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Perspective

Twenty Years of Graphene: From Pristine to Chemically Engineered Nano-Sized Flakes

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ABSTRACT: It is a celebratory moment for graphene! This year marks the 20th anniversary of the discovery of this amazing material by Geim and Novoselov. Curiously, it coincides with the century mark of graphite's layered structure discovery. Since the discovery of graphene with the promise that its outstanding properties would change the world, society often wonders where is graphene? In this context, their discoverers said in 2005, "despite the reigning optimism about graphene-based electronics, "graphenium" microprocessors are unlikely to appear for the next 20 years". Today, possibilities for graphene are endless! It can be used in electronics, photonics, fuel cells, energy storage, artificial intelligence, biomedicine, and even cultural heritage or sports. Additionally, the electronic properties of this material have been modified in fascinating ways. Bilayer graphene sheets have been found to be superconductive when twisted at a "magic angle", leading to a new and exciting field of research known as "moiré quantum materials" or "twistronics". Additionally, small graphene fragments with nanometer sizes undergo a quantum confinement effect of electrons, affording semiconductive materials with applications in optoelectronics. Organic synthesis allows the preparation of molecules with a graphene-like pattern with total control of the shape and size, exhibiting a big catalog of chiroptical and optoelectronic properties. This Perspective shows some of the fascinating milestones raised in the field of graphene-like materials from a chemical point of view, including functionalization strategies employed to chemically modify the topology and the properties of pristine graphene as well as the rising molecular graphenes.

■ AN UNEXPECTED ADVENTURE: THE DISCOVERY OF GRAPHENE

On a Friday afternoon, doing experiments for which there was no time during the rest of the week, Andre Geim and Konstantin Novoselov found the wind sufficiently at their backs. Armed with curiosity, a healthy dose of skepticism, and a humble piece of graphite, they set off on a Friday night quest that would rewrite the textbooks.

Their journey began with a simple observation. Graphite, the material used in pencil lead, is composed of countless layers stacked one upon the other.[1] What if, they wondered, they could somehow peel off just one of these layers? A single, atomically thin sheet of carbon.

With the tenacity of explorers, they began their experiment. Using a mundane tool—Scotch tape—they started to peel away at the graphite.

Layer by layer, they whittled down the material, and the allure of the unknown kept them pushing forward.

Finally, they achieved the "impossible". Before their eyes lay a sheet of carbon, Figure 1.[2] It was a moment of pure exhilaration. They had isolated and discovered graphene, a material with extraordinary properties: stronger than steel, exceptionally flexible, and capable of conducting electricity with unprecedented efficiency.

Their adventure had only just begun. The implications of their discovery were vast and far-reaching. Graphene held the promise for revolutionizing electronics, medicine, and materials science. It was a new frontier waiting to be explored.

Along with the discovery of graphene, the striking electronic properties positioned this material as the best possible "metal" for metallic transistor applications, also offering ballistic transport. In 2005, it was confirmed that the charge carriers in graphene, that mimic relativistic particles with zero rest mass having an effective speed of light, are massless Dirac Fermions.[4] Thus, from the electronic properties point of view, graphene is a zero-gap semiconductor.

Only three years after the discovery, in 2007, Geim and Novoselov reported a compilation of the properties and potential applications already observed, "The rise of graphene", thus providing clear evidence of the rapid interest of the scientific community on this two-dimensional material.[5]

The accessible procedures to obtain high-quality graphene allowed fast progress of the research. Before 2012, the study of the material parameters had already shown outstanding properties. For instance, the electron mobility at room-temperature is 2.5 × 10^5 cm^2 V^{-1} s^{-1},[6] which exceeds the theoretical limit of 2 × 10^5 cm^2 V^{-1} s^{-1}.[7] The Young modulus, which describes the materials stiffness, is 1 TPa, and the tensile strength is 130 GPa.[8] The extreme strength is particularly

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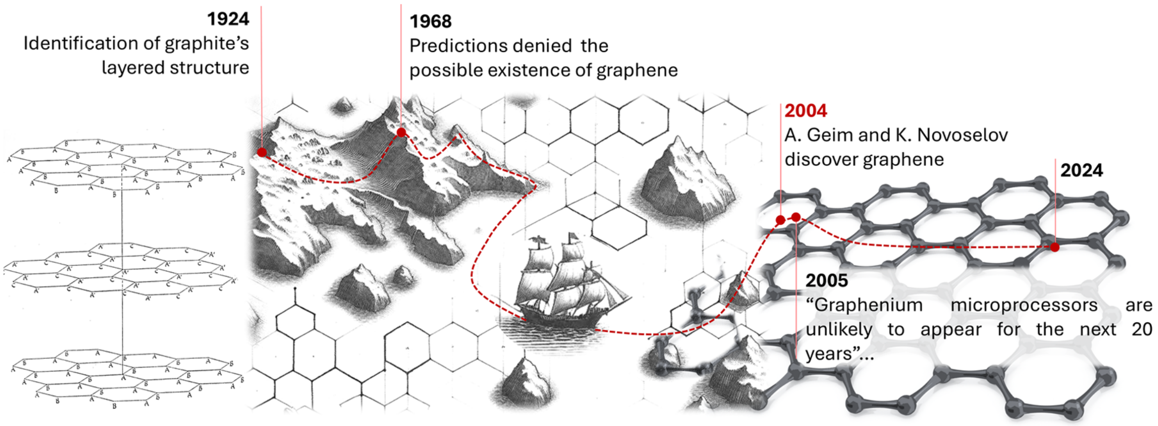


Figure 1. Journey to graphene: from ancient times to the discovery. One century ago, the first milestone by revealing the layered structure of well-known graphite was stablished.[1] After the denied prediction for the possible existence of graphene in 1968,[3] eventually, it became a reality with the seminal discovery by Geim and Novoselov in 2004.[2] This Perspective shows the evolution of graphene along the past two decades from a chemical point of view.

striking in view of it being lightweight (0.77 mg m^{-2}). Furthermore, it presents high thermal conductivity,[9] complete impermeability to gases,[10] transparency, and the ability to support very high densities of electric current (a million times higher than copper).[11] This combination of properties made graphene a promising material for applications in disruptive technologies.[12] However, these properties and, therefore, the potential applications depend on the quality and size of the crystals, which are strongly affected by the production method.

