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*Chapter 11*

**FLUORINATED CARBON NANOTUBES:  
STATE OF THE ART, TRENDS AND  
ADVANCED CONCEPTS**

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**ABSTRACT**

The present contribution details, in an as exhaustive as possible way, the fundamental knowledge acquired on fluorinated carbon nanotubes (CNT), also termed fluorotubes. Since the discrete pioneering articles published in the field a bit more than 10 years ago, around 70 additional references have now appeared which bear witness to the dynamism of this emergent part of the chemistry of nanotubes. As a matter of fact, fluorination stands as the starting point for a great part of the modifications performed on CNT, rendering fluorotubes fundamental intermediates for the integration of CNT in the nanotechnology processes. Many synthesis routes use fluorotubes as precursors in view of the subsequent chemical derivatization of CNT, for instance. In parallel, several attempts of practical developments based on fluorotubes have also lately appeared throughout the literature, covering the tribology, nanocomposites, or electrochemistry sectors, which outline the potential interest of such fluorinated nanostructures. The first part of this chapter compiles the main knowledge reported to date on the subject throughout a still reasonable but increasingly abundant body of literature. The physicochemical properties and special characteristics of the C-F chemical bond in fluorotubes are critically analyzed in a second part, and the last section is devoted to some recent tentative applications and future concepts relating to the fluorination of carbon nanotubes. The present review is essentially depicted from the chemistry of materials standpoint. Some of the concepts illustrated throughout the text are enriched by a few works of unpublished data from our group.

## I. FLUOROTUBES - GENERAL ASPECTS

### 1. Introduction

The covalent addition derivatives of carbon nanotubes are much less diversified than those issuing from the parent fullerenes molecules. Owing to the macromolecular topology of the carbon edifice, a “rough” chemistry consisting of the random fixation of functionalities to the carbon substrate, in a more or less efficient and controlled way and often inducing defects in the continuity of the carbon frame, has succeeded to the fine methodologies employed to functionalize fullerenes. Nanotubes functionalization, most of the time, results from an oxidation of the carbon substrate in harsh conditions, from methods tested and validated decades ago on graphite, carbon fibers, or amorphous to semi-crystalline forms of carbon. Hence, the creation of the basic carbonyl, carboxyl, lactone or hydroxyl functions can be obtained upon treatment of carbon nanotubes with hot nitric acid or with hot aqueous solutions containing the permanganate, peroxodisulfate or perchlorate anions, or still with hydrogen peroxide. If oxygenation turns out to be rather easy, the halogenation of carbon nanotubes is more difficult to obtain, in spite of the strongly oxidizing character of halogen atoms, and only fluorine is known to directly and stably fix to such a carbon matrix. The fluorinated derivatives of carbon nanotubes, the so-called “fluorotubes”, have since proven to be of fundamental importance from both the chemistry of nanotubes and materials standpoints.

The present synthetic approach describes and analyzes the widely diversified classes of materials that arise upon fluorine addition to the different tubular carbon allotropes. The first part reviews the main results reported hitherto concerning the synthesis, structural aspects and physico-chemical properties of both single-walled and multiwalled fluorotubes. The characteristics of the C-F chemical bond in fluorotubes will be analyzed in a second part and the last section of this chapter will be devoted to a prospective overview of the potential valorization of fluorotubes. Further research in the present field would preliminary require a perfect knowledge of the unexpectedly complex nature of the fluorinated derivatives of carbon nanotubes, which is far from being acquired hitherto, as will be shown from a critical analysis of some previously published data.

### 2. Synthesis of Fluorotubes

*Single wall nanotubes:* The fluorination of single wall carbon nanotubes (SWNTs) is usually carried out by direct reaction with an atmosphere of gaseous fluorine, over temperatures ranging from 50 to around 300 °C [1-12]. The latter value is often recognized as the critical threshold before significant degradation of the tubes begins to manifest. Thus, beyond this limit, the introduction of surface defects [1,3] and even combustion may become important, in which case gaseous fluorocarbons will form. The whole set of results reported converge in the sense that, at constant reaction time, the F/C stoichiometric ratio increases in parallel with the synthesis temperature, and the maximum functionalization rate seems to be around 50 to 60%, i.e. C<sub>~2</sub>F.

Extremely efficient plasma fluorination techniques have been recently developed [13-16], allowing access within a few minutes to important fluorination levels. The most common fluorinating agents are  $\text{CF}_4$  or  $\text{SF}_6$ . Hence, such processes remain soft, limiting destruction of the tubular macromolecular edifices, and avoid the use of molecular fluorine, which is expensive and dangerous.

*Multiwall nanotubes:* Morphological differences between SWNTs and multiwall carbon nanotubes (MWNTs) are at the origin of a specific reactivity of each one in regard to fluorine. Hence, MWNTs appear more resistant than SWNTs regarding fluorination at high temperature, owing to their higher outer diameters which reduce the strain associated with the local curvature of the network. Their complete fluorination with an F/C ratio close to 1 has been obtained near 500 °C [17-19], at the expense of the creation of many defects and of a more or less pronounced structural disorder. Note that, in the present case, an insufficient fluorination time will yield surface fluorinated tubes only [19-21]. The use of powerful fluorinating agents such as  $\text{XeF}_2$  has been attempted [22], but similarly results in a partial fluorination, restricted to the outer surface. In parallel, the fluorination of MWNTs can also be performed at low temperature [17,18], following the catalytic process developed several decades ago for graphite [23] and based on the use of gaseous HF. Experimental details in the matter remain scarce, however, since only a few papers on the subject have been published so far [17-22].

### 3. Structure and Fluorination Mechanism

*Single wall nanotubes:* SWNTs represent the macromolecular form of fullerenes molecules. In spite of this direct filiation, the fluorination at high temperature of SWNTs yields covalent addition derivatives resulting from independent and nonhomogeneous addition patterns, in contrast to fullerenes molecules in which case regioselectivity is excellent [24]. The direct observation by scanning tunneling microscopy (STM) [2] of the surface of single-walled fluorotubes (F-SWNTs) indeed showed alternating fluorinated and non-fluorinated sections along the tube axis. The nanotexture is thus seemingly made of individual circular ribbons of F addends wrapping the circumference of each tube.

XPS is a major technique for surface analysis and consequently happens to be suited perfectly to the study of the surface composition of functionalized SWNTs, providing fine details about fluorine addition to SWNTs. Thus, whatever the final stoichiometry of the product and the synthesis route used, the  $\text{C}_{1s}$  XPS spectrum corresponding to F-SWNTs [6,7,10,11,15] typically consists of a first feature centred near 284.5 eV (see Figure 1). The latter is similar to the one present in the  $\text{C}_{1s}$  spectra of raw SWNTs and is therefore, related to bare “graphitic” carbon atoms. It is common knowledge that the  $\text{C}_{1s}$  core level energy undergoes a substantial primary shift in the presence of a strong electron-withdrawing element. Accordingly, the  $\text{C}_{1s}$  signal related to carbon atoms attached to one fluorine atom usually appears in the 287-289 eV binding energy range, with reference to standard tables. A second feature is then observed for fluorotubes in the corresponding region. It is also well established that the existence of carbon atoms not directly linked to a fluorine atom but having fluorinated nearest neighbors gives birth to a secondary shift of the  $\text{C}_{1s}$  energy, which, in the case of fluorotubes, splits the first “graphitic” signal into a second component lying at a

slightly higher binding energy ( $\approx 286$  eV). Complementarily, weak shoulders over the 291-293 eV energy range are always present and arise from  $>CF_2$  and  $-CF_3$  groups that forms on edges or at local defect sites. At last, XPS almost systematically detects a low atomic percentage of oxygen in both pristine and fluorinated carbon materials.

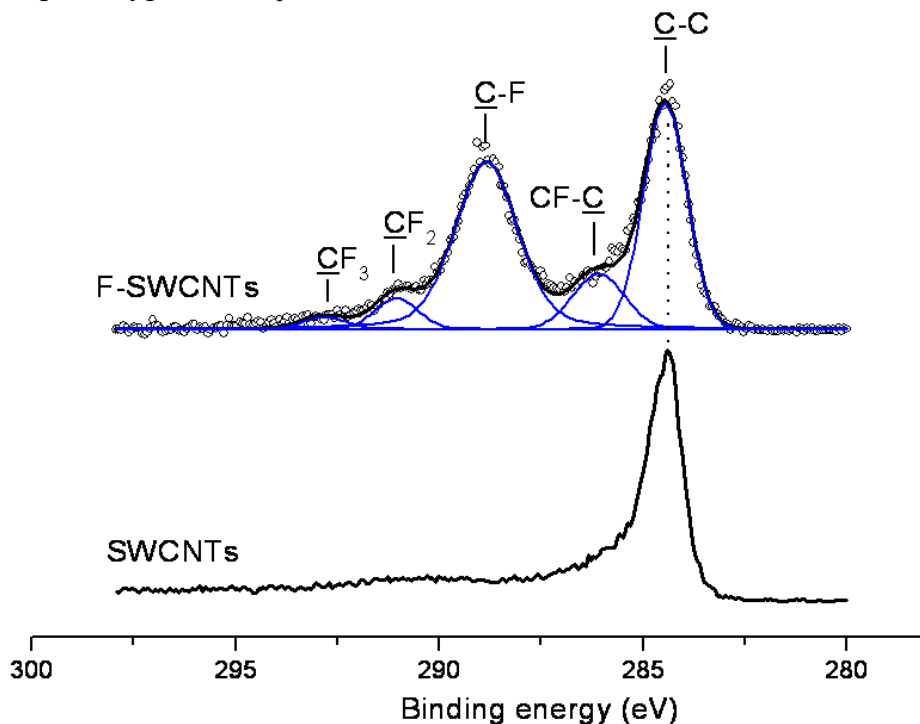


Figure 1. Typical C<sub>1s</sub> XPS spectrum of F-SWCNTs (here: CF<sub>0.5</sub>, obtained after 2 hours under a molecular fluorine gas flow at 300 °C).

