



Carbon Nanotubes in Rotaxanes | Very Important Paper |

VIP Carbon Nanostructures in Rotaxane Architectures

Myriam Barrejón,^{*,[a]} Aurelio Mateo-Alonso,^{*,[b,c]} and Maurizio Prato^{*,[c,d,e]}

Abstract: Considerable research efforts have been devoted to the development of rotaxanes and the study of their unique dynamic properties. This minireview provides an overview of the main advances that have been realized in rotaxane architec-

tures involving different types of carbon nanostructures. In particular, rotaxanes based on fullerenes and carbon nanotubes will be discussed.

1. Introduction

Ever since their discovery,^[1,2] rotaxanes have drawn the attention of many scientists due to their interesting structure and potential applications. Rotaxanes are mechanically interlocked molecules that consist of two individual components, which are not chemically bound to each other (Figure 1).^[3] One of the components consist of a long molecule with bulky parts called stoppers resembling a dumbbell, while the other is a large ring-shaped macrocycle. The stoppers prevent the macrocycle from slipping off the dumbbell avoiding the dissociation of the components. These mechanically interlocked molecules show unique dynamic properties that can adopt multiple translational and rotational isomers as the result of the spatial organization of their submolecular components.^[4] Thanks to this behavior, rotaxanes have been exploited for the design and construction of artificial molecular machines, such as molecular switches and shuttles.^[5,6]

The development of straightforward methods to synthesize rotaxane architectures has been extensively explored since late 1960s,^[7] leading to synthetic procedures which generally follow one of the main three strategies, namely capping, clipping and slipping.^[8] In the capping strategy, the thread is first held within the macrocycle by non-covalent interactions. Then, bulky groups are attached to the ends to avoid dissociation. In the

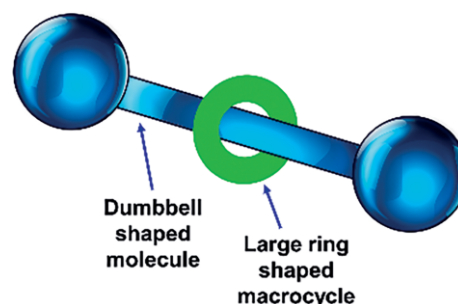


Figure 1. Schematic representation of a rotaxane.

clipping strategy, the thread with the two stoppers is bound by non-covalent interactions to an open macrocycle's precursor that eventually undergoes a ring-closing reaction around the thread giving rise to the rotaxane. Finally, the slipping strategy exploits the thermodynamic stability of the rotaxane. If the stoppers are of the appropriate size the macrocycle can thread the dumbbell at high temperatures and then at low temperatures the macrocycle is kinetically trapped within the two stoppers. In the last decade, a new strategy known as active template method have been introduced, in which the metal plays a dual role, acting as both a template for threading the components and as a catalyst for capturing the interlocked final product by covalent bonding.^[9]

The synthesis of rotaxane derivatives including oligomeric^[10] and polymeric analogs,^[11] porphyrin-stoppered rotaxanes,^[12,13] cyclodextrin-rotaxanes,^[14,15] and rotaxane dendrimers,^[16] has also been reported in the literature through different methods. However, the incorporation of carbon nanostructures into the mechanically interlocked molecular architectures is not a straightforward task and a lot of effort has been dedicated to this goal.^[4] Some representative achievements in this field will be discussed in this minireview focusing attention on the development of hybrid structures based on fullerene- and carbon nanotube-based rotaxanes.

2. A Bit of History ...

The concept of molecular structures based on cyclic molecules whose cavities were threaded by linear molecules was first de-

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scribed as early as 1910 by R. Willstätter, who discussed the existence of interlocked rings during a seminar in Zurich.^[17] However, this subject was not formally reported until 1961 by Frisch and Wasserman.^[16,17] The term rotaxane was introduced in 1967 by Schill and Zollenkopf as a combination of the two Latin words **rota**(= wheel) and **axis**(= axle).^[1] These authors reported the multistep preparation of rotaxanes in which both components were linked by covalent bonds that were subsequently cleaved leaving only mechanical bonds. Two years later, they performed the covalent-template-directed macrocyclization and the subsequent cleavage of the temporary bonds, yielding [2]rotaxanes.^[2] The experimental demonstration of such supramolecular assemblies was also reported by Harrison and Harrison through a statistical approach.^[7] They demonstrated that a polymethylene could thread a C₃₀ ring bound to a Merrifield resin to form a rotaxane (that they called hooplane). In a later study, Harrison described a new approach for the synthesis of rotaxanes which also applied the law of statistics and involved the reversible detachment of the bulky groups of the dumbbell in the presence of macrocycles.^[18] Subsequent regeneration of the bonds resulted in the formation of the rotaxane architecture. During these experiments, they investigated also the effect of the macrocycle ring size on the formation and stability of rotaxanes, establishing that cyclic species of 24 skeletal atoms were needed to provide a cavity large enough to be threaded onto the dumbbell.^[18,19] The relationship between the ring size, molecular length of the linear component, concentration, and blocking group size, was also studied by different authors in the 70s and 80s.^[20–22] However, through the statistical threading method, a mixture of rotaxane, polyrotaxane and unthreaded linear and cyclic compounds was obtained and the efficiency of threading from this method after 70 repetitive steps was as low as 6 %.

In the early 1980, Sauvage and co-workers introduced the so-called templating technique consisting of a transition metal-templated route for the synthesis of catenanes,^[23–25] which was then used by Gibson to synthesize rotaxanes and polyrotaxanes.^[26] Other methods included the use of amides as templates,^[27,28] the use of π -donors/ π -acceptors interactions between electron-rich and electron-deficient aromatics for the design of mechanically bound molecular species^[29–31] and the design and construction of nanoscale switching devices.^[32–34]

While the chemistry of rotaxanes was enjoying its major boom, the emergence of the first interlocked systems equipped with carbon nanostructures occurred.^[35–38] In the next sections, we will take a journey through the most relevant types of carbon nanoform-rotaxane architectures that have been reported in the literature since the synthesis of the first hybrid structure.

3. Rotaxane-Fullerene Architectures

Since the discovery of fullerenes in 1985,^[39] a wide range of covalent and non-covalent chemical strategies involving this carbon allotrope have been developed.^[40–44] The first known rotaxane derivative containing a carbon nanostructure was described in 1995 by Diederich et al. and consisted of a rotaxane containing two fullerene (C₆₀) units as stoppers.^[35] Until this moment, stoppers did not have other role than preventing the macrocyclic component from dissociation. However, the incorporation of C₆₀ units into the rotaxane architectures opened up new possibilities to introduce electro- and/or photoactive species^[45–47] that give rise to molecular systems with interesting electrochemical and electronic properties,^[35,48,49] promising further enhancement of the functionality of such molecular



Myriam Barrejón obtained her PhD in Nanoscience and Nanotechnology in 2015 at the university of Castilla La-Mancha (UCLM) (Spain), under the supervision of Prof. Fernando Langa, working on the functionalization and characterization of graphene and carbon nanotubes for optoelectronic applications, and she received the prize to the best doctoral thesis from the RSEQ-CLM. In September 2016 she joined Prof. Prato's group as a post-doctoral researcher where she has been working on the synthesis of carbon nanostructure-based 3D networks for biomedical applications for two years. Currently she is a postdoctoral researcher at the institute of Nanoscience and Molecular materials (INAMOL), in Toledo (Spain), where she is working on the functionalization of carbon nanostructures for biomedical and energy applications.



