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# Bromine-Substituted Fluorene: Simple Molecular Structure, Strong Br--Br Interactions, and the Resultant RTP and Unique Tri-Color Triboluminescent Properties

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**Abstract:** Organic tribophosphorescence materials are rarely reported and the introduction of Br atoms may be a practicable way to design such materials. Here four bromine-substituted fluorene-based derivatives are presented and BrFlu-CBr with fluorescence-phosphorescence dual-emission induced not only by UV light but also by mechanical stimulus manifests the highest phosphorescence efficiency of 4.56% upon photoirradiation. During grinding process, three different triboluminescent spectra were classified, namely tri-color triboluminescence switching. At the very beginning, upon mechanical stimulus, the triboluminescence emission is cyan; while after a long time, it changed to blue. Excitedly, after stopping mechanical stimulus, green-white phosphorescent emission was observed. Careful research on single crystal structures and theoretical calculations demonstrate that strong Br···Br interactions are vital to facilitate spin-orbit coupling and promote intersystem crossing, thus generating the unique property.

Mechanoluminescence (ML), including piezoluminescence, triboluminescence and sonoluminescence, is luminescence induced by mechanical stimulus on a solid.[1] With potential applications in area such as lighting source, pressure sensor and display device, mechanoluminescence is still attracting widespread interest despite its long-standing history, which could trace back to the first report by Francis Bacon in 1605.[1,2] However, the number of purely organic ML luminogens remains limited and many organic ML compounds only have UV emission band, thus leading to hindrance to explore the ML process and achieve practical application.[1b,3] So there is an urgent need to develop much more ML materials to learn about the relationship between mechanoluminescence phenomena and molecular structures. As necessary process in photoluminescence or electroluminescence for thermally activated delayed fluorescence (TADF) materials and phosphorescence materials, the intersystem crossing (ISC) has been well investigated.[4] However, the ISC transition upon mechanical stimulus is rarely mentioned. Recently, our group presented the first report of unusual mechanophosphorescence luminogen with AIE property and successful marriage of ML and ISC.[5] In consequence, it is possible to rationally design ML luminogens to increase the ISC efficiency.

As a matter of fact, many effective approaches, for instance, crystallization, enhancing π-π interactions, adopting compact face to face packing, expanding conjugation and self-assembly in supramolecular frameworks, have been introduced to organics with phosphorescence at room temperature, to figure out the problem of the highly forbidden triplet-singlet transitions.[6] Besides, heavy atom effect (HAE) is also known as an impactful method to achieve the strong spin-orbit coupling (SOC) between excited singlet and triplet states and increase the intersystem crossing (ISC) rate constant.[7] On the other hand, intermolecular halogen-bonding interactions, especially C-Br···Br-C interactions, are not often investigated on metal-free room temperature phosphorescence (RTP) system.[8] Thus, we wonder whether the introduction of HAE with Br···Br interaction could help to explore compounds possessing high phosphorescence efficiency and ML property.

Thus, in consideration of the HAE and Br···Br interaction mentioned above for the possibly enhanced ISC, we designed four fluorene derivatives, namely Flu-CBr, BrFlu-CBr, 2BrFlu-CBr and BrFlu-C (Figure 1), with simple molecular structure and different number of bromine atoms on the fluorene rings and/or alkyl chains, since fluorene and its derivatives are often used as building blocks for π-conjugated polymers and oligomers in opto-electronic materials, sensing and bioimaging agents and so forth.[9] And actually, a bromo-substituted fluorene derivative has been reported by Takeuchi et al. to display RTP with a phosphorescence yield of 5.9% in solution.[10] Excitedly, BrFlu-CBr crystals demonstrate distinct ML emissions upon grinding and very high phosphorescence quantum yield at room temperature (up to 4.56%) , in comparison with other three crystals and some other RTP materials with simple molecular structures as well, like naphthalimide and aromatic aldehyde.[4c] More importantly, when those crystals were scraped at the very beginning, cyan triboluminescence was observed. After stopping mechanical stimulus, green-white tribophosphorescence emitted out. Additionally, mechanical agitation for a long time produced blue triboluminescence. Thus, tri-color ML emissions switching was successfully realized. The PL and ML characterization, crystal structures and theoretical calculations are presented in detail and help to understand that strong Br···Br interactions contribute to the resultant RTP and ML properties.

