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Crystallization-Induced Phosphorescence of Pure Organic Luminogens at Room Temperature

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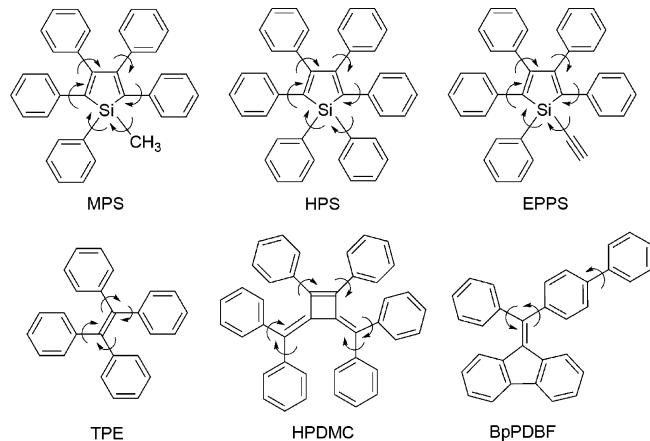
Phosphorescence has rarely been observed in pure organic chromophore systems at room temperature. We herein report efficient phosphorescence from the crystals of benzophenone and its derivatives with a general formula of $(X-C_6H_4)_2C=O$ ($X = F, Cl, Br$) as well as methyl 4-bromobenzoate and 4,4'-dibromobiphenyl under ambient conditions. These luminogens are all nonemissive when they are dissolved in good solvents, adsorbed on TLC plates, and doped into polymer films, because active intramolecular motions such as rotations and vibrations under these conditions effectively annihilate their triplet excitons via nonradiative relaxation channels. In the crystalline state, the intramolecular motions are restricted by the crystal lattices and intermolecular interactions, particularly $C-H \cdots O$, $N-H \cdots O$, $C-H \cdots X$ ($X = F, Cl, Br$), $C-Br \cdots Br-C$, and $C-H \cdots \pi$ hydrogen bonding. The physical constraints and multiple intermolecular interactions collectively lock the conformations of the luminogen molecules. This structural rigidification effect makes the luminogens highly phosphorescent in the crystalline state at room temperature.

Introduction

The development of efficient solid luminophores is a goal of intensive research because of their high application potentials in electronic and optic systems.¹ An obstacle to the development is the fact that many luminophores are highly emissive in dilute solutions but become weakly luminescent or even nonemissive when fabricated into solid films due to the formation of such detrimental species as excimers and exciplexes in the condensed phase.² This thorny problem of aggregation-caused quenching (ACQ) must be solved because luminophors are commonly used as thin films in their real-world applications. Although various chemical, physical, and engineering approaches have been taken to tackle the notorious ACQ effect,³ the attempts have met with only limited success. In most cases, aggregation was impeded partially or temporarily, due to the fact that aggregate formation is a natural process when luminogenic molecules are located in close vicinity in the condensed phase. It would be ideal if a system could be developed, in which emission of a luminophore is enhanced, rather than quenched, upon aggregation. In 2001, we observed an intriguing phenomenon of aggregation-induced emission (AIE): a series of silole molecules, such as 1-methyl-1,2,3,4,5-pentaphenylsilole (MPS; Chart 1), that were nonemissive in the dilute solutions were induced to emit efficiently by aggregate formation.⁴

In an effort to understand the working mechanism of the novel AIE process, we designed a series of experiments to examine

CHART 1: Examples of AIE Luminogens Developed in Our Laboratories



the effects of external and internal perturbations on the emission behaviors of the luminogens. It was found that the luminogenic molecules became more luminescent when their solutions were thickened (viscochromism) and cooled (thermochromism),⁵ their solids are pressurized (piezochromism)⁶ and crystallized (morphochromism),⁷ and their aromatic rotors are locked by covalent bonds or hindered by steric effects.⁸ All these results indicate that restriction to intramolecular motions (RIM) is the main cause for the AIE effect. Thus, in the solution state, the active intramolecular motions such as rotations and vibrations dissipate the energy of the excited states through nonradiative decay pathways, thus making the luminogens nonemissive. In the solid state, however, the intramolecular motions are impeded or the

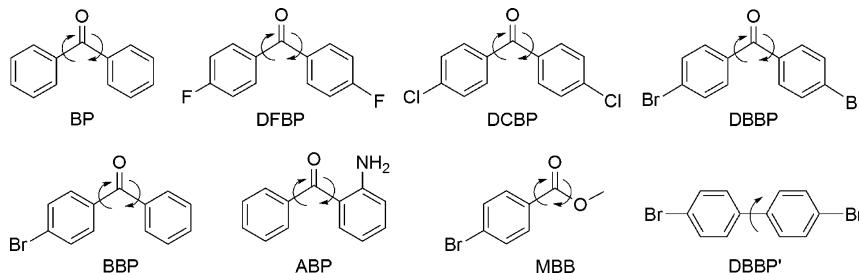
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CHART 2: Luminogens with CIP Characteristics Studied in This Work



RIM processes are activated, hence transforming the luminogens into strong emitters.⁴ On the basis of the mechanistic understanding, we developed a large variety of new AIE luminogens,⁹ representative examples of which are shown in Chart 1. Utilizing the useful AIE feature, we explored the applications of the luminogens in high-tech areas and found that they worked as active materials in the construction of organic light-emitting diodes (OLEDs),¹⁰ optically pumped lasers,¹¹ chemical sensors,¹² and bioimaging systems.¹³

The emissions from all the AIE luminogens developed by our laboratories so far are fluorescence in nature, with none of them being phosphorescence. This is understandable, because it is generally known that phosphorescence from pure organic chromophores is inefficient at room temperature.¹⁴ Although some organometallic, especially cyclometalated, complexes have been recently found to show efficient phosphorescence under ambient conditions,¹⁵ pure organic room temperature phosphors remain rare species.¹⁶ It has been proposed that this is due to the nonradiative decays of their long-lived triplet excited states caused by such detrimental processes as thermal perturbations, intramolecular motions, solute–solute and solute–solvent collisions, and intermolecular interactions with oxygen, humidity, etc. Phosphorescence from pure organic luminogens usually has been observed under conditions free of the interferences mentioned above, typically at cryogenic temperatures (e.g., 77 K) in rigid “glasses” of frozen solvents or mixtures of solvents (e.g., isopentane/methylcyclohexane mixture) in the atmosphere of inert gases (e.g., nitrogen).^{14,17}

