Putting Rings around Carbon Nanotubes

Emilio M. Pérez

Ringing carbon nanotubes

Emilio M. Pérez*

Abstract: In the last five years, we have developed synthetic methods towards encapsulation of single walled carbon nanotubes (SWNTs) into organic macrocycles, to form rotaxane-type molecules. These are the first examples of mechanically interlocked SWNTs derivatives (MINTs). In this article, I discuss our motivation to continue developing chemistry of SWNTs at a time well past their hype. I explain our synthetic strategy and characterization methodology in detail, stressing the general aspects. In particular, I emphasize the importance of adequate control experiments and bulk spectroscopic and analytical data to determine the structure of SWNT derivatives, as opposed to relying only (or mostly) on microscopy. I also use our experimental results as pretext to reflect on more general/conceptual issues pertaining the chemistry of SWNTs and mechanically interlocked molecules.

Introduction

Carbon nanotubes (CNTs) are one of the most promising nanomaterials. Seriously, they still are. After graphene made its flamboyant entrance,[1] Nobel Prize and all,[2-3] followed by a cohort of other bidimensional materials,[4-5] and their mixtures,[6-8] it would seem like CNTs are shying away from the research spotlight, but CNTs still have all the amazing properties that made them candidates to build anything and everything, including a space elevator!

Their extraordinary mechanical properties are still there. Their electronic properties, starring a well-defined bandgap that graphene would die for[9] in semiconducting single-walled carbon nanotubes (SWNTs), are also still there. However, it is only recently that synthetic[10] and purification[11-15] methods have evolved sufficiently to produce affordable samples of CNTs with high purity and homogeneous structural and electronic properties: narrow diameter and length distribution, metallic or semiconducting, or even single-chirality SWNTs.[16-17] Yaw-dropping applications go hand in hand with these synthetic advances.[18] For example, Prato, Ballerini and co-workers are closer and closer to healing spinal cord injuries using implants in which polymer-CNT composites serve as scaffolds to reconnect spinal tissue.[19] Meanwhile, Shulaker et al. have fabricated a working computer based entirely on CNT transistors,[20] and Arnold and co-workers have proven that SWNTs can indeed outperform silicon as semiconducting material in field effect transistors (FET).[21] So CNTs are far from scientifically dead. In fact, none less than Pulickel Ajayan has argued that “now is the best time to work on CNTs”.[22] We do. And that is why I am writing this.

[a] Prof. E. M. Pérez*
IMDEA Nanociencia
Faraday 9, Ciudad Universitaria de Cantoblanco
28049 Madrid, Spain
E-mail: emilio.perez@imdea.org
Twitter: @emiliomperezlab
Web: http://nanoscience.imdea.org/chemistry-of-low-dimensional-materials/home

In particular, we work on developing methods for the chemical modification of SWNTs that combine the best of the covalent (stability) and noncovalent (structural integrity) worlds. We are interested in decorating SWNTs with organic macrocyclic rings, to make rotaxane-type species that we call “mechanically interlocked derivatives of SWNTs”, with a lovely acronym: MINTs.[23] In this Concept article, I will discuss the most relevant aspects of the design, synthesis, characterization, and plausible applications of MINTs.

Why? Covalent chemistry, supramolecular chemistry, and the mechanical bond

SWNTs were first described in 1993,[24-25] and chemists immediately started working on them to soften their sharp edges. There were two tools for the chemist to throw at SWNTs back then: good ol’ covalent chemistry and supramolecular chemistry, which had just earned Cram, Pedersen and Lehn the Nobel Prize in 1987.[26-28] In the covalent chemistry arena, the Haddon group was the first to treat SWNTs with strong mineral acids (H_2SO_4/HNO_3), which results in oxydation of the SWNTs tips to introduce numerous oxygen-containing functionalities, most of which are carboxylic acids. The carboxylic acids can then be manipulated to form amides.[29] The oxydation/amidation or oxydation/esterification protocol remains one of the most popular methods for the chemical manipulation of SWNTs.[30] Direct addition to the SWNT walls is also possible. To name some notable early examples, Haddon’s group described the addition of carbenes to SWNTs,[31] while Hirsch’s reported on the addition of nitrenes, anionic carbenes and radicals,[32] Prato’s on 1,3-dipolar cycloadditions,[33] and Tour’s on their direct arylation through diazonium coupling.[34]

