Carbon Nanotubes

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para-Connected Cyclophenylenes and Hemispherical Polyarenes: Building Blocks for Single-Walled Carbon Nanotubes?

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alkynes · carbon · macrocycles · nanotubes · polyarenes

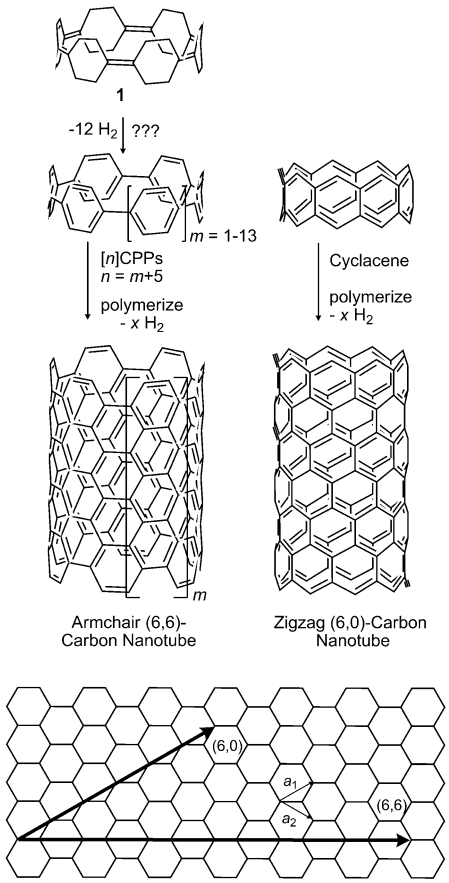
Dedicated to Professor François Diederich on the occasion of his 60th birthday

1. Background

The synthesis and characterization of rigid aromatic macrocycles started when Sondheimer, Eglinton, and Galbraith as well as Raphael, described the synthesis of the cyclic dimer of 1,2-diethynylbenzene.[1] Since then, the synthesis and use of conjugated macrocyclic materials has exploded, as documented in a masterly review by Iyoda et al.[2] An important aspect of this research area is the total synthesis of carbon nanotubes (CNTs) and their cyclic or ribbonlike segments.[3,4]

Carbon nanotubes (CNTs) are attractive for a variety of applications,[3] and come as either armchair (n, n) or zigzag $(n, 0)$ tubes. These two types of single-walled carbon nanotubes (SWNTs) are achiral, whereas all other combinations of indices (n, m) give rise to chiral SWNTs. The (n, m) indices fully define the radius and chirality of a SWNT and determine unequivocally its electronic structure. Only those SWNTs that obey the $n-m=3q$ rule ($q=$ an integer number) are metallic and, therefore, only about one-third of all of the SWNTs are metallic.[3c,d] Both the electronic properties and potential applications of CNTs are thus defined by the diameter and helicity. Therefore, having control over the rational design and chemical preparation of these carbon allotropes by using standard synthetic protocols is of utmost importance. Armchair tubes are built (on paper) by the consecutive stacking of [*n*]-cyclo(*para*-phenylene)s ([*n*]CPPs; where [*n*] denotes the number of phenylene rings connected), while the zigzag tubes are formed (also on paper) by dehydrogenative polymerization of cyclacenes (Scheme 1). The synthesis of both cyclic segments is difficult, and the cyclacenes, despite significant effort, have never been made.[5]

[*n*]CPPs are challenging synthetic targets, even though their partially hydrogenated congeners **1** have been known since the mid-1980s (Scheme 1), although there have been no attempts to dehydrogenate **1** to [6]CPP.[6] However, the synthesis of [*n*]CPPs has flourished since the seminal publication by Jasti and Bertozzi in 2008. Prior to this, Bäuerle and co-workers had synthesized the topologically similar, cyclic 2,5-connected oligothiophene **5** by using a platinum bisphosphine complex to build up the cycle **3**. Treatment of **3** with iodine resulted in the expulsion of the platinum template and



Scheme 1. Structure of CPPs and their relationship to nanotubes (top). Formation of SWNTs from graphene (bottom).

