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# Spectroscopic study of fluorinated carbon nanostructures

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5 Fluorocarbon nanostructures possess an outer halogenated crown playing the role of an interface toward  
their environment and whose properties are then crucial for anticipating integration of the latter materials  
in the nanotechnology processes. Therefore, the result of fluorine addition to nanocarbon frames has been  
here investigated with the help of IR and XPS spectroscopies and the role played by the pristine lattice  
curvature and the addends addition scheme on the physicochemical characteristics of this outermost shell  
10 is experimentally established. The relevant paradigm of supposedly ionocovalent C-F terminations in  
these nanomaterials is definitely shown to be obsolete.

## Introduction

Lately, a broad panel of application attempts has started to  
emerge following the transposition of fluorocarbon materials to a  
15 nanometer scale. As a nice illustration, much attention has been  
paid<sup>1</sup> to the potency of the latter as new synthons, fillers in  
nanocomposites, redox and electrochemically active components,  
lubricants, or as the building blocks of electronic nanocircuits,  
light harvesting nanodevices... The C-F termination proves  
20 essential in tuning the static or dynamic properties of  
fluorocarbon nanostructures and will define in fine their  
conceivable practical uses. Therefore, probing the related  
fundamental bond characteristics happens to be of great  
importance.

25 Hence, while the C/F chemical pairing in conventional  
molecular fluorochemicals is recognized as one of the most  
thermochemically stable combinations, fluorine atoms within the  
solid state fluorinated derivatives of the various carbon allotropes  
can sometimes exhibit a weaker bonding character than expected  
30 (here and in the following, the “bond weakening” terminology  
will refer purely to an increase in the negative absolute bond  
energy). For instance, the C-F bond energy within a macroscopic  
fluorinated inorganic carbon network initially containing  
graphene-like structural units happens to be notably variable,  
35 according to the synthesis conditions. Hence, it has long been  
claimed<sup>2</sup> that, between the different known forms of graphite  
fluorides, fluctuations in the strength of the C-F bond have to be  
related to changes in the nature of the C/F interaction. The latter  
is then well known to be able to progressively evolve from ionic  
40 to covalent,<sup>2,3</sup> including a somewhat exotic intermediate state set  
between ionic and covalent.<sup>2,4</sup> Though rather improperly, the  
terminology “semi-ionic” or “semi-covalent” has been of  
common use to describe the latter supposedly ionocovalent C-F  
bond character.

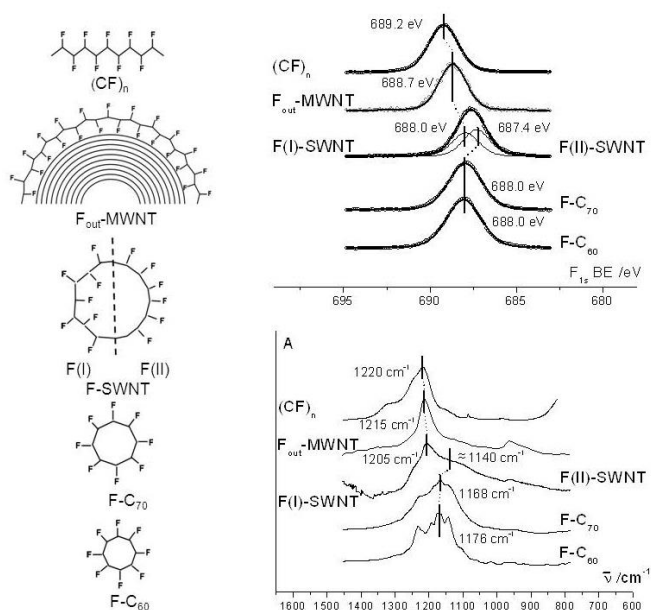
45 Later on, the idea that an apparent C-F bond softening  
phenomenon of similar origin also occurs within the fluorinated  
derivatives of the organized nanostructured forms of carbon, i.e.  
essentially nanotubes and fullerene aggregates, commonly arose.