Nowadays, there are several methods for the mass-production of graphene,[13] which allows control of the size, quality, and price, for particular applications.[14] The methodologies can be classified into two main approaches, top-down and bottom-up. Top-down methods consisting of the exfoliation of graphite are a straightforward and widely used method that can be mechanical, chemical[15] or electrochemical.[16] Conversely, the bottom-up approach involves the formation of graphene from smaller materials at the atomic or nanometer scale. These methods include chemical vapor deposition,[17,18] epitaxial growth,[19] laser induction,[20] laser ablation[21] and electric discharge "flash" synthesis.[22]

Although graphene is less reactive than nanotubes[23] or fullerenes,[24] due to the curvature showed by these other allotropes of carbon, chemical functionalization is one of the most exploited properties of graphene. The functionalization of the edges, especially zigzag edges, occurs more easily than in the less reactive π-surface. However, the functionalization of the honeycomb basal planes is a widely extended method for the chemical preparation of covalent graphene derivatives[25] and supramolecular structures derived from $\pi-\pi$ interactions.[26]

In principle, graphene's chemistry could be considered similar to graphite. The treatment of graphite or graphene with oxidative reagents, commonly acids, entails the oxygenation of the layers in the borders, as well as in the basal planes, providing the commonly known graphene oxide[27] (after exfoliation in the case of graphite). This material exhibits a mixed sp^2-sp^3 carbon system, and due to its nonconductivity and relative hydrophobicity, it has been widely applied in medicine.[28,29] However, for further applications, it is necessary to restore the π-network to recover the electric conductivity. The "reparation" of the carbon network requires the removal of oxygen-containing functional groups in the layers. This reduction process to restore the honeycomb lattice has been achieved by different chemical and nonchemical methods, and the layer obtained is known as reduced graphene oxide. Although the number of remaining defects is important, this material has been used in composites, thermal dissipation films and conducting additives.[30]

The hydrogenation of graphene to obtain graphane was described as the first covalent functionalization,[31] resulting in a drastic change of the conductivity of the material, making it an insulator. From this point on, covalent graphene chemistry has experienced a great boom. Radical chemistry was employed in addition reactions of alkyl chains[32] or aryl substituents, mainly occurring in the basal plane, especially when using diazonium salts (Figure 2a).[33] Interestingly, it has been observed that graphene can undergo classical arene chemistry, such as Friedel–Crafts acylations,[34] as well as more typical alkene transformations, namely 1,3-dipolar cycloadditions,[35] cyclopropanations,[36] [2 + 2] cycloadditions with aryne derivatives[37] and [4 + 2] Diels–Alder cycloadditions acting as a dienophile or even as diene.[38]

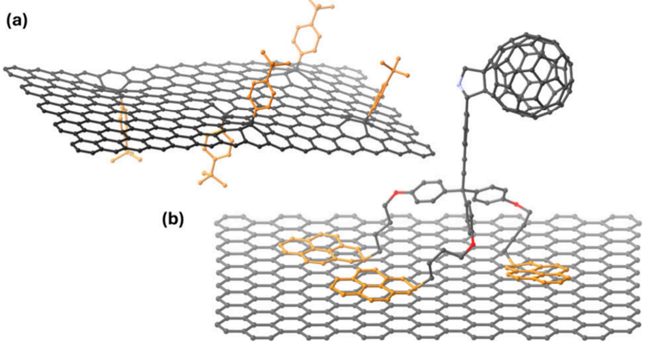


Figure 2. Representative examples of graphene chemistry. (a) Covalent functionalization with diazonium salts.[33] (b) Supramolecular interactions of pyrene functionalized fullerene and graphene.[40]

The high π-extended surface area of graphene has enabled the development of highly effective supramolecular chemistry strategies based on $\pi-\pi$ interactions with polycyclic aromatic hydrocarbons (PAHs). In this way, using triazines,[39] it is possible to compensate the van der Waals interactions between

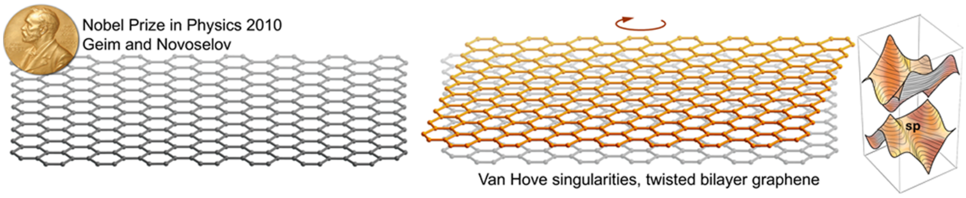


Figure 3. The same year that Geim and Novoselov received the Nobel Prize in Physics for graphene, new possible phases of matter were expected from twisted bilayer graphene.

the layers in graphite, allowing its exfoliation and the stabilization of individual graphene sheets. Additionally, other PAHs namely pyrene (Figure 2b),[40] perylene[41] or porphyrins[42] derivatives resulted in being good substrates to establish $\pi-\pi$ interactions with graphene and an excellent platform for anchoring other chemical entities.

Another technique for fabricating graphene with desired shapes is lithography.[43] This mask-assisted method involves depositing an electron-sensitive polymeric coating on the surface of a graphene sheet. Subsequently, an electron beam can be used to "draw" patterns into the polymeric coating. The exposed graphene regions can be removed through reactive ion etching, and finally, the remaining polymer can be removed.

