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Toward controlled synthesis of carbon nanotubes and graphenes*

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Abstract: A bottom-up synthesis of structurally uniform carbon nanotubes (CNTs) and graphenes is recognized as one of the greatest challenges of primary importance in nanocarbon science. This paper highlights our efforts to address these challenges since 2005. These endeavors have led to (i) modular, size-selective, and scalable synthesis of [*n*]cycloparapheneylenes (CPPs), the shortest segment of armchair CNTs, (ii) design and synthesis of the shortest segment of chiral CNTs, and (iii) efficient synthesis of carbon nanosheets through catalytic C–H bond arylation of polycyclic aromatic hydrocarbons (PAHs). We consider these works as a possible first step toward a controlled synthesis of structurally uniform CNTs and nanographenes.

Keywords: aromatic compounds; carbon nanotubes; catalysts; chemical synthesis; graphenes.

INTRODUCTION

Since the discovery of nanocarbons such as fullerenes, carbon nanotubes (CNTs), and graphenes, their structures, properties, and potential applications have attracted attention. From the standpoint of synthetic chemists, we feel that the development of new synthetic chemistry of nanocarbons is essential for (i) the creation of as-yet unexplored new nanocarbon materials through the chemical functionalization of nanocarbons that can be obtained in a pure form, such as fullerenes, and (ii) the synthesis of structurally uniform nanocarbons that cannot be provided by the current synthetic methods, such as CNTs and nanographenes. Our approach has been to introduce the essence of molecular catalysis in the chemistry of nanocarbons, thereby providing opportunities for markedly different synthetic strategies toward structurally uniform nanocarbons.

Molecular catalysis, in particular transition-metal catalysis, has been a fundamental tool in organic synthesis, enabling a variety of chemical transformations that are otherwise difficult or impossible to achieve with traditional methods. In many instances, remarkable levels of reactivity/selectivity control in chemical transformations can be accomplished. In order to explore new directions in nanocarbon chemistry and molecular catalysis chemistry, we initiated a program aimed at developing new synthetic chemistry of nanocarbons using molecular catalysts in 2005 (Fig. 1). These endeavors have led to (i) the development of a number of new catalytic reactions to functionalize fullerenes [1–7], (ii) the development of modular, size-selective, and scalable synthesis of [*n*]cycloparapheneylenes (CPPs), the shortest segment of armchair CNTs, (iii) the design and synthesis of the shortest segment of chiral CNTs (acene-inserted CPPs), and (iv) the development of efficient synthesis of carbon nanosheets through catalytic C–H bond arylation of polycyclic aromatic hydrocarbons (PAHs). These works, which

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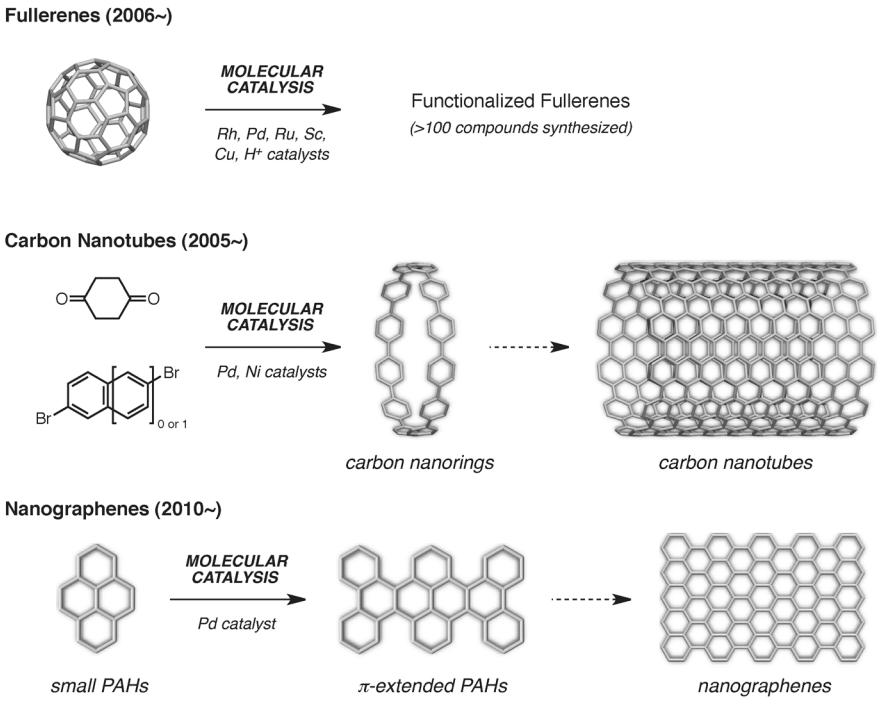