Flu-CBr, BrFlu-CBr, 2BrFlu-CBr and BrFlu-C were conveniently synthesized by the reaction of fluorene or bromosubstituted fluorene and alkyl bromides (Supporting Information, Scheme S1). The molecular structures were fully characterized by $^{1}$H NMR, $^{13}$C NMR, elemental analysis and single-crystal X-ray diffraction. The UV-Vis absorption spectra and

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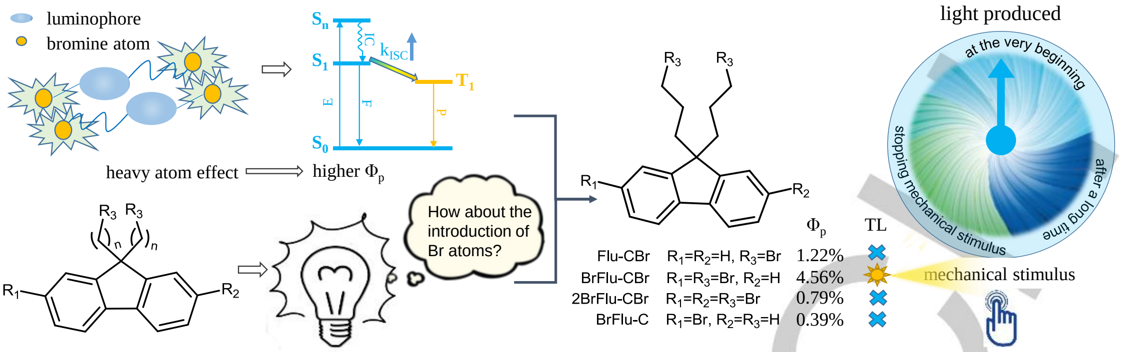

**Figure 1.** The influence of HAE, the combination of fluorene derivatives and HAE and multi-color switching of triboluminescence for BrFlu-CBr upon mechanical stimulus. E: excitation; IC: internal conversion; F: fluorescence; P: phosphorescence; Φp: the quantum yield of phosphorescence emission for crystals of the four compounds; TL: triboluminescence.

photoluminescence (PL) spectra of these four compounds were measured in tetrahydrofuran (THF) solution. They all showed similar shapes (Supporting Information, Figure S1), indicating that there are minor differences for the electronic structures of these molecules, which could be reflected in density functional theory (DFT) results.

The emission patterns of crystals for Flu-CBr, BrFlu-CBr, 2BrFlu-CBr and BrFlu-C all consist of fluorescence and phosphorescence segments with different luminescence efficiencies (Supporting Information, Figure S2). The peaksmainly locate in the ultraviolet region and their lifetimes are similar. The peaks of RTP emissions exhibit microsecond-order delays with tiny discrepancies, whereas BrFlu-CBr has much higher phosphorescence efficiency (4.56%). Accordingly, more than 20 ms after UV excitation off, only the phosphorescence of BrFlu-CBr could be detected (Supporting Information, Figure S3). The photophysical data of crystals of these fluorene derivatives at room temperature are summarized in Table S1 (Supporting Information). It is worth mentioning that the rate constants of intersystem crossing ($k_{ISC}$) and phosphorescence ($k_P$) of BrFlu-CBr are $1.008\times10^{8}$ $s^{-1}$ and 71.40 $s^{-1}$, which are much higher than those of other three luminogens, indicating the most efficient ISC in this process.[11] Therefore, further investigations were performed to find out if BrFlu-CBr was ML-active similar to other ML luminogens[12] with such efficient ISC.

By scraping or grinding the crystalline samples at room temperature, there was cyan triboluminescence produced on BrFlu-CBr as expected, demonstrating its unique ML characteristic. As shown in Figure 2b, BrFlu-CBr crystals exhibit a fluorescence-phosphorescence dual-emission, which is coincident with its PL spectrum with similar proportion of fluorescence and phosphorescence. It is mechanoluminescence at the very beginning. Further serious study helps to make out that after stopping grinding the ML spectrum we recorded (Figure 2c) is different from that at first. Actually, the light is green-white and the difference is apparent under soft light (Figure 2e). The transient ML spectrum corresponds well with the phosphorescence spectrum of BrFlu-CBr crystals, powerfully confirming that triplet excitons could be generated in the ML process. In other words, the mechanical stimulus also induces the transition of excitons from singlet to triplet with efficient ISC.[13] Furthermore, after continuous grinding, the crystalline sample was converted into powder with weak blue emission under the mechanical stimulus (Figure 2d, inset). From the ML spectrum at this state (Figure 2d), we found the relative intensity of the band in long-wavelength region decreased. Different ML emissions with obviously different spectra in various states suggest that the molecular packing is of great importance to the unique ML property. Mechanical grinding or scraping will lead to the loss of crystalline structure, during which, BrFlu-CBr sample undergoes tricolor ML emission switching.

