

Construction and Synthesis of Near-Infrared Emissive Boron Complexes Based on Molecular Orbitals of Nitrogen-Containing Aromatic Heterocycles

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Since near-infrared (NIR) light has various useful properties such as invisibility and high permeability, NIR-emissive materials have been applied in bio-imaging, sensing, and optical transmission. Generally, in order to obtain NIR emission from organic molecules, it is necessary to realize a narrow HOMO–LUMO gap. To fulfill desired electronic structures, there are two conventional strategies: 1) Extension of π -electron delocalization 2) Incorporation of electron-donating and -accepting units.¹

Pyrazine has characteristic frontier molecular orbitals (FMO). There is large contribution from N atoms in its LUMO, while slight contribution in HOMO (Figure 1). Namely, pyrazine has separated FMO. Besides, it is known that boron is electro-negative element, thus stabilization of ligand energy levels can be expected via complexation.² Herein, we anticipated that only the LUMO energy level of pyrazine can be stabilized largely by boron complexation because of the separated FMO of pyrazine, resulting in narrow HOMO–LUMO gaps of the boron complexes.

We synthesized two types of pyrazine-based ligands which are different in the structural symmetry, and we also synthesized subsequent boron complexes based on the ligands (Scheme 1). Optical properties of the boron complexes and the origin of differences in them will be described in presentation.

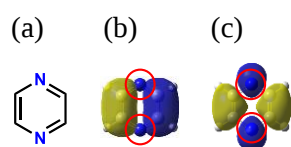
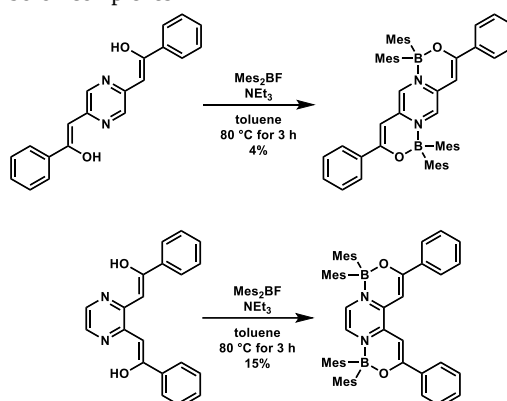


Figure 1. (a) Molecular structure of pyrazine. (b) HOMO-1 and (c) LUMO distributions calculated with the B3LYP/6-31+G(d,p) level of theory. The HOMO of the molecule is composed of a non-bonding lone pair, thus was not considered in our discussion.

Scheme 1. Synthetic scheme of two pyrazine-based boron complexes



1) Fang, L. *et. al. J. Org. Chem.* **2016**, *81*, 4347–4352.

2) Bazan, G. C. *et. al. J. Am. Chem. Soc.* **2011**, *133*, 4632–4644.