

Chem Preview

[Title]

Armchair and Chiral Carbon Nanobelts: Scholl Reaction in Strained Nanorings

[Authors]

Akiko Yagi,¹ Yasutomo Segawa,^{1,2} Kenichiro Itami^{*,1,2}

[Affiliation]

(1) Institute of Transformative Bio-Molecules (WPI-ITbM) and Graduate School of Science, Nagoya University, Chikusa, Nagoya 464-8602, Japan

(2) JST-ERATO Itami Molecular Nanocarbon Project, Nagoya University, Chikusa, Nagoya 464-8602, Japan

[Abstract]

In this issue of *Chem*, Cheung *et al.* have produced an armchair (12,12) and a chiral (18,12) carbon nanobelts through the Scholl reaction of carbon nanoring precursors. The design of the carbon nanorings is the key for the successful synthesis of the carbon nanobelts.

[Body]

Since the first discovery by Iijima in 1991, carbon nanotubes (CNTs) have long been the center of attention in materials science.^[1] Their unique and outstanding properties have contributed the development of basic science and application supported by the improvement of the efficient synthetic methods of CNTs. Single-walled CNTs can be regarded as the rolled up structures of graphene sheets, and the property of each CNT depends on its chiral index (n,m) , which determines the diameter and chirality of CNTs. The CNTs for $m=0$ are called “zigzag”, those for $n=m$ are “armchair”, and the others are “chiral”. (n,m) CNTs are metallic where $n-m$ is a multiple integer of three whereas the other CNTs are semiconductive. Therefore, the chirality-specific synthesis of CNTs is desired to create CNT-based materials with high purity to fulfill their utmost potential.

In recent years, ring-shaped aromatic molecules called “carbon nanorings (CNRs)” has

been the focus of synthetic chemistry.^[2] A representative CNR is cycloparaphenylene (CPP), which consists of *para*-connected benzene rings. Since the breakthrough of CPP synthesis, various CNRs have been synthesized and the CNR chemistry has progressed rapidly. Not only their unique properties derived from their ring structures, but also the potential as the seeds for CNT growth have drawn numerous chemists to CNRs. Among such campaign, in 2013, the synthesis of CNTs by using CPP as a seed in chemical vapor deposition (CVD) was achieved.^[3] This result indicates that the chirality-specific synthesis of CNTs can be accomplished through the growth of the CNT segment molecules.

Following the success of CNT synthesis from CNRs, the next challenge has been the synthesis of belt-shaped molecules called “carbon nanobelts (CNBs)” as more rigid seeds than CPPs. The term “CNB” was defined as cylinder-shaped fully-fused polycyclic aromatic hydrocarbons that represent the segment of CNT structures.^[2] CNBs have been the long-standing targets for synthetic organic chemists; in fact, the earlier attempts to synthesize CNBs were described even before the discovery of CNTs.^[4] Owing to the recent remarkable progress of the CNR chemistry, synthetic chemists have obtained another possible way for achieving CNBs. It is easy to imagine that CNBs can be synthesized through the π -extension of CNRs. For example, oxidative cyclodehydrogenation (Scholl reaction) of polyarylated CPPs is a possible method for constructing CNBs as a straightforward and reasonable strategy. However, such strategy faced significant difficulties due to their high ring strain. In 2015, the group of Müllen reported the unsuccessful Scholl reaction of polyarylated [15]- and [21]CPPs to construct hexabenzocoronene structures (Figure 1(a)).^[5] Instead of the desired product, 1,2-rearranged *meta*-linkage rings were obtained, in which rearrangement was occurred to relieve the ring strain. The group of Jasti also attempted a similar Scholl reaction of tetraarylated [12]CPP, while the products were a complex mixture (Figure 1(b)).^[6] These results implied that Scholl reaction is not suitable for the synthesis of highly strained molecules such as CNBs. In contrast, our group (Itami, Segawa, and coworkers) applied another strategy to achieve the first synthesis of a CNB in 2017. The last step for the construction of the CNB is a nickel(0)-mediated reductive aryl–aryl coupling reaction in order to avoid cationic rearrangeable intermediates (Figure 1(c)).^[7] In addition to the (6,6)CNB, a segment of a (6,6)CNT, the synthesis of (8,8)- and

(12,12)CNB was also accomplished recently.^[8] Such structural variety and commercial availability (since 2017 from TCI) of CNBs will open the door to new CNB science and technology.

