Molecular Machines

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Fullerenes: Multitask Components in Molecular Machinery

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Molecular machines are molecular-scale devices that carry out predetermined tasks derived from molecular motion. This Minireview illustrates how fullerenes can be used as multitask building blocks in molecular machinery, providing new perspectives for fullerenes. Indeed, C_{60} can be applied as a photo- and electroactive stopper owing to its size, as a probe for molecular motion as a result of its well-defined physicochemical properties, and to induce motion through π–π interactions. Such molecular motion can be employed to modulate light-driven electron-transfer events, extending the potential applications of molecular machines to the typical fields of application of fullerenes.

1. Introduction

In the last decades, a lot of effort has been dedicated to the design and synthesis of molecular machines,[1–3] which carry out precise tasks derived from molecular motion. Interlocked architectures, such as rotaxanes, pseudorotaxanes, and catenanes, have come to light as basic components for the preparation of complex artificial molecular machines. Catenanes are comprised of two interlocked rings, while pseudorotaxanes comprise a ring threaded through a molecular wire. If the ring is held in the wire by two bulky stoppers they are called rotaxanes. As a result of the work of many excellent groups, we can benefit now from straightforward protocols for the preparation of rotaxanes, pseudorotaxanes, and catenanes throughout different types of supramolecular interactions. Their interlocked components have a large mobility, and they can be subjected to different types of submolecular motion. In this light, several rotaxanes have been designed in which the position of the ring can be reversibly switched between different and well-defined parts of the thread (stations). In such "molecular shuttles", the translocation of the ring can be achieved by application of an external stimulus that ranges from illumination[4,5] and variation of the electrochemical potential[6–8] to a change in solvent[9,10] or pH.[11,12] Moreover, shuttling can be applied to modify the physicochemical properties of the molecules,[9,10,13–15] providing not only a way to locate the position of the macrocycle but also to modulate the properties at the molecular level.

2. Interlocked Architectures Equipped with C_{60}

Away from such a high level of complexity and performance, the first interlocked systems equipped with fullerene units emerged in 1995. Fullerenes and especially C_{60} have been widely studied and today are valuable building blocks for the preparation of materials with potential applicability in different technological fields including photovoltaics, nonlinear optics, optoelectronics, and medicine.[16–19] Also, they

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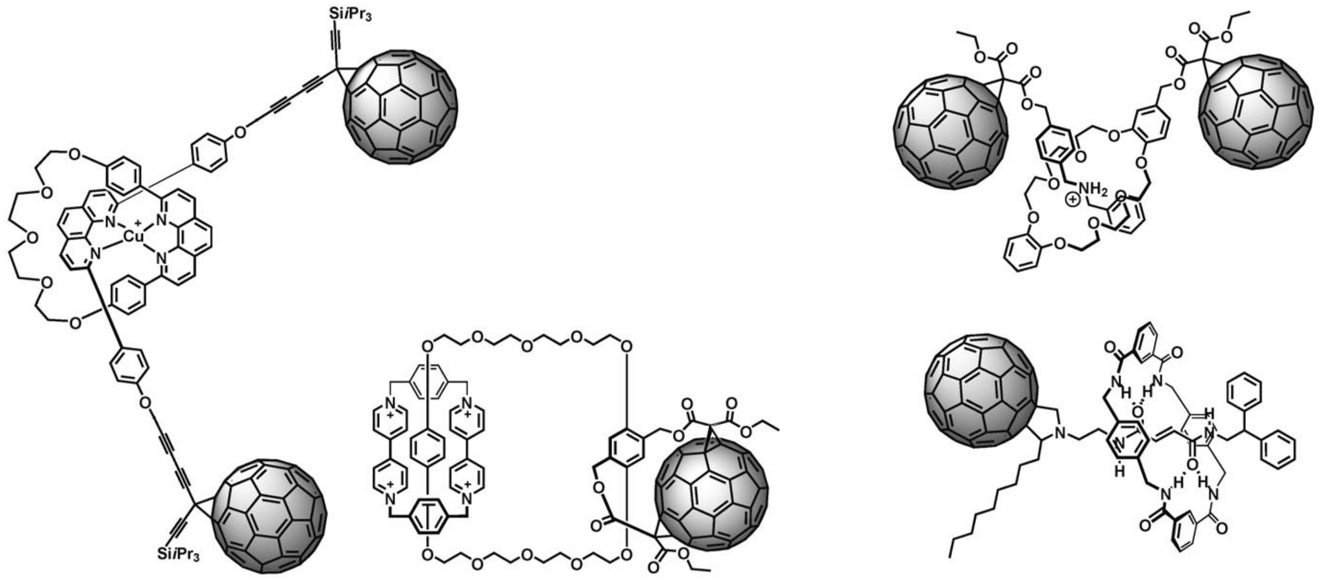