Indeed, the likeliness of the spectral characteristics of fullerenic  
50 to macrofullerenic fluorocarbon architectures<sup>5-10</sup> with those of the  
above-mentioned and supposedly ionocovalent intermediate form  
of graphite fluoride strongly incited to draw a parallel with the  
nature of the C-F bond existing in this latter compound.  
Therefore, most interpretations on chemical bonding within  
55 fluorinated carbon nanostructures have been and still keep on  
being made in a state of mind imposed by the decades-old  
background on fluorographites, namely bond weakening has  
become a synonym of bond polarity. Accordingly, the presence  
of notably polar C-F groups has often been suspected<sup>7</sup> in  
60 fluorofullerene clusters. The nature of the C-F bond within  
different categories of tubular fluorocarbon networks has also  
been customarily explained via this model and the C-F moieties  
in fluorotubes are then still often depicted by numerous authors as  
exhibiting some variable degree of ionic character.<sup>8-10</sup>

65 Herein, the former statement of bond polarization, used to  
explain the apparent evolution between the different  
fluorographite forms and usually extrapolated to the whole  
families of fluorocarbon nanomaterials, is re-examined. In this  
purpose, a series of fluorinated nano to macro-sized carbon  
70 frames has been synthesized, from which fluorine addition to  
carbon networks can be at least partly quantitatively addressed,  
using appropriate spectroscopic techniques. The parameters  
governing the stability of the C/F pair can then be experimentally  
visualized and the relevant fluctuations newly modelled. It  
75 follows that many of the interpretations published so far on the  
origin of properties of some fluorinated carbon nanomaterials are  
widely open to criticism and should be revisited.

## Results

A comparative study of the energetics of fluorine addition to  
80 carbon frameworks is first addressed. Focus was made essentially  
on the influence of the fluorine addition scheme<sup>‡</sup> and radius of



**Fig. 1.** Schematic representation of the successive fluorocarbon samples synthesized and their corresponding (top) XPS spectrum (F<sub>1s</sub>, after background subtraction) (bottom) IR spectrum over the C-F stretching vibration region.

curvature of the carbon skeleton. In this purpose, a prototypical series of fluorocarbon materials offering a smooth evolution in the former parameters has been prepared, by starting from carbon allotropes endowed with progressively varying characteristics. The carbonaceous precursors chosen are graphite, multiwall carbon nanotubes (MWNTs) of arc-discharge origin, CVD-grown single wall carbon nanotubes (SWNTs) and the C<sub>70</sub> and C<sub>60</sub> carbon clusters. The fluorinated derivatives of the former series of carbon frames have been obtained as described in the experimental section and their respective final F/C stoichiometric ratio determined from XPS analysis. Hence, these define two categories of materials, based respectively on a double-side or on a single-side halogenation scheme. Inside a same category, that is, for a given mode of fluorine addition, the radius of curvature of the initial carbon network, characterized by its average cage diameter  $\phi_c$ , is the varying parameter. The series of fluorinated carbons considered consist then of: i) Graphite fluoride (CF)<sub>n</sub> ( $\phi_c = \infty$ ; non curved corrugated layers bound to fluorine in a recto-verso mode and containing purely sp<sup>3</sup> carbon atoms<sup>2,3</sup>); ii) Surface fluorinated multiwalled nanotubes F<sub>out</sub>-MWNT ( $\phi_{c\ out} \approx 30 \pm 10$  nm; fluorination to saturation of the outermost cylindrical layers only, with the preceding (CF)<sub>n</sub> structure<sup>10,11</sup>); iii) 50% fluorinated single wall carbon nanotubes F-SWNT ( $\phi_c \approx 2$  nm; mixture of two main addition modes consisting of one (CF)<sub>n</sub>-like (= double-side addition) plus one exohedral (= single-side addition) subsystem,<sup>6,12</sup> referred to as F(I)- and F(II)-SWNT addends, respectively); iv) 80% fluorinated [70]-fullerene F-C<sub>70</sub> ( $\phi_c = 0.76$  nm; exohedral fluorination<sup>7</sup>); v) 80% fluorinated [60]-fullerene F-C<sub>60</sub> ( $\phi_c = 0.70$  nm; exo-fluorination<sup>7</sup>). In the following, comparisons can be made in conditions where no real influence is exerted by the final stoichiometry, which slightly differs from compound to compound. Indeed, the final fluorination level simply bears witness to the spatial expansion of addition along each carbon framework, but introduces no major

consequence on the average surrounding of a fluorine atom, so that in very good approximation, a constant local surface density of addends can be considered within one same previously defined category of fluorocarbon materials.

