

Light-melting Diketone Crystal with ON-OFF-ON Luminescence Evolution

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ABSTRACT: Crystal melting by light irradiation, that is, the phenomenon of photoinduced crystal-melt transition (PCMT), can dramatically change material properties with high spatiotemporal resolution. However, both the process and mechanism of PCMT remain unknown owing to a lack of suitable probes and the poor diversity of compounds exhibiting PCMT. Here, we report the first instance of PCMT with luminescence evolution. We show that a heteroaromatic 1,2-diketone crystal exhibits ON-OFF-ON luminescence changes under continuous ultraviolet irradiation, which can be ascribed to the sequential PCMT processes of crystal loosening and conformational isomerization before macroscopic melting. Single-crystal X-ray structural analysis, thermal analysis, and theoretical calculations of three diketones revealed that weak intermolecular interactions and the presence of a disordered layer in the crystal are essential for PCMT. Our results provide fundamental insights into the melting process of molecular crystals and should aid the molecular design of PCMT-active materials that are based on emissive compounds, as opposed to the classical molecular designing based on nonemissive photochromic scaffolds such as azobenzenes.

Phase transitions, such as melting and crystallization, can induce drastic changes in the material properties.^{1–6} In particular, the phenomenon of photoinduced crystal-melt transition (PCMT)^{7–19} is extremely useful for applications such as photolithography,¹¹ thermal energy storage,^{15–18} and light-melt adhesion.^{12,13,20,21} However, the process, mechanism, and molecular design principles of PCMT remain largely unknown (Figure 1A). Using synchrotron radiation, Hoshino *et al.* elucidated the structural features of an azobenzene derivative that shows PCMT.^{8–10} However, PCMT has been observed only in three photochromic motifs: azobenzene,^{7–17} hydrazone,¹⁸ and spiropyran.¹⁹ Moreover, owing to a lack of suitable methods/materials, there have been no studies on the real-time and molecular-level observation of the disordering PCMT process. For instance, X-ray diffractometry, which is essentially a method for analyzing ordered structures, does not generally have the temporal resolution required to track the PCMT process.²²

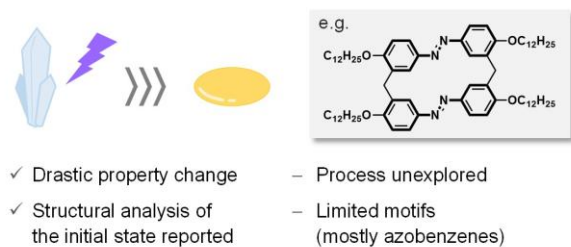
Luminescence is a promising property for the in situ observations of phase transitions because it allows the real-time, high-sensitivity detection of the emissive part in a bulk material.^{1,23–25} Microscopic visualizations of the crystallization process based on time-course luminescence has been reported previously.^{26–30} However, to the best of our knowledge, PCMT has never been studied using luminescence. Azobenzenes are a promising motif for studying PCMT. However, their photoinduced trans-cis isomerization dissipates the excited-state energy nonradiatively (Figure 1B).^{31–33} Moreover, the luminescence properties of materials in the solvent-free liquid state have not been explored extensively.^{34–37} There are only limited examples of liquid materials exhibiting phase-dependent changes in luminescence, and for most of these materials, the luminescence is more intense in the crystal form than that in the liquid form.^{38–41} Such materials would exhibit emission fading during

melting, and this would hinder the visualization of the local disordering process.

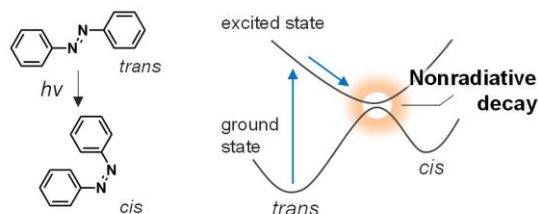
We had previously observed phase-dependent room-temperature phosphorescence (RTP) in a heteroaromatic diketone, **SO** (Figure 1C).⁴² Unlike typical metal-free organic phosphors that only phosphoresce in the crystal form,^{43–45} **SO** exhibits RTP in its supercooled liquid (SCL) state, that is, in the metastable liquid phase at temperatures lower than its melting point. Moreover, **SO** becomes virtually nonemissive (i.e., its emission is too weak to detect with an integrating sphere) after crystallization. Detailed experimental and theoretical investigations revealed that **SO** has distinct rotational isomers, including skew and planar conformers (Figure 1C right). Most notably, while the crystal consists of the poorly emissive skew conformer, the planar conformer is more stable in the excited state and is responsible for the RTP in the SCL state.^{42,46–49} Herein, using **SO** crystals, we demonstrate for the first time the phenomenon of PCMT with luminescence, which is reflective of the molecular environment and allows for the visualization of the local melting process in real time.