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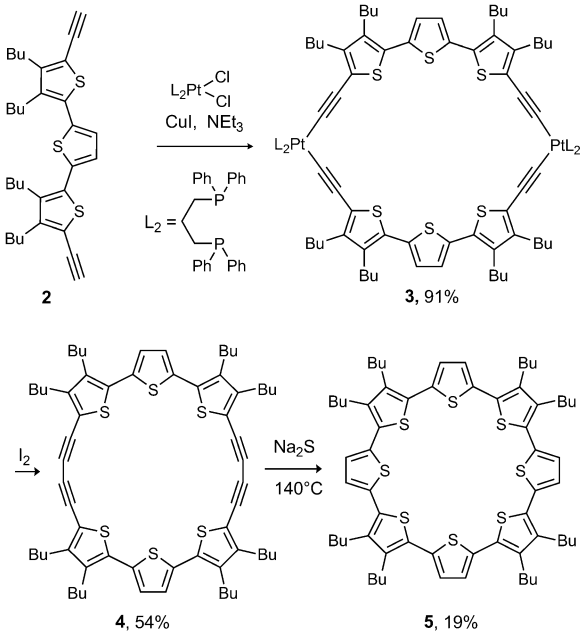
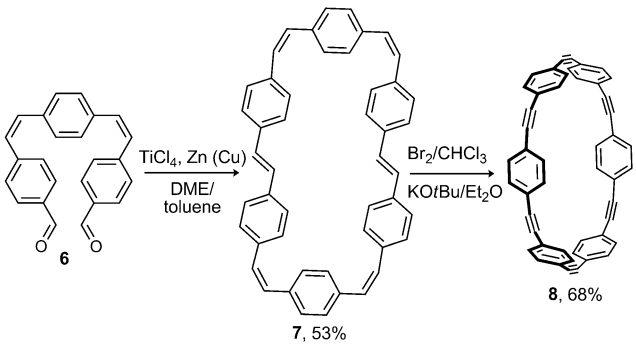
furnished **4**, which transformed into the target structure **5** on reaction with sodium sulfide (Scheme 2).[7]

It is worth mentioning that Kawase, Oda et al. had prepared *para*-connected oligo(phenyleneethynylene)s ([*n*]CPPE, **8**), another molecule class related to the CPPs.



Scheme 2. Synthesis of *para*-cyclothiophene **5**.

The McMurry coupling of **6** produced **7**, which upon bromination followed by dehydrohalogenation afforded **8** (Scheme 3). [*n*]CPPEs with $n = 5$–9 are accessible by this route and display fascinating structures and properties, as reviewed by Kawase et al.[8]



Scheme 3. Synthesis of Oda's hexaene, [6]CPPE. DME = 1,2-dimethoxyethane.

2. Synthesis of CPPs

The approach invented by Bertozzi and co-workers to access the CPPs (Scheme 4) uses dimethoxycyclohexadiene as a hinge to generate the cyclic precursors **13a–c** by Suzuki coupling of **11** to **12**.[9] Reduction of **13a–c** with lithium naphthalenide induces anionic ether cleavage with double expulsion of methoxide under aromatization of the rigid macrocyclic skeleton to give [9]-,[12]-, and [18]CPP.

This concept is general, and the synthesis of [6]CPP proceeds in 48% yield through multiple elimination of methoxide from precursor **16** (Scheme 5).[10] The problematic step in this synthetic sequence is the formation of the ring **16**: it closes in only 12% yield during a Suzuki-type coupling of **15** with a 1,4-phenylenediboronic acid. However, this is an impressive synthetic feat by Xia and Jasti that built upon their earlier successful synthesis of [7]CPP.[11]

There are two other concepts for the preparation of larger CPPs. The sequence used by Itami and co-workers (Scheme 6) to prepare CPPs starts from 1,4-dibromobenzene (**18**) and 1,4-cyclohexanedione (**17**), from which, via a cerium organic compound and subsequent protection of the formed diol, the corner piece **19** is prepared. An efficient Yamamoto coupling generates **20** in respectable yields.[12] Deprotection, double elimination, and subsequent oxidation of **20** in air furnishes [12]CPP in 65% yield. Overall, this is the most practical way to make substantial quantities of large CPPs.

