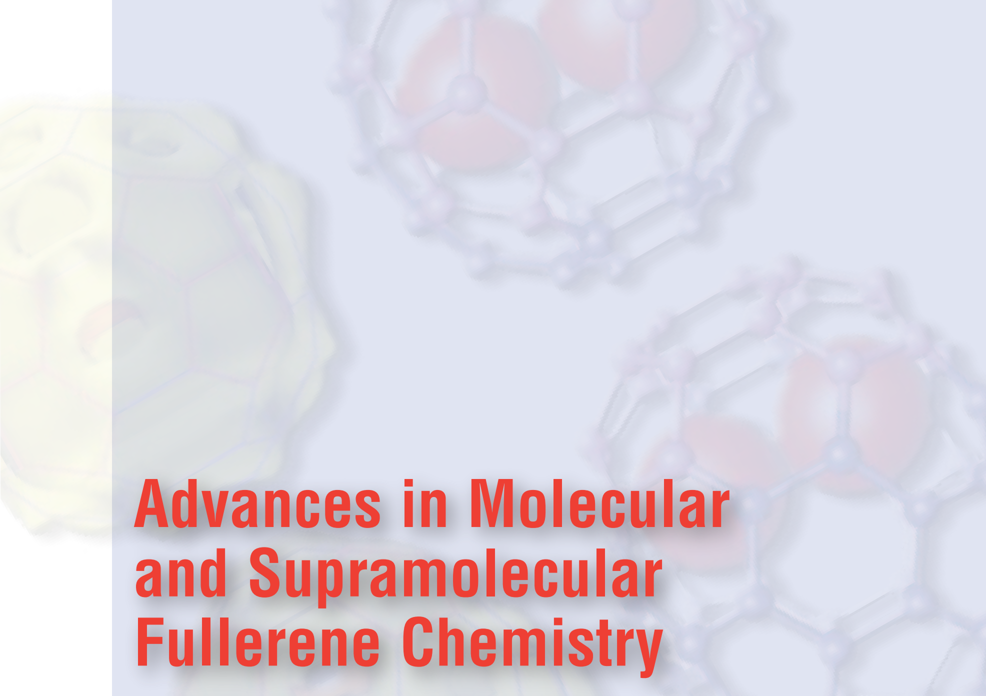

Advances in Molecular and Supramolecular Fullerene Chemistry

by Nazario Martín, Nathalie Solladié, and Jean-François Nierengarten

In 1996 Sir Harold W. Kroto, Robert F. Curl, and the late Richard E. Smalley received the Nobel Prize for the discovery of the fullerenes. After a decade, these round-shaped carbon allotropes still are a major hot topic in chemical research and additional findings are continuously being reported for applying these three-dimensional molecules for practical purposes.[1]

Since the discovery of the fullerenes in 1985,[2] other important breakthroughs in fullerene science occurred in 1990,[3] when Wolfgang Krätschmer and Donald Huffman prepared the fullerene, C_{60}, for the first time in multigram amounts, thus starting in motion, the chemical modification advances and, therefore, the preparation of sophisticated fullerene architectures. Iijima made another major development in 1991 with the discovery of carbon nanotubes (NT),[4] a perfect material to be used in the emerging nanotechnology discipline. The above outstanding findings received scientific and social cachet in 1996 when Kroto *et al.* were awarded the Nobel Prize in chemistry.[5]

This short article highlights some of the more remarkable advances occurring during the last few years in fullerene science and, particularly, on modified fullerenes related to molecular and supramolecular aspects.

