Crystallization-Induced Emission Enhancement of Low Energy Gap Boron Complexes

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Crystallization-induced emission enhancement (CIEE) is a unique photophysical phenomenon in which the compound shows no or weak luminescence in amorphous state but becomes strongly emissive in crystalline states.[1)] CIEE-active organic luminogens have received attracting attention in the application areas of light emitting diodes, optical waveguides, and organic lasers. However, there are very few reports of CIEE compounds because design strategies have not yet been established. In addition, most of them have twisted structures which make their emission blue-shifted. Therefore, it is quite difficult to realize the CIEE phenomenon in a longer wavelength region such as deep-red or near-infrared range. Recently, we reported that four-coordinate boron-fused azomethine complexes (**BAm**) exhibited CIEE property in yellow region.[2)] Furthermore, boron-fused azobenzene complexes (**BAz**) showed bright solid-state emission in red region (Figure 1).[3)] In this work, we developed several kinds of **BAz** derivatives introduced amino groups to achieve the CIEE phenomenon in further longer wavelength range.

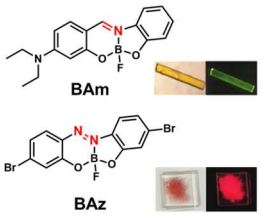


Figure 1. Chemical structures of **BAm** and **BAz**.

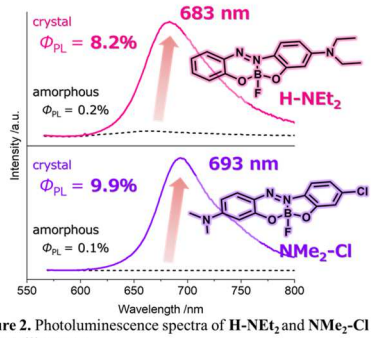
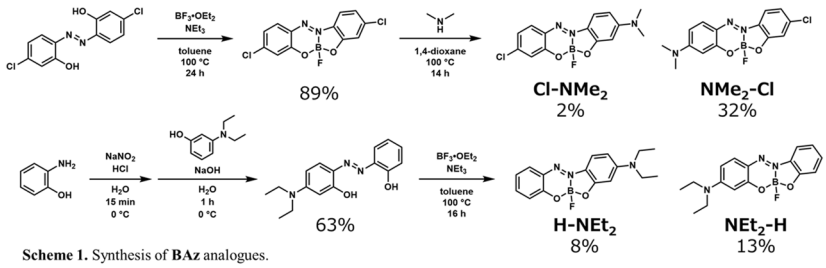


Figure 2. Photoluminescence spectra of **H-NEt$_2$** and **NMe$_2$-Cl** in crystalline state.

We synthesized four kinds of **BAz** analogues according to Scheme 1. Among them, **H-NEt$_2$** and **NMe$_2$-Cl** exhibited CIEE behaviors in deep-red region (Figure 2). Furthermore, we found that there were clear differences between optical properties of each two isomers with different substitution positions in crystal.



Scheme 1. Synthesis of **BAz** analogues.

1) Tang, B. Z. *et al. Chem. Commun.* **2007**, 3255. 2) Chujo,Y. *et al. Chem. Eur. J.* **2017**, *23*, 11827.
3) Chujo, Y. *et al. Macromol. Rapid Commun.* **2021**, *42*, 2000566.