excitons.^[5] In the meantime, the design of TADF emitters has been proposed mainly based on electron donor-acceptor (D-A) compounds, in which spatial separation of the highest occupied and the lowest unoccupied molecular orbital (HOMO and LUMO) effectively reduce the singlet-triplet splitting energy (ΔE_{ST}), therefore facilitating up-conversion of the dark triplet exciton to the luminescent singlet exciton through RISC.^[6] Compared to RTP, TADF requires fast RISC. That is, controlling of excitedstate dynamics plays a central role in tuning RTP and TADF emissions. This, however, remains challenging in the exploration of OLMS, owing to the limited understanding of luminescence mechanisms.

Note that researchers worked on RTP pursued persistent luminescence for and anti-counterfeiting imaging applications,^[2c,7] while those worked on TADF preferred to shorten the exciton lifetime in order to decrease the singlettriplet and triplet-triplet annihilation that leads to OLED efficiency roll-off and device degradation.^[8] Mostly, persistent RTP under ambient condition has been achieved in solid (crystalline) states by stabilization of the triplet state through H-aggregation and by prevention of the penetration of oxygen in the solid-state,^[2c,2e] whereas TADF has been demonstrated exclusively in the guesthost doping films. As a matter of fact, the relationship between the properties of TADF and aggregate states remain largely unexplored. Recently, Yang and co-workers demonstrated coexistence of TADF and RTP dual emission pathways in the crystal form, which are ascribed to separated monomer and dimer states, respectively.^[9] Chi and co-workers reported dynamical triplet-exciton behaviors arising from different conformers in multiple crystalline polymorphs, including RTP, TADF. mechanochromic luminescence (MCL). and mechanoresponsive luminescence (MRL).[10] It is widely accepted that molecular aggregates of different packing arrangements determine the photophysics of OLMs. Therefore,

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exploration of the role of molecular aggregates in controlling RTP and TADF emissions is highly important.^[11] In this paper, we realized the regulation of TADF and RTP properties through the polymorphism of organic molecules, and revealed the relationship between crystal stacking and triplet excitons. We have designed and synthesized a new molecule (E)-1-(((4nitrophenyl)imino)methyl)naphthalen-2-olate•BF2, named \(\beta\)CBF2, (Figure 1a), with the difluoroboron naphthalene as an electron donor (D) moiety and the nitrobenzene as an electron acceptor (A) moiety. Two crystalline polymorphs emitting green and red light have been controllably obtained. Although both belong to the monoclinic system, the green and red crystals are dominated by J- and H-aggregation, respectively, due to different molecular packing arrangements. Experimental and theoretical studies show that J-aggregation not only significantly reduces the energy gap between the lowest singlet and triplet excited states for the realization of RISC process, but also enhances the radiative decay of singlet for the realization of TADF. The Haggregation accelerates the ISC and meanwhile suppresses the radiative decay of singlet, helping to stabilize the triplet exciton for RTP. Our results provide insights into the modulation of TADF or RTP behavior through J- and H-aggregates.

Results and Discussion

The UV/Vis absorption and photoluminescence (PL) spectrum of βCBF_2 in dilute dichloromethane (DCM) solution (10⁻⁵ M) at room temperature are shown in Figure 1b. Table 1 summarizes the related photophysical data. The absorption spectrum (black line) display a strong absorption peak at 412 nm with molar extinction coefficient (ϵ = 13030 L M⁻¹ cm⁻¹, Figure S1), and a shoulder at 354 nm. The PL spectrum (green line) shows a structureless peak around 488 nm with a guantum yield ϕ = 40±1%. In order to further study the properties of excited states, we measured the time-resolved PL (TRPL) using a streak camera (see Figure S2). The PL at 488 nm exhibits a biexponential decay in air, with a short lifetime of 1.16 ± 0.012 ns and a long lifetime of 0.73 ± 0.03 µs, respectively (see the inset in Figure 1c also Figure S3a). Moreover, the prompt spectrum is similar to the delayed one (Figure S2), and both are identical to the steady-state PL spectrum (green line in Figure 1b). Therefore, the PL of βCBF_2 DCM solution exhibits TADF. Moreover, in the case of the de-oxygen conditions, the lifetime of the delayed component was extended to 7.83 ± 0.008 µs (green line in Figure 1c and Figure S3b), revealing the sensitivity of the triplet exciton to oxygen.

