

A sensitive and practical fluorimetric test for CNTs acidic sites determination

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Electronic Supplementary Information

Features of all investigated pristine nanotubes are reported in Table S1.

Table S1 – Features of the 3 different CNTs

Property	<i>p</i> -SW [a]	<i>p</i> -MW1 [b]	<i>p</i> -MW2 [c]
Type	Single walled	Multi walled	Multi walled
Average diameter [nm]	1.3	40-80	10-20
Length (average) [μ m]	1-5	200-400	0.1 - 10

[a] Information on <http://www.nanoledge.com>

[b] Kim YA, Hayashi T, Endo M, Kaburagi Y, Tsukada T, Shan J, Osato K, Tsuruoka S. Synthesis and structural characterization of thin multi-walled carbon nanotubes with a partially faceted cross section by a floating reactant method. Carbon 2005; 43: 2243-2250

[c] Information on <http://www.nanocyl.be>

Oxidation procedure of *p*-MW1

Annealed MWCNTs (labeled *p*-MW1 from now on for brevity purposes), produced by chemical vapor deposition (CVD) and provided by Nano Carbon Technologies Co., Ltd., Akishima-shi, Tokyo (Japan), were soaked in a concentrated acid solution (HNO₃:H₂SO₄ 1:3) and subjected to chemical oxidation. The CNT/acid mixture (0.15 g CNTs/10 ml acid solution) was stirred at 70 °C, for 5 h. The treatment was followed by quenching in ice and water solution. The consequent suspension was centrifuged and filtered. The black powder deposited on the filter was washed with distilled water, then with ethanol and acetone and dried in oven. The as collected filtered powder (*f*-MW1) was then characterized.

Oxidation procedure of *p*-SW

Pristine SWCNTs, purchased from Nanoledge (Sophia Antipolis, France) have been oxidized by acid treatment as following: the SWCNT containing powder was ultrasonicated at 40°C in a highly acidic 3:1 mixture of H₂SO₄ and HNO₃ for 3 hours. The as collected filtered powder (*f*-SW) was then characterized.

Oxidation procedure of *p*-MW2 and *f*-MW2

Both pristine MWCNTs (Nanocyl 7000, labeled *p*-MW2 from now on) and carboxyl-functionalized MWCNTs (Nanocyl 3101, labeled *f*-MW2 from now on) have been purchased from Nanocyl S.A.

Characterization of the nanotubes

Evaluation of lattice defect degree was performed both on pristine and oxidized nanotubes by Raman spectroscopy and by thermogravimetric analysis (TGA) 2050 balance (TA inc.).

- **Raman spectroscopy.** The damaging of the nanotube wall due to the oxidation procedure was apparent in all the samples by comparison of the Raman spectra (Figure S1). After acid treatment the intensity of the “G” band, located at about 1590 cm⁻¹ and typically associated with tangential vibration modes of CNT sidewall C-C bonds, decreases, while the D band, at about 1277 cm⁻¹ and 1344 cm⁻¹ for SWCNTs and MWCNTs respectively, due to the disorder-induced phonon mode of the carbon six-fold rings breathing vibration, is associated with the presence of alterations and sidewall disorder or amorphous carbon.

In order to estimate the structural ordering, of particular interest is the evaluation of the G band narrowing and of the I_D/I_G ratio (S. Osswald, M. Havel, Y. Gogotsi, J. Raman Spectrosc. 38 (2007), 728–36; F. Tuinstra, J.L. Koenig, J. Chem. Phys. 53, 3 (1970) 1126–30). In fact, whereas the intensity

of the G-band (I_G) does not depend on the lattice defect density, the D-band intensity (I_D) decreases as defect density decreases.

Hence, the disorder degree can be estimated by means of the I_D/I_G ratio (Table S2), where I_D and I_G represent the D band and G band intensities respectively.