Scheme 1. Fullerene-interlocked architectures assembled by different supramolecular interactions.

have found applications in molecular machines based on calixarenes.[20–22] The properties of fullerenes derive from the three-dimensional structure of their extended π system that makes them excellent electron acceptors and chromophores. Initially, fullerenes were introduced in catenanes,[23,24] pseudorotaxanes,[25] and rotaxanes[24,26–29] (Scheme 1) as a synthetic challenge, as fullerenes present a low solubility in many solvents and are hard to process, but always with the short-term objective of exploiting their inherent properties.

3. Interlocked Architectures Containing Fullerenes as Supramolecular Donor–Acceptor Ensembles

Once the synthetic methodologies were developed, research efforts were focused on the preparation of photoactive systems where fullerenes had already shown potential applicability, such as organic photovoltaic materials. In these molecular-scale engineered systems, a fullerene electron acceptor contained in one submolecular fragment is coupled with an electron donor contained in the opposite component. Electron-transfer processes extend through many scientific fields of great importance for current technology, including photovoltaics and nonlinear optics. Several systems with different electron donors, such as porphyrins,[30–35] phthalocyanines,[36,37] extended tetrathiafulvalenes,[38] ferrocenes,[39–41] and aromatic amines,[42] were prepared and studied in detail. Photoinduced electron-transfer events were observed, followed by the formation of long-lived radical pairs with lifetimes ranging from nanoseconds to microseconds. The best results to date have been obtained from rotaxanes assembled by metal coordination. Two consecutive electron-transfer events were detected, giving charge-separated states with lifetimes as high as 32 μs (Scheme 2).[33]

4. Probing Molecular Motion through the Properties of C_{60}

Fullerene stoppers have also been introduced in rotaxanes as a way to probe the motion of the ring as a consequence of their well-defined photophysical[43] and electrochemical properties.[44,45] Leigh-like rotaxanes are particularly attractive for this purpose because 1) shuttling and pirouetting can be

