Curved Polycyclic Aromatic Hydrocarbons – A Discipline Still in Its Infancy

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Introduction

With the Nobel Prize winning discovery of graphene[1] (a single layer of the graphite structure) and its unique properties,[2] an area of chemistry devoted to investigating (and potentially replicating) these properties has received fresh impetus. Polycyclic aromatic hydrocarbons (PAHs), a class of compounds consisting of fused conjugated aromatic rings without heteroatoms, can be considered the small extreme within the graphene size spectrum. Within the domain of synthetic chemists, PAHs can be isolated as monodisperse, structurally well defined 'nanographenes' and these have been used as precursors for the synthesis of large graphene sheets in a bottom-up approach.[3,4] However, despite being able to synthesise very large PAHs,[5] structurally perfect graphene sheets by a bottom-up approach have not yet been adequately realised. Many PAHs have been shown to have interesting properties themselves.[6] Depending of the electron configuration, they can show great stability in those examples where electrons can be localised into aromatic sextets.[7] Substituted with solubilising alkyl chains, many large PAHs form liquid crystalline phases that have the ability to carry charge anisotropically and, therefore, have potential roles in molecular electronics.[6] The application of these materials has led to intensive research into PAHs over the past few decades, and as a consequence of this explosion of research there will be few people reading this article who have not heard of PAHs.

An earlier Nobel Prize winning discovery concerning another all-carbon species, that of buckminsterfullerene,[8] has inspired the related area of curved PAHs. Buckminsterfullerene (known more commonly as C_{60}) and graphene are similar in a major way – they are both comprised entirely of nominally sp^2-hybridised carbons.[1,8] However, these molecules are structurally very different. Graphene is planar, whilst C_{60} is spherical (Fig. 1). Despite both being comprised of all sp^2-hybridised carbons, C_{60} has 5-membered rings incorporated into its structure, whilst graphene consists of all 6-membered rings. It is the 5-membered rings that provide the curvature in C_{60}. Based on this observation, the synthesis of curved PAHs has been achieved through the incorporation of 5-membered rings into otherwise planar PAHs.
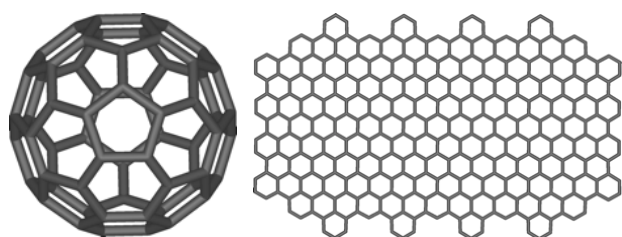

Fig 1. Molecular models of C_{60} and a graphene sheet.

From Buckyball to Buckybowl

The initial foray into curved PAHs was in an attempt to rationally synthesise C_{60}, which has traditionally been prepared primarily through the Huffman electrical discharge method,[9] a method that is low-yielding and produces a fullerene soot mixture that is not trivial to purify.[10] Deconstruction of the spherical C_{60} led to the identification of two fragments from which fullerenes such as C_{60} could potentially be synthesised. These are the 'buckybowls' corannulene and sumanene (Scheme 1).[11,12] Corannulene is a C_{60} fragment that contains a central 5-membered ring surrounded by 6-membered rings. Sumanene, on the other hand, can be thought of as the planar PAH triphenylene with three methylene bridges at the periphery. The trivial name 'corannulene' is derived from the Latin: *cor* = heart and *annulene* = ring,[13] whilst 'sumanene' is derived from the Hindi and Sanskrit name for flower, *suman*, owing to sumanene's flower-like shape.[12]
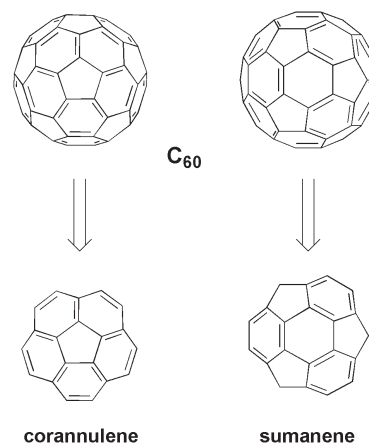

Scheme 1. Identification of the corannulene and sumanene carbon frameworks as fragments of C_{60}.