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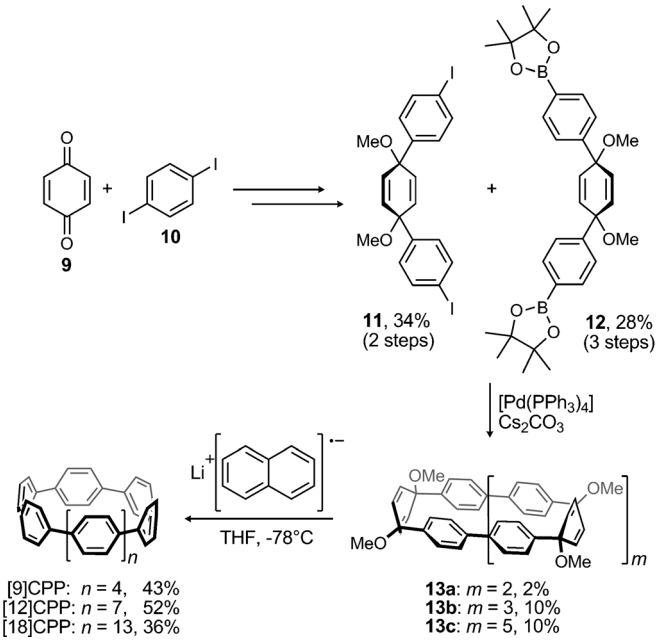
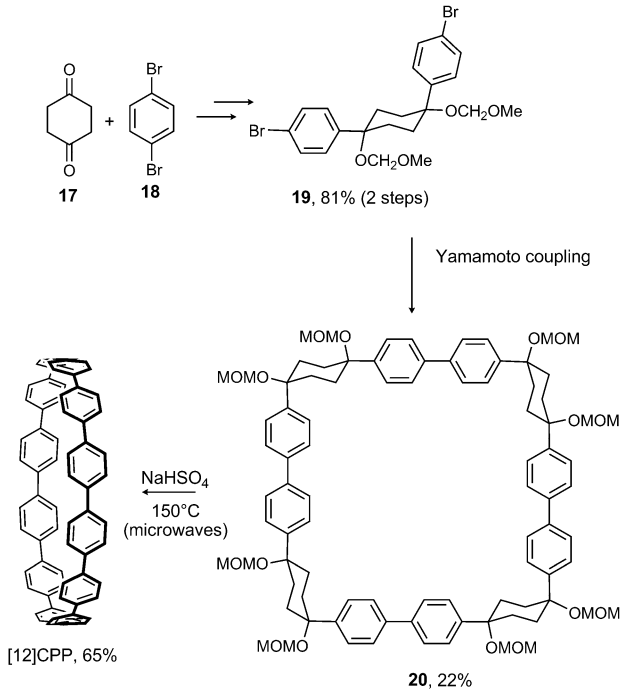
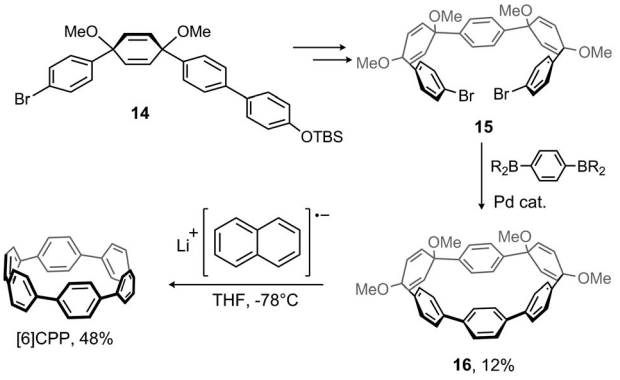


Scheme 4. Synthesis of [*n*]CPPs by Bertozzi and co-workers.



Scheme 6. Synthesis of [12]CPP by Itami and co-workers.



Scheme 5. Synthesis of [6]CPP by Xia and Jasti.

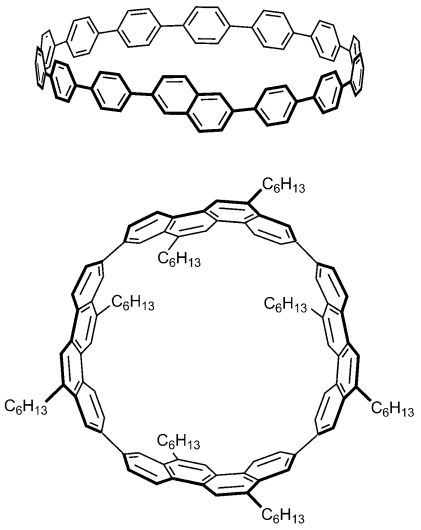


Figure 1. Chiral naphthalene- or phenacene-containing CPP derivatives.[14]