Recent Advances in Molecular Chemistry of Fullerenes

Unlike most organic molecules, the convex surface of fullerenes offers possibilities for the study of reactions and mechanisms under severe geometrical constraints. Although the chemistry of fullerenes is nowadays considered to be an established discipline, a wide variety of important reactions involving alkenes and alkynes have not been studied previously on the fullerene surface. One example of the most successful reactions in organic synthesis is the Pauson-Khand (PK) reaction which has been used extensively for the construction of biologically active five-member carbocycles in a convergent approach. It involves the [2+2+1] cycloaddition of an alkyne, an alkene, and carbon monoxide mediated or catalyzed by a transition metal. Recently, this reaction has been carried out on fullerene C_{60} acting as the alkene component; a highly efficient and regioselective intramolecular PK reaction has afforded a type of fullerene derivative (**2**) showing three (or five) fused pentagonal rings on the same hexagon of the fullerene surface.[6]

The transition metal catalyzed cyclization of enynes represents an active research area which has been studied extensively as a powerful method for the construction of carbo- and heterocyclic molecules. The unique geometry of fullerenes has allowed us to observe a different chemical reactivity to that found for related 1,6-enynes. Recently, it was reported that the thermal treatment of 1,6-fullerenynes (**1**) affords cyclobutene adducts (**3**) without the presence of a catalyst; in a reaction this is the first example of a thermal [2+2] cyclization involving a fullerene double bond as the alkene moiety of the reactive 1,6-enyne[7] (Fig. 1).

A recent example of an unknown chemical reactivity has been found in fulleropyrrolidines, which are among the most studied fullerene derivatives used for many applications in materials science as well as in the search for biological properties.[8] In contrast to other labile fullerene cycloadducts such as those prepared from Diels-Alder or Bingel reactions,[1] fulleropyrrolidines have been considered to be stable fullerene derivatives. However, the thermal quantitative retro-cycloaddition of fulleropyrrolidines to obtain the pristine fullerene together with its typical magenta color in solution (Fig. 2) has been reported only recently.[9] This reaction reveals that the understanding of the reactivity of fullerene derivatives is still far from the level where it is possible to predict the reaction pathway reliably. This reaction constitutes a protection-deprotection protocol which has allowed, for example, the efficient separation of two isomers (I_h and D_{5h}) of endohedral $Sc_3N@C_{80}$.

One of the most successful applications of fullerenes is related to electron/energy transfer processes.[10] Photoinduced electron transfer is a fundamental process in nature because it governs photosynthesis in plants and bacteria. This process occurs through rapid charge separation at the reaction centers with quantitative quantum yield, thus enabling the transformation of sunlight into chemical energy.[11]

In contrast to other well-known electron acceptors such as *p*-benzoquinone derivatives used by nature in the photosynthetic process, the C_{60} molecule accelerates charge separation during photoinduced electron transfer processes to form a charge separated state and simultaneously

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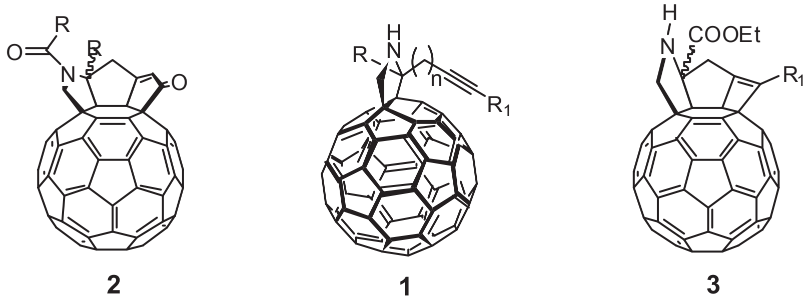

Fig. 1. *1,6-Fullerenynes (**1**) are versatile building blocks.*

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slows the charge recombination process in the absence of light. This behavior has been rationalized by the smaller reorganization energy (λ) of C_{60} compared with other acceptors.[12] These unique electrochemical and photophysical properties of fullerenes have allowed the design of a wide variety of donor-acceptor systems in which the electroactive units are connected by covalent or supramolecular bonds.[13] [*Editor's note: This aspect is also addressed in the third feature article in this issue.*]

To improve the charge separation processes in artificial photosynthetic model systems, photoinduced electron/energy transfer from suitable electron donors, namely, porphyrins, phthalocyanins, tetrathiafulvalenes (TTFs), ferrocene, and other metallocenes, amines, or π-conjugated oligomers, and dendrimers, to electron accepting fullerenes have been studied.[14]