During our program of developing new AIE luminogens, we have discovered a remarkable process of crystallization-induced emission (CIE),¹⁰ with the luminogens being only fluorescent in the crystalline state. Intramolecular motions in these luminogens remain active even in the amorphous phase and can only be suppressed by crystal packing arrangements, thus causing the novel CIE effect. Intramolecular motions are also a main cause for the nonphosphorescence nature of the organic luminogens whose singlet excited states have high probabilities to undergo intersystem crossing transitions to triplet excited states.¹⁴ It is envisioned that the nonradiative relaxation channels of the triplet excited states may be blocked by the RIM process in the crystalline state, thus offering the opportunity to develop pure organic luminogens with efficient phosphorescence at room temperature. Solid phosphors are currently in great demand, because according to the spin-statistic theory they can enable the fabrication of phosphorescent OLEDs with much higher device efficiencies, in comparison to those based on fluorophores. Different from organometallic complexes, organic compounds are easier to synthesize and more stable and their molecular structures are more readily tunable through simple chemical transformations. With these considerations in mind, we embarked on a project of extending the AIE system from fluorescence to phosphorescence and developing organic phosphors in the aggregate state under ambient conditions.

In this work, we investigated luminescence behaviors of a series of “simple” aromatic compounds, particularly benzophenone (BP) derivatives, containing heavy halogen atoms, whose excitons are known to have high probabilities to undergo $S_1 \rightarrow T_1$ transitions (Chart 2). These luminogens are all nonemissive in dilute solutions and as amorphous films but are induced to phosphoresce efficiently at room temperature by crystal formation, thus showing an incredible phenomenon of “crystallization-induced phosphorescence” (CIP). The phenomenon is general and the phosphorescence nature of the emissions is verified by the long lifetimes of the excitons ($\langle\tau\rangle$ up to 4.8 ms). Through detailed crystal structure analyses, the CIP effect is proven to be caused by the RIM processes aided by the physical confinements in the crystalline lattices and the multiple intermolecular interactions, especially the various kinds of special hydrogen bonds, between the luminogenic molecules. The CIP processes of the luminogenic molecules are stable to oxygen and humidity, which rules out these interferences as being the causes for the deactivation of their triplet excitons and makes the CIP effect practically useful.

Experimental Section

Materials. Tetrahydrofuran (THF) and toluene were distilled from sodium benzophenone ketyl and dichloromethane (DCM) was distilled over calcium hydride under nitrogen immediately prior to use. *n*-Hexane, acetonitrile, and ethanol were analytical grades and were used without further purification. BP and its derivatives 4,4'-difluorobenzophenone (DFBP), 4,4'-dichlorobenzophenone (DCBP), 4,4'-dibromobenzophenone (DBBP), 4-bromobenzophenone (BBP), and 2-aminobenzophenone (ABP), as well as 4,4'-dibromobiphenyl (DBBP'), 4-bromobenzoic acid, and poly(methyl methacrylate) (PMMA), were all purchased from Aldrich. Methyl 4-bromobenzoate (MBB) was prepared by esterification of 4-bromobenzoic acid with methanol. Crystals of the luminogenic compounds were grown in common organic solvents, such as ethanol, DCM, and *n*-hexane. The crystallographic data for all the luminogenic molecules were retrieved from the Cambridge Crystallographic Data Center (CCDC) free of charge.¹⁸

Instrumentations. Absorption spectra were measured on a Milton Roy Spectronic 3000 Array spectrophotometer and photoluminescence (PL) spectra were recorded on a Perkin-Elmer LS 55 spectrofluorometer with Xenon discharge lamp excitation. Time-resolved PL spectra were obtained on a Laserstrobe fluorescence lifetime spectrometer (Edinburgh Instruments, FLS920). PL quantum yields (Φ) of the luminogens were estimated in acetonitrile solutions (1 μ M) with 9,10-diphenylanthracene as standard ($\Phi = 90\%$ in cyclohexane) and determined in the crystalline state with a calibrated integrating sphere. Luminogen-doped PMMA film was prepared by dissolving 5 mmol of a luminogen compound and 500 mg of PMMA in 10 mL of THF followed by casting the resulting solution onto the surface of a quartz cell. After slow evaporation

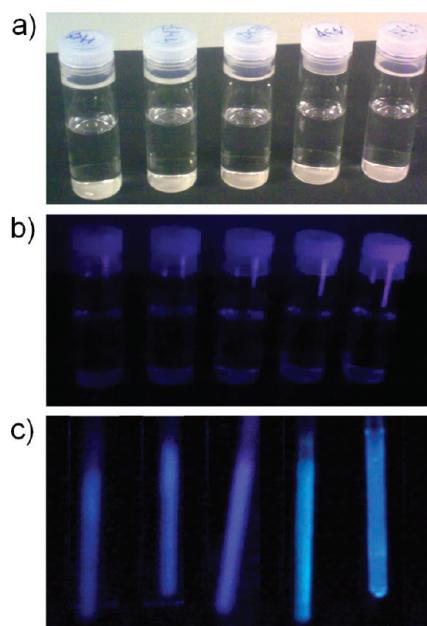


Figure 1. Photographs of BP solutions in different solvents taken under (a) normal laboratory lighting and (b and c) 365 nm UV light illumination at (a and b) room temperature and (c) 77 K. Concentration (c): 0.2 mg/mL. Solvent (from left to right): *n*-hexane, THF, DCM, acetonitrile, ethanol. Solutions shown in panel c are in NMR tubes.

of the solvent, the film was further dried at 40 °C in a vacuum oven for 12 h before it was used for PL measurement.

Results and Discussion

CIP Activity of BP. In our search for pure organic luminogens with CIP feature at room temperature, we chose BP, a typical phosphor at low temperatures¹⁹ with an intersystem crossing efficiency of almost unity,²⁰ for initial test. We first examined whether BP was luminescent in the solution state. Different nonpolar or polar and aprotic or protic solvents, such as *n*-hexane, THF, DCM, chloroform, acetonitrile, and ethanol, were used to prepare the BP solutions. In none of the solutions, however, was BP found to be luminescent at room temperature. Figure 1 shows the photographs of BP in various solvents under different conditions. The solutions of BP are transparent and emit no light upon photoexcitation at room temperature (Figure 1, panels a and b). In sharp contrast, when cooled by liquid nitrogen to 77 K, the solutions become highly emissive under illumination of 365-nm UV light (Figure 1c). Evidently, the phosphorescence of BP is turned on by freezing its molecular motions at the cryogenic temperature.