Several more CPPs were prepared by this route, and the Itami research group also made a chiral, naphthalene-containing CPP (Figure 1).[13,14] The first synthesis of a π-extended carbon nanoring, [9]cyclo-1,4-naphthylene, has also been achieved by this research group.[15]

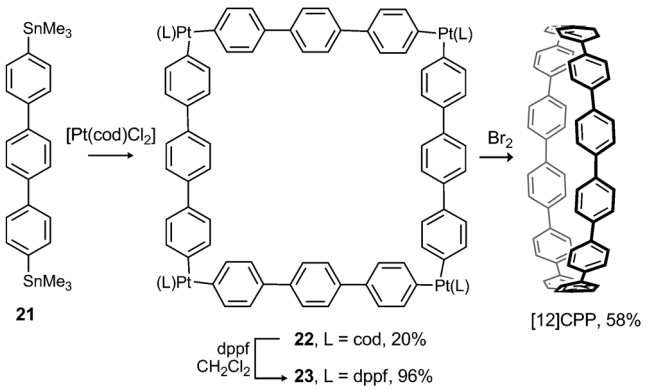
The third synthesis was developed by Yamago et al. (Scheme 7) and is reminiscent of the approach used by Bäuerle and co-workers to access the cyclic oligothiophenes.[16] Reaction of the distannylated terphenyl **21** with $[Pt(cod)Cl_2]$ gives the macrocyclic template **22**. Ligand exchange with dppf to generate **23** is followed by oxidative deplatination, which furnishes the [12]CPP, or, depending upon the precursor, other [*n*]CPPs, in good overall yields. This synthetic approach is clever, but the use of stoichiometric amounts of both dppf and the Pt complexes makes this route expensive to scale-up to generate multigram quantities of CPPs. The three approaches presented, however, have allowed the synthesis of a series of [*n*]CPPs ranging from $n = 6$ to 18 (Table 1). Only [17]CPP is still unknown.

3. Properties and Structures of CPPs

The research groups of Bertozzi, Yamago, and Jasti reported the fluorescence properties of [6]–[13]CPPs. Surprisingly, the smallest representative, [6]CPP, is nonfluorescent, while [7]–[13]CPPs display emission maxima from 592 nm ([7]CPP) to 423 nm ([13]CPP, Table 1)). The trend is

Table 1: Known CPPs, their creators, year of synthesis, their emission properties, and strain energies (calcd in kcal mol^{-1}).

 $n=$	6	7	8	9	10	11	12	13	14	15	16	17	18
Jasti/Bertozzi	2012	2011		2008			2008						2008
Yamago			2010	2011	2011	2011	2011	2011					
Itami				2011			2009		2010	2010	2010		
emission λ_{max} [nm]		592	533	498	474	460	451	442					
strain energy	96	84	72	66	58	54	48	46	41	39	36		32
strain energy/ phenylene ring	16.0	12.0	9.0	7.3	5.8	4.9	4.0	3.5	2.9	2.6	2.3		1.8



Scheme 7. Synthesis of [12]CPP by Yamago et al. cod = cycloocta-1,5-diene, dppf = 1,1′-bis(diphenylphosphanyl)ferrocene.

unexpected, as longer oligomers normally have lower emission energies, as the HOMO–LUMO separations are smaller. The absorption spectra are all similar and display a λ_{max} value at around 340 nm, with a large Stokes shift. The smallest fluorescent CPP ([7]CPP) emits in the orange region—a most unusual finding—while the large ones are blue or green emitters. The optical properties of the linear oligomers and the analogous CPPs become increasingly similar at larger sizes. The counterintuitive red-shift of the emission as the ring size decreases is also observed in the case of the smaller CPPEs.

To explain this behavior, Yamago et al. performed quantum chemical calculations on different-sized CPPs and their linear congeners to examine their HOMO–LUMO gaps (Figure 2).[16b] The observed trend for the emission spectra is reflected in the HOMO–LUMO gaps. The participation of quinoidal resonance structures and perhaps also rehybridization effects are apparently responsible for the abnormally red-shifted fluorescence of the smaller ones.

