

One- and two-dimensional (1D and 2D) nanocarbons such as nanographenes, graphenes nanoribbons (GNRs), carbon nanotubes (CNTs) have received much attention in the field of physical chemistry, synthetic chemistry as well as materials science (ref 8, *Nature Rev. Mater.* **2016**, *1*, 15002). The optoelectronic, physical, magnetic properties of these nanocarbons highly depend on their width, length, and peripheral structure. Therefore, the precise synthesis of structurally well-defined nanocarbons is essential for the application to the electronic, optoelectronic and spintronic devices such as field-effect transistors, light-emitting devices and photovoltaics. However, the current synthetic methodology of nanocarbons lacks the synthetic efficiency and the structural precision.

Toward overcoming these problems, we have developed the novel bottom-up synthetic methodologies for (1) nanographenes and graphene nanoribbons by “APEX reaction” and (2) covalent organic nanotubes by “helix-to-tube methodology”.

(1) Precise synthesis of nanographenes and graphene nanoribbons by APEX reaction

Current synthetic methodologies for nanographenes and graphene nanoribbons are based on the multi-step sequences including the prefunctionalization of aromatics and polycyclic aromatic hydrocarbons (PAHs) such as halogenation and metalation, the molecular assembly by coupling reactions, and the stitching or graphitization by cyclodehydrogenation, thereby diminishing the overall synthetic efficiency. With this background in hand, we have newly developed the efficient, direct and regioselective π -extension methods, namely annulative π -extension (APEX), for the step-economical and precise synthesis of nanographenes and graphene nanoribbons. APEX reaction represents a single-step π -extension reaction of a template aromatic, and is used to construct one or more new fused aromatic rings (review of APEX: ref 14, *Angew. Chem. Int. Ed.* **2017**, *56*, 11144).

First, we found the palladium catalyst effectively catalyzes the APEX reactions of various PAHs such as phenanthrenes and pyrenes with dibenzosilole derivatives or diiodobiaryls (ref 6, *Nature Commun.* **2015**, *6*, 6251; ref 11, *Synlett*, **2016**, *27*, 2081; ref 15, *Angew. Chem. Int. Ed.* **2017**, *56*, 12224). Unfunctionalized PAHs are effectively and directly transformed to the corresponding π -extended PAHs and nanographenes with the perfect K-region (most olefinic concave armchair periphery) selectivity. In addition, we succeeded the synthesis of largely π -extended fused heteroaromatics and precursor of nanographenes by applying APEX methodology to the reaction of unfunctionalized heteroaromatics (ref 15, *Org. Lett.*, **2017**, *19*, 1930; ref 1, *Chem. Sci.* **2013**, *4*, 3416) and diaryl acetylenes (ref 13, *Angew. Chem. Int. Ed.* **2017**, *56*, 1362).

Second, we have recently demonstrated the palladium-promoted APEX polymerization by using silicon-bridged phenanthrene for the synthesis of cove-type GNRs in a single step (ref 20; patent applications 2). By utilizing various monomer units, APEX-copolymerization was also possible to afford coronene diimide-hybridized GNRs with precise edge structure and width. Furthermore, we succeeded to develop the living APEX polymerization using phenanthrene as an initiator and benzonaphthosilole as a monomer for the precise control of width, edge structure and even length of

GNRs for the first time. Obtained fjord-typed GNRs with very narrow polydispersity were also converted to the $N = 8$ armchair-type GNRs in almost quantitative yield. This APEX polymerization methodology represents the first living direct C–H arylation polymerization, the first precise control of length of GNRs, and the first single step solution-state bottom-up synthesis, which will meet the demands for applications using molecularly precise GNRs.

(2) Precise synthesis of covalent organic nanotube by “helix-to-tube method”

Organic nanotubes (ONTs), which are tubular 1D-nanostructures composed of small molecules or macromolecules, are found to be prominent in various applications including molecular recognitions, semiconductors, ion sensor/channels, gas absorption and drug delivery. Organic nanotubes assembled by weak noncovalent interactions have problems such as structure vulnerability and difficulty of molecular design. In contrast, covalent organic nanotubes (covalent ONTs) cross-linked by covalent bond networks like CNTs are expected to solve the problems of conventional organic nanotube by its rigid cylindrical structure. However, the synthesis of covalent organic nanotubes is difficult and its methods have yet to be established.

We newly developed a simple “helix-to-tube method” to construct robust, covalent ONTs from easily accessible poly(*m*-phenylene diethynylene)s (poly-PDEs) possessing chiral amide side chains that can adopt a helical conformation through hydrogen-bonding interactions (ref 12, *J. Am. Chem. Soc.* **2016**, *138*, 11001; patent application 1). The helically folded poly-PDEs subsequently undergo light-induced cross-linking at longitudinally aligned 1,3-butadiyne moieties across the whole helix to form CNT-like covalent ONTs both in solution and solid phases. The structures of poly-PDEs and covalent ONTs were characterised by spectroscopic analyses, diffraction analysis and microscopic analyses. We envisage that this simple yet powerful “helix-to-tube method” will generate a range of ONT-based materials by introducing functional moieties into a monomer.