Synthesis and Optical Properties of *o*-Carborane-Based Solid-State Fluorescent Probes through Electron Transfer

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Fluorescent probes have attracted attention in many fields, such as biology and the environment, because of highly sensitive and non-invasive imaging in a system in real-time. Fluorescent probes through photoinduced electron transfer (PeT) are the most famous, and various have been designed and synthesized. However, there are rarely reported examples of solid-state fluorescent probes due to limitations such as aggregation caused quenching (ACQ). In this study, a combined compound (**CBP-DEA**, Figure 1) of the *o*-carborane derivate as the solid emission material and PeT-activating aniline was synthesized and investigated the optical properties and the acid-base response, compared with **CBP-H** (Figure 1)$^{1)}$.

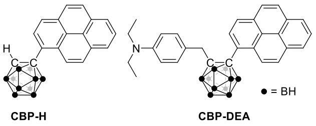

Figure 1. Chemical structures of **CBP-H** and **CBP-DEA.**

Initially, the luminescence properties of **CBP-H** and **CBP-DEA** in THF solution (Figure 2a). The PL absolute quantum yield (Φ_{PL}) of **CBP-DEA** was much lower than that of **CBP-H** in THF. This quenching mechanism can be explained by the typical PeT. This phenomenon was also observed in the crystalline sample. To support PeT characters of the **CBP-DEA**, the quantum chemical calculations were performed (Figure 2b). In the pristine state, because the energy level of the aniline moiety's molecular orbital (MO) exists between the energy level of the *o*-carborane-pyrene moiety's MOs, the fluorescent was quenching by PeT. In contrast, because the MO of aniline moiety in the cation state was stabilized and the energy level was absent between the energy level of the *o*-carborane-pyrene moiety's MOs, **CBP-DEA** can fluoresce. Based on the calculation, we considered that PeT was hindered by the cationization of **CBP-DEA** and investigated the acid-base response of **CBP-DEA**. Exposure of **CBP-DEA** in the crystal state to acid increased Φ_{PL} and exposure to base decreased Φ_{PL} (Figure 2c). In summary, the *o*-carborane-based fluorescent probe **CBP-DEA** shows that PeT can be controlled by acid-base exposure in the solid state, suggesting that *o*-carborane derivate is a promising platform for solid-state fluorescent probes.

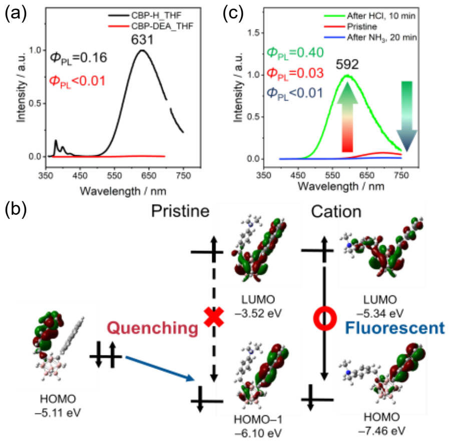

Figure 2. Photoluminescence (PL) spectra and absolute PL quantum yield (Φ_{PL}) of (a) **CBP-H** and **CBP-DEA** in THF (1.0×10^{-5} M) and (c) **CBP-DEA** before and after acid-base exposure in the crystal state. (b) Calculated structure and molecular orbitals of **CBP-DEA** in the excited states at the pristine (left) and the cation (right). (*N*,*N*-Diethylaniline moiety is replaced by *N*,*N*-dimethylaniline.)

1) Nishino, K.; Yamamoto, H.; Tanaka, K.; Chujo, Y. *Org. Lett.* **2016**, *18*, 16, 4064–4067