The era of carbon allotropes

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Twenty-five years on from the discovery of C_{60}, the outstanding properties and potential applications of the synthetic carbon allotropes — fullerenes, nanotubes and graphene — overwhelmingly illustrate their unique scientific and technological importance.

Carbon is the element in the periodic table that provides the basis for life on Earth. It is also important for many technological applications, ranging from drugs to synthetic materials. This role is a consequence of carbon's ability to bind to itself and to nearly all elements in almost limitless variety. The resulting structural diversity of organic compounds and molecules is accompanied by a broad range of chemical and physical properties. The tools of modern synthetic chemistry allow the tailored design of these properties by the controlled combination of structural and functional building blocks in new target systems.

Elemental carbon exists in two natural allotropes, diamond and graphite, which consist of extended networks of sp^3- and sp^2-hybridized carbon atoms, respectively. Both forms show unique physical properties such as hardness, thermal conductivity, lubrication behaviour or electrical conductivity. Conceptually, many other ways to construct carbon allotropes are possible by altering the periodic binding motif in networks consisting of sp^3-, sp^2- and sp-hybridized carbon atoms[1,2]. As a consequence of the expected remarkable physical properties of these elusive carbon allotropes, it has been appealing, for some time, to develop concepts for their preparation in macroscopic quantities. However, diamond and graphite represented the only known allotropes of carbon for a long time. This situation changed in 1985, with the advent of fullerenes (Fig. 1), which were observed for the first time by Kroto *et al.*[3]. This serendipitous discovery marked the beginning of an era of synthetic carbon allotropes. Now, as we celebrate buckminsterfullerene's 25th birthday, it is also the time to reflect on a growing family of synthetic carbon allotropes, which includes the synthesis of carbon nanotubes in 1991[4] and the rediscovery of graphene in 2004[5]. Keeping in mind the numerous possible carbon modifications and the number of scientists investigating this challenge, these revelations have certainly not come to an end.

Synthesis of allotropes

The fullerenes, of which the smallest stable and most prominent is C_{60}, are molecular carbon allotropes. C_{60} consists of a spherical network of sixty structurally equivalent sp^2-hybridized carbon atoms in the shape of a football (or, a soccer ball or, more technically, an I_h-symmetrical truncated icosahedron) composed of 12 pentagons and 20 hexagons. Following the isolation and structural determination of C_{60} by Kroto *et al.*, the first successful preparation of 0-dimensional fullerenes in macroscopic quantities was reported five years later by Krätschmer and Huffman[6]. This involved the evaporation and recondensation of graphite using an arc-discharge method to give C_{60}. Now, fullerenes can be prepared on the ton scale.

Many representatives of higher fullerenes[7] such as D_{5h}-C_{70}, chiral D_2-C_{76}, D_{6h}-C_{84} and more recently D_{5h}-C_{90} (ref. 8) have been isolated and structurally characterized. Furthermore, there are several possible ways of derivatizing fullerene including creating fullerene salts, open-cage fullerenes and quasi-fullerenes (Fig. 2). The latter are spherical, closed structures composed of pentagons and hexagons combined with rings of other sizes. Another family of fullerenes, namely endohedral fullerenes (Fig. 2f), incorporates guest atoms or molecules inside the carbon framework. Examples of endohedral fullerenes include
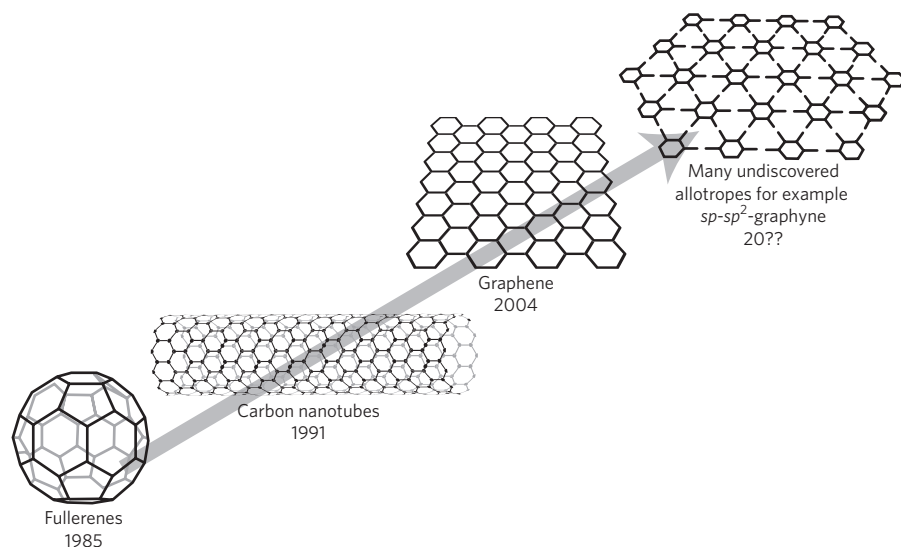

