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Modifying the electronic properties of multiwall carbon nanotubes via charge transfer, by chemical doping with some inorganic fluorides

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Abstract:

The reactivity of multi-walled carbon nanotubes with some inorganic fluorides (BF₃, TiF₄, NbF₅ and WF₆) has been studied. The accommodation of the fluorinated species into the carbon lattice has been shown to result from intercalation and adsorption/condensation phenomena. Charge-transfer, induced by such a chemical doping, has been clearly evidenced by ¹⁹F NMR and ESR spectroscopy. The doped materials exhibit insulating properties. Due to a restriction in size of the intercalated domains, the opportunity of achievement of a homogeneous doping level and of resulting isotropic 1D transport properties in chemically modified carbon nanotubes is discussed.

Keywords :

Carbon nanotubes; Inorganic fluorides; Intercalation.

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1. Introduction

Several ways toward the high yield synthesis of multi-wall carbon nanotubes (MWNTs) are now available, involving either arc-discharge [1] or catalytic processes, in which case numerous carbon sources have proved efficient precursors [2-7].

Chemical doping, usually used to tune the electronic properties of a condensed phase, induces an increase in the density of free charge carriers and, consequently, enhances the thermal and electrical conductivity. We have therefore studied, within the framework of an exploratory approach, the reactivity of MWNTs in regard to a specific category of fluorinated Lewis acids. Indeed, such oxidizing agents, well-known to yield charge transfer intercalation compounds with other allotropic forms of carbon like graphite [8-12] or fullerenes [13-16], stand as ideal candidates liable to give birth to a strong interaction with the carbon matrix, while respecting its structural integrity by avoiding the formation of covalent bonds, associated with electron-trapping. The strategic choice of such a reaction scheme happens to be all the more appropriate that the global morphology of a MWNT suits well the geometrical criterion inherent to intercalation chemistry, since beside the presence of a vacant central cylindrical cavity, the bonding anisotropy along the transversal and longitudinal axes of such a tube generates a van der Waals gap between the concentric carbon layers. Though attractive at first glance, this prospect has been neglected in favour of closely connected studies on single-walled carbon nanotubes bundles [17-21] and so far, only the chemical doping of MWNTs with some alkali metals [22-27] and a few transition metals halides [28-30] seems to have been reported. In the course of some of these earlier studies, it has become common sense to evoke that charge transfer between a strong donor or acceptor intercalated species and the MWNT host-matrix may represent an alternative of chemical nature to the control of the electronic properties of carbon nanotubes. Nevertheless, a detailed description of the

influence of such a doping on the latter carbonaceous host-material properties has never really been tackled. We will therein present results in this sense, characterising the intercalation of several inorganic fluorides into such carbon nanostructures.

2. Experimental

2.1 MWNTs elaboration and purification

MWNTs were prepared via a catalytic method, previously described in ref. [2], and involving the disproportionation of carbon monoxide over alumina-supported Co catalyst particles, at 510 °C (Boudouard reaction). The high yield obtained is partly compensated by the need of a subsequent purification process. Successful chemical treatments with acids under reflux have already been reported but the drawback of this method is the appearance of oxygenated surface groups, when oxidizing reagents are used. In order to avoid the formation of such oxygenated addends, a two-steps purification method was applied, involving a heat treatment in air at 450 °C for 20 minutes, followed by an acid wash with a concentrated HF-HCl mixture (50%-50% in volume). The temperature used in the first step was optimised by thermogravimetric analysis and corresponds to the starting point of decomposition in air of our MWNTs.

