Over the past decade, a growing number of luminescent organic crystals have been developed through appropriate molecular design strategies to overcome the problem of concentration quenching. The development of stimuli-responsive crystals capable of switching luminescence properties is an important target in the field of luminescent organic crystals. Since mechanical stimulation is the ubiquitous external stimulus, particular attention has been paid to mechanochromic luminescence (MCL) of organic crystals. In order to elucidate the relationship between the crystal structure and the mechanoresponsive properties of luminescent organic crystals, an increasing number of polymorphic and multicomponent organic crystals have emerged in recent years.

Recently, we have reported the versatile MCL properties of donor–acceptor (D−A) type benzothiadiazole derivatives [2,3]. These derivatives are composed of an electron-rich heteroaromatic ring and an electron-deficient benzothiadiazole ring. Given that the emission wavelength of D−A molecules is sensitive to the polarity of the surrounding environment, crystalline D−A compounds often change their emission colors when the crystal structure collapses in response to mechanical stimulation.

Recently, we have reported the thienyl-substituted benzothiadiazole derivative 1 as a new donor–acceptor-type MCL dye [4]. Both bicolor and tricolor MCL have been realized by the three polymorphic crystals of 1 (Figure 1a). The emission color of these polymorphic crystals should be determined by the dihedral angle between benzothiadiazole and thiophene rings as well as the packing mode. Both crystal a and b formed isolated dimers, whereas extended intermolecular stacks were observed for crystal g.

The control over the mechanoresponsive luminescence of crystalline 4-(2-thienyl)-2,1,3-benzothiadiazole (2) has also been achieved by doping a trace amount of 4,7-di(2-thienyl)-2,1,3-benzothiadiazole (3) [5]. Most remarkably, the mechanoresponsive shift in the maximum emission wavelength has been extended from 10 nm to 69 nm by preparing the doped mixed crystals 2·3 (Figure 1b). The larger shift in the emission band of the doped mixed crystals 2·3 compared with the single-component crystals of 2 should be attributed to the mechano-induced on–off switching of the Förster resonance energy transfer from 2 to 3.

Figure 1. (a) Multi-color mechanochromic luminescence of three polymorphic crystals of 1. (b) Extension of the mechanoresponsive luminescence shift of 2 by doping with 3.

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