The design of C_{60}-based photosynthetic mimics has been directed to the formation of long-lived charge separated states in a highly efficient way. For this purpose, the different factors which influence the competition between energy *vs.* electron transfer have been analyzed, and factors such as nature of the photo- and electroactive units, solvent, donor-acceptor distance, molecular topology in which donor and acceptor are connected and arranged in space, and the nature of the spacer connecting them, have a strong influence on the photophysical results. Unusually slow charge recombination dynamics has been reported in some molecular dyads which, despite the proximity between the donor and acceptor units, appear to be electronically isolated due to their singular geometry.[14] As a representative example, lifetimes of 230 µs in benzonitrile at 25°C, an exceptionally long-lived intermediate for a simple molecular dyad, have been reported recently.[15]

Recently, Martín and co-workers have shown the molecular wire behavior of oligo-*p*-phenylenevinylene (oPPV) as π-conjugated oligomers in a series of supermolecules of the type C_{60}-oPPV-donor [donor = TTF or zinc porphyrinate (ZnP)] ranging from the monomer to the heptamer (Fig. 3). Photophysical studies revealed an exceptionally low attenuation factor ($\beta \sim 0.01$ Å^{-1}) and a strong electronic coupling element ($V \sim 5.5$ cm^{-1}) even at distances as large as 5 nm.[16]

These examples clearly show the high versatility of fullerenes for the study

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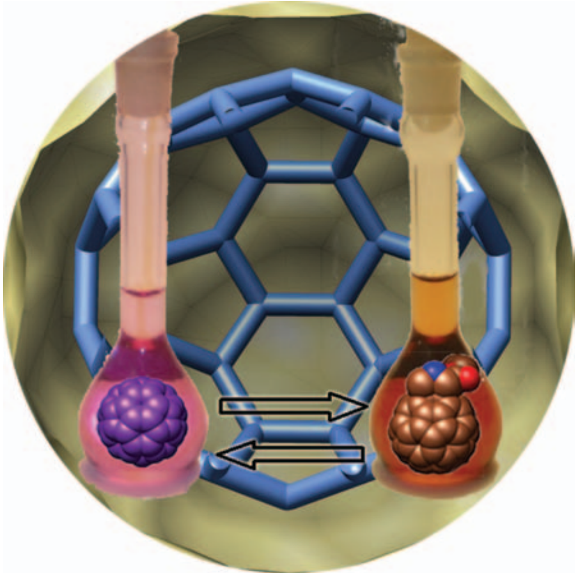

Fig. 2. *Pristine fullerene C_{60} can be recovered quantitatively from the corresponding fulleropyrrolidine.*

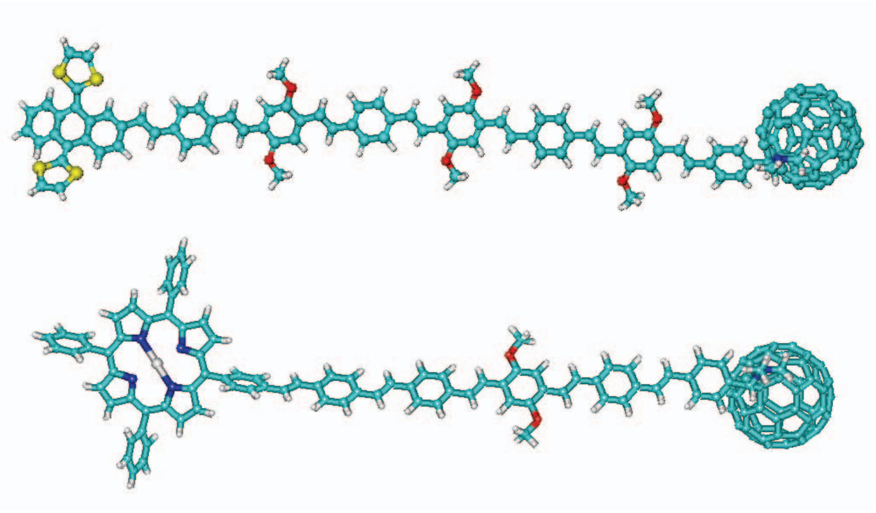

Fig. 3. *Molecular modeling of photo- and electroactive exTTF-oPPV-C_{60} (top) and ZnP-oPPV-C_{60} (bottom) triads.*