2.2 MF_n elaboration and intercalation conditions

The inorganic fluorides employed were BF₃, TiF₄, NbF₅ and WF₆. The present experimental conditions reproduce those previously used for the intercalation of the same fluorides into graphite, as described in [11]. Purified MWNTs (10-20 mg) were put in an

alumina crucible, placed in a reactor connected with a fluorine and nitrogen gas flow. The fluorides were prepared by direct reaction of a pure fluorine atmosphere with each element, placed in a separate crucible next to the MWNTs and heated at the specific temperature of formation of its fluoride. In order to increase the reaction rate for the most volatile fluoride, i.e. WF_6 , MWNTs were put in a secondary reactor cooled at $-20\text{ }^\circ\text{C}$ with a salt-ice bath, so that the formed fluoride condense on the inner side of the container. The system was then isolated and placed at the desired specific reaction temperature, during 24 hours. After reaction, all MF_n -MWNTs materials were stored and handled under argon. The different reaction conditions are summarised in table 1.

2.3 Characterisation

The pristine MWNTs and MF_n -MWNTs samples were conditioned in sealed capillaries of 0.5 mm diameter. Powder X-ray diffraction (XRD) measurements were performed using a Philips X'Pert Pro diffractometer, working with the $Cu\ K\alpha_1$ radiation. Diffraction patterns were collected in the transmission mode with a position sensitive detector.

Transmission electron microscopy (TEM) was performed with a Jeol microscope operating at 200 kV to characterise the initial MWNTs.

ESR spectra were recorded using a X Band Brüker EMX spectrometer equipped with a standard variable temperature accessory and operating at 9.653 GHz. Diphenylpicrylhydrazyl (DPPH) ($g=2.0036 \pm 0.0002$) was used to calibrate the resonance frequency. In order to avoid distortion of the spectrum, the modulation amplitude of the static field was maintained at less than or equal to one third of the smallest peak-to-peak linewidth (ΔH_{pp}) each time. Non-saturated microwave power levels were used when determining the g -

values and ΔH_{pp} . Data processing and simulations were performed using Brüker WIN-EPR and SimFonia software, respectively.

Solid state ^{19}F NMR spectra were obtained at room temperature at 282.3 MHz (CFCl_3 as external reference) with a Brüker DSX 300 Spectrometer, under static conditions and using a classical $\pi/2$ acquisition sequence.

3. Results

The final number of layers in the batch of MWNTS synthesised has been modulated in order to enhance the efficiency of the purification process, aiming at the elimination of the ferromagnetic catalyst particles. This sounds a prerequisite before any further physical characterisation involving a magnetic field can be performed.

The TEM observations confirm the quasi total removal of residual alumina and cobalt particles after purification. The number of layers seems to vary around 9 ± 2 for each tube (fig. 1). Thus, the corresponding carbon thickness appears to be insufficient to resist a complete opening of the tubules extremities via the preliminary oxidative treatment in air. The metal particles, located at the tips and freed from their initial protective carbon coating are then completely removed by the acid wash. Their final amount in the sample thus purified is sufficiently low for the usual very broad ESR response with a g-factor close to 2, characterising such ferromagnetic residues, to remain unobservable when a large scan width is used.

Consequently, X-ray diffraction (fig. 2) shows no persistence of any signal arising from Co particles. The pattern is composed of broad lines, related to the reduced coherence length in the material. The average wall thickness, extrapolated from the FWHM of the main reflection, which is equivalent to the (002) reflection of graphite and in which the finite-size

effect contribution to the global profile is supposed to be largely predominant, corresponds to 8 successive stacked layers, complying with the HRTEM observations. The distribution of interlayer spacing is centred on 0.346 nm.

After exposure to the different gaseous reagents vapours, according to the experimental procedures previously mentioned, the nominal composition of the MF_n-MWNTs compounds has been determined by weight uptake. The corresponding chemical formula in each case is given in table 1.