Figure 1 | The world of synthetic carbon allotropes. In this family, fullerenes represent the most intensively investigated class. Fullerene chemistry is a mature field and many well-defined derivatives with outstanding properties have been synthesized. The first fullerene-based products such as organic solar cells have already entered the market. The materials properties of the carbon nanotubes and especially those of graphene are considered to be even more promising. However, it is still difficult to control their chemistry and also the bulk production of uniform monodisperse samples, for example, mass production of tubes with single helicities remains a challenge. Graphene chemistry is in its early infancy. Thinking to the future, there are a huge number of elusive carbon allotropes whose predicted properties are unprecedented. Synthetic chemists are developing concepts at present for their preparation and have already synthesized partial structures.

Figure labels: Fullerenes 1985; Carbon nanotubes 1991; Graphene 2004; Many undiscovered allotropes for example sp-sp^2-graphyne 20??

$La@C_{82}$ and $Sc_3N@C_{80}$ and, most recently, the first endohedral fullerene containing an I_h-symmetrical C_{60} cage, $Li@C_{60}$, was structurally characterized[9]. Exohederal fullerenes — those that have been modified externally — are discussed in further detail below.

Soon after the discovery of the fullerenes, the formation of quasi-one-dimensional carbon nanotubes out of evaporated graphite was reported[4]. Later, a series of alternative production methods for carbon nanotubes, such as chemical vapour deposition methods, were developed[10]. Depending on the preparation conditions, either single-walled or multiwalled carbon nanotubes are obtained. Carbon nanotubes can be considered as seamless, rolled-up graphite sheets. These tubular networks of bent sp^2-hybridized atoms are characterized by a pronounced one-dimensionality because of a very high aspect ratio: typical diameters of single-walled carbon nanotubes are around one to two nanometres, but their lengths can easily reach millimetres and above. Present production methods of carbon nanotubes lead to the formation of mixtures consisting of tubes with many different helicities, characterized by so-called m,n-values of the roll-up vectors[10].

> Synthetic carbon allotropes represent a growing family of fascinating and aesthetically pleasing architectures with outstanding materials properties.

The youngest synthetic carbon allotrope is two-dimensional graphene, representing a single graphite sheet[5]. Graphene, the ultimate example of expanded aromatic carbon, was considered for a very long time to be an exclusively theoretical material. Recently, however, single graphene layers were prepared successfully by means of a simple mechanical exfoliation of graphite using Scotch tape[5]. Andre Geim and Konstantin Novoselov, who headed the team behind the discovery of the exfoliation method and an associated investigation of the electronic properties of graphene, were awarded the 2010 Nobel Prize in Physics. Of the three families of carbon allotropes, graphene is the most structurally uniform material where only the sheet extensions and nature of edges can differ.

Properties of fullerenes

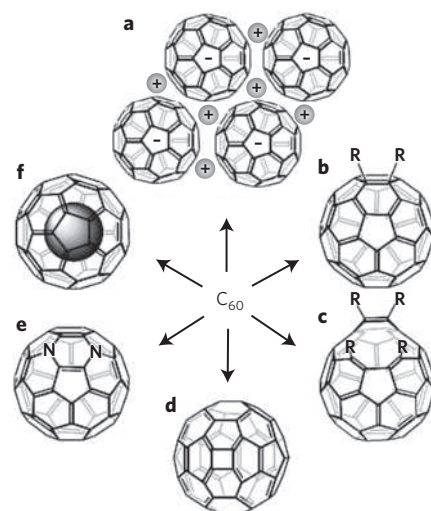What makes synthetic carbon allotropes so attractive for scientists is not only the

Figure 2 | Possible derivatizations of C_{60} (ref. 6): **a**, fullerene salts; **b**, exohedral adducts; **c**, open-cage fullerenes; **d**, quasi-fullerenes; **e**, heterofullerenes; **f**, endohedral fullerenes.