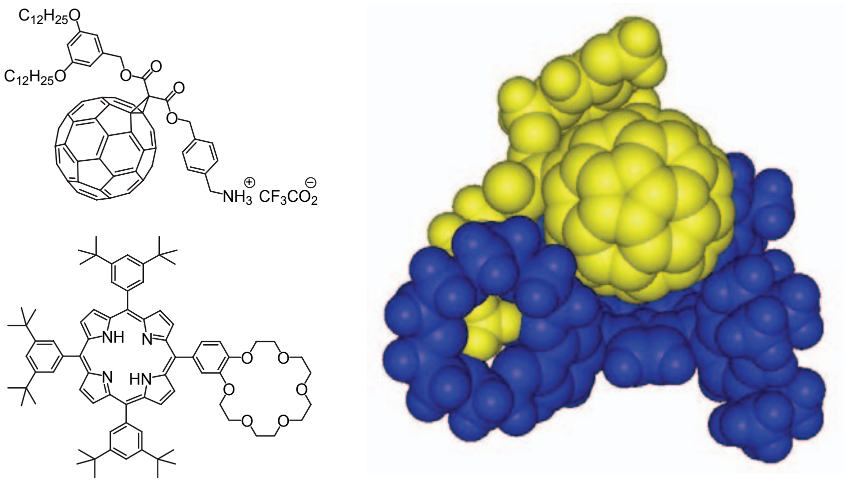

Fig. 4. *In addition to the ammonium-crown ether recognition, π-stacking interactions between the C_{60} sphere and the porphyrin moiety have been observed in a supramolecular complex obtained from a porphyrin-crown ether conjugate and a fullerene derivative bearing an ammonium unit.*

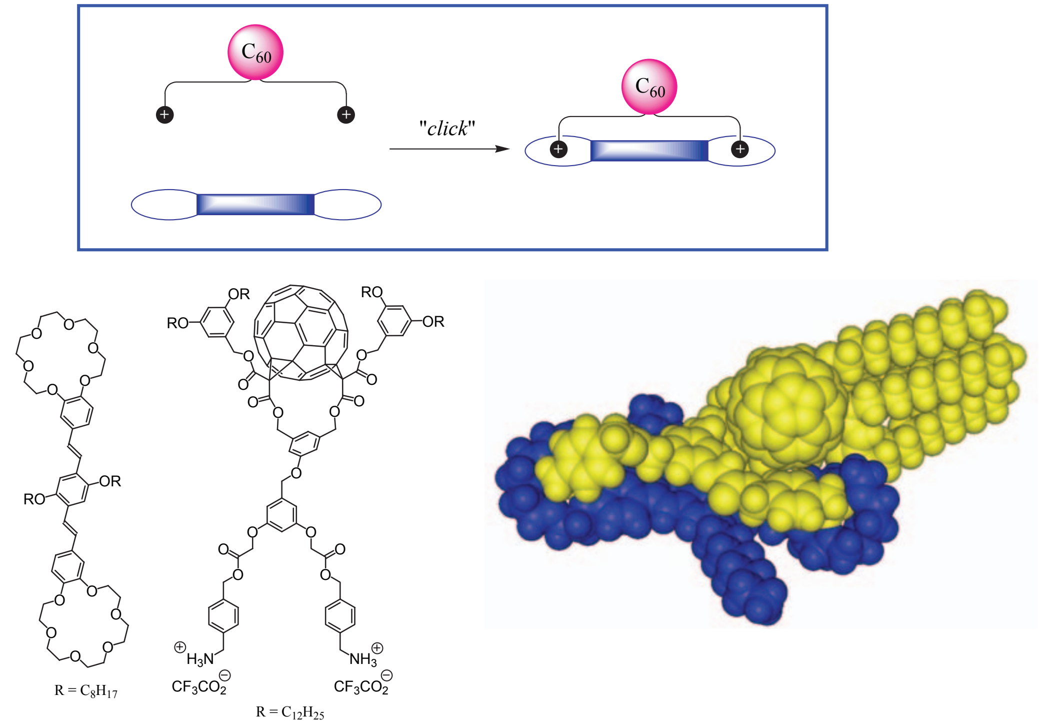

Fig. 5. *Schematic representation of the supramolecular click chemistry principle and calculated structure of the clicked supramolecular complex resulting from the association of a bis-crown ether derivative and a bis-ammonium fullerene ligand.*

