

POLYCYCLIC AROMATICS

On-surface molecular engineering

Rational synthesis of large polycyclic molecules is on its way. A bottom-up strategy for molecular assembly to tailor-make new molecules has been applied to fabricate nanographenes.

José A. Martín-Gago

The appearance on the technological scene of new electronic devices based on organic molecules is eagerly awaited, as they promise to be inexpensive, flexible, faster and smaller than those based on silicon technology. But molecular electronics faces important challenges before the jump can be made from the research laboratory to the technological centre. To make this jump, one of the new trends in the field aims to assemble organic molecules at specific locations on nanostructured surfaces, where they can subsequently be used as building blocks for fabricating the active or passive electronic elements of a circuit. Rather than using the present top-down techniques successfully applied in solid-state electronics, it seems clear that the groundwork for building molecular devices should start with a bottom-up strategy, which is currently missing from the molecular engineer's toolkit. Although the core ideas have been on the table for more than 40 years, the design of robust methodologies for assembling molecular objects at the nanoscale continues to be one of the main stumbling blocks. Innovative strategies involving accurate control of molecular structures on well-defined surfaces are imperative before bottom-up assembly can be exploited in its full beauty.

This is the scenario into which catalytic surfaces are now emerging as essential tools. As in heterogeneous catalysis, transition metal surfaces can conveniently be used to synthesize new molecular species directly. They not only furnish a two-dimensional template on which molecules can more easily associate, but also provide an efficient means of shrinking the reaction activation barriers to values that are easily attained using thermal energy. Moreover, the two-dimensional system created by the surface directionally drives the molecules and kinetically enhances reactions that are difficult to obtain with three-dimensional systems. These surface attributes lead to the possibility of true on-surface synthesis of large organic molecules and polycyclic aromatic hydrocarbons through rational and well-controlled reactions.

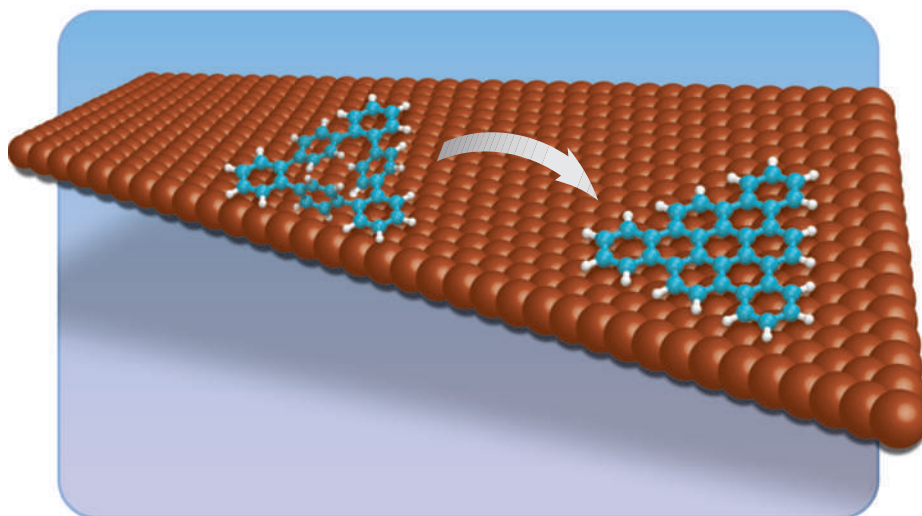


Figure 1 | Cyclohexa-*o-p-o-p-o-p*-phenylene (left) can be converted into tribenzocoronene (right) by means of a thermally induced, surface-assisted cyclodehydrogenation process. This aryl-aryl on-surface coupling reaction leads to the formation of planar nanographene on the surface and opens a way for fabrication of tailored-made large graphene nanoribbons.

As they report in *Nature Chemistry*, Roman Fasel and colleagues¹ make use of these ideas to form new molecular structures from molecular precursors by means of controlled cyclodehydrogenation processes assisted by surface catalysis. They show that it is possible to synthesize “nanographene”, or tribenzocoronene, a highly strategic molecule, from less complex polyphenyls, a strategy that can be easily extended to the assembly of nanographenes of varying dimensions (see Fig. 1). Fasel and co-workers show that on-surface chemistry could be the missing ingredient needed for a new, efficient recipe for bottom-up assembly.

An assortment of different reactions for large tailor-made organic molecules has been recently reported. In less than five years, new fullerene species (triazafullerenes)², graphene nanoribbons³ and nanotube end-cups (molecular hemispheres)⁴ have been synthesized from their respective precursors. Other examples include the formation of porphyrin unimolecular chains⁵, polymeric networks that can only be created through

this methodology⁵⁻⁷ and, in this case, nanographene¹. This new form of on-surface chemistry presents some advantages for technological applications. It can be combined easily with nanostructured surfaces, and highly stable species can be formed, leading to reduced thermal degradation of their structural properties. Another figure of merit of these covalent assemblies is an efficient electron transport through the structure formed. This brings the networks or molecular species formed in this way nearer to possible applications, opening the door to new and valuable molecular objects with tunable properties for molecular electronics.

