Crystal-to-Amorphous Phase Transitions of Mechanochromically Luminescent Organic Molecules

(*Faculty of Engineering, YOKOHAMA National University*) ○Suguru Ito

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

Mechanochromic luminescence (MCL) describes the reversible color change of the solid-state luminescence induced by mechanical stimuli. Typical organic MCL molecules exhibit a bicolor emission-color switching based on crystal-to-amorphous phase transitions. A second external stimulus such as heating or exposure to solvent is generally required to recover the original emission color from the mechanically changed state (Figure 1).[1] We have developed novel organic fluorophores that exhibit versatile MCL behaviors.[2–4] Two-component dyes have also been investigated to control the MCL properties of organic fluorophores.[5,6] In this talk, I will discuss the behavior of amorphous states in the MCL of organic molecules.

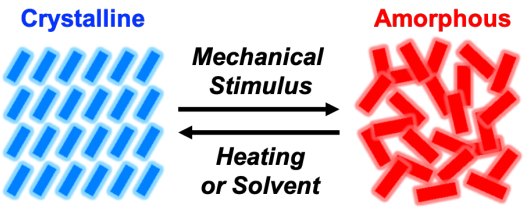

Figure 1. Typical MCL of organic molecules

1. Donor-acceptor-type benzothiadiazoles that exhibit versatile MCL behaviors

Indolylbenzothiadiazoles **1** exhibited self-recovering MCL, whereby the original emission could be recovered autonomously at room temperature after grinding (Figure 2a). The self-recovering nature should be rationalized by a spontaneous recrystallization of **1** from the amorphous states.[2,3] The MCL of phenanthroimidazolylbenzothiadiazoles **2** could be tuned by changing the substituent Ar on the benzothiadiazole ring (Figure 2b). Red-shifted or blue-shifted MCL as well as two-step MCL were observed for these dyes owing to the formation of different crystal structures by introducing various substituents.[4]

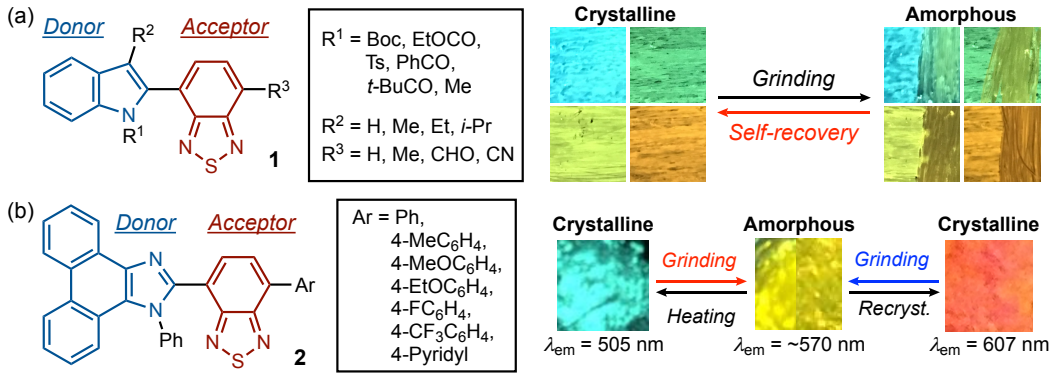

Figure 2. (a) Self-recovering MCL of indolylbenzothiadiazoles **1**. (b) Red-shifted and blue-shifted MCL of phenanthroimidazolylbenzothiadiazoles **2**.

2. Two-component systems for controlling the MCL properties of organic molecules

The preparation of two-component organic fluorophores is a useful method to tune the range of the mechanical-stimuli-induced shift of the emission wavelength ($\Delta\lambda_{em}$). The two-component mixture of a poorly MCL-active dipyrenylbithiophene ($\Delta\lambda_{em}$ = 13 nm) and non-MCL active *N*,*N*′-dimethylquinacridone (**DMQA**) exhibited tricolor MCL ($\Delta\lambda_{em}$ = 135 nm) based on the transition of the fraction of the MCL dye between one crystalline and two amorphous phases.[5] The self-recovering nature of 2-alkyl-4-(pyren-1-yl)thiophenes **3** was tunable by changing the length of alkyl group R. Upon mixing the hexyl derivative of **3** with **DMQA**, a high-contrast self-recovering MCL ($\Delta\lambda_{em}$ = 194 nm) could be achieved (Figure 3a).[6] Furthermore, a wide-range MCL over 300 nm ($\Delta\lambda_{em}$ = 340 nm) was realized based on the transition between segregated crystals and an amorphous mixture composed of a bis(1-pyrenylmethyl)diamine derivative and a far-red-emissive organic dye (Figure 3b).