We then checked whether BP was luminescent when it had been adsorbed on a plate of thin-layer chromatography (TLC) but saw no light emitted from the BP-adsorbed TLC plate. During our study of AIE systems, we have found that some luminogenic molecules, such as HPS, HPDMC, and BpPDBF (cf., Chart 1), show the CIE effect.^{10,21} An amorphous film of BpPDBF, for example, emits a faint yellow light of 550 nm but its crystals emit a bright blue light of 450 nm in a 32-fold higher efficiency.²⁰ Tolbert²² and Wang²³ have also observed similar CIE phenomena in their systems and shown that the CIE effect is associated with specific intermolecular interactions in the crystalline state. Inspired by the CIE effect, we examined emission of the BP crystals. Excitingly, the crystals of BP emitted a strong blue light at room temperature (Figure 2b)! In other words, the phosphorescence of BP is rejuvenated by crystal formation. The above results imply that in the solution state

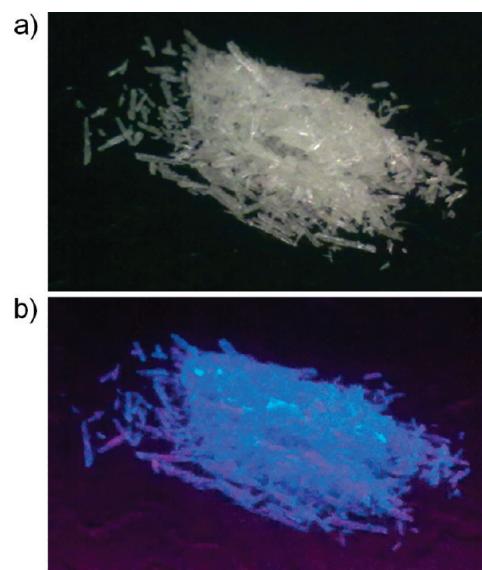


Figure 2. Photographs of crystals of BP taken under (a) laboratory lighting and (b) UV illumination at room temperature.

and on the TLC plate, the BP molecules can undergo active intramolecular motions that cause nonradiative decays of their excitons. In the crystalline phase, the intramolecular motions are restricted or the molecular conformations are locked by the ordered molecular packing lattices. This RIM process endows BP with CIP activity and turns on its phosphorescence emission at room temperature.

To gather more information about the CIP process and to gain mechanistic insights into its origin, we measured the PL spectra of BP by a spectrometer. Figure 3a shows the PL spectra of a dilute solution of BP in THF at different temperatures and its crystals under ambient conditions. Intense PL signals are collected from the BP crystals at room temperature, whereas the PL spectrum in the THF solution is so weak that it is basically a flat line parallel to the abscissa.²⁴ To examine the details, the spectrum is greatly magnified, from which it is seen that BP emits weak fluorescence at 310 and 380 nm in the THF solution. When cooled to 77 K, besides the “old” fluorescence signal at 310 nm, three new peaks corresponding to phosphorescence emission emerged at 410, 440, and 472 nm.²⁵ In other words, BP emits both fluorescence and phosphorescence at 77 K. No fluorescence signals at wavelengths shorter than 380 nm, however, are detected in the crystals of BP and its PL spectrum displays peaks at 420, 449, and 483 nm, which match well with those of the cooled THF solution. To confirm the phosphorescence nature of the BP emission in the crystalline state, we investigated its PL spectral decay behavior using a time-resolved technique. As shown in Figure 3b, the emission of the BP crystals decays through three relaxation pathways with a mean lifetime ($\langle \tau \rangle$) as long as 316.5 μ s, verifying that emission originates from the radiative decay of triplet excited states.

For almost all the AIE luminogens, their light emissions can be turned on by doping them into films of polymers such as PMMA, due to the activation of the RIM process in the solid state.⁹ We carried out a solid-state “dilution” experiment to see whether BP would become luminescent when its molecules had been doped into a PMMA film. No light, however, is emitted from the BP-doped polymer film at room temperature (Figure 4), suggesting that the triplet excited states are highly sensitive to the intramolecular motions, although such motions should be weakened after the luminogenic molecules have been doped into the solid matrix. The film becomes phosphorescent when

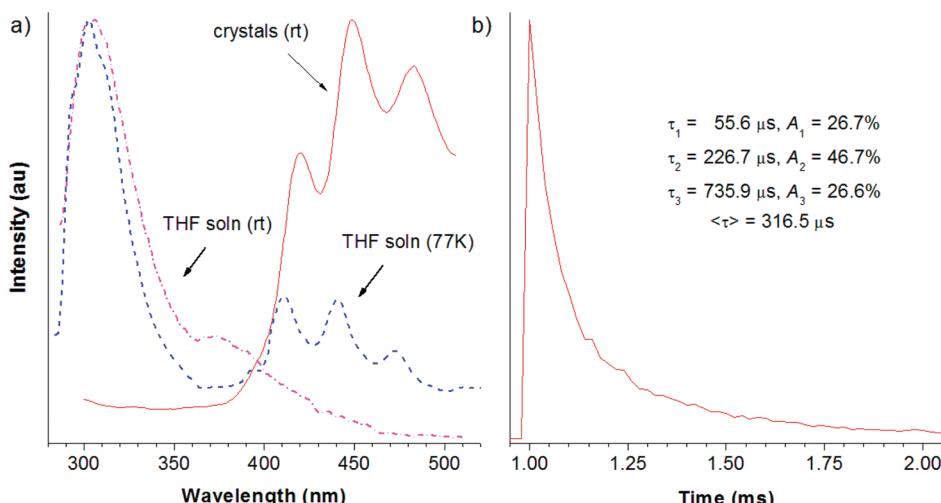


Figure 3. (a) PL spectra of BP in the THF solution and crystalline state at room temperature and 77 K. Luminogen concentration (c): 1 μM . Excitation wavelength (λ_{ex}): 270 nm. The original spectrum in the THF solution at room temperature was extremely weak and the spectrum shown here has been greatly magnified to make it visible. (b) Phosphorescence decay curve of BP crystals at room temperature.

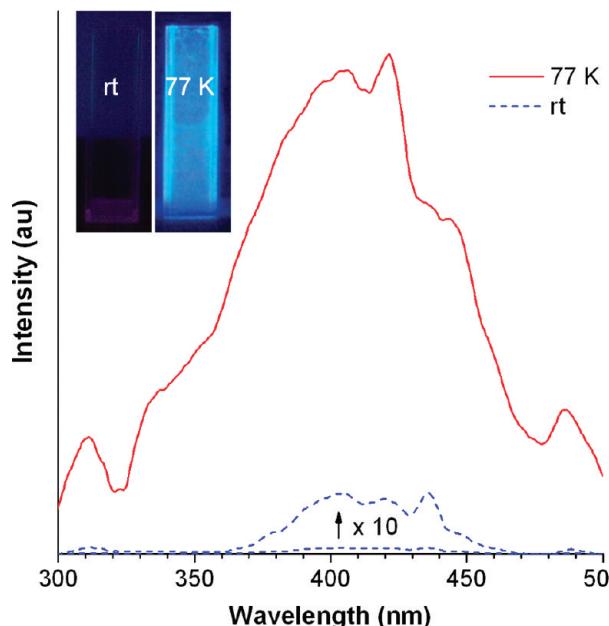


Figure 4. PL spectra of BP-doped PMMA film at room temperature and 77 K. Inset: Photographs of the BP-doped polymer films on quartz cells at room temperature and 77 K taken under UV illumination.

it is cooled to 77 K, verifying that it is the conformation rigidification and the associated RIM process that has played a decisive role in making BP phosphorescent at the cryogenic temperature.

