



Editorial/Éditorial

Warmest congratulations to Jean-Pierre Sauvage on the occasion of the award of the Nobel Prize in Chemistry 2016



The Nobel Prize in Chemistry 2016 was awarded jointly to Jean-Pierre Sauvage, Sir J. Fraser Stoddart, and Bernard L. Feringa “for the design and synthesis of molecular machines”. Chemists worldwide are delighted and congratulate the three laureates for their spectacular achievements and the development of new concepts associated with fundamental synthetic chemistry.

Jean-Pierre Sauvage (Fig. 1) did his PhD thesis under the supervision of Professor Jean-Marie Lehn, on macrobicyclic compounds (cryptands and cryptates) and their complexing properties. He obtained his Doctorate degree from Strasbourg University in 1971. He then spent a year as a post-doctoral fellow at Oxford University, under Dr. M.L.H. Green, after which he came back to Strasbourg, where he joined Jean-Marie Lehn as a CNRS researcher. After 1976, he became more and more involved in photochemistry. In particular, with Jean-Marie Lehn, he developed new photochemical systems related to photochemical splitting of water to H_2 and O_2 . In 1977, they proposed one of the very first systems leading to the catalytic reduction of H_2O to H_2 under the action of light and, in 1979, symmetrical reactions (oxidation of H_2O to O_2 by visible light irradiation) were made possible, using related reactions and photochemical principles.

Jean-Pierre Sauvage created his own research laboratory in 1980, within the University and in association with the CNRS (“Laboratoire de chimie organo-minérale”). Through his early work on catenanes and rotaxanes, he rapidly established himself as a master of molecular topology. Catenanes and rotaxanes are essential components of molecular systems displaying novel properties in relation to electron transfer, organic materials, polymers, etc. Presently, the most popular field utilising catenanes and rotaxanes is that of controlled dynamic systems, often referred to as “molecular machines” or “molecular motors”.

When Sauvage and his group started to work in the field of interlocking rings, the situation was very different from what it is now. These compounds had been much discussed in the 1960s. Because of their intriguing topology, they seemed to have triggered a lot of interest among molecular

chemists, even very long ago (from the beginning of the 20th century to the 1970s). Unfortunately, their synthesis was exceedingly difficult. Elegant work, based on pure organic chemistry, had been carried out in the 1960s and in the 1970s by German chemists (Schill and coworkers). In spite of the elegance of the synthetic route proposed by German chemists, a practical synthesis of catenanes seemed to be out of reach and the organic chemistry community lost gradually interest in such compounds. At the beginning of the 1980s, there were virtually no research teams working on catenanes and rotaxanes anymore and, as expected, only very few—if any—publications dealing with these compounds could be found in the literature.

In 1983, Sauvage and Dietrich-Buchecker proposed a novel strategy for making interlocking rings (catenanes), based on the three-dimensional template effect of a metal centre (copper(I)). The templating core is able to gather two (or several) organic ligands and to dispose them in a given geometrical arrangement. Subsequent reactions allow one to incorporate these fragments into desired chemical structures and, in particular, to synthesize catenanes. This first report clearly demonstrated that catenanes are accessible species that can be obtained on a macroscopic scale. It was a new birth for molecules which had fascinated chemists for decades, but which were more discussion objects or laboratory curiosities than real chemical species. This early report was followed by other studies describing the templated synthesis of new catenanes, either using purely organic templates (Stoddart et al., 1989; Hunter, Voegtler, 1992) or based on transition-metal-incorporating assemblies (Fujita, 1994), to cite just a few. Many groups then joined the field and, subsequently, proposed various efficient synthetic routes also based on template effects.

Since 1983, the concept has been generalized and used to create a whole family of topologically and chemically fascinating molecules in Sauvage's group. Among the catenanes, the record, reported in 1991, consisted of a gigantic cycle (132-membered ring) and, separately interlocked to it, six smaller rings. Some of the catenanes prepared in the team could be crystallized and characterized by X-ray



Fig. 1. Jean-Pierre Sauvage (photo: Catherine Schroder).

diffraction. In particular, the molecular arrangement of a 3-ring system is particularly appealing from a chemical and an aesthetic viewpoint. The compound and its derivatives are also of interest in relation to energy and electron-transfer processes. In addition, they constituted the prototype of future macromolecular systems consisting of interlocking rings arranged in a chain.