Itami and co-workers calculated the strain energies of the [*n*]CPPs (Table 1) by DFT methods.[17a] The smallest hitherto prepared [6]CPP has a significant strain energy of 96.0 kcal mol^{-1}, which calculates to 16 kcal mol^{-1} strain energy per phenylene unit. The strain is accommodated by a bending of the benzene ring into a slight boat conformation. For the larger CPPs ($n > 10$), the strain energies are only modest on a per ring base, and the bond angles are only slightly distorted.

Crystal structures have been determined for the [6]-, [9]-, and [12]CPPs (Figure 3). The calculations (Figure 4) and crystal structures both show that neighboring benzene rings are not coplanar in CPPs but twisted with respect to each other. The reason for the perimeter phenylene rings not being planar is the steric interaction between the *ortho*-hydrogen atoms of adjacent phenyl rings.

The crystallographically observed conformation (Figure 3) of [12]CPP is not the calculated minimum energy D_{6d}-symmetrical one (Figure 4), but rather resembles the D_{3d}-symmetrical one, which is calculated to be 3.7 kcal mol^{-1} higher in energy. Packing effects are probably responsible for the difference in the calculated and observed conformations. In the case of the odd-numbered CPPs, here [9]CPP, the canted back-and-forth-type of arrangement is not feasible and the *ortho* interactions are

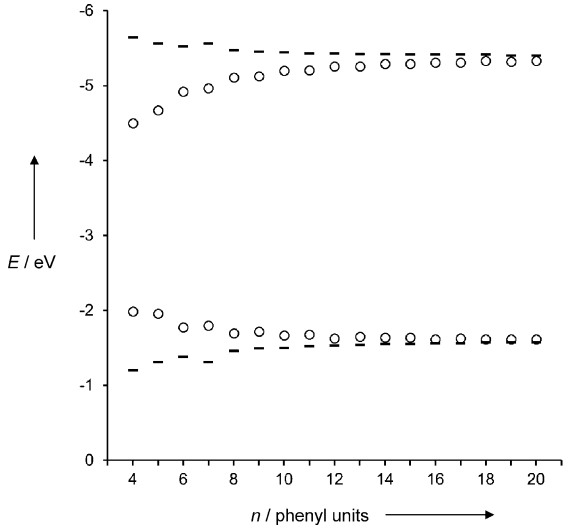


Figure 2. Calculated HOMO and LUMO positions for CPPs (○) and linear oligomers of the same size (——). Top: data indicate the HOMO position, bottom: data indicate the LUMO position.

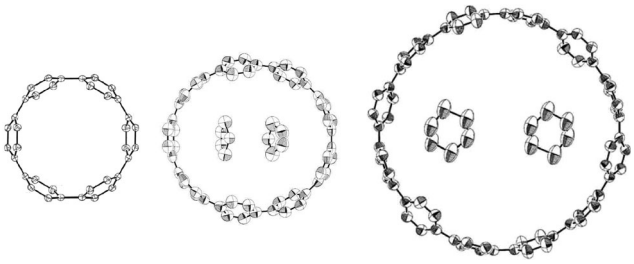


Figure 3. Single-crystal structures of [6]-, [9]-, and [12]CPP. Reprinted with permission from Refs. [10, 12]

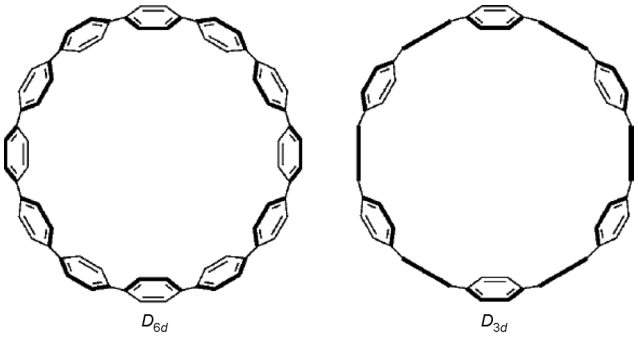


Figure 4. Two optimized structures of [12]CPP. The left conformation represents the energy minimum, while the right one is 3.7 kcal mol^{-1} higher in energy. Reprinted with permission from Refs. [12, 17].

avoided by a somewhat more complicated twisting pattern, perhaps induced by the presence of the two THF molecules that fill the void. The torsion angles between adjacent phenylene groups in the X-ray crystal structure of [9]CPP range from 0 to 42°. In the crystal structure of [6]CPP, the torsion angles between two adjacent phenylene units, symmetry-bound, strictly alternate between 25.7 and 27.1°. These torsion angles are somewhat different to that calculated for biphenyl (41.2°, B3LYP 6-311 G**) in the gas phase.