The result of the polymer doping experiment is similar to that observed on the TLC plate, indicating that intramolecular motions in the BP molecules have not been completely suppressed in the amorphous state. The BP crystals are strongly phosphorescent at room temperature, implying that there exist some special interactions in the crystalline state to aid the RIM process. To address this issue, we scrutinized the crystal structure of BP. Figure 5 shows part of the packing arrangements of BP molecules in the crystalline state. Two benzene rings between two adjacent BP molecules are linked by two nonclassic C–H \cdots O hydrogen bonds. The hydrogen bonds extend over the whole crystal structure and the multiple intermolecular interactions help lock the molecular conformations. The thus stabilized conformations are resistant to intramolecular motions

induced by the thermal agitation. This structural stiffening effect populates the radiative decays of the triplet excitons, thus making BP crystals phosphorescent at room temperature.

Phosphorescence of DFBP. It is well-known that heavy atoms are helpful to $S_1 \rightarrow T_1$ transition.²⁶ It is thus conjectured that halogenated BP derivatives are CIP active. To verify this assumption, we first investigated the light emission behaviors of DFBP, a BP derivative carrying two fluorine atoms at the 4,4'-positions. Figure 6 shows the photographs of DFBP solutions in different solvents taken under normal laboratory lighting and 365-nm UV light illumination. Similar to its BP parent, DFBP is nonemissive in solutions at room temperature but becomes luminescent when its solutions are cooled to 77 K by liquid nitrogen. The “lighting up” of the phosphorescence is ascribed to the rigidification of the molecular conformation and the activation of the RIM process in the frozen “glasses” of the organic solvents.

The emission of the crystals of DFBP is then examined. As shown in Figure 7, its tabular crystals are strongly emissive under UV illumination. The PL behaviors of DFBP are similar to those of its parent form BP. Thus, the magnified PL spectrum of a dilute solution of DFBP in THF at room temperature²⁴ shows a peak at around 302 nm along with a shoulder at 375 nm (Supporting Information, Figure S1), which should be associated with the radiative decay of its singlet excited states. When the solution is cooled to 77 K, new phosphorescence peaks emerge in the visible spectral region at 414, 444, and 476 nm, besides the fluorescence peak in the UV region at 302 nm. The spectrum of the DFBP crystals exhibits no signal at 302 nm but displays strong phosphorescence peaks at 409, 437, and 467 nm. Time-resolved PL measurement reveals long-lived excited states with a $\langle \tau \rangle$ value as long as 1.3 ms, indicative of the phosphorescence nature of the light emission.

The emission behaviors of DFBP doped into PMMA films and adsorbed on TLC plates were also studied. While the DFBP-doped polymer film is nonemissive at room temperature, it emits a blue light at a low temperature of 77 K, whose intensity is 96-fold higher than that at room temperature (Figure 8a). The DFBP-adsorbed TLC plates were prepared by spotting tiny amounts of a THF solution of DFBP ($c = 0.2 \text{ mg/mL}$) onto the plates, using glass capillaries. By varying the spotting times, e.g., one time for spot A and six times for spot B, spots with different amounts of DFBP adsorbed on a TLC plate are formed,

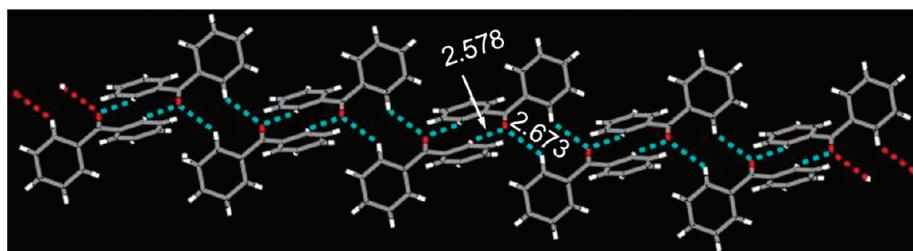


Figure 5. Perspective view of molecular packing arrangement in the crystal of BP, with the C–H...O hydrogen bonds marked by dotted lines.

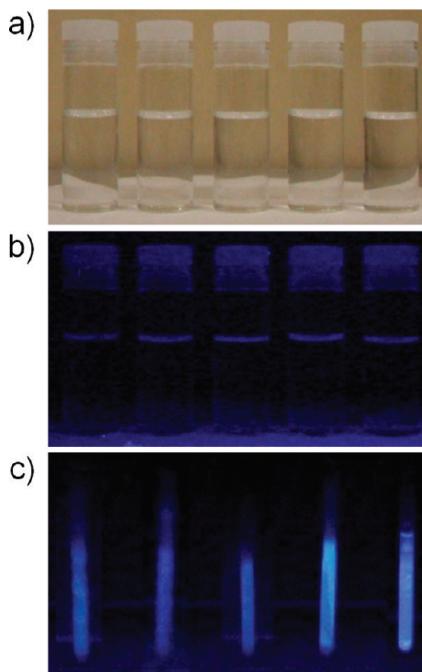


Figure 6. Photographs of DFBP solutions in different solvents taken under (a) normal laboratory lighting and (b and c) UV light illumination at (a and b) room temperature and (c) 77 K. $c = 0.2 \text{ mg/mL}$. Solvent (left to right): *n*-hexane, THF, DCM, acetonitrile, ethanol. Solutions shown in panel c are in NMR tubes.

as visualized under 254-nm UV illumination (Figure 8B, upper panel). When illuminated with a 365-nm UV light, spot A is invisible, whereas the outer rim of spot B is emissive. Both spots become luminescent when the plate is cooled to 77 K. The whole spot A and the inner core of spot B return to the nonemissive state when the plate is warmed to room temperature. The nonphosphorescent nature of the DFBP molecules at room temperature dispersed in the PMMA film and on the TLC plate suggests that the luminogen molecules are still undergoing intramolecular motions in the solid “solutions”, which consumes the energy of the excitons through nonradiative channels. The thermally activated molecular motions are effectively suppressed by the cooling process, thus making the DFBP spots emissive at the cryogenic temperature. Increasing the spotting times results in accumulation of more DFBP molecules and formation of microcrystals at the outer edge of the spot (B). Because intramolecular motions are restricted in the crystallites, this part becomes phosphorescent at room temperature.

