メチル置換有機ホウ素錯体の分子構造，結晶構造，および蛍光特性の相関

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Correlation of the Molecular Structure, Crystal Structure, and Fluorescence Property of Methyl-substituted Organoboron Complexes

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We previously proposed that an organoboron complex *p*-**1** (Fig. 1a) with methyl groups at the *p*-positions exhibits "excited multimer luminescence" which is characterized by π-stacking structure and orbital fusion over multiple molecules in crystals.[1] To verify the generality of the phenomenon, in this work, we synthesized several methyl-substituted organoboron complexes and investigated the correlation of molecular structure, crystal structure, and fluorescence properties.

In the crystal of *m,m*-**1** with four methyl groups, the π-stacking structure similar to that of *p*-**1** was observed (Fig. 1b). Time-dependent density functional theory calculations using the crystal data show orbital fusions over more than three molecules, suggesting that the luminescence of *m,m*-**1** (Fig. 1c: light blue, 464, 480^{sh}, and 508^{sh} nm) involves "excited multimers". After considering the results of other derivatives, it was suggested that derivatives with high crystallographic symmetry exhibit "excited multimer luminescence".

Keywords : Organoboron Complex; Organic Crystal; Fluorescence; X-ray Crystallographic Analysis; Density Functional Theory Calculation

我々は以前，*p* 位にメチル基をもつ有機ホウ素錯体 *p*-**1**（Fig. 1a）が，結晶中でπ積層構造と多分子の軌道融合を特徴とする“励起マルチマー発光”を示すことを提唱した[1]．この一般性を検証するため，本研究では種々のメチル置換有機ホウ素錯体を合成し，分子構造，結晶構造，および蛍光特性の相関を検討した．

メチル基を 4 つもつ *m,m*-**1** の結晶中において，*p*-**1** に類似したπ型積層構造が見られた（Fig. 1b）．結晶データを用いた時間依存密度汎関数理論計算で，3 分子以上に及ぶ軌道融合が見られたことから，*m,m*-**1** の発光（Fig. 1c: 薄青色，464, 480^{sh}, および 508^{sh} nm）には“励起マルチマー”の関与が示唆された．他の誘導体の結果も考慮した結果，高い結晶学的な対称性をもつ誘導体が，“励起マルチマー発光”を示すことが示唆された．

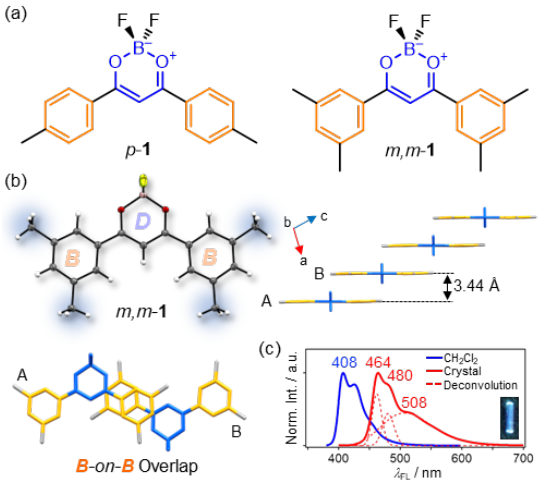

Fig. 1. (a) Molecular structures of *p*-**1** and *m,m*-**1**. (b) Crystal structures of *m,m*-**1**. (c) Fluorescence spectra of a CH_2Cl_2 solution (*ca.*1 × 10^{-5} M, $\lambda_{EX} = \lambda_{ABS,max}$) and crystals ($\lambda_{EX}$ = 365 nm) of *m,m*-**1**.

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