Several competing fixation modes to the carbon substrate are to be considered. In order to decrease the influence of physisorption at the outer surface and that of a possible condensation in the hollow core, at local defect sites or even in the mesoporosity of the bulk, several temperature conditions have been tested. Increasing the temperature has indeed resulted in a systematic decrease of the final MF_n/C ratio. While a simple “deposit” of fluorinated species on the carbon substrate can most of the time not be evidenced by XRD (some relevant narrow extra-lines are sometimes apparent, see fig. 2), intercalation phenomena can usually be characterised by the emergence of new reflections in the low angle region of the pattern and beside the main line of the pristine material [22, 23, 28, 30]. Such additional features can be distinguished in most cases (fig. 2), supporting an effective, though partial, intercalation process. Largely as a consequence of the size-broadening effect, the diffraction data are in any case not much modified in regard to the overall profile observed for the raw material and the intercalated domains exhibit roughly defined X-ray signatures with excessive peak overlapping. Hence, the determination of their corresponding stage number happens to be quite uncertain and has not been considered in the present work. The relevant Bragg peaks even become hardly discernible as the synthesis temperature increases, showing that this latter effect affects intercalation at least as much as adsorption/condensation. A high

temperature may therefore result either in less extended intercalated zones or in the formation of higher order stages. Whatever the reaction conditions used, both previous accommodation modes occur and their respective influence on the global composition of the different samples varies in an indefinite way.

As mentioned in introduction, the chemical modification of nanotubes may appear to be an alternative to the problematic control of their electronic properties via their helicity and diameter. Hence, we have investigated charge transfer, a necessary condition for an efficient modulation of the electronic properties, between MWNTs and the accommodated fluorides. The MF_n-MWNTs compounds have then been further characterised by ESR spectroscopy, in a second place. While the pristine purified nanotubes are ESR silent in the limit of detection of the spectrometer, all ESR spectra of the doped compounds exhibit two lines, broad and narrow respectively. For a given fluoride, these distinct signals differ by their relative intensities according to the synthesis temperature and the contribution of the narrow component to the global spectrum is all the more important that this temperature is high (fig. 3 a-f). This observation parallels the evolution of the diffraction patterns, i.e. the higher the preparation temperature is, the lower the diffracted intensities issuing from the intercalated domains are. We thus infer that the broad signal is related to the intercalation phenomenon whereas the narrow one originates from the adsorption and/or condensation of fluorides.

It may be worth noticing that no contribution from potential unsaturated dangling bonds is expected here, since the presence of elemental fluorine in the initial medium should rapidly lead to an addition reaction at such sites. The presence of the previous fluorine atmosphere also precludes the reduction of fluorides, which may result in the formation of paramagnetic halides and accordingly, no direct contribution from any neutral or charged fluorinated species mentioned in the following is awaited either.

The origin of the intercalation-induced appearance of unpaired spins is thus not supposed to differ from that already established in the case of homologous graphite intercalation compounds (GIC's), formed under similar conditions [8-12]. Charge transfer arises from the formation of interplane anionic species according to the following symbolic notation: $C + MF_n + p/2 F_2 \rightarrow C^{p+} + MF_{n+p}^{-}$, where $p=1$ or 2 . The latter phenomenon has been clearly evidenced by ^{19}F NMR spectroscopy in the case of a BF_3 -treated MWNTs sample. The relevant spectrum on fig. 4 exhibits a dominant peak whose chemical shift $\delta_{\text{F}} = -161$ ppm unambiguously corresponds to the BF_4^- anion (from standard tables δ_{F} ref. ≈ -150 ppm). Downfield peaks at $\delta_{\text{F}} = -120$ and -62 ppm are attributed to the presence of some neutral BF_3 species (δ_{F} ref. ≈ -129 ppm) and $-\text{CF}_3$ groups on edges (δ_{F} ref. ≈ -69 ppm), respectively. Furthermore, while attempting to insert WF_6 , it has been observed that the absence of an initial oxidizing fluorine atmosphere results in an extremely slow reaction rate, thus indirectly confirming the above mechanism and the necessary formation of anionic species in the interlayer space for intercalation to occur.

The ESR signal assigned to adsorption/condensation of fluorides is in favour of a charge exchange of similar origin, involving the formation of surfacic anionic species. The previously described independent schemes result in different interactions of spins with their respective environment and in a subsequent spectral decomposition.