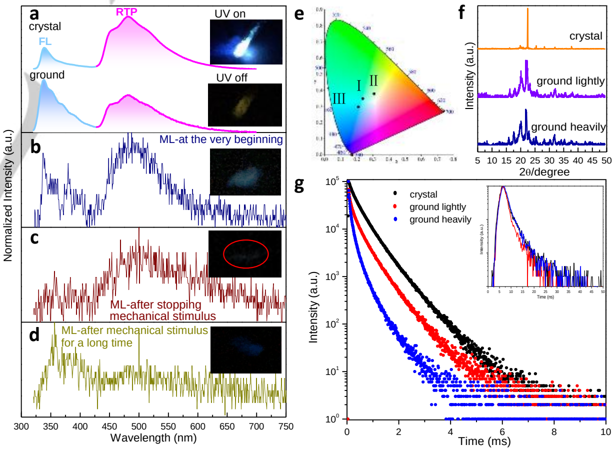

**Figure 2.** a) PL spectra of crystals (top) and powder after ground lightly (bottom) for BrFlu-CBr. Inset: The luminescent photos of crystals for BrFlu-CBr before and after UV excitation (365 nm) off. b) ML spectrum of BrFlu-CBr in the beginning. Inset: The corresponding ML image. c) ML spectrum of BrFlu-CBr after stopping mechanical stimulus. Inset: The corresponding ML image. d) ML spectrum of BrFlu-CBr after mechanical stimulus for a long time. Inset: The corresponding ML images. e) The calculated CIE coordinates in CIE 1931 color space chromaticity diagram based on the ML spectra at different time: I. at the very beginning; II. after stopping mechanical stimulus; III. After mechanical stimulus for a long time. f) XRD patterns of BrFlu-CBr in different states. g) Phosphorescence decay curves of BrFlu-CBr in different states. Inset: Fluorescence decay curves of BrFlu-CBr in different states.

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The mechanochromism (MC) effect of BrFlu-CBr was also investigated. Accompanying with grinding, dropping of the phosphorescence band could be observed (Figure 2a, bottom). Powder X-ray diffraction (PXRD) patterns were also carried out to evaluate the changes in crystals (Figure 2f). BrFlu-CBr crystals exhibit intensely sharp peaks, illustrating the good crystallinity. After light grinding, these peaks decrease with diminished intensity, which convert to broader peaks upon heavy grinding. This means the crystals were destroyed to some extent under the mechanical stimulus, and some strong intermolecular interactions should disappear or largely weaken. In addition, Figure 2g shows an apparent decrease of phosphorescence lifetime upon grinding, while fluorescence lifetime does not have evident change in different states. It proves that intersystem crossing is weakened after grounding, which facilitates a quantitative analysis of the mechanical process. It comes to a preliminary estimate that crystallization is important to the photophysics properties of the compounds.[6a,14]

