Modulating Room-Temperature Phosphorescence-To-Phosphorescence Mechanochromism by Halogen Exchange

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Modulating the stimulus-responsiveness of a luminescent crystal is challenging owing to the complex interdependent nature of its controlling factors, such as molecular structure, molecular conformation, crystal packing, optical properties, and amorphization behavior. Herein, we demonstrate a halogen-exchange approach that disentangles this problem, thereby realizing the modulation of room-temperature phosphorescence-to-phosphorescence mechanochromism. Replacing the bromine atoms in a brominated thienyl diketone with chlorine atoms afforded isostructural crystals; i.e., molecules with different halogen atoms exhibited the same molecular conformation and crystal packing. Consequently, amorphization behavior toward mechanical stimulation was also the same, and the phosphorescence of amorphous states originated from the same conformer of each diketone. In contrast, the phosphorescence properties of each conformer were modulated differently, which is ascribable to heavy atom effects, resulting in the modulation of the mechanochromism. Thus, halogen exchange is a promising approach for modulating the stimulus-responsive photofunctions of crystals involving spin-forbidden processes.

Keywords: mechanochromism, heavy atom effects, isostructural crystals, amorphous, halogen exchange, room-temperature phosphorescence, metal-free

INTRODUCTION

Mechanochromic luminescence is a phenomenon in which the luminescence color changes when mechanical stimulus is applied and is recovered by other external stimuli, such as heat (Sagara et al., 2016; Ito, 2021). Such phenomena have received significant interest not only because they visualize otherwise invisible force histories, but also because of their mechanism involved in transducing macroscopic force to the molecular level. Basically, the color change is due either to a change in the molecular environment, the intermolecular arrangement, the molecular conformation, or a combination thereof.

Phosphorescent organic molecules are particularly promising mechanochromic materials because phosphorescence is highly sensitive to changes in the molecular environment (Xue et al., 2016; Huang et al., 2020). Phosphorescence is a spin-forbidden form of luminescence that involves a change in the spin multiplicity. Unlike metal complexes, such as Ir and Pt, which benefit from the heavy atom effect that accelerates spin-forbidden processes, metal-free organic molecules seldom show room-temperature phosphorescence (RTP) (Hirata, 2017; Kenry et al., 2019). However, the crystalline states of some metal-free organic molecules were reported to exhibit RTP as early as 1939
(Clapp, 1939; Bilen et al., 1978). More recently, significant interest has been directed toward “crystallization-induced phosphorescence” (CIP) following the seminal report published in 2010 by Tang et al. (Yuan et al., 2010). A rigid environment is generally regarded to be crucial for observing RTP from a metal-free organic molecule; otherwise, RTP is quenched by molecular motions (Baroncini et al., 2017). Indeed, the conventional RTP of an organic crystal is quenched by applying mechanical stimulation, which amorphizes the crystal. While such mechanoresponsive RTP turn-off behavior has been used to achieve RTP-to-fluorescence mechanochromism, (Gong et al., 2015; Mao et al., 2015; Xu et al., 2017; He et al., 2019; Huang et al., 2019; Ma et al., 2019; Wang et al., 2019a; Liu et al., 2021a; Liu et al., 2021b) the RTP mechanorespones is largely limited to the turn-off type, with a molecular design that modulates mechanochromic RTP behavior remaining elusive.

To establish design principles for mechanochromism, two types of structure-mechanochromic-property relationship are important: the molecular-structure-property and the crystal-structure-property relationship. However, in many cases, the molecular structure and crystal structure are strongly interdependent, which prevents revealing the essential causal relationship. Polymorphic crystals, in which the same molecule forms different crystal structures, provide practical bases for studying the crystal-structure-property relationship (Wang and Li, 2017). On the other hand, the molecular-structure-property relationship can be elucidated when different molecules form isostuctural crystals; i.e., crystals with the same space group, lattice constants, crystal packing, and molecular conformations (Fábián and Kálmán, 1999; Kálmán et al., 1993). The differences in isostuctural crystal structures are so small that they usually do not disturb the properties derived from the molecular structure itself.