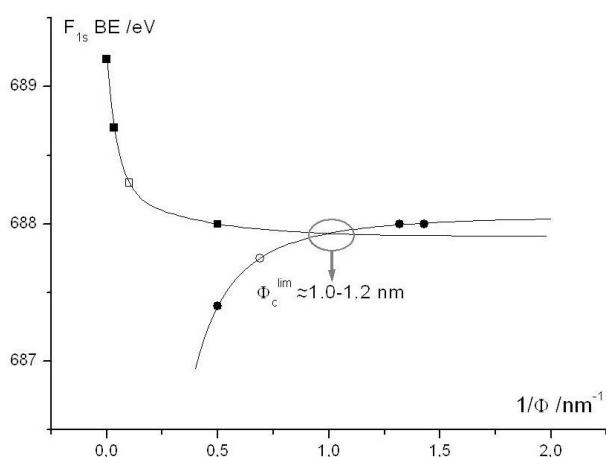
It has become customary to characterize changes in the C-F bond strength of solid fluorocarbons from the shift in the position of the corresponding stretching vibration band in the IR region.<sup>2,4</sup> However, the extent to which a normal vibrational mode of a network can be identified with the stretching mode of one individual bond might deserve a critical analysis. Furthermore, the intuitive assumption that bond strengths thus observed with the help of IR spectroscopy should also reflect absolute bond energies does not appear straightforward. As a matter of fact, bond strengths could rigorously reflect bond energies only under the condition that the state of each atom (hybridization, electrons localization) can be kept unchanged in the fragments formed following dissociation. In practice, a correlation between the absolute bond energy and the stretching frequency can therefore be expected only if the relaxation energies following a given bond cleavage are almost constant, which is at best roughly satisfied for a series of structurally parent compounds. Therefore, XPS can alternatively be considered as a better direct means of comparison between absolute bond energies, upon implicit but reasonable admission that changes occurring at the core level mirror those occurring at the valence level. In order to allow direct comparisons from an energetic standpoint, care must simply be taken to refer to one unique initial state. The reference fluorination process considered here will be  $C_{\text{graphite}} + x/2 F_2 \rightarrow CF_x$ , where the final product stands for any fluorinated carbon allotrope. We may thus define in a pragmatic way a normalized standard enthalpy of formation for one C-F bond, concretely representing the difference between the absolute  $E_{C-F} + E_{(F)C-C(F)}$  bond energies within a final fluorinated compound and the absolute energy of one C/C bond in graphite. Assuming that, from one fluorocarbon material to another one, variations in the absolute C-F bond energy prevail over those that may occur at the level of the final (F)C-C(F) bonds, the evolution in the position of core level features then directly reflect changes in  $E_{C-F}$ . Hence, the former spectroscopic technique happens to be intimately related to the energetics of fluorine addition to a carbon network and may benefit to a generalized thermochemical approach of the phenomenon.

As a starting point, a compilation of the XPS data collected over the whole fluorocarbon series considered and showing a regular shift of the F<sub>1s</sub> core level is displayed in figure 1a. A similar effect is also systematically recorded from the C<sub>1s</sub> photoelectron peak of those carbon atoms directly bound to fluorine (table 1). Therefore, it happens possible to clearly correlate a gradual variation in the average C-F bond energy with a progressive evolution in the intrinsic characteristics of each sample. The complementary IR data of figure 1b show an exactly similar trend for the main C-F stretching band, illustrating an acceptable strength/energy parallel for a carbon-fluorine atomic pair in a nearly constant C<sub>3v</sub>-like local environment.