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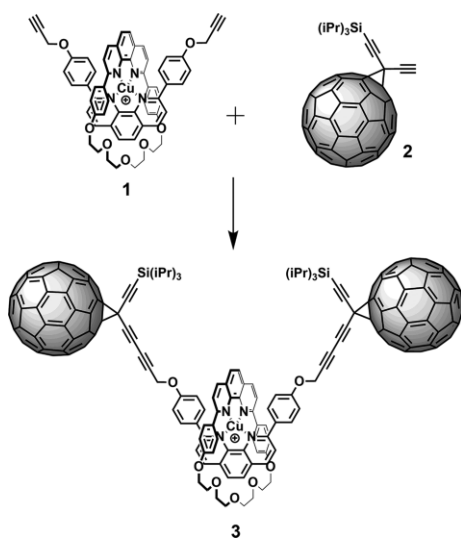


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assemblies. This will be discussed more in detail in the following sections.

3.1. Synthetic Approaches

Due to the intrinsic low solubility of fullerenes,^[50] the initial studies involving fullerene-based rotaxane architectures were aimed at addressing the synthetic challenges. In this regard, several synthetic strategies involving different types of supramolecular interactions have been employed over the years to incorporate C₆₀ molecules into the rotaxane structure.^[4] The first fullerene-based rotaxane complex was prepared via metal complexation through a copper complexed rotaxane (Scheme 1).^[35] The removal of the coordinated copper (I) center yielded the desired rotaxane **3** that was not completely isolated in a pure form.



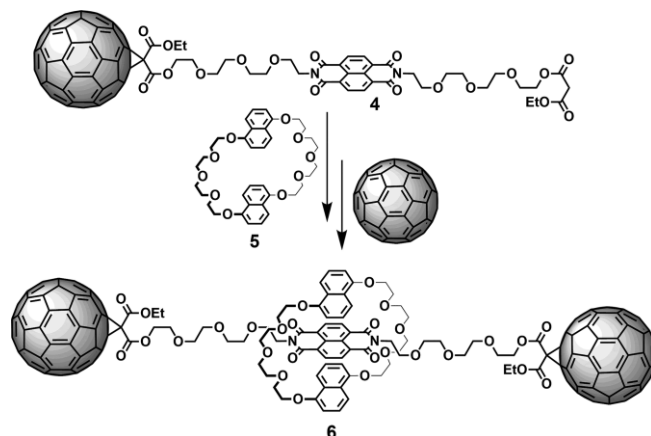
Scheme 1. Synthetic approach for the synthesis of fullerene-stoppered rotaxanes via metal complexation of copper.

A synthetic strategy based on π - π interactions was used by Nakamura and co-workers^[51] to prepare fullerene-rotaxane architectures. The interaction between an electron-poor naphthalenetetracarboxylic diimide with an electron-rich 1,5-dihydroxynaphthalene, yielded a pseudorotaxane. The subsequent capping with C₆₀ gave the rotaxane **6** (Scheme 2).

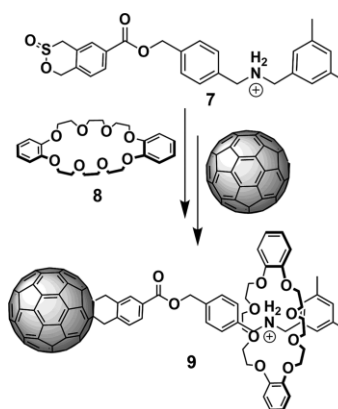
Hydrogen bonding interactions have been also employed to prepare fullerene-rotaxanes.^[4] Through this approach, rotaxanes were synthesized by preassembling a pseudorotaxane through hydrogen bonds between aromatic crown ethers and ammonium salts. Then, a Diels-Alder end-capping reaction with a C₆₀ unit was accomplished to yield the final rotaxane architecture **9** (Scheme 3).^[49,52,53]

Solvophobic interactions between cyclodextrin and polymeric chains have been also exploited for assembling polyrotaxanes.^[54,55] Here, the C₆₀ molecules were employed as the end-capping agent after polyrotaxane formation (Scheme 4).

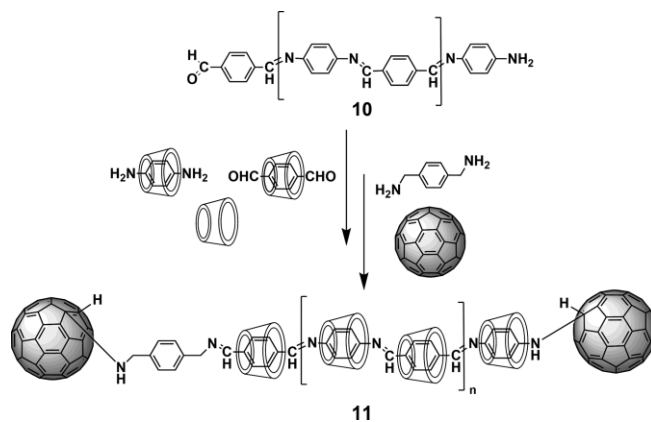
Recently, a new synthetic approach has been reported that employs C₆₀ as a template.^[56] This method exploits the π - π concave-convex complementarity between C₆₀ and [10]cyclo-



Scheme 2. Synthetic approach for the synthesis of fullerene-stoppered rotaxanes via π - π stacking.

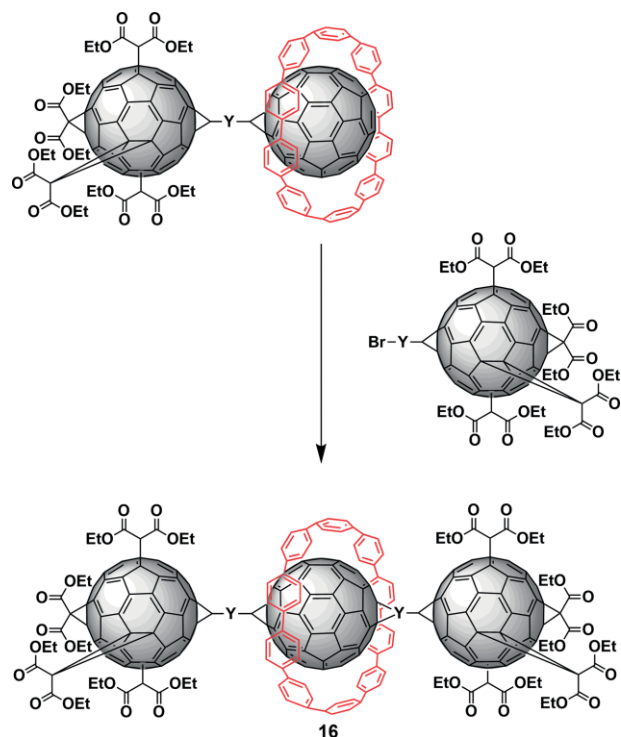


Scheme 3. Schematic representation of the synthesis of fullerene rotaxanes via hydrogen bonding.



