Supplementary Data

Grafting of adipic anhydride to carbon nanotubes through a Diels-Alder cycloaddition/oxidation cascade reaction

Rui Filipe Araújo [a], Maria Fernanda Proença [*,b], Carlos Jorge Silva [b], Tarsila G. Castro [b,c], Manuel Melle-Franco [c], Maria Conceição Paiva [a], Silvia Vilar-Rodil [d], Juan Manuel D. Tascón [d]

[a] Instituto de Polímeros e Compósitos/I3N, Universidade do Minho, 4800-058 Guimarães, Portugal

[b] Centro de Química, Universidade do Minho, 4710-057 Braga, Portugal

[c] Departamento de Informática, Centro ALGORITMI, Universidade do Minho, 4710-057 Braga, Portugal

[d] Instituto Nacional del Carbón, INCAR-CSIC, Apartado 73, 33080 Oviedo, Spain

[*] *Corresponding Author. E-mail address:* ***fproenca@quimica.uminho.pt***

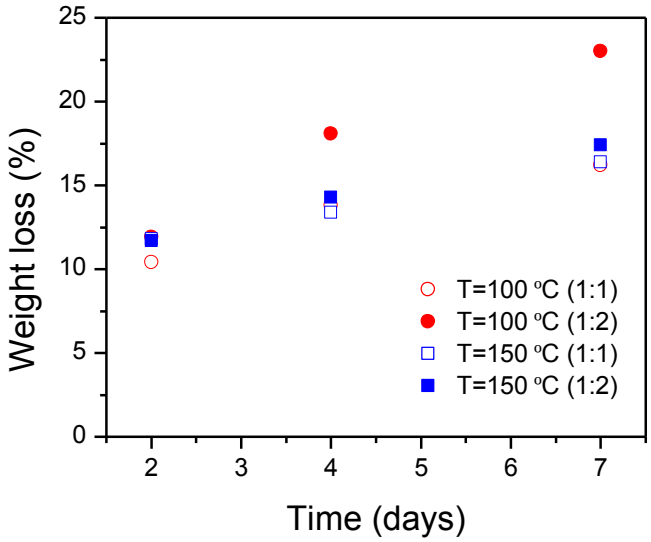


Fig. S1 - Weight loss (%) recorded by TGA in nitrogen atmosphere at 800 ºC for functionalized CNT after 2, 4 and 7 days of reaction.

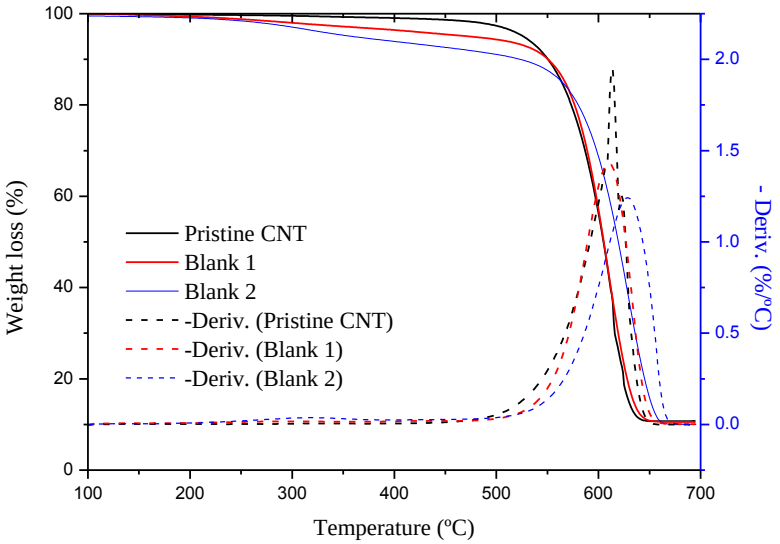


Figure S2. TGA curves (solid lines) and first derivative (dash lines) of CNT-Blank 1, CNT-Blank 2 and pristine CNT. The TGA experiments were performed in air atmosphere.

