

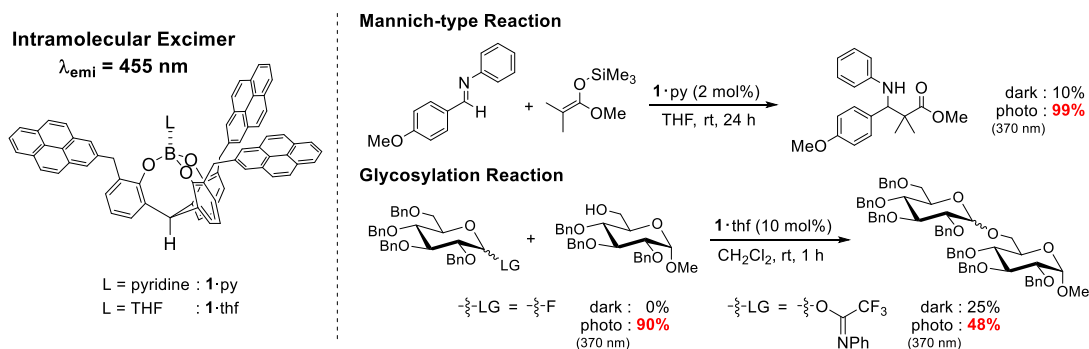
Properties of Photo-Activated Lewis Acid Catalyst and Application to Glycosylation

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Recently, the reactions mediated by photoexcited species have attracted much attention in organic chemistry. A number of photochemical reactions involving by transition metals¹ and organic dyes² have been developed, however, the mediations of Lewis acids have been limited to few reports. Our group has investigated the Lewis acidity and catalytic activities of tripodal triphenoxy boranes.³ Because the properties of the borates are readily controlled by the introductions of substituents, the tripodal structure should be a promising platform for a photo-activated Lewis acid. In this study, we designed and synthesized a cage-shaped borate with pyrenes through linkers. The structural changes induced by intramolecular excimer formation should be reflected in the reactivity of Lewis acid.

The fluorescence spectrum of the cage-shaped borate **1**·py gave a broad emission at 455 nm. The emission is notably observed even in the dilute conditions, thus we assigned the emission to an intramolecular excimer. The borate **1**·py worked as a photo-activated Lewis acid catalyst. When the Mannich-type reaction of imine with silyl ketene acetal in the presence of catalytic amount of **1**·py was performed under the photoirradiation of 370 nm light, the catalytic efficiency was dramatically improved compared to dark condition. Furthermore, the same acceleration of the reaction under photoirradiation was observed in the glycosylation using both glycosylfluorides and glycosyl imidates. From the investigation of fluorescence quenching and ligand dissociation behavior, we believe that the formation of the intramolecular excimer assists the regeneration of the catalyst and the activation of the substrates. The detailed mechanism will be presented.



1) D. A. Nicewicz, D. W. C. MacMillan, *Science* **2008**, 322, 77. 2) D. P. Hari, P. Schroll, B. König, *J. Am. Chem. Soc.* **2012**, 134, 2958. 3) a) M. Yasuda, S. Yoshioka, S. Yamasaki, T. Somyo, K. Chiba, A. Baba, *Org. Lett.* **2005**, 8, 761. b) M. Yasuda, H. Nakajima, R. Takeda, S. Yoshioka, S. Yamasaki, K. Chiba, and A. Baba, *Chem. Eur. J.* **2011**, 17, 3856. c) D. Tanaka, Y. Tsutsui, A. Konishi, K. Nakaoka, H. Nakajima, A. Baba, K. Chiba, and M. Yasuda, *Chem. Eur. J.* **2020**, 26, 15023.