The invariable nature of the XPS spectra of F-SWCNTs also reflects their texture at the nanometer scale and provides a compelling evidence of an inhomogeneous fluorine addition pattern, besides the direct view of this phenomenon by scanning tunnelling microscopy previously mentioned. Indeed, a uniform halogenation pattern with an F/C ratio close to  $\frac{1}{2}$  would constrain each carbon atom to have at least one fluorinated neighbor in its immediate surrounding, suppressing the photoelectron peak assigned to bare carbon atoms. The systematic persistence of the latter then necessarily implies a non homogeneous distribution of fluorine atoms along the longitudinal axis of a tube and the presence of fluorine depleted zones alternating with fluorinated sections.

The former experimental STM observation has seemingly provided support for a circumferential exo-addition pattern being the most probable architecture. Different regular exo-addition pathways may allow to reach the apparently optimal experimental C<sub>2</sub>F composition, but the conclusions of theoretical approaches on the subject [2,25-29], performed most of the time on virtual fragments of fluorotubes, exhibit too much divergence to shed light on the point here addressed. The results of computations are indeed highly dependent on the spatial extension of the system, its initial helicity/diameter parameters, the fluorination rate introduced and on the level of approximation. Somehow, at constant parametrization except fluorine location, the modest variations in energy from one model to

another probably reveal the thermodynamical origin of the random addition of fluorine to SWNTs. Lately, some experimental evidence in favor of 1-2 addition instead of a more exotic 1-4 pattern have been seemingly obtained throughout measurement of the  $^{13}\text{C}$  NMR chemical shift of F-SWNTs [30].

From the crystal chemistry standpoint, a high temperature fluorination process does not necessarily imply destruction of the bundle configuration, provided the latter was initially present within the pristine tubes sample, as shown on the following micrograph. The bi-dimensional cell parameter characterizing the compact triangular arrangement of the tubes becomes then notably expanded upon fluorine addition [7], independently confirming the location of some fluorine addends on the outer side of each tube.

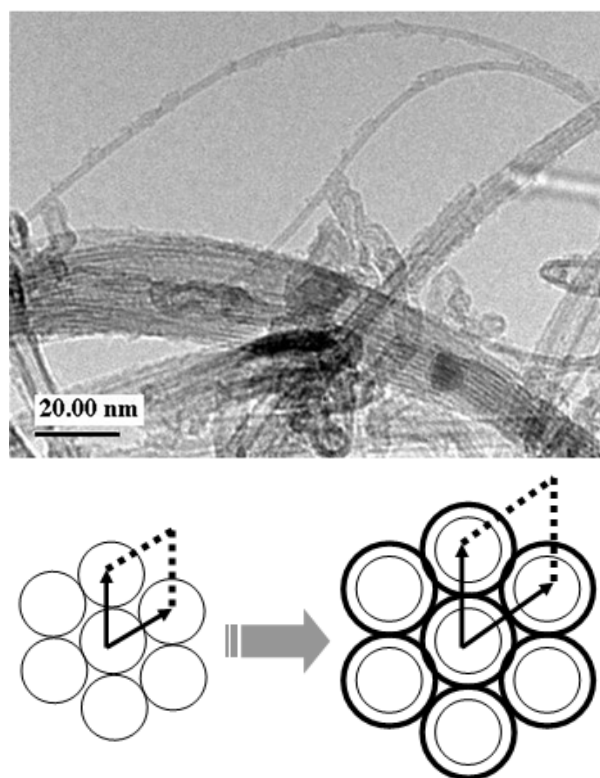


Figure 2. TEM observation of SWNTs bundles fluorinated at 300 °C for 2h.

Double-walled carbon nanotubes consist of two nested carbon cylinders. They represent the first step toward MWNTs. Their fluorination has been successfully achieved at room temperature via the use of a fluorinating agent [31,32], which represents much milder conditions than heating under molecular fluorine, but some authors reported that direct fluorination at 200 °C does not break the double-layered morphology [33]. Overall, their apparent fluorination pattern somewhat recalls the one of SWNTs, consisting of surface addends grafted to the outermost sidewall, but interestingly, the core carbon shell remains preserved. Indeed, the radial breathing mode characterizing the Raman signature of the inner shell is kept unchanged upon fluorination, indicating that addition is effective at the level of the outermost framework only. The evolution of optical absorption spectra upon fluorination

reinforces the former conclusion. These findings offer a soft transition toward the MWNTs case.

*Multiwall nanotubes:* In comparison to SWNTs, the reduced curvature within MWNTs diminishes reactivity, and the conditions required for fluorinating the latter approach those required to fluorinate their flat homologue, graphite. Hence, the formation of covalent fluoro-derivatives of MWNTs (F-MWNTs) necessitates significant thermal activation and fluorine atoms tend to graft to the sidewalls of multiwalled nanotubes from 300 °C, near the surface first. Higher temperatures (500-550 °C) can lead to the bulk fluorination of MWNTs [17-19]. The resulting fluorocarbon compounds still exhibit wiry imprints after undergoing such harsh conditions and their overall structure consists of a superposition of more or less fragmented fluorinated shells, some examples of which are displayed on figures 3 and 4. XRD usually shows still reasonably resolved (00l)-type Bragg peaks (see example, Figure 3) which reflect some degree of coherence in the stacking of the fluorinated shells. Their average separation becomes close to that characterizing the interlayer distance in the graphite fluoride (CF)<sub>n</sub>, obtained at 600 °C. Note that the final morphology turns out to strongly depend on the nature of the precursor MWNTs (Figure 3 and 4): the higher the rate of sidewall discontinuities in the pristine material is, the higher the disorder in the final fluorinated compound is. Accordingly, a well-ordered succession of fluorinated domains along both axial and radial directions can be obtained only by starting from a well organized MWNT. This has been tentatively explained through the “zipper” model [19], in which the fluorination mechanism is chronologically decomposed according to the following steps: i) Fluorination of the outermost sidewall, accompanied by radial inflation of the latter following change in the C/C bond order ii) Diffusion of F in the increased interlayer space with the underlying sidewall made possible, resulting in the attack of the latter by fluorine, on edge first iii) Radial inflation of the second outermost sidewall upon fluorination, inducing progressive cracking of the above fluorinated shell... and so on. Some authors consequently mentioned [21] that delamination of the outer fluorinated shells could occur in the course of progression of the fluorinated front.

Globally, essential divergences arise when comparing the high temperature fluorination of MWNTs and SWNTs. The maximum stoichiometry that is usually reported for F-SWNTs is close to F/C  $\approx$  0.5, whereas fluorination to saturation of the carbon shells occurs in the case of F-MWNTs, without degradation of the substrate. In the latter case, according to XRD, the microstructure locally looks like that of the graphite-derived phase poly-monocarbon monofluoride (CF)<sub>n</sub>, indicating that more or less ordered rolled perfluorographene sheets form. This consequently implies that both sides of the carbon shells must be fluorinated according to a regularly alternating inner/outer addition pattern. Note that partial fluorination rates, i.e.  $x < 1$  in the CF<sub>x</sub> formula, can also be obtained upon fluorination of MWNTs, but must be interpreted as the superposition of a set of completely fluorinated layers over a set of non-fluorinated carbon layers [19,20] (see an example Figure 4). Saturation with fluorine at the level of a layer is rigorously confirmed by XPS measurements performed on such phases [21], which do not exhibit the photoelectron peak typical of bare carbon atoms having fluorinated first neighbors (see peak assignment in Figure 1). In sharp contrast with MWNTs, the fluorination of SWNTs seems to take place on one side only, according to the current opinion, though this point needs to be addressed in more details in the following.

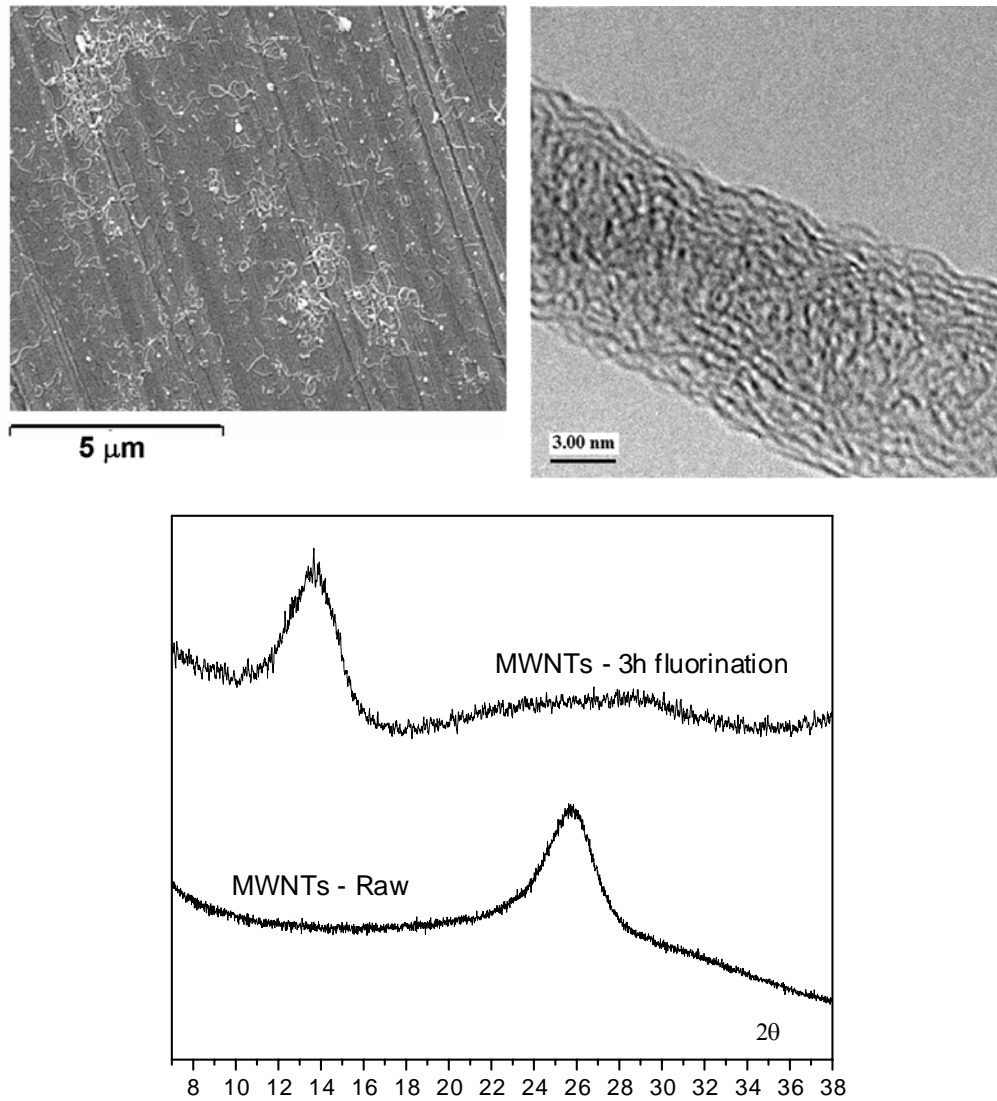


Figure 3. CVD-grown MWNTs fluorinated to saturation at 520 °C for 3h ( $F/C = 1.1$ ) - (Upper left) SEM observation: dispersion by spin coating from an ethanol suspension - (Upper right) TEM micrograph: lattice fringes provide evidence for some residual partial order in the stacking of the successive fluorinated layers - (Bottom) X-ray diffraction pattern ( $K_{\alpha Cu}$ ): the average intershell distance expands from 0.34 to about 0.65 nm upon fluorination.