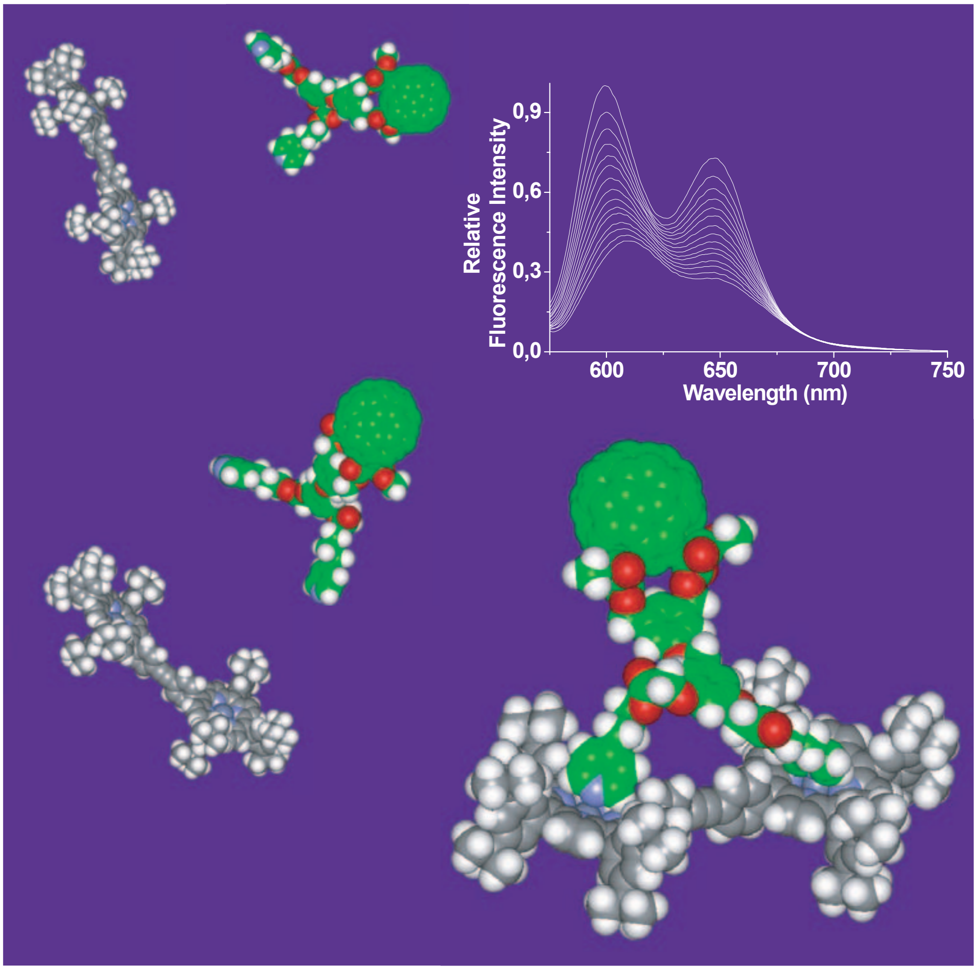

Fig. 6. *A fullerene derivative bearing two pyridine subunits has been designed to allow the assembly of a macrocyclic clicked edifice with a bis-Zn(II)-phorphyrinic receptor, the K values deduced from the emission data reveal an increased stability of the macrocyclic complex as a result of the simultaneous coordination of the two Zn centers by the two pyridine moieties.*

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of artificial photosynthetic systems in which it is possible to control the lifetime of the photogenerated charge separated states by different strategies.