Despite being readily identified as fragments from which to synthesise fullerenes, the buckybowls did not prove easy to synthesise, with gas-phase flash vacuum pyrolysis (FVP) failing to produce sumanene from viable precursors.[14] Both sumanene and corannulene have since been synthesised in very low yields.[14,15] The synthesis of corannulene is particularly long and complicated, relying on the low-yielding FVP technique and resulting in a total yield of less than 1%. The synthesis of sumanene, however, is more concise, involving the cyclotrimerisation of norbornadiene (**1**) to give the *syn*- and *anti*-isomers of **3** in a ratio of 1:3 (Scheme 2). The *syn*-isomer can be transformed to the more thermally stable **4** in a tandem ring-opening and ring-closing metathesis reaction with a Grubbs' first generation catalyst under an acetylene atmosphere. Compound **4** can then be readily oxidised to sumanene (**5**) with DDQ. The overall yield for this synthesis is only 2%.[14]
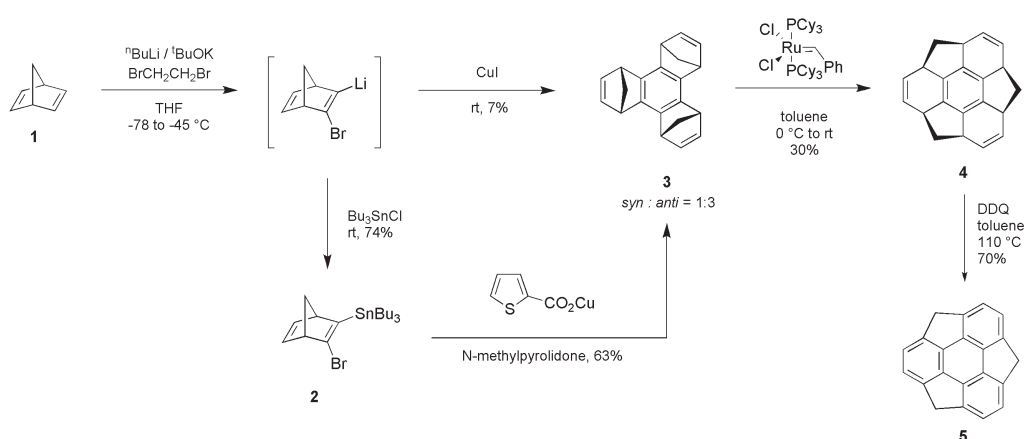
**Scheme 2.** Sakurai's original synthesis of sumanene.[14]