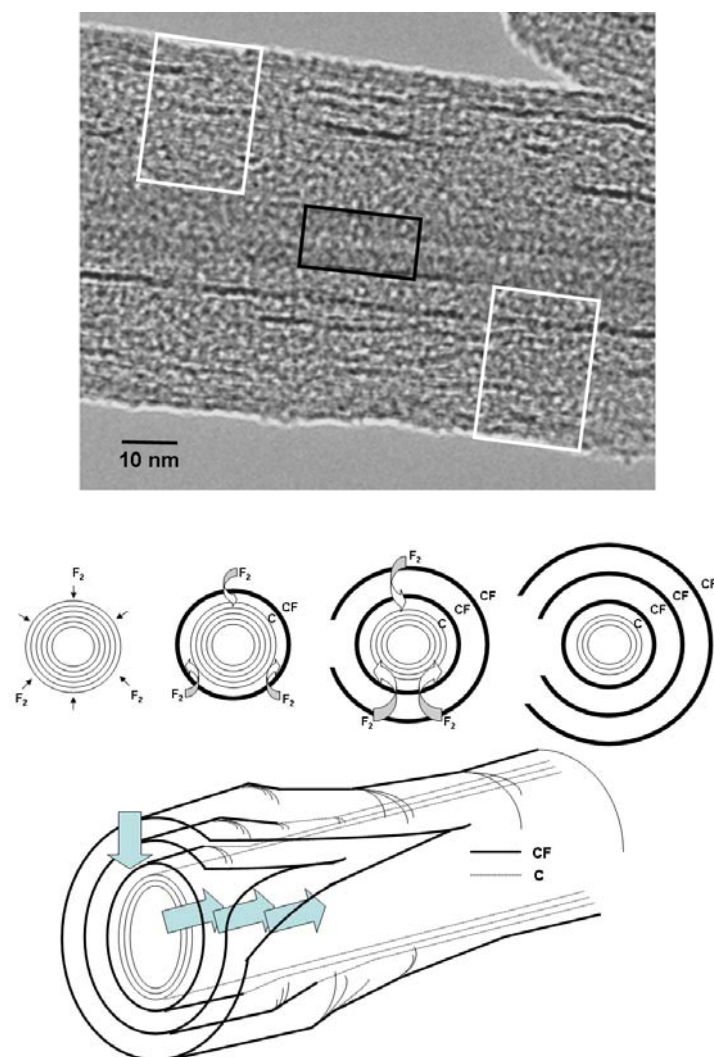


Figure 4. TEM micrograph showing details of a partially fluorinated MWNT - (Top) The black and white framed zones indicate fluorinated and non-fluorinated regions, respectively. The central channel of the tube can be easily distinguished - (Bottom) The “zipper” model: a layer by layer fluorination mechanism likely accounting for the formation of such organized F-MWNTs. The successive and progressive rips recall the opening of zippers. *Reprinted from ref. [19], with permission from Elsevier © 2008.*

In parallel, and adding further difference between the respective fluorination processes of SWNTs and MWNTs, multiwalled fluorinated products differing from the former covalent addition derivatives have also been observed. Two independent studies indeed showed [17,18] that the catalytically assisted low temperature fluorination of MWNTs gives birth to a surface fluorine intercalation phenomenon. It is characterized by an increase of the average intershell distance, while the initial stacking sequence seems preserved, as directly observed by TEM. This specific behavior is made possible when the topology of the carbon network is changed from single to multi-walled, creating an interlayer Van der Waals gap that affords accommodation of guest-species. Such a scenario requires some wall disjunctions to be

initially present or to be created in the course of the fluorination process, however, so that to allow local inflation of the structure upon intercalation of fluorine atoms [34]. Though the intercalation phenomenon remains limited to the most external shells in the present case, the formation of stages was even inferred by Nakajima et al. [17]. Indeed, the related X-ray signatures recorded presented a good analogy with those of the homologous phases obtained from graphite. Beyond 60 °C, the latter authors gave evidence for a quantitative diminution of the intercalation phenomenon, first evidenced by an increase of the stage number, and by further limitation of insertion to areas closer and closer to the outer surface above 100 °C.

#### 4. Physicochemical Properties

##### *a) Individual Fluorotubes*

*Stability:* From the thermochemical standpoint, fluorinated nanotubes constitute unstable entities in regard to their transformation into perfluoroalkanes. The expression of their overall unstable character is activated upon simple annealing. Thus, F-SWNTs simply lose part or all of their fluorine upon moderate heating in an inert atmosphere [8,11,12] but start to frankly decompose beyond about 300 °C under the form of gaseous fluorocarbons (mainly CF<sub>4</sub>) and COF<sub>2</sub> [9,35] (nanotubes always typically contain around 3% atomic oxygen before and after fluorination), turning back to damaged SWNTs. High temperature (>500 °C) pyrolysis results in short fragments of SWNTs [9], following gasification of the surface fluorinated sections.

In compliance with their synthesis temperature higher than that of F-SWNTs, F-MWNTs appear more resistant to thermal decomposition and show almost no degradation when annealed at reasonably high temperatures under inert atmosphere (see Figure 5). TEM observations on SWNTs fluorinated at 300 °C showed the starting coexistence of some multi-walled fluorinated phases [36], seemingly arising from the transformation of the single-walled phase, that further confirms that the multilayered state constitutes a better intermediate level of stability. Alternatively, F-SWNTs have even been observed to evolve toward multi-walled structures under simple extensive electron-beam irradiation in a TEM [36].

*Electronic structure:* Contrarily to fullerene molecules, the random addition that takes place on SWNTs renders the concept of an “electronic structure” somewhat meaningless. Indeed, anticipating any individual behavior implies to consider a unique residual conjugation scheme at the surface of an “addended” tube, which requires a regular isomeric structure of the carbon substrate plus a periodical distribution of motifs at its surface. Some theoretical investigations [38-40] have shown that in such conditions, the fluorination of SWNTs can open or close gaps in the band structure of the final material. This kind of approach suffers less from the level of approximation used than from its unrealistic confrontation with actual experimental results, since in practice, the former requirements can not be gathered. So far, the only practically useful data then lies in the prediction of a global lowering of the Fermi level [39] induced by the presence of fluorine. Hence, each fluorinated carbon nanotube individually constitutes a potentially oxidizing species. This draws a direct link with the electronic properties of the parent fluorofullerene molecules, well-known to be able to yield stable fluorofulleride anions [24].

Given the structural divergences previously evoked between F-SWNTs and F-MWNTs, differences in their respective electronic structures emerge. Thus, multiwalled fluorotubes should not exhibit electronic and macroscopic properties too different from those characterizing the analogous graphite-derived phase  $(CF)_n$ . However, this will only hold true for tubes saturated with fluorine and yet unexplored hitherto, the expected mixed properties of surface fluorinated MWNTs should be described on the basis of a two-phases model including the core and outermost levels of the structure.

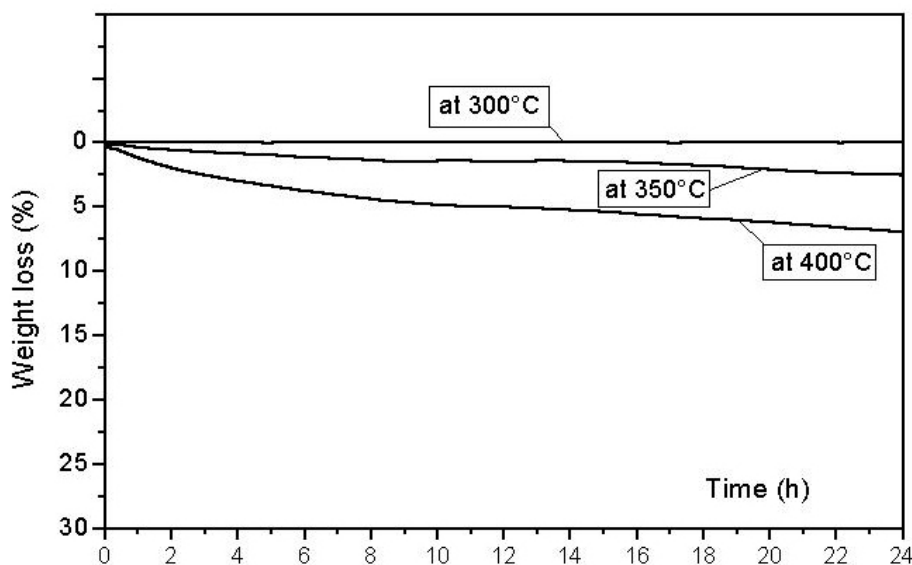


Figure 5. TGA curves (constant temperatures) illustrating the stability of the C-F chemical bond within a sample of F-MWNTs, bulk-fluorinated at high temperature (520 °C, here).