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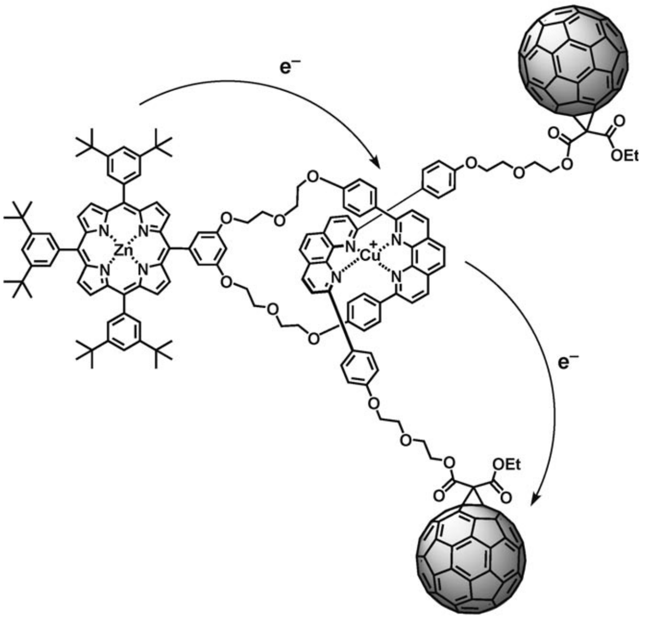
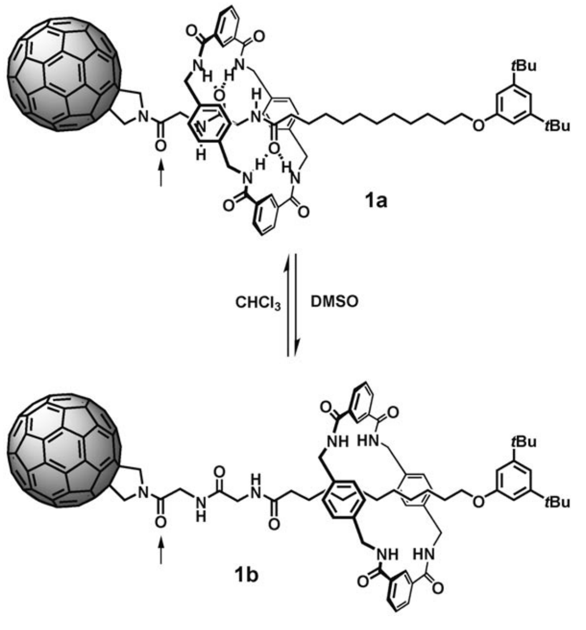


Scheme 2. Donor–acceptor rotaxanes.



Scheme 3. Solvent-switchable molecular shuttle. Arrows indicate the amide group relevant to the discussion in Section 5.

achieved through a wide variety of stimulus, such as light,[4,13,14,46,47] electrons,[4,7] solvent change,[9,10,48,49] temperature,[46,47] pH variation,[12] electric field,[50] coordination,[51,52] and chemically,[53] and 2) they are not built from chromophores or redox groups and are therefore the perfect backbones for studying the effect of submolecular motion on photo- and electroactive components. A good example is molecular shuttle **1**,[9] in which some selected photophysical properties of the fullerene were applied to detect the position of the macrocycle along the thread (Scheme 3). Rotaxane **1** comprises 1) a fullerene stopper, 2) a glycylglycine template, 3) an alkyl chain, and 4) a di-*tert*-butylphenyl stopper. In solvents that do not disturb hydrogen bonds, such as CH_2Cl_2 and $CHCl_3$, the macrocycle resides preferentially over the glycylglycine template by complementary hydrogen-bond recognition (co-conformation **1a**). Instead, in solvents that interfere strongly with hydrogen bonds, such as DMSO, the macrocycle resides over the alkyl chain (co-conformation **1b**) as a result of the solvation of the hydrogen-bonding sites. This behavior is typical of this class of rotaxanes and is independent of the stopper used.[10,54] The position of the macrocycle along the thread is clearly observed by NMR spectroscopy, as the macrocycle shields the protons of the thread over which it is located. Additionally, the location of the macrocycle can be also monitored by means of time-resolved spectroscopy. The triplet–triplet features of the fullerene are nearly independent of the solvent in the case of the thread and are similar to those of rotaxane **1** in DMSO. When rotaxane **1** was studied in CH_2Cl_2 and $CHCl_3$, the proximity of the macrocycle to the fullerene sphere induced visible differences in the triplet–triplet spectra and the triplet lifetime, which was shorter by a factor of 1.7.