Fasel and co-workers followed the dehydrogenation process by means of surface science techniques in an ultra-high vacuum environment. To visualize the catalytic mechanism, they used a model single-crystal metal surface, Cu(111), and unequivocally distinguished the molecule adsorbed on the surface with scanning tunnelling microscopy images. After

annealing at about 500 K, they visually followed the molecular transformations in images that were interpreted in the context of large-scale calculations performed within the frame of density functional theory. These model systems are highly relevant for establishing reaction mechanisms. Although the work was performed in ideal conditions, the conclusions obtained are far from unrealistic. The use of other more suitable substrates, as Fasel and colleagues discuss, or alternatives such as the inclusion of nanoparticles², are among the undemanding strategies needed to transfer these concepts to more relevant environments and to scale up the processes for bulk synthesis. Moreover, this highly controlled experimental set-up provided the authors with accurate information on the process at an atomistic level, which allowed them to depict the progress of the chemical reaction in a movie. They were able to visualize several intermediate reaction stages as snapshots, accomplishing the dream of many chemists: to be a front-row spectator

at a chemical reaction. These pictures, complemented by in-depth theoretical analysis, show that the transformation of polyphenyl into nanographene occurs through a cascade of consecutive dehydrogenation reactions.

Fasel's work, and the work cited previously, point towards the real possibility of rational bottom-up molecular assembly at the nanoscale. The starting point lies with the organic chemist, who generates the molecular precursor that must be either combined with other precursors, as one would construct a molecular puzzle, or transformed into others, akin to molecular origami. This suggests a new way forward for chemistry: the design, with accurate calculations, of the desired molecule for specific properties, the synthesis of their constituent pieces, and their assembly using the catalytic properties of a nanostructured surface at specific locations required for addressing an electrical signal. This new approach is intrinsically interdisciplinary and can only be successful after convergence of the approaches of each discipline. In

fact, the work of Fasel and co-workers falls between the use of catalytic properties of transition metals to generate new carbonaceous species, and the synthesis of graphene as an essential element for future electronics, two key areas highlighted by the 2010 Nobel Prizes in Chemistry and Physics. It is a beautiful demonstration that through on-surface synthesis there is indeed a path to the development of molecular electronics. □

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References

1. Treier, M. *et al. Nature Chem.* **3**, 61–67 (2011).
2. Otero, G. *et al. Nature* **454**, 865–868 (2008).
3. Cai, J. *et al. Nature* **466**, 470–473 (2010).
4. Rim, K. T. *et al. Angew. Chem. Int. Ed.* **46**, 7891–7895 (2007).
5. Grill, L. *et al. Nature Nanotech.* **2**, 687–691 (2007).
6. Weigelt, S. *et al. Angew. Chem. Int. Ed.* **46**, 9227–9330 (2007).
7. Côté, A. P. *et al. Science* **310**, 1166–1170 (2005).

MOLECULAR HELICES

Breaking free of chiral symmetry

Helical macromolecules are ubiquitous in nature, and almost always adopt a one-handed conformation. Synthetic systems, in contrast, are typically obtained in racemic right- and left-handed mixtures. A helical phenylene oligomer has now been prepared that forms a non-racemic mixture on crystallization, and on oxidation locks one conformation in.

Eiji Yashima

Biological macromolecules, for example DNA and proteins, are often found to form helices. These molecules are typically composed of chiral components (such as D-sugars, or L-amino acids) but, moreover, helical structures are also inherently chiral — their right- and left-handed conformations are exact mirror images of each other. This means that molecules that are composed of non-chiral components can also be optically active, if they are selectively prepared in one conformation. In such cases, chirality arises solely from the arrangement of the helix. Inspired by beautiful biological helices as well as the widespread need for chiral molecules — for example in the sensing or separation of enantiomers, or in asymmetric catalysis — chemists have long endeavoured to synthesize and control helical compounds¹.

A number of helical polymers and oligomers have now been prepared that

show interesting chiroptical properties, including amplification or inversion of the helicity, or stimuli-responsive conformational changes. These systems have been achieved in most previous instances by relying on the presence of chiral components — either a DNA- or protein-based backbone, or chiral pendant groups — to prevent helices from rapidly interconverting in solution and giving racemic mixtures of right- and left-handed helices². Writing in *Nature Chemistry*, Takuzo Aida and co-workers³ now describe a series of discrete long oligomers, formed by non-chiral phenylene units, that crystallize in a non-racemic mixture, and whose helical inversion in solution can be suppressed by oxidation.

Polyphenylenes are a class of π -conjugated polymers, whose *para*- and *meta*-connected analogues have been studied extensively⁴. In contrast, the chemistry of the *ortho*-linked counterpart

has received much less attention on account of its challenging synthesis. A tight, twisted aromatic connection endows *o*-phenylenes with a strong tendency to fold into a compact one-handed '3,' helical conformation (with three repeating phenylene units for one helical turn). Helices form in which three aromatic rings are stacked closely together — as revealed in analysis of crystal structure by X-ray diffraction — but their proximity means that these oligomers easily undergo cyclization on oxidation⁶.

Aida and co-workers found that this sensitivity can be overcome by using nitro terminal groups. Copper-mediated oxidative coupling of lithiated precursors allowed the preparation of *o*-phenylene oligomers with a variety of terminal functionalities such as -Br, -H and -NO₂. The Br-terminated *o*-phenylene octamer could then be used for chain-extension reactions, yielding uniform oligomers