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Allosteric Guest Binding Behavior of Triple-stranded Helicates based on Calix[4]arenes

Yutaro Yamasaki,[1] Ryo Sekiya,[1] Takeharu Haino[1]

[1] Department of Chemistry, Graduate School of Science, Hiroshima University

A coordination-driven self-assembly has been a well-established methodology that offers the effective way to construct functional supramolecular structures. A variety of self-assembled supramolecular complexes have been developed when combining metal ions and organic ligands. Notably, Metallohelicates are a class of motifs that attract exceptional interests due to the distinctive structural features. However, there are limited examples of the chiral induction of triple-stranded helicates having cavities that encapsulate chiral guests. We have reported the synthesis and guest binding behavior of triple-stranded dinuclear helicate 1.[1)] Here, we report the triple-stranded multinuclear helicates 2,3 possessing multiple guest-binding cavities surrounded by the three calix[4]arene moieties (Figure 1). The preparation of 2,3 was determined by DOSY experiments, UV-Vis spectroscopy, and ESI-MS measurements. The complexation of the chiral guests 4 determined the absolute helicity of the triple-stranded helicates that induced the CD signals as shown in Figure 2. Binding constants of 2,3 with 4 were given by non-linear curve fitting analysis. The positive allostery in guest binding was observed. The changes in the ICD intensity with respect to the enantiomeric excess of 4 resulted in a strong chiral amplification (Figure 3).

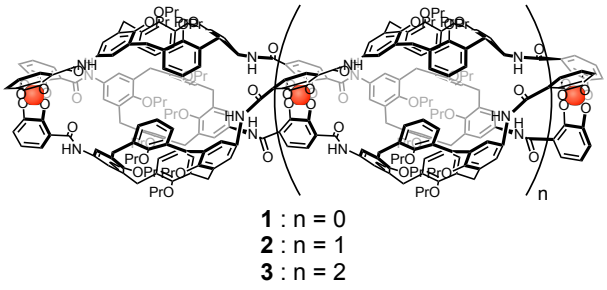

Figure 1 Structure of triple-stranded helicates.

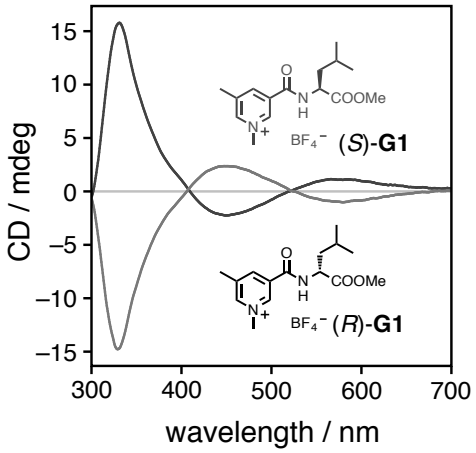

Figure 2 CD spectrum of **3** and **G1** in methanol.

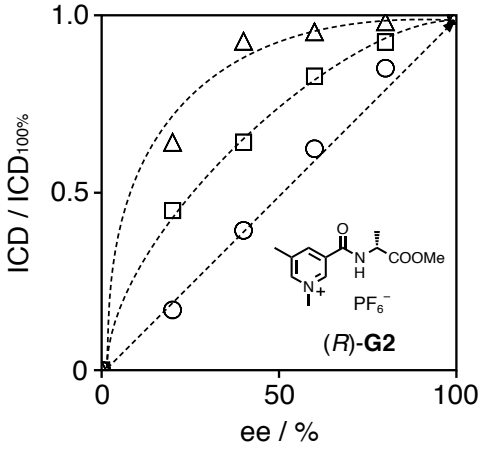

Figure 3 Changes in ICD intensity of **3** versus the %ee of **G2** (100eq).

References

1) Haino, T.; Shio, H.; Takano, R.; Fukazawa, Y. *Chem. Commun.* **2009**, 2481-2483.