To sum up, the possibilities to obtain graphene are currently wide and technically diverse. However, it is important to note that the production methodology is directly related to the quality of the material and its properties, which determine its potential applications.

Since the early years of graphene's rise as a tangible and manipulable material, its discoverers quickly realized its potential applications. Although, they warned: "despite the reigning optimism about graphene-based electronics, "graphenium" microprocessors are unlikely to appear for the next 20 years".[4] Currently, graphene has been applied to a wide range of fields, including electronics, photonics and optoelectronics,[44] fuel cells,[45] energy storage,[46] artificial intelligence,[47] biomedicine,[48] and even cultural heritage.[49] Thus, in a situation in which graphene is produced in a several thousand tons/year scale[50] in the present times, it is worthy to question, what else can be done?

In this regard, although it formally cannot be considered as a graphene layer or a derivative, a most amazing and remarkable carbon-based material coined as graphullerene has recently been reported. These singular layered materials are an extended quasi-two-dimensional network of C_{60} molecules in a planar 2D array whose properties are currently being unveiled. Interestingly, regardless the optoelectronic properties, these new materials are of interest as a multicontact platform for constructing superlubric interfaces with layered materials.[51]

TWIST TO SUPERCONDUCTIVITY: BILAYER AND MULTILAYER GRAPHENE

Paradoxical though it may seem, one of the current challenges and hot topics in graphene is the overlapping of a fixed number of graphene layers by controlling the relative twist angle between them. Interestingly, this growing interest, especially in graphene bilayers, started in the same year in which Andre Geim and Konstantin Novoselov were awarded with the Nobel Prize in Physics (2010) "for groundbreaking experiments regarding the two-dimensional material graphene" (Figure 3).

In 2010, Eva Y. Andrei and co-workers reported the observation of van Hove singularities in overlapping 2D crystals of graphene with a 1.79° relative twist between the layers.[52] This observation resulted in the very intriguing consideration that new phases of matter can arise near the van Hove singularities (saddle point in the electronic band structure leading to a divergence in the density of states, sp in Figure 3).[53] Thus, this indicates the possibility of modulating graphene properties without changing its chemical structure, just controlling the number of layers and their relative twist angle. These early observations were the starting points for the development of new metamaterials.

The stacking of two or more atomically thin materials with a relative twist angle or a lattice mismatch leads to so-called "moiré quantum materials". In 2018, Jarillo-Herrero and co-workers described the results expected from the previous observations, a new phase of matter in twist bilayer graphene, unconventional superconductivity.[54]

The interlayer interaction between two stack graphene layers induces the hybridization of their bands, entailing modifications in the low-energy band structure depending on the stacking order. Additionally, the relative twist angle between the layers modulates the hexagonal moiré patterns, consisting of alternating stacked regions, in the resulting superlattice. The precise control over the twist angles revealed that at the particular twist angle of 1.1°, termed as the first magic angle, the phase diagram of twisted bilayer graphene is similar to that of high-temperature superconductors.

In view of these results and the properties reported so far,[55] it is expected that twisted bilayer and multilayer graphene will follow the successful path of monolayer graphene, with new applications where carbon materials were not sufficiently competitive. It is striking that a simple layer with a honeycomb pattern and the thickness of a carbon atom, whose existence was so often questioned, has revolutionized the science of materials and condensed matter, allowing the development of disruptive technologies already introduced in society 20 years after its discovery.

MINIMIZING LIMITATIONS: GRAPHENE AT THE NANOSCALE

The zero-gap semiconducting nature of graphene limits its application on optoelectronics. In contrast, the quantum confinement of the electrons in smaller fragments (flakes) opens the gap between the conduction and the valence bands, thus broadening the range of applications in sensing, electronics, or photovoltaics. The substantial interest in graphene-based semiconductors exhibiting optoelectronic properties, such as photoluminescence, stimulated the emergence of novel research topics focused on graphene nanofragments.

Within this class of nanomaterials inspired by the 2D graphene sheet, graphene quantum dots and molecular nanographenes can be primarily differentiated. This distinction is contingent upon the synthetic strategy employed. Top-down approaches, which involve the polydisperse fragmentation of graphite or graphene into laminar fragments with dimensions below 100 nm, result in graphene quantum dots. Conversely, bottom-up approaches, rooted in organic synthesis, yield monodisperse molecular nanographenes with dimensions not exceeding 10 nm.

■ GRAPHENE QUANTUM DOTS

The top-down approach to nanographenes could be described as "cutting graphene sheets" into nanosized fragments. The resulting nanographenes are typically known as graphene quantum dots (GQDs, Figure 4), which are defined as graphene nanosheets with lateral dimensions lower than 100 nm in single-, double-, and/or few-layers (up to 10). Typically, GQDs exhibit crystalline structures with disk-like shapes and surface functional groups derived from the preparation method.[56] These functionalities are predominantly oxygen-related groups, such as carbonyl and hydroxy, although nitrogen groups can also be present, rendering GQDs dispersible in aqueous solution or even soluble. The synthetic strategies of GQDs usually are top-down methods starting from graphitized carbon materials such as graphite,[57] carbon black,[58] carbon fiber,[59] graphene,[60] or graphene oxide.[61] The most extended method is the oxidative cleavage of these bulk materials,[62] but other strategies such as nanolithography,[63] hydrothermal[64] and solvothermal[65] cutting of graphene sheets and electrochemical scissoring[66] have also been used.

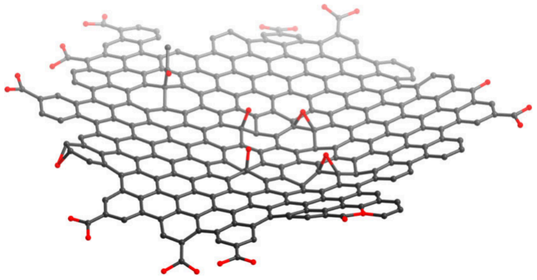


Figure 4. A chemically modified structure with oxygen-containing groups of graphene quantum dots.