Scheme 4. Synthetic approach for the synthesis of rotaxanes through solvophobic interactions.

paraphenylene. The thread is constituted by a fullerene dimer with one fullerene hexa-adduct that acts as a stopper and one fullerene monoadduct that acts as the template. The [10]cycloparaphenylene macrocycle is able to π -stack to the fullerene monoadduct which is trapped by a Bingel reaction with another fullerene hexa-adduct stopper (Scheme 5).



Scheme 5. Synthetic approach for the synthesis of a cycloparaphenylene-fullerene rotaxane synthesized by concave-convex π - π templating strategy.

During the study, electron transfer experiments revealed that the presence of the mechanically interlocked [10]cycloparaphenylene did not affect the electrochemical behavior of the fullerene bis-adduct, but supported the existence of charge separation in a “bound” and “unbound” state where the [10]CPP ring was located on the central fullerene or somewhere over the thread, being the charge recombination process much slower in the “unbound” state.

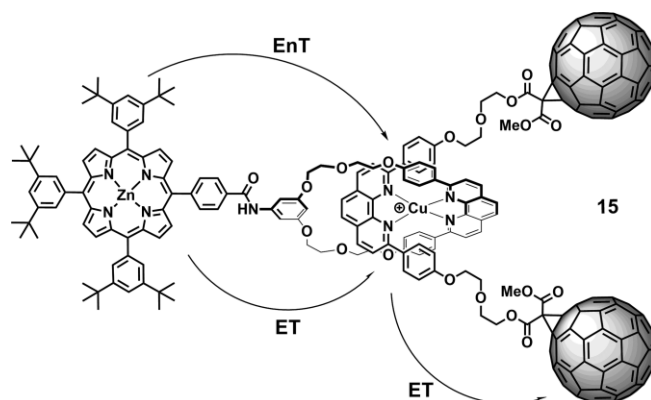
3.2. Electron Transfer in Rotaxane Architectures

C_{60} has proven to be an excellent electron-acceptor in the preparation of photoactive systems in which a cascade of several electron and energy transfer processes can be orchestrated one after the other.^[44,57] Rotaxane architectures allow placing different electron/energy mediating units in different submolecular components and therefore favor through-space communication rather than through-bond.^[58] Depending on the number of photo/electroactive units the systems are called dyads, triads, tetrads, etc.

Dyads

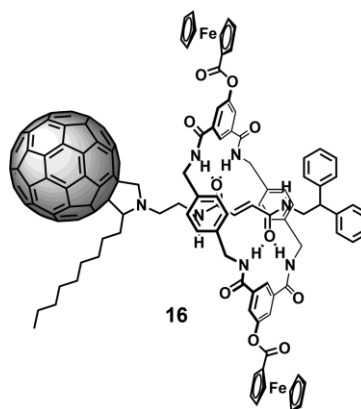
Rotaxanes containing C_{60} as the electron-acceptor component and different types of electron-donors have been reported in the literature. Among them, porphyrins and phthalocyanines have been widely explored as the electron-donors,^[59–68] in which charge separation (CS) process can occur through the singlet or triplet excited states, depending on the distance between the components.^[58,65] Furthermore, changes in the relative distance between donors and acceptors seems to play a

key role in the photoinduced electron transfer (PET) process.^[65] Similarly, the lifetimes of the charge separated states have been found to depend strongly on the positions of the donor and the acceptor.^[4] Thus, changes in topology have shown to result in substantially longer lifetimes, greater than analogous covalently linked Zinc porphyrin- C_{60} (ZnP- C_{60}) systems, showing lifetimes as long as 32 μ s in the case of dyad **15** (Scheme 6), in which the bisphenanthroline template act as an energy or electron transfer mediator.^[62]



Scheme 6. Schematic representation of the rotaxane dyad combining C_{60} and Zn-porphyrin.

Dyads have been also prepared with extended- tetrathiafulvalenes (extTTFs) as donors, where the ammonium groups bind the fullerene derivatives with a crown-ether functionality leading to architectures that could mimic the natural photosynthetic process.^[69,70] Ferrocene is also an useful electron donors in donor-acceptor rotaxane architectures. In addition, ferrocenes are bulky enough to be used as stoppers in some cases.^[71] For these reasons, rotaxane architectures combining fullerene and ferrocene have been described which have provided a lot of information on the CS process of the spatial arrangement of C_{60} and ferrocene (Scheme 7).^[71–73]



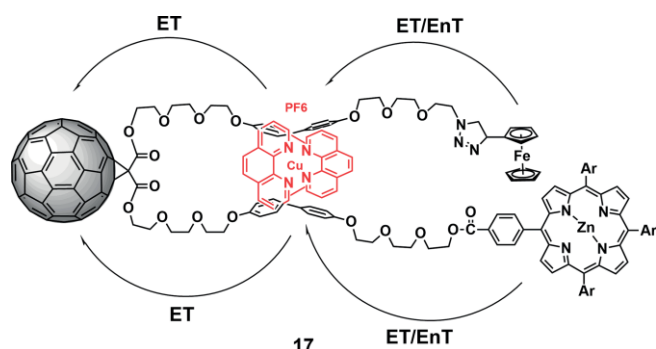
Scheme 7. Representative ferrocene-rotaxane dyad.

Rotaxane systems constituted of aromatic amines and fullerene moieties have also received a lot of attention. In these systems, the intermolecular electron-transfer route via the singlet excited state was predominant at high amine concentrations,

whereas the electron-transfer via the triplet state became predominant at low concentrations.^[74] Furthermore, the comparison of simple triphenylamines (TPA) with bis-biphenylamines (BBA) demonstrated that the CS process of systems containing TPA predominantly took place via $^3C_{60}^*$,^[74] whereas in the presence of BBA the CS process via $^1C_{60}^*$ was increased.^[75] This was attributed to the higher donor ability of BBA to $^1C_{60}^*$ than that of TPA, probably because of its larger area.^[58] However, when comparing the charge recombination constants, in the presence of TPA these values were slightly larger than those of BBA, probably due to the wider fluctuation of the distance between C_{60} and TPA moieties compared with the bulky BBA.^[58,74,75]

Triads

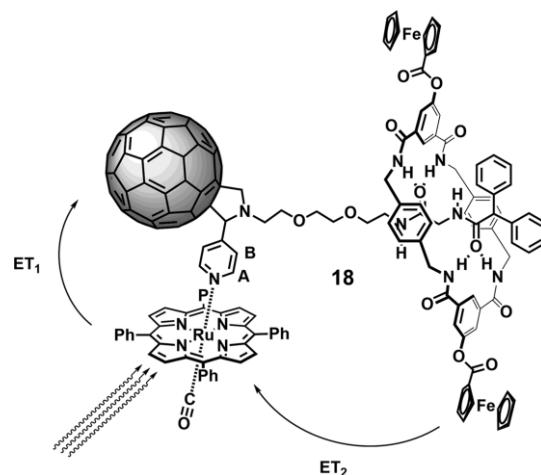
Structures containing more than two electron donating/accepting molecules have been also described in the literature, which in some cases results in a considerable improvement of charge separation. A good example is triad **17**, showing lifetime values as high as 61 μ s (Scheme 8).^[66] In this triad, the authors demonstrated that photo-excitation triggered a cascade of multi-step energy and electron transfer events leading to remarkably long-lived charge separated states that involve one-electron reduced C_{60} radical anion ($C_{60}^{\cdot-}$) and either one-electron oxidized porphyrin ($ZnP^{+\cdot}$) or one-electron oxidized ferrocene ($Fc^{+\cdot}$).