However, this poor yield can mostly be explained by the poor selectivity in the cyclotrimerisation reaction for the *syn-* isomer and the inability of the major (*anti-*) isomer of **3** to react in the metathesis reaction to give **4** owing to its lack of strain. This issue of selectivity was not only overcome, but overcome in such a way that sumanene could be derivatized at the aromatic (as opposed to the benzylic) positions. This was achieved by converting enantiopure norbornandione (**6**) into iodonorbornanone (**7**), followed by cyclotrimerization to afford the *syn*-isomer of **8** selectively in a 55% yield (Scheme 3). The ketone functionalities could then be readily converted to methyl groups and the tandem ring-opening and ring-closing metathesis achieved in a yield of 24%, followed by final oxidation.[16]
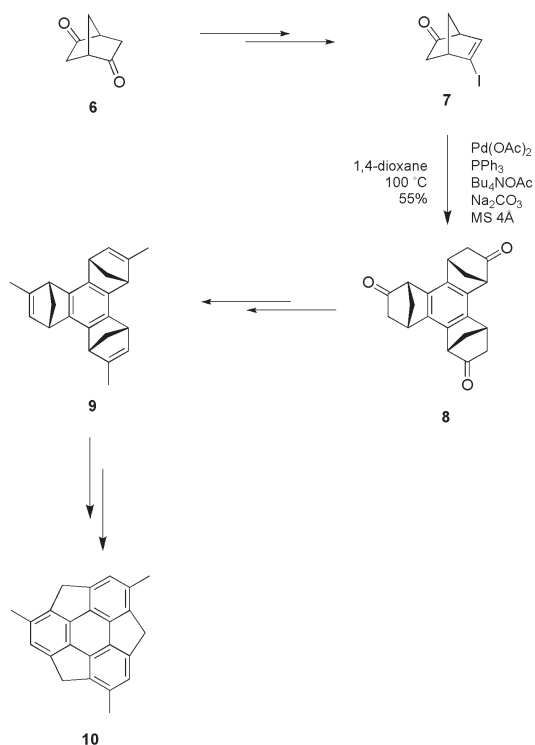
Scheme 3. Sakurai's improved synthesis of sumanene derivatives.[16]

The synthesis of corannulene has also been improved, so that FVP is not required. This was facilitated by a new protocol developed by Sygula *et. al.* that forms the corannulene core by a nickel-mediated intramolecular coupling (Scheme 4).[17] A key advantage of this method over other recent solution-phase syntheses is the greater tolerance for functional groups. In fact, each of these syntheses is a refinement on the previous methods, with the nickel-mediated coupling being the most refined.[18] As such, each of these syntheses involves the coupling of benzyl and benzylidine bromides.[19,20,21,22]
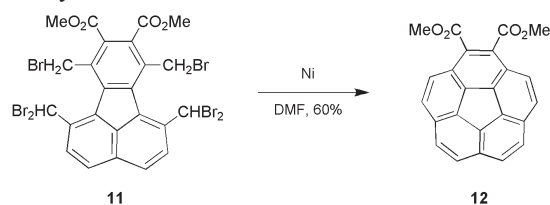
Scheme 4. Sygula *et. al.*'s improved synthesis of corannulene derivatives.[17]

Constructing Fullerenes

Synthetically, most attempts at constructing C_{60} have started from corannulene-based fragments (Scheme 5).[23,24,25]
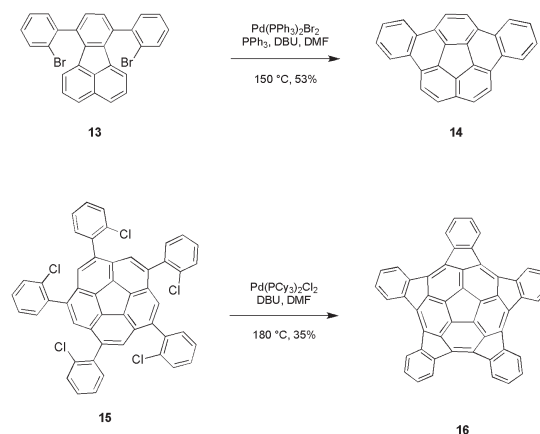
Scheme 5. Corannulene and corannulene precursor-based syntheses of curved PAHs.[23,25]

The resulting curved PAHs have been able to be mapped onto the surface of C_{60},[25] but the synthesis of a curved PAH large enough to be closed-up to form a fullerene has yet to be achieved using this methodology. Other approaches have involved starting with planar materials and then forming rings that cause enough strain to induce curvature. This was shown to work for the synthesis of **17** (see Fig. 2), but it proved to be a very long synthetic pathway and achieved yields no better than starting with curved precursors such as corannulene.[26] One advantage

