

Synthesis of Armchair- and Chiral-Types Cyclophenylene-Naphthylene Belts by Rhodium-Catalyzed Intramolecular [2+2+2] Cycloaddition

(¹Sch. Mater. & Chem. Tech., Tokyo Tech., ²IMS, ³Grad. Sch. of Pharm. Sci., The Univ. of Tokyo, ⁴Sch. Sci., Tokyo Tech., ⁵RIKEN) ○Juntaro Nogami,¹ Yuki Nagashima,¹ Haruki Sugiyama,² Kazunori Miyamoto,³ Yusuke Tanaka,³ Hidehiro Uekusa,⁴ Atsuya Muranaka,⁵ Masanobu Uchiyama,³ Ken Tanaka¹

Keywords: Carbon Nanobelt; Cycloparaphenylene; Rhodium; Cyclotrimerization; Asymmetric Synthesis

Belt-shaped π -conjugated molecules such as carbon nanobelts (CNBs) have fascinated organic chemists for decades due to their aesthetic structures and potential applications.¹ Several bottom-up syntheses of these belt molecules have been reported in recent years, however, there are still unachieved synthetic targets. For example, the bottom-up synthesis of $[n]$ cyclophenacene,² which is the simplest and shortest belt-type segment of armchair carbon nanotube (CNT), has not been achieved. The synthesis of chiral-type CNBs is also limited to a single racemic synthesis in Miao's report,³ and the synthetic research is hardly advanced compared with the zigzag- and armchair-types CNBs.

Herein, we report the synthesis of cyclophenylene-type cyclophenylene-naphthylene (CPN) belt **1** in 57% yield, and the enantioselective synthesis of chiral-type CPN belts (*P*)-**2** and (*M*)-**3** with up to >99% ee by the cationic rhodium(I)-catalyzed intramolecular [2+2+2] cycloadditions of cyclic polyynes (Figure 1). The cylindrical unimolecular structures and the packing structures of these CPN belts were successfully confirmed by X-ray crystallographic analyses. Unfortunately, in the attempted synthesis of vertically expanded CPN belt, the final intramolecular [2+2+2] cycloaddition did not proceed and one triyne unit remaining was isolated in a low yield of 15%. These successful and unsuccessful reactions showed the capability and limitation of the cationic rhodium(I)-catalyzed intramolecular [2+2+2] cycloaddition of the cyclic polyynes.

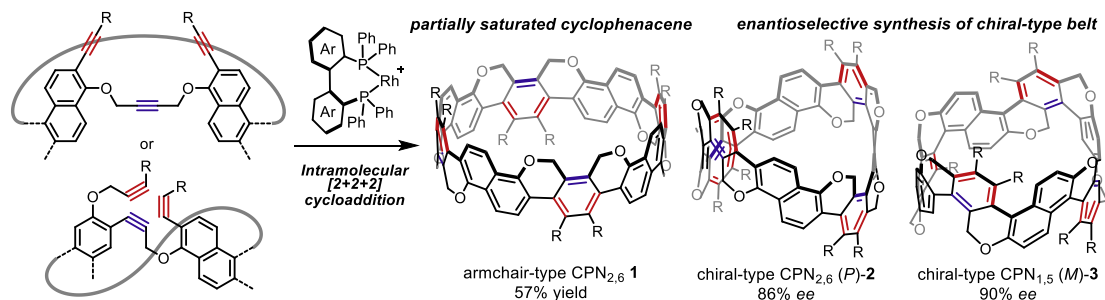


Figure 1. Synthesis of cyclophenylene-naphthylene (CPN) belts.

1) E. R. Darzi, R. Jasti, *Chem. Soc. Rev.* **2015**, *44*, 6401. 2) K. Y. Cheung, S. Gui, C. Deng, H. Liang, Z. Xia, Z. Liu, L. Chi, Q. Miao, *Chem* **2019**, *5*, 838. 3) E. Nakamura, K. Tahara, Y. Matsuo, M. Sawamura, *J. Am. Chem. Soc.* **2003**, *125*, 2834.