The properties of GQDs depend on a variety of factors, the most important being the size of the flakes, that can be controlled by reactions times, temperature or reactants concentration.[67] Larger size leads to smaller gaps between the conduction and the valence bands and hence longer wavelengths of fluorescence. The oxidation degree, the number of oxygenated groups presented in the GQD, has also an important role on the properties of the material.[68] Usually, the more functionalized the GQD, the less energetic the photoluminescence. However, removal of these groups makes them less dispersible, although it increases the quantum yields and blue-shifts the emission. Heteroatom doping also modifies the properties of GQDs, with N, S and P being the most used heteroatoms, altering the bandgap structures and the catalytic activities.[69]

Additionally, the properties of GQDs can be postsynthesis modified by the functionalization of the edges or the surface. The conjugation with polyaromatic molecules narrows the band gap,[70] but it is also possible to introduce new properties such as photoinduced electron transfer processes from the substituent to the GQD,[71] or even the appearance of chiroptical properties by anchoring chiral substituents.[72]

While the tuning of GQDs' properties is a highly impactful field with applications in photovoltaics, light-emitting diodes, photodetectors, batteries, catalysis, and biomedical engineering, the real control over their size, shape, and therefore properties is mostly achieved by employing the bottom-up synthesis of molecular nanographenes.

■ MOLECULAR NANOGRAPHENES

Polycyclic aromatic hydrocarbons have attracted the interest of the scientific community since the discovery of benzene by Michael Faraday in 1825. The multidirectional evolution of sp^2-hybridized carbon materials ranges from the development of simple molecules to more sophisticated 0D fullerenes[73] (discovered by Kroto, Curl and Smalley in 1985), 1D carbon nanotubes[74] (discovered by Iijima and Ichihashi in 1991), and 2D graphene.

The knowledge gained in modern organic reactions and new characterization techniques has enabled the continuous evolution of emergent carbon-based materials. It is therefore not surprising that organic stepwise synthesis is one of the most powerful tools for producing graphene molecular fragments. However, it is interesting that the greater development of these nanometric-size fragments, with a honeycomb pattern, took place in parallel to the emergence of single-layered graphene and its derivatives.

The smallest and most frequently investigated graphene molecule, namely hexa-*peri*-hexabenzocoronene (HBC, **1**), was described for the first time and simultaneously by Halleux[75] and Clar[76] in 1958. This flat structure formed by 42 carbon atoms and a diameter close to 1 nm was for a long time the largest fully characterized polycyclic aromatic hydrocarbon (Figure 5). However, the development of different methodologies based on stepwise organic synthesis has made possible the monodisperse preparation of significantly larger polycyclic aromatic hydrocarbons with different sizes and shapes.[77] For instance, in 2002, Klaus Müllen et al., pioneers in the preparation of large molecular graphene fragments, reported one of the largest structures described so far (**2**) (formed by 222 carbon atoms and a diameter of 3 nm), demonstrating the potential of organic synthesis for obtaining large and precise graphene molecules (Figure 5).[78]

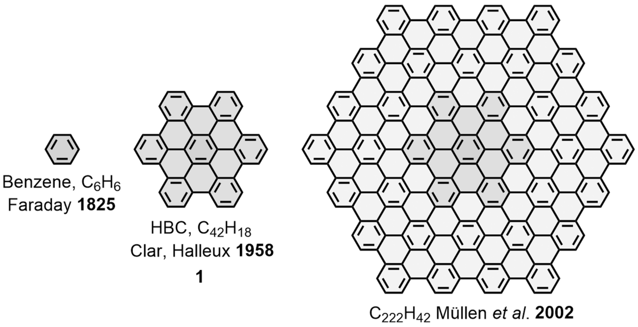
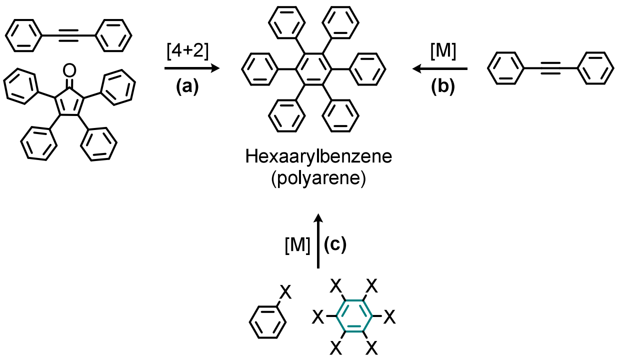


Figure 5. From benzene to synthetic small polycyclic aromatic hydrocarbons and molecular nanographenes.

In 2012 Müllen and co-workers defined as nanographenes those graphene fragments ranging from 1 to 100 nm in size.[77a] The past decade has marked the boom of nanographenes,[79] and several review articles can be found regarding the advances in synthetic methodologies, from the first flat molecules to increasingly sophisticated structures that have demonstrated amazing optoelectronic and chiroptical properties.

The methodology to obtain these nanographenes is based on a bottom-up approach by stepwise organic synthesis, which allows the monodisperse preparation of graphene molecular fragments with atomic control. In the first half of the 20th century, Roland Scholl and Eric Clar were pioneers to report the synthesis and characterization of large polycyclic aromatic hydrocarbons.[80] Nowadays, several strategies can be found in the literature for the synthesis of nanographenes.[81] Typically, it requires the preparation of a polyarene-like precursor, whose preparation can be addressed by three main approaches, Diels–Alder [4 + 2] cycloadditions (Scheme 1a),[82] metal-mediated cyclotrimerizations of alkynes (Scheme 1b)[83] and metal-catalyzed cross-couplings (Scheme 1c).[84] These methodologies allow the design and synthesis of a great variety of structures with suitable topology and substitution pattern to obtain the desired nanographenes.