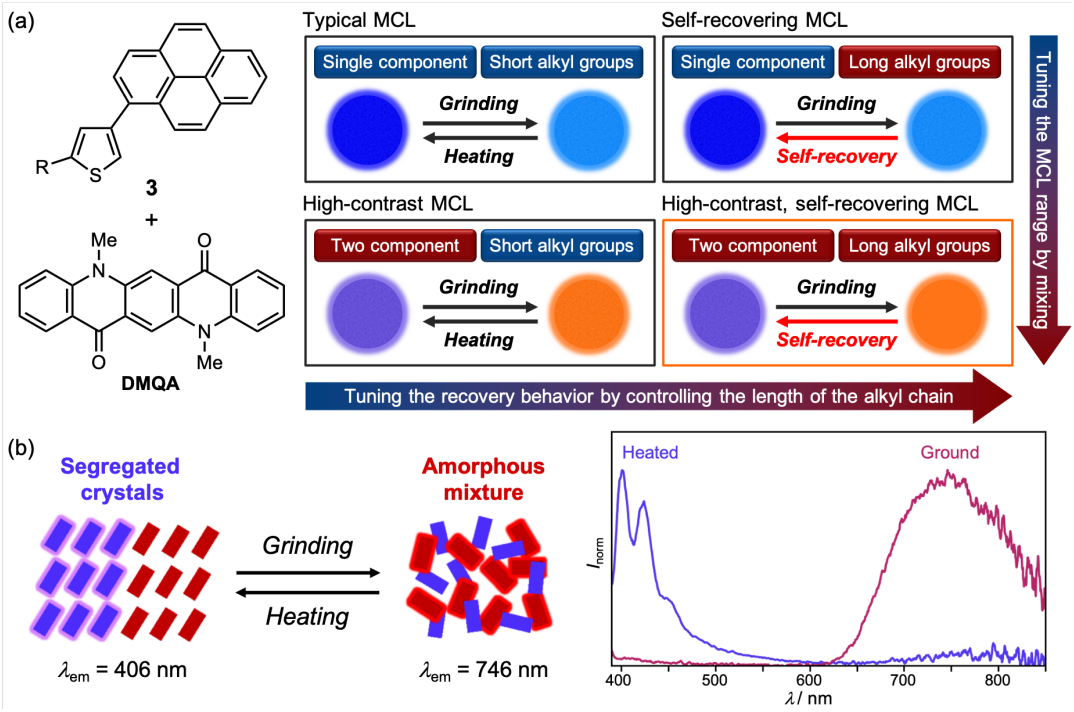

Figure 3. (a) Tunable MCL of 2-alkyl-4-(pyren-1-yl)thiophenes. (b) Wide-range MCL based on the transition between segregated crystals and an amorphous mixture.

References: [1] S. Ito, *Chem. Lett.* **2021**, DOI: 10.1246/cl.200874 (***Review***). [2] S. Ito, T. Yamada, T. Taguchi, Y. Yamaguchi, M. Asami, *Chem. Asian J.* **2016**, *11*, 1963. [3] S. Ito, T. Taguchi, T. Yamada, T. Ubukata, Y. Yamaguchi, M. Asami, *RSC Adv.* **2017**, *7*, 16953. [4] S. Nagai, M. Yamashita, T. Tachikawa, T. Ubukata, M. Asami, S. Ito, *J. Mater. Chem. C* **2019**, *7*, 4988 (***Inside Back Cover***). [5] S. Ito, G. Katada, T. Taguchi, I. Kawamura, T. Ubukata, M. Asami, *CrystEngComm* **2019**, *21*, 53 (***Back Cover***). [6] M. Ikeya, G. Katada, S. Ito, *Chem. Commun.* **2019**, *55*, 12296 (***Back Cover***).