To further confirm the occurrence of TADF, we measured the temperature-dependent steady-state PL and TRPL. First of all, the PL intensity decreased significantly with the decrease of temperature (Figure S4a). And the PL intensity at 77 K is only about 1/5 of that at 298 K. Meanwhile, the long-lived component in the PL decay decreases with decreasing the temperature (Figure S4d and orange line in Figure 1c for 77 K), confirming the TADF observed at 298 K (green line in Figure 1c). The photophysical behavior of a thin-film with molecules doped in the polymethylmethacrylate (PMMA) matrix further confirmed the TADF properties (Figure S5). Note that the PL spectrum at 77 K exhibited multimodal emissions at 465, 488 nm and 590, 640 nm (orange line in Figure 1b and Figure S3b). The TRPL spectrum at 77 K on a nanosecond time scale shows an emission maximum approximately at 488 nm (green line in Figure S4c), which decays with a lifetime of 1.90 ± 0.015 ns (blue line in Figure 1d) and thus can be attributed to the fluorescence emission from S1 to S0. Furthermore, the TRPL spectrum recorded with a delay time of 10 ms presents the main emission peak at 590 nm and a shoulder at 640 nm (red line in Figure S4c), which decay with a lifetime as long as 976 µs (inset in Figure 1d) and is ascribed to the phosphorescent emission from T_1 to $S_0.$ Therefore, the S_1 and T_1 energies can be estimated from the fluorescence and phosphorescence spectra at 77 K and are determined to be 2.65 and 2.1 eV, respectively (Table 1), giving rise to a ΔE_{ST} as large as 0.55 eV. Note that such a large energy gap between S_1 and T_1 makes the RISC directly from T_1 to S₁ almost impossible. As shown below by theoretical calculation results, TADF of βCBF_2 in dilute DCM might be enabled by an ultra-fast RISC between high-lying T_n and S₁ states.[12]



Figure 1. a) Chemical structures of βCBF_2 . Inset show photographs of βCBF_2 solution in DCM under 365 nm ultraviolet lamp at room temperature and 77 K. b) Steady-state absorption and PL spectra of βCBF_2 in dilute DCM solutions. The green and orange lines represent PL spectra recorded at RT and 77 K. c) The PL decay of βCBF_2 in DCM without O₂ at RT (green line) and 77 K (orange line). Inset: PL decay curves of βCBF_2 :DCM solution in air at room temperature. d) PL decay and fitted curves of fluorescence at 488 nm (blue line) and phosphorescence at 590 nm (red line) at 77k. e) Energy level diagrams and spin–orbit coupling (SOC) constant for βCBF_2 . f) Hole-electron analysis (holes and electrons are shown in lilac and green, respectively) of the S₁, T₁, and T₂ for βCBF_2 in DCM based on the optimized geometries.

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Figure 2. a) PL spectra of green (green line) and red crystals (red line), respectively. Inset: photographs of the green and red crystals under UV excitation. b, c) Transient PL decay of green (b) and red crystals (c) at RT (blue line) and 77 K (red line). Inset: PL decay curve of fluorescence emission measured at 510 nm.

Table 1.	Photophysical	parameters of	βCBF ₂ monomers	in the dilute	solution and	l solid-state	aggregation
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Sample	<i>λ</i> ⊧ [nm]	$\lambda_{ m Phos}$ [nm]	<i>т</i> ⊧ [ns]	<i>τ</i> _{DF} [μs]	TPhos [µS]	<i>k</i> r [s ⁻¹] ^[b]	kisc [s ⁻¹] ^[b]	Es/ET [eV] ^[c]	$\Delta E_{\text{ST}} [eV]^{[d]}$	$arPhi_{pl}$ [%]
solution	488	590 ^[a]	1.16	0.73	976 ^[a]	2.04×10 ⁸	3.52×10 ⁸	2.54/2.10	0.44	40±1
green crystals	514	558	0.56	0.93	-)	3.04×10 ⁸	6.18×10 ⁸	2.41/2.22	0.19	26±1
red crystals	505	598	0.41	_	9 µs	6.31×10⁵	2.44×10 ⁹	2.45/2.07	0.38	2.8±1