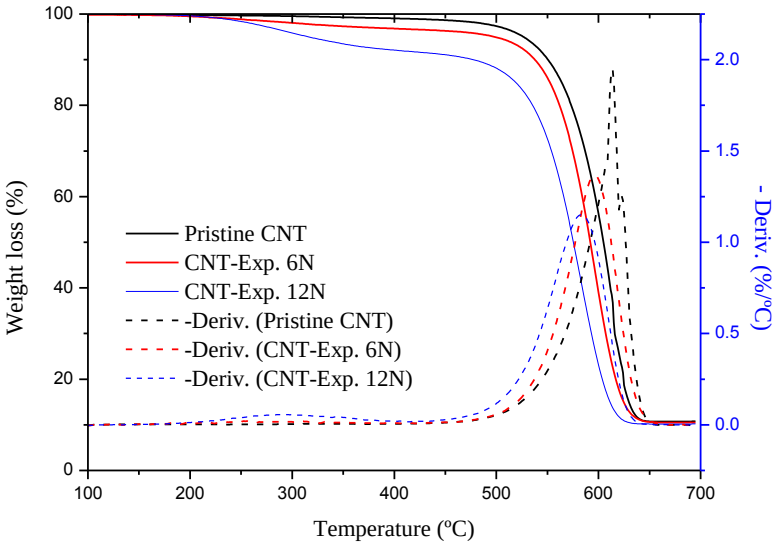


Figure S3. TGA curves (solid lines) and first derivative (dash lines) of CNT-Exp. 6N, CNT-Exp. 12N and pristine CNT. The TGA experiments were performed in air atmosphere.

