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Crystal Multi-Conformational Control Through Deformable Carbon–Sulfur Bond for Singlet–Triplet Emissive Tuning

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Abstract: Crystal-state luminophores have been of great interest in optoelectronics for years, whereas the excited state regulation at the crystal level is still restricted by the lack of control ways. We report that the singlet-triplet emissive property can be profoundly regulated by crystal conformational distortions. Employing fluoro-substituted tetrakis(arylthio)benzene luminophores as prototype, we found that couples of molecular conformations formed during different crystallizations. The deformable carbon-sulphur bond essentially drove the distortion of the molecular conformation and varied the stacking mode, together with diverse non-covalent interactions, leading to the proportional adjustment of the fluorescence and phosphorescence bands. This intrinsic strategy was further applied multicolor emissive conversion for solid-state and mechanoluminescence, probably offering new insights for design of smart crystal luminescent materials.

Solid-state organic luminogens play a significant role in modern optoelectronics, light-emitting materials, luminescent displays and light sources.^[1-11] In particular, luminogens that can work in the crystal phase have generated a considerable interest due to their material anisotropy, stability and the potential to construct perfect optoelectronic devices with low defect density.^[12-16] The past years witnessed substantial progress in developing crystalstate emissions, the study and application of which have been principally focused on luminescent color tuning, brightness adjustment and device fabrication.[17-22] Nevertheless, regulation of emissive pathways (e.g. regarding singlet-triplet excited state features or the transfer in between) on single materials by crystal engineering has received little attention, probably because such a excited state regulation often lacks sensitivity in a crystalline system.^[14] In contrast, it is known that emissive pathways can basically respond to diverse structural and selfassembly factors in amorphous phases.^[23-28] This factor makes it desirable to develop an intrinsic strategy of enrolling molecular

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conformational deformability to control the emissive pathways at the crystal level.

Since fluorescence and phosphorescence in a single system generally cover individual spectral regions with a sizable energy difference, the regulation of singlet-triplet emissive pathways has raised significant concerns for advanced luminescent materials.^[29, 30] Here we present a strategy of imposing crystal multi-conformational control for achieving the tunable dual emission. The strategy is inspired by that molecular conformation, not only molecular structure, can largely affect the material photophysics including the intersystem crossing (ISC) rates.^[31-34] We are intended to introduce deformable covalent bonds upon molecular crystallization to produce distortable conformations with different stackings, for manufacturing a material with fluorescent–phosphorescent proportion adjustable.

Multi-sulfurated aromatic compounds are prone to take effect metal-free room-temperature phosphorescence emitters in which the ISC process is environmentally adjustable.^[35-38] The compounds can be readily synthesized from low-cost precursors with different functional groups modified for postprocessing.^[39-41] Herein, we designed and synthesized two fluoro-substituted tetrakis(arylthio)benzene molecules (compound 1 and 2, Figure 1), based on the anticipation that the multiple C-S bond can be deformable for tuning the molecular conformation with diverse intermolecular non-covalent interaction (e.g. CH–F bond, CH– π , S–S interaction, π – π stacking, etc.). Thus, the conformational distortion and stack ability to different degree can be achieved during different crystallizations, followed by a regulation of the singlet–triplet emissive pathways.

The crystal growth of 1 and 2 can be affected by a variety of applied solvent conditions. We here investigated six representative single-crystal materials of 1, namely a DCM-IPR one (from dichloromethane and isopropanol), an ETH-EA crystal (prepared from ethanol and ethyl acetate), a TOL-BUT one (from Toluene and Butanol), an ACN one (from acetonitrile), a THF-IPR one (from Tetrahydrofuran and isopropanol) and an EA one (from ethyl acetate). These crystals show distinct photoluminescence properties (Figure 2a). The DCM-IPR and ETH-EA reveal a multiband emission spectrum with 420 nm signal dominance with a blue luminescent color. The TOL-BUT, ACN and THF-IPR crystals show even stronger emission band of 475-550 nm relative to the 420 nm one, resulting in cyan to deeper cyan luminescent colors. In the EA crystal, the emission band around 420 nm is extremely suppressed, and exhibits instead a higher emission band of 450-560 nm with a green luminescent color. The difference in luminescent color originates from the synergy of these multi-band emission signals dominated by discrete wavelengths. The CIE chromaticity diagram signifies the color parameters of the corresponding crystals (Figure 2b). Meanwhile, time-resolved emission measurements upheld the fluorescence or phosphorescence components in the multi-band emission (Figure 2c, 2d, 2e, S11, and S12).

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Figure 1. Illustration of the formation of various single-crystal structures of 1 and 2 under different crystal growth conditions. The deformable C-S bond with diverse non-covalent interactions dominate the crystal polymorphism nature, and the multi-color labelling of these single-crystal structures represents the corresponding luminescent color of fluorescence–phosphorescence emission, along with the multi-conformational change. The luminescence mechanism is linked to the degree of the molecular conformational distortion, namely, higher tense conformations give rise to a fluorescence-dominant emission since ISC is weakened by relatively restricted molecular vibrations, whereas the lower tense conformations are prone to produce phosphorescence-dominant emission when lacking the restrictive factors and allowing for an effective ISC process.

