

Circularly Polarized Dual-Emission Properties of *o*-Carborane Derivatives with [7]Helicene Units

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Keywords: Carborane; Helicene; Optical Property; Circularly Polarized Luminescence; Stimuli-Responsiveness

The differential emission of right- and left-handed circularly polarized light is known as circularly polarized luminescence (CPL), which is an optical property of chiral luminescent system. CPL property is evaluated with its sign. When the left CPL is stronger than the right one, CPL sign is determined as plus. If otherwise, sign becomes minus. Recently CPL-active molecules often show sign-switching of CPL accompanying changes in luminescent species.¹ Such sign-switchable molecules are useful in security technologies and sensing devices. In this context, we are focusing on icosahedral boron cluster, *o*-carborane as an inducer of dual-emission property for CPL sign-switching materials. Aryl-substituted *o*-carborane derivatives spontaneously exhibit two emission species: locally excited (LE) emission of aryl-units and intramolecular charge transfer (ICT) emission dependent on relative orientation of clusters' carbon-carbon bond and aryl-units.² Owing to its spherical structure, *o*-carborane can induce changes in luminescent species even in densely packed solid-state, which is an advantage for material applications.

In this work, we developed novel derivatives incorporated with [7]helicene as a CPL-active chiral unit and investigated their chiroptical properties. We synthesized [7]helicene-substituted *o*-carborane (**1**) and its methoxy-derivative (**2**) (Fig. 1a) and measured their chiroptical properties in dispersed film state (Fig. 1b). We found that both compounds showed sign-difference in shorter wavelength (LE emission) and longer wavelength (ICT emission) regions. The temperature dependence on PL and CPL of **2** indicated that sign-switching of CPL upon increase in relative PL intensity of ICT emission (Fig. 1c). We also discuss solution-state chiroptical properties and theoretical analyses in our presentation.

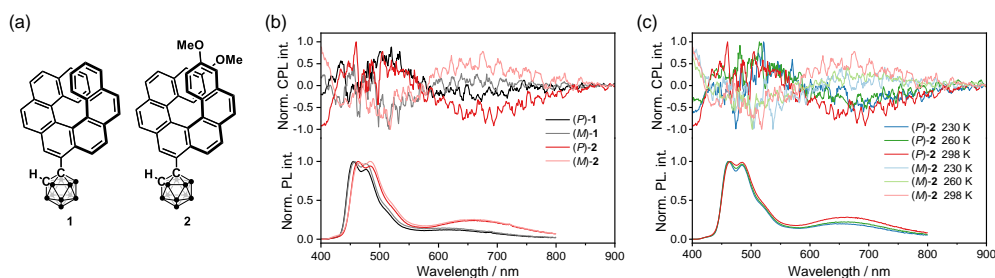


Figure 1. a) Structures of [7]helicene-incorporated *o*-carboranes, **1** and **2**. b) PL and CPL spectra at 298 K and c) temperature dependence of PL and CPL for **2** in β -estradiol dispersed film (1 wt%).

- 1) Zhao, C. *et al. Chem. Eur. J.* **2019**, 25, 15441–15454.
- 2) Chujo, Y. *et al. Angew. Chem. Int. Ed.* **2017**, 56, 254–259.