At around the same time, Weisman and co-workers used supramolecular chemistry to disperse individual SWNTs in water with the help of surfactants. The individualization of the SWNTs allowed for the identification of more than 30 individual SWNT chiralities using photoluminescence excitation (PLE) spectroscopy, arguably one of the most significant feats in the characterization of SWNT.[35] Dai’s[36] and Nakashima’s[37] reports on the use of pyrene as a noncovalent anchor to attach functionality to SWNTs were the debut of what would become the workhorse of the supramolecular chemistry of SWNTs.[38]

The advantages of using covalent chemistry for the functionalization of SWNTs are quite clear: it is usually based on well-known reactions, in most cases previously tested on fullerenes,[39] and the products obtained are typically (not always!)[31] very stable. The main disadvantage, on the other hand, is that making covalent bonds to SWNTs necessarily implies a modification of their native structure, from which all their outstanding properties are derived. Although the change in structure/properties need not be necessarily detrimental,[40] it is in principle counterintuitive to praise SWNTs for their unique structure and then meddle with it. Which leads us to the main advantage of using supramolecular chemistry, its complete respect for the SWNTs’ native structure. On the negative side, supramolecular constructs are inherently labile, so the

functionalization can be lost at later stages, for instance during device fabrication. To circumvent this problem, Stoddart and co-workers have reported on a variety of devices in which SWNTs were functionalized *after* fabrication,[38] but most often, chemical modifications are the first step towards active materials.

A few decades before these developments on the covalent and supramolecular chemistry of SWNTs took place, an entirely new type of bond, the mechanical bond, was born[41] and raised.[42-43] Mechanically interlocked molecules (MIMs) are composed of different parts that are linked together as a consequence of their topology, so that separating them implies the breaking of the covalent structure of at least one of the constituents. Rotaxanes are archetypical examples of MIMs in which one or more macrocycles encapsulate a dumbbell-shaped thread, from which they cannot detach due to the presence of bulky "stoppers" (Figure 1).[44]

The main driving force in MIMs research has been using the dynamic nature of the mechanical bond to synthesize molecular machinery, a fascinating field that has very recently been recognized with the Nobel Prize in Chemistry 2016[45] to two MIM pioneers, Jean-Pierre Sauvage[46] and Sir J. Fraser Stoddart,[47] together with the most notable non-MIM molecular machinist, Ben L. Feringa.[48] However, the mechanical bond has another very interesting feature: it can be used to connect two covalent entities very intimately, with stability equal to their weakest covalent bond, *and* without modifying their structure.

So this was our initial idea: to use SWNTs as threads to make rotaxane-type derivatives in which macrocycle and SWNTs are mechanically interlocked (MINTs, Figure 1), taking the best of both the covalent and the supramolecular worlds.[49]

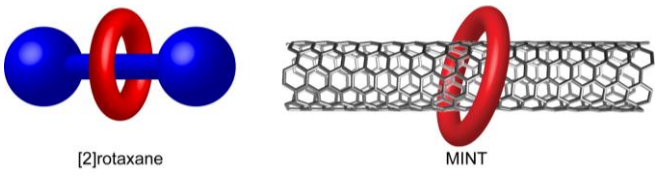

Figure 1. Cartoon of a [2]rotaxane: the red macrocycle remains on the blue thread thanks to the presence of the bulky stoppers at its ends. Cartoon of a MINT: experimentally, the SWNT thread is so long that no stoppers are needed to prevent the macrocycle(s) from falling off (see main text). In that way, the red macrocycle and the SWNT thread are intimately but respectfully linked.

