Synthesis and Properties of Two Boron-containing Electron-deficient Heteroacenes

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Xanthene is one of the most widely used π-conjugated scaffolds for organic dyes, as exemplified by fluorescein and rhodamine. To produce attractive π-electron materials using this scaffold, various chemical modifications have been conducted, such as the extension of the π-skeleton and the replacement of an oxygen atom at the 10-position with other main-group elements. Among them, the incorporation of boron atoms is effective to furnish significantly red-shifted absorption and emission through lowering the LUMO level due to the electron-accepting effect of the boron atom. As such example, we previously succeeded in the synthesis of borafluorescein,[1] which exhibited absorption and emission in the near-infrared (NIR) region.

Herein, we report the synthesis of diboron-containing heteroacene **1** in which two xanthene skeletons are fused. This molecule exhibited intense absorption and emission in the NIR region due to the electronic effects of the boron and oxygen atoms as well as the effective π-extension. Replacement of the central benzene ring with a thienothiophene scaffold in **2** resulted in further bathochromic shifts of the absorption bands. Furthermore, these molecules showed multi-step reversible redox processes. In this presentation, we will discuss about their synthesis, crystal structures, electronic properties, and photophysical properties.

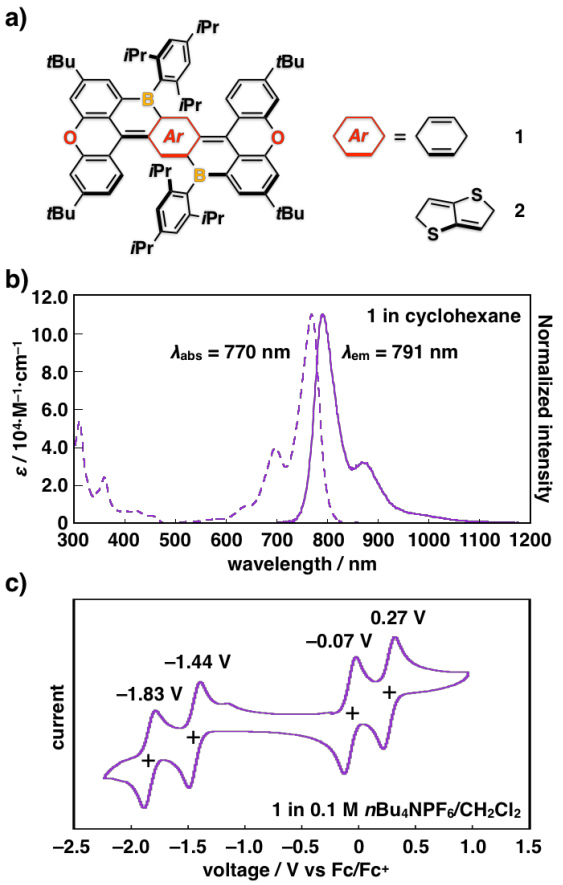

Figure 1. a) Molecular structures. b) Absorption and emission spectrum of compound **1** in cyclohexane. c) Cyclic voltammogram of compound **1** in CH_2Cl_2: scan rate: 0.05 V s^{-1}; supporting electrolyte: [nBu$_4$N][PF_6] (0.1 M); all potentials referenced vs. Fc/Fc^+.

1) N. Ando, H. Soutome, S. Yamaguchi, *Chem. Sci.* **2019**, *10*, 7816.