Room-Temperature Phosphorescence of Iodine-substituted Dibenzoylmethanatoboron Difluoride

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Metal-free materials that display room-temperature phosphorescence (RTP) are interesting substances. However, these materials are not common because of the requirement for enhanced intersystem crossing (ISC) and/or suppressed thermal deactivation of their excited triplet states. In this work, in the efforts for elucidating photoluminescence (PL) properties of organoboron complexes,[1] we found out that bis(4-iodobenzoyl)methanatoboron difluoride (**1BF$_2$**, Fig. 1a) emits not only fluorescence (FL) but also green RTP in the crystalline state though it exhibits only blue FL in degassed *n*-BuCl solution.[2]

The PL spectrum of **1BF$_2$** in degassed *n*-BuCl at 298 K is composed of a fluorescence band at 421 nm (Fig. 1b, broken curve). At 77 K, **1BF$_2$** in a glassy *n*-BuCl matrix exhibits FL bands at 421 nm together with bands at 512 nm (gray). The PL at 512 and 545 nm was assigned to phosphorescence (PH) since these bands were decayed with long τ of 3.6 ms. In contrast, the crystals of **1BF$_2$** emit PL consisting of FL at 460 nm (τ = 0.5 and 4.0 ns) and PH at 527 nm (1.3 ms) even at room temperature (black). X-Ray crystallographic analysis revealed that one molecule of **1BF$_2$** possesses van der Waals contacts with 14 neighboring molecules in the packing structure (Fig. 1c). The major interactions are classified into π-stacking (–17.1 kcal mol^{-1}), H•••F hydrogen bonding (–9.9), and I•••F halogen bonding (3.0) whose intermolecular interaction energies were evaluated by density functional theory calculations. These results suggest that these intermolecular interactions should provide a rigid crystal packing structure to suppress a thermal deactivation of T_1 state of **1BF$_2$**.

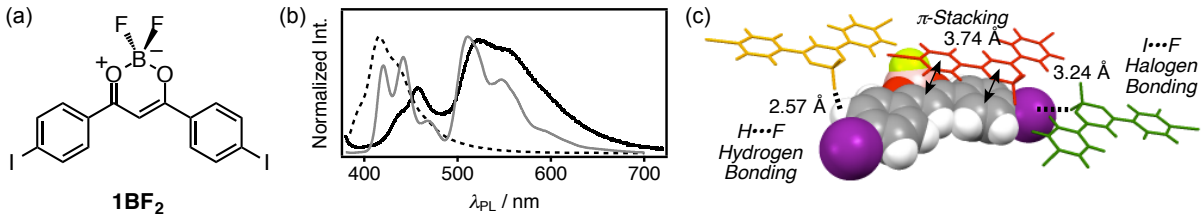

Fig. 1. (a) Molecular structure of **1BF$_2$**. (b) PL spectra of **1BF$_2$** in degassed *n*-BuCl at 298 (broken curve) and 77 K (gray) and in the crystalline state (black). (c) Intermolecular interactions of **1BF$_2$** operating in the crystal packing structure.

References:

[1] A. Sakai, E. Ohta, Y. Matsui, H. Ikeda, *et al. Chem. Eur. J.* **2015**, *21*, 18128–18137.
[2] A. Sakai, E. Ohta, S. Tsuzuki, Y. Matsui, H. Ikeda, *ChemPhysChem* **2016**, *17*, 4033–4036.