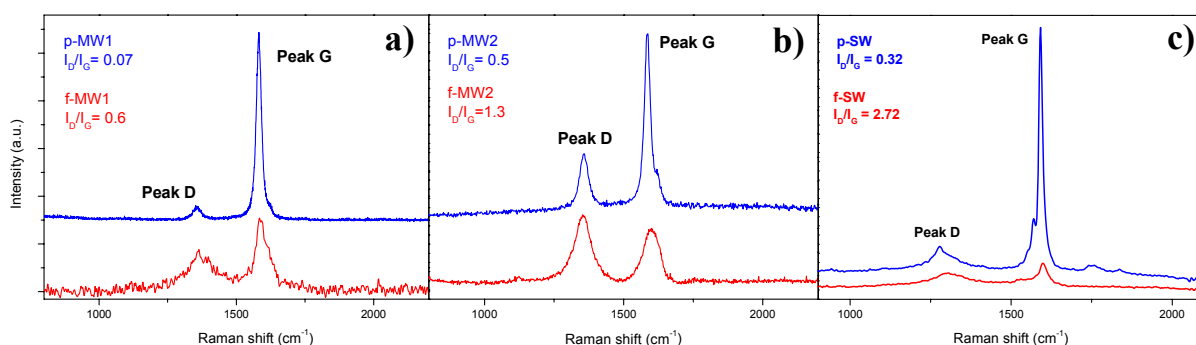


Figure S1. Raman spectra for the pristine and oxidized **MW1** (a) and **MW2** (b) samples (MicroRaman Renishaw Ramascope, Ar⁺ laser 514.5 nm excitation), and Fourier Transform Raman spectra (NXR FT-Raman Thermo Fisher Scientific, excitation laser 1064 nm) for the pristine and oxidized) SWCNT samples (c).

	I_D/I_G ratio
p-MW1 f-MW1	0.07 0.6
p-MW2 f-MW2	0.5 1.3
p-SW f-SW	0.13 0.6

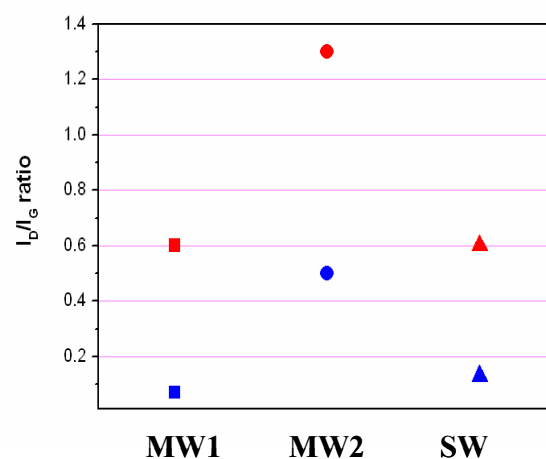


Table S2 – I_D/I_G ratio for the nanotubes, both before and after chemical oxidation

-Thermogravimetric analysis. TGA experiments were performed on approximately 10 mg of the samples with a 60 cm³/min nitrogen flow (99,999 % purity) and with a 10 °C/min heating ramp. The comparison of the thermal degradation curves of the nanotubes, both before and after functionalization treatment, allowed us to evaluate the presence of functional groups (Figure S2). In fact, the functionalized CNTs exhibited a not negligible weight loss in a temperature range (100-400°C) where pristine nanotubes were extremely stable. This can be explained with the fact that the functional groups tend to be significantly desorbed by the CNT surface. Moreover the overall thermal stability of f-CNTs is lower than p-CNTs due to the high amount of lattice defects.

Thermogravimetric analysis have been also performed on the samples after the interaction with THA (Figure S3). Since THA shows a significant thermal degradation at approximately 200°C (Figure S3a), we tried to evaluate the amount of THA absorbed on the nanotubes by comparing the different weight loss of the nanotubes before and after intimate contact with THA solution (Figure S4 and S5).