of this pathway is that the final step that induces curvature is functional-group tolerant, potentially allowing further extension of the curved PAH. This avenue was not explored, however.
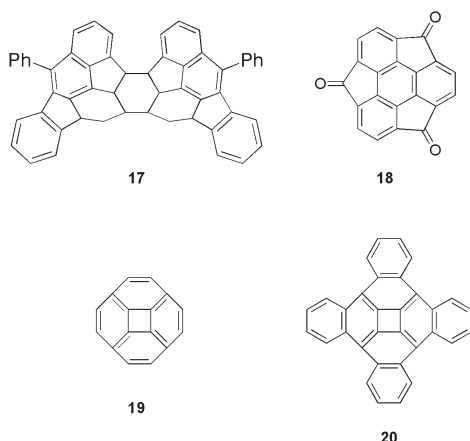

Fig 2. Structures of **17**, **18**, **19** and **20**.

Recently, interest in the synthesis of C_{60} from sumanene-based fragments has grown. This is because sumanene can be more readily derivatised than corannulene owing to the benzylic positions around its periphery (as opposed to the all aromatic periphery of corannulene).[27] The oxidation of sumanene to trioxosumanene (**18**) was shown to be highly successful and that the carbonyls are readily accessible for substitution. Derivatization of trioxosumanene is currently being investigated.[28] Other researchers have investigated the synthesis of curved PAHs through computational chemistry. By examining different potential synthetic pathways, it was shown that some methodologies would encounter greater issues relating to strain associated with the formation of curvature.[29,30] An interesting example of a highly strained curved PAH is quadrannulene (**19**). Quadrannulene is analogous to corannulene, containing a central four-membered ring as opposed to corannulene's five-membered ring. The trivial name of quadrannulene is even based on the trivial name of corannulene. Tetrabenzoquadrannulene (**20**) has been successfully synthesised, and its synthesis opens the possibility of obtaining the non-classical, truncated octahedral fullerene C_{24}.[31]

Physical Properties of Curved PAHs

Despite being unable to achieve the original goal of rationally synthesising fullerenes with useful yields, the synthesis of curved PAHs was not in vain. The buckybowls were found to have properties quite different from those of their planar counterparts. These properties included wider absorption and emission spectra, and more efficient transport of charge.[14] The optical properties can be explained by the curvature of the molecule, as the frontier orbitals are less parallel and therefore have less overlap. This results in the HOMOs and LUMOs being modified, leading to a change in optical properties.[32] As the buckybowls can invert in solution, a range of different orbital environments will exist, leading to broadening of the absorption and emission spectra. Some corannulene derivatives have even been tuned to be blue emitters,[33] an area of considerable interest for light-emitting diodes.

The more efficient transport of charge, however, is a consequence of self-assembly in solution and solid-state packing.[34] Planar PAHs, when appropriately substituted, have the ability to self-assemble into columns owing to intermolecular π-stacking interactions. However, in the solid state the discotic components are tilted with respect to columnar axis owing to the affinity of the protons at the periphery of the PAHs for the electron-rich aromatic regions of the neighbouring molecules.[6] Because of the bowl shape in curved PAHs, there is no latitudinal freedom between stacked molecules, and therefore only one orientation in which curved PAHs can stack: linearly. This linear stacking (Fig. 3) can enhance the molecular orbital overlap between molecules, leading to greater charge-carrier mobility.[34]
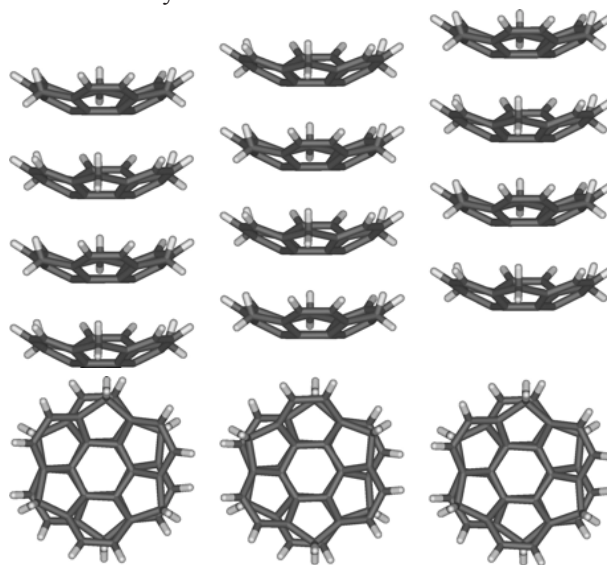