How? Nano-horseshoe throwing: the clipping strategy

If you want encapsulate SWNTs in a synthetically viable organic macrocycle, they'd better be thin (diameter ≤ 1nm). The purest and most affordable samples that meet this requirement are (7,6) or (6,5)-enriched CoMoCAT® SWNTs, which show diameters around 0.9 and 0.8 nm, respectively, and lengths in the μm range. With this extreme aspect ratio, and the tendency of SWNTs to bundle up, it is no surprise that under transmission electron microscopy (TEM) it is nearly impossible to locate their tips (Figure 2a). This suggests that direct threading of SWNTs through previously formed macrocycles is perhaps not the best plan to synthesize MINTs. However, in the same picture, it is common to find sections of individualized SWNTs, which would be available for association by adequate U-shaped molecules that could later be closed around them following a classic "clipping" strategy for the synthesis of rotaxanes (Figure 2b). To introduce recognition elements for SWNTs that facilitate the association of the U-shaped molecules, we have focused on a simple, symmetric design, in which two recognition units are linked through an aromatic spacer, and subsequently decorated with alkene terminated alkyl spacers. The long alkenyl chains provide the flexibility and the functionality to close the U-shapes around the SWNTs via ring-closing metathesis (RCM). We have initially focused on molecules that were already known to associate SWNTs, such as electron-donor π-extended derivatives of tetrathiafulvalene (exTTF)[23, 50] electron-acceptor naphthalene diimides (NDI),[51] and electronically "neutral" pyrenes (pyr).[52] So the idea is relatively simple, let's see how it works, and more importantly, how we can prove that it works.

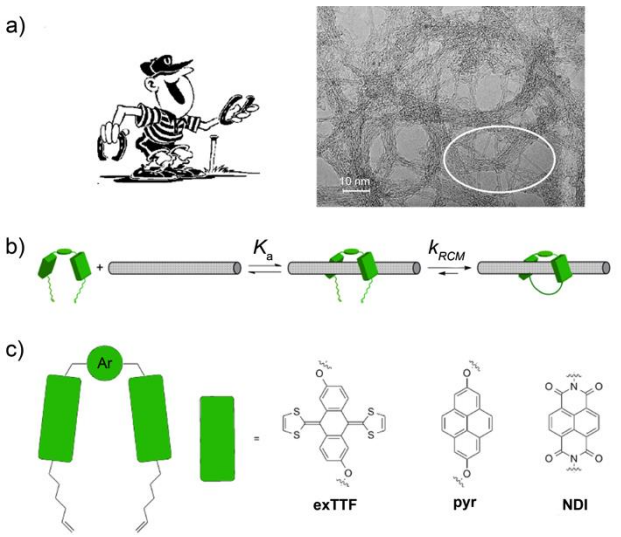

Figure 2. a) Nano-horseshoe throwing: several areas of the TEM image show sections of individualized (6,5) SWNTs, one of them is highlighted with a white elipse (TEM image from SigmaAldrich Co.). b) Clipping strategy for the synthesis of MINTs: U-shaped molecules featuring two units of a recognition motif for SWNTs are allowed to interact with them via a supramolecular equilibrium, governed by its association constant (K_a), the associates are then stitched around the SWNTs via RCM, a process which shows pseudo-first order kinetics (k_{RCM}). c) Schematic structure of the U-shaped molecules and some of the recognition motifs that we have used so far to synthesize MINTs, including electron donor **exTTF**,[23] electron acceptor **NDI**,[53] and electronically neutral **pyr**.[52]

The characterization challenge: comparing cartoons to reality

Experimentally, nano-horseshoe throwing is rather simple. We suspend SWNTs in an adequate solvent (usually tetrachloroethane, TCE, or dimethylformamide, DMF) using ultrasonication, then add a solution of the U-shaped host and

Grubb's 2nd generation catalyst. We let this mixture stir at room temperature for 48-72 hours, and then filter it through polytetrafluoroethylene membranes of 0.2 µm pores. Since U-shape, catalyst, non-threaded macrocycles, U-shape oligomers formed in-situ, etc. are all very soluble in organic solvents, we then wash the solid profusely with dichloromethane (DCM) under ultrasonication, filter, wash, filter, wash, etc. The final solid contains only SWNTs and whatever is very tightly attached to them. Thermogravimetric analysis (TGA) shows that organic material remains attached to the SWNTs after this treatment. More importantly, it shows that there is a direct relationship between the size of the cavity of the macrocycle, the diameter of the SWNT, and the loading of organic material. *And* it also shows that the functionalization remains stable even after boiling in TCE for 30 min and repeating the purification procedure. Control experiments without Grubb's catalyst with either the U-shaped molecules or the preformed macrocycles show very little functionalization, proving that direct supramolecular attachment and/or threading is highly unlikely. So whatever is stuck to the SWNTs requires Grubb's catalyst to get attached, it is very firmly anchored, and there is more of it if macrocycle cavity and SWNT diameter match.[23, 54] Raman spectroscopy shows that the functionalization is noncovalent (no increase in the relative intensity of the D band with respect to the G band), and solid state NMR shows signals that correspond to the macrocycle (or indeed the U-shape, or oligomers of the U-shape).[55] So far, so good. But obviously not good enough.