5. Inducing Shuttling with Fullerene Stoppers

Rotaxane **2**[55] was designed with an analogous chemical structure to that of rotaxane **1** (Scheme 4): 1) a fullerene stopper, 2) an alkyl chain, and 3) a smaller (diphenyl) stopper at the other end. In this case, the succinamide and glycylgly-

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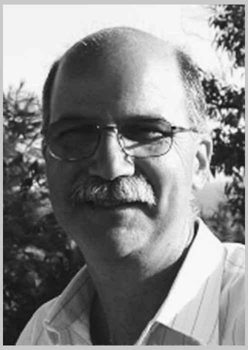
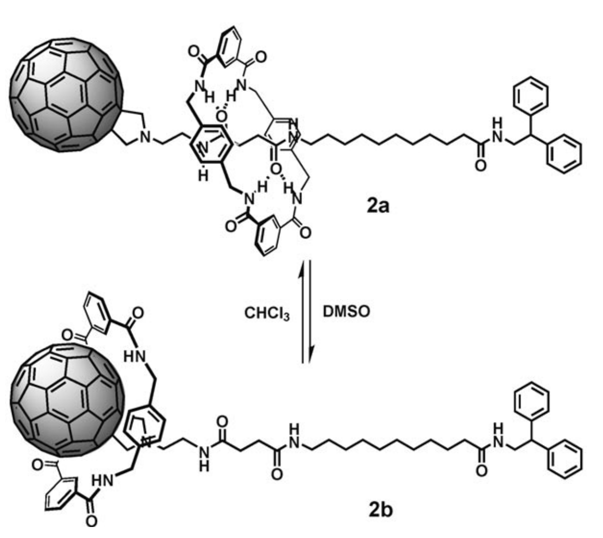


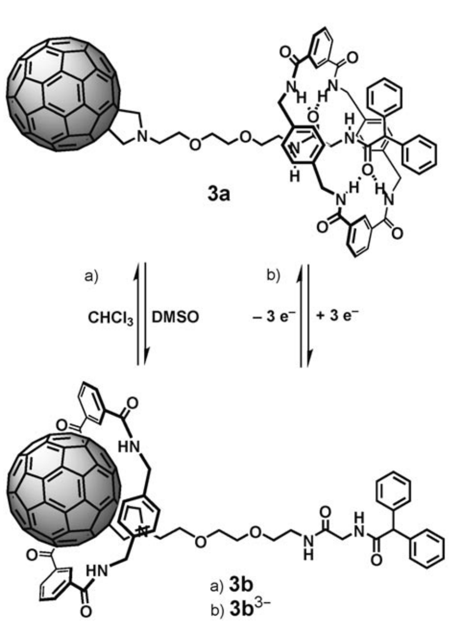
Maurizio Prato received his degree in 1978 from the University of Padova (Italy), where he was appointed Assistant Professor in 1983. He accepted a position as Associate Professor at Trieste in 1992 and was promoted to Full Professor in 2000. He spent sabbatical terms at Yale University (1986–1987) and the University of California, Santa Barbara (1992–1993), and was Professeur Invité at the Ecole Normale Supérieure, Paris (France) in 2001. His research focuses on the functionalization chemistry of fullerenes and carbon nanotubes.



Scheme 4. Reverse shuttling.

cine templates can be considered equivalent as they bind the macrocycle weakly, allowing its translocation.[47] However, when rotaxane **2** was dissolved in DMSO, the typical shielding of the alkyl signals due to translocation of the macrocycle was not observed by NMR spectroscopy. This result was rather puzzling, and 2D NMR experiments were subsequently carried out to understand exactly what was going on. After careful assignments, it was noted that the signals corresponding to the fulleropyrrolidine ring were shielded, confirming that the macrocycle switched in the opposite direction to that expected and was positioned next to the fullerene stopper. A series of electrochemical experiments centered on the fullerene were carried out in different solvents in order to clarify this behavior. From cyclic voltammetry it was seen that the presence of the macrocycle next to the fullerene spheroid stabilizes the electrochemically generated anions. This was confirmed by comparing the reduction potential of rotaxane **2** in DMSO with those of the thread, in which the anodic half-wave potential shifts ($\Delta E_{1/2}$) between 8 and 23 mV were discernable. Instead, in THF, smaller shifts between 4 and 9 mV were measured. This suggested that π–π interactions might take place between the negatively charged fullerene and the macrocycle. Reverse shuttling was explained as a result of solvation and weak interactions between the macrocycle and the fullerene. Rotaxane **1** presents an extra amide between the template and the fullerene (Scheme 3), which only allows shuttling towards the alkyl chain because of solvation of the hydrogen-bonding sites that are very close to the fullerene. However, the succinamide template of rotaxane **2** is connected to the fulleropyrrolidine stopper by two methylene groups. This allows shuttling in both directions, but the macrocycle displaces preferentially towards the fullerene to adopt co-conformation **2b** (Scheme 4).

