

Development of Thermo-responsive Solid-State Luminescent Materials Utilizing Intermolecular Interactions between Carboranes and Nitrogen Atoms

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o-Carborane is an icosahedral cluster composed of ten boron and two carbon atoms with three-center two-electron (3c2e) bonds. Its three-dimensionally delocalized skeletal electrons through 3c2e bonds can be an origin of various unique luminescent properties.^[1] Moreover, the electronically polarized structure has the potential to form electrostatic interactions and therefore to be a versatile scaffold to develop functional materials (Fig. 1).

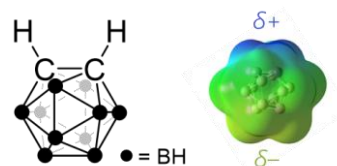


Fig. 1 Chemical structure of *o*-carborane (left). Electrostatic potential map of *o*-carborane (right).

In this research, we synthesized three types of acridine-modified compounds **Ac-M1**, **Ac-E1**, and **Ac-E2** (Fig. 2). From single-crystal X-ray analyses, it was revealed that the nitrogen-containing acridine unit induced intermolecular CH \cdots N interactions. All three compounds formed a dimer structure and each dimer was π -stacked via acridine moieties (Fig. 3). They showed structureless broad emission bands with long emission lifetimes from the crystalline samples. After the series of measurements under various conditions, we attributed those broad emission bands to solid-state excimer emission derived from the π -stacking in the crystalline state. In addition, crystalline acridine-modified *o*-carboranes showed thermochromic luminescence (Fig. 3). The fluorescence band shifted continuously depending on the temperature, probably because the degree of π -stacking could be gradually changed. These results strongly indicate that CH \cdots N interaction-induced dimer formation should be a powerful tool for designing thermochromic luminescence materials.

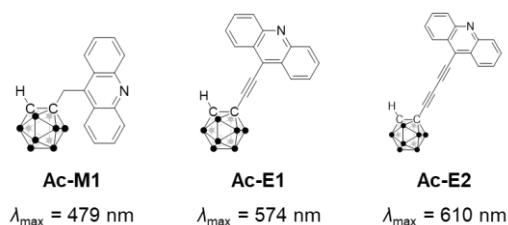


Fig. 2 Chemical structure and fluorescence wavelengths of acridine-modified *o*-carboranes.

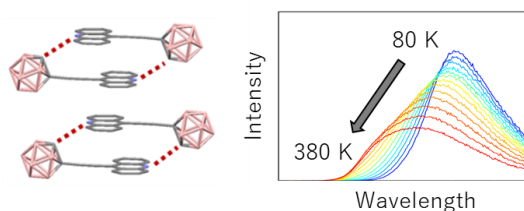


Fig. 3 Single-crystal X-ray structure (left) and thermochromic luminescence (right) of **Ac-E1**.

1) Tanaka, K. *et al. Angew. Chem. Int. Ed.*, **2019**, 59, 9841.