If we go back to our clipping strategy (Figure 2b), there formation of MINTs relies on two steps: a supramolecular association, and a covalent bond formation. Luckily, both of them can be measured separately and directly from bulk data. The first one is a supramolecular binding equilibrium. Unfortunately, after nearly 15 years of supramolecular chemistry of SWNTs, there was no standard method to measure association (or adsorption, if you will) constants (K_a) towards nanotubes. The problem is that the inhomogeneity and insolubility of the SWNTs samples prevents determining their exact molar concentration, so standard titration experiments to determine K_a are no good.[56] As supramolecular chemists, this was a challenge that excited us. So we went back to basics: Connor's "Binding Constants. The Measurement of Molecular Complex Stability".[57] The first thing you come accross is that the simplest form of the standard 1:1 binding isotherm depends on the concentration of free host *only* (Equation 1).

$$\theta = \frac{K_a \times [\mathrm{H}]_{free}}{1 + K_a \times [\mathrm{H}]_{free}} \text{ (eq. 1),}$$

where θ is the fraction of occupied binding sites.[58]

No need to know the total concentration of host. In fact, classic titration methods were developed because it is next to impossible to determine the concentration of free host in solution. "In solution", that is the key. In supramolecular equilibria involving SWNTs, it is safe to assume that both free and bound SWNTs are in suspension, and can therefore be precipitated by centrifugation or directly filtered, to separate them from the solution, where...only the free host remains! So you just need to run several experiments varying the initial concentration of the host, filter, measure the concentration of free host in the filtrate, plot your binding isotherm, and calculate K_a. As usual, experiments are not quite that straightforward. Turns out it is actually easier to measure the concentration of bound host attached to the SWNTs by TGA, and then calculate the concentration of free host by subtraction (mainly because small SWNTs and/or other carbonaceous impurities in the SWNT sample get in the filtrate). There is one more assumption to be made: the surface of the SWNT exposed to solution has N binding sites available, each of which can only be occupied by one host molecule (Figure 3). In other words, the stoichiometry is necessarily 1:1. Much to our advantage, this assumption can be proven right or wrong by simply looking at the shape of the binding isotherm, which will look like a square hyperbole, Langmuir-type binding isotherm, if our approximation is correct. We have shown that this method works well for measuring binding constants in the 10-10^4 M^{-1} range.[59] Of more relevance to the subject in hand, we have shown that our U-shapes do associate SWNTS, and they do so with respectable binding constants around 10^3-10^4 M^{-1} in several organic solvents at room temperature (Figure 3). So the first part of the MINT formation reaction (Figure 2b) is experimentally proven.