Fig. 1 Our molecular catalysis approach toward controlled synthesis of nanocarbons.

we believe to be important initial steps toward a controlled synthesis of nanographenes, are highlighted in this paper. Owing to the limitation in space, our functionalization chemistry of fullerenes is not described here [1–7].

TOWARD BOTTOM-UP SYNTHESIS OF STRUCTURALLY UNIFORM CARBON NANOTUBES

Currently CNTs can only be produced as mixtures in terms of diameter and chirality (armchair, chiral, or zigzag) [8,9]. Depending on the way a graphene sheet is rolled up (starting and end points of chiral vector), CNTs can form armchair, chiral, and zigzag structures (Fig. 2). Given that the electric properties of CNTs are primarily determined by the sidewall structures (metallic for armchair structures and semiconducting for most zigzag and chiral structures), electrical uniformity is critically important for CNT-based electronics [10,11]. Therefore, the selective and predictable synthesis of structurally uniform CNTs has been recognized as the "Holy Grail" both in nanocarbon chemistry and synthetic chemistry.

We envisioned that the bottom-up synthesis of structurally uniform CNTs could be achieved through a controlled growth process from a short carbon nanoring (template) that corresponds to the target structure of CNTs [12–17]. Such a simple retrosynthetic analysis would lead to the identification of CPPs, acene-inserted CPPs, and cyclacenes [18] as the shortest sidewall segments of armchair, chiral, and zigzag CNTs, respectively (Fig. 2). Herein we summarize our campaign for the synthesis of CPPs [19–23] and acene-inserted CPPs [24]. In parallel to our work, Bertozzi/Jasti [25,26] and Yamago [27,28] also reported the successful synthesis of CPPs. Very recently, Isobe reported the synthesis of [4]cyclo-2,8-chrysenylene as the second example of a short segment of chiral CNTs [29].

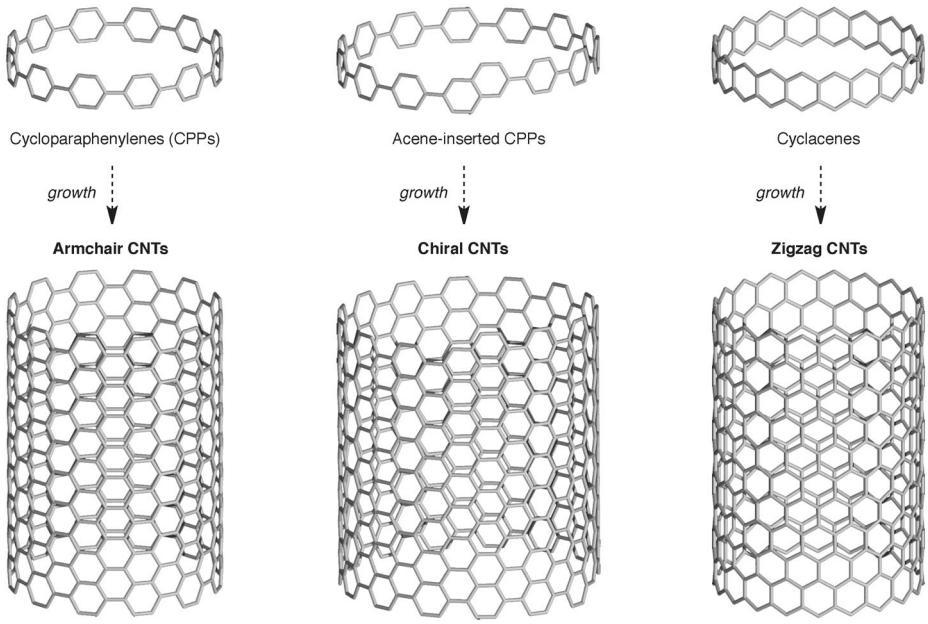


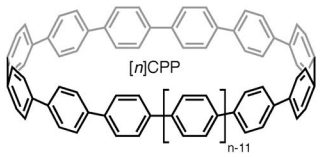
Fig. 2 Structures of armchair, chiral, and zigzag CNTs and their shortest sidewall segments.