Experimental ESR spectra can be correctly fitted from a Lorentzian description of each separate contribution (fig. 3). The analysis of the broad features shows that the peak-to-peak linewidth (ΔH_{pp}) and Landé factor are almost independent of temperature over the 110-300 K range (table 2), suggesting that the spin carriers are localised, contrary to the metallic character of some parent GIC's. The insulating behaviour inferred is further confirmed by the observation of increased signals intensities with decreasing temperature, which supports a susceptibility of the Curie type for each material studied. Figure 5 displays the variation of

$\ln(\Delta H_{pp})$ as a function of $\ln(Z)$, where Z stands for the atomic number of the intercalated coordinated metal. It is found that ΔH_{pp} varies as Z^α , with $\alpha = 0.9 \pm 0.2$. A similar relation was already reported for alkali metal-based GIC's [31] and some alkali-ion-doped low dimensional organic polymers [32,33], where such an evolution of ΔH_{pp} with Z indicated that the spin-orbit interaction at the dopant atoms was the major contribution to the line broadening of the ESR signal. The low value of α obtained here and the deviation from perfect linearity suggest that the spin relaxation rate is not dominated by spin-orbit coupling effects.

In the case of the narrow signal due to adsorbed/condensed fluorides at the inner or outer surface of nanotubes, ΔH_{pp} does not vary as Z^α , indicating different electronic interactions governing the ESR parameters. In any case, the previously noticed intensity vs temperature correlation is maintained. Further insight into the influence of temperature is provided for two samples of composition $C_{82}WF_6$ and $C_{33}BF_3$ and it has been found that ΔH_{pp} slightly decreases from 110 to about 200 K (fig. 3h). The variation remains of weak amplitude, however, and motional narrowing of the linewidth induced by thermally activated hopping could explain the behaviour observed.

4. Discussion

In regard to the experimental results described in the above sections, the tuning of the electron density of carbon nanotubes through doping seems full of promise and the question that may be addressed is whether such a chemically modified carbon nanostructure is suitable for potential nanotechnology applications.

From a steric point of view, an expansion of the interlayer spacing is necessary for an accommodation of guest-species into the interstitial channels of a MWNT to be possible. The

required dilatation of interatomic distances then necessary implies the presence of non-closed curved graphitic shells and was at the origin of the scroll structural model of MWNTs originally proposed by Zhou et al. [22], instead of the commonly admitted Russian doll model. A possible extension to a continuous imbrication of disrupted graphene layers, spirally rolled up, was also mentioned.

The most salient feature in the diffraction patterns of the present doped samples is characteristic of some raw MWNTs and accordingly, intercalation happens to be only partial in all cases. The underlying scheme was elucidated in earlier works by microscopy observations [23, 28, 29] of successive intercalated and non-intercalated sequences along the longitudinal axis of each tube, producing an heterogeneous swelling effect. The particular morphology of the intercalated materials has then to be related to a successive alternation along the tube axis of intercalable zones, consisting in non-closed graphitic fragments, and non-intercalable zones, consisting in perfectly nested shells. This inhomogeneity in the basal structure implies that a regular and continuous doping of the tube and consequently, the achievement of isotropic 1D transport properties, can only be expected from a precursor consisting in a perfect scroll-like structure over its entire length. The controlled synthesis of such entities remains unfortunately an unsolved difficulty and as a corollary, the tuning of the electronic properties of carbon nanotubes by the chemical way remains as delicate to circumvent as the current limitation inherent to the control of these same properties via some of the intrinsic characteristics of the tubes.

The surface effect described above may represent a better alternative since it could more easily be applied to a single-walled carbon nanotube, a prototype of topologically regular nanostructure, the elaboration of which is now well advanced. Simple filling of the core by capillarity, with a properly selected charge transfer agent, should ensure electron

exchange from the inner side and lead to the desired shift of the Fermi level and modification of transport properties.

5. Conclusion

Novel fluorinated intercalation compounds have been obtained from catalytically-grown MWNTs. Several modes of fixation of the fluorinated molecules to the carbon lattice have been evidenced, leading to an effective electron transfer between the host and guest species. Direct exploitation of such a charge exchange within the frame of a chemically controlled tubule can turn out to be a fruitful concept only with a precise category of MWNTs, still unavailable yet.