By applying a strategy derived from that described in the first report on catenanes, the first molecular knot, namely *the trefoil knot*, was synthesized in 1989 by Sauvage and Dietrich-Buchecker. The compound is a topologically fascinating object (the simplest non-trivial knot), and it is clear that its preparation represents an interesting link between topology, art, and biology. In fact, many of the interlocking ring systems and knots made in the group display topological properties identical to those of the molecular objects formed by DNA in the course of recombination or replication processes, and recognized by molecular biologists since the beginning of the seventies. This first chemical knot can also be considered as a real synthetic achievement, since chemists had discussed knots as hypothetical chemical objects for several decades before they were actually made.

In recent synthesis, performed in collaboration with Grubbs (Nobel laureate 2005) and coworkers (Caltech, USA), the original preparation of the [2]catenane (consisting of two interlocking rings), published in the 1980s, was improved in a spectacular fashion by using a methodology based on the ring-closing metathesis of olefins. In a few steps from commercially available compounds, a [2]catenane was obtained with an overall yield of about 70%, the cyclisation reaction, which is certainly the key reaction, being almost quantitative. Furthermore, the use of a second metal centre (Pd(II)) to make the rings allowed the catenane to be formed under thermodynamic control, allowing

the system to reach the most stable situation, which is indeed the catenane. This work, carried out in association with M. Fujita and his group (Tokyo), demonstrated that catenanes can be obtained quantitatively and very simply, from organic fragments, using the concepts of coordination chemistry.

Another spectacular synthesis improvement was the trefoil knot, which could be made in only small amounts (50 mg) 15 years ago, but which could be obtained at the gram scale thanks to new preparative methodologies.

A fascinating aspect of knots is their chirality. A trefoil knot could be resolved into its enantiomers (right- and left-handed knots) and their absolute configuration could even be determined by X-ray crystallography. The chiroptical properties of these resolved knots show in particular huge optical rotation.

The original copper(I)-templated synthesis of catenanes was generalised and afforded a broad family of porphyrin-containing catenanes and rotaxanes. In association with photophysicists (Harriman et al., Austin, USA, and Flamigni and colleagues, Bologna, Italy), it was shown that ultrafast electron transfer takes place between a photoexcited electron donor and an acceptor, in a way which is reminiscent of the natural photosynthetic reaction centre, or that long-range energy transfer processes are operative in transition-metal-assembled multiporphyrins.

Controlling and triggering motion at the molecular level became a rapidly expanding field of research. In molecular biology, several extremely important systems contain motor-like assemblies. Given parts of the ensemble are set in motion under the action of an external signal (most of the time, of chemical nature), while other fragments are regarded as motionless. ATP-synthase is probably the most spectacular example, acting as a *rotary motor*. Bi- or multi-stable highly functional [2]catenanes, which can be set in motion in a precisely defined fashion, have been elaborated in Sauvage's group as early as in 1994. One ring glides within the other ring under the action of an electrochemical signal, the process being reversible. Further improvements afforded new "pirouetting" machines, able to move within milliseconds or even less, after an electrochemical signal has been sent to the molecule.

Another contribution from the group of Sauvage is a rotaxane dimer whose behaviour is reminiscent of natural *muscles*. In this particular case, two filaments can glide along one another in a controlled fashion. The overall effect is that the synthetic rotaxane dimer can be stretched or contracted at will, using a chemical signal. The linearly arranged two-component assembly is about 85 Å long in its stretched geometry. After the chemical stimulus has been sent to the molecular system, contraction occurs so as to afford a species whose overall length is only 65 Å.

Electrochemically driven machines, based on the copper(I)/copper(II) couple, have also been assembled on electrode surfaces, with the hope that real electronic and memory storage devices will be fabricated.

Sauvage's group also developed a new family of dynamic systems, incorporating octahedral ruthenium(II) complexes of the rotaxane or catenane family. These new compounds behave as *light-driven molecular machines*, photonic or thermal energy being the only source of energy

responsible for the motion. They represent an important class of controlled dynamic systems besides the now well-established electrochemically driven systems. Two-dimensional interlocking networks were also assembled, which could lead to highly flexible and dynamic membranes, whose pore size could be controlled by an external stimulus.

These chemically or electrochemically driven machine-like molecules, as well as recently proposed photoactive species based on ruthenium(II) complexes, can be thought of as the molecular components of future nano- or microscopic chemo-, photo-, or electromechanical devices. Molecular machines and motors could find applications in, e.g.,

the elaboration of microrobots or nanometric systems acting as information storage and processing devices.

The pioneering role of Jean-Pierre Sauvage in chemical synthesis towards controlled molecular topology has been recognized by a number of national and international awards. He was elected a member of the French “Académie des sciences” in 1997 and belongs to the Editorial Board of *Comptes rendus Chimie*.

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