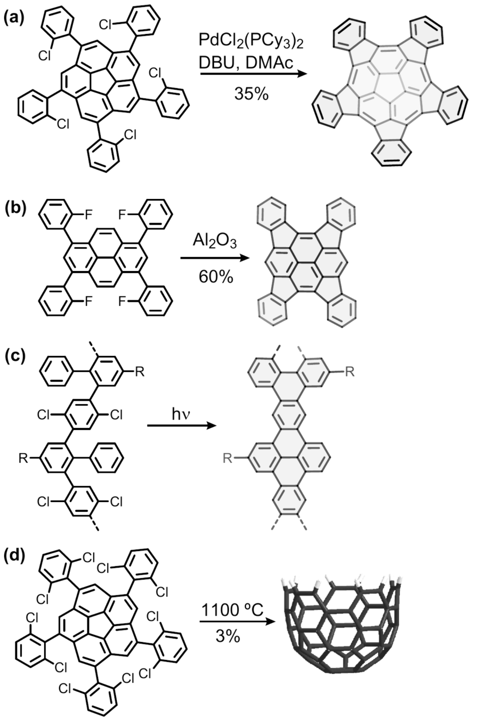
Scheme 1. Synthetic Approaches to Polyarenes, Precursors of Nanographenes



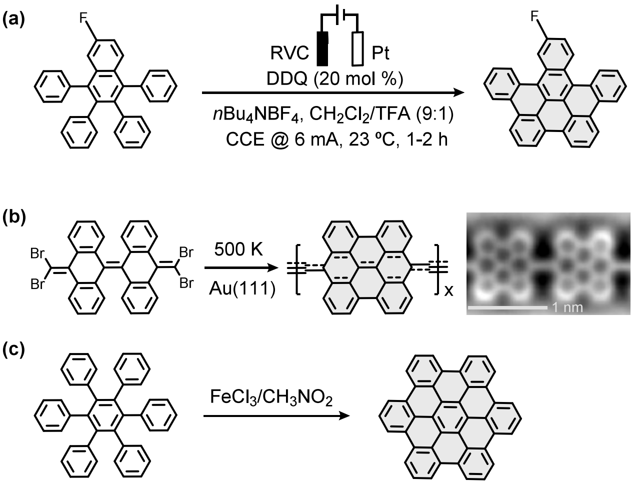
However, the key step in the synthesis of nanographenes is the graphitization of the polyarene precursor. To this end, different reactions can be found in the literature. For instance, it can be accomplished by intramolecular catalyzed couplings (Scheme 2a),[85] C–F bond activation, methodology developed by Amsharov et al. (Scheme 2b),[86] photochemical cyclization (Scheme 2c),[87] or flash vacuum pyrolysis, as described by Scott et al., to achieve the formation of a highly curved π-extended corannulene (Scheme 2d).[88] These reactions require the previous functionalization of the polyarene precursors, commonly with halogens.

Nevertheless, the most widely used reactions in the synthesis of molecular nanographenes are those that do not require the introduction of reactive functional groups for subsequent graphitization. In this context, electrochemical and on-surface reactions are rapidly developing methodologies. Kong et al. reported an electrochemical cyclodehydrogenation methodology that requires catalytic equivalents of DDQ (2,3-dichloro-5,6-dicyano-1,4-benzoquinone) (Scheme 3a).[89] On-surface reactions have proven to be suitable for the graphitization of planar structures. The interaction of the starting molecules with a metal surface after temperature treatment nicely induce graphitization (Scheme 3b).[90]

Scheme 2. Graphitization Reactions Starting from Functionalized Polyarenes: (a) Intramolecular Metal-Catalyzed Cross-Coupling; (b) C–F Bond Activation; (c) Photochemical Cyclization; (d) Flash Vacuum Pyrolysis



Scheme 3. Graphitization Reactions Starting from Unfunctionalized Polyarenes: (a) Electrochemical Cyclodehydrogenation; (b) On-Surface Au(111) Graphitization; (c) Scholl Cyclodehydrogenation



However, most molecular nanographenes reported in the past decade have been obtained by conventional organic chemistry in solution. For this purpose, the preferred graphitization reaction is Scholl oxidation (Scheme 3c). Reported by Roland Scholl in 1910,[91] this reaction is a cyclodehydrogenation that occurs by double aryl C–H activation leading to the formation of multiple C–C covalent bonds.[92] The reagents to perform this oxidation are typically Lewis acids (commonly $AlCl_3$, $MoCl_5$ and $FeCl_3$) or oxidants in the presence of Brønsted acids (as 2,3-dichloro-5,6-dicyano-

1,4-benzoquinone, DDQ, or *para*-chloranil in combination with methanesulfonic acid or trifluoromethanesulfonic acid).

Thus, the stepwise synthesis of nanographenes offers a precise method for modulating the topology, shape, and size. Furthermore, the introduction of topological defects disrupts the planar structure, introducing asymmetry and potentially leading to chirality. Such symmetry breaking requires the absence of both symmetry planes and inversion centers. Thus, nonhexagonal rings can induce curvature within the nanographene structure. Rings smaller than six atoms result in positive Gaussian curvature, while larger rings produce negative Gaussian curvature.[93] In addition, the generation of sterically congested structures can induce the torsion of the hexagonal networks if the energy cost of the torsional strain, or deformation, minimizes the steric interactions (e.g., helicenes, twistacenes, and chiral nanobelts), Figure 6.[94]

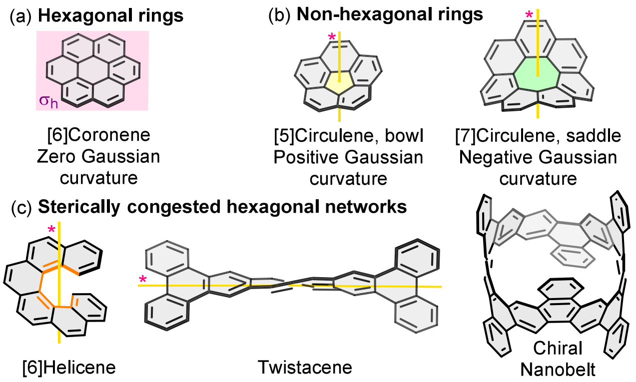


Figure 6. (a) Csp^2 atoms in a hexagonal network provide planar structures with a symmetry plane (σ_h), in light pink, preventing chirality. (b) *Nonhexagonal rings diverting the structures from planarity, positive Gaussian curvature (bowls), and negative Gaussian curvature (saddles). (c) Strain-induce deviation from planarity. Chiral axes are represented in yellow. *Corannulene and [7]circulene should be substituted to fulfill the symmetry conditions for chirality.