All three cycles pack in a tubular fashion, but in the cases of [9]- and [12]CPP, the stacks are tilted and the molecules offset from each other (Figure 5), while in [6]CPP the packing axis is perpendicular to the ring, thereby preforming a carbon nanotube (Figure 6).

The binding constant ($K_{bind} = 3–4 \times 10^6$) between [10]CPP and C_{60} was determined through a Stern–Volmer quenching experiment by the research group of Yamago.[18] This value is high, probably because of the excellent fit of C_{60} within the belt-shaped cavity. Figure 7 displays the quantum chemical

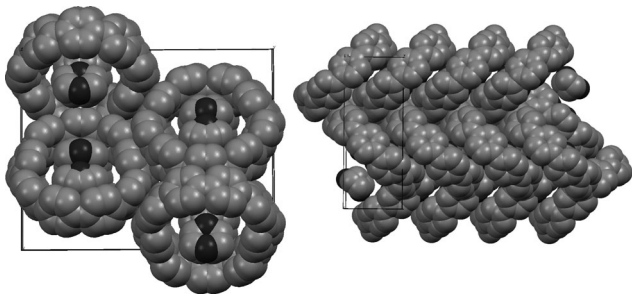


Figure 5. Two views of the tubular stacking of [9]CPP.

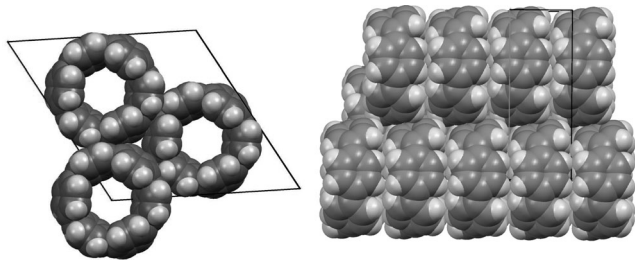


Figure 6. Two views of the tubular stacking of [6]CPP.

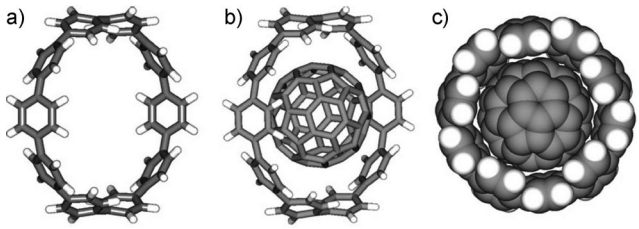


Figure 7. Structure of a) [10]CPP, b) [10]CPP·C_{60} complex (side view), and c) its space-filling model (top view) optimized at the M06 2X/6-31G* level of theory. Reprinted with permission from Ref. [18].

calculations on the formed, well-fitting complex. The smaller and larger CPPs also bind C_{60}, but to a much lesser extent, because of the poor spatial fit. [10]CPP has the perfect size for this task; it might, therefore, be used as a means to separate C_{60} from a mixture of other larger fullerenes.

4. Geodesic Polycyclic Aromatic Compounds

CNTs are produced chemically by using "heterodox" methods.[19] In principle, a plausible rational chemical design for growing carbon nanotubes (CNTs) in a controlled way could be carried out starting from small curved hydrocarbon templates. As an alternative to the nanorings, the elongation of the curved hydrocarbon template by the repetitive addition of carbon atoms to annulate new rings would result in CNTs in which the diameter and orientation of the rings formed along the sidewalls would be identical. The material thus produced would allow control of the type and chirality of the CNTs produced and, therefore, of the physical (conducting versus semiconducting) and chemical properties (Figure 8).