[a] Phosphorescence spectra and lifetime measured at 77k. [b] k_r , and k_{SC} represent the rate constant of radiative (S₁ \rightarrow S₀), intersystem-crossing (ISC) rate constant (S₁ \rightarrow T₁), respectively. [c] Singlet (E_S) and triplet (E_T) energies estimated from the emission spectra at 77 K respectively. [d] Δ E_{ST} = E_S- E_T.

Density functional theory (DFT) and time-dependent DFT (TD-DFT) at B3LYP/6-31G(d) level combined with polarization continuum model (PCM) were used for theoretical calculation to explore the mechanism of TADF characteristics of βCBF_2 molecule. The ground-state structure exhibit a dihedral angle (θ) between the difluoroboron naphthalene plane and the nitrobenzene plane about θ = 36.9° (Table S1). And the calculated vertical energy is 3.09 eV, consistent with the absorption maximum at 412 nm. Upon geometry optimization, the adiabatic energies of S_1 and T_1 have been determined to be 2.60 and 1.94 eV (Figure 1e), corresponding well to $\lambda_{\rm F}$ = 488 nm (2.54 eV) and λ_{Phors} = 590 nm (2.10 eV) (see Table 1). These results validate the calculation methods adopted in our study. It can be seen from Figure 1e that there are two triplet excited states (T1 and T2) below S1. The adiabatic energy difference between S1 and T2 is only 0.11 eV, allowing the RISC process to occur between S_1 and T_2 . According to the analysis of the density distribution of "hole" and "particle" (Figure 1f), in the S₁ state, the hole distribution is mainly controlled by the naphthalene ring donor part, and the electron distribution is mainly located in the acceptor unit of nitrobenzene, exhibiting obvious CT excitation characteristics. This CT characteristic is further confirmed by the positive solvatochromism, i.e., the gradually red-shifted PL peaks with increasing the polarity of the solvents (Figure S6). In contrast, the T1 state is actually locally excited (LE) in nature. Notably, the T2 state demonstrates a coexistence of LE and CT features (HLECT), which is 0.11 eV lower than S₁ (see Figure 1f and Figure S7). Moreover, we found that S₁ and T₂ have similar geometric structures with $\theta = 26.4^{\circ}$

and 27.7°, respectively (Figure 1f and Table S1). The SOC value of 1.40 cm⁻¹ between S₁ and T₂ is much larger than that of 0.45 cm⁻¹ between S₁ and T₁ (Figure 1e). Therefore, we speculate that the effective RISC between T₂ \leftrightarrow S₁ is responsible for efficient TADF observed for β CBF₂ molecules in DCM.

What is interesting is that slow evaporation of the solution of βCBF₂ in DCM at 5 and 30 °C generates two polymorph singlecrystals (see the supporting information for the detailed process and Figure S8). Upon ultraviolet light (330-380 nm) excitation, these two polymorphs exhibit green and red emissions, as indicated by their μ -PL images of the insets of Figure 2a. Singlecrystal X-ray diffraction (XRD) measurements indicate that they belong to two different polymorph crystals (Figure S9). Figure 2a depicts the PL spectra of pure-phase green and red crystals. Compared with the PL spectrum of dilute solution, the PL of green crystals show a slightly red-shifted maximum at 514 nm with $\phi = 26\pm 1\%$ (Table 1).^[13] In sharp contrast, the PL of red crystals exhibit a maximum at 598 nm, which is very similar to the phosphorescence spectrum of the solution measured at 77 K (Figure S4b), together with a weak peak around 505 nm; meanwhile, the PL quantum yields is significantly reduced to ϕ = $2.8 \pm 1\%$