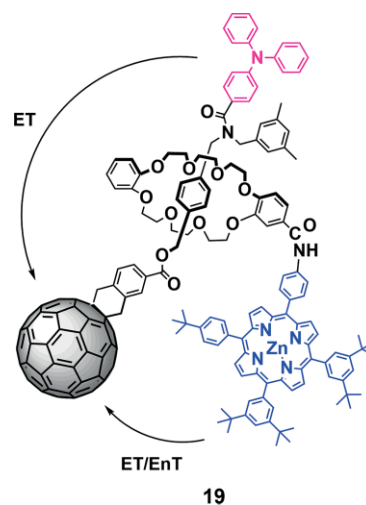
Scheme 8. Schematic representation of a triad rotaxane combining C_{60} , Zn-porphyrin and ferrocene.

In another study, the introduction of a pending pyridyl group between the C_{60} and the ferrocene units allowed the coordination of a ruthenium carbonyl tetraphenylporphyrin (Scheme 9).^[76] In this case, the redox gradient promotes a unidirectional cascade of charge-transfer reactions between the three units upon excitation of the porphyrin, with an initial electron transfer from the porphyrin to the fullerene, which is followed by a charge shift from the porphyrin to the ferrocene.

In a triad rotaxane consisting of one electron-acceptor (C_{60}) and two electron-donors (ZnP and TPA moieties), it was demonstrated that the position of the components made possible an efficient CS process.^[67] The authors carried out a comparison with previously synthesized triad rotaxanes showing longer axles,^[77,78] concluding the existence of longer lifetimes in this particular case, where a short axle with C_{60} and TPA at both terminals was penetrating through a crown-ether as an electron acceptor and a hole-shift. The main advantage of this system was that the ZnP moiety was positioned quite near the C_{60} and TPA moieties (Scheme 10).



Scheme 9. Ferrocene-porphyrin- C_{60} triad rotaxane.



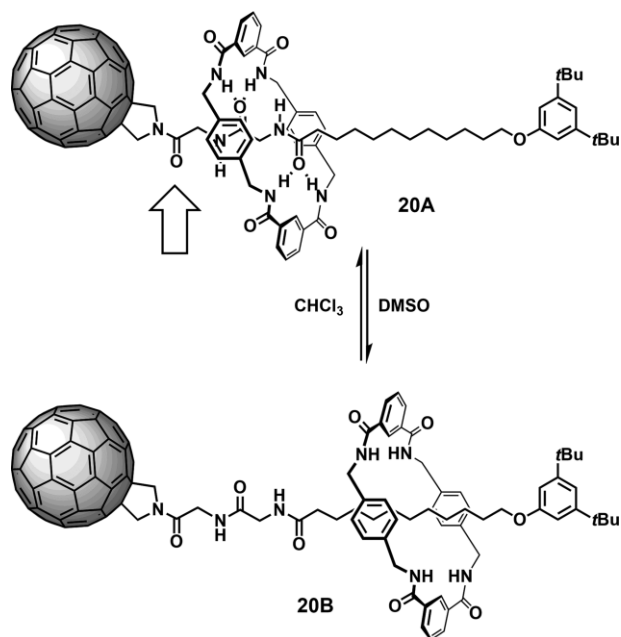
Scheme 10. Schematic representation of the triad rotaxane based on C_{60} -ZnP-TPA.

3.3. Bistable Rotaxanes

One of the most useful properties of rotaxanes is their intrinsic multi-stability. The different components in rotaxanes are held together only by mechanical linkages, which allows the macrocycle to be positioned along different parts of the axle called stations. In the particular case of bistable rotaxanes, the macrocycle of the rotaxane can switch between two different stations from the axle.^[79] In rotaxanes containing C_{60} units, the positional switching of the macrocycle can be used to modulate the optoelectronic properties of C_{60} .^[79] Furthermore, controlling the position of the macrocycle allows the rotaxane to function as a molecular switch with potential use as a molecular switching element or molecular shuttle.^[80]

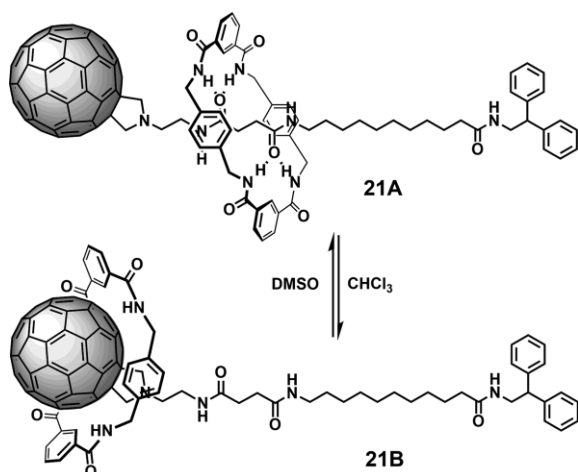
The first bistable rotaxane containing a fullerene was reported in 2003 and consisted of a C_{60} stopper and a benzylic amide macrocycle (Scheme 11).^[81] In this rotaxane, the amphiphilic nature of the rotaxane allowed the shuttling of the macrocycle, being close to the C_{60} unit in the presence of non-polar solvents, such as chloroform, and far away in polar solvents such as dimethyl sulfoxide (DMSO). The position of the

macrocycle was monitored through time-resolved spectroscopy, by looking at the triplet-triplet absorption characteristics of C_{60} , that was affected by the proximity of the macrocycle to the C_{60} unit.



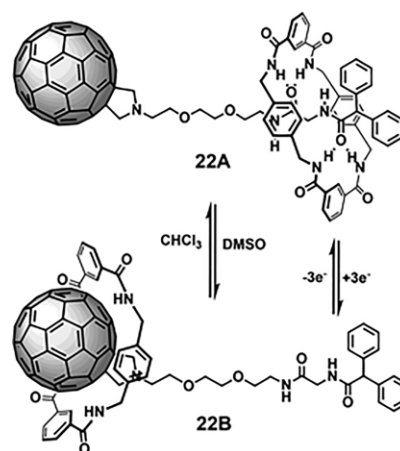
Scheme 11. Molecular shuttle controlled by solvent polarity.

An analogous solvent-switchable rotaxane was designed (Scheme 12).^[82] In this case, the presence of polar solvents triggered a reverse shuttling of the macrocycle that was explained by the existence of π - π interaction between the macrocycle and the fullerene. The main difference between rotaxanes **20** and **21** was the presence of an extra amide between the macrocycle and the fullerene in the former case that prevented the macrocycle from getting close to the C_{60} , avoiding the existence of π - π interactions.^[82] The position of the macrocycle in the different stations of the rotaxane **21** was identified through changes in the electrochemical and excited-state absorption measurements.