The main drawback of the synthetic strategies is the controlled synthesis of the curved polyarenes—the necessary starting materials.[20] Bowl-shaped π-conjugated compounds or geodesic polyarenes are of interest not only as model compounds of fullerenes but also as possible synthetic intermediates for the synthesis of fullerene derivatives,

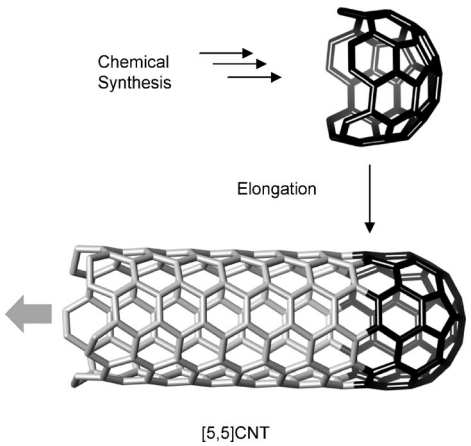


Figure 8. Strategy for the rational chemical synthesis of [5,5]-carbon nanotubes of uniform diameter and single chirality from the hemispherical $C_{50}H_{10}$ template.

heterofullerenes, and endohedral fullerenes.[21–24] For many years, the synthesis of geodesic polyarenes or "fullerene fragments" has been a difficult challenge for chemists.[25] Corannulene ([5]circulene) is a relatively simple polyarene formed from a cyclopentane ring fused with five benzene rings. It exhibits a concave shape (buckybowl) and was first synthesized in 1966 and produced on a large scale in 2000 (Figure 9).[26,27] More recently, corannulene has been prepared by Siegel and co-workers in kg quantities.[28]

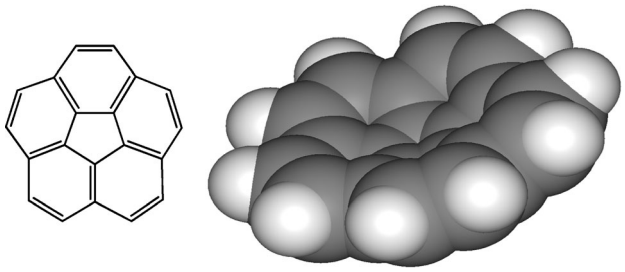
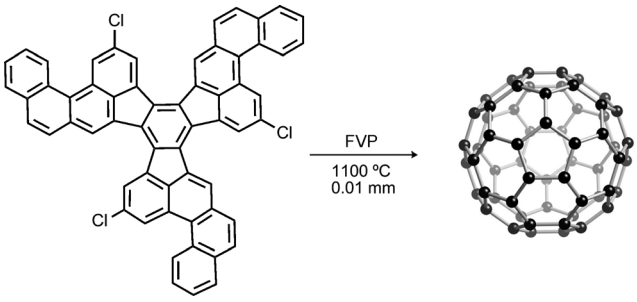


Figure 9. Bowl-shaped corannulene or [5]circulene ($C_{20}H_{10}$).

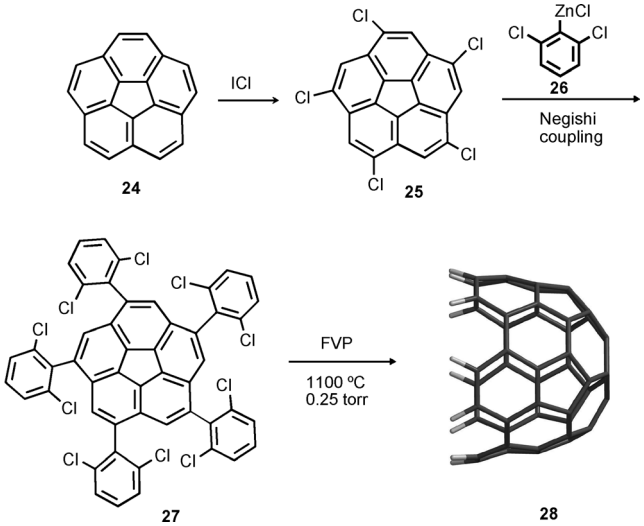
Corannulene is formally a constituent fragment of all the fullerenes which follow the isolated pentagon rule (IPR), such as [60]fullerene. This rule states that the stable fullerenes are those in which all the pentagons are surrounded by hexagons, thus generating the corannulene moiety.[29,30] However, the first rational chemical synthesis of [60]fullerene did not use the corannulene molecule as a starting material. It was accomplished in 2002 by Scott et al. Their synthesis involved 12 synthetic steps from commercially available materials and led to C_{60} in isolable quantities and in around 1% yield. The last step required flash vacuum pyrolysis (FVP) of the chlorinated polycyclic aromatic hydrocarbon $C_{60}H_{27}Cl_3$ at 1100°C (Scheme 8). Interestingly, the absence of other fullerenes, such as C_{70} and higher fullerenes, in the final product can be taken as good evidence that the chlorinated hydrocarbon "zips up" intramolecularly to form C_{60} through C–C coupling reactions.[31]