sheer manifold of aesthetically pleasing structures but their outstanding, and often unprecedented, properties. Common to fullerenes, carbon nanotubes and graphene is the presence of fully conjugated π-electrons confined in either zero-, quasi-one- or two-dimensions. This characteristic conjugation leads to pronounced redox activity and outstanding electronic properties. However, what about the chemical properties of the synthetic carbon allotropes and their (and derivatives') application as high-performance materials? Let us start by taking a look at C_{60}: immediately after its availability in macroscopic quantities, it was realized that chemical functionalization was the key to full exploitation of its vast potential. For example, chemical functionalization enables a dramatic increase in the solubility of fullerenes, in any solvent, which is required for their development as new materials or as bioactive redox drugs. Most importantly, however, chemical functionalization provides the possibility of combining the unique properties of fullerenes with those of other compounds. Exohedral addition reactions to the conjugated π-system represent the most important functionalization methods realized so far[7] (Fig. 2b). The driving force for exohedral additions is the reduction of strain energy stored in the spherical carbon framework. Additions usually occur regioselectively at fusions of two six-membered rings, because in contrast to the neighbouring [5,6]-bonds, these [6,6]-bonds are shorter and have more double-bond character.

Over the past couple of decades, thousands of well-characterized adducts of C_{60} and other fullerenes have been synthesized and show remarkable properties. For example, the exohedral covalent binding of organic donor molecules such as porphyrins has attracted a lot of attention[7], to simulate natural photosynthesis or to transform light into chemical energy. Donor–acceptor dyads or oligoads such as compound **1** (Fig. 3) undergo photoinduced electron transfer from the porphyrin donor to the fullerene acceptor and serve as ideal model compounds for organic solar cells. Indeed, no other compound class surpasses fullerenes as electron acceptors in photovoltaic devices[11]. Adduct **2**, namely phenyl-C_{61}-butyric acid methyl ester (PCBM), serves as an n-type conductor in very inexpensive and comparatively efficient plastic solar cells[11] (bulk heterojunctions) that have already entered the market. Water-soluble fullerenes, such as adduct **3** and **4**, exhibit remarkable biological properties with regard to anti-HIV activity[12] and metal-free superoxide dismutation, respectively. The latter is a principal mechanism for efficient neuroprotection[13]. Further applications of fullerene adducts in materials science include the fields of non-linear optical properties[14] and liquid crystals[15].

Other types of fullerene derivative show unprecedented properties: for example, salts, such as K_3C_{60} or $(TDAE)C_{60}$ are superconductors[16] and ferromagnets[17], respectively. Cluster-opened fullerenes have been prepared that can be filled with small molecules, such as hydrogen, and subsequently reclosed to form $H_2@C_{60}$ (ref. 18). This opens the door to a whole