It could be found that either conformational pairs in a triclinic lattice (P 1) or a single conformation in a monoclinic lattice (P 21/c) can be formed during the crystallization of 1. The conformational pairs include a symmetrical and an unsymmetrical conformation. All of them are distinct as monitored by the C-S-C bond angles in the crystal form (Figure 2f), which reflect the conformational change and significantly affect the band ratio of the dual emission. Figure 2g shows the average C-S-C angles in these conformations of the crystals. We infer that solvent molecules with different sizes can facilitate the deformation of the C-S bond to different degree. Once the rigid crystals formed, the molecular conformation is fixed with the removal of solvents (verified by the single-crystal analysis without solvent molecules). The deformability of the C-S bond induced the distinguishing intermolecular interactions among the crystals (Figure 3a), resulting in different crystal confinement environment.

For deeply understanding the photophysical mechanism, the low-temperature (77 k) emission spectra of 1 was collected for its altered states (Figure S13). For the monomeric state of 1 in pure DMF, a smooth and broad phosphorescence band is observed. In contrast, it is split in EA-ETH, TOU-BUT and ACN crystals (Figure 2a, S14), reflecting the aggregated state only contained one phosphorescent component that can be assigned into vibrational structures rather than multiple species.[42] Furthermore, the singlet-triplet energy gap (Δ Est) varies ^[24] little among these crystals as described by the identical band wavelength of both the fluorescence and phosphorescence in Figure 2a. Another, the HOMO-LUMO orbital gap show little separation as displayed by the typical conformations upon computational simulation (Figure S15). Hence an effect of twisted intra-molecular charge-transfer on the luminescence of molecular crystals can be also excluded. [21] Therefore, it further suggests that the photophysics of the crystals can be related to the crystal restriction effect from the varied molecular conformations which induced the different ISC effectiveness. The conformational difference as well as the deformation of the C-S bonds also resulted from the assistance of diverse non-

covalent interactions in the singlet crystal system, confirmed by the intermolecular short actions marked in Figure S16-S20, namely, CH–F bond, CH– π , S–S interaction and π – π stack can be seen in these conformations (Figure 3a-c). After obtaining the spin-orbit coupling (SOC) (ξ) change (Figure 3d) in different crystal through computational simulation and the KISC change from the experiments (Table S1),^[43a] we found that the evaluated SOC § (S1, T1; S0, T1) increased largely from DCM-IPR crystal (1.198 eV; 0.957 eV) to TOU-BUT crystal (1.201 eV; 1.157 eV) and to THF-IPR crystal (1.222 eV; 1.294 eV). That is to say, in the more rigid crystals, strong intermolecular interactions promote the ISC from singlet to triplet state and lead to the higher ratio of phosphorescence at room temperature. This was further clarified by an ISC rate increase from DCM-IPR crystal $(1.1 \times 10^7 \text{ s}^{-1})$ to TOU-BUT crystal $(1.9 \times 10^8 \text{ s}^{-1})$ and to THF-IPR crystal (4.1 \times 10⁸ s⁻¹). Such an improvement in ISC may be due to the stronger intermolecular interactions that can induce stronger out-of-plane vibration to contribute to the spin orbit coupling.^[43b] The fluorescence and phosphorescence ratio change is due to the deformability of the C-S-C bond, which determined the molecular conformation and the crystal environment assisted by a variety of intermolecular interactions. Compared to those fluorescence dominant crystals (Figure 3a), the intermolecular interactions in the phosphorescencedominant crystals (Figure 3b, 3c) enhanced the degree of molecular confinement, thereby improving the SOC and resulting in an increased ratio in phosphorescence.

To better clarify such a unique behaviour, we also crystallized molecule 2 and selected two typical single-crystal forms, namely an ACE–ETH crystal (from acetone and ethanol) and an ACN crystal (from acetonitrile). Although both of the two crystals exhibit a single symmetrical conformation, they still show a polymorphism nature with the change of C-S-C bond angles, similarly resulting in a tunable dual emission band as well as an emission color difference (Figure 4). The symmetrical conformation may be due to the strong O···H interaction (Figure S21) originating from methoxy group between two adjacent molecules. This interaction makes the system easy to form an

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edge-to-edge stacking, thus to avoid the close π - π stacking that may cause the overcrowding of the molecules and the unsymmetrical conformation like compound 1 (Figure S16-S20). From the emission lifetime and spectra study (Figure S22 and

S23), we can also find it contains a triplet emission property. Similarly to compound 1, the varied C-S-C angles imply a different crystal environment and induced the fluorescence and phosphorescence ratio tuning.