Previously, we reported the thienyl diketone BrTn (Figure 1A), the first metal-free organic molecule to exhibit RTP-to-RTP mechanochromism (Tani et al., 2019); in contrast to RTP quenching observed for conventional organic phosphors, mechanical stimulation amorphizes the BrTn crystals, resulting in RTP color change. Detailed investigations revealed that mechanical stimulus turns off the initial RTP from a skew conformer while providing a small amount of the highly emissive trans-planar (TP) conformer. In addition, we desymmetrized the C2-symmetrical BrTn structure. (Tani et al., 2020; Komura et al., 2021) Notably, replacing one of the two Br atoms with a hydrogen atom led to the formation of a crystal that is isostuctural with that of BrTn (Tani et al., 2020). Interestingly, the crystal of the unsymmetrical diketone was non-emissive, which was attributed to the presence of voids that result from the volumetric difference between Br and H (Figure 1B top). Hence, the difference in the crystal structures were highly localized, facilitating the stringent crystal-structure-property relationship study.

Herein, we report the first RTP-to-RTP mechanochromism modulated by halogen-atom exchange. We envisaged that halogen-atom exchange in BrTn (e.g., bromine to chlorine) would afford isostuctural crystals (Reddy et al., 2006; Saidykhán et al., 2021; He et al., 2017; Wen et al., 2019; Lai et al., 2021) that retained the mechanoresponsive nature of BrTn, as observed for our previous system (Figure 1B top). On the other hand, altering the heavy atoms is expected to affect the molecular phosphorescence properties, thereby modulating the responsiveness to RTP color. Heavy atom effect—the enhancement of the rate of a spin-forbidden process by the presence of an atom of high atomic number—has been widely used to modulate or achieve phosphorescence from metal-free organic molecules. (He et al., 2017; Wen et al., 2019; Lai et al., 2021; Wang et al., 2019b; Liao et al., 2021) With these aims in mind, we designed new diketone CITn, in which the Br atoms in BrTn are replaced with Cl atoms (Figure 1B bottom). As a result, the fundamental stimulus-responsive nature of BrTn is retained, while the sensitivities of RTP color to mechanical/thermal stimuli are modulated. Our study demonstrates the usefulness of the halogen-exchange strategy for modulating the stimulus-responsive photofunctions of crystals that involve spin-forbidden processes.

**EXPERIMENTAL SECTION**

**Instrumentation and Chemicals**

1H and 13C [1H] NMR spectra were recorded on a JEOL ECS400 spectrometer. Chemical shift values (δ) are reported in ppm and are calibrated to tetramethysilane (0.00 ppm) for 1H and to CDCl3 (77.0 ppm) for 13C NMR. Melting points were measured between cover glasses with Yanaco MP-S3. Elemental analysis (EA) was conducted on a Yanaco MT-6 recorder. Analytical thin-layer chromatography (TLC) was performed on aluminum plates bearing a layer of Merck silica gel 60 F254. Column chromatography was carried out on silica-gel 60N (Kanto Chemical Co., Inc., spherical, 63–210 μm). Unless otherwise noted, chemicals were obtained from commercial suppliers and used without further purification.