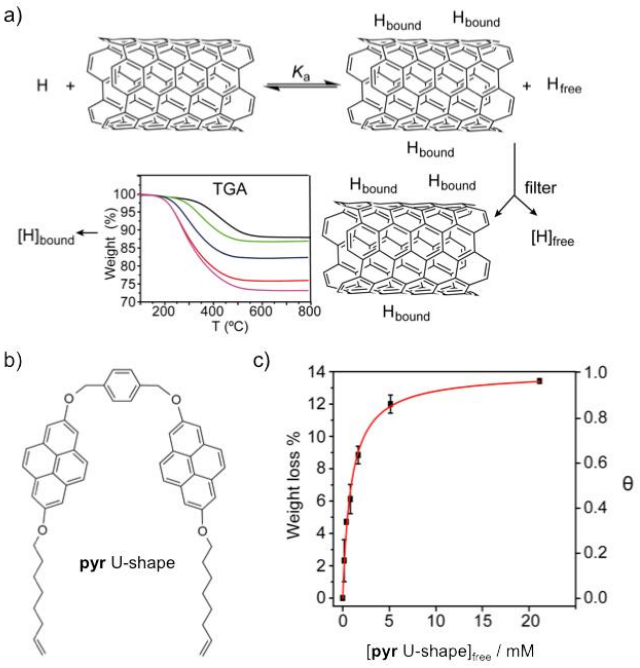

Figure 3. a) Procedure for the measurement of $[H]_{bound}$ and $[H]_{free}$. A known concentration of host L and SWNTs are allowed to reach equilibrium, and then complex and free species are physically separated through filtration. The concentration of $[H]_{bound}$ is measured by TGA (typical results for a real titration experiment described in ref. [59] are shown). The concentration of $[H]_{free}$ can then be calculated by subtraction or directly measured in the filtrate. b) Chemical structure of one of the pyr-based U-shapes that we have used to synthesize MINTs.[52] c) Binding isotherm for the pyr U-shape depicted in b in THF at room temperature, which affords $K_a = 7 \pm 2 \times 10^3$ ($r^2 = 0.951$).[59]

The covalent part of the MINT-forming reaction seems more troublesome. As immediately pointed out by referees of our first communication, under RCM conditions, bisalkene molecules can react both to form the macrocycle or through acyclic diene metathesis polymerization (ADMP) to form oligomers of the U-shape, which might attach to the SWNT particularly strongly, as many other oligomers/polymers do, most notably single-stranded DNA[12] and fluorene-based polymers.[60] To complicate matters further, all the spectroscopic data for the possible oligomer of the U-shape conjugates with the SWNT are expected to be very similar to MINTs.

The good news is that we can differentiate RCM from ADMP by looking at the kinetics of formation of the product. RCM is known to follow pseudo-first order kinetics, while ADMP is expected to be (at least) second order in bisalkene.[61] So we went on to analyse the kinetics of the synthesis of MINTs. The results, shown in Figure 4, clearly demonstrate that the rate-determining step to form our products is RCM and not ADMP. So, the second part of the clipping scheme is also proven experimentally, and, much to our delight, strictly from bulk data.[54] Remarkably, we have later learned how to induce substantial oligomer formation, either by increasing the amount of catalyst,[54] or by using NDI-based U-shapes under adequate conditions,[53] and we have identified the differences with the pure MINT products in TGA (Figure 4b).

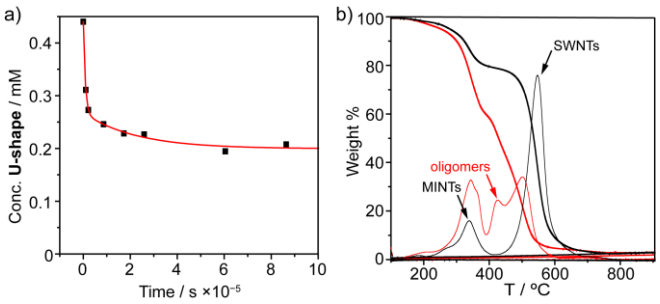

Figure 4. a) Kinetic profile for the formation of MINTs (black squares), and its fit to a pseudo-first order kinetics model (red solid line). b) TGA of MINTs (black lines) and a mixture of MINTs with oligomer-wrapped SWNTs (red lines), synthesized by increasing the amount of catalyst. Thinner lines show the derivative of the TGA curves, and are assigned to the different products in the mixture by comparison with adequate control experiments.[54]

Seeing is believing... or is it?

In the previous section, we have shown that the final products of our clipping reaction are indeed (mostly) MINTs. We have based our conclusions on techniques that explore the bulk sample, and which require little to no sample preparation, but that are directly connected to the mechanism of formation of MINTs. In this section, we will discuss the advantages and disadvantages of transmission electron (TEM) and atomic force (AFM) microscopies for characterization, and show some our best TEM micrographs of MINTs.

The typical procedure we use to prepare of a sample for TEM or AFM analysis involves sonication in a solvent to disperse the nanotubes, often complemented with centrifugation, followed by deposition on the TEM grid or substrate for the AFM, mica in our case, by direct dropcasting, spincoating, or by suction filtration, and finally drying of the sample. In our (limited) experience, the final results depend crucially on the sample preparation. That is, for the same sample, with identical spectroscopic and analytical data, you will observe anything from heavily bundled to nearly completely individualized SWNTs. If your interest is in the structure of the possible attachments to the SWNTs, bundling will limit the number of accessible nanotube walls you observe in TEM and will result in huge shades in AFM that will prevent extracting conclusions, so we *have* to focus on individualized SWNTs. More often than not, these represent a small percentage of the sample, particularly in TEM, where the low contrast of C requires the use holey TEM grids, so that only relatively large SWNT conglomerates remain on the grid after deposition. The AFM samples present their own challenges, including residual solvent (or solvent impurities), contamination (dust specks, skin flakes, etc.), and substrate-sample adhesion issues. All of these can be moderated, mostly using trial and error, but are nearly impossible to suppress completely.