Our research was initiated by an unexpected observation of the photoinduced turn-on RTP^{50–55} and melting of pristine **SO** powder under a fluorescence microscope (Figure 2A). The luminescence of the powder was negligible initially but increased under ultraviolet (UV) irradiation (160 mW/cm², $\lambda_{\text{max}} = 365$ nm). Moreover, the powder melted into an isotropic liquid, as evident from the disappearance of the birefringence (Figure 2A, inset). As reported previously, **SO** forms a kinetically super-stable SCL at room temperature.⁴² Hence, its melting is a crystal-to-SCL transition, that is, a transition to the metastable phase. The resulting emission ($\lambda_{\text{max}} = 575$ nm) was similar to that of the SCL state and can be ascribed

A. Photoinduced Crystal-Melt Transition (PCMT)



B. Nonemissive Photoisomerization of Azobenzenes



C. PCMT with Luminescence Evolution (This Work)

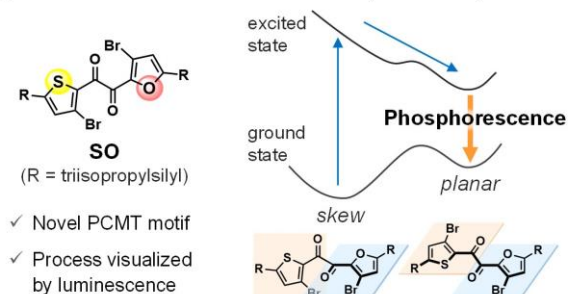
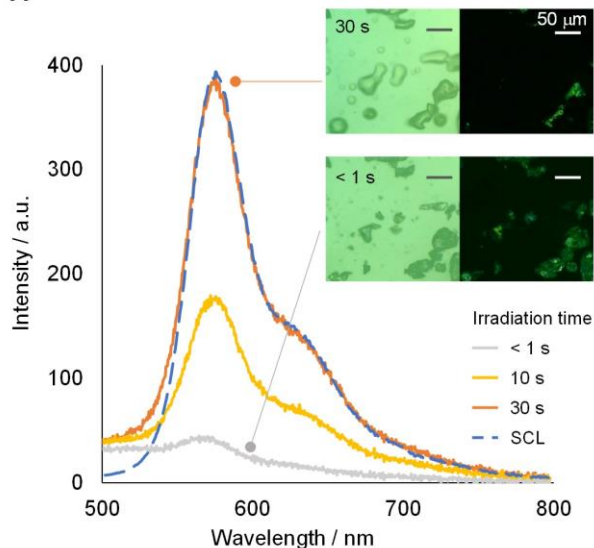


Figure 1. (A) Background of photoinduced crystal-melt transition. (B) Photophysical pathway of azobenzene. (C) Structure and simplified photophysical pathway of **SO**.

to the RTP from the planar conformer (Figure 2A).⁴² Note that the phosphorescence of the SCL state disappears at higher temperatures (lower than the melting point, which is 59.5 °C, see Figure S2). Therefore, the melting is not caused by heating.

Next, we evaluated the changes in the crystallinity and luminescence simultaneously using a single crystal. UV light was irradiated on the top-left part of the crystal (Figure 2B, top right). After 220 s, only the irradiated area exhibited the yellow emission and melted (Figure 2B, bottom row). The sharp boundary indicates that the melting transition does not propagate to the unirradiated crystal region and is not caused by heating. In addition, the recrystallization of the melt is sufficiently slow owing to the high kinetic stability of the SCL state. Most notably, the turning-on of the luminescence preceded the macroscopic melting of the irradiated area. Based on the bright-field and polarizing optical images, the area was still crystalline after irradiation for 60 s. However, a distinct emission was observed simultaneously (Figure 2B, middle row). Thus, the emission is clearly indicative of microscopic melting, which is not evident from the light reflection, transmission, and absorption characteristics.

