Toward Rational Control of Mechanochromic Luminescence by Organic Crystals

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Keywords: Organic Crystals; Solid-state Emission; Mechanochromism; Intermolecular Interaction; Energy Transfer

In recent years, there has been increasing interest in mechanochromic luminescence (MCL) of organic crystals, where the emission color of fluorescence or phosphorescence changes in response to mechanical stimuli.[1,2] The MCL exhibited by organic crystals often originates from alterations in molecular arrangement and conformation induced by amorphization or phase transition to another polymorphic crystal upon mechanical stimulation. However, the design of organic crystals that manifest the desired MCL properties remains a challenging task. This presentation will discuss the current research progress toward the rational control of MCL.

1. Control of MCL properties through the two-component segregated crystals

The mechanoresponsive shift of the maximum emission wavelength could be extended by preparing two-component segregated crystals of pyrene derivatives with other fluorophores. Significant shifts in emission wavelength were achieved by mechanical stimulation-induced amorphization of the segregated crystals, resulting in energy transfer from the excimer of pyrene to the other fluorophore.[3,4] This method could be applied to the bispyrene derivative **1**, which exhibited MCL between the monomer and excimer emission of the pyrene moieties (Figure 1).[5] When **1** was mixed with 3,4,9,10-perylenetetracarboxylic diimide (**PTCDI**), a wide-range MCL exhibiting the MCL shift of 340 nm was realized. In addition, when mixed with 9,10-anthraquinone (**AQ**), a two-step MCL from blue to blue-green and orange was achieved in response to the intensity of mechanical stimulation.

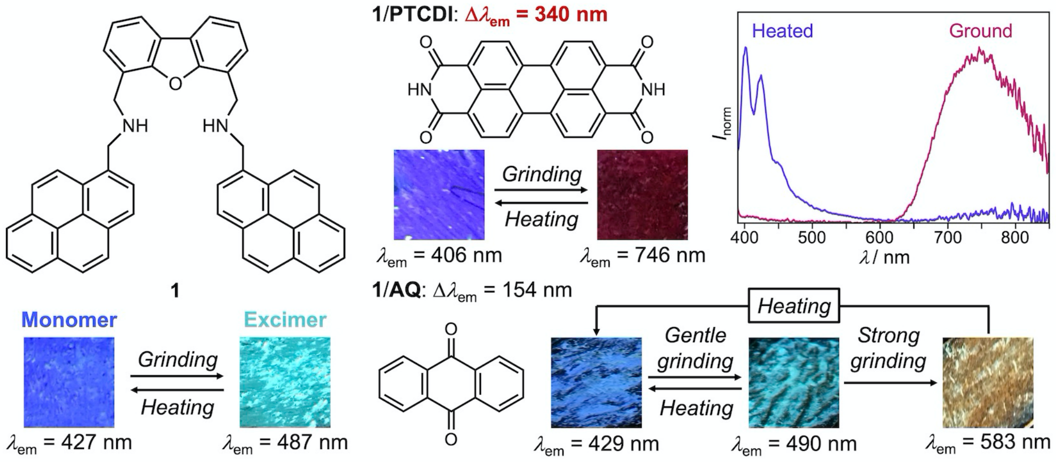

Figure 1. Wide-range MCL of **1**/**PTCDI** and two-step MCL of **1**/**AQ**.

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2. Extension of the mechanoresponsive luminescence shift via formation of doped crystal

Crystalline benzothiadiazole derivatives substituted with electron-rich heteroaromatic rings exhibit versatile MCL properties.[6–9] While substituted thienylbenzothiadiazole derivatives showed significant hypsochromic shifts of luminescence upon grinding, the mechanoresponsive luminescence shift of the unsubstituted derivative **2** was only 10 nm.[10] However, by doping with a trace amount of dithienylbenzothiadiazole **3**, the mechanoresponsive shift could be extended to 69 nm (Figure 2).[11] Specifically, the emission color of crystalline **2** was changed from green (λ_{em} = 502 nm) to yellow (λ_{em} = 559 nm) by doping with 250 ppm of **3**. Mechanistic studies revealed that the yellow emission from the doped crystal **2·3** was due to Förster resonance energy transfer (FRET) from **2** to **3**. When a mechanical stimulus was applied to crystalline **2·3**, the emission color shifted in the hypsochromic direction to light blue (λ_{em} = 490 nm). The fluorescence spectrum of ground **2·3** was in good agreement with that of ground **2**, indicating the significant decrease in FRET efficiency in ground **2·3**. This doping strategy represents a new design principle to rationally control the mechanoresponsive properties of luminescent organic crystals.

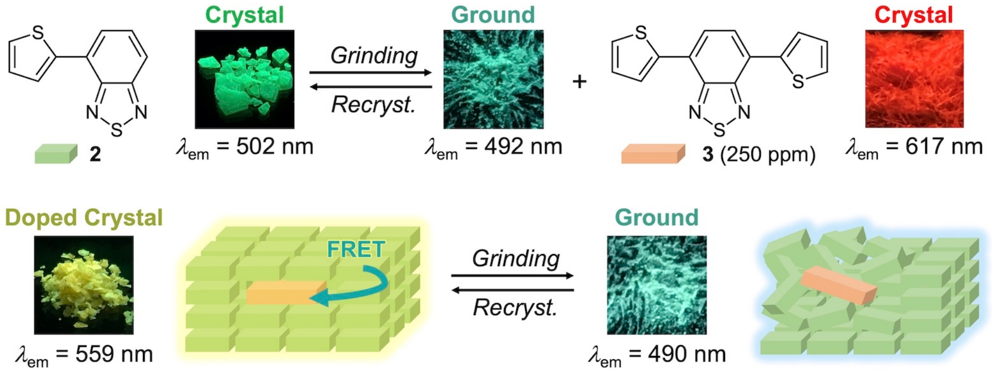

Figure 2. Extension of mechanoresponsive luminescence shift of **2** by doping with **3**.

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