Fascinated by the possibility of using fullerenes to induce shuttling, we further investigated these systems to identify, understand, and exploit the interactions between the fullerene unit and the macrocycle. Thus, we prepared rotaxane **3**,[56] in which the hydrogen-bonding station was placed far away from the fullerene by a triethylene glycol spacer (Scheme 5). As expected, in solvents such as CH_2Cl_2, $CHCl_3$, and THF, the macrocycle stays preferentially on the peptidic station (co-conformer **3a**). In solvents such as DMSO and DMF, the hydrogen bonds are weakened, which releases the macrocycle from the template. This allows the establishment of π–π interactions between the macrocycle and the fullerene, which induce a large positional change of the macrocycle to assume co-conformation **3b**. Careful photophysical experiments carried out in different solvents with increasing hydrogen-bond basicity confirmed that in the neutral state shuttling takes place through π–π interactions between the fullerene and the macrocycle and therefore the conformation of the macrocycle must change from chairlike to boatlike to increase the π contact with the fullerene stopper. In the excited-state absorption measurements, nearly solvent-independent behavior was observed for the thread, while measurements carried out on rotaxane **3** showed that the fluorescence of the fullerene is quenched by the proximity of the macrocycle by 28% and 44%, respectively, in DMF and DMSO. The residual fullerene fluorescence in DMSO is 51% of that in CH_2Cl_2. These experiments provided not only a way to identify the interactions that take place between the macrocycle and the fullerene but also provide a much simpler way to monitor shuttling than with transient absorption measurements. Photophysical detection of shuttling is easier in comparison with rotaxane **1** as the macrocycle interacts directly with the fullerene stopper.

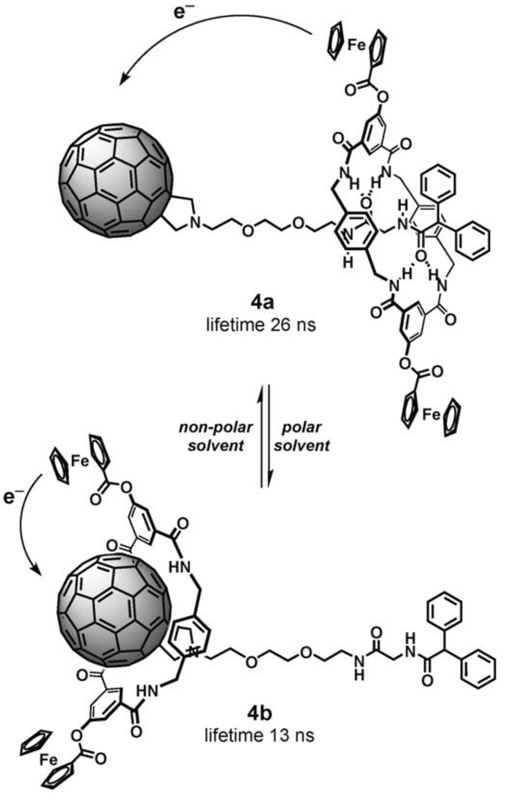


Scheme 5. Solvent- and electrochemically controllable molecular shuttle.