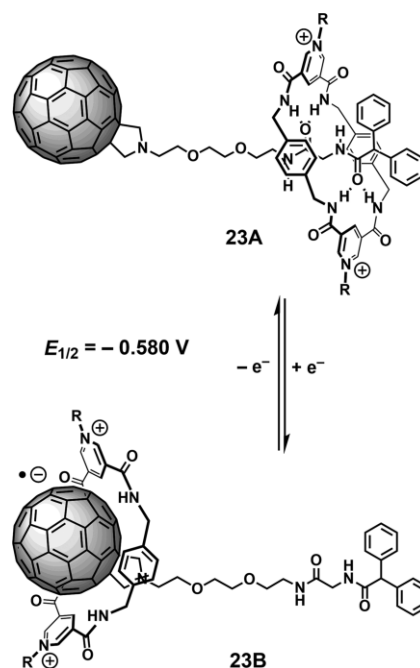
Scheme 12. Molecular shuttle controlled by solvent polarity and electrochemical behavior.

In another study, shuttling over long distances was demonstrated by designing a rotaxane complex in which the hydrogen bonding diamide station was far away from the C_{60} unit (Scheme 13).^[83,84] In this case, also the solvent polarity was determinant. In the presence of polar solvents, the hydrogen bonds were weakened and the macrocycle established π - π interactions with the C_{60} unit, showing a large positional change and changing its conformation. The translocation of the macrocycle can also be triggered electrochemically. By reducing the fullerene stopper to the trianion selectively, the macrocycle leaves the hydrogen bond binding sites to bind the macrocycle by π - π stacking in order to stabilize the negative charge present on the fullerene.



Scheme 13. Solvent and electrochemically controllable molecular shuttle.

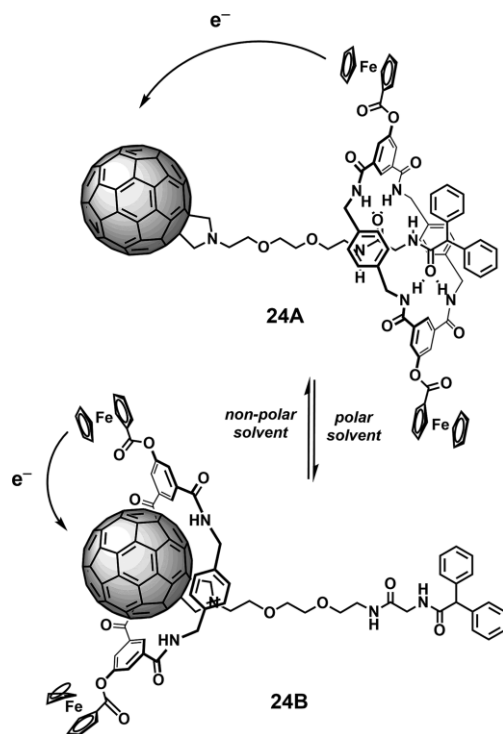
The introduction of the pyridinium salts in the macrocycle resulted in a similar positional discrimination but at much lower reduction potentials (Scheme 14).^[84,85] For instance the reduction of the fullerene to the radical-anion is enough to trigger



Scheme 14. Molecular shuttle controlled by radical-anion recognition.

the relocation of the macrocycle because of the stronger interactions between the pyridinium cations and the radical-anion of the fullerene.

When two ferrocene electron-donors were incorporated into the macrocycle of rotaxane **22** (Scheme 15),^[86] the same shuttling behavior was observed and translocation of the macrocycle in the resulting rotaxane **24**. Indeed, the relocation of the macrocycle can also be triggered by changes in solvent polarity

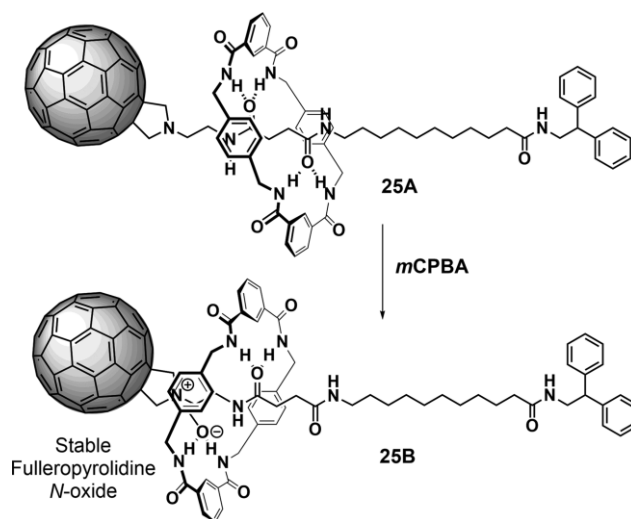


Scheme 15. Molecular shuttle controlled by solvent polarity with tunable PET and NLO.

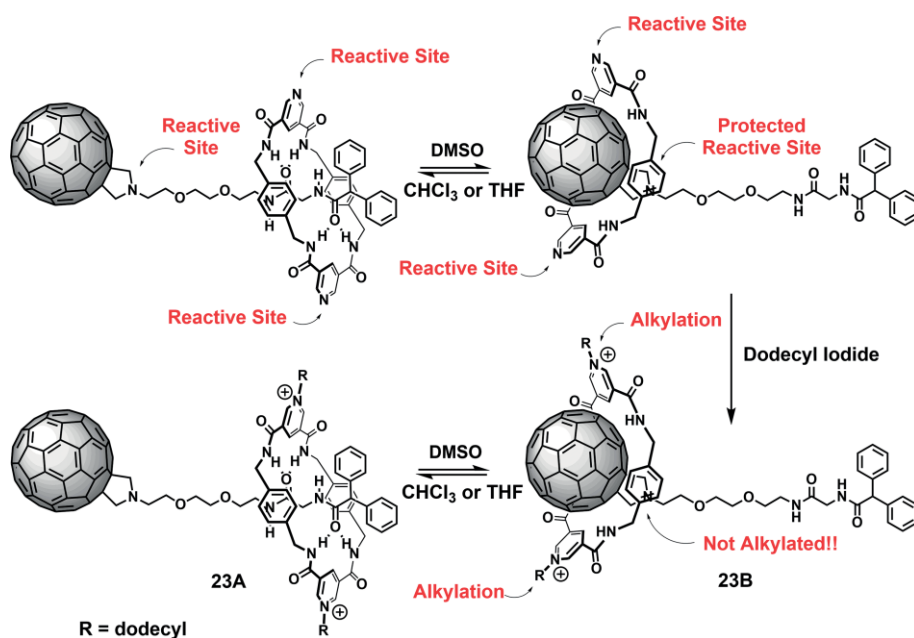
or the redox state of the fullerene. However, in this case, photo-physical studies revealed the existence of a PET process between the fullerene and the ferrocene. Most importantly the lifetime of the photogenerated can be affected by controlling the spatial separation between the donor and the acceptor.

Another important aspect of rotaxanes **22** and **24** is the fact that the different positions of the macrocycle along the thread results in changes in the non-linear optical (NLO) response of fullerene stoppers. These changes were also explained in terms of the existing π - π stacking between the macrocycle and the fullerene.^[87]

Fullerene rotaxanes can be also switched chemically.^[79] A good example^[88] is rotaxane **25** in which the benzylic amide macrocycle is initially sitting on the succinimide station (**25A**) by hydrogen bonding (Scheme 16). When the fulleropyrrolidine



Scheme 16. Chemically stimulated switching by oxidation of fulleropyrrolidines.