Recent Advances in Supramolecular Chemistry of Fullerenes

In 1987 Jean-Marie Lehn together with two other supramolecular chemistry pioneers, Donald J. Cram and Charles J. Pedersen, received the Nobel Prize for the development and utilization of molecules with highly selective structure-specific interactions. Supramolecular chemistry and fullerenes crossed each other to give rise to an interdisciplinary field in which the imagination of chemists has facilitated the design and construction of unprecedented fullerene-based supramolecular architectures.[17] Examples are rotaxanes,[18] catenanes,[19] self-assembled coordination compounds,[20] liquid crystalline inclusion complexes,[21] and photoactive supramolecular devices.[22]

As part of this research, supramolecular donor-fullerene systems based on the self-assembly of C_{60} derivatives bearing an ammonium unit with crown ethers have been reported.[23,24] The ammonium-crown ether interaction itself is weak. Consequently, the binding constants are low and only a small fraction of the two components are effectively associated in solution. This prompted several groups to design systems with additional recognition elements to increase the binding constants. For example, π-stacking interactions between the C_{60} sphere and the porphyrin moiety have been evidenced in a supramolecular array obtained from a porphyrin-crown ether conjugate and a fullerene derivative bearing an ammonium unit (Fig. 4).[25] In this particular case, the association constant (K_a) for the complex is increased by two orders of magnitude when compared to K_a values found previously for the complexation of the same ammonium cation with other crown ether derivatives. More recently, the preparation and the characterization of a stable supramolecular complex obtained from a bis-crown ether receptor and a bis-ammonium fullerene ligand have been described.[26] Owing to the perfect complementarity of the two components, the bis-cationic substrate can be clicked on the ditopic crown ether derivative thus leading to a non-covalent macrocyclic 1:1 complex (Fig. 5).

Comparison with thermodynamic data available in the literature for closely related systems (crown ether and ammonium derivatives) shows coordination stronger by more than three orders of magnitude. This is associated mainly to the two-center host-guest topography. Similar to the click chemistry concept of Sharpless,[27] the supramolecular click chemistry principle described herein is a powerful and selective process for the preparation of stable macrocyclic non-covalent arrays. This approach is modular and appears applicable to a wide range of functional groups for the preparation of supramolecular architectures with tunable structural and electronic properties. In particular, Trabolsi *et al.* have shown that supramolecular click chemistry is perfectly suited for the preparation of a stable non-covalent fullerene-porphyrin hybrid system.[28] The bis-Zn(II)-phorphyrinic receptor has been selected as a platform with two equivalent Zn binding sites separated by about 20 Å. A fullerene ligand bearing two pyridine subunits has been designed to allow the assembly of a macrocyclic clicked edifice with the bis-porphyrinic receptor. Binding studies revealed the formation of a single complex with $\log K_1 = 5.09 \pm 0.07$. The sizeable increase of stability compared to that of C_{60} derivatives bearing a single pyridine moiety and metalloporphyrins through coordination to the metal ion emphasized the peculiar structure of the complex in which the bis-pyridyl fullerene substrate is clicked on the ditopic receptor (Fig. 6). Similar increases in the association constants have been reported by D'Souza and co-workers for supramolecular systems resulting from the axial coordination of the C_{60}-pyridine ligand to Zn(II)-porphyrins and possessing an additional recognition element.[29]

Concluding Remarks

Fullerenes have shown a wide range of unique physical and chemical properties that make them attractive for the preparation of advanced materials. Applications encompass a wide range of technologies and many developments rely on new materials and our abilities to understand their intimate properties. Modern organic synthesis is the starting point of this research, as compounds must first be made and studied and then modified to improve their properties toward projected applications. Novel synthetic methodologies for the preparation of new fullerene derivatives have still to be discovered and remain a key step toward the elaboration of fullerene-based molecules and materials displaying unique properties. Despite some remarkable recent achievements, clearly, the examples discussed above represent only the tip of the iceberg in the design of fullerene-based molecular assemblies which can display functionality at the macroscopic level. More research in this area is needed to fully explore the possibilities offered by these materials, for example, in nanoscience or in photovoltaics. ■

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