Cycloparaphenylenes: Shortest armchair CNTs

Despite its structural simplicity, no successful synthesis of CPP had been reported when we started our work in 2005. The challenge for synthesizing CPPs lies in the increased strain energy that results from ring closure [19]. The strain energies of [*n*]CPP (n = 6–20) are estimated to be 96–28 kcal mol^{-1} by the density functional theory (DFT) calculation (Fig. 3B) [20]. We hypothesized that a suitably substituted cyclohexane moiety could function as a bent benzene-convertible unit in the synthesis of CPPs (Fig. 3C). Namely, we envisioned that 1,4-*cis*-diphenylcyclohexane-1,4-diol derivatives (terphenyl-convertible L-shaped units) would undergo macrocyclization without having serious build-up of strain energy. For example, DFT calculation revealed that the strain energy built up during the cyclotetramerization of 1,4-*cis*-diphenylcyclohexane-1,4-diyl units is only ca. 5 kcal mol^{-1} [19]. The aromatization of cyclohexane rings in the thus-formed macrocycles would then generate the target CPP structures.

The requisite L-shaped monomers can be synthesized by the twofold addition of 4-halophenyllithium [19] or cerium reagents [21] (prepared from 1,4-dihalobenzene) to cyclohexane-1,4-dione, followed by appropriate functional group manipulations such as methoxymethyl (MOM) protection of hydroxyl groups and/or Pd-catalyzed borylation of phenyl–halogen bonds (Fig. 3C) [19]. The X-ray crystal structure analysis of L-shaped monomer revealed its nearly ideal "included" angles around 80º [22]. In our first-generation method, we synthesized cyclic tetramer by the cyclizative Suzuki–Miyaura coupling of L-shaped diiodide and L-shaped diboronate in a stepwise manner (*3* + *3* + *3* and then *9* + *3*) using different Pd catalysts (Fig. 3C) [19]. We anticipated that the treatment of cyclic tetramer with acid would lead to a sequence of (i) deprotection of MOM groups, (ii) dehydration (dihydroxycyclohexane → cyclohexadiene), and (iii) oxidation (cyclohexadiene → benzene) to provide the target [12]CPP. After many investigations, we identified that the aromatization of cyclic tetramer could be achieved by treatment with (i) *p*-toluenesulfonic acid in *m*-xylene under microwave irradiation [19], or (ii) $NaHSO_4 \cdot H_2O$ in refluxing *m*-xylene/DMSO under air [21].

(A) Structure of [*n*]cycloparaphenylene



(B) Strain energies and diameters of [*n*]CPPs [ref 20]

n in [*n*]CPP	strain energy (ΔH, kcal·mol^{-1})	diameter (Å)
6	96	8.4
8	72	11.1
10	58	13.9
12	48	16.6
14	41	19.4
16	36	22.1
18	32	24.9
20	28	27.6

(C) Modular synthesis of [*n*]CPPs (*n* = 12, 14, 15, 16)