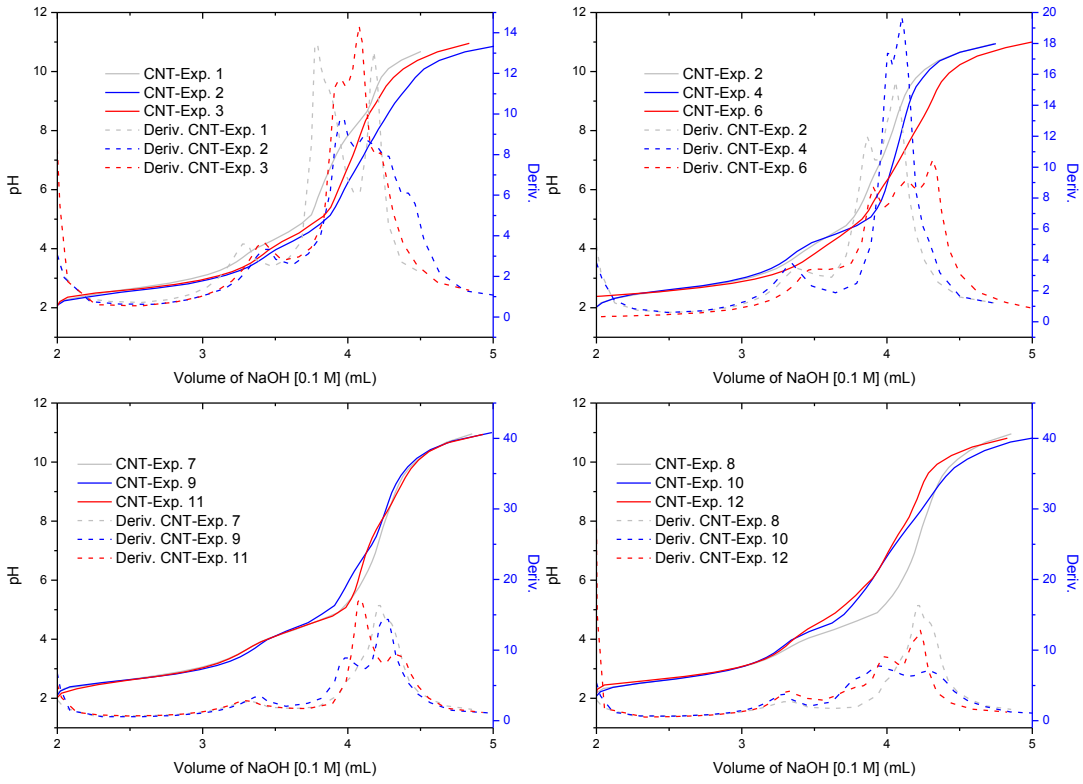


Fig. S4 - Titration curves of functionalized CNT.

Table S1. Total amount of released species obtained by integration of the TPD profiles.

Sample code	Total amount of species released (μmol/g)	
	CO_2	CO
exp. 3	499	500
exp. 6	831	918
exp. 9	493	454
exp. 12	726	706

Table S2. Deconvolution of the TPD profiles into different bands. Temperature of the maximum and μmol g^{-1} of evolved species are indicated for each component.

	CO_2 (μmo/g)				CO (μmol/g)			
Temperature (º C)→	150	318	481	550	103	341	726	837
		-326	-484	-588	-129	-363	-774	-879
Assignment (*) →	1	2	3	3	4	2	5	6
Sample code↓								
exp. 3	40	373	-	86	46	401	53	-
exp. 6	39	721	-	71	68	813	37	-
exp. 9	27	380	21	65	3	374	48	30
exp. 12	48	568	35	75	37	563	48	58

(*) 1: carboxylic acids; 2: carboxylic anhydrides; 3: lactones; 4: not known, maybe labile hydroxyls or epoxies created on the MWCNT basal planes upon oxidation; 5: carbonyl; 6:quinone.

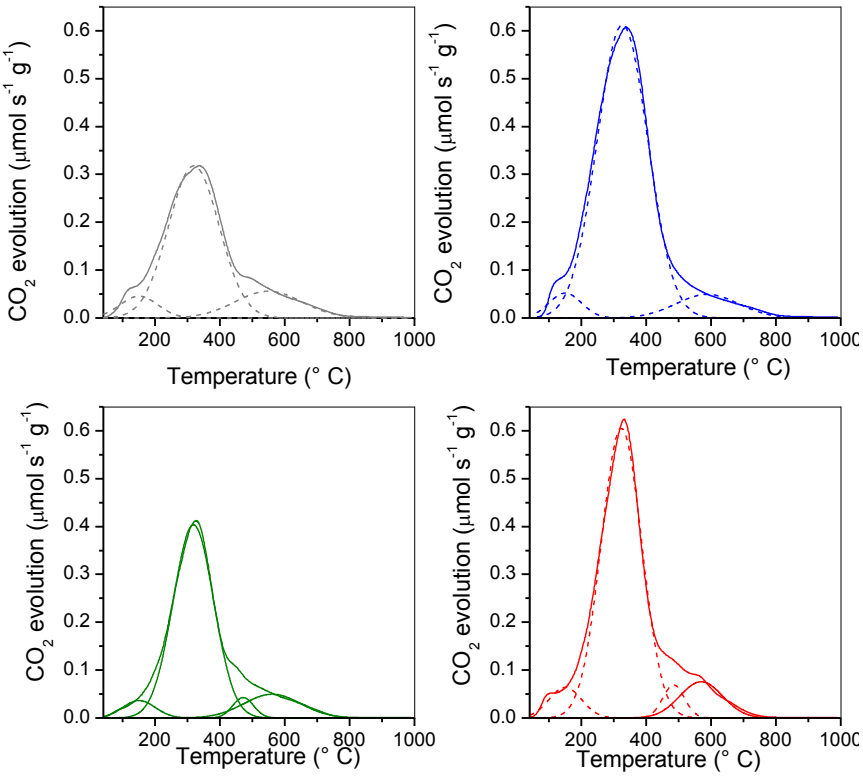


Figure S5. Deconvolution of the CO_2 TPD profiles of exp. 3 (gray), exp. 6 (blue), exp. 9 (green), and exp.12 (red). The components are shown in dashed lines.