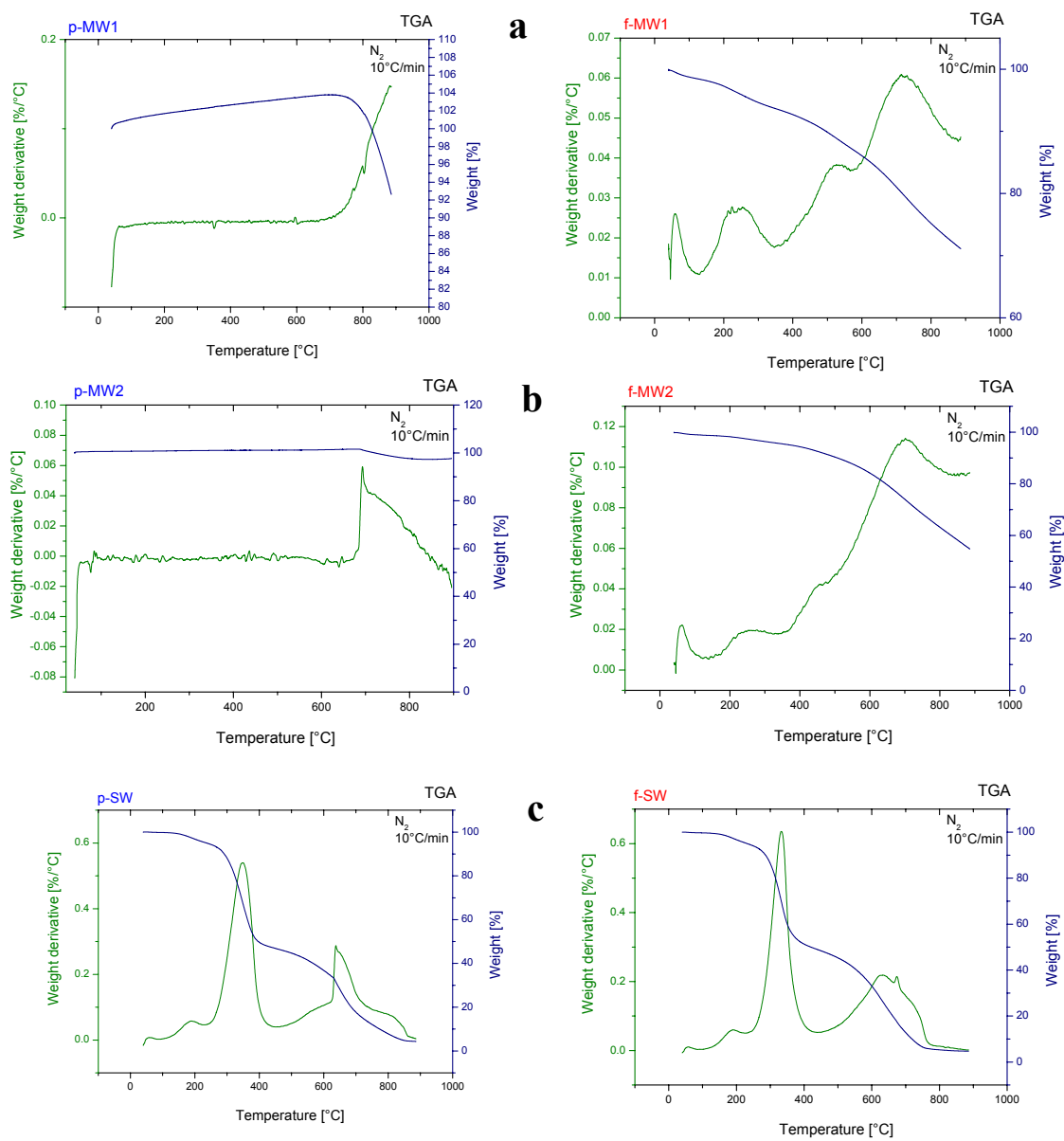


Figure S2. Thermogravimetric analysis in nitrogen flow of the pristine (left) and oxidized (right) MW1 (a), MW2 (b), SW (c).