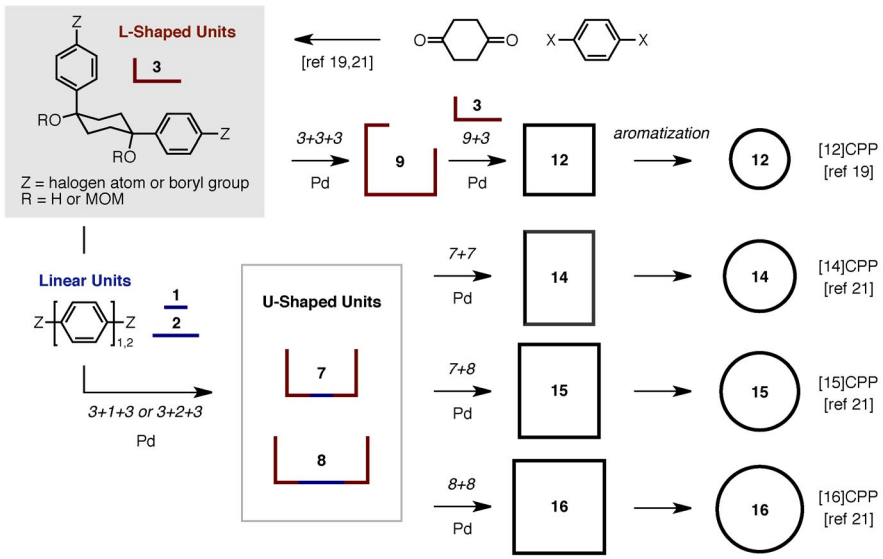


Fig. 3 Structures, strain energies, diameters, and modular synthesis of [*n*]CPPs.

Our CPP synthesis is very flexible, assembling bent (cyclohexane) and linear (benzene) building blocks in a controlled and programmable manner. By strategically varying the number of bent and linear building blocks, a range of [*n*]CPPs become accessible. For example, by assembling a L-shaped diphenylcyclohexane unit and a linear benzene/biphenyl unit in a *3* + *1* + *3* or *3* + *2* + *3* mode by Suzuki–Miyaura coupling, we synthesized U-shaped 7- or 8-benzene unit (Fig. 3C). The cyclizative dimerization of these U-shaped units by Suzuki–Miyaura coupling and follow-up aromatization led to [14]CPP (*7* + *7*), [15]CPP (*7* + *8*), and [16]CPP (*8* + *8*) with reasonable efficiency [21]. As the number of benzene rings in the U-shaped units can be easily increased, this method can be a uniform synthetic strategy for [*n*]CPPs ($n \geq 14$). The use of cyclohexane ring is extremely important in our CPP synthesis not only because the L-shaped structure of cyclohexane attenuates the build-up of strain energy during the macrocyclization but also because the chair-flipping aptitude of cyclohexane provides a strategic basis for accessing both even- and odd-numbered [*n*]CPPs in a selective and predictable manner [21].

Although these studies established the synthetic viability of long-awaited CPPs, important issues remain unresolved. For example, any synthetic route must be more concise, cost-effective, and scalable route in order to provide CPP in useful quantities ensuring further studies of this interesting molecular entity. The disadvantages of our Pd-based synthetic methods include the need of preparing two cross-coupling partners and the need for stepwise reactions to access the macrocyclic precursors for CPPs. After many investigations, we developed a Ni-mediated concise synthesis of [12]CPP and [9]CPP [22,23] (Fig. 4A). We determined that L-shaped *cis*-1,4-bis(4-bromophenyl)cyclohexane monomer

