Photochromic Luminescence Derived from Photochemical Reaction in Complexes of Four-Coordinate Group 13 Elements

(*Graduate School of Engineering, Kyoto University*) ○Yuto AOYAMA, Shunichiro ITO, Kazuo TANAKA

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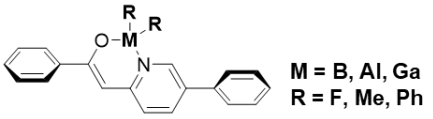
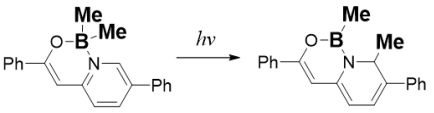
Complexes of four-coordinate group 13 elements have been known as excellent photoluminescent materials. On the other hand, recent studies reported that some complexes showed photochemical reactions in which the bonds on the central elements are dissociated by photoexcitation.[1,2] Herein, we focused on pyridylenolate complexes capable of efficient luminescence in various states and stimuli-responsiveness.[3] The pyridylenolate complexes of group 13 elements showed photochemical migration of substituents from the central elements to the π-conjugated ligand (Schemes 1 and 2).

We synthesized the pyridylenolate complexes with various substituents and central elements (Scheme 1). Among them, the complex with methyl groups on the boron atom (**BMe**) showed a photochemical migration reaction in the solution state (Scheme 2). Interestingly, the luminescent color changed after photoirradiation in the solution and solid states (Figure 1). Quantum calculation suggested the red-shift of the luminescent band originated from the electronic interaction between the resultant three-coordinate boron center and the π-conjugated system. The photochromic luminescence exhibited temperature dependence in the solid state. Utilizing the responsiveness to light and temperature, we demonstrated the applicability of the complexes to luminescence thermography, which can visualize, memorize, and measure the temperature when and where they are irradiated by UV light. In the presentation, we will discuss the effects of the substituents and the central elements on the reaction and photoluminescence.

Scheme 1. Chemical structures of synthesized pyridylenolate complexes



Scheme 2. Photochemical migration reaction of **BMe**



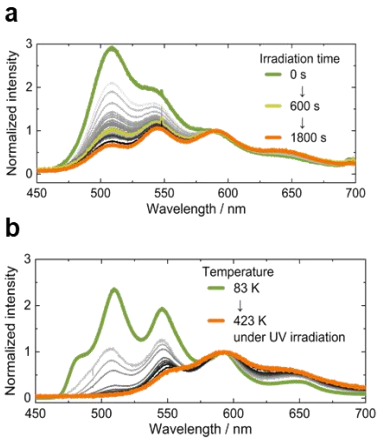


Figure 1. a) Photochromic luminescence of **BMe** and b) the temperature dependence in the powder state.

1) Tanaka, Ken *et al. Nat. Commun*. **2023**, *14*, 652. 2) Ohmiya, H. *et al. J. Am. Chem. Soc.* **2020**, *142*, 9938. 3) Tanaka, Kazuo *et al. Macromolecules* **2024**, *57*, 6559.