A



B

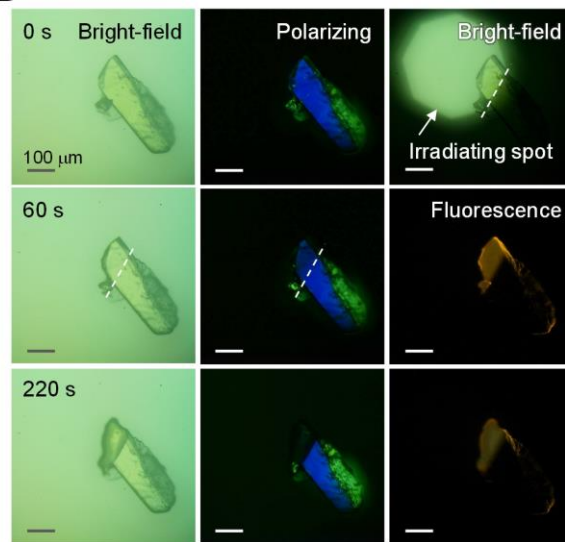


Figure 2. (A) Photoluminescence spectra of **SO** in SCL state and powder form under continuous UV irradiation. Inset: photographic images obtained using (left) bright-field and (right) polarizing optical microscope. (B) Photographic images of **SO** crystal obtained using (left and top right) bright-field and (center) polarizing optical and (right) fluorescence microscopes.

Next, we tracked the time-dependent changes in the luminescence spectrum of a single crystal under continuous UV irradiation (Figure 3A). Surprisingly, UV excitation initially resulted in a weak green luminescence peak at approximately 520 nm, which disappeared within seconds (Figure 3A, red trace). The yellow emission from the planar conformer ($\lambda_{\text{max}} = 575$ nm) turned on only after an inductive period. These ON-OFF-ON changes in the luminescence were qualitatively reproducible and visually observable using a large crystal (Figures 3B and S5 and Movie S1). Considering that **SO** exhibits the skew conformation in crystal form

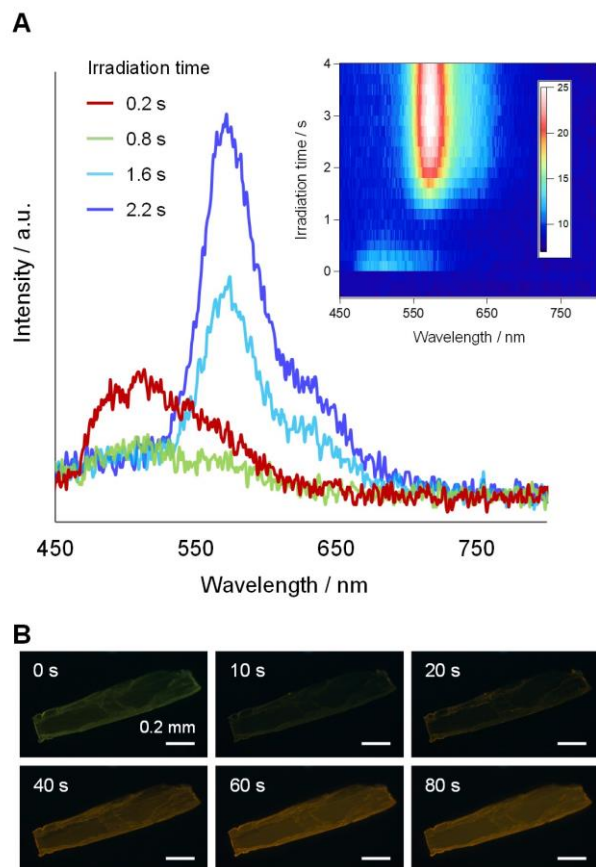


Figure 3. Evolution of (A) photoluminescence spectrum and (B) fluorescence microscope image (clipped from Movie S1) of **SO** crystal during continuous UV irradiation. Note that crystal size and light source for panels A and B are different.

(see below),⁴² the initial green emission is caused by the skew conformer (Figure S6).^{42,46–48} Therefore, the changes in the luminescence reflect the local melting process, namely, how the molecular conformation changes from skew to planar.^{56–58} Hence, the intermediacy of the nonemissive regime must be the key to understand the process.

To elucidate the emission turn-off mechanism, we investigated the crystal structure and examined its relaxation after UV excitation. We were able to successfully perform a single-crystal X-ray structural analysis of **SO** at 300 K (Figure 4A). Compared with the structure at 123 K,⁴² the thermal ellipsoids become remarkably large, particularly in the silyl moieties. The silyl moieties form disordered layers along the (10–1) plane while the heteroaromatic diketone cores are relatively more ordered (Figure 4B).⁵⁹ Furthermore, according to density functional theory calculations, the silyl moiety moves along the disordered (10–1) plane because of excited-state structural relaxation (Figures S10 and S12); thus, the relaxation is allowed, as the disordered layer mitigates the mechanical stress in the crystal, thereby accelerating the disordering of the entire crystal. In general, the RTP disappears when the ordered crystalline lattice is disturbed.^{43–45} Therefore, the disappearance of the skew emission is due to pronounced nonradiative decay and indicates crystal loosening

owing to UV irradiation.⁴⁶ Moreover, the presence of the inductive period for the planar emission implies that crystal loosening is necessary to overcome the barrier for the formation of the planar conformer.