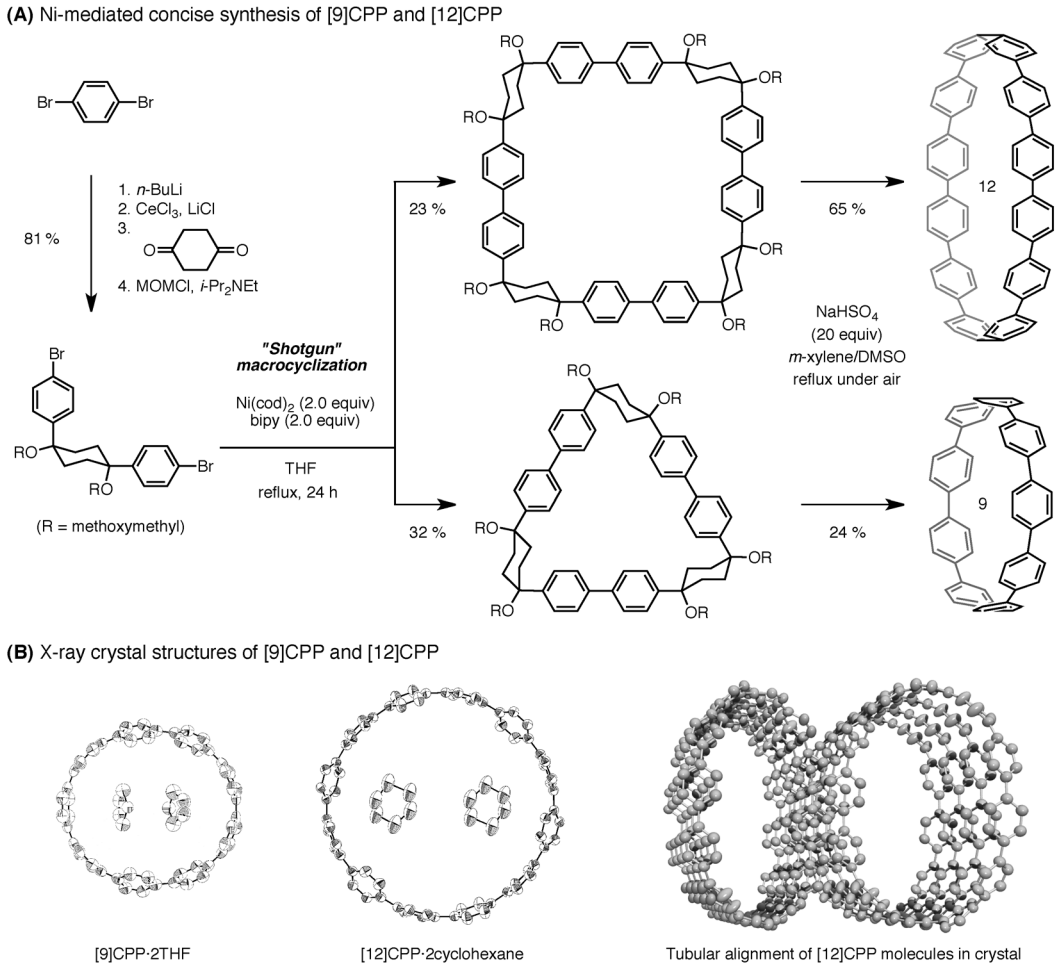


Fig. 4 Concise synthesis and X-ray crystal structures of [9]CPP and [12]CPP.

underwent "shotgun" macrocyclization in the presence of $Ni(cod)_2$ and 2,2'-bipyridyl in refluxing tetrahydrofuran (THF) to furnish the corresponding cyclic tetramer and trimer in 23 and 32 % yield, respectively. The aromatization of thus-formed macrocycles under the influence of $NaHSO_4 \cdot H_2O$ furnished [12]CPP and [9]CPP in reasonable yield.

During these studies, we have successfully validated the molecular structures of [12]CPP and [9]CPP by X-ray crystallography [22,23] (Fig. 4B). It was found that CPP molecules always incorporate solvent molecules within the ring during crystallization. In addition, we verified that the benzenoid characters are reasonably preserved in these CPPs, even though each benzene ring in the crystal structure is slightly folded owing to the inherent ring strain of the cyclic system. Interestingly, C_{ipso}–C_{ipso} and C_{ortho}–C_{ortho} bond lengths of [9]CPP are shorter than those of [12]CPP. This clearly shows that the contribution of "quinoid" property of CPP becomes larger as the ring size of CPP decreases. The packing mode of CPP molecules in the crystal is also interesting. As shown in Fig. 4B, concurrently with herringbone packing, CPP molecules align nicely to form a tubular structure. The emergence of such a surprising channel structure obviously provides various possibilities of crystalline-state CPP chemistry.

Acene-inserted cycloparaphenylenes: Shortest chiral CNTs

In parallel to establishing the synthetic chemistry of [*n*]CPPs, which represent the shortest sidewall segments of [*n*,*n*]CNTs (armchair CNT structures), we also designed and synthesized a shortest chiral CNT structure (chiral carbon nanoring) for the first time [24]. Our design of chiral carbon nanorings is straightforward, inserting an acene unit into [*n*]CPP structures (Fig. 5A). For example, when inserting a naphthalene unit with 2,6-linkage, the resulting cyclo[*n*]paraphenylene-2,6-naphthylene ([*n*]CPPN) will become the shortest segment of a [*n* + 2, *n* + 1]CNT. Similarly the incorporation of anthrylene-2,6-diyl and tetracenylene-2,8-diyl will result in the shortest segments of a [*n* + 3, *n* + 1]CNT and a [*n* + 4, *n* + 1]CNT, respectively. By inserting these acenes with appropriate linkages, all possible chiral structures of CNTs can be created. Indeed, by incorporating 2,6-diborylated naphthalene into our well-established Pd-catalyzed stepwise cross-coupling using L-shaped monomers [21], we synthesized [13]CPPN (the shortest segment of [15,14]CNT) in reasonable overall yield (Fig. 5B) [24].