Fig 3. Crystal structure showing linear stacking of three columns of sumanene (**5**), viewed from side-on (top) and down the columnar axis (bottom).[34]

This effect has now been observed from the original buckybowls to a wide range of curved PAHs. One study has been particularly insightful into the effects of bowl-depth and curvature on the stacking of these larger curved PAHs. By characterising the solid-state stacking of the indenocorannulene family, Filatov *et al.* showed that more highly curved PAHs stacked to form more ordered one-dimensional columns (as for larger PAHs) and have greater intermolecular orbital overlap.[35] Bowl-depth and curvature are parameters that are characterised by π-orbital axis vector (POAV) analysis, which indicates the degree to which the molecule is pyramidalised (curved). One particular curved PAH, **16**, was shown to be actually more highly curved than C_{60} itself.[24]

Heteroatomic PAHs have long been of interest for advanced materials.[36] The most accessible of these compounds were deemed to be the heterosumanenes, with heteroatoms replacing the benzylic carbons of sumanene. Whilst two sulfur atoms were able to bridge the periphery of triphenylene, a third sulfur could not be incorporated by starting from triphenylene precursors.[37] However, bromination of **21**, followed by Sonogashira-Hagihara cross-coupling, treatment with hydrochloric acid, and then FVP yielded the trithiasumanene, **25** (Scheme 6).[36] Trisilasumanene, however, was actually synthesised from

a triphenylene-based precursor.[38] These heterasumanenes were found to be flatter than sumanene, and their electronic properties were more related to coronene than sumanene.[36] However, the presence of the heteroatoms was proposed to impart some unique electronic properties that could be used to expand sumanene chemistry.[14]
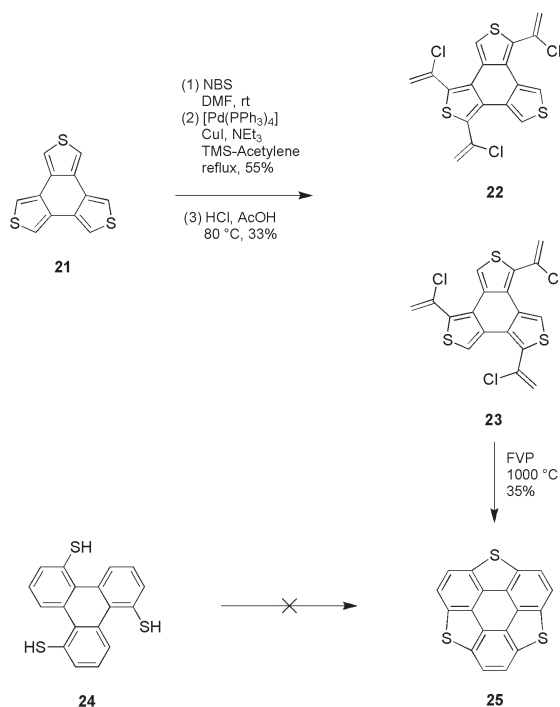
Scheme 6. Synthesis of trithiasumanene.[36]

Chirality

Another property that has sparked interest in non-planar PAHs is bowl-chirality. Chirality in these molecules is imparted from the chemical environment on the concave (*endo-*) face of the molecule being different from that on the convex (*exo*) face (Fig. 4). For example, the benzylic protons of sumanene can be oriented either axially or equatorially and are therefore in two unique chemical environments. Variable-temperature NMR spectroscopy can be used to differentiate between these two environments.[39]
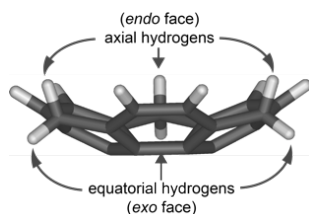

Fig. 4. Benzylic proton environments in sumanene **5**.