*Chemical bonding:* At this stage, we have to first point out that the forthcoming approach considers an average C-F bond, convenient for the purpose of generalization, but that, in practice, non-energetically equivalent C-F moieties should sometimes be distinguished, as detailed in a further section. Globally speaking, a weakening of the C-F bond strength occurs in curved fluorocarbon networks in comparison to conventional fluorochemicals, but the amplitude of variation will strongly depend on the characteristics of the carbon substrate. Thus, if the stability of different fluorinated carbon structures is compared, one essential factor strongly influencing the C-F bond strength intrinsically lies in the respective topologies of the carbon lattices considered. For instance, as clearly illustrated from figure 6, the evolution of the C-F stretching frequency in the IR region shows a concomitant decrease in the averaged bond strength with the radius of curvature of the carbon network. Admitting that bond strength also reflects absolute bond energy, the former phenomenon can be basically explained by a softened covalence between carbon and fluorine. Indeed, bending, when present, imposes valence angles that prevents the realization of a purely  $sp^3$  state at the level of “addended” carbon atoms in the final fluorinated structure, which would be associated with too important local strain. Some  $sp^2$  character is then partly retained in such a case,

necessarily implying that the overlap between the hybridized lobes pointing outward the carbon frame and the fluorine atomic orbitals becomes less efficient.

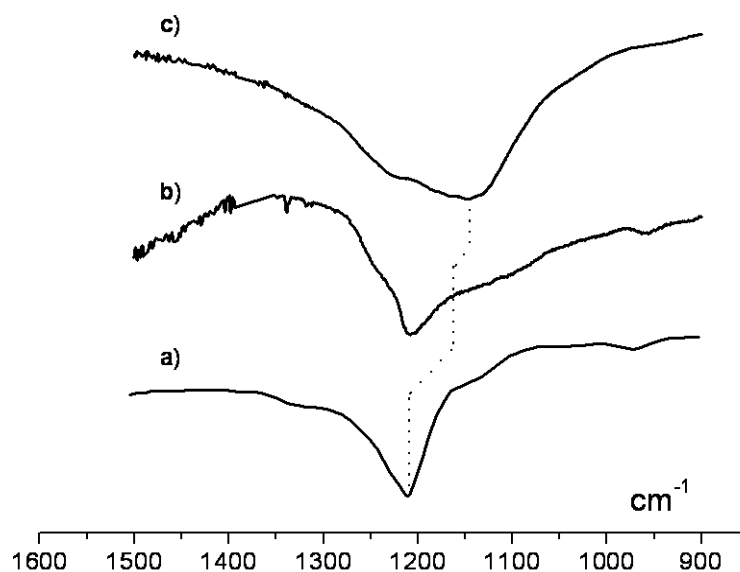


Figure 6. Experimental IR spectra showing a progressive shift of the approximate intermediate position of the C-F stretching band toward lower wave numbers, following an increase in the carbon substrate curvature - a) Bulk-fluorinated MWNTs (520 °C, composition  $CF_{1.1}$ ) b) SWNTs fluorinated at 300 °C (composition  $CF_{0.5}$ ) c) 80% fluorinated [70]-fullerene.

If curvature presently plays a significant role in diminishing the thermochemical stability of fluorotubes, some additional factors may potentially contribute to further weaken the C-F bond. Thus, an accumulation of adjacent fluorine atoms on one side of a carbon sidewall should create steric hindrance. Yet, this can not hold for F-MWNTs, in which case nearest neighbors fluorine alternatively stand on both sides of a carbon sheet, as seen before. According to theoretical calculations [27], when a given exo- fluorine addition pattern is envisaged, steric repulsion would tend to stabilize those F-SWNTs endowed with the smallest diameters (i.e. the most curved). A pronounced curvature indeed lengthens the separation between nearest neighboring addends. At last, one may also legitimately wonder whether the initial helicity of the tubular substrate can play a role on the thermochemical stability of the C-F moiety within fluorotubes. Computational investigations [27,37] showed that the latter factor has a minor influence compared to that exerted by diameter.

Alternatively, it has often been inferred that bond weakening within fluorotubes arises from a polarization of the C-F bond, an opinion issued from the several decades long earlier background dedicated to fluorographites. However, in spite of the ability of fullerenic carbon frames to undergo charge withdrawal [34], such a bonding concept happens definitely obsolete, as discussed later on. To close this paragraph, we then have to point out that a more reasoned overview on chemical bonding in fluorotubes must be provided but appears so unexpectedly complex that a whole detailed part will be devoted to it in the following. The present short section aims only at being a useful preliminary guide to account for some of the properties described below.

*Reactivity:* Standard fluorocarbons are known for their chemical inertness, a property inherent to the generally extreme intrinsic robustness of their C-F bonds. One may then expect the less energetically stable C-F bond present in fluorotubes to confer the latest an enhanced chemical reactivity. This naïve picture is at the origin of a frequently committed mistake in the interpretation of the physicochemical properties of fluorotubes, described below.

The notion of reactivity will be essentially restricted to single-walled fluorocarbon matrices only, since as seen previously, F-MWNTs consist of rather stable perfluorographene-like shells, resembling their chemically inert flat homologue, graphite fluoride (CF)<sub>n</sub>. In contrast, F-SWNTs can undergo defluorination upon simple prolonged annealing [8,11,12] at moderate temperature or upon chemical reduction with hydrazine [1,10,43,47] or with some solid halides and sulfides [43], turning back to their initial SWNTs state. More importantly, the latter fluorocarbon matrices are prone to nucleophilic attack, as well. Important pioneering works [41,42] had similarly led to the grafting of functionalities to the [60]-fullerene cage by starting from a fluorinated precursor, whereas some of these reactions may otherwise be more difficult to obtain from the C<sub>60</sub> molecule, especially when a high functionalization rate is desired. The interested reader may refer to wider review articles on the subject [24]. Originally initiated within the framework of the study of the chemical reactivity of fluorofullerenes, investigations on this latter aspect have since been intensively extended to fluorine atoms grafted to the surface of a SWNT and have shown the ability of the halogen atom to be readily displaced. Hence, the attachment of alkyl chains and various oxygen or nitrogen-based functional groups [1,43-47] to the sidewall of SWNTs has been reported, by starting from F-SWNTs. So far, simple substitution of mobile fluorine species, which are initially easy to fix to the carbon substrate, turns out to be the best means to enhance the rates of derivatization of fullerenic carbon networks (= fullerenes and tubes).

One should be careful to a common confusion when interpreting the above properties. Indeed, the ability of some fluorotubes to undergo defluorination does not arise from the previously illustrated diminution of the absolute average C-F bond energy, but instead likely possesses a kinetic origin [48]. Indeed, absolute bond energies stand with respect to the free atoms and provide information on thermochemical stability, once the energy offset corresponding to the constitutive elements in their more conventional thermodynamic standard state is introduced. Thus, in comparison with “normal” bonds in common fluorochemicals, especially poly-monocarbon fluoride (CF)<sub>n</sub>, C-F moieties in fluorotubes happen to be destabilized, i.e. the creation of C-F bonds according to  $C_{\text{graphite}} + x/2 F_2 \rightarrow CF_x$  is less energetic when the final CF<sub>x</sub> network is bent. But interpreting the formerly described physicochemical properties of fluorotubes from an energetic standpoint implies to rather consider the bond dissociation energy (BDE), which itself contains an enthalpy contribution relating to the formation of the pristine carbon network. It turns out that the latter term exerts the major influence on the BDE value, as shown from the following example. In the absence of direct thermochemical measurements on fluorotubes, a parent fluorofullerenic framework is compared to the fluorinated derivative of graphite. Hence, direct defluorination of a gaseous fluoro[60]-fullerene molecule according to  $C_{\text{full.}F_x} \rightarrow C_{\text{full.}} + x F$  necessitates on good average 291 kJ/mol C-F [49,50], while the equivalent complete defluorination of one poly-monocarbon fluoride (CF)<sub>n</sub> sheet necessitates only 254 kJ/mol C-F [51] (cohesive energies in the fluorinated and non-fluorinated condensed states of graphite are of nearly the same order, due to only weak van der Waals interaction between layers, so that the corrective terms

involved in the transition to isolated layers can be safely neglected). Overall, the C-F bond cleavage happens then to be +37 kJ/mol more endothermic for an isolated  $C_{60}F_x$  molecule than for a perfluorographene sheet. This energy amount compares very favorably with the +42 kJ/mol C representing the enthalpy of formation of a gaseous  $C_{60}$  molecule from graphite. Consequently, it can be extrapolated that fluctuations in the average BDE of any fluorocarbon lattice turn out to be almost entirely contained in the sole enthalpy of formation of the pristine carbon frame. It follows that the average BDE of a fluorocarbon matrix will increase concomitantly with the radius of curvature of the bare carbon precursor.

Consequently, great care should then be taken when evoking poorly bound fluorine atoms, while referring to the physicochemical properties of fluorotubes previously recalled. In fact, regarding the above mentioned energetic considerations, fluorine atoms within fluorotubes turn out to be tightly bound to their carbon substrate since defluorination of a tubular network will require more energy than that of graphite fluoride. Yet, it turns out that this energetic statement appears in strong contradiction with all experimentally established trends, since, as seen before, F-SWNTs can readily release fluorine throughout different processes, whereas graphite fluoride  $(CF)_n$  is an extremely stable compound until around 500 °C under inert atmosphere, decomposes beyond into gaseous fluorocarbons instead of undergoing defluorination, and is chemically inert. Such a paradox, opposing thermodynamics, clearly means that the easy fluorine departure from F-SWNTs compounds has a pure kinetic origin, so that a terminology like “labile fluorine” should be rigorously preferred. The underlying kinetics can be reasonably understood by referring to hybridization states in conjunction with activation energies. In pristine SWNTs, the  $sp^2$  character of the carbon atom is limited by the pyramidalization angle imposed by curvature, while the  $sp^3$  character of the carbon atom in the fluorinated derivatives is in turn limited for similar valence angle reasons. Consequently, in the course of either a fluorination or defluorination process, part of the hybrid character initially present is retained, which should then lower the energy barrier over which to pass to reach the transition state involved in the transformation. This makes an initially bent carbon skeleton easier to fluorinate and in parallel, its fluorinated homologue also easier to defluorinate. In contrast, the fluorination/defluorination of graphite is a total  $sp^2 \leftrightarrow sp^3$  transformation involving complete conversion of the hybridization state of carbon. This introduces kinetic limitation which can be overcome only under harsher experimental conditions.

Though fundamentally correct and laying the foundation stone of the physico-chemistry of F-SWNTs, we have to here again emphasize that the present approach implicitly stands for an averaging of the chemical bonding properties and that, in practice, partial distinction should be introduced between the C-F moieties, as described later on.