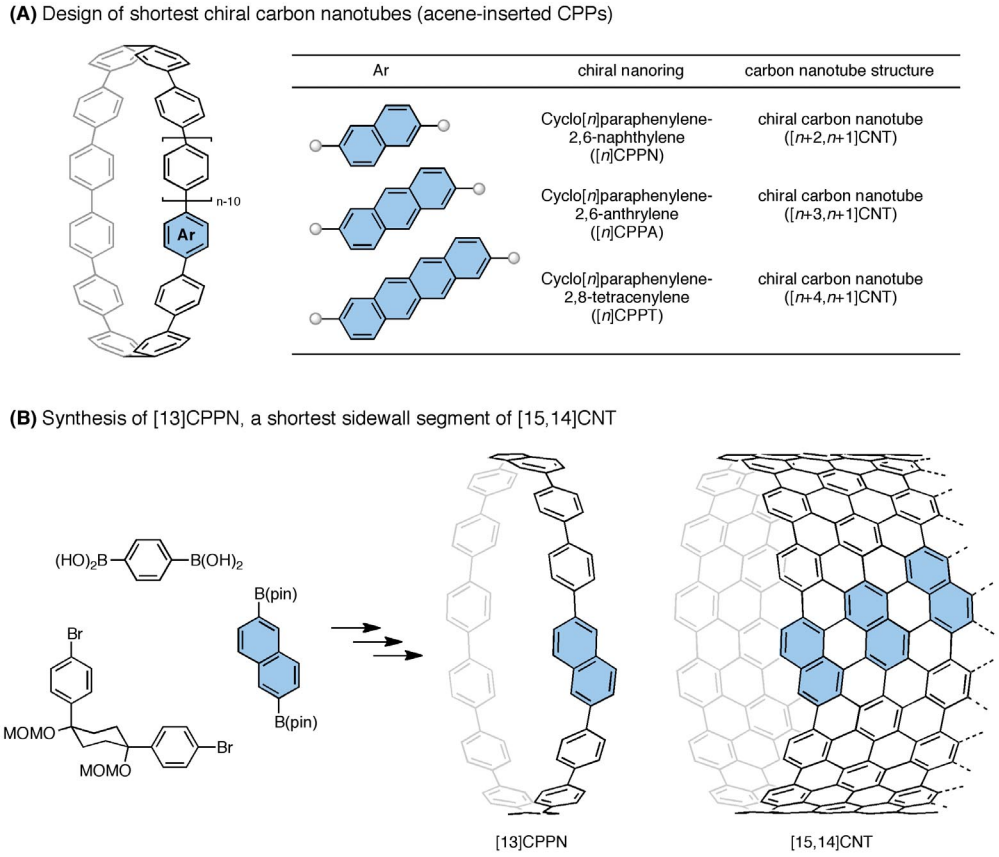


Fig. 5 Design of shortest chiral CNT and synthesis of [13]CPPN.

Chiral carbon nanorings such as [13]CPPN possess helical chirality corresponding to the helical chirality of chiral CNTs. The racemization of chiral carbon nanorings occurs via the rotation of the acene unit (naphthalene for [13]CPPN) around the two C–C bonds that connect it to the neighboring benzene units. By using DFT calculations, we determined the racemization barriers ($\Delta G^{\ddagger}$) of a series of chiral carbon nanorings (acene-inserted CPPs) and clarified the effect of ring size and acene unit in racemization process [24]. In general, the $\Delta G^{\ddagger}$ value increases (i) as the number of benzene units

decreases (as the ring size decreases) or (ii) as the acene unit becomes larger. As for the synthesized [13]CPPN, the racemization barrier was estimated to be 8.4 kcal mol^{-1}. Based on these studies, we are now in a position to rationally design a chiral carbon nanoring with target racemization aptitude.

In summary, we successfully opened the door for the modular and controlled synthesis of short sidewall segments of armchair and chiral CNTs (CPPs and acene-inserted CPPs) by simply introducing a cyclohexane ring as a bent benzene-convertible unit. With these small templates in hand, we are currently trying to find a way to grow these templates (seeds) into the targeted CNT structures.