An important feature of **3** is that the translocation of the macrocycle is also achieved by the reduction of the fullerene to its trianion, which is both effected and observed by cyclic voltammetry.[56] In DMSO, the proximity of the macrocycle to the fullerene substantially stabilized the electrogenerated fullerene trianion ($\Delta E_{1/2} = 46$ mV) through π–π interactions. Surprisingly, in THF where the macrocycle is preferentially positioned on the peptide station, a similar behavior was observed ($\Delta E_{1/2} = 40$ mV). Although contradictory, these results can be easily rationalized in terms of electrochemically induced shuttling. A co-conformational change takes place, transforming **3a** into **3b** (Scheme 5), to the benefit of the stabilization of the negative charge present on the fullerene. The fact that this phenomenon is solely observed in this particular system, in comparison with previous fullerene rotaxanes,[29,55] is explained as a consequence of the less efficient binding between the peptidic template and the macrocycle, which is in agreement with the relative binding strengths of the different templates (fumaramide $\gg$ succinamide > glycylglycine).[7,29,57] We have calculated by combination of cyclic voltammetry and digital simulation that switching takes place with 89 % efficiency.

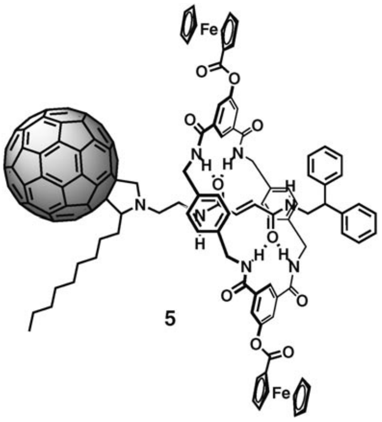
6. Tuning Electron Transfer through Molecular Motion

The possibility of fine-tuning properties such as electron-transfer through molecular shuttling is very attractive. For this reason, we modified the protocol of rotaxane formation in order to obtain molecular shuttle **4** with ferrocene electron donors on the macrocycle (Scheme 6).[58] Molecular shuttle **4** behaves exactly as the analogue **3**; the translocation of the macrocycle is triggered through a solvent change or through changes in the redox state of the fullerene by cyclic voltammetry. Steady-state and transient absorption photophysical measurements revealed through-space photoinduced electron transfer between the fullerene stopper and the ferrocenes on the macrocycle. In CH_2Cl_2, a lifetime of 26.2 ns was measured for the radical ion pair state. This value is consistent with the larger relative separation of the electroactive units that gives longer lifetimes. Addition of HFIP (hexafluoro-2-propanol) to **4** shortens the lifetime to 13.0 ns, a consequence imposed by weakening the hydrogen bonds that decreases the relative spatial separation between the donor and the acceptor while increasing the shuttling rate.



Scheme 6. Tuning photoinduced electron transfer through shuttling.

In rotaxane **5**, the relative position of the macrocycle along the thread, and therefore the relative separation of the donor and the acceptor, is fixed independently of the solvent used as a result of the greater affinity of the fumaramide template for the macrocycle.[28,29,58] By comparing the photophysical data obtained for **4** with that of rotaxane **5**, we demonstrated that shuttling contributes by at least 28 % to the effects observed on the lifetime of the photoinduced radical pair (Scheme 7).



Scheme 7. Reference rotaxane dyad.

The ultrafast positional exchange has a bigger impact on fluorescence owing to electron transfer, which allows easier monitoring of the position of the macrocycle. The residual fluorescence of the fullerene in rotaxane **5** in CH_2Cl_2/HFIP, DMF, and DMSO is respectively 46 %, 77 %, and 85 % of that observed in CH_2Cl_2. This result also gives an insight to the positional discrimination between the different stations in different solvents.

7. Summary and Outlook

In conclusion, we have shown that fullerenes are active components in molecular machinery, as they can be applied to perform different tasks. Steady-state and time-resolved photophysical measurements centered on the fullerene unit have proved to be very useful to monitor very fast submolecular motion such as shuttling. Additionally, fullerenes can be applied to induce submolecular motion through a solvent change or electrochemically through π–π interactions. Such motion can be applied to modulate physical properties such as the electrochemical potential, fluorescence, or electron-transfer events by controlling the separation of the different units to the fullerene. The manipulation of these properties at the molecular level might lead to the design of materials with enhanced properties for applications in fields where fullerenes currently play an active role.

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