Supplementary Data

The solvent effect on the sidewall functionalization of multi-walled carbon nanotubes with maleic anhydride

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Supplementary Figures

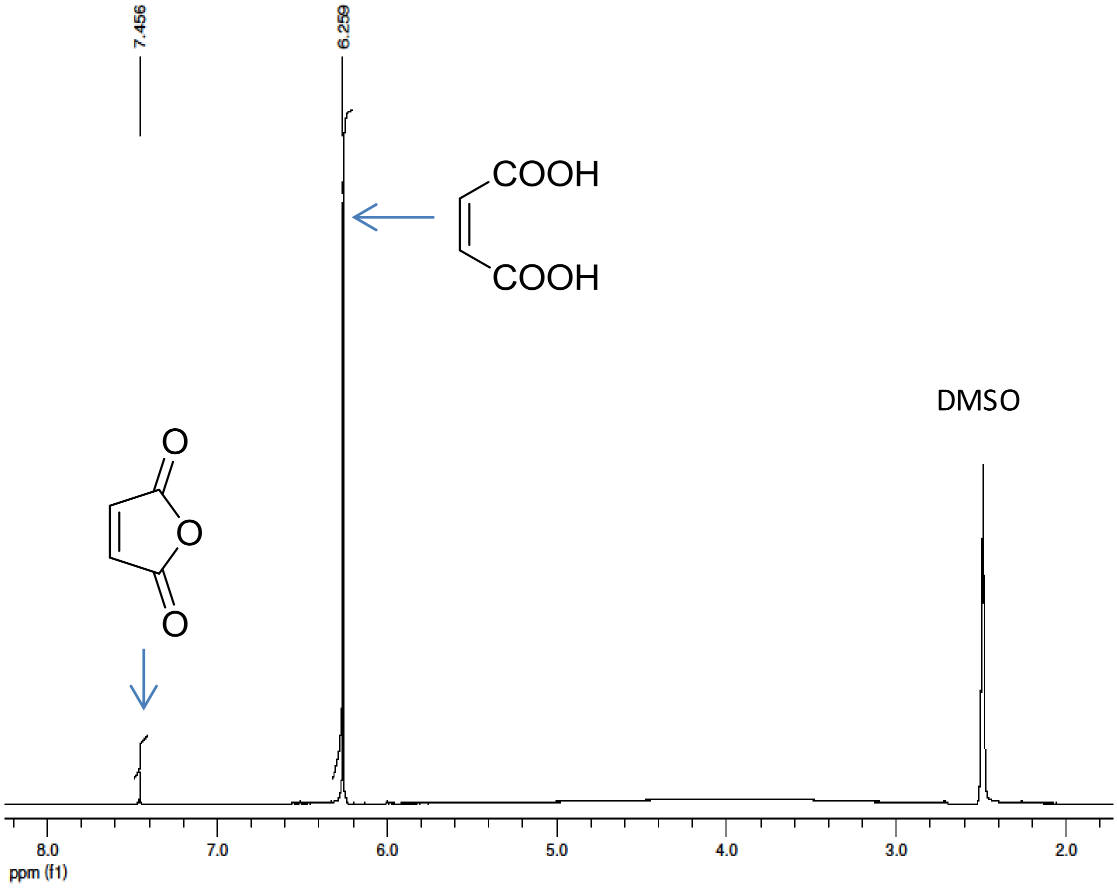


Fig. S1 - ^{1}H NMR spectrum of the compounds soluble in DMSO-d_6 and extracted from the solid mixture of CNT and MA, after 24 h at room temperature.