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1141

Tables and figures captions

Table 1: Synthesis conditions of the MF_n -MWNTs compounds. The bracketing of the final C/MF_n ratio has been established on the basis of a reasonable margin error of ± 0.5 mg on the weight uptake measured. (*) data from ref. [30].

Table 2 : Parameters of the ESR lines at 110 and 300 K.

Figure 1: HRTEM image of the pristine nanotubes.

Figure 2: Diffraction patterns of the samples prepared at the lowest (a) and highest (b) temperatures. (*) point out reflections arising from probable condensation products.

Figure 3: (a)-(g) Experimental and deconvoluted EPR spectra of the different MF_n -MWNTs samples ((a) Gain $G=10^5$, (b) $G=5.10^4$, (c)(d) $G = 5.10^4$, (e)(f) $G = 4.10^4$, (g) $G = 2.10^4$; the lower signal to noise ratio in (b) is due to a smaller amount of material). A very broad additional contribution (not shown) has been used as baseline correction. (h) Evolution of the parameters of the narrow signal with temperature for C_{33}BF_3 (top) and C_{82}WF_6 (bottom).

Fig. 4: Room temperature ^{19}F NMR spectrum of the C_{23}BF_3 sample.

Fig. 5: Variation of $\ln(\Delta H_{pp})$ as a function of $\ln(Z)$ ($Z =$ atomic number of M in MF_n) for the different intercalated metal atoms considered.

Table 1

Element	Temperature of formation of the fluoride (°C)	Reaction temperature with the MWNTs (°C)	Reaction time (h)	Final composition
B	250	250	4	$C_{23 \pm 3} BF_3$
	300	300		$C_{33 \pm 6} BF_3$
Ti	320	320	4	$C_{23 \pm 2} TiF_4$
	380	380		$C_{33 \pm 3} TiF_4$
Nb	170	170	4	$C_{32 \pm 3} NbF_5$
	220	220		$C_{35 \pm 4} NbF_5$
W	300	20	24	$C_{36 \pm 3} WF_6$ (*)
	300	60		$C_{82 \pm 13} WF_6$

Table 2

	Broad line				Narrow line			
	ΔH_{pp} (± 1 G)		g-factor (± 0.0002)		ΔH_{pp} (± 1 G)		g-factor (± 0.0002)	
	110 K	300 K	110 K	300 K	110 K	300 K	110 K	300 K
$C_{23}BF_3$	9	9	2.0034	2.0033	6	4	2.0030	2.0029
$C_{33}BF_3$	9	8	2.0032	2.0032	6	4	2.0027	2.0027
$C_{23}TiF_4$	22	23	2.0041	2.0040	7	8	2.0030	2.0024
$C_{33}TiF_4$	22	22	2.0041	2.0039	7	8	2.0028	2.0028
$C_{32}NbF_5$	81	78	2.0034	2.0033	16	17	2.0029	2.0033
$C_{35}NbF_5$	75	77	2.0034	2.0034	40	41	2.0030	2.0032
$C_{82}WF_6$	69	70	2.0024	2.0021	19	16	2.0025	2.0020