TOWARD BOTTOM-UP SYNTHESIS OF STRUCTURALLY UNIFORM NANOGRAPHENES

Graphenes, two-dimensional sheets of sp^2-hydridized carbon, have received a tremendous amount of interest from almost all areas of science and technology [30–32]. As the shape, width, and edge periphery (topology) determine the properties of graphenes, a bottom-up synthesis of structurally uniform nanographenes is recognized as one of the greatest challenges of primary importance in this research field [33,34]. Among various potential strategies, a two-step approach through (i) controlled organic synthesis of relatively large PAHs with various topologies [35], followed by (ii) the surface-assisted polymerization of these π-extended PAH monomers [36] or (iii) the amplification sheet-growth using these π-extended PAHs as a template [37], holds promise for a controlled synthesis of nanographenes.

A possible first step in this strategy is the arylation of small PAHs. Typically, arylation of PAHs has been executed by a two-step sequence consisting of either (i) halogenation of PAHs followed by Pd-catalyzed cross-coupling reactions, or (ii) Ir-catalyzed C–H borylation of PAHs followed by Pd-catalyzed cross-coupling with aryl halides. However, given the issue of step- and atom-economy and our own experience [38–47], we decided to take a more challenging direct C–H bond arylation strategy (Fig. 6). After many investigations, we discovered that the combination of $Pd(OAc)_2$/*o*-chloranil can catalyze the direct C–H arylation (C–H/C–B coupling) of PAHs with arylboron compounds (Fig. 7) [48]. Among various forms of arylboron reagents, arylboroxin turned out to be the first-choice agent in terms of reaction efficiency. For example, under the influence of $Pd(OAc)_2$/*o*-chloranil catalytic system, various electronically and structurally diverse arylboroxins were found to react with pyrene to give the corresponding 4-arylpyrenes in moderate to good isolated yields (Fig. 7). Very interestingly, the C–H/C–B cross-coupling took place exclusively at the C4 position of the pyrene ring, which is quite unusual in pyrene functionalization. In addition, it was found that the C–H arylation also occurs with various PAHs, such as phenanthrenes and benzoanthracenes, with high regioselectivity [48]. The use of

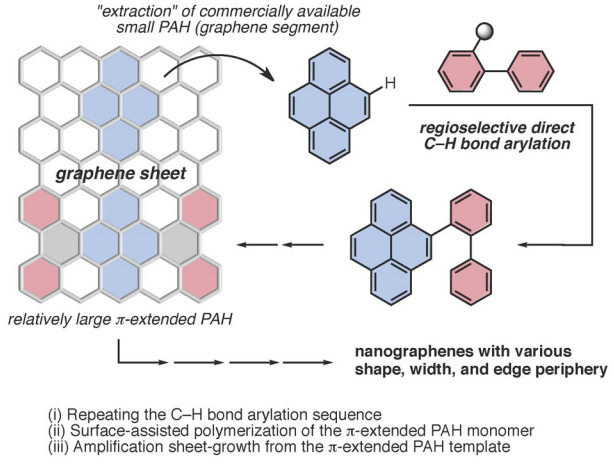


Fig. 6 Direct arylation of small PAHs as a possible initial step toward controlled synthesis of nanographenes.