Figure 9 shows the partial view of crystal packing of DFBP. Similar to the case of the BP crystal, there exist multiple nonclassic intermolecular C–H...O hydrogen bonds in the DFBP crystal. In addition, C–H...F interaction, another kind of special hydrogen bond, is involved in the packing arrange-

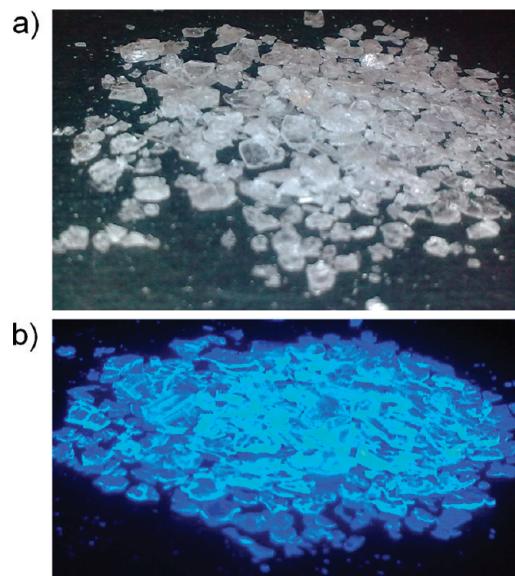


Figure 7. Photographs of crystals of DFBP taken under (a) normal laboratory lighting and (b) UV illumination at room temperature.

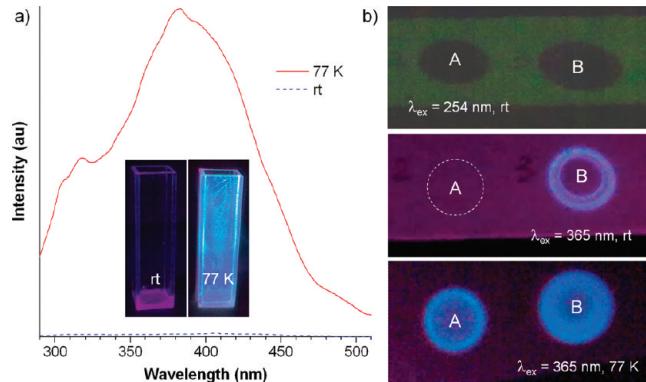


Figure 8. (a) PL spectra of DFBP in PMMA films at room temperature and 77 K. $\lambda_{\text{ex}} = 270 \text{ nm}$. Inset: Photographs of polymer films of BP coated on quartz cells taken under 365-nm UV light illumination at room temperature and 77 K. (b) Photographs of DFBP adsorbed on TLC plates taken under (upper panel) 254- and (middle and lower panels) 365-nm UV light irradiations at (upper and middle panels) room temperature and (lower panel) 77 K.

ment of the crystal.²⁷ The multiple C–H...O and C–H...F hydrogen bond interactions collectively rigidify the conformations of the DFBP molecules. This structural stiffening effect obstructs the photonic energy of the triplet excited states from being consumed by the thermal relaxation processes, thus enhancing the phosphorescence of the DFBP crystal at room temperature.

Owing to the long lifetime of the triplet excited state, the phosphorescence process has been reported to be extremely sensitive to many external perturbations, particularly oxygen²⁸

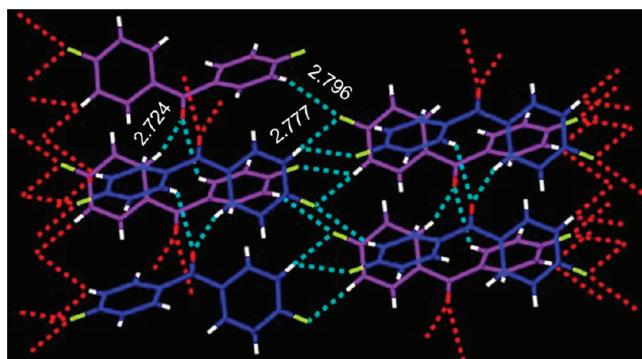


Figure 9. Perspective view of molecular packing arrangement in DFBP crystal. Cyan dotted lines denote intermolecular interactions, and red dotted lines denote suspended contacts.

and humidity.²⁹ In the DFBP-doped PMMA film, the luminogens are molecularly dispersed and are physically shielded and protected from the attacks from oxygen and water by the polymer matrix. However, the luminogen is still nonemissive at room temperature.³⁰ Furthermore, its spots adsorbed on the TLC plates remain incapable of emitting light even after they have been placed under a nitrogen atmosphere. On the contrary, the fine powders obtained by crushing the big crystals of DFBP remain luminescent even after they have been exposed to oxygen and immersed in water. Similar phenomena are observed in the case of BP. These results suggest that the light emissions of the phosphors are not quenched by molecular collisions, oxygen, and humidity but intramolecular motions at room temperature, noticing that the luminogens are comprised of rotatable phenyl blades (cf., Chart 2).

Other BP Derivatives. The CIP behavior of DFBP prompted us to check the emission properties of other halogen-containing BPs, such as DCBP, DBBP, and BBP (cf., Chart 2). We delightfully found that they were all CIP active. The ordered packing arrangements and strong intermolecular interactions in the crystals of these luminogens should be responsible for their phosphorescence emissions at room temperature. As to be elaborated below, the intermolecular interactions in the crystals are associated with different kinds of special hydrogen bonds. A natural question is then whether a BP derivative whose molecules form “classic” hydrogen bonds in the crystalline state would be phosphorescent. ABP (Chart 2) is a good example to test this idea, because its molecules can form classic intermolecular N–H \cdots O hydrogen bonds. The emission and lifetime measurements reveal that ABP is CIP active, thus proving that all kinds of hydrogen bonds are helpful to make the crystal of a luminogen phosphorescent under ambient conditions.

Figure 10 shows the photographs of the crystals of DCBP, DBBP, BBP, and ABP taken under room lighting and 365-nm UV irradiation. DCBP and DBBP emit orange lights upon photoexcitation, due to their heavier halogen atoms, in comparison to the lighter fluorine atom in DFBP. Blue and bluish-green lights are emitted from BBP and ABP crystals, respectively. The emission of ABP is red-shifted from that of BBP, owing to the push–pull interaction between the donor (NH_2) and acceptor ($\text{C}=\text{O}$) groups in ABP. It should be stressed that none of the luminogens are phosphorescent when they are dissolved in good solvents or adsorbed on TLC plates at room temperature.