Therefore, it has been possible to develop complex structures with atomic control. Thus, a variety of synthesized molecular nanographenes can be classified according to the topology of the network into planar, curved, and helical structures.

Planar molecular nanographenes have been extensively studied since the pioneering works by Klaus Müllen in the first decade of the 21st century.[95] The semiconductor properties of these molecules are highly dependent on the size of the structure: the larger the molecule, the smaller the gap between the HOMO and LUMO orbitals, giving rise to red-shifted photoluminescent properties and smaller oxidation potentials. Another important aspect to take into account in planar nanographenes is the shape taken by the edges, which has a great influence on the stability of the nanographene (Figure 7a), as well as on the electronic properties. According to Clar's sextet rule, benzenoid nanographenes with armchair or cove edges typically show high stability. However, nanographenes with zigzag edges have higher chemical reactivity, and can showcase magnetic properties due to the formation of open-shell species (Figure 7b).[96]

One of the most recent and successful techniques employed to prepare planar structures is the on-surface synthesis,[97] that it is commonly used to stabilize large zigzag radicaloid nanographenes.[98] This technique permits the execution of chemical reactions on crystalline metal surfaces, which are not feasible in solution. By such manner, it is also possible the polymerization of "nanographene monomers" leads to the formation of structures with higher dimensionality namely, 1D graphene nanoribbons[99] or 2D porous graphene derivatives.[100] Additionally, $\pi-\pi$ stacking of different molecules is avoided, enabling the physical characterization by high resolution STM, STS and noncontact AFM.

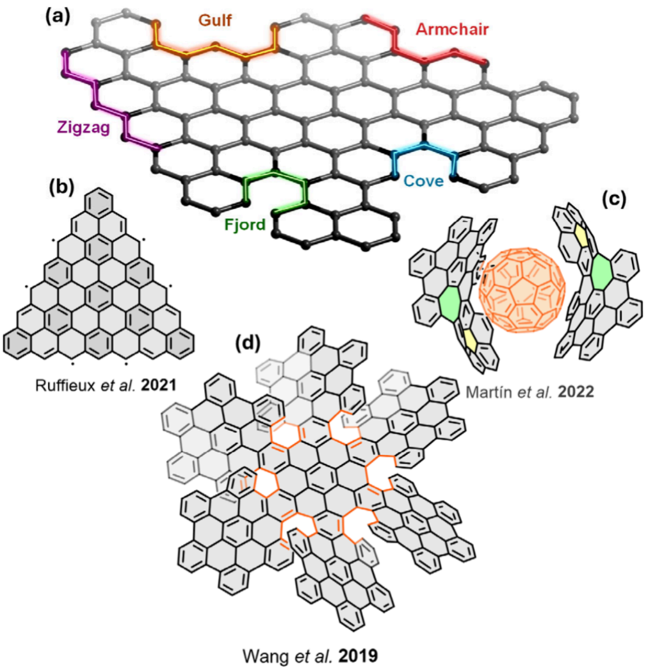


Figure 7. Representative examples of nanographenes with different topologies (*tert*-butyl groups have been removed for clarity): (a) Edge effects in nanographene; (b) Open-shell planar nanographene;[96d] (c) Curved nanographene as host with for C_{60} fullerene guest;[104a] (d) Helical nanographene with propeller shape.[107a]

The introduction of curvature bends the honeycomb planar lattice of molecular nanographenes out of the plane.[101] This bending usually generates chiral structures, but the rapid bowl-to-bowl or saddle-to-saddle interconversions lead to racemization processes, making the chiroptical properties of curved nanographenes unstable along time.[102] However, curved nanographenes have interesting features, the presence of curvature sometimes inducing exotic photophysical properties such as thermally activated delayed fluorescence (TADF).[103] Additionally, curved nanographenes have suitable geometries to host other chemical entities through concave−convex interactions (Figure 7c).[104] This behavior led to interesting applications such as artificial photosynthetic systems through the formation of supramolecular complexes able to undergo photoinduced electron transfer, thus mimicking the natural photosynthesis, or metal storage systems with special interest in new-era alkali-ion batteries.[105]

However, the real chiral molecular nanographenes are those with helicenes embedded in their structure.[106] By this way, π-extended helicenes and molecular nanographenes with propeller shapes (Figure 7d)[107] have been developed in recent years. The high values of the inversion barriers presented by helicenes larger than [5]helicenes guarantee the stability of the chiroptical properties of chiral molecular nanographenes. Additionally, the π-extension of helicene systems in more graphitized structures boost significantly the chiral properties leading to larger values of dissymmetry factors, g_{abs} and g_{lum}, circular dichroism (CD) and circular polarized luminescence (CPL).[108]

■ BILAYER NANOGRAPHENES: A NEW FRONTIER

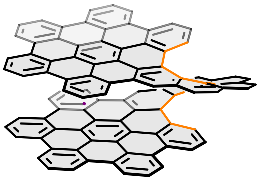
The variety of structures reported in the literature gives evidence of the numerous possibilities for modifying the size, shape, and properties of these graphene molecular fragments. The main approaches are the variation of the π-extension and the topological modification of the hexagonal networks, allowing the induction of inherent chirality. However, with the synthetic tools, imagination is the limit, and more recently, special interest has been focused on the design of bilayer nanographenes.