**Synthesis of CITn**

To a heat gun-dried Schlenk flask under Ar were added BrTn (69.9 mg, 0.101 mmol) (Tani et al., 2019), copper chloride (I) (50.2 mg, 0.507 mmol), and N,N-dimethylformamide/ o-dichlorobenzene (3:1, 2.4 mL). The solution was degassed by typical freeze-pump-thaw cycling three times. Then, the mixture was stirred at 140°C overnight, quenched by adding aq. NH4Cl, and extracted with CHCl3 (10 ml × 3). The combined organic extracts were washed with aq. NH4Cl (10 ml × 2) and water (10 ml × 2), dried over MgSO4, and concentrated under reduced pressure. The crude product was passed through a silica-gel column (eluent: CHCl3), and all the volatiles were removed. The residue was further purified in reflushing MeOH (5 ml) at 75°C (bath temperature) for 20 min, and then filtered at room temperature. The solid was then suspended in hexane (2 ml) and reflushed at 80°C (bath temperature) for 20 min, cooled in a freezer, and filtered to give 34.5 mg (57.1 µmol, 57%) of CITn as a yellowish-white powder. m. p. 156–158°C. 1H NMR (400 MHz, CDCl3) δ: 7.17 (2H, s), 1.38 (6H, sep, J = 7.3 Hz), 1.12 (36H, d, J = 7.3 Hz), 1.29 (66H, d, J = 7.3 Hz). 13C NMR (100 MHz, CDCl3) δ: 182.21, 148.75, 137.33, 134.64, 133.89, 18.38, 11.51. EA Calcd for C28H32Cl2O2S2Si2: C, 55.69; H, 7.34. Found: C, 55.79; H, 7.41.
Single-Crystal X-Ray Structure Analysis of ClTn

A single-crystal of ClTn suitable for X-ray structure analysis was obtained by a liquid-liquid diffusion of CHCl₃/MeOH solution. Data were collected on a Rigaku XtaLab P200 diffractometer with graphite monochromated MoKα radiation (λ = 0.71075 Å) in the ω-scan mode. The crystals were cooled by a stream of cold N₂ gas. Collection, indexing, peak integration, cell refinement, and scaling of the diffraction data were performed using the CrystalClear software (Rigaku). The structures were solved by direct methods (SIR97) and refined using full-matrix least-square refinement on F² (SHELXL2014). The non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed on the calculated positions and refined using the riding model. The crystallographic data have been deposited at the Cambridge Crystallographic Data Centre (CCDC) under deposition number CCDC-2119698, and can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

Preparing and Characterizing ClTn-G and ClTn-Y

Typical procedure: to a stirred solution of ClTn (70.2 mg) in CHCl₃ (4 ml) was added dropwise MeOH (30 ml). The precipitate was collected by vacuum filtration and washed with MeOH to obtain ClTn-G, which was then uniformly ground for 1 hour with an agate mortar and pestle to give ClTn-Y. The materials were characterized at room temperature in air. The steady-state photoluminescence (PL) spectra of ClTn-G and ClTn-Y were acquired using a JASCO FP-8200 spectrofluorometer with an L37 sharp-cut filter (HOYA, long pass, >370 nm) and a U340 band-pass filter (HOYA). Powder X-ray diffraction (PXRD) patterns were collected on a Rigaku MiniFlex 600 diffractometer with CuKα radiation (λ = 1.5418 Å). The PL quantum yields of ClTn-G and ClTn-Y were determined by the absolute method using a Hamamatsu photonics C11347-01 spectrometer augmented with an integrating sphere while excited at (λex) 368 nm. The PL decay curves were acquired with a HORIBA DeltaFlex multichannel scaling system using a DeltaDiode for excitation (368 nm). The PL intensity decay curves were recorded at 520 nm for ClTn-G and 560 nm for ClTn-Y. The area-weighted average lifetimes τ were determined with EzTime software (HORIBA) using a single-exponential fit for ClTn-G and a double-exponential fit for ClTn-Y.