Figure S2a in the Supporting Information shows the PL spectra of DCBP, DBBP, BBP, and ABP in the solution and crystalline states. In the THF solutions, all the spectra share similar profiles with emission peaks at 299 and 346 nm,

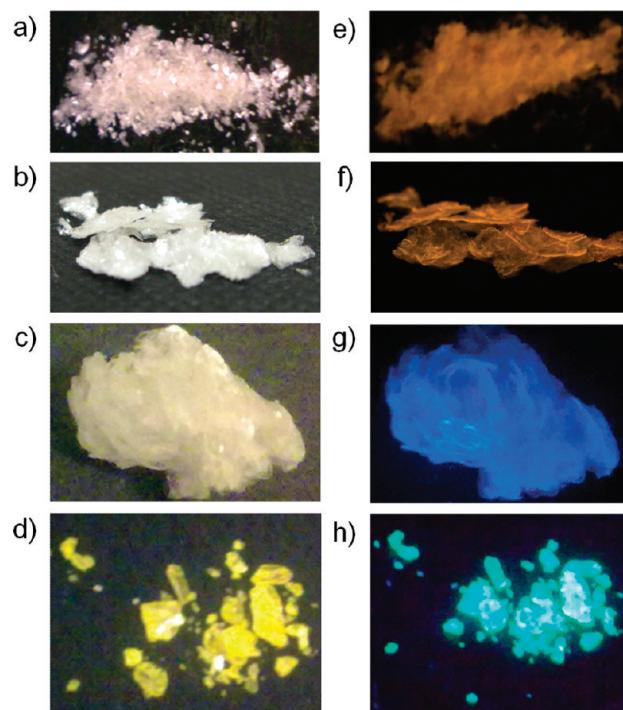


Figure 10. Photographs of crystals of DCBP, DBBP, BBP, and ABP taken under (a–d) normal laboratory lighting and (e–h) 365-nm UV light illumination at room temperature.

regardless of the molecular structures of the luminogens. The crystals of the luminogens, however, behave differently. The DCBP, DBBP, and BBP crystals emit both fluorescence in the UV spectral region and phosphorescence in the visible spectral region. The phosphorescence peaks are affected by the halogen substituents. The luminogen with one bromo substituent (BBP) shows phosphorescence peaks at 421, 450, and 482 nm, while the emissions from DCBP and DBBP that have two chlorine and bromine substituents are peaked at 421, 448, 483, and 517 nm and 428, 457, 486, 495, and 535 nm, respectively. On the other hand, ABP gives only a phosphorescence peak at 479 nm. The triplet excited states of the luminogens are long-lived (Figure S2b, Supporting Information), with longest lifetime achieved by DBBP (τ up to \sim 15 ms).

Figure 11 shows the packing arrangements in the crystals of DCBP, DBBP, BBP, and ABP. Similar to BP and DFBP, all the luminogens adopt twisted molecular conformations, which are locked by various intermolecular forces. Besides C–H \cdots O hydrogen bonds, there exist special C–H \cdots X ($\text{X} = \text{Cl}, \text{Br}$)³¹ and C–Br \cdots Br–C³² interactions in the crystals of the halogen-substituted BPs. C–H \cdots Cl and C–H \cdots Br hydrogen bonds with distances of 2.895, 2.939, and 3.236 Å are observed in the crystals of DCBP and BBP, while C–Br \cdots Br–C interconnect with a distance of 3.788 Å and an angle of 153.81° is seen in the crystal of DBBP. Intermolecular N–H \cdots O hydrogen bonds with a distance of 2.118 Å are formed in the crystal of ABP, thanks to its amino group. These attractive intermolecular forces rigidify the molecular conformations, which accounts for the strong phosphorescence of the crystals of the BP derivatives at room temperature.

Other Luminogenic Systems. The CIP effects of BP and its halogenated derivatives manifest that the carbonyl group and the heavy atom are important structural parameters that make them phosphorescent. The nonplanar molecular conformation of the BP derivatives is another factor that favors the spin–orbit coupling and promotes the phosphorescence process. Keeping

