Design and synthesis of a phenine nanocage with chirality

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The chemistry of sp^2-hybridized carbon atoms started from the studies of its two-dimensional networks with benzene/graphite/graphene. Types of the sp^2-network were further expanded by the discovery of curved variants such as fullerene and carbon nanotubes. The discovery of these carbon allotropes ignited interests of chemists in exploring unique nanocarbon molecules with large sp^2-networks via organic syntheses. In our group, the nanocarbon molecules are being diversified by a synthetic strategy that adopts "phenine (1,3,5-trisubstituted benzene)" as a fundamental trigonal planar unit to be assembled.[1] Herein, the phenine strategy is expanded to design a nanometer-sized cage **1** with chirality (Figure 1a). Phenine nanocage **1** possessed 14 phenine vertices, and the synthesis was completed by forming 15 edges between them via coupling reactions. The synthetic route was versatile enough to introduce various substituents, and nanocage **2** with 26 phenine units was also synthesized to install radiating phenine substituents on the cage. The atomic-level structure of the phenine nanocage **1** was revealed by X-ray diffraction analysis of a single crystal (Figure 1b). Although there were potentially 5600 isomeric structures arising from (*R*)/(*S*) atropisomerism at 15 biaryl edges, phenine nanocage **1** existed as a singly pair of enantiomers in the crystal. The chirality of **1** originates from the helicity around the major C_3 axis, and we propose the stereochemistry to be described with "(*P*)" and "(*M*)" descriptors. Although stereochemical non-rigidity of **1** and **2** obscured their chirality, structural rigidification with a dimethylated linkage allowed for the chiral resolution of the enantiomers of phenine nanocages. Our perspective over the chiral phenine nanocage will be disclosed and discussed in the presentation.

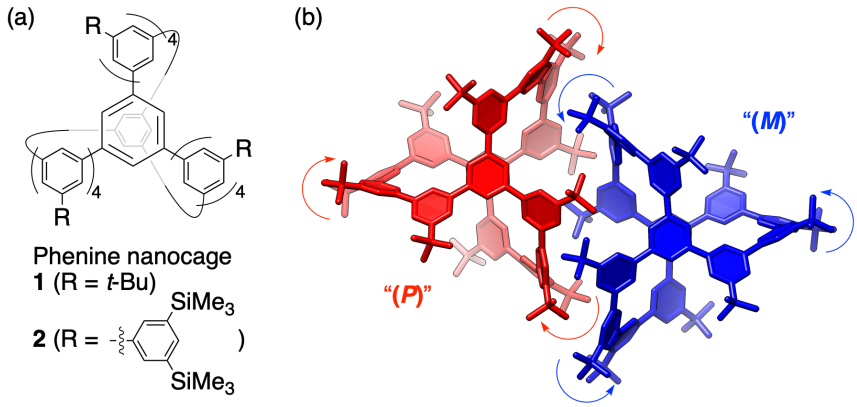

Figure 1. Phenine nanocages. (a) Chemical structures. (b) Crystal structures of **1**.

1) K. Ikemoto, H. Isobe, *Bull. Chem. Soc. Jpn.* **2021**, *94*, 281.