

Poster Presentation

MS43.P29

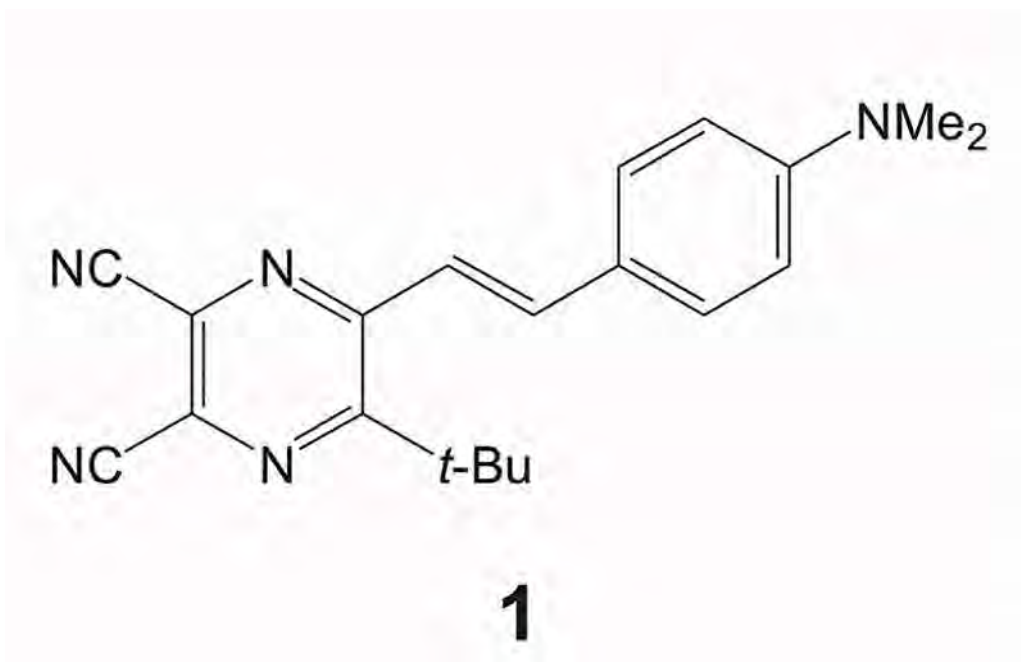
Optical Properties of Three Crystal Modifications of a 2,3-Dicyanopyrazine Dye

N. Okada¹, R. Eto¹, E. Horiguchi-Babamoto², S. Matsumoto¹

¹Yokohama National University, Department of Environmental Sciences, Yokohama, Japan, ²Musashino University, Department of Pharmaceutical Sciences, Tokyo, Japan

Some pyrazine dyes are known to display strong fluorescence not only in solution but also in the solid-state. 5-*t*-Butyl-2,3-dicyano-6-[4-(dimethylamino)styryl]pyrazine (**1**) is a 2,3-dicyanopyrazine dye synthesized for an examination of substituent effects on thin-film growth [1]. Dye **1** was found to exhibit three crystal modifications with different color appearance (I: red, II: black, III: reddish purple). Modification I is a solvate crystal including one chloroform per one dye molecule [2], and modifications II and III are polymorphs. In this work, optical properties of these three modifications were interpreted on the basis of their crystal structures. The absorption spectra of the modifications were measured using optical waveguide spectroscopy. The absorption maxima of modifications I, II and III were found at 559 nm, 462 nm and 571 nm, respectively. A bathochromic absorption shift of reddish modifications I and III from that of **1** in toluene was 79 nm (-2944 cm⁻¹) and 91 nm (-3320 cm⁻¹), respectively. On the other hand, a hypsochromic absorption shift of 18 nm (812 cm⁻¹) was observed in modification II. The fluorescence maxima of modifications I, II and III were found at 619 nm, 734 nm and 668 nm, respectively. The energy displacement corresponding to the observed spectral shifts was characterized in terms of an exciton interaction. The exciton interaction for a dimer was estimated using the extended dipole model, and the nearest-neighbor approximation was applied for evaluating a total energy displacement due to crystallization. The calculation results were qualitatively in good agreement with the observed spectral shifts. The result also revealed that molecular pairs in two-dimensional stacking structure in these modifications play a significant role in the total energy displacement.

[1] S. Matsumoto, T. Yano, E. Horiguchi-Babamoto, et al., *Mol. Cryst. Liq. Cryst.*, 2007, 472, 105-112, [2] S. Matsumoto, E. Horiguchi-Babamoto, R. Eto, et al., *Dyes Pigm.*, 2012, 95, 431-435



Keywords: Organic Dye, Polymorphism, Optical Property