Figure 1

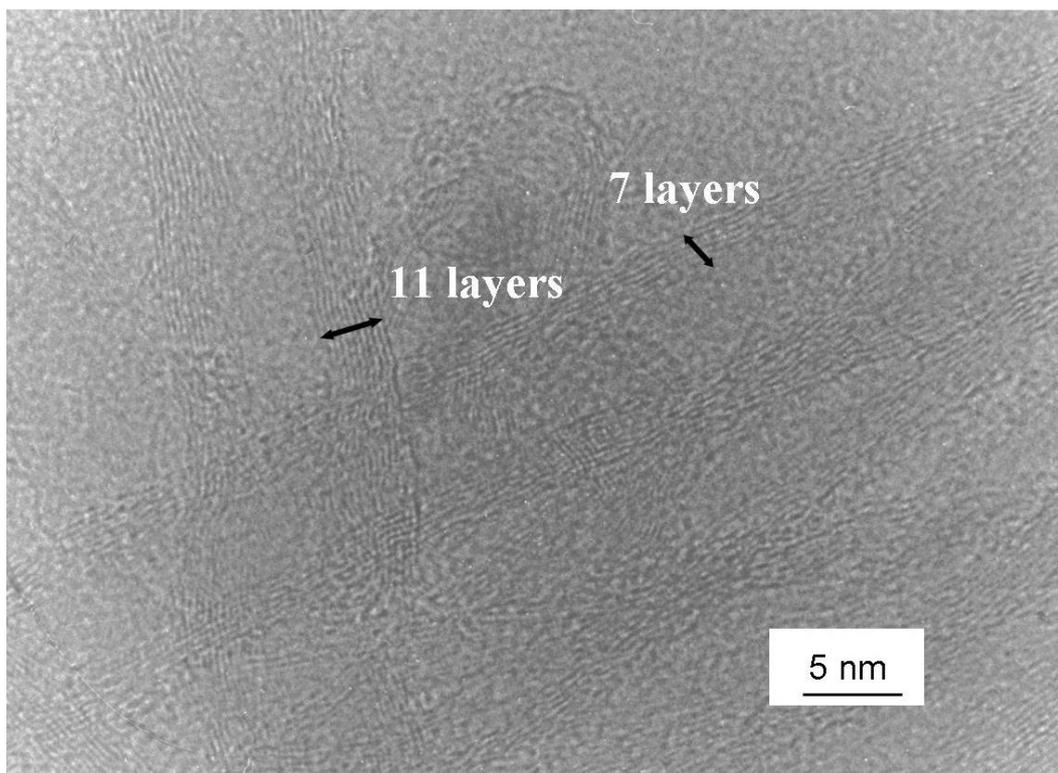


Figure 2