It has been shown that the benzylic positions of sumanene can be sequentially deprotonated and then reacted with trimethylsilylchloride to selectively give a trisubstituted species, with all trimethylsilyl groups in the equatorial positions (toward the *exo* face). This facial selectivity was proposed to be caused by steric repulsions if the trimethylsilyl groups were to approach from the *endo* face.[34] Furthermore, this selectivity for approach from the *exo* face results in the syn-isomer forming exclusively. Selectivity was further investigated, without the use of bulky

trimethylsilyl groups; deprotonation of the benzylic positions followed by deuteration also showed facial selectivity, resulting in the formation of the syn-isomer.[39] An added bonus associated with the deuterated analogue of sumanene is that bowl-inversion kinetics can be studied by variable-temperature NMR spectroscopy. Methylation of trioxosumanene was also shown to be selective for the syn-adduct, showing that nucleophiles also approach from the *exo*-face of the molecule.[28]

Supramolecular and Organometallic Chemistry

Supramolecular chemists quickly latched onto the fact that the curved nature of buckybowls makes them ideal candidates as molecular receptors with the ability to recognise the curved surface of fullerenes.[18] These molecular receptors were given the trivial name 'buckycatchers'.[40] The first example of a curved PAH that could recognise C_{60} is the decathioaryl-substituted corannulene, **26**. The crystal structure of **26** as a benzene solvate, exhibits a "fly-trap" arrangement where two molecules of **26** surround one molecule of benzene (Fig. 5).[41] This inspired the formation of supramolecular complexes of **26** with fullerenes. It was shown that the electron-rich **26** could form π-donor / π-acceptor complexes with the electron-poor (good π-acceptor) C_{60} and C_{70}, with K_{assoc} values of *ca.* 1420 and 1080 M^{-1}, respectively.[42]
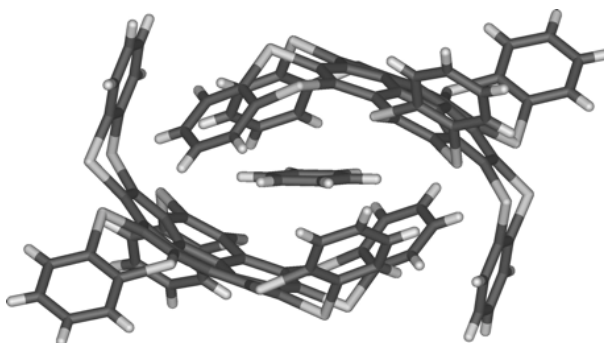

Fig 5. X-ray crystal structure of "fly-trap" encapsulation of benzene by **26**.[41]

The first true buckycatcher was a molecular tweezer with two corannulene subunits attached to a central dibenzocyclooctadiene subunit, **30** (Scheme 7). The saddle shape of the dibenzocyclooctadiene subunit positions the corannulene subunits such that they are ideally located to act as a molecular host for fullerene guests. This buckycatcher was synthesised in a Diels-Alder cycloaddition reaction between isocorannulenofuran (**27**) and dibenzocyclooctadiyne (**28**), followed by deoxygenation with Ti(0) to give **30**.[40] The crystal structure of **30** (see Fig. 6) shows that the corannulene subunits exist in the conformation most ideal for fullerene recognition, with the two concave faces facing each other, creating a significant cleft in the middle.