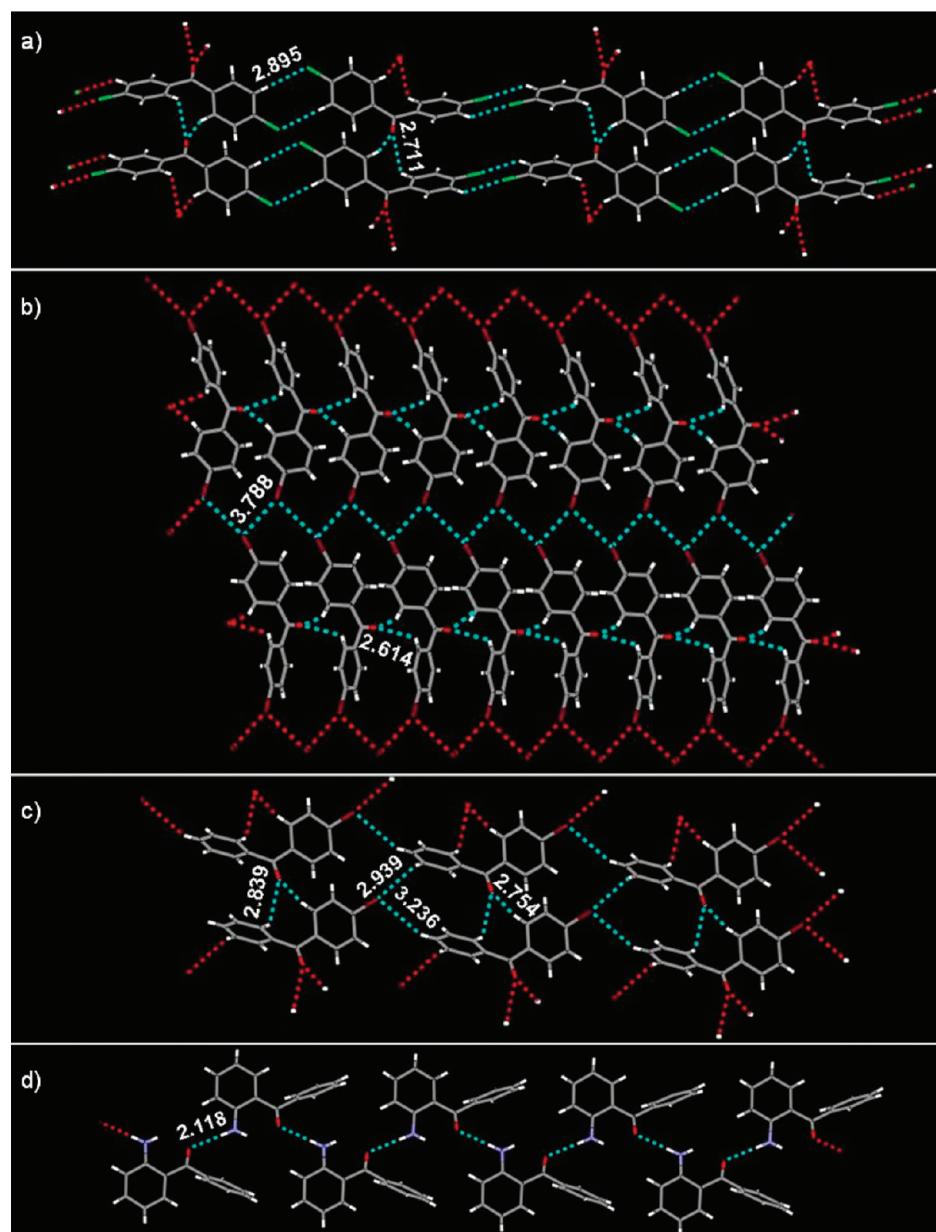


Figure 11. Perspective view of packing arrangement in crystals of (a) DCBP, (b) DBBP, (c) BBP, and (d) ABP, with C—H \cdots O, C—H \cdots Cl, C—Br \cdots Br—C, C—H \cdots Br, and N—H \cdots O intermolecular interactions marked by dotted lines.

these structural features (carbonyl group, heavy atom, and nonplanar conformation) in mind, we searched for potential CIP luminogens other than BP derivatives. MBB and DBBP' (cf. Chart 2) are not BP derivatives but possess part of the structural features discussed above. Delightfully, both of them are luminescent in the crystalline state, although their dilute solutions and adsorbed TLC plates are nonemissive. Measurements of their time-resolved PL spectra reveal long-lived excited states, confirming the phosphorescence nature of the emissions. Figure 12 shows the photographs of the crystals of MBB and DBBP' taken under ambient conditions. The crystals look pure white under normal room lightning but emit strong green lights upon 365-nm UV irradiation.

Figure S3a in the Supporting Information shows the PL spectra of MBB and DBBP' in the solution and crystalline states at room temperature. The spectra of their THF solutions contain only fluorescence signals in the UV region. Their crystals, however, emit in both the UV and the visible region, with their PL spectra dominated by the emissions in the long wavelength

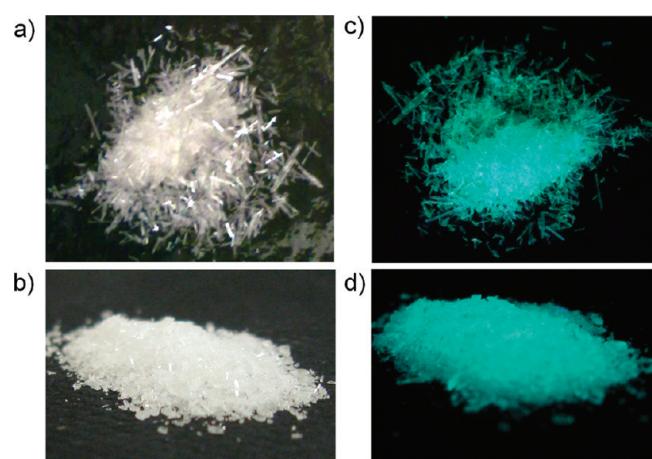


Figure 12. Photographs of crystals of MBB and DBBP' taken under (a and b) normal laboratory lighting and (c and d) UV light illumination at room temperature.

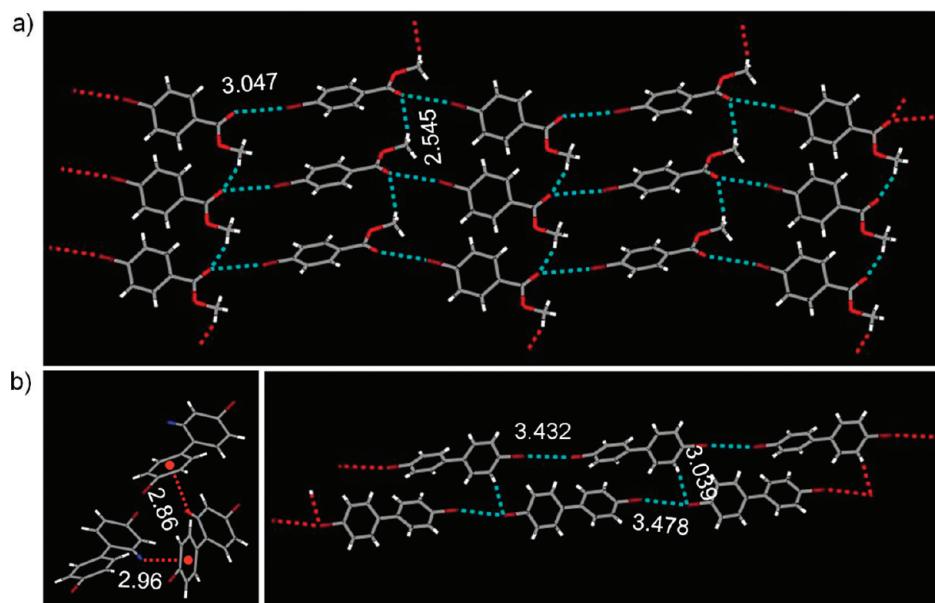


Figure 13. Perspective view of molecular packing arrangement in crystals of (a) MBB and (b and c) DBBP', with (a) C—H \cdots O and C=O \cdots Br—C and (b) (left) C—H \cdots π and (right) C—Br \cdots Br—C and C—H \cdots Br intermolecular interactions marked by dotted lines.