### ***b) Solid State***

*Solubility/dispersion:* Bulk samples of F-SWNTs prepared at 250 °C exhibit excellent dispersion properties upon sonication in alcohols [47], whereas perfluorinated solvents happen surprisingly quite inefficient in this purpose, in spite of the “like dissolves like” tendency. This was tentatively attributed to an enhanced dipolar moment of the C-F chemical bond that may facilitate the formation of hydrogen bonds from the partly charged fluorine atoms, but this initial explanation can clearly not be retained anymore.

*Conductivity:* It can be readily foreseen that the functionalization of carbon nanotubes should generate insulating materials, following random breaking of conjugation. Thus, not surprisingly, the resistivity of an initially conducting film of SWNTs was found to increase by six orders of magnitude after fluorination [1]. In another study [5], the resistivity was also found to increase in parallel with the level of fluorination. Let's note that such phenomena, though intimately correlated with the evolution of the "overall" electronic structure, reflect a sum of individual behaviors within a sample rather than a true collective behavior.

In regard to the resemblance that F-MWNTs bear to poly-monocarbon fluoride, it can be taken for granted that the latter similarly exhibit strong insulating properties. Nevertheless, when not bulk-fluorinated, it is expected that they can also exhibit a mixed behavior combining the insulating properties of their outer fluorinated shells with those of their conducting to semi-conducting inner pure carbon core.

## II. CHARACTERISTICS OF THE C-F CHEMICAL BOND IN FLUOROTUBES

### 1. A Weakened Plus Versatile C-F Bond

As for summary of the essential points established in the former part I, one may first basically recall that the high affinity of carbon for fluorine usually makes this combination one of the most energetic simple bonds. Thus, in thermodynamic equilibrium conditions, the simple pairing of one fluorine atom and one carbon atom yields a stable  $\cdot\text{CF}_{(g)}$  radical fragment, called fluoromethylidyne, whose bond dissociation energy is 540 kJ/mol [52,53]. We then evoked, independently of any local structural aspect, how the global stability of the latter atomic association in the solid state is made dependent on the carbon frame. The present part II aims at providing a final description of the fluorine addition pattern to carbon nanotubes. Focus will be made on the variability of the C-F binding energy that can appear in fluorotubes, which arises from its ability to be frozen in local minima.

*MW Fluorotubes:* The tendency toward metastability of the C-F bond in fluorotubes is clearly exemplified throughout the low and high temperature forms of multiwall fluorotubes, which clearly denote the opportunity of formation of kinetic products. We have depicted in the first part how the multi-walled tubular carbon allotrope mimics by several ways the chemistry of graphite, especially from the point of view of its reactivity with fluorine. Thus, the high temperature fluorination of MWNTs yields products that compare well with the graphite fluoride form  $(\text{CF})_n$  prepared at high temperature, whereas low temperature catalytic conditions yields a surface phase analogous to the so-called intercalation compounds of graphite with fluorine. It can be intuitively guessed that the varied addition modes of fluorine to a MWNT, under the form of either intercalation or addition final compounds, are intrinsically associated with changes in the nature of the C-F chemical bond. The experimentally checked quenching of the intercalation process upon increase of the synthesis temperature is the signature of rapid thermal decomposition, providing evidence for the instability of the C-F bond involved in it. The increase in the synthesis temperature alleviates

kinetic limitations and then turns the fluorination process toward the formation of a true addition compound involving the thermodynamically stable covalent C-F moiety.

*SWNTs*: Though manifesting in a different way, the versatile character of the C-F bond in F-SWNTs has also asserted itself and several authors have explicitly mentioned the coexistence of mixed bonding properties in their samples of single-walled fluorotubes [5,9,12-14,61]. These have been evidenced most of the time by an apparent splitting of the associated  $F_{1s}$  XPS signal [5,13,14], or through the wide wave number range associated to the stretching of the C-F bond [9,12,61]. Simple gravimetric techniques exploiting controlled thermolysis have recently provided a quantitative determination of the different bonding modes present in F-SWNTs [12]. As illustrated below, three different modes of fluorine chemisorption can be unambiguously evidenced within single-walled fluorotubes prepared at 100 °C, for instance. The TGA curves of such samples exhibit distinct steps of fluorine desorption, tentatively interpreted as the successive rupture of weak to stronger C-F bonds over the respective ranges  $50\text{ °C} < T < 150\text{ °C}$ ,  $150\text{ °C} < T < 250\text{ °C}$  and  $T > 250\text{ °C}$ . The respective amounts of each C-F bond type can then be quantified when selective thermal desorption is used, a sequential cleavage of the three different types of C-F bonds progressively taking place. Thus, figure 7 shows that the thermolysis of such fluorotubes stabilizes after one day at 150 °C, providing evidence of the complete removal of a first category of F atoms, involved in the weakest bond type. A further and again stabilized weight loss can be achieved at 250 °C, after a similar duration, signing for the complete removal of another kind of bonds. Note that about 24h are required to overcome kinetic limitations each time. By weight difference with respect to the initial total fluorine content of the sample, the existence of a third bonding mode of fluorine is deduced, supposedly representing the strongest and therefore, thermodynamically stable interaction.

A first tentative explanation of such a gradual classification might be that the C-F bond dissociation energy in F-SWNTs correlates to the diameter and/or helicity of a tube, as seen previously. Since samples of SWNTs consist of mixtures of individual entities with different intrinsic characteristics, their fluorination might indeed be expected to result in fluctuating bond strengths inside a same sample. However, variation in the tube diameter seems to be the parameter having the greatest influence on bond strength and the size distribution in SWNTs samples being usually narrow, it seems that the present hypothesis can not contribute significantly to the drastic variations observed. According to computational investigations [25], isomeric addition configurations usually exhibit too small energy differences and can again not account for so large fluctuations in the C-F binding energies. At this stage, the ultimate hypothesis of metastability becomes fully justified. From the experimental standpoint, the increased amount of the most stable bonding mode with the increase of the synthesis temperature seems to confirm an influence of kinetic factors. It is then highly likely that owing to a high activation energy regarding the formation of the most thermodynamically stable bond and/or difficulty in getting ordered at the surface of a tube, some fluorine atoms can be trapped into local energy minima. Accordingly, out of equilibrium C/F subsystems should provide a satisfying explanation for the non-homogeneous bonding scheme experimentally revealed in F-SWNTs. Their origin lies in the existence, dictated by the topology of the carbon substrate, of secondary binding sites that can readily allow fluorine storage.



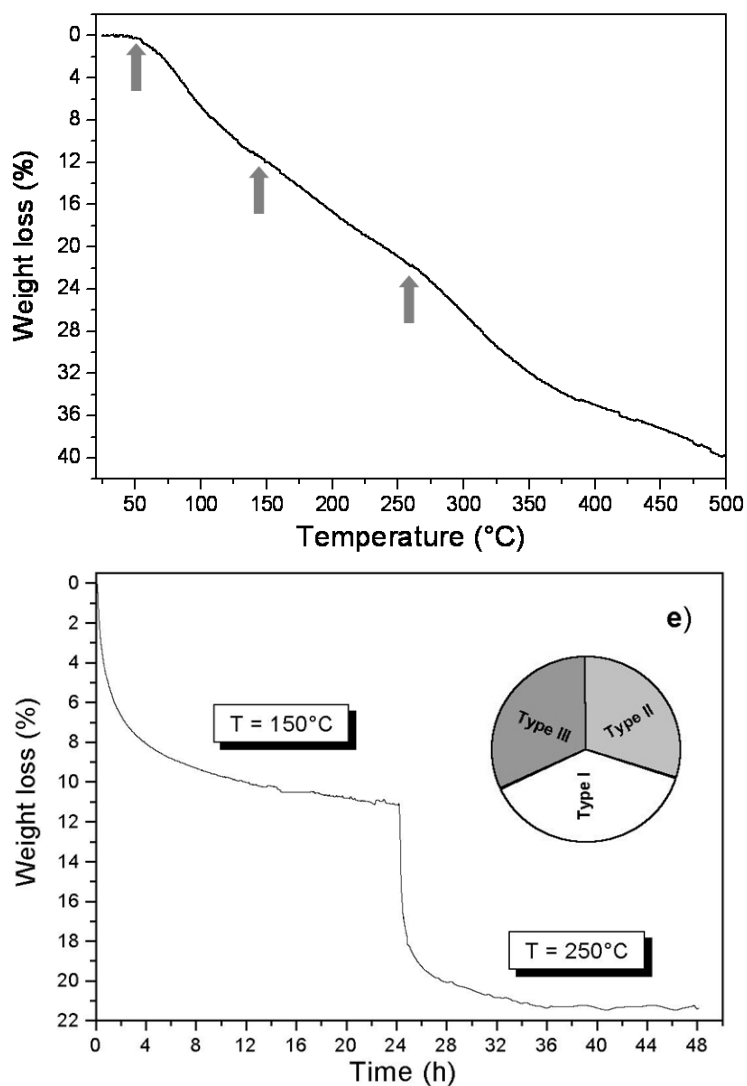


Figure 7. (Top) Thermogravimetric analysis curve of a sample of SW fluorotubes prepared at 100 °C for 4h (composition  $\text{CF}_{0.34}$ ), showing successive fluorine desorption steps. (Bottom) Relative amounts of the different C-F bond types in the same sample, as revealed by sequential thermal desorption. Reprinted from ref. [12], with permission from Elsevier © 2007.

In preliminary conclusion, F-SWNTs exhibit exaggeratedly important deviations in their bonding properties for a regular bonding scheme to be inferred and further characterization is required to really find out about the different ways fluorine can bind to the tubular carbon substrate. Alternatively, it has sometimes been argued [5,9,13,14] that the former differentiation in the C-F bond strength within single-walled fluorotubes has to be related to the emergence of an ionic character at the level of some bonds. Such arguments are manifestly wrong, as shown in the next section.

## 2. C-F Bond Strength Versus C-F Polarity: Revision Required?

The C-F bond within a fluorinated inorganic carbon network containing graphene-like structural units usually possesses constant characteristics within a same sample, but can be variable from sample to sample according to the synthesis conditions. Hence, it has long been claimed that the C/F interaction in this case is able to evolve from ionic to covalent, including a somewhat exotic intermediate state set between ionic and covalent. Though rather improperly, the terminology “semi-ionic” or “semi-covalent” has been of common use to describe the latter intermediate state, instead of “ionocovalent”.