To gain deeper insight into the origin of the above phenomena, single crystal structures and molecular packing of Flu-CBr, BrFlu-CBr, 2BrFlu-CBr and BrFlu-C were examined carefully. It is determined to be the intermolecular interaction when the distance is within the critical value of 4 Å. Thus, it is significant to note that there are one kind of Br⋯Br interaction (−C−Br⋯Br−C− interaction with a distance of 3.577 Å) in Flu-CBr crystals (Figure 3a) and two kinds of Br⋯Br interaction (=C−Br⋯Br−C− interaction with a distance of 3.125 Å and −C−Br⋯Br−C− interaction with a distance of 3.528 Å) in BrFlu-CBr crystals (Figure 3b), while there are no Br⋯Br interaction in 2BrFlu-CBr and BrFlu-C crystals (Figure 3c and 3d), which give rise to different intersystem crossing efficiency among these four compounds. Indeed, each molecule shares two Br⋯Br interactions with neighboring molecules in the single crystal structure of Flu-CBr (Figure 3a, inset), while the number for BrFlu-CBr is four (Figure 3b, inset). Wayne White *et al.*[15] noted that the addition of sodium iodide to 2-naphthalene sulfonate solution at room temperature dramatically increases the phosphorescence intensity, which is known as the external heavy atom effect. Here, Br⋯Br interactions play a pivotal role like the external heavy atom effect to increase the SOC and promote the ISC between singlet and triplet states. Moreover, with the aid of strong Br⋯Br interactions, they form rigid structures, through which, the vibrational loss of triplets and molecular slippage under a stimulus of mechanical force are largely suppressed. The synergy between efficient ISC and the stabilization of triplet excitons is accountable for the high phosphorescence efficiency of dual-emissive BrFlu-CBr. Molecular slippage may cause energy loss through non-radiative relaxation channels upon mechanical stimulus, as described in previous literatures.[16] Once being ground, the ordered crystal lattice collapses and transforms into microcrystals. Excited states produced during this process including stable triplet states mentioned above could return to the ground state via radiative pathway, as the result, mechanofluorescence and mechanophosphorescence appear. Once crystals are crushed, the restrictions on non-radiative transition of triplets diminish and the phosphorescence emission efficiency decreases evidently. And the destabilization of triplet states for BrFlu-CBr could be reflected in its ML spectrum. As to 2BrFlu-CBr, the steric hindrance of bromine atoms could not be balanced with the Br⋯Br interaction. Consequently, it could only adopt stable conformation with long distances between bromine atoms. Thus, there are many bromine atoms but no strong Br⋯Br interactions and low phosphorescence efficiency for 2BrFlu-CBr crystals.

Furthermore, some theoretical calculations were carried out. The configurations of the excited state and possible ISC of monomers and dimers were calculated by the time-dependent density functional theory (TD-DFT). When triplet state ($T_n$) contains the same transition configuration components as that in singlet state ($S_1$) with its energy level difference determined to be within ±0.3 eV, the transition from $S_1$ to $T_n$ is commonly considered to be the ISC channel.[5,13] For isolated BrFlu-CBr, although there are two main channels with two minor channels, a smallest energy gap of 0.1052 eV can be only found in a minor channel between $S_1$ and $T_5$ (Figure 4). When it comes to dimers of the compound, increased number of ISC channels and decreased gap of energy levels are both obtained. In BrFlu-CBr crystals, $T_{11}$ and $T_{12}$ in dimer1 and $T_9$ and $T_{11}$ in dimer2 are close to $S_1$, and the transitions from $S_1$ to them are main ISC channels. They show small energy gaps from 0.0087 to 0.0302 eV, which are reduced by a large margin compared to those in monomers. Additionally, three minor channels exist in dimer1. As to Flu-CBr, the main channels in dimers have quite low value of $\Delta$ ($S_1$-$T_n$), but they are also the single channel in each dimer (Supporting Information, Figure S17). The energy levels of $T_n$ of main channels for 2BrFlu-CBr and BrFlu-C lie more far from $S_1$ (Supporting Information, Figure S18 and S19). Thus, it is obvious that strong Br⋯Br interactions help to develop effective interactions in dimers, such as C−H⋯Br−C and C−H⋯π interactions. Strong SOC and enhanced ISC are realized while energy loss through non-radiative relaxation channels is restricted, thus achieving high phosphorescence efficiency upon photo or mechanical force excitation.

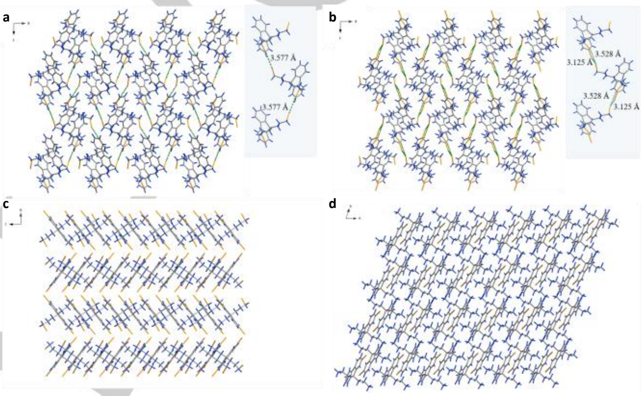

**Figure 3.** Molecular stacking of four fluorene-based derivatives: a) Flu-CBr, b)BrFlu-CBr, c)2BrFlu-CBr, d)BrFlu-C. The green dot lines represent Br⋯Br interactions. The pictures inset show the examples of molecules with Br⋯Br intermolecular interactions.