Toward the chiral-specific synthesis of CNT, further progress in the synthesis of CNBs is demanded. In this issue of *Chem*, Cheung *et al.* overcame the difficulty of the Scholl reaction of CNRs and succeeded in the synthesis of two kinds of CNBs. One is an armchair (12,12)CNB, which was synthesized from the [12]CPP derivative bearing 12 aryl groups (Figure 1(d)). The authors designed the precursor CNR to reduce the increase of strain by minimizing the number of Scholl reaction. Notably, in this synthesis, Scholl reaction in the CNR precursors worked well unlike the previous reports.^{[5],[6]} The authors commented that the key for successful Scholl reaction is the low reaction temperature ($-78\text{ }^{\circ}\text{C}$) to prevent undesired rearrangement and introduced propoxy groups to facilitate the cyclization by lowering oxidation potential. Additionally, the authors have achieved the first synthesis of a chiral (18,12)CNB by Scholl reaction from a chiral-type CNR, the derivative of cycloparaphenylene-2,6-naphthylene (Figure 1 (e)).^[3] The high reactivity of the alpha-position of naphthalene ring facilitates Scholl reaction and raises the efficiency of overall 12 C–C bond formation to 66%. The thus-obtained two CNBs were identified by HRMS, NMR and STM analyses whereas the X-ray crystal structure analysis was not achieved. The design of the precursors and well-tuning of the Scholl reaction conditions led the successful synthesis of both armchair and chiral CNBs.

The strain energies of the two CNBs and their precursors were discussed in detail. By using the previously established method,^[10] the strain energies of the armchair (12,12) and the chiral (18,12)CNBs were estimated to be 54.2 and 28.1 kcal·mol⁻¹, respectively. These values are significantly lower than that of (6,6)CNB (119.5 kcal·mol⁻¹)^[8] reflecting the difference of their diameters. Considering the small differences in the strain energies between CNBs and corresponding precursors (armchair: 45.8 to 54.2 kcal·mol⁻¹, chiral: 39.1 to 28.1 kcal·mol⁻¹), it is quite reasonable that Scholl reaction took place successfully without undesired rearrangement reactions.

The present work represents the first synthesis of chiral CNB, which should be a significant step forward the chirality-specific synthesis of CNTs. The synthesis of CNBs

through the Scholl reaction of CNRs has been recognized to be difficult for years. As shown in this issue, the design of the precursors and the fine-tuning of the reaction conditions were essential to work Scholl reaction in the strained structures well. This work would become a novel “ring-to-belt” methodology to access a range CNBs. We envision that the synthesis of diverse CNBs will be achieved in the near future.

- [1] Iijima, S. (1991). *Nature* 354, 56–58.
- [2] Omachi, H., Nakayama, T., Takahashi, E., Segawa, Y., Itami, K. (2013). *Nat. Chem.* 5, 572–576.
- [3] Segawa, Y., Yagi, A., Matsui, K., Itami, K. (2016). *Angew. Chem. Int. Ed*, 55, 5136–5158.
- [4] Fragments of Fullerenes and Carbon Nanotube: Designed Synthesis Unusual Reactions, and Coordination Chemistry (Eds.: M. A. Petrukhina, L. T. Scott), Wiley, Hoboken, 2012.
- [5] Quernheim, M., Golling, F.E., Zhang, W., Wagner, M., Räder, H.-J., Nishiuchi, T., and Müllen, K. (2015). *Angew. Chem. Int. Ed.* 54, 10341–10346.
- [6] Sisto, T.J., Zakharov, L.N., White, B.M., and Jasti, R. (2016). *Chem. Sci.* 7, 3681–3688.
- [7] Povie, G., Segawa, Y., Nishihara, T., Miyauchi, Y., and Itami, K. (2017). *Science* 356, 172–175.
- [8] Povie, G., Segawa, Y., Nishihara, T., Miyauchi, Y., and Itami, K. (2018). *J. Am. Chem. Soc.* 140, 10054–10059.
- [9] Cheung, K. Y., Gui, S., Deng, C., Liang, H., Xia, Z., Liu, Z., Chi, L., Miao, Q. (2019) *Chem* 5 (this issue), 1-10.
- [10] Segawa, Y., Yagi, A., Ito, H., and Itami, K. (2016). *Org. Lett.* 18, 1430–1433.