Accordingly, the most part of interpretations regarding chemical bonding within fluorofullerenic networks (the term stands for fluorofullerenes + fluorotubes) have been and still keep on being performed in a state of mind imposed by the several decades long earlier background on fluorographites, that is, bond softening has become a synonym of bond polarity. For instance, the presence of notably polar C-F groups was claimed [54-56] in fluorofullerenes, following shifts observed in their IR and XPS features. The versatility of the C-F bond in fluorotubes has also often been explained via this model and depending on the fluorination conditions, bonds qualified by the authors as covalent or “semi-covalent” can form and seemingly even coexist [5,9,13,14]. While the temperature threshold ensuring the formation of as covalent as possible bonds seems to be sample dependent, a general consensus was reached in that the higher the synthesis temperature is, the more developed the covalent character of the final C-F bond in the sample is.

If the role played by the curvature of the carbon network in regard to the softening of the C-F bond within fluorotubes has not to be demonstrated anymore, may one complementarily see in the latter weakening effect the signature of a polarization of the C-F moiety? In this context, it may be interesting to have a closer look at the extent to which some of the ideas that have prevailed for decades on fluorographites should be reconsidered in the light of some late investigations, unhappily never taken into account. It follows that many of the interpretations published so far on the nature of chemical bonding in fluorotubes and fluorofullerenes are widely open to criticism and should be properly revisited. Indeed, while the either ionic or covalent characters of the C/F interaction in some graphite fluorides seem well established and have obtained general acknowledgement among researchers involved in the physico-chemistry of inorganic fluorocarbons, the pertinence of the ionocovalent (“semicovalent”) bonding mode happens obsolete in the light of some experimental and theoretical data.

Thus, as early as 1999, Panich [23] noted that the covalent  $(CF)_n$  and supposedly ionocovalent  $CF_x$  forms of graphite fluoride exhibit similar  $^{13}C$  NMR chemical shifts. The shielding effect being partly function of the electron cloud symmetry around the nucleus, no real change in the hybridization state of the carbon atom must consequently occur from one form to the other, which would otherwise induce sensitive difference in their respective  $\delta_C$  values. In other words, no significant modification in the bond character must occur from one form to the other. He also noted that the respective positions of the  $^{19}F$  lines are reversed in regard to what would be expected from an increased partial charge on the fluorine atom, therefore sharply contrasting with the idea of a variation in bond polarity between the two fluorographitic forms. He then concluded that variation in the ionicity of the bond should not stand as a correct explanation of the bond strength weakening in the intermediate form of graphite fluoride, hitherto thought as ionocovalent. Further NMR studies [57] have since

confirmed that the so-called “semicovalent” fluorographite form consists of a mixture of  $C_{sp^2}$ -C and  $C_{sp^3}$ -F carbons, implying that the C-F bond has a true covalent character. Recent neutron diffraction results by Sato et al. [58] have provided further highlight in favor of the non-existence of an ionocovalent bonding mode in the latter compound. Their analysis of the carbon environment has led to an estimated carbon-fluorine separation of 0.140 nm. This represents only a slight elongation with respect to the  $0.136 \pm 0.003$  nm bond length present in any common fluorochemical, while one may intuitively expect interatomic distances to strongly vary in case of charge separation. A structural model was proposed in which the carbon planes are buckled, contrarily to all previous models, indicating that orbital overlap between fluorine and  $sp^3$  carbon, i.e. a normal covalence state, prevails. An independent computational study [59] has also confirmed that the energetically favorable configuration necessitates the realization of a  $sp^3$  hybridization state for those carbon atoms directly linked to a fluorine atom. In other words, the C-F bond in the intermediate form of graphite fluoride appears as a conventional, but softened, covalent bond. The reason for bond weakening was shortly discussed by Sato et al. [58] who proposed that the latter effect results from the participation of the valence shell of the fluorine atom in a hyper-conjugation phenomenon, involving the subsisting conjugated  $\pi$ -scheme present in each partially “addended” carbon layer.

Given the obsolescence of the ionocovalent model in the case of fluorographites, it seems clear that the same must hold true for fluorofullerenes and fluorotubes and that weakened, but nevertheless fully covalent bonds do form in these compounds. Consequently, both the overall softening effect and the mixed character of the C-F bond in fluorotubes are independent of any variation in the polarity of the bond, as sometimes inferred earlier. The respective contributions to the overall softening of the bond strength remain curvature and potential steric hindrance, to which we will now add the metastable location of some fluorine. These effects naturally go in parallel with a soften IR frequency associated to the main vibration mode, while a higher core molecular level also results for fluorine, which accounts for the upshifting effect sometimes recorded from the  $F_{1s}$  XPS signal. The present conclusion that partial ionicity can not stand as a correct explanation for bond weakening in fluorofullerenic compounds is further reinforced by an independent computational study [27], who established that the Mulliken charges on the fluorine atoms in PTFE,  $CH_2F_2$  and a  $C_2F$  fluorotube isomer are similar, rendering the existence of an exotic charge state in the latest highly doubtful.

### 3. Anticipating the True Bonding Scheme of F-SWNTs

The set idea considering exo fluorine chemisorption on the surface of SWNTs has intuitively prevailed hitherto, guided by the initial STM view [2] on the outer morphology of a single-walled fluorotube and probably also influenced by antecedent findings regarding the parent, exo-functionalized, fluorofullerene molecules [24]. Yet, attention should be drawn on the facts that STM does not allow observation of inner regions, which might well bias our empirical apprehension of such systems, and that fullerene molecules are closed cages which only permit external addending, while this might not be the case for tubes, usually open on tips. Consequently, a more rigorous state of mind on the question is necessary and in parallel, seems also dictated by the most recent experimental characterizations.

It happens then obvious that beside the outer surface of a tube, different regions can contribute to fluorine fixation. Hence, the simplest structural model [60] that forces itself upon us and that would well account for versatile C-F bonding modes through a multiple location of F atoms is depicted in figure 8. From the energetic standpoint, one can intuitively postulate stability in the respective order: group I > II > III, so that II and III appear as metastable subsystems that may be at the origin of softened covalent bonds. Indeed, fluorine atoms of group I abide by the architecture of the stable  $(CF)_n$  compound, while group II addends undergo higher local strain at the level of the carbon frame plus probable steric hindrance between nearest neighbors in eclipsed position, if 1-2 addition is respected. The group III endo-addition pattern possesses a still more reduced stability, owing to the concave deformation generated at the surface of a convex carbon surface plus also probable steric hindrance. Therefore, the maintenance of group II and III with respect to the more energetically favorable group I must arise from kinetic limitation that is progressively overcome by increasing the synthesis temperature and/or reaction time, favoring evolution of the global addition pattern toward the most stable of the three subsystems.

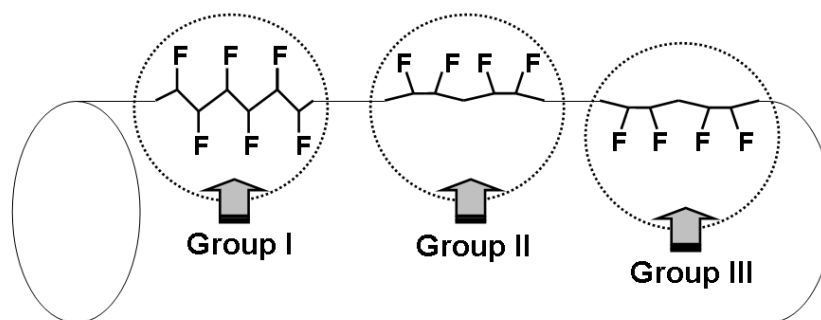


Figure 8. Provisional and schematic overall fluorine addition pattern to SWNTs.

The pertinence of this multi-site model [60] finds at least partial justification throughout different experimental and theoretical facts. First, the structure of F-MWNTs was claimed to be made of rolled  $(CF)_n$ -like sheets [17-20], so that at least partial filiation is highly likely to occur with F-SWNTs. In parallel, the scarce computational investigations [39,40] that considered an a priori exotic succession of exo/endo fluorine addends on the sidewall of an F-SWNT, concluded in the enhanced or competing thermodynamic stability of the latter in regard to an equivalent but purely exo functionalization pattern. Finally and more importantly, the  $^{19}F$  NMR spectrum of high temperature prepared F-SWNTs is made of a broad hump centered on -175 ppm [47], which is very close to the -180 ppm chemical shift recorded for the  $(CF)_n$  compound [23]. This suggests almost unambiguously that  $(CF)_n$ -like sections should constitute a notable, if not dominant, part of the fluorine addition pattern of F-SWNTs. IR spectroscopy strictly confirms this assumption. Indeed, the IR spectrum displayed in figure 6 spreads over a wide wave number range but distinctly shows a first tooth at  $1205\text{ cm}^{-1}$ , approaching the  $1220\text{ cm}^{-1}$  feature that characterizes the  $(CF)_n$  compound. The small frequency downshift simply occurs as a manifestation of the curvature effect on bond strength, as seen before. In the second place, IR spectroscopy seems to also confirm the existence of fluorine atoms belonging to the second group envisaged. Indeed, a broad but distinct feature is also apparent over the  $1100\text{-}1170\text{ cm}^{-1}$  zone in figure 6, which is the typical

absorption range of C-F moieties in fluorofullerene molecules (see Figure 6). The presence of a fluorofullerene-like subsystem in the overall addition pattern of F-SWNTs is therefore highly likely, as well. The existence of the third group of addends happens to be more difficult to evidence since no equivalent reference compound is known. However, some authors reported [7] that, at constant final F/C ratio, the fluorination of open versus closed-end SWNTs generates a lesser intertubular expansion in the case of open tubes. This might be an indirect indication that part of the fluorine can be located on the inner side of tubes. Our own most recent work (Claves et al., unpublished) has also confirmed the possible endo-functionalization of SWNTs.

At last, the influence of synthesis conditions on the final constitution of the mixed bonding scheme in F-SWNTs may be discussed. Experimental observations indeed indicated that the synthesis temperature is a key parameter affecting the respective proportions of each bonding mode [12] in the final fluorotubes sample, but the fluorination method retained (gaseous fluorine vs fluorinating agents, plasma techniques...), the reaction time and some morphological characteristics (average diameter size, bundled or individual tubes...) at the level of the precursor SWNTs batch may also more or less significantly influence the final result. The dependence of the final global addition pattern on the experimental conditions undoubtedly explains why characterization of F-SWNTs has often led to different results throughout the literature, depending on the chemisorption mode that prevailed within each sample studied.