Consequently, XPS and secondarily, IR data, give formal experimental evidence that the creation of a C-F bond is more

**Table 1.**  $C_{1s}$  binding energies for carbon atoms directly bound to fluorine and experimental  $F_{1s}$ - $C_{1s}$  energy gap.

Sample	$C_{1s}$ -F BE (eV)	$\Delta(F_{1s}-C_{1s})$ (eV)
$(CF)_n$ :	290.1	+399.0
$F_{out}$ -MWNT:	289.8	+398.9
F-SWNT:		
F(I)	289.4	+398.6
F(II)	288.6	+398.8
F- $C_{70}$ :	289.2	+398.8
F- $C_{60}$ :	289.2	+398.8



**Fig.2**  $F_{1s}$  core level energies vs  $1/\phi_c$  (open square: data from [10] on surface fluorinated MWNTs around 10 nm in outer diameter; open circle: data from [13] on exo-fluorinated double-walled nanotubes).

energetic, when:

*At constant addition scheme,*

- i) bending of the initial carbon lattice decreases, in case of double-side addition
- ii) bending of the initial carbon lattice increases, in case of single-side addition

*At constant initial carbon cage radius*

- iii) a recto-verso mode of addition takes place, beyond a critical threshold  $\phi_c^{lim} \approx 1.0-1.2$  nm
- iv) a single-side mode of addition takes place, below a critical threshold  $\phi_c^{lim} \approx 1.0-1.2$  nm

The estimation of the critical value  $\phi_c^{lim}$  is shown in figure 2, where the x-axis is represented as  $1/\phi_c$  for convenience and fits are obtained from heuristic exponential decay and inverse power functions as guides to the eye. A few judiciously chosen spectroscopic results previously reported<sup>10,13</sup> can usefully complete the set of data presently obtained. This cross-checking with some other literature data also emphasizes the global convergence between measurements issuing from independent sources. Rules iii) and iv) above imply that single-side and double-side additions become energetically equivalent processes

near this particular carbon frame size  $\phi_c^{lim}$ . Note that since the latter critical threshold typically falls in the range of diameters adopted by conventional SWNTs, these have then usually the choice between two energetically competitive functionalization modes with fluorine, as supported by some theoretical calculations,<sup>14</sup> which is highly likely the reason why they practically adopt mixed bonding schemes.<sup>6,9,12</sup>

## Chemical bonding

It has often been argued<sup>7-10</sup> that C-F bonds in fluorotubes and fluorofullerene clusters possess a partially ionic character, inducing a weakening in their strength/energy in comparison with the reference  $(CF)_n$  compound. In spite of the ability of fullerene cages to undergo charge withdrawal,<sup>15</sup> such an argument is purely dictated by the earlier background on the different fluorographite forms, shortly reviewed in the introductory part. This section will consequently aim at showing whether the bond evolution observed throughout the series studied here could not be understood independently of the paradigm involving a progressive change in the bond polarity, before examining the pertinence of the latter concept in the discussion part.

It will first be shown unambiguously that the partial ionic character of the bond claimed earlier<sup>7-10</sup> for halo-(macro)fluorofullerene materials is absolutely not compatible with the present experimental data. Indeed, in the context of an ionocovalent model, any supposedly bond polarized fluorinated carbon skeleton should possess an increased charge density at the fluorine site and a decreased one at the carbon site. Since XPS is widely known as a sensitive probe for charge states, core level energies being highly sensitive to internal electron screening, the former charge separation should therefore cause shifts of the respective carbon and fluorine 1s levels in opposite directions. Yet, as seen in the first part, it can be noticed that the corresponding signals are systematically found to shift together in the same direction and the  $C_{1s}$ - $F_{1s}$  binding energy gap happens to be rigorously constant from sample to sample (table 1) within experimental error. Though never pointed out hitherto, this universal invariability can also be checked from independent work.<sup>5,7,10,13</sup> It follows that the evolution observed in the bonding properties can definitely not be explained by progressive modifications in the polarity of the C-F pair. Instead, given the present quasi-constant chemical architecture consisting of alternating  $>(CF)-$  moieties, electron density in the valence shells has few chance to significantly vary and so do the extra-atomic contributions to the chemical shift, so that in such conditions, the evolution of XPS spectra must simply reflect charge-independent changes in the overall  $\sigma_{C-F}$  bond energy diagram. The present preliminary conclusion refuting the standard ionocovalent C-F model is further reinforced by an independent computational study,<sup>16</sup> that has established that the Mulliken charges on the fluorine atoms in PTFE,  $CH_2F_2$  and a  $C_2F$  fluorotube isomer are similar, rendering highly doubtful the existence of an exotic charge state in any fluorinated carbon nanotube, and by extrapolation, in any fluorinated carbon lattice.

