Steering the asymmetric folding of a nanographene

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Steering the asymmetric folding of a nanographene layer

An asymmetric folding of a planar nanographene molecule has been achieved by the enantioselective generation of inherently chiral elements in its structure. A stereocontrolled graphitization process has enabled the synthesis, separately, of both enantiomers of a two-layer nanographene, thus paving the way for chirality controlled all-carbon nanographenes.

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SECTION 1: The problem

Chirality, or handedness, is the property of an object or molecule that is not superimposed to its mirror image (enantiomer), being ubiquitous in Mother Nature. The broad interest in chirality-related properties in materials science and nanoscience faces a major obstacle in the access to materials in enantiopure forms.[1] A wide variety of so-called nanographenes have mostly been synthesized in a racemic manner, that is a 1:1 mixture of both enantiomers (racemate). Therefore, to get enantiomerically pure nanographenes requires the further separation of both enantiomers by chiral cromathography, which is expensive and time consuming and not always possible.[2] Furthermore, the most extended syntheses of nanographenes rely in a last synthetic step involving a graphitization (aromatization) process consisting in an oxidative dehydrogenation under acidic conditions (Scholl reaction).[3] This reaction has so far been carried out in a racemic manner, being unable to direct the stereochemical pathway.

SECTION 2: The solution

We were faced with the need to use a heteroatom as an anchor point for the transfer of chirality, which could not be maintained in an all-carbon molecule. To solve this problem, we made a virtue of necessity, using the stereocontrolled removal of an OH group for the ring closure required for the synthesis of the nanographene precursor (Fig.1).
The accomplishment of these key steps enabled the unprecedented stereocontrol of the Scholl reaction, which is widely used to obtain polycyclic aromatic hydrocarbons (PAHs) in a graphitization process. As a result, we demonstrate that is possible to precisely direct the folding of a nanographene layer and, therefore, its handedness.

The experiments performed in our laboratory revealed that both enantiomers of a nanographene could be obtained in a highly efficient manner, thus avoiding the use of chiral chromatography. It is important to note that the number of synthetic steps in these enantioselective syntheses is the same to that of the racemic synthesis, which allow preparing chiral nanographenes at will in multigram amounts. These findings reveal that the preparation of nanographenes in an enantioselective manner (only one of the two enantiomers at will) it is possible, and that the useful Scholl graphitization reaction can be also used for this purpose. The main conclusion is that the discovery of the enantioselective Scholl oxidation reaction developed in this work opens a new avenue to the rational synthesis of these elusive all-carbon chiral materials, whose chiroptical and photophysical properties are mostly unexplored, particularly in those areas involving the use of circularly-polarized light.

SECTION 3: Future directions

The enantioselective synthesis of nanographenes is at its infancy and, hopefully, many other synthetic groups will address the synthesis of other chiral nanographenes, thus opening a new scenario on these appealing all-carbon materials. Furthermore, the introduction of chirality in nanographenes will fuel the study of the chiroptical and photophysical properties of these materials, such as circular dichroism and circularly-polarized luminescence as well as other subtle properties like phosphorescence, dual emission or thermally activated fluorescence, to name a few in which chirality is the issue.[4]

The expected limitation for our work is related with the difficulties in the preparation of large nanographenes due to the limitations imposed by the presence of large aromatic areas which favour the aggregation and, therefore, the lack of solubility. Although solubilizing groups are present in most of the nanographenes reported so far, this solubility and large aromatic moieties are serious concerns for the top-down synthetic processes, including the enantioselective approach. Moreover, the acidic conditions of the Scholl reaction prevent the presence of certain functionalities in the nanographene, which are not compatible with these experimental conditions.]

The obvious next questions are related with the scope of the synthetic methodology for the enantioselective synthesis of chiral nanographenes and, particularly, to determine the scope of the this first enantioselective Scholl graphitization reaction. The perspectives are promising and the reward of new properties highly encouraging. [46 words]

Avoiding the use of heteroatoms in these all-carbon structures as a means of activating and controlling chiral induction would significantly expand the synthetic tools for preparing larger ones.

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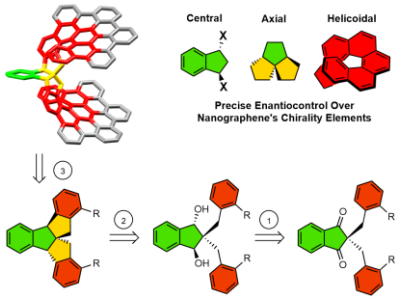
FIGURE

Fig.1 | Enantioselective synthesis of an all-carbon nanographene.
An inherently chiral two -layer nanographene has been designed and synthesized by building three types of chiral elements, namely central, spiro and helicoidal, in the backbone structure A fully enantioselective process was achieved through the precise stereochemical control of three key steps: 1. introduction of chiral information by asymmetric ketone reduction; 2. exploitation of a ring closing reaction in nanographene preparation to remove oxygen in a stereocontrolled form 3. enantiospecific graphitization to produce nanographene layers with a single handedness.



BEHIND THE PAPER

The genesis of this work relies on the interest of our group in introducing chirality into emergent carbon nanostructures. In 2009, we carried out the synthesis of chiral fullerenes at will by using asymmetric catalysis, whose first paper was published in a brand-new sister journal, Nature Chemistry.[5] After synthesizing a variety of molecular nanographenes with fascinating shapes and properties, we realized that the development of a new synthetic methodology based on the stereoselectivity was necessary.
The results now reported required around two years of attempts and the use of over one hundred reagents. The most exciting day was when, eventually, we were able to obtain the first reaction with a poor enantioselectivity. At that moment, we realized that the way was open. Now it is done!

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This paper reports on the photophysical studies of several molecular nanographenes by using time-resolved and temperature-dependent photoluminescence (PL) spectroscopy. Amazingly, dual fluorescence, as well as dual phosphorescence at low temperature were found, as well as thermally activated delayed fluorescence (TADF) at low temperatures.

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This paper reports the enantioselective catalytic synthesis of chiral fullerenes, which proceeds in high yields under very mild

conditions at low temperatures, through the combination of a particular metal catalyst—Ag(I) or Cu(II)—and a chiral ligand to direct the reaction selectively to one of both enantiomers.