Figure 2. Single-crystal luminescence and conformational study of 1: (a) Emission spectra upon 365 nm excitation in DCM–IPR, EA–ETH, TOL–IPR, ACN, THF– IPR and EA crystals. Inset shows the crystals photographs under a 365-nm UV lamp. (b) CIE 1931 chromaticity diagram signifying the luminescent color coordinates for the corresponding crystals. PL lifetime in DCM–IPR crystal measured at (c) 420 nm, (d) 475 nm, 505 and 550 nm emission upon excitation at 365 nm. (e) Time-resolved emission spectra upon 365 nm excitation with delay of the DCM–IPR crystal. (f) Unit cell display of the symmetrical and the unsymmetrical conformations of different crystals. The C-S-C bond angles are highlighted. (g) An average distribution of the C-S-C bond angles in the different conformations.

In addition to the ratio change between the fluorescence and phosphorescence, an increase in luminescent quantum yield (QY) was also observed among most of the crystals.^[44] Namely, a more rigid crystal environment can effectively enhance the ISC process and reduce the non-radiative relaxation so as to improve the emission efficiency, which can be explained by the K_{ISC} (Table S1) and calculated SOC.^[23] In addition, the P21 EA crystal only exists in a stacking mode through a strong S- π stacking instead of π – π stacking, as compared with the other P1 kind of crystals. This relatively deteriorated aggregation is unfavorable for the emission efficiency. Table S2 shows the average torsion (C-S-C dihedral angel) of the symmetrical and unsymmetrical conformations in different crystals of 1. Diminishing of the torsion reflects a strengthening of the conformational coplanarity, which also facilitates molecular rigidity for improving the QY.

With understanding the crystal nature, we turn to study the related films for practical use. As a complete isolation all of the conformations of compound 1 at film state by routine approaches is not possible as compared with single crystals, three typical solid films of compound 1 from ethanol (Eth film), dichloromethane (DCM film) or ethyl acetate (EA film) were straightforwardly obtained from the corresponding solution-processing. Figure S24 shows a solid-state multi-band emission of compound 1 in different films with proportional differences among the crystalline forms. With a facile calculation through a CIE Colorimetric diagram (Figure S25), a multi-color luminescent property among these different solid-state materials can be featured.

The dual-emission material here is highly sensitive to mechanical stimuli.^[45, 46] The dual-emission peaks of a typical EA film of 1 greatly decreased during grinding (Figure 5a), with an equilibrium state was reached after grinding for 30 s. The

On the other hand, no emission blue-shift or red-shift was

observed in the ground film, suggesting that the excimer

formation in the grinding process can be excluded.

phosphorescent ratio here decreased more significantly than the fluorescent one, because the grinding can weaken the crystal rigidity (proved by the reduction of the XRD peaks, Figure 5c).



Figure 3. Crystal stacking modes with ISC regulation: Molecular packing display of (a) DCM–IPR, (b) TOU–BUT and (c) THF–IPR crystals. π – π , S–S,CH- π and CH-F short-contacts were shown in these stacked molecular conformations. d) Spin-orbit matrix elements (cm⁻¹) for the studied molecules calculated within INSO/S approximation. The energy of S₁ and T₁ states (in eV) corresponds to the vertical excitations calculated by the (TD)DFT/B3LYP/6-31G(d).



Figure 4. Single-crystal luminescence and crystal conformational study of 2: (a) Emission spectra upon 365 nm excitation in ACE–ETH and ACN crystals. The inset shows the crystal photographs under a 365-nm UV lamp. (b) Unit cell display of the conformations of different crystals. The C-S-C bond angles are highlighted. (c) An average distribution of the C-S-C bond angles in the symmetrical conformations.

Such a mechanical response was also found to be reversible and the initial emission signal could be restored when the film was fumed with EA (see Figure 5a and 5b). Furthermore, the crystalline peaks in the XRD spectra of the pristine film vanished after grinding and could be restored by fuming (Figure 5c). These results suggest that the molecular crystal form altered along with luminescent color change during the mechanical response process.

In conclusion, we have demonstrated a strategy for crystal multi-conformational control of organic luminophore with a regulation of their singlet and triplet emissive characteristics. Using fluoro-substituted tetrakis(arylthio)benzene-based luminophores as a demonstration case, we found that the deformation of multiple C-S bond resulted in a varied conformation that strongly connected to ISC to control the dualband ratio. Meanwhile, the molecular stacking mode in the crystals plays a crucial role in regulating their emission efficiency. Based on the multi-conformational control, in this way, a manipulation of the unimolecular fluorescence and phosphorescence emission was accomplished making solidstate multicolor emission adjustable and making mechanoluminescence possible. We believe that this strategy could be valuable for further exploitation of materials with intrinsically tunable crystal-state emission with order and low defect density.



Figure 5. Reversible mechanoluminescence of 1: (a) Emission spectra of pristine, grinded and fumed EA film under 365 nm excitation. (b) The photographs of the pristine and grinded EA film under daylight and 365-nm UV light. (c) PXRD traces of pristine, ground and fumed EA film.

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Entry for the Table of Contents (Please choose one layout)

Layout 1:

COMMUNICATION

The deformable carbon–sulfur (C–S) bond with diverse non-covalent interactions essentially drives the crystal conformational distortion of asterisk-shaped luminogen, the fluorescence–phosphorescence of which can be profoundly regulated by such a crystal multi-conformational control.



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