To gain further insights into the factors controlling PCMT, we examined the photoresponse and crystal structures of the analogous diketones **OO** and **SS** (Figure 4C). Despite the high similarity in their chemical structures, their behavior upon UV irradiation was different: PCMT did not occur in the case of the **SS** crystal, while the **OO** crystal melted (without luminescence) (Figures S13 and S14). Single-crystal structural analysis revealed that **OO** exhibits packing features similar to those of **SO**, but **SS** does not (Figures 4C–4E). While all three diketones have a lattice plane facing the silyl moieties, in the cases of **SO** and **OO**, the two silyl moieties within a single molecule face the same plane, while in **SS**, they face a different plane. Moreover, the silyl moieties of **SO** and **OO** are disordered while those of **SS** are well ordered even at room temperature (Figure S15). These results further confirm the importance of a structure with a disordered layer with respect to the occurrence of PCMT.⁷

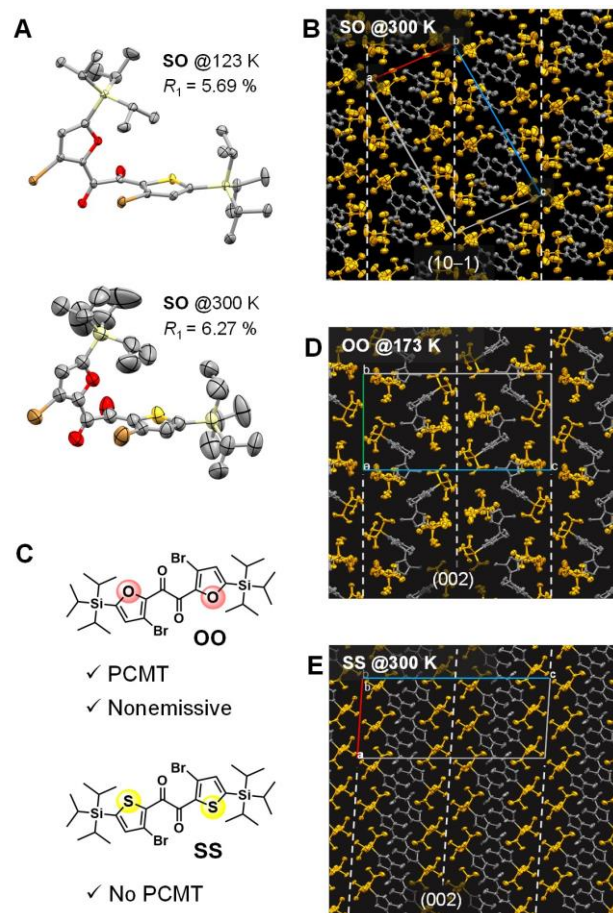


Figure 4. ORTEP drawings of (A) molecular structures of **SO** at 123 and 300 K and packing structure of (B) **SO** at 300 K, (D) **OO** at 173 K, and (E) **SS** at 300 K. Thermal ellipsoids are set at 50% probability level, and hydrogen atoms are omitted for clarity. Lattice planes facing silyl moieties are drawn as white dotted lines. (C) Chemical structures of **OO** and **SS**.

Energetically, the skew-to-planar photoisomerization is favorable in all three diketones (Table S3). However, the barrier to the structural change should increase if the intermolecular interactions in the crystals increase. Using differential scanning calorimetry, the enthalpy of fusion (ΔH_m) values of the **SO**, **OO**, and **SS** crystals were determined to be 22, 29, and 40 kJ/mol, respectively (Figures S17–S19). That the values for **SO** and **OO** were much smaller indicated that the intermolecular interactions in these PCMT-active crystals were weaker. Moreover, the Gibbs free energies for the crystal-to-SCL transition at 300 K for **SO**, **OO**, and **SS** were estimated to be 2.2, 2.7, and 12 kJ/mol, respectively. Clearly, PCMT is less endothermic in the cases of **SO** and **OO**. These results suggest that a subtle atomic replacement can significantly modulate the bulk thermal properties, resulting in PCMT in aromatic diketones.