To verify the PL origin of the two crystals, we measured temperature-dependent PL and TRPL spectra. For comparison, their related photophysical parameters were also summarized in Table 1. Similar to the DCM solution, the PL of green crystals decays bi-exponentially with a prompt component of 0.56 ± 0.008 ns (inset in Figure 2b) and a delayed component of 0.93 ± 0.05 µs (blue line in Figure 2b). However, at 77 K, the delayed

component significantly reduced (Figure S10b and red line in Figure 2b); meanwhile, the PL intensity at 77 K decreases to about 1/2 of that at 298 K (Figure S10a). Therefore, the green crystals of β CBF₂ also exhibit TADF just like its dilute solution.^[14] Notably, the phosphorescence of green crystals measured at 77 K by setting a delay gate of 10 μ s was found at 558 nm with a lifetime of 0.05 \pm 0.008 ms (Figure S10c and d), giving rise to $\Delta E_{\text{S-T}} = 0.19$ eV, much smaller than that of monomers in the dilute solution (Table 1).

In sharp contrast, the red crystals exhibited distinct RTP phenomenon. As shown in Figure S12, the PL spectra of red crystals remain the same with decreasing the temperature, presenting a maximum around 598 nm; meanwhile, the PL intensity at 77 K is significantly enhanced about 15 times (peak top intensity) higher than that at 298 K (Figure S11a). It should be noted that these temperature-dependent behaviors observed for red crystals are completely different from characteristics of TADF. Furthermore, the PL lifetime at 77 K is determined to be 0.44 \pm 0.02 ms (red line in Figure 2c), longer than 9 \pm 0.8 μs at 298 K (blue line in Figure 2c). Therefore, the PL of red crystals around 598 nm originates from phosphorescence. Notably, the PL of red crystals also exhibit a very weak band around 505 nm, which does not exhibit long-lived component (Figure S12) and can be ascribed to fluorescence with a lifetime about 0.41±0.01 ns (inset of Figure 2c and Table 1). Therefore, the $\Delta E_{S-T} = 0.38$ eV of red crystal is larger than that of green crystal but smaller than that of the dilute solution (Table 1).



Figure 3. a, b) Single crystal structures of (a) green crystal and (b) red crystal. c, d) The molecular packing mode of (c) green crystal and (d) red crystal.

In order to understand the conversion mechanism between TADF and phosphorescence of βCBF_2 in different polymorph crystals, the single crystal structures were determined (CCDC Nos. 2045851 and 2045853). In the green crystal, βCBF_2 shows a highly twisted molecular conformation with $\theta = 40.4^{\circ}$ (Figure 3a), close to $\theta = 36.9^{\circ}$ optimized for S₀ in dilute solution. While in red crystal, βCBF_2 adopts a more planar conformation with $\theta = 19.8^{\circ}$ (Figure 3b), approximately similar to $\theta = 21.6^{\circ}$ optimized for T₁ in dilute solution. In both cases, there are abundant intermolecular interactions that solidify molecular conformations in green and red crystal, including $\pi \cdots \pi$ and X-H $\cdots \pi$ (X = B, F, O) interactions (Figure S14). It should be noted that the distorted molecular structure leads to loosely molecular packing in green

crystals that possess a density of (1.209 g /cm³), while planar structure give rise to tight molecular packing in red crystals as evidenced by a larger density of 1.536 g /cm³ (Table S2).