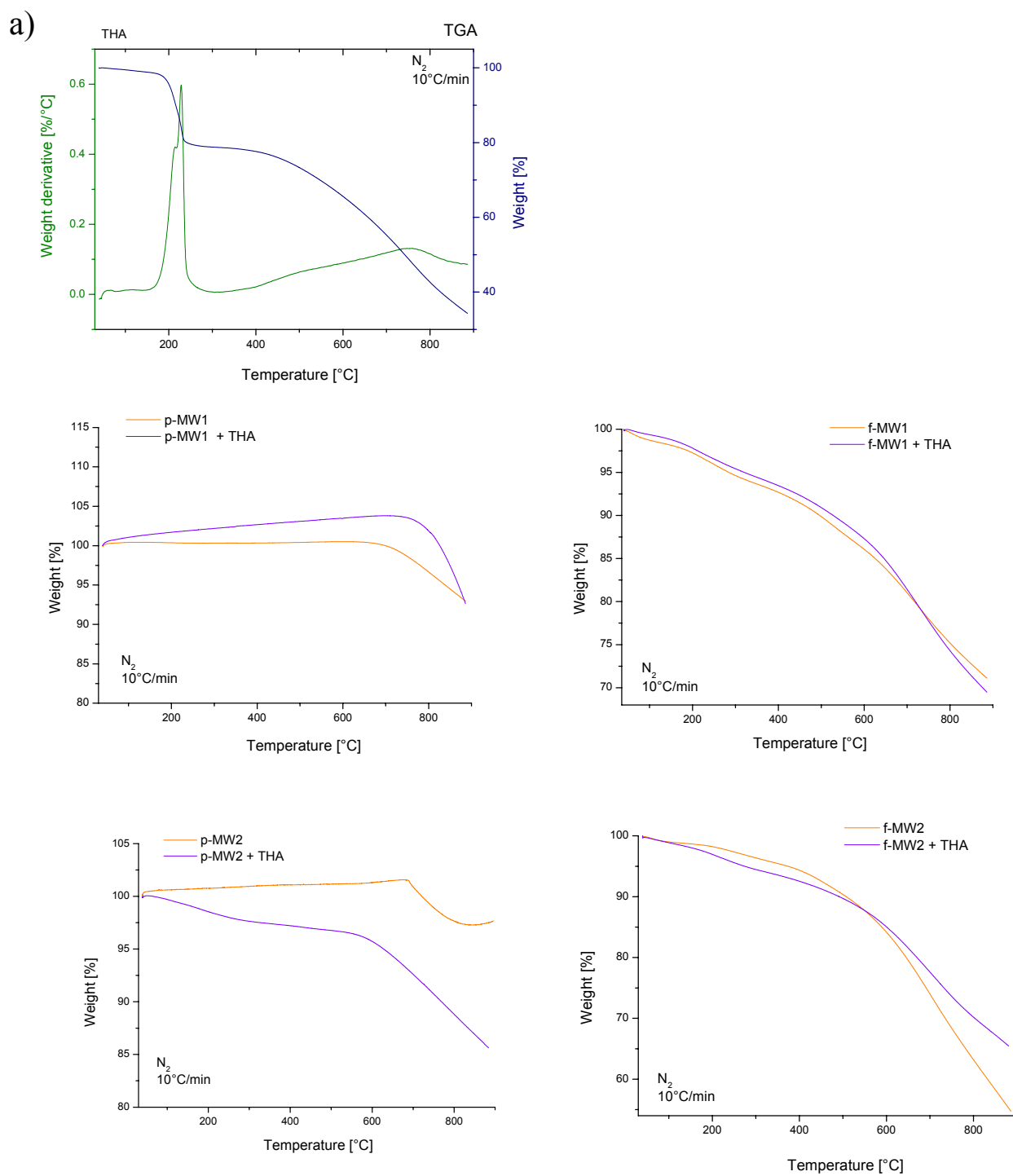


Figure S3. Thermogravimetric analysis in nitrogen flow of THA (a) and of the nanotubes with and without THA.