The first hypothesis inferred to interpret the origin of kinetic effects is that the formation of bonds necessitates an increased activation energy in the order: group III < II < I. It can indeed be anticipated that the final p character of an "addended" carbon atom regularly diminishes from group I to III. Therefore, the final hybridization state of a carbon atom linked to fluorine is all the more close to its initial hybridization state in the precursor carbon substrate that the group number of the addend is high. Consequently, the pathway to the transition state might be energetically facilitated in the order III easier than II easier than I. The second and more reliable assumption is that the group I pattern likely derives from group II and III motives, after "backside completion" of the latter, which additionally implies potential rearrangement if 1-2 addition initially prevails. Indeed, in terms of probability, the direct formation of group I motives seems difficult because simultaneous attack on opposite sides by two fluorine molecules is required. Therefore, the creation in two steps of addends of the first group may slow down their apparition, so that high temperature and time will be required to observe their proliferation over the surface. At last, some complementary mechanistic grounds responsible for endo-fluorination can be reasonably anticipated, as well. Indeed, an arrangement under the form of bundles often prevails in SWNTs samples. Owing to the compactness of such nano-ropes, diffusion of fluorine molecules into the carbon lattice is hindered from the lateral sides. Fluorine admission must then rather occur from the bundles tips, where different apertures pre-exist. Consequently, fluorine species diffuse into the compact carbon lattice either via migration in the intertubular channels or directly through the hollow core of a tube. The cross section of a tube being about ten times that of an interstitial channel, the contact of fluorine molecules with the inner side of a tube rather than with the outer side should be clearly favored, facilitating endo-addition. In such conditions, a high temperature route is necessary to initially provide sufficient kinetic energy to the fluorine molecules and carbon lattice, so that to force "de-cohesion" within the ropes and to allow the parallel formation of the other subsystems.

### III. APPLICATIONS AND PROSPECTS: ADVANTAGES OF A WEAK AND VERSATILE ENERGETIC BONDING SCHEME

#### 1. Developments and Future Progress

In this last section, it will be dealt with the potency of fluorinated nanotubes in regard to advanced technological developments. So far, attempts of valorization of research performed on fluorotubes have been mostly driven by some antecedent industrial exploitation of fluorochemicals. Graphite fluorides or some fluorinated polymers are indeed currently used under the form of lubricants, cathode materials, or fibers entering into composite materials and textiles. In comparison to the standard fluorocarbon materials previously cited, the C-F bond weakening in fluorotubes is at the origin of an enhanced mobility of the fluorine atoms which may allow optimization of some performances. In parallel, it is expected that fluorotubes may benefit to new kinds of applications. Indeed, fluorination stands so far as the starting point for a great part of the modifications performed on carbon nanotubes, rendering fluorotubes fundamental intermediates for the integration of nanotubes in the nanotechnology processes.

*Functionalization:* We will first briefly recall that, in sharp contrast with the very bad nucleofugal properties of the fluorine atom in classical fluoroalkanes, fluorine atoms in fluorotubes can be readily displaced, rendering fluorotubes important synthons in the context of nanotubes chemistry. Thus, many synthesis routes use F-SWNTs as precursors [1,43-47] in view of the subsequent chemical derivatization of SWNTs. The basic aspects of fluorine displacement by some functions have been formerly depicted and we will then restrict this paragraph to an example of the new synthesis developments recently achieved [61]. It turns out that the differentiated bonding scheme of fluorine atoms within F-SWNTs can be turned to good account in some advanced synthesis patterns yielding to the controlled bi-functionalization of the SWNTs surface by heteroelements.

Hence, it has been observed [61] that in an acidic aqueous medium, partial pre-fluorination stimulates the subsequent grafting of hydroxyl terminations to the sidewall of SWNTs via the classical substitution of F by O, resulting in an oxyfluorinated compound. A significant upshift in the position of the  $F_{1s}$  peak (Figure 9) in the course of the XPS analysis of the products indicated an evolution in the strength of the C-F bonds before and after acid treatment. This resulted in the conclusion that a selective substitution of fluorine by oxygen can be achieved through the displacement of the sole most weakly bonded, and therefore nucleofugal, F atoms, since only the strongest C-F bonds subsist after substitution. The selectivity encountered here in the substitution mechanism should directly relate to the mixed bonding scheme evoked on figure 8. Such a tunable reactivity of the F atoms in a fluorotube paves the way toward a quantitative functionalization process of the SWCNT surface by hetero-elements. In practice, the advantage of the concept remains limited, yet, the selectivity in the exchange power of the F atoms being seemingly quenched in the presence of too strong nucleophilic reagents [61,62].

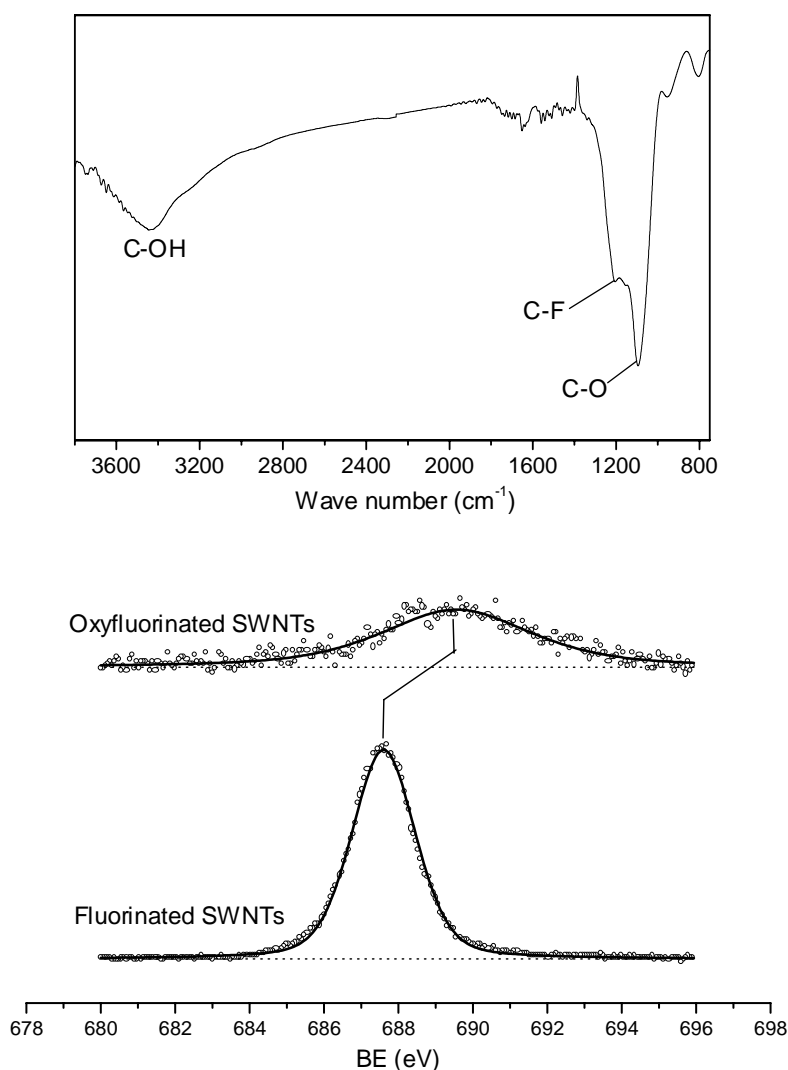


Figure 9. (Top) IR spectrum of oxyfluorotubes obtained upon acid treatment of F-SWNTs. (Bottom) F<sub>1s</sub> XPS spectra of F-SWNTs before and after treatment in acidic conditions, showing an evolution in the strength of the C-F bonds. Reprinted from ref. [61], with permission from Elsevier © 2008.

*Electrochemistry:* The covalent perfluoro-derivative of graphite (CF)<sub>n</sub> has been commercialized as a primary lithium battery component for several decades, now. Cathode materials are probably the field par excellence where the weakening of the C-F bond can benefit to optimized performances. Indeed, the thermodynamics of a CF<sub>x</sub>/Li battery is governed by the Gibbs energy of decomposition of the fluorocarbon phase into carbon, which acts as an unfavorable factor, compensated by the free enthalpy of formation of LiF upon discharge. The higher the (negative) bond energy is, the higher the increase in the absolute value of the Gibbs energy of the cell reaction is, so that any loss in the C-F bond strength is interestingly recovered under the form of power for the battery. Fluorotubes show interesting open circuit voltages when used as cathodes materials in lithium batteries, but preliminary tests [63-65] also globally displayed modest performances owing to a significant potential

drop in the course of discharge and to a limited Faradaic capacity. Future developments are required to achieve a more competitive system, in which partially fluorinated MWNTs could play a role. As seen in a former section, the latter indeed consist of fluorinated shells superposed to a pure carbon core, i.e. consist of an outer electrochemically active layer wrapping an electron conducting central part that might limit Ohmic drop in the cell.

Supercapacities are the second main electrochemical energy storage device. Samples of fluorotubes do not offer good capacitances but fluorination followed by defluorination at high temperature seems to constitute an efficient means to develop the porosity within a sample of raw carbon nanotubes, and as a corollary, to increase its specific capacitance [66].

*Mechanical properties:* Some theoretical calculations predicted [67] that the exceptional intrinsic mechanical properties of carbon nanotubes are preserved upon addition of fluorine. Additionally, the presence of surface C-F groups offers a way to favorably tune the strength of interfacial interaction or adhesion between SWNTs and another external medium. Such fundamentals clearly render fluorotubes potential reinforcing agents for composite materials. The discovery of the homogeneous dispersion properties of fluorotubes represents one concrete step in view of such a practical development. Let's here recall that fluorinated tubes form stable suspensions in alcohols over a long time and that they also seem to present a good affinity for polymers, satisfying one more key requirement for their processing under the form of tentative fillers for polymer matrices. Thus, a growing number of studies now report the use of F-SWNTs [68-70] or F-MWNTs [71-73] as reinforcing agents in nanocomposites made from different kinds of polymers. A significant increase in the mechanical properties is claimed most of the time, in parallel with the fluorination level and/or load percentage of fluorotubes. Fluorination happens to strongly improve interfacial adhesion since fluorine atoms can be removed and subsequently substituted by direct covalent bridges with the matrix [69,70].