Therefore, a more pertinent interpretation of changes in C-F bond energies should be given based on the role played by each

influential parameter experimentally identified here. As a starting point, the effect of the addition scheme should be examined. Clearly, systems adopting the double-side halogenation mode are energetically favored over those consisting of contiguous exo-addends in eclipsed position. This obviously stems from the cancelling of steric hindrance when nearest neighbour fluorine atoms alternatively stand on both sides of a carbon sheet. In the second place comes the effect exerted by the carbon lattice topology. Basically, a correlation between the C-F bond energy and the radius of curvature of the carbon precursor is naturally expected, since the pyramidalization angle at the level of the carbon frame will affect the quality of orbital overlap between carbon and fluorine. Qualitatively, surface bending imposes some residual  $sp^2$  character at the level of each fluorinated carbon atom, which therefore partially reduces the extension of hybrid lobes pointing outward the carbon cage. This slightly reduces orbital overlap with fluorine and consequently, results in bond softening. At last, the reversed bond energy vs lattice curvature trend observed between the double-side and single-side addition schemes can be intuitively understood. Neighbouring exo-addends are taken away from each other upon bending, which decreases their mutual steric repulsion. This improves the stabilization of the latter exo-addition mode with curvature, as shown in a theoretical work by Bettinger et al.,<sup>16</sup> making it in fine competitive with the recto-verso mode below the critical threshold previously identified. All above-described effects act to influence the carbon-halogen bond strength/energy, so that the chemical bonding properties of fluorinated frameworks of fullerenic origin can be commonly rationalized without the help of the old standard model based on a variation in the ionicity of the C-F bond.

## Discussion

At this stage, it may be interesting to have a closer look at the extent to which some of the ideas that have prevailed over decades about fluorographites, and which falsely inspired most anterior interpretations of the C-F bond nature and its related properties within fluorofullerenic materials, should be reconsidered in the light of some late and unfortunately, too often overlooked, investigations. It then turns out that the ionocovalent description of the intermediate fluorographites appears manifestly erroneous. In the purpose of clarifying the situation, the state of the art on the whole family of fluorographe compounds is critically detailed in the following. Thus, beside the covalent addition derivative  $(CF)_n$ , usually obtained via the fluorination of graphite near 600 °C, and its parent sub-fluoride  $(C_2F)_n$  that forms at lower temperature, some non-stoichiometric graphite fluorides, denoted  $CF_x$  and possessing a low fluorine content ( $x < 0.1$ ), can be obtained near room temperature when a gaseous fluoride is used as catalyst.<sup>2,3</sup> Such phases are then rather considered as lamellar intercalation compounds of graphite, in which the carbon-fluorine interaction has notably evolved. Structural information has strongly contributed to settle the notoriety of the existence of a charge transfer between carbon and fluorine in such graphitic fluorocarbons. Indeed, the carbon-fluorine interatomic distance directly deduced from the value of their identity periods along the c axis is close to 0.30 nm.<sup>2</sup> Interestingly, such a value corresponds exactly to the sum of one