Scheme 17. Molecular shuttle controlled by the translocation of the macrocycle as a selective protecting group.

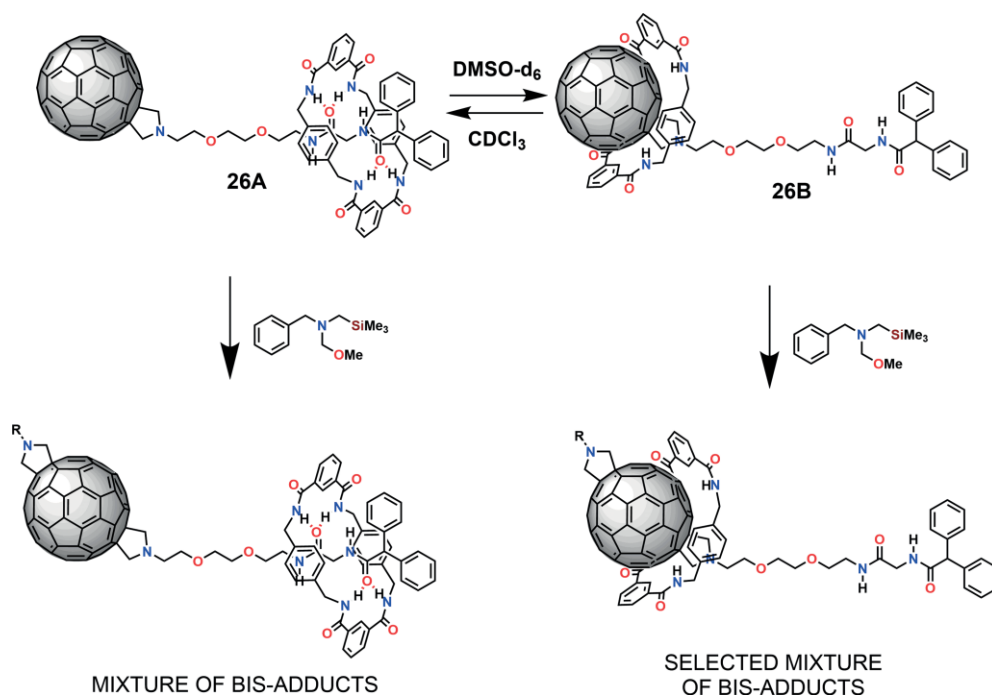
of rotaxane **25** was chemically oxidized to the corresponding fullerene di-*N*-oxide, the macrocycle switched to bind preferentially the *N*-oxide and the adjacent amide (**25B**).

The position of the macrocycle along the thread can be used to modulate the chemical reactivity of different functionals groups as an effect of encapsulation. For instance, the encapsulation of fulleropyrrolidine *N*-oxide (Scheme 16) by means of intrarotaxane hydrogen bonds results in the stabilization of fulleropyrrolidine *N*-oxides that otherwise are easily transformed into the parent fulleropyrrolidines in the presence of alcohols.^[79]

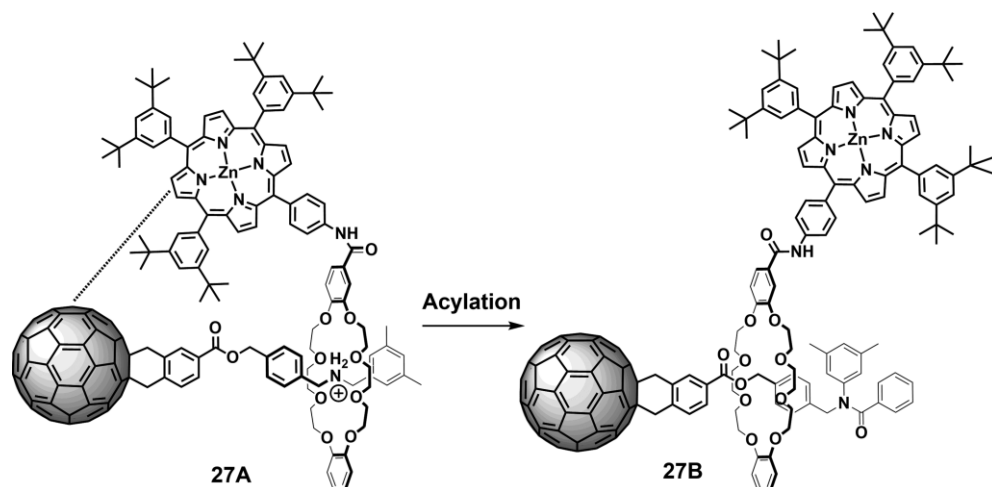
Another example is the synthetic route of molecular shuttle **23**^[85] described above, which has been accomplished by exploiting the controlled and reversible translocation of the mac-

rocycle as a selective protecting group.^[30] The reaction of the thread with dodecyl iodide in DMSO yields the corresponding fulleropyrrolidinium salt. Conversely, when rotaxane **23** was allowed to react with an excess of dodecyl iodide (3, 27 and 45 equivalents) in DMSO, only the alkylation of the macrocycle took place, since the alkylation of the fulleropyrrolidine was inhibited because it was encapsulated by the macrocycle. This led directly to rotaxane **23** (Scheme 17).

The switchable nature of rotaxane **26** (Scheme 18) has been recently exploited to control the reactivity of the fullerene towards a second cycloaddition reaction.^[89] The results demonstrated that close proximity of the macrocycle to the fullerene sphere was able to allosterically influence the selectivity of the bis-additions.

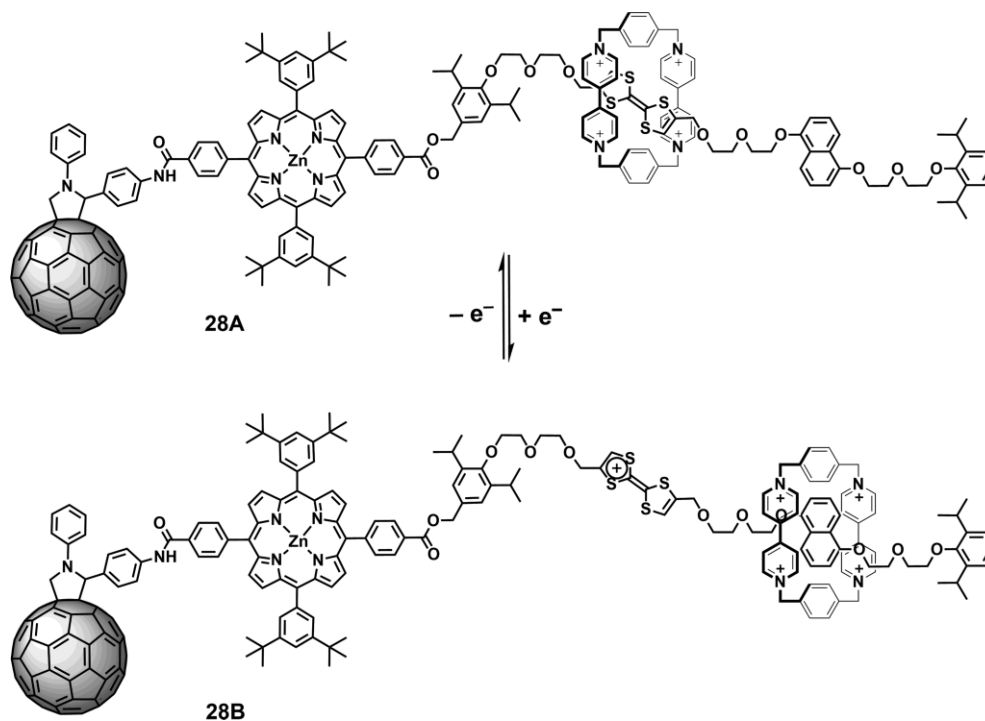


Scheme 18. Molecular shuttle used to control the reactivity of second cycloaddition reactions.