Resembling the multilayer structure of graphite, planar nanographenes tend to aggregate by $\pi-\pi$ intermolecular interactions. Taking advantage of this behavior, in 1999 Müllen et al. reported the first supramolecular aggregates of HBC derivatives forming ordered columnar structures.[109] Thus, in the early 2000s a great development in ordered HBC-based liquid crystals[110] took place due to the potential in organic electronics.[111]

However, it has not been until the past few years that discrete persistent bilayer and multilayer systems could be prepared in a controlled manner, i.e. with a fixed number of overlapping layers stacked by $\pi-\pi$ interactions.

Chiral Bilayer Nanographenes. As previously described (Figure 6), chirality in nanographenes involves the deviation from planarity by the introduction of topological defects. Therefore, an accessible approach is synthesizing bilayer structures with adjustable optoelectronic and chiroptical properties, in which the overlapping layers are linked by covalent bonds.

In this context, our research group was a pioneer in describing the first helical bilayer nanographene in 2018.[112] The structure of the new molecular nanographene **3** consisted of two hexa-*peri*-hexabenzocoronene moieties annulated to a helicene backbone resulting in a totally conjugated [10]helical bilayer nanographene, Figure 8. The formation of the helical feature diverts the structure from planarity, inducing chirality and disposing the layers face-to-face at an interlayer distance of 3.6 Å. In the same year, Jux and co-workers reported helical nanographene **4** consisting of an oxa[7]helicene fused to two HBC layers.[113] The main difference between these structures is the length and shape of the helical backbone, which determines the overlapping between the graphitized layers and the optoelectronic and chiroptical properties.


Martín *et al.* 2018
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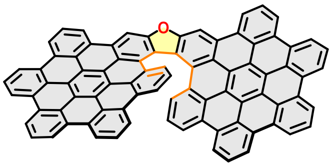
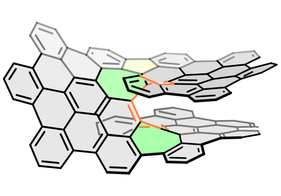

Jux *et al.* 2018
4

Figure 8. Helical bilayer nanographene and π-extended oxa[7]-helicene, *tert*-butyl groups have been removed for clarity.

The number of turns of the helicene—and the overlapping between the layers at the ends—depends on the number and geometry of the *ortho*-fused rings. The presence of five-membered rings opens the inner rim of the helicene, decreasing the number of turns (defined as the cycle number of helix). Thus, [10]helical nanographene **3** is a partially overlapped structure, with 14 rings involved in the $\pi-\pi$ intramolecular interactions, while the length and shape of the helicene in oxa[7]helical nanographene **4** prevent the overlapping between the graphitized layers.

Moreover, seven-membered rings embedded in the helical feature close the inner rim, increasing the number of turns. In this regard, Feng and co-workers reported in 2023 the nonbenzenoid [10]helical bilayer nanographene **5** (Figure 9).[114] The presence of two seven-membered rings in the helicene backbone entails the closing of the inner rim leading to the total overlapping between the layers and a small interlayer distance of 3.24 Å. The in situ registration of UV−vis−NIR spectra upon oxidation revealed an intervalence charge transfer band in the NIR region for the oxidized species. TD-DFT calculations supported through-space electronic communication between the layers. In addition, these helical nanographenes are showing highlighting chiroptical absorption (circular dichroism, CD) and emission (circularly polarized luminescence, CPL) properties, determined by the dissymmetry factors of absorption (g_{abs}) and luminescence (g_{lum}). For instance, the enantiomers of nanographene **5** present a luminescence dissymmetry factor g_{lum} of 1.3×10^{-3}.


Feng *et al.* 2023
5

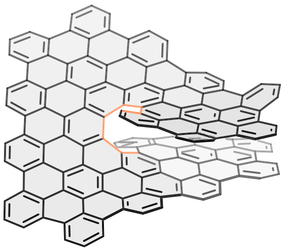

Gong *et al.* 2023
6

Figure 9. π-Extended helical bilayer nanographenes, *tert*-butyl groups have been removed for clarity.

Also in 2023, Gong et al. reported helical bilayer nanographene **6** consisting of a pentadecabenzo[9]helicene core and four fused hexabenzocoronene units (Figure 9).[115] The rigidity of the structure, due to the π-extension of the helicene, and the large overlapping of the layers (28 benzene rings involved in the $\pi-\pi$ interactions) afford an interlayer distance of 2.9 Å. The dissymmetry factors for the isolated enantiomers of this nanographene **6** are among the highest reported for organic molecules, $g_{lum} = 4.5 \times 10^{-2}$ for the *P* isomer, and $g_{lum} = 4.22 \times 10^{-2}$ for the *M* isomer.

CPL-active materials[116] have attracted considerable interest due to their potential applications in different fields, including photoelectronic devices, data storage, sensing, organic light-emitting diodes, chiroptical switching, etc.[117] As previously mentioned, the CPL intensity is described by the dissymmetry factor g_{lum}, which represents the ratio of the difference in intensity and the average total luminescence intensity: $g_{lum} = (I_L - I_R)/[(1/2)(I_L + I_R)]$, I_L intensity of left-circularly polarized light, and I_R intensity of right-circularly polarized light. Theoretically, the dissymmetry factor can be calculated as a function of the electric (μ) and magnetic (m) dipole transition moments, $g_{lum} = 4R_e[(\mu \cdot m)/(|m|^2 + |\mu|^2)]$. For organic molecular CPL emitters, the transitions are usually electric dipole allowed and magnetic dipole forbidden. Thus, the magnetic dipole term is much smaller than the electric dipole, and the denominator is dominated by $|\mu|^2$, which results in $|g_{lum}|$ values in the order of 10^{-5} to 10^{-2}.[118]