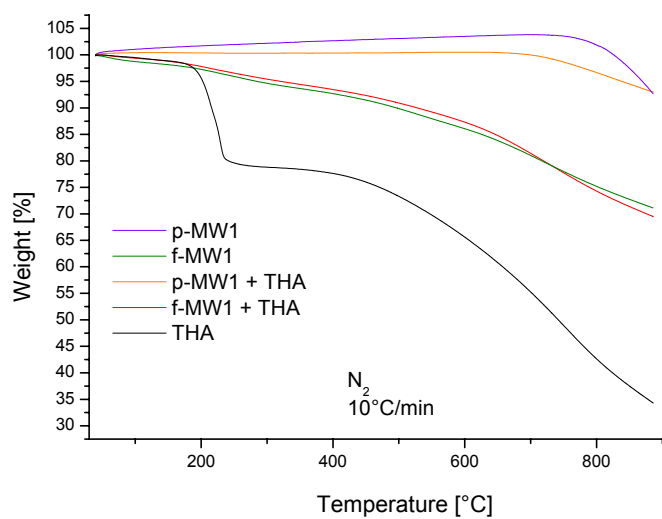


Figure S4. Summary of the thermogravimetric analysis in nitrogen flow of **MW1** nanotubes with and without THA

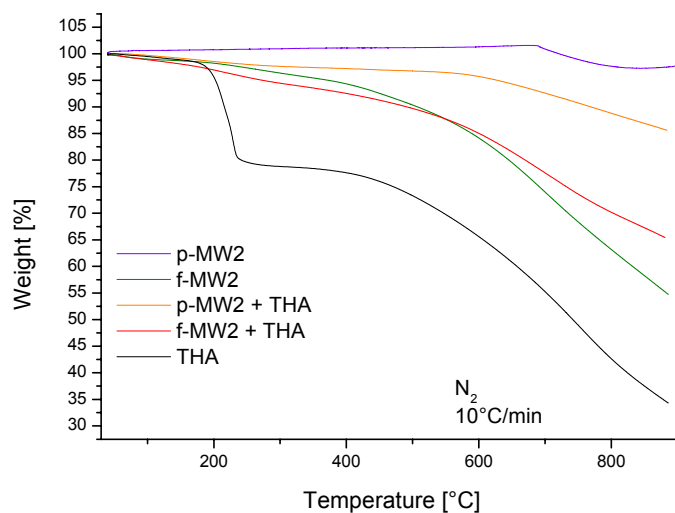


Figure S5. Summary of the thermogravimetric analysis in nitrogen flow of **MW2** nanotubes with and without THA

Spectrochemical titration

An ethanolic solution of THA (4.3×10^{-6} M) was added to small amount (2mg) of CNTs; the solid was trodden (pH = ca. 6), and the mixture is allowed to stir at room temperature for 30 min. After centrifugation (10000 rpm for 10 min) CNTs have been removed and the solution filtered on a $0.45 \mu\text{m}$ pore filter. Steady-state fluorescence intensity measurements were performed on a Perkin Elmer LS 55 spectrofluorimeter equipped with a xenon lamp source and a 5 mm path length quartz cell.

Fluorescence spectra (scan speed 100 nm/min) were recorded in the range of 600–700 nm upon excitation at 594 nm. Excitation and emission slit were 10.0 nm and 5.0 nm respectively.

A daily fresh five points (from 9.7×10^{-8} to 2.4×10^{-7} ; stock solution 9.7×10^{-5}) calibration graph of THA was done using the fluorimetric method herein described ($R^2 = 0.999$).

