Creation of Three-Dimensional Nitrogen-Containing Nanocarbons Aimed at Developing Innovative Foundational Materials

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The properties of π-conjugated materials depend strongly on their repeating structures (periodicity). To date, π-conjugated materials with one-dimensional and two-dimensional periodicity have been extensively studied. In contrast, π-conjugated materials with three-dimensional periodicity, although investigated theoretically, remain in an unexplored research field. Therefore, the aim of this study is to pioneer **three-dimensional periodic π-conjugated chemistry**. Specifically, I seek to construct three-dimensionally periodic π-conjugated organic frameworks from saddle-shaped amines and planar ketones, thoroughly elucidate their physical properties, and explore unusual properties and phenomena unique to 3D π-conjugated systems. The final goal is the creation of innovative foundational materials, beginning with the development of three-dimensionally periodic π-conjugated crystals.

Since the planar ketone has already been reported in the literature, **the imine became the initial target for synthesis**. Starting from dimethoxybenzene, terphenyl boronate ester was synthesized in three steps. Subsequent Suzuki–Miyaura cross-coupling with dibromodimethoxybenzene afforded a macrocyclic compound in 18% yield. The following oxidative dehydrogenative cyclization to construct the saddle-shaped structure proved extremely challenging due to the strain inherent in the saddle geometry and the destabilization and poor solubility arising from the expanded π-conjugated system. After extensive optimization, we succeeded in obtaining saddle-shaped [8]circulene in 48% yield by treating the intermediate with iron(III) chloride under light-shielded conditions in the presence of molecular sieves. Subsequent demethylation and triflation furnished the triflate-functionalized [8]circulene in 17% yield.

In the final stage of saddle-imine preparation, the Buchwald–Hartwig amination, achieving amination at all eight reactive sites and purifying the resulting product pose significant challenges. However, using the insights gained from handling the saddle-shaped molecules synthesized thus far, we aim to establish optimal reaction and purification conditions. Thereafter, through reversible dehydrative condensation with the planar ketone, we plan to construct a **3D nitrogen-containing nanocarbon crystal**.