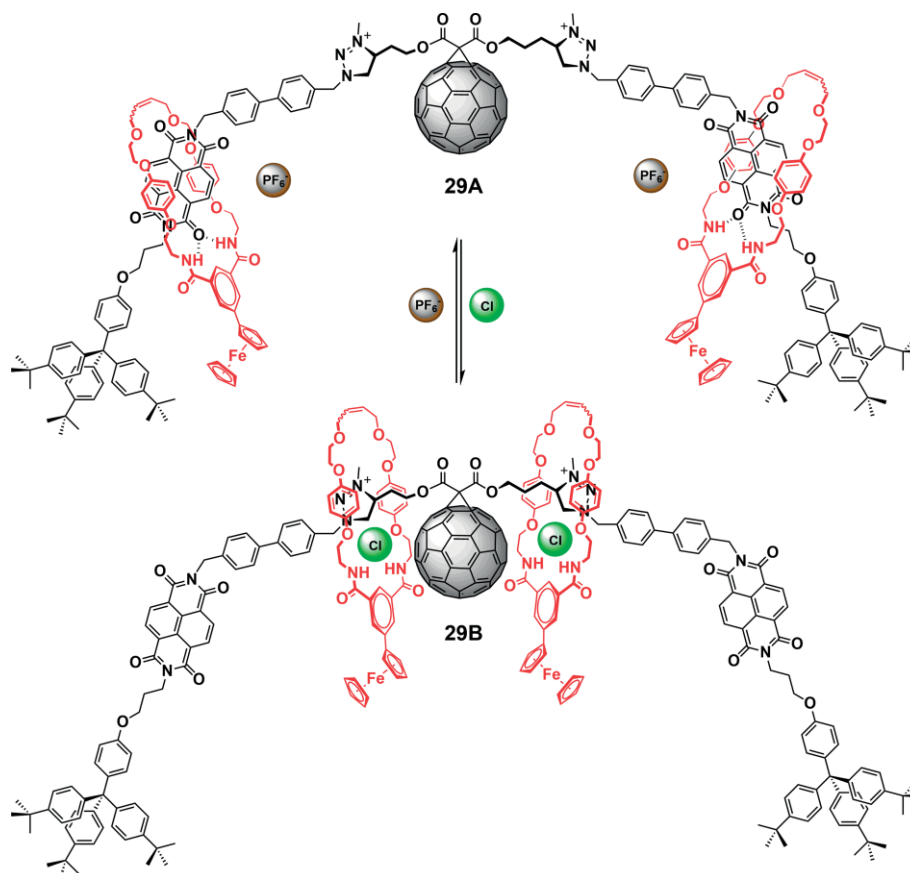


Scheme 19. Chemically stimulated switching by acylation of the ammonium salt.

In another example, a bistable rotaxane consisting of a hydrogen-bonded complex between an aromatic crown ether and an ammonium salt, switched into a new co-conformation after acetylation of the ammonium salt,^[78] in which the macro-



Scheme 20. Electrochemically switchable molecular shuttle.



Scheme 21. Schematic representation of a four-station bis-naphthalene diimide C₆₀-rotaxane.

cycle was positioned closer to the fullerene and the π - π interactions between the porphyrin and the fullerene were disrupted (Scheme 19). Photophysical studies revealed the existence of photoinduced electron transfer between the porphyrin and C₆₀ in **27A**.^[78]

Stoddart and co-workers have reported an electrochemically-driven bistable multicomponent rotaxane consisting of two electron-rich stations (tetrathiafulvalene (TTF) and 1,5-dihydroxynaphthalene (DNP)) (Scheme 20).^[90] In this shuttle, the electron-deficient macrocycle sits preferentially over the TTF station because is more electron rich than the DNP station. Upon electrochemical oxidation, the TTF unit oxidizes to the radical cation and therefore is no longer the more electron-rich station. Therefore, the electron-deficient macrocycle switches to accommodate over the DNP station. The idea underneath the fullerene stopper was to photochemically generate the radical-cation of TTF by two consecutive electron transfer processes from the porphyrin to the fullerene and then from the TTF unit to the porphyrin.

Recently, a novel multifunctional dynamic rotaxane consisting of a four-station bis-naphthalene diimide (NDI), a centrally positioned electron-deficient C₆₀ unit and two mechanically bonded ferrocenyl-isophthalamide anion binding site-containing macrocycles has been reported (Scheme 21).^[91] In this system the macrocycle can bind the NDI unit by hydrogen bonding, but in the presence of chloride anions the macrocycle switches to bind the triazolium salt through the chloride. ¹H NMR spectroscopy was used to demonstrate the anion-mediated translational motion of the electron donor and acceptor motifs. Further studies based on absorption and emission spectroscopy and electrochemical analysis probed the anion-dependent positional macrocycle-axle station state of the molecular shuttle, revealing a switchable emission response induced by anion binding. Photophysical studies revealed that when the macrocycle is sitting on the NDI station electron transfer takes place between the ferrocene and the NDI unit and later on the electron shifts to the fullerene. On the contrary when the macrocycle is sitting on the top of the triazolium station the electron is directly injected from the ferrocene into the fullerene upon irradiation.

4. Carbon Nanotube-Rotaxane Architectures

Since the discovery of carbon nanotubes (CNTs) in 1991 by Iijima,^[92] these materials have attracted great interest owing to their extraordinary mechanical,^[93] thermal,^[94,95] and electronic^[96] properties that allow their application in a wide number of fields.^[97] Over the years, the chemistry of carbon nanotubes has been focused in their modification through covalent and non-covalent approaches.^[98,99] However, covalent chemistry leads to the disruption of the π - π structure of CNTs while non covalent approaches yield materials that lack in kinetic stability.^[100]

In recent years, an unexplored alternative for the chemical modification of single-walled carbon nanotubes (SWCNTs) has been described,^[101] in which a macrocycle is threaded by a SWCNT. This approach has allowed the chemical attachment of

useful components to the sidewall of SWCNTs, combining the best of covalent and non-covalent approaches and yielding mechanically interlocked rotaxane-type CNTs (MINTs) (Figure 2).^[101,102]

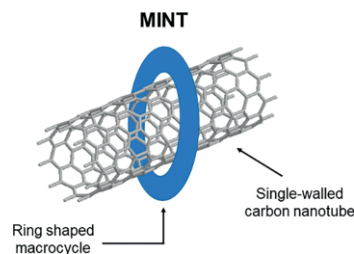


Figure 2. Schematic representation of a mechanically interlocked CNT (MINT).