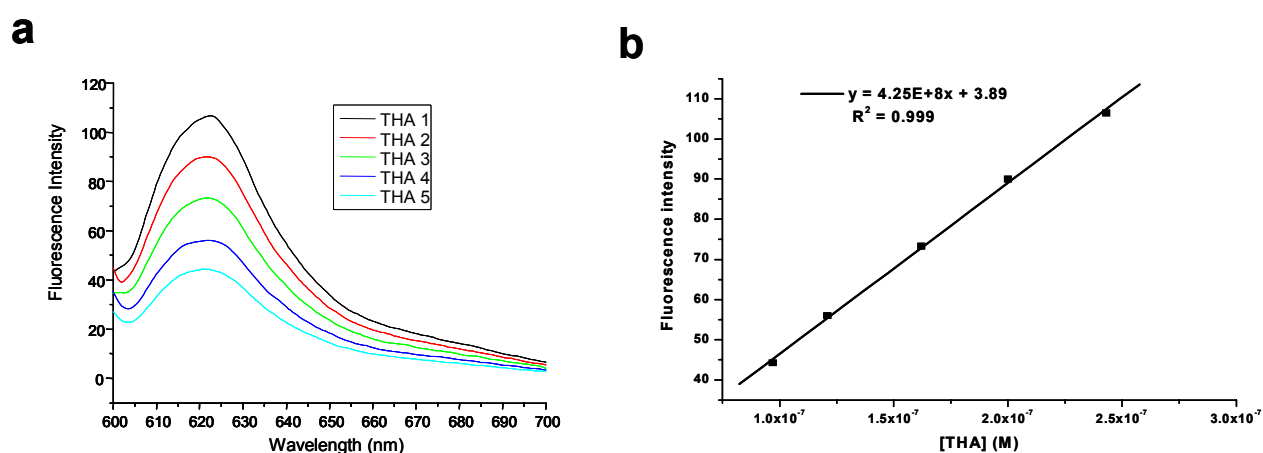


Figure S6. In panel **a** fluorescence spectrum of THA at different concentrations; **b** calibration curve.

In Figure S7 examples of fluorescent spectra of THA reacted with different CNTs are reported. For non oxidized nanotubes the resulting THA solution was diluted 400 times