It is widely accepted that the optical and electronic properties of solid-state OLMs is significantly influenced by molecular aggregate states, which depend strongly on the molecular packing arrangement. The Kasha's exciton model represents a milestone, leading to often found descriptions of "head-to-tail" arrangement for J-aggregates and "face-to-face arrangement" for H-aggregates in literatures.^[15] As shown in Figure 3c and 3d, BCBF₂ molecules are packed in an antiparallel arrangement in both green and red crystals, forming dimer-like structures. In green crystals, owing to large twisted molecular conformation, the nitrobenzene units of the two molecules are anti-parallelly packed by face to face with a separation of 3.3 Å, while the difluoroboron naphthalene groups point to opposite directions without any overlapping (labeled as g-dimer, Figure S16), which seriously affects the π - π interaction between adjacent molecules. The longitudinal displacement between the two molecules is 4.99 Å (Figure S16), and the intermolecular center-to-center distances (d_{c-c}) is 8.84 Å (Figure S17). We then used the energy splitting method to calculate the exciton-coupling between neighbored molecules, which works well for identical molecular dimer.^[16] The sign of the coupling is determined by the relative orientation of the transition dipole moments within the selected molecular pair, that is, negative for J-type and positive for H-type couplings. According to our calculation results, the head-to-tail arrangement of g-dimer exhibit a negative exciton coupling of $\Delta \varepsilon = -16$ meV, which is dominant among total seven selected molecular pairs (Figure S18), suggesting moderate J-type coupling in green crystals. In sharp contrast, it can be seen from Figure 3d that in red crystals, planar BCBF2 molecules lead to anti-parallel packed dimers (labeled as r-dimer) with a π - π distance of 3.39 Å (Figure S19). And further crystal analysis revealed that the pitch angle was 90°, and there was no longitudinal displacement between adjacent molecules, showing typical H-aggregate characteristics (Figure S20). Indeed, the exciton coupling value of r-dimer is calculated to be positive ca. +91 meV, much larger than other selected dimers, indicating strong H-aggregation effect in red crystals (see Figure S21).

To model the effect of solid-state environment, the quantum mechanics/molecular mechanics (QM/MM) method was used to evaluate a single molecule (QM level) embedded in the crystal lattice, with the surrounding molecules defined as the rigid MM part (Figure S22 a and b). We found that the geometric changes of molecules in different electronic states (S_0 , S_1 and T_1) characterized by the root mean square displacement (RMSD) are quite small^[17], indicating small geometry relaxation owing to strong intermolecular interactions in crystals (Figure S22c).

Note that QM/MM method is not suitable for calculating high-lying triplet T_n states for large systems such as dimers. Therefore, DFT and TD-DFT-D3 calculations at B3LYP-D3/6-31g(d) level were performed to calculated the vertical energy levels of monomers and dimers extracted from green and red single-crystal structures. It can be seen from left panels of Figure 4a and 4b that both the calculated S₁ and T₁ energies of

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twisted g-monomer (θ = 40.4°) is blue-shifted than that of planar r-monomer (θ = 19.8°). This is consistent with the observation of λ_{Phors} of green crystal at 558 nm and λ_{Phors} of red crystal at 598 nm (Table 1). However, the calculated ΔE_{ST} between S₁ and T₁ are similar between g-monomer (0.92 eV) and r-monomer (1.02 eV).



Figure 4. a, b) The vertical energy levels for monomer and dimer of green (a) and red (b) based on TD-B3LYP-D3/6-31G(d) calculations in gas phase. c, d) Nature transition orbital analysis of S₁ state for the dimers of green (c) and red (g). e, f) Energy level diagrams for g-crystal (e) and r-crystal (f) emissions.

Figure 4c show the frontier molecular orbitals (FMOs) of the lowest singlet of green dimer. The hole and electron distributions of S1 are located on the difluoroboron naphthalene and the nitrobenzene parts, respectively, showing obvious CT feature. In sharp contrast to the delocalization of S₁ of the green dimer, hole and electron distributions of S1 are more localized and extended over the whole red dimer (Figure 4d), showing LE characteristics, also is T₁ (see Figure S25). As compared with those of monomers (left panels of Figure 4a and 4b), the energy level splitting in both g-dimer (right panel of Figure 4a) and rdimer (right panel of Figure 4b) caused by molecular aggregation significantly reduces the energy level of S1, but has little effect on T₁. Moreover, the calculated $\Delta E_{ST} = 0.48 \text{ eV}$ of gdimer between S₁ and T₁ is found to be smaller than that of ΔE_{ST} = 0.68 eV of r-dimer, consistent with the experimental results (Table 1). It should be noted that the number of high-lying triplet states between $\Delta E_{ST} \approx \pm 0.3$ ev increases in both the cases of gand r-dimers (Figure 4a and b), suggesting that more ISC channels are available in crystalline states. As a matter of fact, the $k_{\rm ISC}$ values of both g-crystal and r-crystal are faster that of the solution (Table 1). Therefore, consideration of only ISC and RISC processes cannot explain the distinct difference between TADF of g-crystal and RTP of r-crystal.