The same strategy was used with a different technical protocol for the synthesis of C_{60} and the triazafullerene $C_{57}N_3$ from aromatic precursors through a highly efficient surface-catalyzed cyclodehydrogenation process.[32] Deposition of the starting hydrocarbon onto a Pt(111) surface and heating to 750 K resulted in the precursors being quantitatively transformed into the corresponding fullerene and triazafullerene molecules. This approach might allow the production of different fullerenes and heterofullerenes from suitable precursors. Although it has also been claimed that conducting the process under an atmosphere containing guest species might even allow the encapsulation of atoms or small molecules, thus affording endohedral fullerenes, no results have so far been reported.[33]



Scheme 8. FVP formation of [60]fullerene from $C_{60}H_{27}Cl_3$.

The most intriguing step in the synthesis of buckybowls is the deformation of simple planar or nearly planar polyarenes. This key transformation has been carried out by flash pyrolysis, first applied to these systems by Scott et al. and subsequently used by many others interested in fullerene fragments.[34] Geodesic polyarenes have recently attracted attention as a result of the stepwise chemical synthesis of the first geodesic hemispherical polyarene $C_{50}H_{10}$ by Scott et al.[35] The synthesis of **28** was carried out in three synthetic steps from corannulene (**24**; Scheme 9). Chlorination of **24** afforded pentachlorinated compound **25**, which underwent a five-fold Negishi coupling with 2,6-dichlorophenylzinc chloride (**26**) to give **27** ($C_{50}H_{20}Cl_{10}$, X-ray analysis). Flash vacuum pyrolysis (1100°C/0.25 Torr) gave **28**. Cleavage of the C–Cl bonds under these conditions is expected to result in the sequential formation of highly reactive (multi)radical species. The high temperature also provides the conditions for distortion of the intermediate species, thus allowing generation of the geodesic compounds. The final compound **28** was isolated as a red-orange solid in 2–3% yield.



Scheme 9. Synthesis of hemispherical polyarene $C_{50}H_{10}$ (**28**) from corannulene (**25**).

Compound **28** is stable to air, heat, and light and soluble in common organic solvents, thus allowing its complete chemical and spectroscopic characterization. X-ray crystallographic analysis of **28** revealed a diameter of 9.4 Å, which is close to the diameter of C_{60} or a (5,5)-nanotube.

The synthesis of this hemispherical geodesic polyarene **28** paves the way for the preparation of other buckybowls, whose diameters and rim structures can be designed and synthesized

at will. Furthermore, the controlled elongation of the hemispherical compounds should allow carbon nanotubes to be obtained in which the diameter and rim structure are well defined and, therefore, with the required chirality and conducting properties. This vision, although closer, is still a great challenge for chemists.

5. Conclusion and Outlook

Since 2008, [6]–[18]CPPs have been prepared by three different synthetic routes. All of the CPPs are surprisingly soluble in common organic solvents, as they apparently cannot form efficient intermolecular π–π interactions. Hexiphenyl, the linear congener of [6]CPP, on the other hand, is already insoluble as a result of efficient π–π interactions in the solid state. The emissive properties of the CPPs starkly defy intuition, as the emission wavelengths are red-shifted as the CPP size decreases, which is opposite to that found for the linear oligophenylenes and other conjugated oligomers.[36]

The promise of CPPs lies in the directed wet-chemical synthesis of segments of single-walled carbon nanotubes with a perfectly defined diameter. One could employ either thermal fusion in the solid state or a Scholl-type oxidation of [*n*]CPPs in solution. For the former approach, the latest member of the family, [6]CPP, seems to be ideal, as it already packs in a nanotube-like manner in the solid state, while the latter approach would probably require oligomers of CPP, which could then be dehydrogenated under suitable oxidative conditions. A radically different approach would be to start with a CPP, then modify the rim, and build the desired nanotube up level by level. Any of these concepts could bring exciting progress to this enthrallingly suspenseful area.

In addition to the CPPs, the geodesic polyarenes represent a realistic and attractive approach to generate templates from which to grow structurally uniform CNTs. However, finding the right synthetic methods to elongate the starting hemispherical buckybowl, such as **28**, remains a challenge. This, however, should be achievable with the repertoire of available modern synthetic methods.

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