The important role of Br⋯Br interactions in crystalline state at room temperature also could be indirectly proved at low temperature.[17] At 77 K, the lifetime of delayed component of BrFlu-CBr solution is not very different from others. Relatively, the phosphorescence lifetime of BrFlu-CBr crystals has a huge increase (Supporting Information, Figure S4d). After UV excitation off, BrFlu-CBr crystals showed more intense phosphorescence emission and slow decay rate in transient spectra (Supporting Information, Figure S5). The totally different lifetime and intensity of phosphorescence for BrFlu-CBr crystals at low temperature confirm that Br⋯Br interactions are the key determinant for intersystem crossing and the resultant RTP and ML properties.

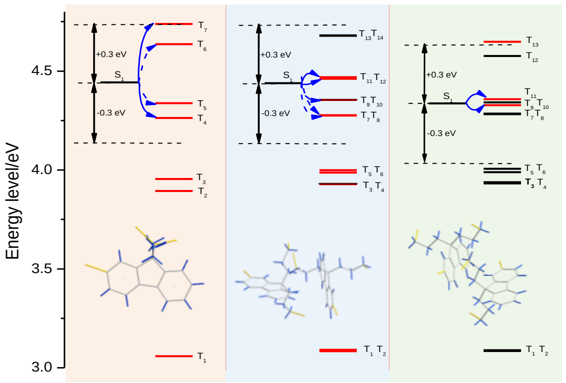

**Figure 4.** Energy level diagrams and possible ISC channels from singlet $S_1$ to triplet $T_n$ ($S_0$ = 0 eV) for the monomer and two types of dimers in BrFlu-CBr crystal. The solid arrows and dotted arrows refer to main and minor ISC channels, respectively.

In summary, we have designed and synthesized four fluorene based derivatives to combine heavy atom effect with fluorene. BrFlu-CBr crystals exhibit fluorescence-phosphorescence dual-emission under UV light or mechanical stimulus. Upon mechanical stimulus for a long time, the ML emission of BrFlu-CBr could change from cyan to blue because of the destruction of the crystalline structure, while after stopping mechanical stimulus, green-white phosphorescence could be observed. This is the first example of multi-color switching of triboluminescence tuning by phosphorescence intensity in purely organic compound. On the basis of careful investigation of single crystal structure and theoretical calculation, it is concluded that strong Br⋯Br interactions are vital to facilitate SOC and promote ISC, resulting in unique properties for BrFlu-CBr. This validates that adopting strong halogen interactions with external HAE may be feasible to develop more RTP and tribophosphorescence materials, opening a new avenue for the further development of ML luminogens with RTP property.

## Acknowledgements

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**Keywords:** triboluminescence • room-temperature phosphorescence• heavy atom effect • multi-color switching

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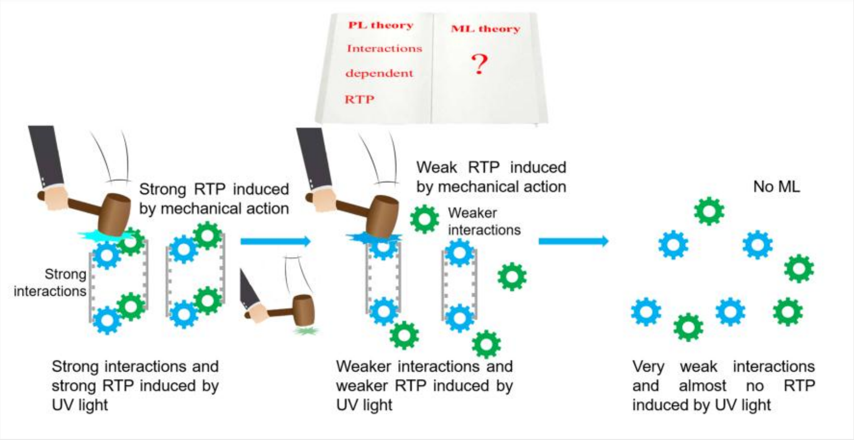
# COMMUNICATION



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***Bromine-Substituted Fluorene: Simple Molecular Structure, Strong Br···Br Interactions, and the Resultant RTP and Unique Tri-Color Triboluminescent Properties***

BrFlu-CBr crystals exhibit fluorescence-phosphorescence dual-emission under mechanical stimulus wihout excitation by a UV lamp. Upon mechanical stimulus for a long time, the TL emission of BrFlu-CBr could change from cyan to weak blue, while after stopping mechanical stimulus, green-white phosphorescence could be observed, which is multi-color switching of triboluminescence tuning by phosphorescence intensity.