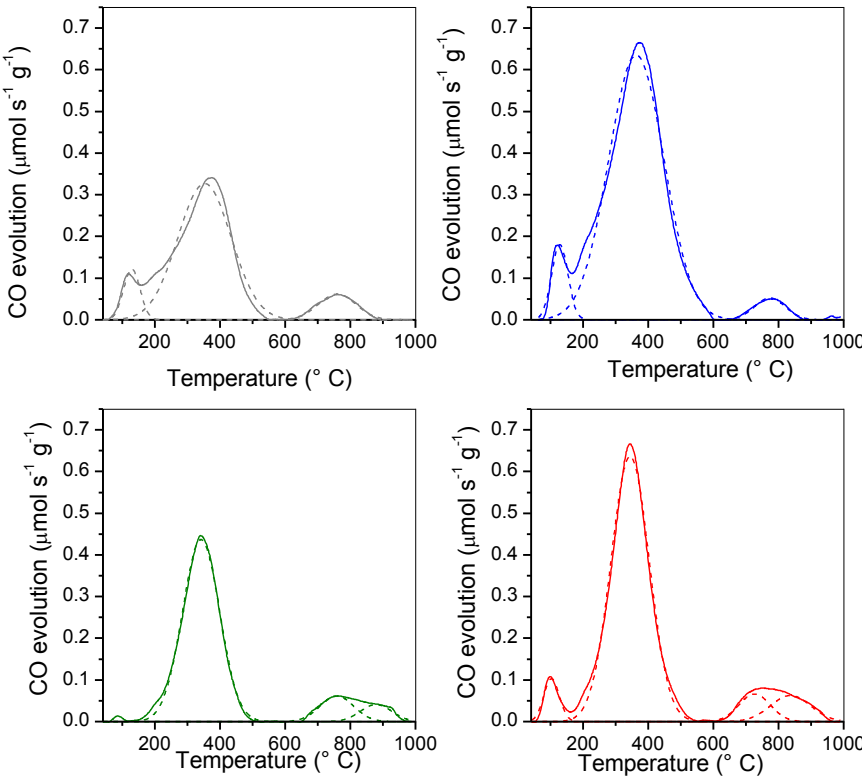


Figure S6. Deconvolution of the CO TPD profiles of exp. 3 (gray), exp. 6 (blue), exp. 9 (green), and exp.12 (red). The components are shown in dashed lines.

Table S3. Deconvolution of the high resolution C1s XPS band into six components

	Relative amount (%)					
Binding energy (eV) →	284.4	285.4	286.4	287.7	289.1	291.0
Sample code ↓						
exp. 3	62.2	11.7	13.3	5.7	2.6	4.6
exp. 6	57.9	12.3	17.6	6.4	3.4	2.4
exp. 9	60.4	10.4	13.6	7.2	4.0	4.5
exp. 12	57.6	11.8	17.9	5.8	2.7	4.3

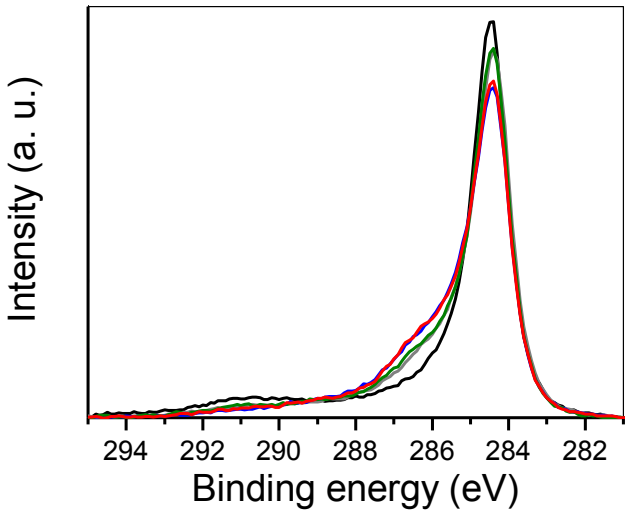
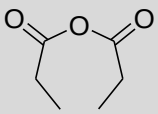
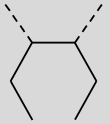
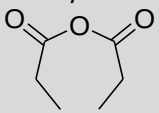