Evaluating Reversibility and Sensitivity

To evaluate reversibility of mechano/thermochromism and heat-induced recovery, ClTn-G was placed between two quartz plates and rubbed for 1 min, after which the PL spectrum was acquired (λex = 320 nm). The plates were placed on a preheated copper plate and heated on a hot plate (IKA C-MAG HS 7) for 1 h, with the temperature of the copper plate maintained at 138–143°C. The sample was cooled to room temperature while on the plate (with the heater turned off), after which the PL spectrum was acquired (λex = 320 nm). This treatment protocol was repeated four times to test repeatability. PL spectral change was evaluated as the color change ratio: First, the normalized difference in intensity D = (I₅₂₀ – I₅₆₀)/(I₅₂₀ + I₅₆₀) was determined for each spectrum to provide the relative intensity of the skew/TP emission, where I₅ is the intensity at x nm. The color change ratio was then calculated as (D – D₀)/(D₀ – D₀) × 100 (%), where D₀ and D are the D values for the ClTn-G and ClTn-Y, respectively. All photographic images were acquired using a SONY NEX-5N camera while irradiated with a hand-held UV light (365 nm). Temperature was controlled in a similar manner to evaluate sensitivity toward thermal stimulation. The recovery ratio is defined as (D – D₀)/(D₀ – D₀) × 100 (%), where D₀ is the D value for sample h₀ (ClTn-G rubbed for 1 min between two quartz plates). The color change and recovery ratios of BrTn were determined using I₅₂₀ instead of I₅₆₀.

Constructing the ΦP-Weighted PL Spectrum of ClTn-Y

The spectrum of ClTn-G, which is purely derived from the skew conformer, was subtracted from that of ClTn-Y after normalizing the intensity at λmax (the emission maximum) of ClTn-G. The
difference spectrum corresponds to the pure PL spectrum of the TP conformer. The difference spectrum and the spectrum of CITn-G were multiplied by $\alpha_Y = [\Phi_p$ of BrTn-Y]/[$\Phi_p$ of CITn-G], respectively, and summed to construct the $\Phi_p$-weighted PL spectrum of CITn-Y.
RESULTS AND DISCUSSION

Diketone CITn was synthesized by reacting BrTn with CuCl. The X-ray structure of a single-crystal of CITn revealed that it is isostructural to that of BrTn (CCDC), with superimposable molecular geometries, the same space group, and very similar lattice constants (Figure 2 and Table 1). The conformation of aromatic 1,2-diketones is well represented by two torsion angles: the vicinal-dicarbonyl torsion angle $\theta$ and the thiophene–carbonyl torsion angle $\phi$ (Mukai et al., 1992; Singh et al., 2002). A comparison of these angles in CITn and BrTn highlights their almost identical crystal conformations ($\theta$: 114.0(1) vs. 109.5(2); $\phi$: −19.1(2) vs. −17.2(3)). In addition, the diketones have three kinds of intermolecular interactions (a total of 12 interactions from one molecule), which are also comparable in both systems due to their identical crystal packing (Figure 2C). Hence, these isostructural crystals provide both conformationally and environmentally consistent systems that are ideal for investigating structure–property relationships.

CITn was found to exhibit RTP-to-RTP mechanochromism in a qualitatively similar manner to BrTn (Tani et al., 2019); the RTP color changed from green (G-phase) to yellow (Y-phase) upon grinding. To investigate these photophysical properties in detail, we prepared samples of CITn-G and CITn-Y; CITn-G is a crystalline powder precipitated from CHCl3/MeOH, while CITn-Y was prepared by uniformly grinding CITn-G using an agate mortar and a pestle (see Experimental Section for details). The photoluminescence (PL) emission maximum of CITn-Y ($\lambda_{PL}$ = 560 nm) was observed to be redshifted by $\sim$40 nm compared to that of CITn-G ($\lambda_{PL}$ = 522 nm) (Figure 3A). By comparing the behavior of BrTn with that of CITn (Figure 3B), (Tani et al., 2019) we conclude that the PL spectrum of CITn-Y consists of an emerging emission from the TP conformer and a remaining small emission from the skew conformer (vide infra). The PL lifetimes of CITn-G and CITn-Y were determined to be 66 and 122 $\mu$s, respectively, without any nanosecond-order decay component, confirming that these are phosphorescence emissions (Figure 4).