In addition to the independent study of bilayer molecular nanographenes due to their highlight of optoelectronic and chiroptical properties, the past two years have witnessed a boom in structure/property relationship studies on bilayer nanographenes. Considering the great interest of these structures, our research group (Martin and co-workers) has recently described a family of helical bilayer nanographenes, Figure 10, following the synthetic approach described in 2018.[119] The number of *ortho*-fused rings forming helicenes modifies the degree of overlapping between the graphitized layers attached to the ends. Remarkably, the layers overlapping determines the variation of the optoelectronic and chiroptical properties. Thus, the lower π-extended structure, [9]helical bilayer nanographene (HBNG) **7**, presents the larger overlapping degree (with 26 rings involved in the $\pi-\pi$ intramolecular interactions) and the strongest electron-donor character. In the case of this family of bilayers, the larger the helicene, the lower the overlapping degree, which conditions the variation of the properties. The values for the first oxidation potentials follow the order [9]HBNG **7** < [10]HBNG **3** < [11]HBNG **8**, and the maxima wavelengths of the principal emission bands show the trend [9]HBNG **7** > [10]HBNG **3** > [11]HBNG **8**. Then, it is worth mentioning that the properties follow the order opposite to that expected if the modification of the π-extension. In addition, these bilayer nanographenes present highlighting chiroptical properties; a $|g_{lum}|$ value as high as 3.6×10^{-2} was recorded for the totally overlapped structure [9]HBNG **7**, followed by [10]HBNG **3** ($g_{lum} = 1.0 \times 10^{-2}$), and [11]HBNG **8** ($g_{lum} = 0.9 \times 10^{-2}$).

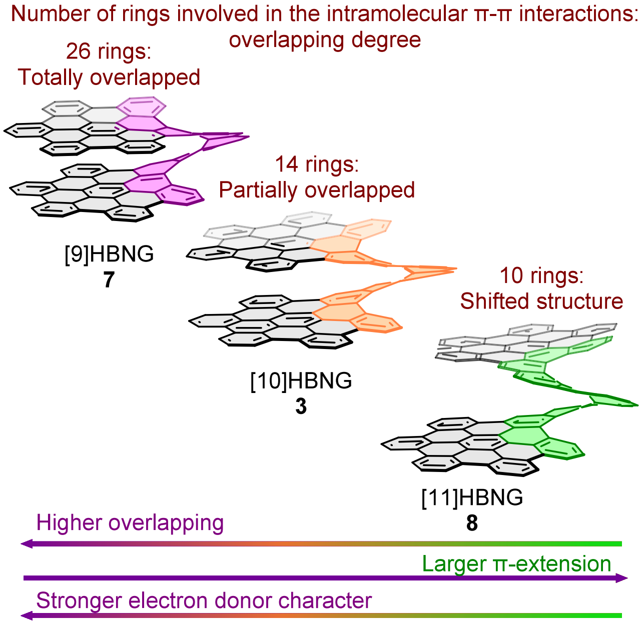


Figure 10. Family of helical bilayer nanographenes (HBNGs) with different helicene lengths, [9]HBNG, [10]HBNG and [11]HBNG, and the variation of the overlapping and the properties determined by the length of this structural feature. *tert*-Butyl groups were removed for clarity.

The results observed for bilayer nanographenes so far may pave the way for the development of new CPL active materials. Additionally, the influence of the overlapping degree provides a new alternative for modification of the optoelectronic properties.

Bilayer nanographenes are an exciting and emerging area of research. Similar to their larger graphene counterparts, they consist of two layers of graphene-like structures stacked together. However, due to their molecular character, they exhibit unique properties and potential applications, and the large possibilities to modify the hexagonal networks allow the fine control of the properties.

■ CONCLUSIONS AND OUTLOOK

Is graphene a gift from the gods? Twenty years after the discovery of graphene, it can be stated that this new carbon allotrope has provoked a scientific, technological, and also social revolution due to the expectations raised by this first 2D material.

The scientific curiosity led to something difficult to imagine which, eventually, paved the way to the new science of 2D carbon-based materials and, by extension, to 2D materials involving other elements of the Periodic Table (transition metals calcogenides, black phosphorus, boron nitrides, etc.), metamaterials, and, more recently, the moiré quantum materials. Thus, twistronics is a new coined term used to refer to those materials whose electronic properties result and depend on the angle existing between the layers of similar or different nature.

The aim of controlling the size and shape of the carbon flakes resulting from the top-down approach has led chemists to use the arsenal and power of modern organic synthesis to the obtention of nanometer-size polycyclic aromatic hydrocarbons, the so-called nanographenes. Interestingly, due to the reduced electronic confinement in these systems, these nanographenes exhibit a variety of amazing optoelectronic properties that are not found in pristine graphene. Furthermore, the introduction of defects in these carbon structures provides other amazing chiroptical properties, which sets a precedent for a variety of applications, including those stemming from the existing circularly polarized fluorescence.

It is worth mentioning that, in contrast to the fascinating properties shown by twisting bilayer or multilayer pristine graphene, giving rise to "twistronics", the dimensions and molecular nature of bilayer or multilayer nanographenes prevent the existence of similar properties. However, instead, a variety of interesting properties have been found due to the electronic interactions existing between the layers at the molecular scale.

To answer the question posed above, no doubt graphene can be considered a gift from the gods whose limits are still far away to be realized, not only for practical applications but also at the scientific level where the fascination for these 2D carbon materials is opening new questions and challenges in the broad scientific community.

Our motivation to write this Perspective is show gratitude for the discovery of this seminal finding and to encourage the scientific community to highlight how graphene has impacted and broadened different scientific areas after these first 20 years of existence of graphene. However, as the famous Frank Sinatra's song says, "The best is yet to come!"

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Notes

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