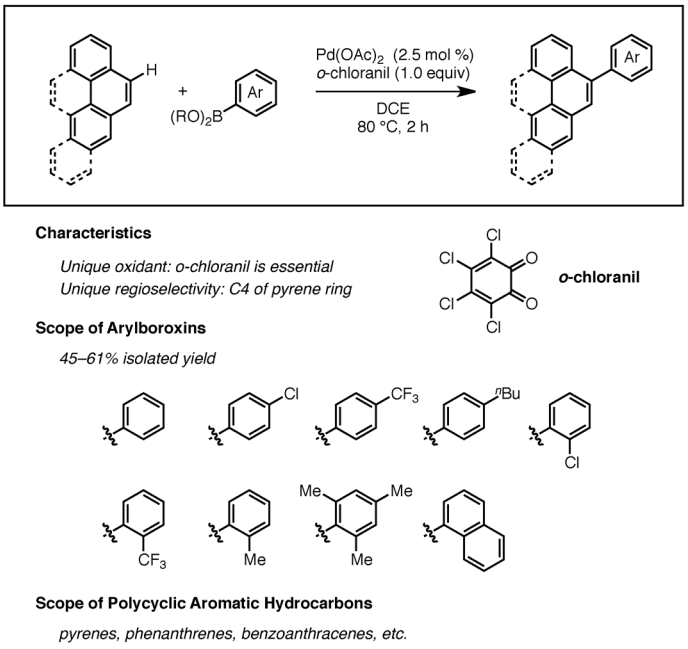


Fig. 7 Direct C–H arylation of PAHs with arylboron compounds.

o-chloranil as an oxidant is critically important for the present reaction to occur. It became clear from the reactions using other oxidants that the high reactivity of *o*-chloranil stems not only from its high oxidation aptitude but also from the *o*-quinone structure. Although further investigations are needed, Pd species bound with two oxygen atoms of *o*-chloranil (*o*-quinone, *o*-semiquinone, or catecholate form) might be responsible for the unique reactivity in C–H/C–B coupling.

We also found that the sequential integration of Pd-catalyzed direct arylation of PAHs and $FeCl_3$-mediated cyclodehydrogenation (Scholl reaction) [49] is particularly effective in rapidly extending a parent PAH π-system with high directionality (Fig. 8). For example, phenanthrene cross-coupled with *o*-biphenylboroxin under the action of $Pd(OAc)_2$/*o*-chloranil to afford 9-biphenylated phenanthrene. The follow-up treatment with $FeCl_3$ in $CH_2Cl_2/MeNO_2$ at room temperature successfully closed the "fjord region" of the initial coupling product to furnish dibenzochrysene in 60 % overall yield. Two-directional π-extension of PAHs is even more effective. For example, a double C–H bond arylation of 2,7-di-*tert*-butylpyrene with *o*-biphenylboroxin, followed by cyclodehydrogenation provided hexabenzotetracene in 60 % yield in two steps (Fig. 8). It is noteworthy that the reaction can be conducted on a gram scale.

In summary, we have demonstrated that the newly developed $Pd(OAc)_2$/*o*-chloranil system is an effective catalyst for the oxidative direct arylation of PAHs with arylboron compounds. The unexpected emergence of unique C4-regioselecivity for pyrene arylation is particularly interesting not only because it provides information about the mechanism, but also because it can be utilized complementarily with the other π-extendable reactions such as bromination (C1) [50] and Ir-catalyzed C–H borylation (C2) [51]. We also demonstrate that the sequential integration of Pd-catalyzed direct arylation of PAHs and $FeCl_3$-mediated cyclodehydrogenation is particularly effective in rapidly extending a parent PAH π-system with high directionality. The application of $Pd(OAc)_2$/*o*-chloranil catalysis to various planar and geodesic PAHs and the controlled synthesis of nanographenes are currently ongoing in our laboratory.

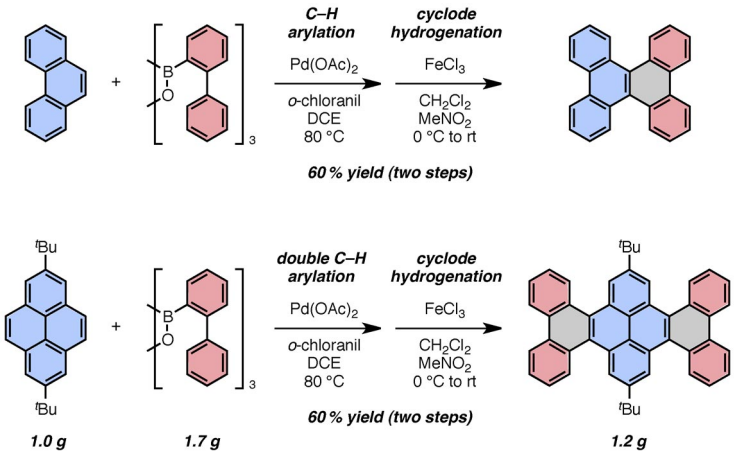


Fig. 8 Synthesis of extended PAHs through sequential C–H arylation and cyclodehydrogenation.

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