TABLE 1: Photophysical Properties of CIP Luminogens^a

compd	λ_{ab} (nm)	λ_{em} (nm)	Φ (%) ^b		phosphorescence decay ^c			
			soln	cryst	A_1 (%)/ τ_1 (μ s)	A_2 (%)/ τ_2 (μ s)	A_3 (%)/ τ_3 (μ s)	$\langle \tau \rangle$ (μ s)
BP	269	420, 449, 483	0.001	15.9	27/55.6	47/226.7	26/735.9	312.9
DFBP	259	409, 436, 467	0.003	39.7	56/660.4	44/2107.1		1296.9
DCBP	266	421, 448, 483, 517	0.091	8.30	99.5/16.8	0.5/488.5		19.2
DBBP	268	428, 457, 486, 535	0.565	12.0	79/2127.8	21/14855.2		4800.6
BBP	263	421, 450, 482	0.010	6.70	18/25.1	44/66.2	38/156.3	93.0
ABP	236	479	0.001	8.60	39/24.5	61/220		143.8
MBB	243	338, 476, 504	0.044	5.90	76/585.2	24/11991.7		3322.8
DBBP'	269	480	0.001	13.9	57/240.4	43/1555.9		806.1

^a Abbreviations: λ_{ab} = absorption maximum, λ_{em} = emission maximum, Φ = quantum yield, soln = solution, cryst = crystal, A = molecular fraction, τ = phosphorescence lifetime, and $\langle \tau \rangle$ = mean lifetime. ^b Determined in acetonitrile solution (1 μ M) with 9,10-diphenylanthracene as standard (Φ = 90% in cyclohexane) or in crystalline state with a calibrated integrating sphere. ^c Measured in the crystalline state.

region. The emissions in the visible spectral region are from the triplet excitons, as proved by the data from the time-resolved PL measurements. As shown in Figure S3b (Supporting Information), the excited states of the MBB and DBBP' crystals slowly decay in a double-exponential manner, with mean lifetimes of 3.28 ms and 808.7 μ s, respectively.

As can be seen from Figure 13a, the conformations of MBB molecules are locked and stabilized by the multiple C—H \cdots O ($d = 2.545$ \AA) and C=O \cdots Br—C ($d = 3.047$ \AA) intermolecular interactions³³ in the crystal packing arrangement. In the crystal of DBBP', there exist not only multiple C—H \cdots π hydrogen bonds but also C—Br \cdots Br—C and C—H \cdots Br interactions between the luminogen molecules (Figure 13b), which work cooperatively to hamper the phenyl rings from undergoing conformational changes. Thus, similar to the cases of BP derivatives, the structural rigidification effect reinforced by the multiple special hydrogen bonds between the MBB and DBBP' molecules in the crystals blocks the nonradiative decay channels and enables the luminogens to phosphoresce efficiently under ambient condition.

To make a quantitative comparison between the CIP-active luminogens, we measured their Φ values in acetonitrile solutions using 9,10-diphenylanthracene as standard and in the crystalline state using a calibrated integrating sphere. The efficiency data are summarized in Table 1. The Φ values for all the luminogens in acetonitrile are extremely low (down to 0.001%), indicative

of their nonluminescent nature in the solution state. In the crystalline state, their Φ values are increased dramatically. While the crystal of BP shows a Φ value of \sim 16%, its fluorinated derivative (DFBP) enjoys the highest Φ value (\sim 40%) among all the studied BP derivatives. It is remarkable that the Φ value of the DFBP crystal is 4 orders of magnitude higher than that of its solution! The quantum yields of MBB and DBBP' crystals are \sim 6% and \sim 14%, respectively, which are \sim 140- and \sim 14 000-fold higher than those in the acetonitrile solutions. Although it is technically difficult to obtain well-resolved absorption spectra of the crystals, the differences between the absorption maxima of the luminogens in the solution state and their emission peaks in the crystalline state are all very large (up to 267 nm), which serves as a proof for the phosphorescence nature of the light emissions.

The phosphorescence nature of the light emissions is further substantiated by the long lifetimes of the excited states. Although the PL signals of the luminogen crystals decay in different manners (double or triple exponential), most of the decay components are in the time scale of microseconds, with some being even in the millisecond region. This excludes the possibility of the emission being fluorescence, because singlet excitons generally decay in much shorter time scale (nanoseconds). The mean lifetime for the triplet excited states of BP is \sim 213 μ s, while those for its fluorinated and brominated derivatives DFBP and DBBP are lengthened to \sim 1.3 and \sim 4.8

ms, respectively. Although MBB and DBBP' are not BP derivatives, their mean lifetimes are also impressively long (up to ~ 3.3 ms). This unambiguously attests that CIP is a general phenomenon for not only BP derivatives but also other luminogens, provided that their intramolecular motions are restricted and that their molecular conformations are stiffened by the physical constraints in the crystalline lattices and by the intermolecular interactions in the packing arrangements.

Concluding Remarks

Efficient phosphorescence has seldom been observed in pure organic chromophore systems at room temperature. In this work, we discovered a novel, general, and useful phenomenon of CIP: a series of organic luminogens, including BP and its halogenated derivatives (DFBP, DCBP, DBBP, and BBP), as well as other luminogens with similar molecular structures (ABP, MBB, and DBBP'), are induced to phosphoresce at room temperature in high efficiencies (Φ up to $\sim 40\%$). A carbonyl group, halogen atoms, and nonplanar conformation have been found to be key structural features for the CIP luminogens.

These luminogens are nonphosphorescent when they are dissolved in good solvents, adsorbed on TLC plates, and doped into polymer films. The intramolecular motions of the lumino-genic molecules under these conditions nonradiatively consume the photonic energies of their triplet excitons through rotational and vibrational energy relaxation channels. The ordered molecular packing arrangements and the multiple specific intermolecular interactions, such as C—H \cdots O, N—H \cdots O, and C—H \cdots π hydrogen bonds and C—H \cdots X (X = F, Cl, Br) and C—Br \cdots Br—C interconnects, cooperatively lock the molecular conformations of the luminogens and hamper their aromatic rings from undergoing the conformational variations caused by the intramolecular motions. This structural rigidification effect activates the RIM process and makes the lumino-genic molecules highly phosphorescent in the crystalline state at room temperature. All the luminogens are phosphorescent at cryogenic temperature. The emission spectra of their crystals taken under ambient conditions closely resemble those measured at the low temperature. The phosphorescence nature of the emissions is further supported by the long lifetimes of the excited states of the luminogens.

The information on the structure—property relationships and the insights into the working principle of the CIP process gained in this study are helpful and of guiding value for the exploration of new organic phosphors with high efficiencies under ambient conditions. The phosphorescence emissions of the luminogens are dramatically affected by their molecular packing arrangements and intermolecular interactions in the crystalline state. This offers a large platform for “crystal engineering” in the design and fabrication of advanced optoelectronic devices based on organic phosphors in the technologically useful solid state. It is worth pointing out that organic phosphors are more stable and more readily processable, in comparison to their organometallic counterparts.

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Supporting Information Available: Emission spectra of DFBP, DCBP, DBBP, BBP, ABP, MBB, and DBBP' in crystal

and solution states and phosphorescence decay curves of their crystals at room temperature. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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