Moreover, the yellow RTP of CITn-Y returned to green upon heating (Figure 5); this color-change cycle was repeated for five-times, thereby demonstrating reversible mechano/thermoresponsiveness. The observed RTP mechanochromism is based on crystal amorphization, because the PXRD pattern of CITn-G reveals sharp diffraction peaks, while that of CITn-Y shows peak broadening (Figure 6). Overall, the RTP-to-RTP mechanochromism of BrTn was well reproduced by CITn.
FIGURE 7 | Normalized PL spectra of (A) ClTn-G and (B) BrTn-G upon mechanical stimulation (λex = 320 nm). Angles in the legends are the rotating angles as depicted in the bottom right. (C) Sensitivity of RTP color to mechanical stimulation. See Experimental Section for definition of the color change ratio.

FIGURE 8 | (A) Sample preparation for heat-induced-recovery experiments. (B, C) Normalized PL spectra (left, λex = 320 nm) and corresponding PXRD profiles (right) of (B) ClTn-Y and (C) BrTn-Y upon heating. (D) Sensitivity of the RTP color and (E) FWHMs of the PXRD peaks at 2θ = ~6° toward the thermal stimulation. See Experimental Section for definition of the recovery ratio.
however, close inspection revealed notable differences in stimulus-responsiveness that are compared and mechanistically rationalized below.

Despite its isostructural nature, the RTP color of CI\textsubscript{Tn} responds to mechanical stimulus more slowly than that of Br\textsubscript{Tn}. For comparison, crystalline powder (CI\textsubscript{Tn-G} or Br\textsubscript{Tn-G}) was placed between two quartz plates, ground by rotating the upper plate while being pressed, with PL spectra acquired at rotating angles of 0, 90, 180, and 360° (Figure 7). The RTP color of CI\textsubscript{Tn} changed gradually; the relative intensity of the emission from the TP conformer ($\lambda_{PL} = 560$ nm) continuously increased with the application of the mechanical stimulus. On the other hand, the TP emission of Br\textsubscript{Tn} emerged rapidly; its RTP color changed dramatically during the first quarter turn and remained almost unchanged thereafter (Figure 7C). These results may seem to suggest that Br\textsubscript{Tn-G} is more easily amorphized than CI\textsubscript{Tn-G}; however, we note that what responds faster in Br\textsubscript{Tn} is the RTP color, for which the ease of amorphization is just one of the possible factors. Evaluating/monitoring the rate of amorphization (loss of crystallinity) during mechanical stimulation is difficult because the preferred orientation may also affect the PXRD peak, the full-width at half-maximum (FWHM) of which is a measure of crystallinity, and can be alleviated by mechanical stimulation.

Monitoring the heat-induced recovery from the Y phase to the G phase is expected to provide a better understanding of the crystallinity–RTP color relationship, as heating does not disturb the orientation of the powder. With this in mind, PL spectra and PXRD profiles were acquired after heating the Y phase samples (h0) at the temperatures and times indicated in Figures 8A–C. In contrast to the mechanical response observed for CI\textsubscript{Tn}, its PL spectrum responded faster to temperature than the spectrum of Br\textsubscript{Tn}. More interestingly, CI\textsubscript{Tn} and Br\textsubscript{Tn} exhibited the same crystallinity response; the FWHMs of the PXRD peaks at $2\theta = 6^\circ$ were observed to decrease at the same rate (Figures 8D,E). These results indicate that, while the crystallinity of the powder is important for determining the RTP color, the stimulus-responsiveness of RTP color is not associated with ease of amorphization.