half the interlayer separation between carbon sheets in the pristine host material (0.335 nm) with the conventional ionic radius of fluorine (0.133 nm). Under the condition that the staged structural model proposed earlier is valid, this can be considered as a good indication of an ionic nature of the intercalant fluorine atoms in such a case. In conjunction with the former interpretation of XRD patterns, XPS has also proven an additional probe of the occurrence of a charge transfer from carbon to fluorine. Indeed, in comparison with the high temperature form of graphite fluoride  $(CF)_n$ , the  $F_{1s}$  chemical shift characterizing the former  $CF_{x < 0.1}$  graphite intercalation compounds moves toward a position typical of anionic fluorides.<sup>2</sup> Other spectroscopies, particularly NMR,<sup>3</sup> have since brought further evidence in favour of negatively charged fluorine atoms in the present case. Hence, the corresponding narrow  $^{19}F$  signal recorded<sup>3</sup> indicates motional averaging of the dipolar interactions, implying mobility of the intercalant species in the interlayer space, which necessarily means non-directionally (i.e. ionically) bonded F atoms. To date, no reason has ever appeared for calling into question the present description of chemical bonding in such low halogen content fluorographitic compounds.

Secondly, if always under catalytic conditions and at moderate temperature, the F/C ratio is increased in the non-stoichiometric  $CF_x$  phases, the  $F_{1s}$  photoelectron peak happens to shift to an intermediate position, set between those characterizing the ionic and covalent F atoms.<sup>2</sup> This phenomenon led pioneering researchers<sup>4</sup> to imagine, seemingly legitimately, the creation of an intermediate ionocovalent (“semicovalent”/“semi-ionic”) C-F bonding mode beyond  $x \approx 0.1$ . In parallel, for this intermediate graphite fluoride form, the frequency of the C-F stretching vibration becomes notably downshifted to 1100-1125  $cm^{-1}$ ,<sup>2,4</sup> in comparison with the homologous IR feature at 1215-1220  $cm^{-1}$  characterizing the high temperature fluorographe forms  $(CF)_n$  or  $(C_2F)_n$ . Since one may expect the stretching force constant to be lowered concomitantly with a decreased covalence of the C-F bond (in other words, an increased ionicity), this phenomenon apparently further confirmed the existence of an intermediate ionocovalent state with respect to the previously evoked covalent and ionic states of the  $(CF)_n$  and  $CF_{x < 0.1}$  phases.

However, while the either ionic or covalent character of the C/F interaction within graphite fluorides has obtained general acknowledgement, the pertinence of the latter ionocovalent bonding model happens definitely obsolete if account is taken of still recent experimental and theoretical data on the subject, seldom taken into account. Thus, as early as 1999, Panich<sup>3</sup> 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 the respective  $\delta_c$  values. In other words,  $sp^3$  hybridization for the carbon atom must be present in both compounds, which can only mean covalent bonding with fluorine, and no significant modification in the bond character must occur from one form to the other. Further NMR studies<sup>17</sup> have since confirmed that the so-called “semi-ionic”/“semicovalent” fluorographe form consists of a mixture of  $C-C_{sp^2}$ -C and  $C_{sp^3}$ -F carbons, implying

that the C-F bond possesses a true covalent character. Panich also noted that the respective positions of the  $^{19}\text{F}$  lines corresponding to the covalent and supposedly ionocovalent graphite fluorides are reversed in regard to what would be expected from an increased partial charge on the fluorine atom within the latest form, therefore sharply contrasting with the idea of a change 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 apparent bond weakening in the intermediate form of graphite fluoride. Since then, recent neutron diffraction results<sup>18</sup> have provided further highlight in favor of the non-existence of an ionocovalent bonding mode in the latter compound, in which the analysis of the carbon environment has led to an estimated carbon-fluorine separation of 0.140 nm. This represents only a modest elongation with respect to the  $0.136\pm 0.003$  nm bond length present in any common organic fluorochemical, while one may 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  $\text{sp}^3$  carbons, i.e. covalence, prevails. Some theoretical calculations<sup>19</sup> have since also confirmed that the energetically favourable configuration in the intermediate form of graphite fluoride necessitates the realization of an  $\text{sp}^3$  hybridization state for those carbon atoms directly linked to a fluorine atom, again refuting the statement of ionocovalence.