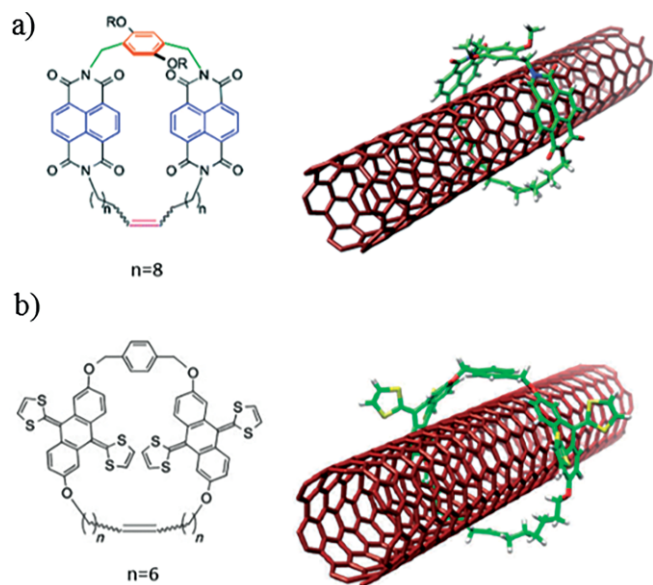
For the successful threading of SWCNTs into the ring shaped macrocycle component (Figure 2) one of main requirements is the use of thin SWCNTs, being the most suitable those with diameters around 0.8 and 0.9 nm, diameter that show the (7,6) and (6,5)-enriched CoMoCAT SWNTs.^[102,103]

In the first reported synthesis of MINTs, the direct threading of SWCNTs through previously formed macrocycles was considered. However, the results indicated that this threading process was indeed highly unlikely,^[101] which was later attributed to the extreme aspect ratio required for the proper encapsulation of SWCNTs into the macrocycle and the tendency of SWCNTs to bundle up.^[102]

In the same work, they demonstrated that the clipping strategy was the most suitable synthetic approach for the mechanical bonding of SWCNTs, in which the macrocycles were formed around the CNTs by ring-closing metathesis.^[101] In particular, they employed π -extended derivatives of tetrathiafulvalene that behaved as a U-shape for the recognition of SWCNTs precursors. Based on these studies, the introduction of different recognition elements for SWCNTs, able to facilitate the association of different U-shaped molecules has been realized in recent years, focusing on symmetric designs where two recognition units were linked through an aromatic spacer decorated with long alkenyl chains that provided the required flexibility.^[102] Thus, molecules with high affinity binding to CNTs via non-covalent interactions have been employed, such as electron-donor π -extended derivatives of tetrathiafulvalene,^[103] electron-acceptor naphthalene-diimides,^[104] and neutral pyrenes (Scheme 22).^[105]

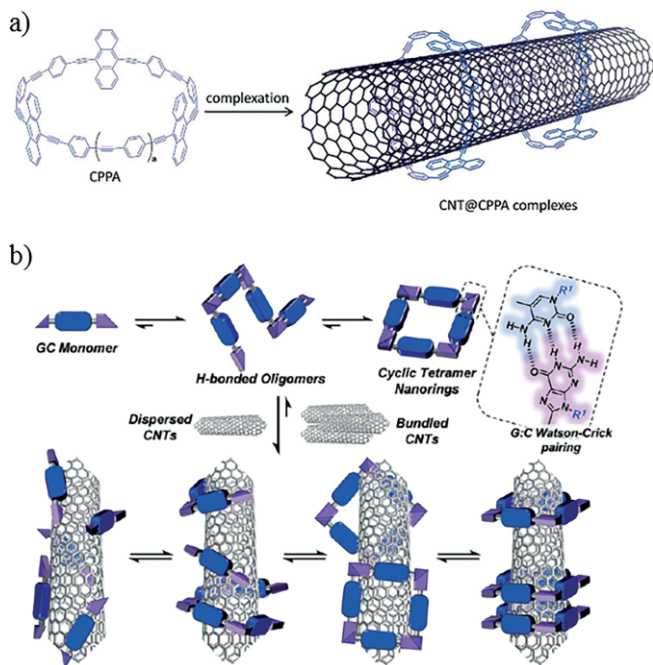
Recently, the incorporation of porphyrins into the macrocyclic ring of CNT rotaxane-like architectures has been reported.^[106] In this work, the authors have demonstrated that the mechanical bonding between the porphyrin derivatives and CNTs proceeds with chiral selectivity towards the smaller diameter SWCNTs. Furthermore, transient-absorption and steady-state fluorescence measurements demonstrated the existence of electronic interactions between the porphyrins and the SWCNTs with the smaller diameters.

A novel strategy for the preparation of interlocked architectures of CNTs, known as the "ring toss" method, have been recently reported by Miki et al.^[107] To prove the efficiency of the method, the authors employed various derivatives of cyclo-



Scheme 22. (a) Molecular model of a pseudorotaxane comprising a naphthalenediimide macrocycle and SWCNT. Reproduced from ref.^[104] with permission from The Royal Society of Chemistry. (b) Molecular model of a pseudorotaxane comprising a π -extended tetrathiafulvalene macrocycle and SWCNT. Reproduced from ref.^[101]

paraphenyleneacetylene that efficiently interact with CNTs thanks to their π -conjugated structure (Scheme 23a). The complexation efficiency of the method was demonstrated to depend on the size of the π -conjugated macrocycle and the diameter of the CNTs.



Scheme 23. (a) Synthesis of CNT@CPPA complexes through the "ring toss" approach. Reproduced from ref.^[107]. (b) Schematic representation of the formation process of CNT-rotaxane like structures through non-covalent macrocyclization processes. Reproduced from ref.^[110] with permission from The Royal Society of Chemistry.

Finally, a novel approach has been recently described that relies on a cooperative clamping process where dinucleoside monomers that are able to form nanorings are assembled around the tubes. The method affords stable CNT dispersions through a non-covalent macrocyclization process which supplies the required reversibility to simply and effectively recover the pristine CNTs. (Scheme 23b).^[110]

Once established the control over the synthetic strategies for the preparation of CNT-rotaxanes with different macrocycle motifs, the most promising applications of the MINTs have been recently explored.^[108,109] Thus, the MINTs have proved to be promising architectures for the reinforcement electrospun polystyrene fibers when they are used as polymer fillers.^[109] As a matter of fact, just by adding 0.01 wt.-% of MINTs to the polymer, an increase of the Young's moduli and tensile strength of up to 200 % was observed.

More recently, MINTs have been used as catalysts.^[108] In this work the authors have reported the control of the catalytic activity of SWCNTs towards the reduction of nitroarenes by the encapsulation of the CNTs with different types of n- or p-doping macrocycles forming MINTs.

5. Conclusions

The combination of different types of carbon nanostructures and mechanically interlocked molecular architectures has been reviewed here. The examples discussed highlight the important role of C₆₀ as an electron-acceptor unit in mechanically interlocked donor-acceptor systems, as a unit able to induce submolecular motion and also as template in the synthesis of rotaxanes. Also, the recent incorporation of SWCNTs into mechanically interlocked molecular architectures have shown that SWCNTs are a promising template to prepare complex architectures with rings of different nature that can further modify and enhanced the existing properties of SWCNTs.

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