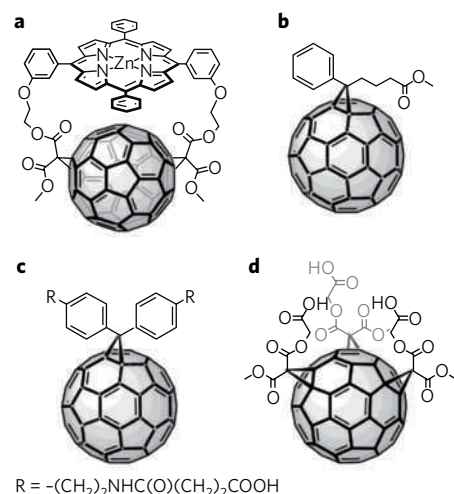$R = -(CH_2)_2NHC(O)(CH_2)_2COOH$

Figure 3 | Some examples of fullerene derivatives with outstanding materials or biological properties.
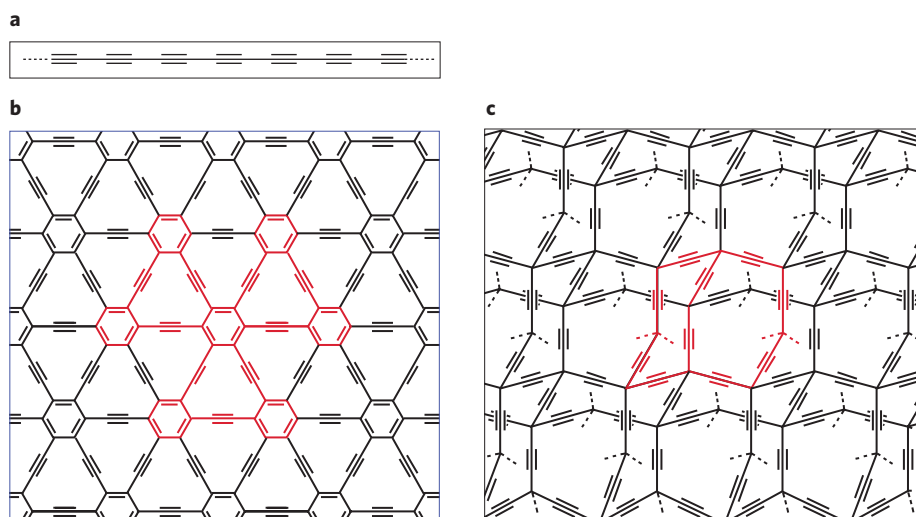
Figure 4 | Some examples of elusive synthetic carbon allotropes: **a**, one-dimensional *sp*-carbyne; **b**, two-dimensional *sp-sp²*-graphyne; **c**, three-dimensional *sp-sp³*-yne-diamond.

world of new endohedral derivatives. The substitution of carbon atoms with heteroatoms such as nitrogen, realized in the heterofullerene $(C_{59}N)_2$ (Fig. 2e) allows for further variation of the electronic properties of the fullerene core[19].

Nanotubes and graphene

The electronic and materials properties of carbon nanotubes and graphene are at least as remarkable as those of fullerenes. Depending on their helicity, carbon nanotubes are either semiconducting or metallic. Both properties are appealing for applications in the field of molecular electronics or for the refinement of materials, such as antistatic paints and shieldings. Indeed, metallic carbon nanotubes and graphene are the first representatives of stable organic metals where no further activation, doping or charge transfer is required for the establishment of extremely high charge-carrier mobilities. A fascinating recent example for the performance of carbon nanotubes is their ability to act as single-electron pumps[20]. This could be a key for the development single-electron transistors; devices that can confine charges down to single-electron level and hence, are applicable for quantized current generation. Carbon nanotubes hold the record for the mechanically strongest material, making them useful for the reinforcement of polymers in composite materials. For example, coating cotton thread with conductive carbon nanotubes leads to the formation of a lightweight thread that can be easily woven into fabrics[21].

Compared with fullerenes, chemical functionalization of carbon nanotubes is considerably less mature and graphene chemistry is still in its earliest infancy. Nevertheless, graphene-based technology is at present considered to have the greatest potential for applications. In this regard, Nobel Laureate Frank Wilczek from the Nobel Symposium on Graphene held in May 2010 said: "Graphene is probably the only system where ideas from quantum field theory can lead to potential applications." The idea of using graphene for digital electronics was born in 2004 with the realization of a graphene-based field effect transistor[5] driven mainly by three extraordinary properties: extremely high charge-carrier mobilities at room temperature; an enormous current-carrying capability; and the fact that graphene is the ultimate thin material. Already it has been shown that graphene meets the electrical and optical requirements for transparent conductive electrodes used in touch screens and displays[22]. However, in contrast to the material used at the moment, indium tin oxide, the graphene electrodes are flexible and mechanically more robust. To proceed with these developments and to gain access to mass production, chemical functionalization of graphite/graphene could be a powerful tool to solve a number of problems, such as increased solubility and processability, stabilization in solution, separation and purification, as well as device fabrication.

Elusive allotropes

During the investigation of *sp²*-hybridized allotropes, attention has also been paid towards the development of further synthetic carbon allotropes[23].

The extension of the construction principle by incorporating both *sp*- and *sp³*-hybridized atoms into carbon networks offers almost limitless structural possibilities. The simplest example for such synthetic carbon allotropes is one-dimensional carbyne consisting of infinite chains of *sp*-hybridized carbon atoms (Fig. 4a). Whereas the parent allotrope itself is still elusive, a number of model compounds, namely end-capped polyynes, have been synthesized and characterized.

The combination of *sp*-, *sp²*- and *sp³*-hybridized carbon atoms leads to many possible two- and three-dimensional carbon allotropes, such as graphyne[23] (Fig. 4b). Significantly large molecular segments of graphyne (pictured in red in Fig. 4b) have been synthesized and their study suggests the material has attractive optoelectronic and self-assembly properties. Allotropes with a skeleton of *sp*- and *sp³*-hybridized carbon are the least-studied class of hybrid allotropes, and the only notable example reported thus far is expanded cubane[23]. The study of these materials is motivated by the prediction of impressive mechanical properties, such as hardness for allotropes like yne-diamond, which is composed of the hypothetical building block adamantyne (pictured in red in Fig. 4c). Although a variety of low-molecular partial structures of these networks have been synthesized, preparative access to these designer allotropes is still elusive.