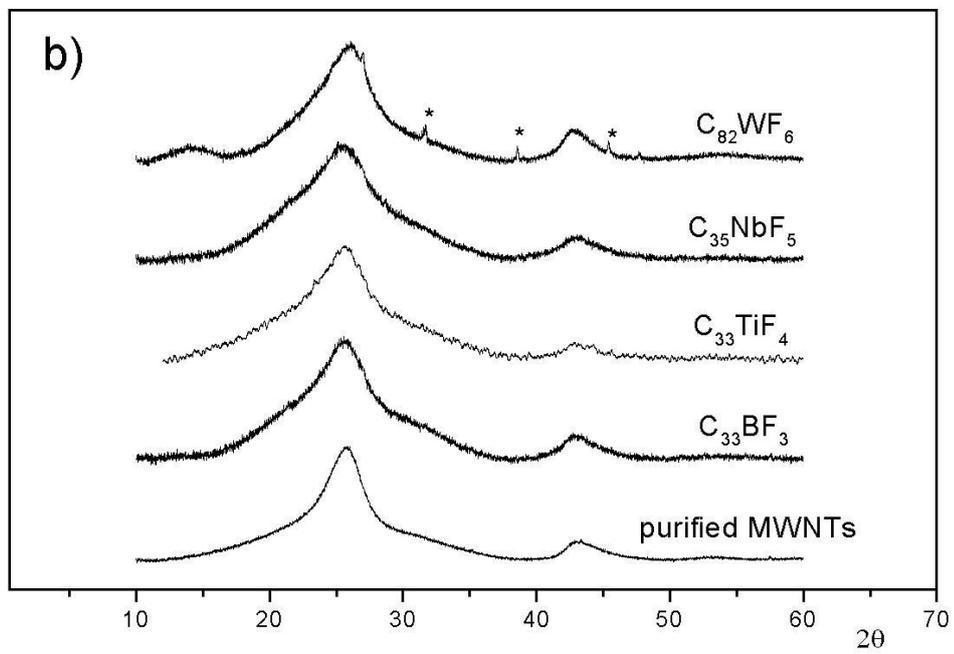
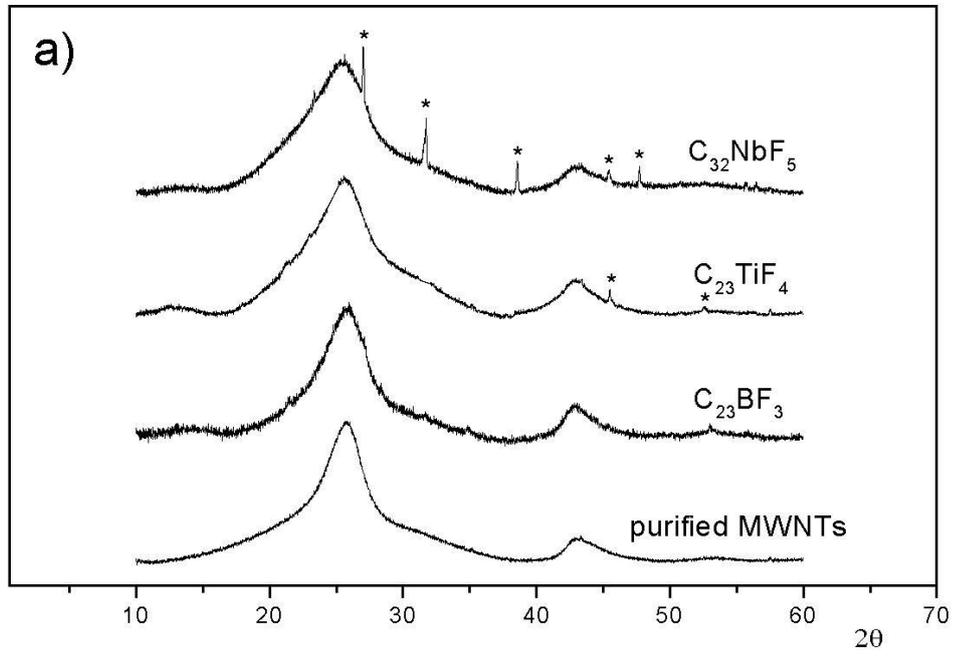


