

# Original Research Paper

J. Jpn. Soc. Colour Mater., 93 [9], 288–291 (2020)

—Special Edition Central (Japan) Section : New colorant technologies—

## Relationship between Crystal Packing and Solid-State Fluorescence Quantum Yield in Pyrazine Monoboron Complexes

Yasuhiro KUBOTA<sup>\*,†</sup>, Yuki HAISHIMA<sup>\*</sup>, Kazumasa FUNABIKI<sup>\*</sup> and Masaki MATSUI<sup>\*</sup>

<sup>\*</sup> Department of Materials Science and Technology, Faculty of Engineering, Gifu University, 1-1 Yanagido, Gifu, Gifu 501-1193, Japan

<sup>†</sup> Corresponding Author, E-mail: kubota@gifu-u.ac.jp

(Received May 26, 2020; Accepted August 17, 2020)

### Abstract

The relationship between crystal packing and solid-state fluorescence quantum yield ( $\Phi_f$ ) in pyrazine monoboron complexes **1**–**6** was investigated. The maximum fluorescence wavelength ( $F_{\max}$ ) of the BPh<sub>2</sub> complexes **4**–**6** was blue-shifted (524–628 nm) and the  $\Phi_f$  values were higher (0.13–0.29) than those of the corresponding BF<sub>2</sub> complexes **1**–**3** ( $F_{\max}$ : 531–672 nm,  $\Phi_f$ : 0.04–0.13), probably due to inhibition of the intermolecular interactions. Despite weaker intermolecular interactions of the dimethylamino-substituted BPh<sub>2</sub> complex **6** compared to non-substituted BF<sub>2</sub> complex **1**, **6** ( $\Phi_f = 0.13$ ,  $F_{\max} = 628$  nm) had the same  $\Phi_f$  value as **1** ( $\Phi_f = 0.13$ ,  $F_{\max} = 542$  nm) due to red-shifted  $F_{\max}$ , which promoted non-radiative processes.

**Key-words:** Boron complex,  $\beta$ -iminoenolate ligand, Pyrazine, Solid-state fluorescence, Crystal packing

### 1. Introduction

Despite the wide-ranging applications of solid-state fluorescent organic dyes in a variety of areas such as organic light-emitting diodes<sup>1)</sup>, solid-state dye lasers<sup>2)</sup>, and organic light-emitting field-effect transistors<sup>3)</sup>, the development of these dyes is still challenging. Common organic dyes that fluoresce in dilute solution often quench or reduce the fluorescence intensity in the solid state; this phenomenon is called aggregation-caused quenching (ACQ) or concentration quenching<sup>4)</sup>. The solid-state fluorescence properties of organic dyes are known to be strongly dependent on the molecular packing<sup>5)</sup>. In many cases, the intermolecular  $\pi$ - $\pi$  interactions in the solid state lead to ACQ<sup>6)</sup>. The introduction of bulky substituent group in organic dyes should prevent the formation of intermolecular  $\pi$ - $\pi$  interactions and is often used for the expression of fluorescence and enhancement of the fluorescence quantum yield in the solid state<sup>7)</sup>.

Organoboron complexes are some of the most vital fluorescent dyes. Due to the rigid molecular skeleton, organoboron complexes often fluoresce in solution<sup>8,9)</sup>. Additionally, the photophysical properties such as absorption and fluorescence wavelengths can be controlled by the type of ligand. However, similar to the common organic dyes, organoboron complexes exhibit the ACQ phenomenon in the solid state. In the course of our studies on the organoboron compounds<sup>10-14)</sup>, we have found that the introduction of

bulky substituent groups, particularly on the boron atom, is a good strategy for enhancement of the fluorescence quantum yield of organoboron compounds. We have also reported pyrazine monoboron complexes featuring a  $\beta$ -iminoenolate ligand that show interesting fluorescence properties in solution such as fluorescence solvatochromism<sup>15)</sup>. In this paper, we reported the relationship between crystal packing and solid-state fluorescence quantum yield in the pyrazine monoboron complexes.

### 2. Experimental

The synthesis and fluorescence properties of pyrazine monoboron complexes **1**–**6** in solution were reported in our previous paper<sup>15)</sup>. Fluorescence spectra in the solid state were measured with a Jasco FP-8600 spectrofluorometer. Fluorescence quantum yields in the solid state were recorded with a Hamamatsu Quantaurus-QY instrument. The single crystals of **1**, **4**, and **6** were obtained by the slow diffusion of hexane into chloroform solutions of the corresponding compounds. Single-crystal X-ray diffraction measurements were performed on a Rigaku Mercury 375R/M CCD (XtaLAB-mini) diffractometer with graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71075$  Å). The crystal structures were solved using direct methods with SHELXS-97 or SHELXS2013 and refined by full-matrix least-squares methods with anisotropic thermal parameters for non-hydrogen atoms on  $F^2$  using SHELXL-97 or SHELXL2013. All hydrogen atoms were placed using AFIX instructions. The Cambridge Crystallographic Data Center (CCDC) numbers for **1**, **4**, and **6** are 1567751, 1567752, and

[Figures and illustrations] Figures and illustrations published in black and white in the journal can be seen in color at our public website [J-STAGE]. Please make use of it.