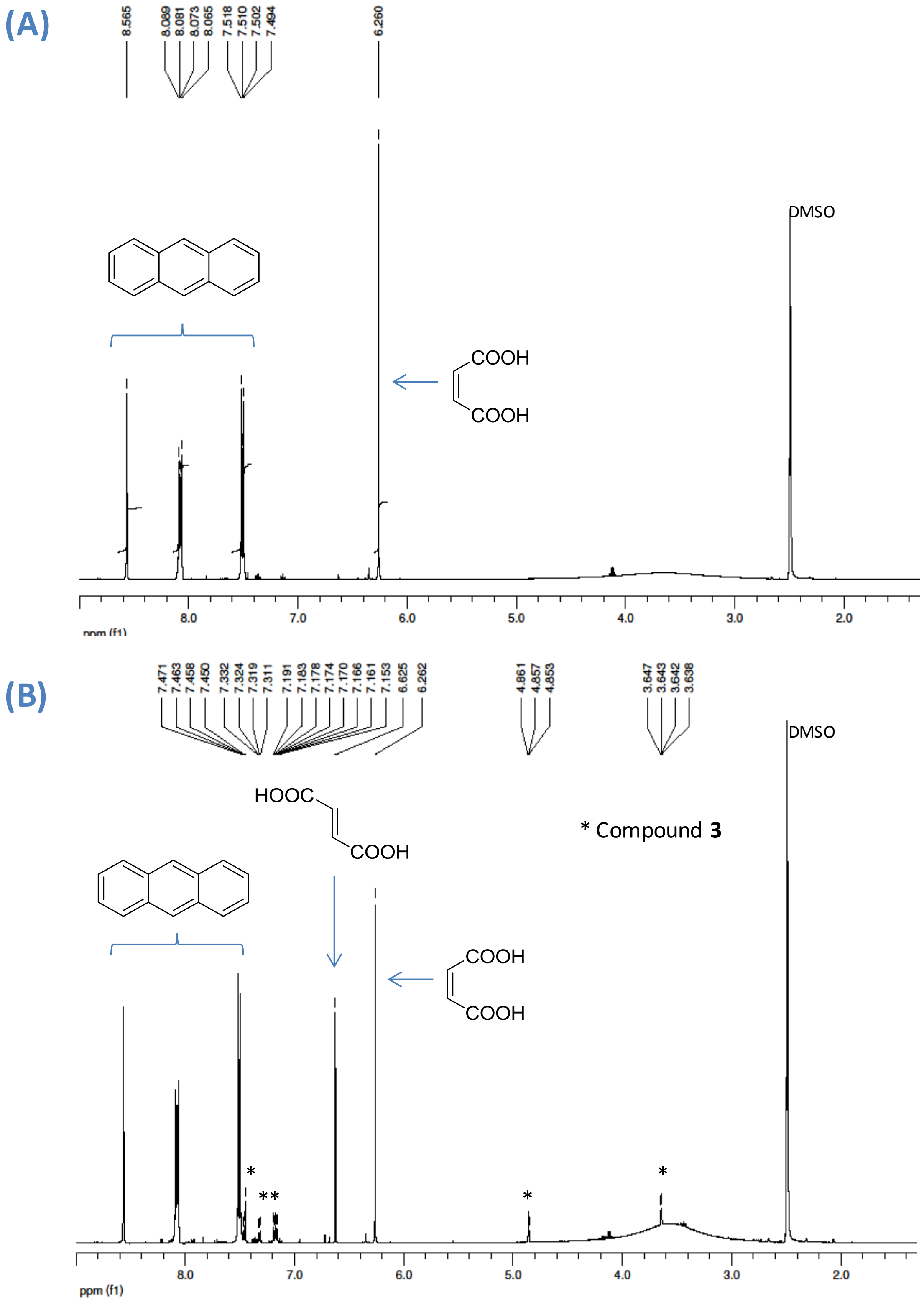


Fig. S2 - ^{1}H NMR spectra of the compounds soluble in DMSO-d_6 extracted from the mixture of CNT and MA, A) immediately after addition of anthracene, and B) after addition of anthracene and heating at 185 ºC for 45 min..