Figure 3

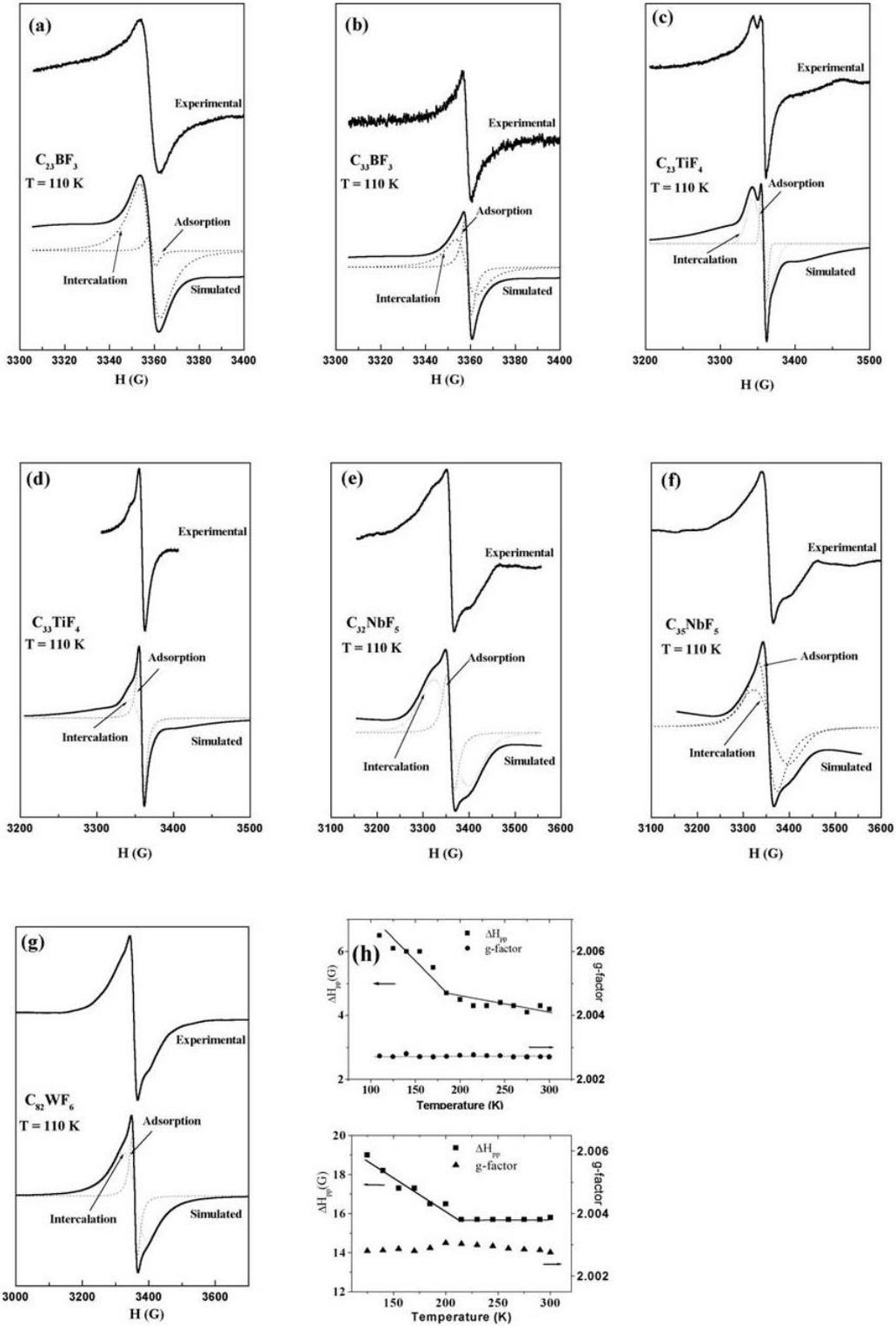


Figure 4

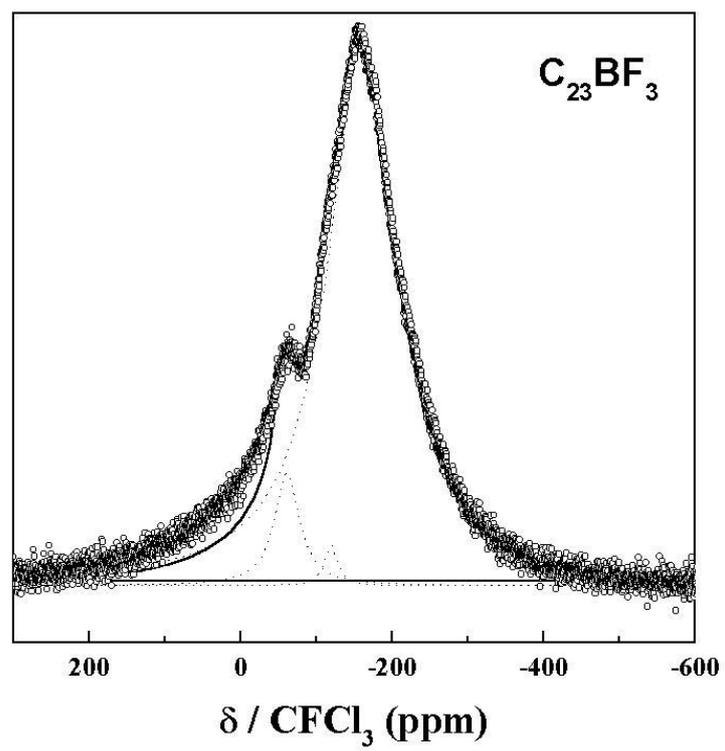


Figure 5