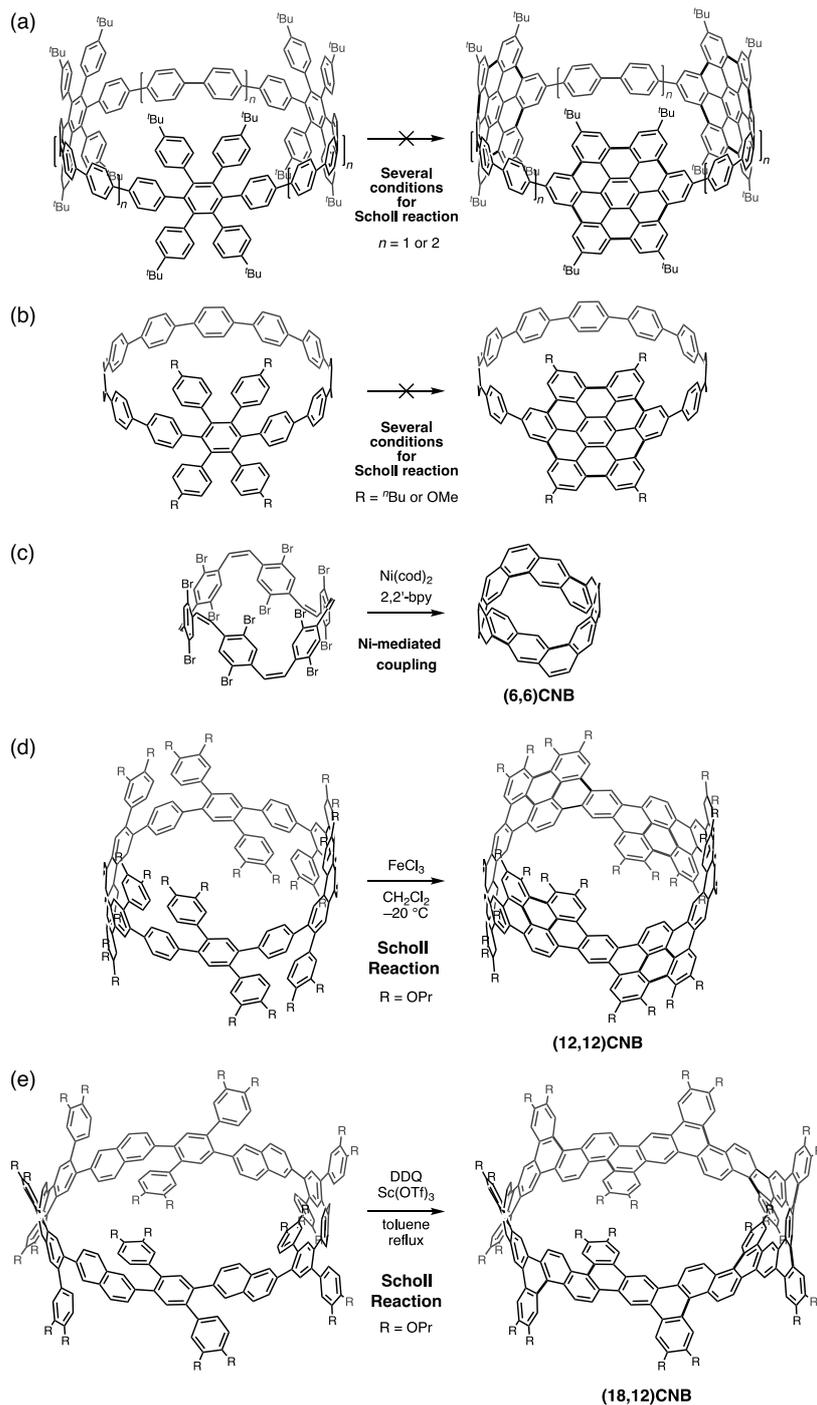


Figure 1. (a),(b) The attempts to construct hexabenzocoronene structures on CNRs by Scholl reaction reported by (a) Müllen and (b) Jasti. (c) The synthesis of a (6,6)CNB by the Itami group. (d),(e) The synthesis of (d) an armchair (12,12)CNB and (e) a chiral (18,12)CNB by Scholl reaction described in this issue of *Chem. cod*: cyclooctadiene, bpy: bipyridyl, DDQ: 2,3-dichloro-5,6-dicyano-*p*-benzoquinone, OTf: trifluoromethanesulfonate