Come to the microscope, and issues keep arising. In TEM, the main one is the stability of the sample under electron beam (e-beam) irradiation. SWNTs are particularly stable forms of C, due to their extended π-conjugation, but most organic molecules, including our macrocycles, decompose rapidly under e-beam irradation at voltages ≥ 80 kV,[62] so we are limited in voltage, and hence in resolution.[63] With the right microscope, and perhaps more importantly, with the right microscopist, you can still obtain absolutely outstanding TEM micrographs down (or close) to atomic resolution. The group of Nakamura has been one of the pioneers in observing organic molecules in or around SWNTs under TEM.[64] The group of Khlobystov in Nottingham has also provided brilliant examples.[65] But the size of the problem is perhaps best exemplified by the size of one of the solutions thrown at it, the Sub-Angstrom Low Voltage Electron microscopy (SALVE) project, based in the University of Ulm.[66]

In our case, the nanotubes we use, (6,5) or (7,6)-enriched SWNTs, are particularly thin, and hence more sensitive to the e-beam, the macrocycle(s) are placed around the SWNTs, directly exposed to the e-beam, and the degree of functionalization is rather high (around one macrocycle every 400-800 SWNT C atoms, depending on U-shape and conditions)... so no, it is not easy to spot individual macrocycles around SWNTs in MINTs e-photocalls. Nevertheless, we have succeeded enough to make some pretty slides that are consistently the ones that get more attention at conferences. Figure 5 shows some of our best EM images to date. In figure 5a, four segments of individualized SWNTs around which at least five approximately circular objects of adequate size to be the macrocycle are clearly visible (red circle). Besides these, the image also shows much uglier areas, which correspond to bundled and damaged SWNTs, solvent residues, and/or unknown impurities, and will be familiar to anyone who has ever recorded TEM images of SWNTs (Figure 2a, for instance). Figures 5b and c are higher magnification TEMs, this time focusing on individual macrocycles around SWNTs. Note that the walls of the SWNT in Figure 5c are

already starting to wriggle and wrinkle under the e-beam, so the macrocycle is most likely damaged too. Finally, figure 5d shows an aberration-corrected STEM image of two exTTF macrocycles around a (7,6) SWNT. In this case, the irregular shape of the macrocycles and the parts on top and below the macrocycle are clearly distinguishable. With these micrographs, the formation of rotaxane-type MINTs is proven beyond reasonable doubt...but they are just a complement, the cherry on the cake of the control experiments and the bulk data described in the previous sections. Without them, they would be meaningless, because they depend heavily on sample preparation and are necessarily very local, so they don't represent the whole sample.