Figure S7. Background-corrected, normalized high resolution C1s XPS spectra of pristine MWCNT (black), exp. 3 (gray), exp. 6 (blue), exp. 9 (green), and exp.12 (red).

Table S4. Hydrogen, oxygen and sulphur wt. (%) and mmol. % of pristine CNT and CNT-Exp. 6 determinate by elemental analysis and it surface acidity.

	Elemental Analysis								H^+ equiv. (mmol)
CNT-Exp. 6	**Total C**		**Total H**		**Total O**		**Total S**		**0.05**
	Wt%	At%	Wt%	mmol. %	Wt%	mmol. %	Wt%	mmol. %	0.05-**0.029** = 0.021 of COOH
	77.69	6.47	2.14	**2.14**	14.29	**0.89**	0.93	**0.029**	
			0.029 mmol.% of H in SO3H 0.021 mmol.% of H in COOH **0.32 mmol.% of H in pristine CNT** In 0.02390.239 mmol. % of:  0.956 mmol. % of H 2.14-0.029-0.021-0.32-0.956=0.841 0.814/6=0.239 mmol. % of:  0.814/6 = 0.136		3*0.029 = 0.087 mmol. % of O in SO3H 2*0.021 = 0.042 mmol. % of O in COOH **0.044 mmol. % of O in pristine CNT** 0.89-0.087-0.042-0.044=0.717 0.717/3=0.239 mmol. % of: 		Based on the XPS analysis the content of sulfur was attributed to-SO3H functional group (**0.029 mmol.% of –SO3H)**		

Grafting ratio of Anhydride molecules on the CNT

The grafting ration of Anhydrides on the CNT was calculated using the a similar approach reported in reference [S1]

Grafting ratio of Anhydrides on the CNT calculated from elemental analysis (EA). It should be noted that the key data for the grafting density calculation are the carbon and oxygen content in modified CNT-Exp.6. Therefore the calculated carbon (*C%*) and oxygen (*O%*) contents (excluding the sulphur and hydrogen contents). Pristine CNT were employed to calculate the grafting density (***σ*CO**) in *wt.* %. Only the amount of O from anhydride was considered (Table S3).

$$\sigma CO = \frac{\text{O\% Sample} - \text{O\% Pristine CNT}}{\text{O\% A}} .100 \text{ (wt.\%)} \qquad \textbf{Eq. S1}$$

Equation S1 for determining the grafting density wt.% from elemental analysis.

Grafting ratio of Anhydride (mol/g) on the CNT calculated from wt. % determined by EA (Eq. S1). After the estimation of the amount of degraded Anhydrides (σCO) and the amount of residue at 700°C (*x* residue (EA) in *wt.* %), the grafting density (***σ***) in mol/g was calculated based on the weight loss, the Anhydride molecular weight *M*n and PF the predicted wt. % loss calculated from the mmol. % of functional groups on the CNT surface (Table S3).

In summary, the grafting density (mol/g) is given by the **Equation S2**.

$$\sigma = \frac{\sigma CO}{Mn .(100 - \text{PF} - x \text{ residue at } 700\ ^{\circ}\text{C})} \text{ (mol/g)} \qquad \textbf{Eq. S2}$$

Equation S2 for determining the grafting density from grafting density wt.% (Eq. S1).

References

[S1] 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.