Remarkbly, the calculated emission oscillator strength (*f*) of S₁ states for g-dimer is 0.64, much larger than 0.006 for r-dimer, suggesting enhanced radiative decay in g-crystal and suppressed radiative decay in r-crystal according to the Einstein spontaneous emission expression of $k_{r,F} = f E_g^2/1.499$, where f is the dimensionless oscillator strength and E_g is the energy gap in units of cm⁻¹.^[18] It can be seen from Table 1 that the $k_{r,F}$ of g-crystal (3.04×10⁸ s⁻¹) is indeed much larger than that of r-crystal (6.31×10⁵ s⁻¹, Table 1), consistent with Kasha's theory. That is, H-aggregates can suppress fluorescence, which facilitates crossover between systems and enhances phosphorescence. On the contrary, J-aggregates are beneficial to fluorescence.^[19]

Based on the above discussion, we proposed energy diagrams of Figure 4e and 4f. The twisted molecular conformation induces the molecular arrangement of Jaggregates in the g-crystal. The formation of J aggregates significantly reduces ΔE_{ST} and accelerates the rate of radiative decay $k_{\rm r,F}$. The accelerated $k_{\rm r,F}$ deactivates those singlet excitons generated through RISC process enabled by small ΔE_{ST} , leading to TADF of g-crystal (Figure 4e). In sharp contrast, the nearly planar molecular structure results in H-aggregation in r-crystal (Figure 4f). Similar to the case of g-crystal, both ISC and RISC might be fast in r-crystal. [The large number of transition channels in r-crystal and related SOC values (0.65 cm⁻¹ for $S_1 \rightarrow$ T_4 , 0.26 cm⁻¹ for $S_1 \rightarrow T_6$, 0.33 cm⁻¹ for $S_1 \rightarrow T_8$, 0.93 cm⁻¹ for $S_1 \rightarrow$ T₁₀,) even lead to enhanced ISC (Figure S23).] However, even though the RISC process can take place, the suppressed radiative decay of H-aggregates recycles those delayed generated singlets into triplet manifold again via enhanced ISC, and subsequent Internal conversion within triplet manifold helps to stabilize T₁ states. Finally, large SOC value of 4.16 cm⁻¹ for T₁ \rightarrow S₀ leads to an increase in the radiation rate T₁ to S₀ and thus promotes phosphorescence emission in r-crystal (Figure 4f).

Conclusion

In summary, we demonstrated that the emission characteristics of TADF and RTP are affected by the aggregation state. We designed and synthesized a novel organic molecule BCBF2, and obtained green and red crystalline polymorphs through simple temperature control. Importantly, the two polymorphs exhibit different photophysical processes, i.e., green crystals exhibit TADF properties and red crystals shows the behavior of RTP. Single crystal data indicate that there are significant differences in the molecular stacking arrangements between the two types of polycrystalline, with green and red crystals dominated by J- and H- aggregates, respectively. Experimental and theoretical investigations further elucidate that J-aggregates can significantly reduce ΔE_{ST} to achieve ultra-fast RISC process, followed by enhanced radiative decay leading to TADF. The H-aggregates accelerate the ISC and meanwhile suppress the radiative decay of singlet, helping to stabilize the triplet exciton for RTP. These results deepen the understanding of the effect of aggregation on the luminescence mechanism, and provide new strategy to tuning TADF and RTP OLMs.

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J-aggregates significantly reduce the energy gap between the lowest singlet (S_1) and triplet (T_1) excited states and contribute to the reverse intersystem crossing (RISC) process; while H-aggregates will accelerate ISC and suppresses radiation transition of S_1 to realize phosphorescence. This provides crucial information for deeply understand of the internal mechanism of the excited state dynamics controlled by different aggregates.