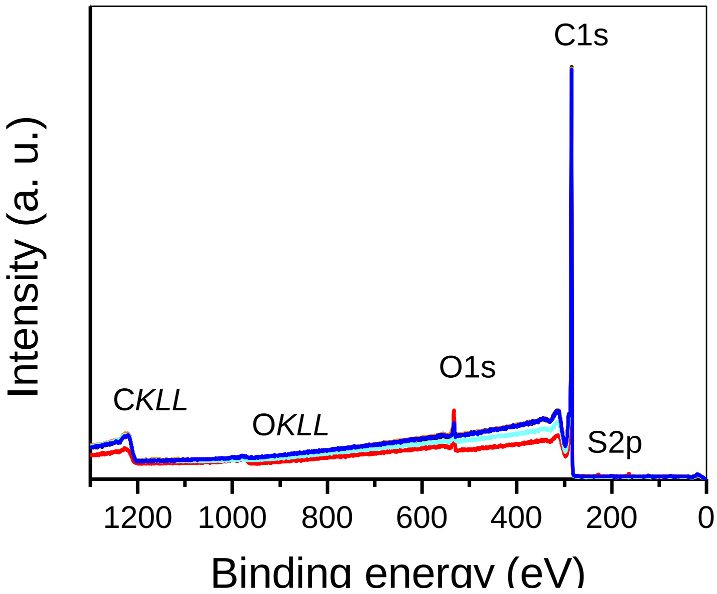


Fig. S3 - XPS survey spectra of pristine CNT (black), exp. 1 (red), exp. 2 (orange), exp. 4 (blue), exp.5 (cyan).

Supplementary Tables

Table S1. Oxygen at. (%) of pristine CNT determinate by XPS and it surface acidity.

Sample	**XPS analysis**	**H^+ equiv. (mmol)**
Pristine CNT	Total oxygen (at. %)	**-**
	0.71	
	Functional groups	
	Phenolic -OH [S1]	

Table S2. Oxygen and sulphur at. (%) of CNT-Exp.2 determinate by XPS and it surface acidity.

<table>
<tr><td>Sample</td><td colspan="6">XPS analysis</td><td>H^+ equiv. (mmol)</td></tr>
<tr><td rowspan="6">CNT-Exp. 2</td><td colspan="3">Total oxygen (at. %)</td><td colspan="3">Total sulphur (at. %)</td><td rowspan="6"><u>0.03</u></td></tr>
<tr><td colspan="3"><u>2.07</u></td><td colspan="3"><u>0.25</u> -S- ; -SO3H
Assumption 50% : 50%, however a small amount of sulfoxide groups cannot be excluded</td></tr>
<tr><td colspan="6">Functional groups</td></tr>
<tr><td>-OH</td><td>-COOH (calculated from 0.02 mmol of H+ [total mmol H+ - mmol SO3H] 0.03-0.01)</td><td colspan="2">-OH; -SMe</td><td colspan="2">-OH; -SO3H
(**0.01 mmol-calculated from XPS analysis)</td></tr>
<tr><td>O (at. %)</td><td>O (at. %)</td><td>O (at. %)</td><td>S (at. %)</td><td>O (at. %)</td><td>S (at. %)</td></tr>
<tr><td>2.07-0.486-0.125-0.125-0.375=0.959</td><td>*0.243 COOH groups (C-O 0.243; C=O 0.243)</td><td>0.125</td><td><u>0.125</u></td><td>3*0.125 = 0.375
C-O 0.125</td><td><u>0.125</u></td></tr>
</table>

Note: **<u>values in bold and underlined are experimental results;</u>**

Values in blue were calculated from the experimental results.

**<u>Acidity calculated from the XPS analysis attributed to sulfonic acids.</u>

Molecular weight calculated from the XPS analysis (once the XPS do not determine the hydrogen atoms they won't be considered in following calculus):

Mw(CNT-Exp.2)=2.07*16+0.25*32+97.68*12=1213.28 g/mol

By XPS it is Known that there are 0.125 groups of SO_3^-

$\%SO_3^- = \frac{80 * 0.125}{1213.28} * 100$ =0.824 % , so in 100 mg we have 0.824 mg of SO_3^- groups

$n(SO_3^-)=n(H^+)$

$n(H^+)$ from sulfonic acids $= \frac{0.824}{80} = 0.01\ \mathrm{mmol}$

* number of carboxylic acids calculated from the total acidity minus the acidity calculated in **

By titration it is known that the total acidity in 100mg of functionalized CNT it is 0.03 mmol

Subtracting to the total acidity the contribution of sulfonic acids it is determined the mmol of H^+ associated to carboxylic acids:

0.03-0.01 = 0.02 mmol of COO^-

Determination of the mass of COO^- (n=m/M) in 100 mg

$0.02 = \frac{m(COO-)}{44}$ <=> $m(COO^-)=0.88$ mg

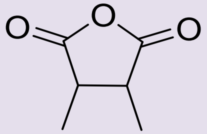
% COO- = 0.88 %

Determination of the number (x) of COO^- groups

$\%COO^- = \frac{x * (MCOO-)}{Mw(CNT - Exp.2)} * 100$ <=>

<=> $x = \frac{0.88 * 1213.28}{100 * 44}$ =0.243 COO^- groups

Table S3. Oxygen and sulphur at. (%) of CNT-Exp. 1 determinate by XPS and it surface acidity.

Sample	**XPS analysis**									**H$^+$ equiv. (mmol)**
CNT-Exp. 1 *CNT+MA(1:1)+DMSO* *190ºC* *24h*	Total oxygen (at. %)					Total sulphur (at. %)				**0.04**
	7.18 C=O + S=O; C-O; SO3H 49.9% : 43.9% : 6.4% (C=O+S=O = **3.58**) (C-O = **3.15**) (SO3H = **0.45**)					**1.20** -S- ; S=O; SO3H 69.7% : 18.8% : 13.2% (**0.836**; **0.226**; **0.158**)				
	Functional groups									
	-COOH calculated from 0.027 mmol of H$^+$ [total mmol H$^+$ - mmol SO3H] 0.04-0.013)	-OH; -SMe		-OH; -SO3H (**0.013 mmol-calculated from XPS analysis)		-OH; -SOMe				
	O (at. %)	O (at. %)	S(at. %)	S(at. %)	O (at. %)	S(at. %)	O (at. %)	O (at. %)		
	* **0.338** COOH groups (C-O 0.338; C=O 0.338)	C-O (0.836)	← **0.836**	**0.158** ↳	SO3H (**0.45**) ~ (0.158*3)=0.474 OH (0.158)	**0.226** →	S=O (0.226) C-O (0.226)	C-O (1.59) C=O (3.02) Aprox. ratio 1:2		

Determination of the ratio of C-O and C=O bonds without the contribution of alcohol, carboxylic acid and sulfoxide groups. The expected ratio of C-O and C=O in anhydride groups it is 1:2 respectively.	
C-O (**3.15** at. % of O)	C=O + S=O (**3.58** at. % of O)
3.15-0.338-0.836-0.226-0.158= 1.59	C=O **3.58**-0.338-0.226= 3.02

Note: **values in bold and underlined are experimental results;**

Values in blue were calculated from the experimental results.

**Acidity calculated from the XPS analysis attributed to sulfonic acids.

Molecular weight calculated from the XPS analysis (once the XPS do not determine the hydrogen atoms they won't be considered in following calculus):

Mw(CNT-Exp.1)=7.18*16+1.20*32+91.62*12=1252.72 g/mol

By XPS it is Known that there are 0.158 groups of SO_3^-

$\%SO_3^- = \frac{80 * 0.158}{1252.72} * 100$ = 1.01 % , so in 100 mg we have 1.01 mg of SO_3^- groups

$n(SO_3^-)=n(H^+)$

$n(H^+)$ from sulfonic acids $= \frac{1.01}{80} = 0.013\ \mathbf{mmol}$

* number of carboxylic acids calculated from the total acidity minus the acidity calculated in **

By titration it is known that the total acidity in 100mg of functionalized CNT it is 0.04 mmol

Subtracting to the total acidity the contribution of sulfonic acids it is determined the mmol of H^+ associated to carboxylic acids:

0.04-0.013 = 0.027 mmol of COO^-

Determination of the mass of COO^- (n=m/M) in 100 mg

$0.027 = \frac{\mathbf{m(COO-)}}{\mathbf{44}}$ <=> $m(COO^-)$=1.19 mg

% COO- = 1.19 %

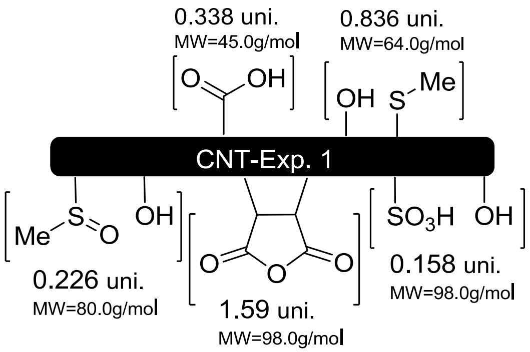
Determination of the number (x) of COO^- groups

$\%COO^- = \frac{\mathbf{x * (MCOO-)}}{\mathbf{Mw(CNT-Exp.1)}} * \mathbf{100}$ <=>

<=> $x = \frac{1.188 * 1252.72}{100 * 44}$ =0.338 COO^- groups

Values in red from total at. (%) of oxygen in C-O and C=O+S=O, less the contribute of the other functional groups introduced during the functionalization.

Determination of the relative percentage of MA grafted to the surface of CNT:



$$\% \text{ MA} = \frac{1.59 * 98.0}{(1.59 * 98.0 + 0.836 * 64.0 + 0.338 * 45.0 + 0.226 * 80.0 + 0.158 * 98.0)} = 60.4\ \%$$

Grafting ratio of MA on the CNT

The grafting ration of MA on the CNT was calculated using the same procedure reported in reference [S2]

Grafting ratio of MA on the CNT calculated from TGA. The amount of degraded MA was calculated on the basis of the weight loss between 370 and 500 ºC, when the TGA was performed under air atmosphere. After the estimation of the amount of degraded MA (x MA) and the amount of residue at 700°C (x residue at 700°C in *wt.* %), the grafting density (σ) in mol/g was calculated based on the weight loss, the MA molecular weight Mn and by assuming the remaining sample is constituted purely of carbon.

In summary, the grafting density is given by the **Equation S1**.

$$\sigma = \frac{x\ \mathbf{MA}}{Mn\ .\ (\mathbf{100} - x\ \mathbf{MA} - x\ \mathbf{residue\ at\ 700\ ºC})} \quad \text{(mol/g)} \qquad \textbf{Eq. S1}$$

Equation S1 for determining the grafting density from TGA.

Grafting ratio of MA on the CNT calculated from elemental analysis (EA). The grafting density (***σ*1**) was determined by the same procedure as described above for the thermogravimetric analysis. It should be noted that the key data for the grafting density calculation are the carbon and oxygen content in modified CNT-Exp.1 and CNT-Exp. 4. Therefore the calculated carbon (*C%*) and oxygen (*O%*) contents (excluding the nitrogen, sulphur and hydrogen contents) from CNT-Exp. 2 or CNT-Exp. 5 and MA were employed to calculate the grafting density (***σ*CO**) in *wt.* %. According to the following **Equation S2**, the results provide a slightly underestimated grafting density (***σ*CO**) for CNT-Exp.1 and CNT-Exp.4, since the oxygen content (*O%*) from CNT-Exp. 2 or CNT-Exp. 5 was directly used and not recalculated according to the composition of the sample.

$$\sigma\mathbf{CO} = \frac{\mathbf{O\%\ Sample} - \mathbf{O\%\ CNTreference}}{\mathbf{O\%\ MA}}\ .\mathbf{100} \quad \text{(wt.%)} \qquad \textbf{Eq. S2}$$

Equation S2 for determining the grafting density from elemental analysis.

From this value, the grafting density σ1 can then be expressed using the **Equation S1**

References

[S1] Paiva MC, Simon F, Novais RM, Ferreira T, Proença MF, Xu W, Besenbacher F. Controlled Functionalization of Carbon Nanotubes by a Solvent-free Multicomponent Approach. *ACS Nano* 2010, 4: 7379-7386.

[S2] Zydziak N, Hübner C, Bruns M, Barner-Kowollik C. One-Step Functionalization of Single-Walled Carbon Nanotubes (SWCNTs) with Cyclopentadienyl-Capped Macromolecules via Diels-Alder Chemistry. *Macromolecules* 2011, 44: 3374-3380.