Conclusions

Synthetic carbon allotropes represent a growing family of fascinating and aesthetically pleasing architectures with outstanding materials properties. The existing representatives, namely fullerenes, carbon nanotubes and graphene, will be complemented in the future by new carbon forms whose construction principles are based on the numerous possibilities to assemble carbon atoms in one, two and three dimensions. At a time when silicon-based technology is approaching its fundamental limits, the possible incorporation of synthetic carbon allotropes in the production of electronic devices is welcome. As a result of their spectacular electronic, thermal and mechanical properties they are expected to offer an exceptional choice. However, fully realizing their application in nanoelectronics, sensors, nanocomposites, batteries and supercapacitors still requires much fundamental research, keeping chemists, physicists, materials scientists and engineers busy for years to come. ❑

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Green carbon as a bridge to renewable energy

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A green use of carbon-based resources that minimizes the environmental impact of carbon fuels could allow a smooth transition from fossil fuels to a sustainable energy economy.

Carbon-based resources (coal, natural gas and oil) give us most of the world's energy today, but the energy economy of the future must necessarily be far more diverse. Energy generation through solar, wind and geothermal means is developing now, but not fast enough to meet our expanding global energy needs. We advocate that 'green carbon', which enables us to use carbon-based sources with high efficiency and in an environmentally friendly manner, will provide our society time to develop alternative energy technologies and markets without sacrificing environmental or economic quality. Green carbon will help to reduce the loss of our precious carbon resources, which are better reserved for high-value chemicals, and it will ensure that those hydrocarbons used for fuels will minimize carbon emissions. Through intensive research and development in green carbon, our society can guarantee an energy future that uses carbon strategically, without smokestacks, greenhouse gases and extensive environmental damage.

Building a solid bridge
There is a chasm between the diminutive proportions of renewable energy currently available and our overwhelming dependence on fossil fuels that currently propel society. The energy policy review of the Obama administration makes this soberingly clear: "The use of renewable energy today and even in the next 5 to 10 years is still extremely limited when put into the context of total world use of fossil fuels. For example, the world used the equivalent of 113,900 terawatts hours [TWh] of fossil energy to fuel economic activity, human mobility, and global telecommunications, among other modern day activities in 2007. Replacing those terawatts hours with non-fossil energy would be the equivalent of constructing an extra 6,020 nuclear plants across the globe or 14 times the number of nuclear power plants in the world today. In renewable energy terms, it is 133 times the amount of solar, wind and geothermal energy currently in use on the planet."[1]

Barring a huge reduction in our global standard of living, we will need to rely on carbon-based energy for some time. Whether this will last for several decades or into the next century is unclear, but what is apparent is that renewable approaches to energy generation are increasing at an annual rate of 7.2% compared with 1.6% for non-renewable growth[2], and the continued growth of renewables will demand sustained government support. During this transition we propose a green carbon bridge that minimizes the environmental impact of carbon fuels and lowers our reliance on these resources for primary energy generation. Ultimately, green carbon will use hydrogen from renewable sources, while at the same time producing basic chemical feedstocks.

The concept of a bridge to a renewable energy future is not new, and many strategies have been offered as near-term alternatives to conventional carbon resources[3]. Although some of these concepts appear at first glance to be 'green' solutions, further scrutiny that takes into account the energy lifecycle and environmental consequences suggests a more murky set of trade-offs. Biodiesel, for example, has led to destruction of vast areas of tropical rainforest to make palm oil[4]. A shift of transportation to lithium battery-powered cars requires enormous amounts of fossil fuels to mine vast stretches of the Earth in search of lithium, and the vehicle would need to be driven tens of thousands of kilometres entirely on renewable energy just to accrue back the ~1.7 GJ energy per kilowatt hour capacity used for the lithium mining and battery manufacture[5]. The electric grid promised to serve the purportedly clean electric-car technology may just become a long tailpipe connecting the plug-in batteries to coal-fired power plants[6]. And even if renewable energies could supply the electricity, the current electrical grids could not sustain the vast increase in demand. We need to quantify the full environmental or lifecycle consequences of various options for our energy bridge if we are to build it from the proper technologies.

We must also consider energy technology options in a broader context. In