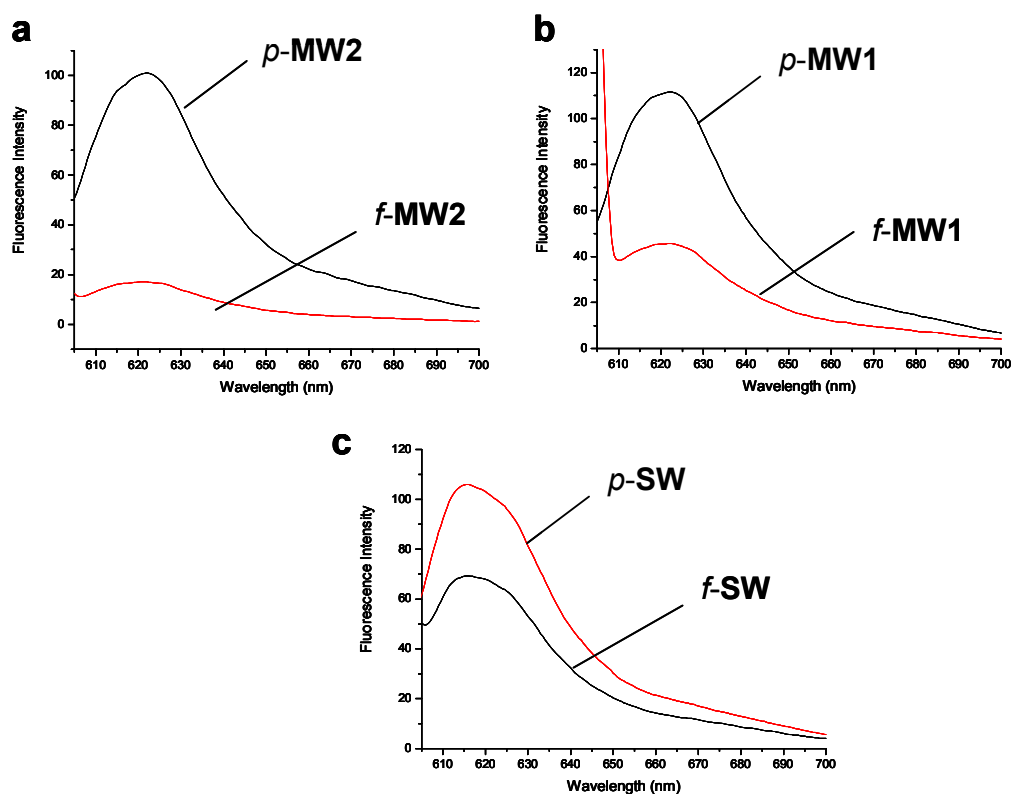


Figure S7. Fluorescent spectra of THA in the presence of *p*- and *f*-MW1, MW2 and SW.

The quantity of thionin absorbed by *p*-MW1, *p*-MW2 and *p*-SW was evaluated by determining the fluorescence emission intensities decrease of the initial dye solution. The reported results are mean values of six experiments, results are shown in figure S8.

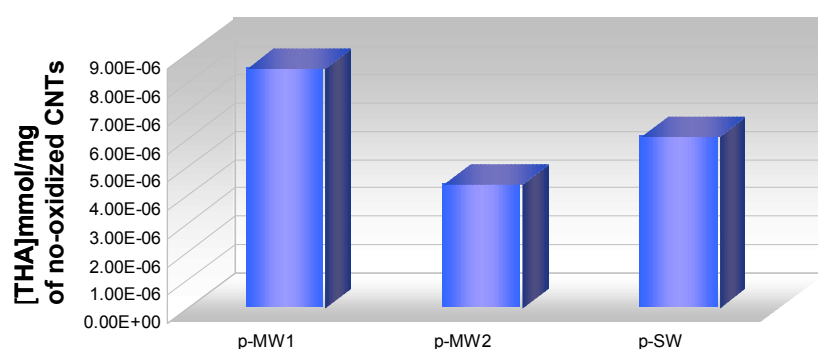


Figure S8. Concentration of THA solution of non oxidized CNTs

The concentration of the acidic moieties of an oxidized CNT sample was evaluated by determining the fluorescence emission intensities decrease of the initial dye solution and subtracting the amount due to unspecific interaction evaluated on the corresponding non-oxidized CNT sample (figure S9). The content of carboxylic groups (equivalent to THA concentration because of 1:1 stoichiometry) was expressed as mmol of COOH/mg of oxidized CNTs. Also in this case data reported are mean values of six experiments and results are shown in figure 2 of the communication.

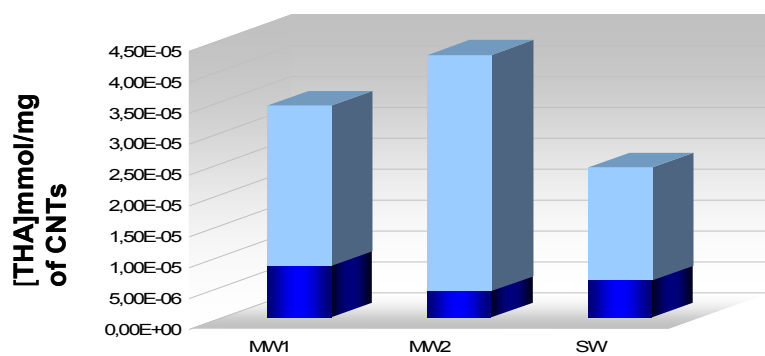


Figure S9. Concentration of THA linked to oxidized CNTs (light blue) and corresponding concentration of THA unspecifically bonded to non-oxidized CNTs (dark blue).