Based on our results, a possible three-step mechanism for PCMT in the **SO** crystal is suggested (Figure 5). Initially, **SO** exhibits a skew conformation in the crystal form, which is weakly emissive at 520 nm. As the first step, the crystal packing is loosened because of the photoinduced conformational relaxation. In the loosened environment, the skew emission disappears because of the activated molecular motions.⁴⁶ Meanwhile, as the second step, a larger conformational change is allowed, resulting in the planar conformer: the yellow RTP occurs despite the loosened environment, because the planar conformer is inherently more emissive than the skew conformer.^{42,46–48} This loosening and the corresponding conformational changes occur repeatedly in the crystal during continuous UV irradiation, finally leading to greater disordering in the longer range and the eventual macroscopic melting of the bulk crystal (the third step). Thus, the stepwise changes in the luminescence of the PCMT-active crystal allowed the visualization of its molecular-level melting process in real time.

The proposed PCMT mechanism is based on a conformational change around the single bonds. This is distinct from the reported mechanisms based on the double-bond *E/Z* isomerization^{7–18} or the cleavage/formation of the σ -bond,¹⁹ which has a high energy barrier for the backward reaction in the ground state. The corresponding barrier for **SO** is not high (calculated to be 6.86 kcal/mol in vacuum, Figure S11). However, the SCL state of **SO** exhibits exceptionally high kinetic stability (greater than 3 months). We had previously demonstrated that SCLs do not crystallize readily even in the presence of crystal seeds.⁴² This is likely because the diketone core has several conformers, including axially chiral enantiomers (Figure S8). Thus, the backward recrystallization process is too slow to compete with the melting process. The elucidation of this mechanism should help improve the molecular design of PCMT-active materials and lead to the development of materials other than the conventional photochromic motifs.

In summary, we report the first instance of PCMT with luminescence evolution. The stepwise changes in the luminescence during UV irradiation suggest that the macroscopic melting process is preceded by the loosening of the crystal packing and subsequent conformational isomerization. Moreover, the present study introduces aromatic diketones as a new class of compounds exhibiting PCMT. This study furthers our understanding of the melting phenomenon at the molecular level and should lead to the development of novel molecular designs of stimulus-responsive materials based on phase transitions.

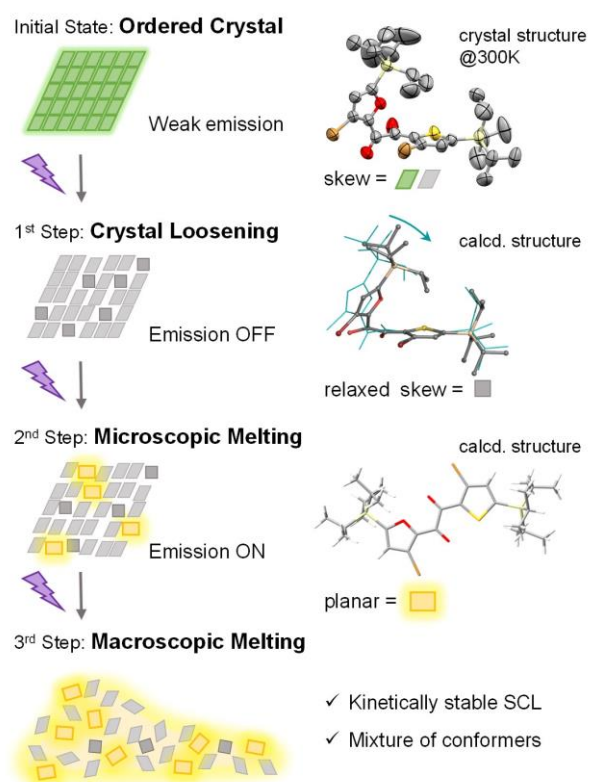


Figure 5. Schematic illustration of plausible PCMT mechanism.

ASSOCIATED CONTENT

Supporting Information.

Experimental procedures, additional spectral, photographic, crystallographic, and thermal analysis data, and computational details (PDF)

Optimized geometries and energies of molecules (xyz)

Movie S1: Luminescence changes of **SO** crystal during continuous UV irradiation under fluorescence microscope (mp4)

These materials are available free of charge via the Internet at <http://pubs.acs.org>.

Accession Codes. CCDC 2189550–2189553, 2095928, and 1986446 contain the supplementary crystallographic data for this paper. This material is available free of charge via a www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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