In summary, the ionocovalent model in the intermediate phases of fluorographites should be replaced by a conventional covalent bonding mode, softened by some effects to be clarified in future works. Sato et al.<sup>18</sup> shortly discussed the reason for bond weakening in this kind of compounds and reasonably inferred that the latter effect should result from the participation of the valence shell of the fluorine atom in a hyper-conjugation phenomenon with the subsisting conjugated  $\pi$ -scheme present in a carbon sheet. Such an effect is indeed well-known to occur in some conjugated organic fluorocarbon molecules.

## Conclusions

Given the now firmly established obsolescence of the ionocovalent description of some fluorographites, it seems clear that the same must hold true for any fluorinated carbon nanostructure and that less energetic, but nevertheless fully covalent bonds do form in these compounds. Consequently, extrapolation of the latter bond polarization model to the interpretation of their reactivity, solution or surface/interface properties and of their spectral data must be discarded.

The main effects contributing to the evolution of the C-F bond energy in fluorocarbon materials have been here experimentally visualized and arise from the carbon lattice initial curvature and fluorine addition scheme.

## Experimental section

Fluorinated samples were prepared by heating the former carbonaceous materials under a molecular fluorine gas flow in a Monel reactor, initially purged with nitrogen until the synthesis temperature was reached. Temperatures of 600, 520, 300, 320, 320 °C and reaction times of 8, 1, 2, 3, 8 hours were used, with

respect to the order first cited in the text for the different carbon allotropes used. All samples were rapidly cooled under fluorine. Further details about the experimental procedures might be found in previous work.<sup>6,11</sup>

The standard white compound poly(monocarbon monofluoride)  $(\text{CF})_n$ , saturated with fluorine,<sup>2,3</sup> resulted from the high temperature fluorination of graphite. The short duration employed to fluorinate the MWNTs ensured halogenation to saturation of the outermost layers only, while maintaining a pure inner carbon core.<sup>10,11</sup> The associated apparent average composition, deduced from weight uptake after fluorination, was  $\text{CF}_{0.2}$ . The SWNT-based fluorotubes prepared present surface fluorine addends under the form of two major distinct addition schemes.<sup>12</sup> These two main categories of bonds are clearly revealed in the corresponding IR spectrum, while the large width features inherent to C-F bonds can be resolved with 2 components in the  $\text{C}_{1s}$  and  $\text{F}_{1s}$  spectra (fig. 1 + table 1). XPS analysis indicated a final composition  $\text{CF}_{0.5}$ . Finally, the fluoro[70]- and [60]-fullerenes each correspond to a  $\text{CF}_{0.8}$  compound (i.e.  $\text{C}_{70}\text{F}_{56}$  and  $\text{C}_{60}\text{F}_{48}$ , respectively).

FTIR spectra were obtained in the transmission mode from anhydrous KBr pellets. Preliminary TEM observations performed on the raw single-walled and multi-walled tubes showed outer diameters set near 2 nm and  $30\pm 10$  nm, respectively. XPS spectra were collected twice from two different spectrometers equipped with hemispherical analyzers (pass energy 20 eV) and Mg or Al  $\text{K}_\alpha$  radiations (240-300 W), respectively. The curve-fitting of the spectra was carried out with Gaussian/Lorentzian product functions (G/L mixing ratio of about 0.7). The relative sensitivity factor F:C was adjusted from PVDF as standard. Care was taken to properly correct binding energies with respect to possible charging effects, especially for non-conducting samples, and all spectra were referenced against the position of the  $\text{C}_{1s}$  peak from non-halogenated carbons at 284.6 eV, of either adventitious origin or from some samples themselves. The minor  $\text{C}_{1s}$  signal of  $>\text{CF}_2$  groups, forming on edges or at local defects sites upon fluorination of the carbonaceous precursors, could sometimes also be used as an additional check of the correctness of the respective peak positions. The accuracy expected in the binding energies comparisons is thus better than  $\pm 0.1$  eV in the absence of excessive peak overlap.

## Notes and references

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‡ Indicates the exo, endo, or recto-verso way addition can take place on a carbon sidewall and should be distinguished from the term « addition pattern », which refers to isomerism within a same addition scheme.

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