Molecular modelling calculations were consistent with this, indicating that the other potential conformations (convex faces together, and one convex face facing a concave face) are higher energy conformations.[40] Despite previous work concluding that "the attractive force of the concave-convex interactions is not so significant, if at all",[43] it was shown that **30** did indeed form a supramolecular complex
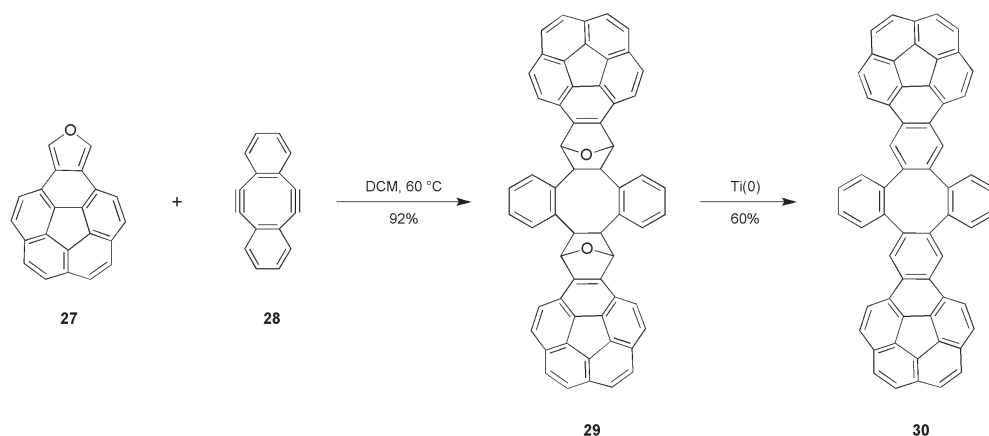
Scheme 7. Synthesis of the buckycatcher **30**.[40]

with C_{60}, confirmed by X-ray crystallography and NMR titration, which was used to estimate a K_{assoc} of 8600 M^{-1}.[44] This association is without the contribution of heteroatoms or polar substituents; it was therefore believed that the strength of interaction comes from pure π-π interaction between the convex fullerene and properly aligned concave corannulene subunits of **30**.[40]
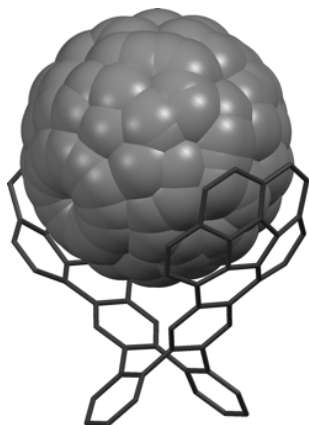

Fig. 6. X-ray crystal structure of Sygula *et. al.*'s buckycatcher **30** in a supramolecular complex with C_{60}.[40]

It has been shown that the highly charged tetraanionic corannulene could form an octaanionic dimer in the presence of eight lithium cations.[45] This was further extrapolated by reducing pentamethyl- and pentaphenyl-C_{60} to pentaanions, forming a green solution. The compatibility of the fullerene guest and buckybowl host was such that when tetraanionic corannulene was introduced, the solution turned black, indicative of the formation of the heterodimer. NMR data are also consistent with this non-anionic heterodimer being formed.[46]

The co-ordination of transition metals to buckybowls has also been investigated, as there are multiple sites present to which a metal can bind in a π-fashion.[18,47,48] It has been shown that the reaction between sumanene and ferrocene or ruthenocene, in the presence of aluminium and aluminium trichloride, led to the formation of the η^6-sumanene complexes **31** and **32** (Scheme 8).[49,50] It is particularly interesting that the iron complex was found exclusively as the *endo*- isomer, with the iron present on the concave face,[49] whereas the ruthenium complex was found as a mixture of *endo*- and *exo*- isomers and dynamic bowl inversion observed; the *endo*- isomer was found to be the