In the short term, new synthesis routes allowing a controlled chemical modification of carbon nanotubes could play a key role in the expansion of nanotube-based composites. The previous example of oxyfluorotubes offers a nice overview on one essential realization that might be achieved in this field. One may indeed imagine that the relative proportions of each type of C-F bond in a fluorotube may be modulated according to its preparation conditions, and that so may be the selective exchange of fluorine by oxygen (or by some other hetero-element) and the consequent final O/F/C stoichiometric ratio. The practical interest of such hetero-functionalized derivatives as reinforcing materials is obvious, since the filler-matrix interactions might be tuned through the ratio of the hetero-elements, opening a window on materials with desired mechanical performances. At last, one may also try to anticipate to which extent partially fluorinated MWNTs as those displayed in figure 4 may efficiently ensure the mechanical reinforcement of composites. Their use would indeed involve a complex combination of effects, including that of a fluorinated outer surface improving dispersion and/or interactions at the fibre-matrix interface and that of a sliding and highly resilient inner carbon core.

*Tribology:* The exceptional friction properties of C-F covered surfaces are well-known and commercially exploited under the form of Teflon<sup>®</sup> or poly-monocarbon fluoride based lubricants. This fully justifies the initial suspicion that similar or even better properties might



be obtained from fluorotubes. However, the lubrication durability of F-SWNTs was shown [74] to be limited by cracking, owing to the weakening of the frame induced by fluorination.

In this context, F-MWNTs might here again appear as a possible alternative, at first glance. Indeed, the partial fragmentation induced by fluorination results in a relaxation of the internal strain which improves flexibility and hence, might help in the preservation, under a mechanical constraint, of tubular-shaped nanoparticles playing the role of nano-bearings.

*Nanoelectronics:* One of the most promising and exciting future development, that has boosted expansion of research on carbon nanotubes, is the integration of the latter as nanometer scaled components into a new generation of electronic circuits. At first glance, functionalization does not appear as adding value at this level, because its random character makes difficult the control of the electronic properties of tubes by this means. Yet, surface fluorinated MWNTs couple insulating outer properties with conducting inner properties that make these fluorocarbon architectures look like nano-sized electric wires. One might then expect the latter to be used to carry electricity inside nanodevices, so that to ensure connections between nanocomponents.

*Processing:* Finally, we will shortly emphasize the potential impact of fluorination as a “processing method” for carbon nanotubes. Due to the reversibility of fluorination, fluorotubes might well be seen as simple intermediates in the course of an overall transformation scheme of raw carbon nanotubes. Thus, an etching effect on the carbon skeleton following high temperature pyrolysis of fluorotubes was reported [9], but sounds rather anecdotic since a similar effect can be obtained upon simple prolonged sonication of a suspension of raw tubes.

The key point slowing down the development of carbon nanotubes-based devices is the control of the intrinsic characteristic of the tubes during their synthesis, which, so far, results in a mixture of conducting and semi-conducting entities. Trends in this field have lately turned toward post-synthesis chemical sorting methods. Though reported several times from different kinds of oxidizing reagents [34], the selective “sorting effect” accompanying the reaction of raw SWNTs with fluorine seems worth being noticed. As a matter of fact, the selective quenching of Raman and optical absorption features observed during a [room temperature fluorination/ high temperature defluorination] cycle showed that a preferential destruction of small diameter metallic tubes occurs in this case [75], providing a basis to an enrichment process. The latter results have been seemingly confirmed by an ab initio study [76] stipulating that metallic tubes interact more favorably with fluorine than semi-conducting tubes, beyond a critical diameter threshold.

## 2. Prospects

As for conclusion to this chapter, we will detail below a few concepts, remaining speculative at this stage, but that may stimulate future research in the field. Some are inspired with commercially exploited applications of other perfluorocarbons, a fact reflecting in itself a promising potency in regard to future valorization.

*Gas storage:* From kinetic grounds, we have previously justified why F-SWNTs contain rather labile fluorine atoms. If synthesis conditions favoring metastable addition are employed, the labile character of the fluorine atom happens to be highly reinforced. In such a case, simple heating at moderate temperatures can rapidly permit the removal of important amounts of fluorine (see Figure 10). The precursor carbon matrix could then be advantageously envisaged for fluorine storage. An obvious underlying interest arises, regarding some potential energy storage devices, given the highly exothermic reactions to which elemental fluorine, once liberated, can give birth.

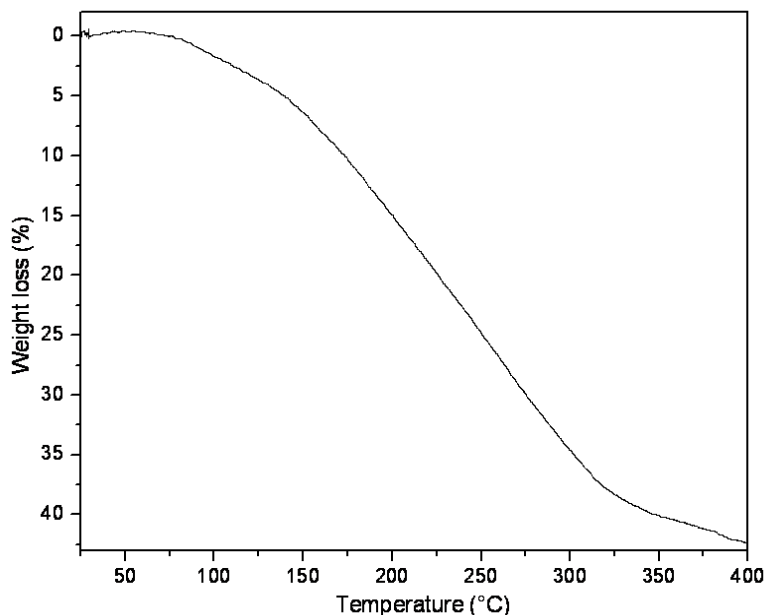


Figure 10. TGA curve of a SWNTs sample fluorinated at room temperature, showing how some fluorine can be rapidly given off.

*Soft fluorinating agents:* Alternatively, transforming an initially weak C-F bond into a stronger one, by transferring the fluorine atom to another compound in which the C-F energy level would be deeper, appears straightforward from the thermochemical standpoint. Therefore, due to their ability to release fluorine, some fluorotubes are good candidates likely to act as donors and could probably be employed as soft fluorinating synthesis agents. The fluorine exchange process may be activated upon heating a mixture of the respectively donor and acceptor solid phases, for instance, and might be efficient regarding H substitution in  $-\text{CH}_x$  groups or for the halogenation of pure carbonaceous materials.

*Smart textiles:* The notoriety of some fluorine containing synthetic fibers has entered our everyday life, the most famous being probably Gore-Tex<sup>®</sup>, which is nothing else than thermo-mechanically expanded PTFE. Like their non-fluorinated precursor, fluorotubes can likely be processed under the form of fibers, paving the way toward their integration into tissues and canvas. In this framework, the combination of the robustness of their carbon frame with the specific properties of the C-F bond may provide a bunch of interesting characteristics. The

well known hydrophobicity of the C-F group intuitively suggests fluorotube-made anti-soil and/or water proof textiles, or highly resistant and water repellent surface coverage tissues, for instance. Furthermore, the stabilization of the C-F bond in F-MWNTs may render them compatible with biological tissues, opening the door toward novel implant materials or growth templates, which require chemical inertness.

*...and much more:* Nanosized particles are known to modify the barrier properties of polymers. In parallel, the introduction of  $-CF_n$  groups in a polymer chain is also known to have a similar influence. Fluorotubes are a perfect example of a nanoload that would combine both effects and that may, for instance, benefit the tuning of the separation properties of membranes. Alternatively, the reasonable resistance to thermolysis of F-MWNTs (see Figure 5) might also render the latter useful agents for improving the fireproof performances of some polymers.

## CONCLUSION

Still at an exploratory stage only a few years ago, the development of research on fluorinated carbon nanotubes is now becoming routine. Its evolution is well reflected by a growing number of contributions to the subject year after year, a picture of which is given below (Figure 11). Among all possible future work directions, one is clearly emerging. Indeed, some key knowledge concerning some characteristics of the C-F chemical bond in fluorotubes still remains to be ascertained before application attempts can confidently build on a solid fundamental basis. In parallel, one may regret that most studies have been performed on fluorinated SWNTs, so far, leaving fluorinated MWNTs on the fringe of research in this field. The latter really possess an appealing applicative potential that I have tried my best to emphasize throughout this chapter.

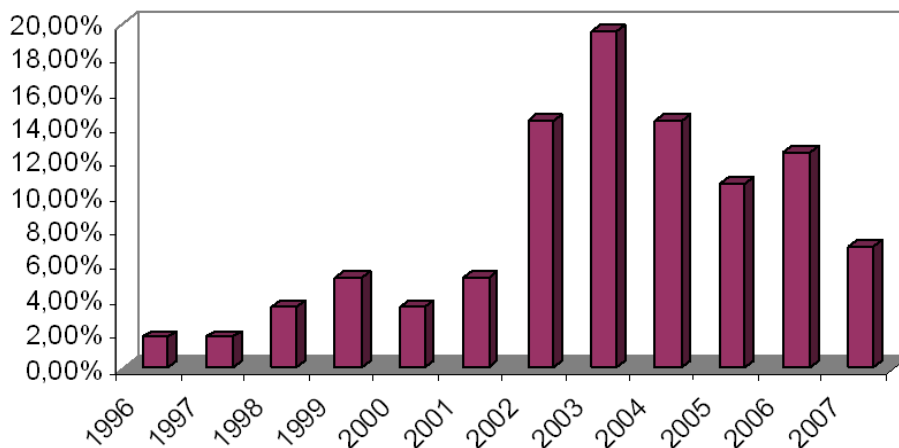


Figure 11. Annual publication trend, estimated on the basis of the whole bibliography herein referenced, and reflecting evolution in the research effort dedicated to fluorinated carbon nanotubes over the past 12 years.

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