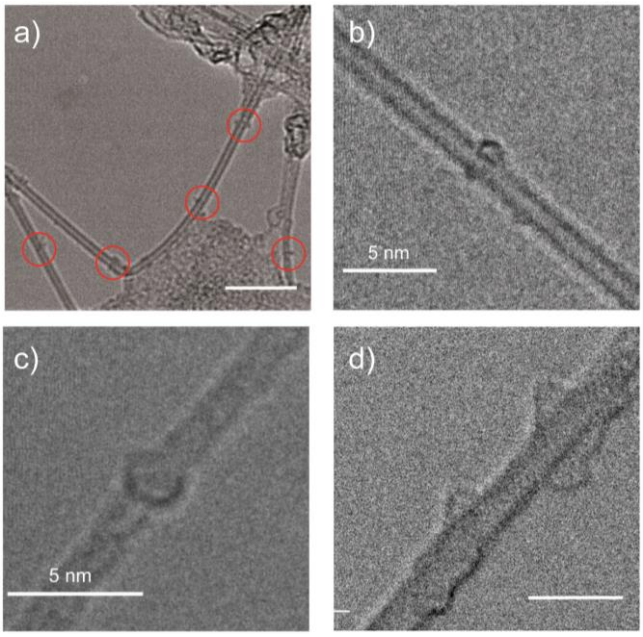

Figure 5. Some of our best EM images of MINTs to date. All correspond to exTTF-based macrocycles. Image a) shows a low magnification TEM image, in which up to five different macrocycles are visible (red circles). Note that large areas of the image correspond to bundled SWNTs, solvent residues, and/or unknown impurities. b-c) High magnification TEM images of individual macrocycles around SWNTs. d) Aberration corrected HR-STEM image of two macrocycles around a (7,6) SWNT. Scale bars are a) 20 nm; b and c) 5 nm; d) 2nm. The sizes of all macrocycles are commensurate with the expected dimensions...but are they still macocycles after e-beam irradiation?

Where are the stoppers? Are MINTs rotaxanes or pseudorotaxanes?

At first sight, the difference between rotaxanes and pseudorotaxanes is the presence or absence of stoppers. But is that really the key? If we systematically decrease the size of the stoppers, when does a rotaxane become a pseudorotaxane? A few years back, Schalley and co-workers addressed these questions experimentally.[67] Their findings proved that the kinetics of de-threading respond to a complex mixture of parameters, including the size and shape of the stoppers, the length of the thread, the affinity between thread and macrocycle, etc. So it is not easy to discern between rotaxanes and pseudorotaxanes based on the size of the stoppers, or, ultimately, their presence. In fact, regardless of the presence of stoppers, rotaxanes are *not* MIMs from a mathematical standpoint, as their topology is trivial, and identical to that of pseudorotaxanes (or any other macrocycle host-guest complex, for that matter).[68] The chemical translation of the mathematical terms, however, is quite straightforward. Two objects are topologically identical if they can be transformed into one another by compressing and/or stretching, without cutting and/or pasting. In chemistry terms, if separating the macrocycle and thread requires breaking at least one covalent bond (i.e. "cutting"), we are talking of a rotaxane and we can consider it a MIM. If macrocycle and thread can be dissociated without breaking a covalent bond (at any temperature and rate), we are talking of a pseudorotaxane. Therefore, we believe a solid criterion to decide if species are mechanically interlocked is the integrity of the covalent connectivity of the constituent parts *after* separation.[69]

Experimentally, we have only been able to separate macrocycles and SWNTs in MINTs by calcination of the macrocycles. We have proven that the main reason behind it is the extreme length-to-diameter ratio of the SWNTs we use for the synthesis of MINTs (typically tens of µm long). Shortening the SWNTs by oxydation to 0.2-5 µm leads to a substantial decrease in MINT formation. We have also shown that the reverse process, threading of the SWNTs by preformed macrocycles is next to impossible.[23] Taking all this into account, we believe that MINTs are better defined as rotaxanes (and MIMs) than as pseudorotaxanes.

Possible applications of MINTs: polymer fillers, catalysis, sensors, ...and molecular machines

With the synthetic and characterization routes of MINTs established, the next logical question is: are MINTs any use? How do they compare to covalent and supramolecular derivatives of SWNTs? This is the main problem we are working on right now, and our first results seem promising.

One of the fields where SWNTs have excelled is as fillers in polymer-SWNT composites.[70] The main idea behind is to combine the mechanical and/or electronic properties of the SWNTs with the processability of the polymers. That is, to make polymers stronger and/or conductive by adding small amounts of SWNTs. In the reinforcement area, the key parameter for the polymer to make the most of the nanotubes' extraordinary mechanical strength is the polymer-SWNT interface. Ideally, the polymer chains should align along the SWNT longitudinal axis, and interact strongly with its walls.

In collaboration with Dario Pisignano and Juan J. Vilatela, we have recently shown that the encapsulation of SWNTs to form MINTs results in significant improvements in the reinforcement of electrospun polystyrene (PS) fibers.[71] In fact, the Young's moduli and tensile strength were bettered up to 200% in the PS-MINT samples, with just 0.01 wt.% of MINTs. More importantly,

supramolecular models with *identical* chemical composition and loading had no effect, or even weakened the final fibres. To make sure our observations were due to the topology of the MINT samples, we tested combinations of two different macrocycles (**exTTF** and **pyr**) and three different SWNT samples, and the reinforcement is consistently observed for the MINTs only (Figure 6). That is, a change in topology from non-interlocked supramolecular compounds to MINTs results in a major change in macroscopic properties! Molecular dynamics simulations allowed us to understand such delightfully surprising results. Upon interaction with the MINT fillers, PS adopts an elongated conformation parallel to the SWNT, independently of the chemical nature of the macrocycle. In contrast, when faced with the supramolecular models, PS adopts a more globular structure, which prevents the polymer from benefitting fully of the SWNT longitudinal properties.

