

Substituents on Boron of Organoboron Complexes Modulates Luminescent Properties via Excited Triplet States

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Abstract

Organoboron complexes have attracted attention because of their electron-accepting character and remarkable luminescent properties. Recently, we have synthesized β -diketiminato boron complexes that exhibit functional luminescence in solid states. Furthermore, these boron complexes exhibit phosphorescence with long lifetime (~ 1 sec) at 77 K as well as fluorescence.^[1] This fact indicates that the intersystem crossing from the singlet excited states to triplet ones is fast enough to compete with fluorescence. However, the detailed mechanism of such a fast intersystem crossing of this class of compounds is unclear. Herein, we demonstrate that substituents on their boron atom modulate their luminescent properties via excited triplet states, *i.e.* phosphorescence and delayed fluorescence. We will describe their synthesis and photophysical properties.

Results and Discussion

We synthesized boron complexes with different substituents at the boron center. The typical examples of the obtained compounds were shown in Figure 1. Interestingly, their photophysical properties highly depended on the substituents on the boron atom. Biphenyl-substituted complex **BBiph** exhibited room-temperature phosphorescence, while phenyl substituted one **BPh** showed thermally activated delayed fluorescence.

Density functional theory calculations suggested that the intersystem crossing would occur between locally excited (LE) and charge transfer (CT) excited states. The relative location of the LE and CT states could be modulated by the substituents. We will describe the detailed mechanisms of these photoluminescence properties and demonstrate further functionalization of these complexes.

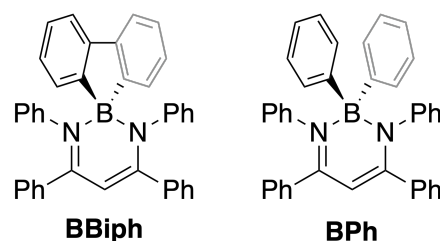


Figure 1. Chemical structures of synthesized organoboron complexes.

Reference

[1] (a) Yoshii, R.; Hirose, A.; Tanaka, K.; Chujo, Y. *J. Am. Chem. Soc.* **2014**, *136*, 18131; (b) Yoshii, R.; Hirose, A.; Tanaka, K.; Chujo, Y. *Chem. Eur. J.* **2014**, *20*, 8320; (c) Yamaguchi, M.; Ito, S.; Hirose, A.; Tanaka, K.; Chujo, Y. *J. Mater. Chem. C* **2016**, *4*, 5314; (d) Ito, S.; Yaegashi, M.; Tanaka, K.; Chujo, Y. *Chem. Eur. J.* **2021**, *27*, 9302.