We hypothesize that the difference in the stimulus-responsiveness of the RTP color originates from a conformation-dependent heavy atom effect. To test this hypothesis, we determined the phosphorescence quantum yields $\Phi_p$ of each compound/phase and constructed the $\Phi_p$-weighted PL spectrum of CI\textsubscript{Tn-Y}. As expected from the weaker heavy atom effect of Cl compared to Br, the $\Phi_p$ of CI\textsubscript{Tn} is smaller than that of Br\textsubscript{Tn} (Table 2). Interestingly, the amorphous Y phase exhibited a larger quantum yield ratio ($\alpha = [\Phi_p$ of Br\textsubscript{Tn}] / [\Phi_p of CI\textsubscript{Tn}]) than the crystalline G phase, implying that the extent of the heavy atom effect depends on conformation. Next, we subtracted the PL spectrum of CI\textsubscript{Tn-G}, which is purely derived from the skew conformer, from that of CI\textsubscript{Tn-Y} (Figure 9A). The difference spectrum corresponds to the pure PL spectrum of the TP conformer. Indeed, other PL spectra of CI\textsubscript{Tn} with partial amorphization (e.g., 180° in Figure 7A) can be reconstructed from the obtained spectra of the skew and TP conformers (Figure 9B), which indicates that the PL spectra are

### Table 2: Phosphorescence maxima, quantum yields, and lifetimes.

| Compound | $\lambda_p$/nm | $\Phi_p$ (%) | $\tau$/μs |
|----------|----------------|--------------|----------|
| CI\textsubscript{Tn-G} | 522 | 1.7 | 122 |
| Br\textsubscript{Tn-G} | 527 | 3.9 | 103 |
| CI\textsubscript{Tn-Y} | 560 | 1.4 | 66 |
| Br\textsubscript{Tn-Y} | 571 | 10 | 51 |

**FIGURE 10** | Schematic representation of the proposed mechanism for different mechanoresponse of RTP color, describing the change in conformation and RTP color along amorphization. The relative color depth represents relative PL efficiency.
composed of the two emissions. Finally, we corrected the PL spectrum of CITn-Y by multiplying the spectra of each conformer by $\alpha$ and then recombining them. The $\Phi_p$-weighted PL spectrum of CITn-Y (Figure 9C, blue trace) obtained in this manner matches the PL spectrum of BrTn-Y. Therefore, we concluded that the conformational composition of amorphous CITn-Y is similar to that of BrTn-Y, and that the differences in spectral shape are attributable to the difference in PL efficiency. A proposed mechanism for the different stimulus-responsiveness of RTP color is described in Figure 10. Even though the ease of amorphization is similar as expected for the isostructural crystals, different PL efficiency (represented by color depth) makes the RTP color response different. Upon amorphization, the PL quantum yields are increased in BrTn-G/Y (3.9/10%) while slightly decreased in CITn-G/Y (1.7/1.4%) (Table 2). Thus, the mechanoresponse in the RTP color is different. We emphasize that, in the present system, isostructural crystals exhibited a similar amorphization behavior, enabling the stimulus-responsiveness of the bulk solid to be modulated by tuning the molecular properties.

CONCLUSION

The RTP-to-RTP mechanochromism of a thienyl diketone was successfully modulated by Br-to-Cl halogen exchange. Modulating the molecular structure does not disturb the crystal structure, with both diketones forming isostructural crystals. The stimulus-responsiveness of the crystallinity is also retained, as evidenced by PXRD peak widths. In contrast, relative RTP efficiency is affected, which is ascribable to a conformation-dependent heavy-atom effect. Consequently, we were able to successfully modulate the stimulus-responsiveness of RTP color. We are currently investigating the conformation-dependent heavy atom effect, which will be reported in due course.

DATA AVAILABILITY STATEMENT

The datasets presented in this study can be found in online repositories. The names of the repository is Cambridge Crystallographic Data Centre. Following are the accession numbers CCDC-2119698 CCDC-1906440.

AUTHOR CONTRIBUTIONS

YT (last author) conceived the idea and designed research. YT (1st author) synthesized and characterized the materials. All authors analysed data and wrote the paper. All authors contributed to the article and approved the submitted version.

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SUPPLEMENTARY MATERIAL

The Supplementary Material for this article can be found online at: https://www.frontiersin.org/articles/10.3389/fchem.2021.812593/full#supplementary-material

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