メチル置換有機ホウ素錯体の結晶構造と蛍光特性

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Crystal Structures and Fluorescence Properties of Methyl-substituted Organoboron Complexes

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We previously proposed that crystals of organoboron complex **1a** (Fig. 1a) with methyl groups at the *p*-positions of phenyl groups exhibit "excited multimer luminescence" which is the luminescence from the multiple molecules with the interaction in the excited state.[1] To gain further insights into the proposal, in this work, we synthesized some organoboron complexes **1a**–**e** with methyl groups at various positions.

Two crystal polymorphs were obtained for complex **1b** (*m*-Me), and crystals **1b-B** and **-Y** exhibited blue (λ_{FL} = 460 nm) and yellow (536 nm) luminescence (Fig. 1b,c), respectively. The long-wavelength luminescence of **1b-Y** was assigned to an excimer from two facts: 1) π-stacked dimers exist in the crystal, and 2) time-resolved photoluminescence spectroscopy of the crystal showed-a rise of a *ca.* 550-nm component associated with a decay of a *ca.* 400-nm component attributable to the excited monomer luminescence. In the presentation, we will discuss new findings on "excited multimer luminescence" based on the results of **1a** and **1c**–**e**.

Keywords: Organoboron Complex; Organic Crystal; Fluorescence; X-ray Crystallographic Analysis; Time-resolved Photoluminescence Spectroscopy

我々は以前，フェニル基の *p* 位にメチル基をもつ有機ホウ素錯体 **1a**（Fig. 1a）の結晶が，励起状態で複数分子が相互作用した発光である“励起マルチマー発光”を示すことを提唱した[1]．さらなる知見を得るべく，本研究ではメチル基を種々の位置にもつ有機ホウ素錯体 **1b**–**e** を合成し，結晶構造と発光特性の関係を調べた．

錯体 **1b**（*m*-Me）では 2 種の結晶多形，結晶 **1b-B**，**-Y** が得られ，それぞれ青色（λ_{FL} = 460 nm），黄色（536 nm）の発光を示した（Fig. 1b,c）．結晶 **1b-Y** の発光については，1）結晶中に積層二量体が存在すること，2）時間分解発光分光で励起モノマーに帰属可能な短波長（*ca.* 400 nm）発光成分の減衰に伴う長波長（*ca.* 550 nm）発光成分の増加が観測されたことの 2 点から，エキシマー発光と帰属した．発表では，他の誘導体（**1a**，**1c**–**e**）の結果も含め，“励起マルチマー発光”の新しい知見について議論する．

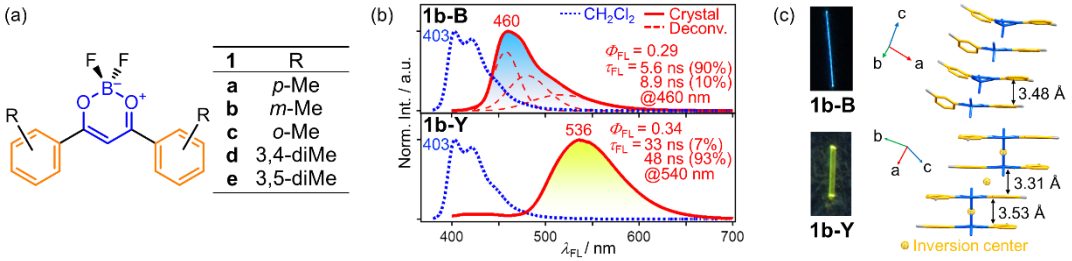

Fig. 1. (a) Molecular structures of **1a**–**e**. (b) Fluorescence spectra of **1b-B** and **1b-Y** in CH_2Cl_2 (*ca.* 1 × 10^{-5} M, λ_{EX} = $\lambda_{AB,max}$) and crystal (λ_{EX} = 365 nm). (c) Crystal structures of **1b-B** and **1b-Y**.

1) Sakai, A.; Tanaka, M.; Matsui, Y.; Ikeda, H. *et al. Chem. Eur. J.* **2015**, *21*, 18128–18137.