Synthesis and Functionalities of Luminescent Conjugated Polymers Based on Dialdiminate Boron Complexes

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Abstract

Solid-state luminescent molecules are essential for the development of advanced optical materials and devices, such as organic light-emitting diodes, chemical sensors, and organic lasers. Luminescent boron complexes have attracted attention because of their electron-accepting character and stimuli-responsive properties. We have developed solid-state emissive materials based on group 13 elements *β*-diiminate complexes with crystallization-induced emission.[1] Herein, we synthesized *β*-diiminate boron complexes and their polymers with highly efficient luminescence both in the solutions and solids. Moreover, a series of conjugated polymers composed of the complex were obtained by coupling reactions. We will describe their molecular design, syntheses, and luminescent properties.

Results and Discussion

We synthesized boron complexes with aromatic groups at different positions as shown in Figure 1. The compounds with aromatic rings at R_1 position are named as diketiminates, while dialdiminates possess hydrogen atoms at R_1 position. Conjugated polymers composed of these complexes were obtained by using metal-catalyzed copolymerization with fluorene, bithiophene, or phenylene comonomers. Furthermore, homopolymers were synthesized by nickel-mediated Yamamoto coupling with dibrominated boron complexes.

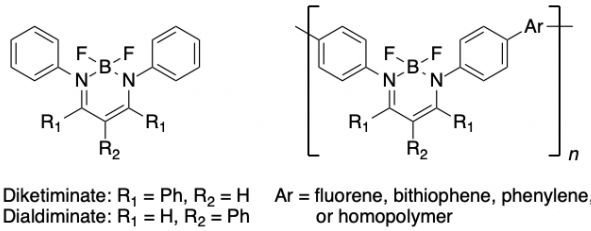

Figure 1. Chemical structures of synthesized complexes and polymers.

Diketiminate complexes showed fluorescence at the crystalline state, meanwhile they were not emissive in their solutions. On the other hand, dialdiminate complexes showed not only at the crystalline state but also in the solutions. It was suggested that non-radiative quenching processes would be accelerated by the aromatic substituents at R_1 positions.

The polymers of diketiminates exhibited solid-state emission, but their solutions hardly emitted light. On the other hand, the polymers of dialdiminates were luminescent at both solid and solution states as well as the corresponding dialdiminate small molecules. Furthermore, the homopolymers of dialdiminates showed solvent-dependent change in emission color and intensity, which was not observed from the small molecules.

Reference

[1] Yoshii, R.; Hirose, A.; Tanaka, K.; Chujo, Y. *J. Am. Chem. Soc.* **2014**, *136*, 18131.