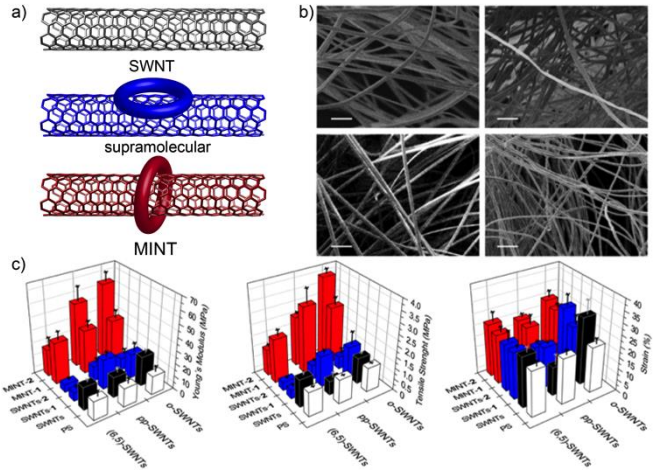

Figure 6. a) Cartoons showing the structure of the fillers tested. The supramolecular and MINT fillers contain the same amount of organic macrocycle b) SEM images of the electrospun fibers. Left to right and top to bottom: pure PS fibers, with SWNTs filler, with MINT filler, and with supramolecular filler. All scales are 10 μm. c) Measurements of the Young's moduli, tensile strength, and strain to break. Note that the MINT samples (in red) show consistently larger Young's moduli and tensile strength, compared to pristine PS (white), SWNT filler (black), and remarkably, also to supramolecular complexes (blue). This effect holds true for two different types of macrocycles and three types of SWNTs, so the effect can be safely attributed to the topology of MINTs.

Conclusions

The development of synthetic methods for MIMs and the study of their properties, including the design of molecular machinery, is one of the most attractive areas of noncovalent chemistry (at least from my heavily biased perspective). Very recently, the area has started to move beyond small-molecule MIMs, to the synthesis of mechanically interlocked materials, including polymers[72] and MOFs.[73] The synthesis of MINTs developed by our group is the first application of the mechanical bond to the chemistry SWNT. In this concepts article, we have dealt with why and how to put organic rings around SWNTs.

We have also dedicated a significant portion of the article to characterization. In that sense, as synthetic chemists dealing with inherently impure and inhomogeneous SWNTs samples, we have dedicated our best efforts to obtain and analyze data that represent the whole sample. The reader might have been surprised by the relatively little importance that we have given to the microscopic characterization. We did not mean to disrespect the techniques, much less a community of scientific colleagues that have produced astonishing advances. We just wanted to highlight that very local techniques are adequate to address very local problems, in the single or few molecule limit, but are perhaps not the best choice for chemical characterization.

Finally, we have also shown evidence that MINTs show distinct properties from supramolecular SWNT complexes. This is not at all new in the chemistry of MIMs, but is particularly exciting for the case of SWNTs, and might be applicable in areas where other types of chemical functionalization have not succeeded (or not entirely).

Our eyes are now set on the development of other applications for MINTs, and the construction and operation of MINT-based molecular machinery, for which we have some not entirely crazy ideas...but that is another story and it will be told in a different place.

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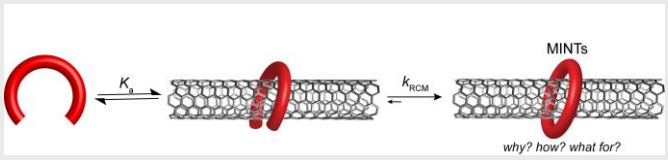

*E. M. Pérez**

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Putting rings around carbon nanotubes

If you liked'em then you should've put a ring on them! We discuss why it is interesting to make rotaxane-type derivatives of SWNTs, how to do it, and what they might be useful for.