most thermodynamically stable, however.[50] This dynamic behaviour, dependent on the metal present, was proposed as a means to tune the physical properties of coordinated buckybowls.[14]
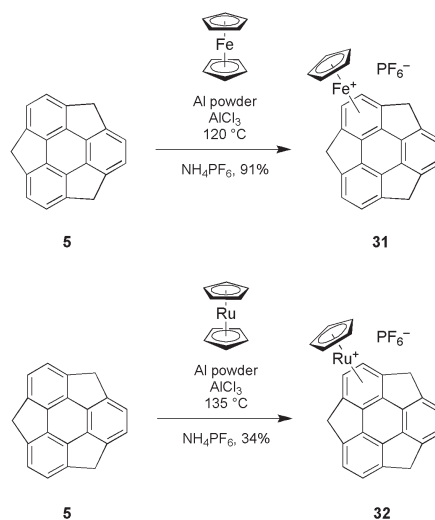
Scheme 8. Amaya *et. al.*'s syntheses of metallosumanenes **31** and **32**.[49,50]

Constructing Carbon Nanotubes

Recently, interest in this field has taken another turn. Although the synthesis of fullerenes has always been a goal of synthetic chemists, existing preparations are efficient enough that a rational synthesis is not an urgent need. However, the preparation of another family of all-carbon compounds that show interesting properties, the single-walled carbon nanotubes (SWCNTs), is due further attention. SWCNTs can have either armchair or zigzag arrangements. The armchair SWCNTs are conductive and show promise as molecular wires.[51] The zigzag SWCNTs are typically semiconducting and also show size-dependent optical properties. This makes them of high interest as materials for molecular electronic devices.[52] However, before getting carried away about the possibilities of zigzag SWCNTs, there is a catch. As with fullerenes, the primary syntheses of SWCNTs involve electrical discharge, laser ablation or flash vacuum pyrolysis (FVP) methods. These methods are somewhat capricious, and result in low yields and high polydispersity.[53] Also, the task of isolating SWCNTs from multiple-walled CNTs and to differentiate the different size SWCNTs is not trivial.[54] Therefore, a synthetic approach that can synthesise specific size SW-

CNTs is highly desirable. To accomplish such a synthesis, a hemispherical end-cap is required from which to template the growth of a nanotube.[55]

The first such end-cap, **33**, was reported only this year.[56] This particular end-cap had previously been predicted to be the simplest capped molecule. X-ray crystallography confirms an enormously high degree of curvature, showing the molecule to be a potentially good template for nanotube formation (Fig. 7). However, the molecule was synthesised using FVP methods, resulting in a very poor yield. It also has no functionality from which to rationally extend nanotubes. Therefore, it could only act as a template for one of the aforementioned methodologies. Despite this, it is the first example of a hemispherical cap molecule and proves that they are synthetically accessible. It is pertinent to note that larger end-caps will likely have less strain and therefore be more accessible targets.
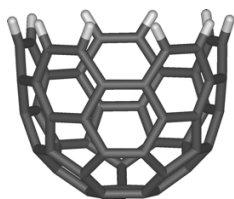

Fig 7. X-ray crystal structure of proposed nanotube end-cap **33**.[56]

Previous studies have also identified potential hemispherical targets from which to direct nanotube growth, and recognised that FVP is a less than ideal technique to use because of its low functional group tolerance.[57] This has led researchers to investigate palladium-catalysed cross-coupling reactions to induce the curvature, owing to their high functional group tolerance and success of such methods under ambient conditions. Curved PAHs have been successfully synthesised in respectable yields, proving the concept of palladium-catalysed cyclisation to form strained systems, and chemists are currently working towards targets that can template nanotube growth.

Conclusion

The desire to rationally synthesise difficult, curved macromolecules like fullerenes and carbon nanotubes has led to a recent rise in research toward curved PAHs. The unique physical properties of these materials have also sparked much interest. However, it is evident that the syntheses of curved PAHs still need to be refined to be efficient and functional-group tolerant. There have been great advances on this front, but functional curved PAHs are still proving elusive. The next step is to properly characterise the behaviour of these materials, so as to rationally design materials that utilise the unique charge-carrying and optical properties of these fascinating molecules.

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