

Supporting information

Ionic liquids plus microwave irradiation: A general methodology for the retro-functionalization of single-walled carbon nanotubes

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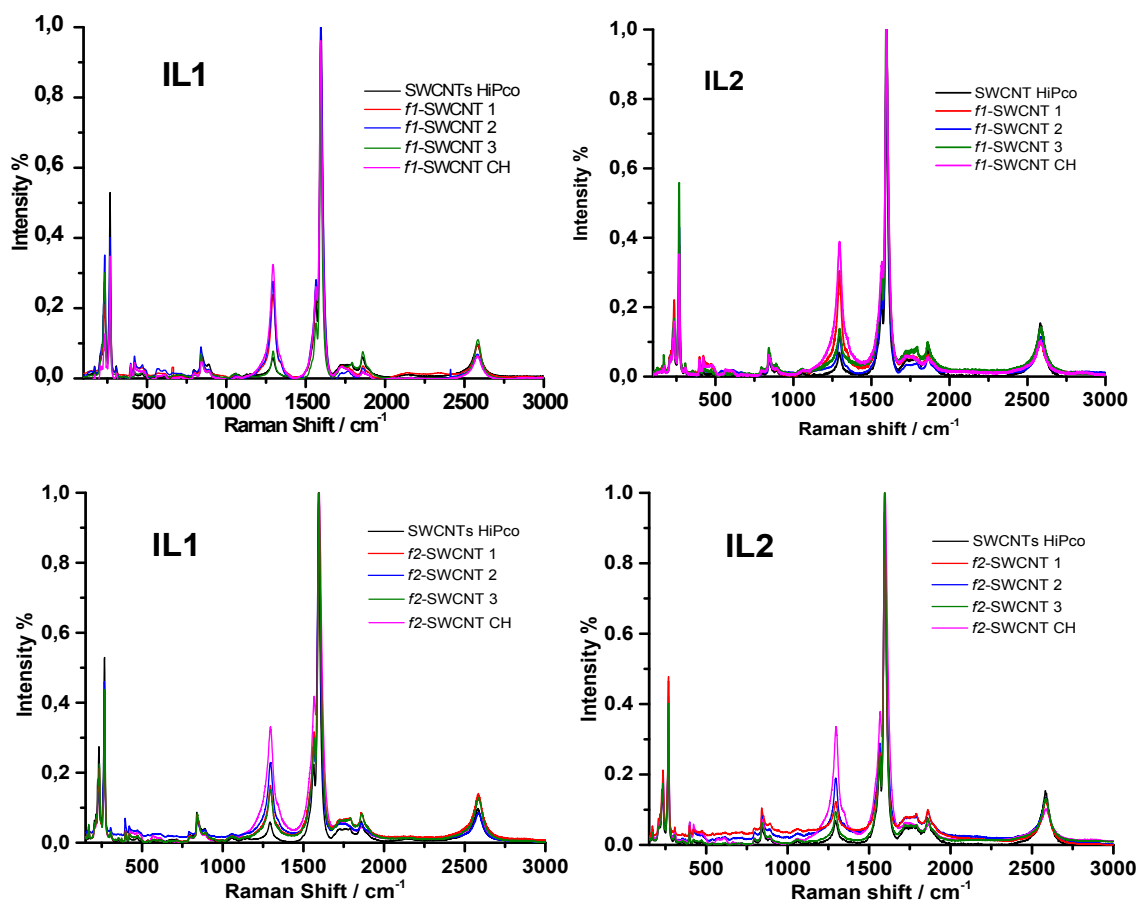


Figure S1. Raman plots IL-1/Salt-1 (top-left); IL-2/Salt 1 (Top-Right); IL-1/S2 (Bottom-Left) and IL-2/S2 (Bottom-right).

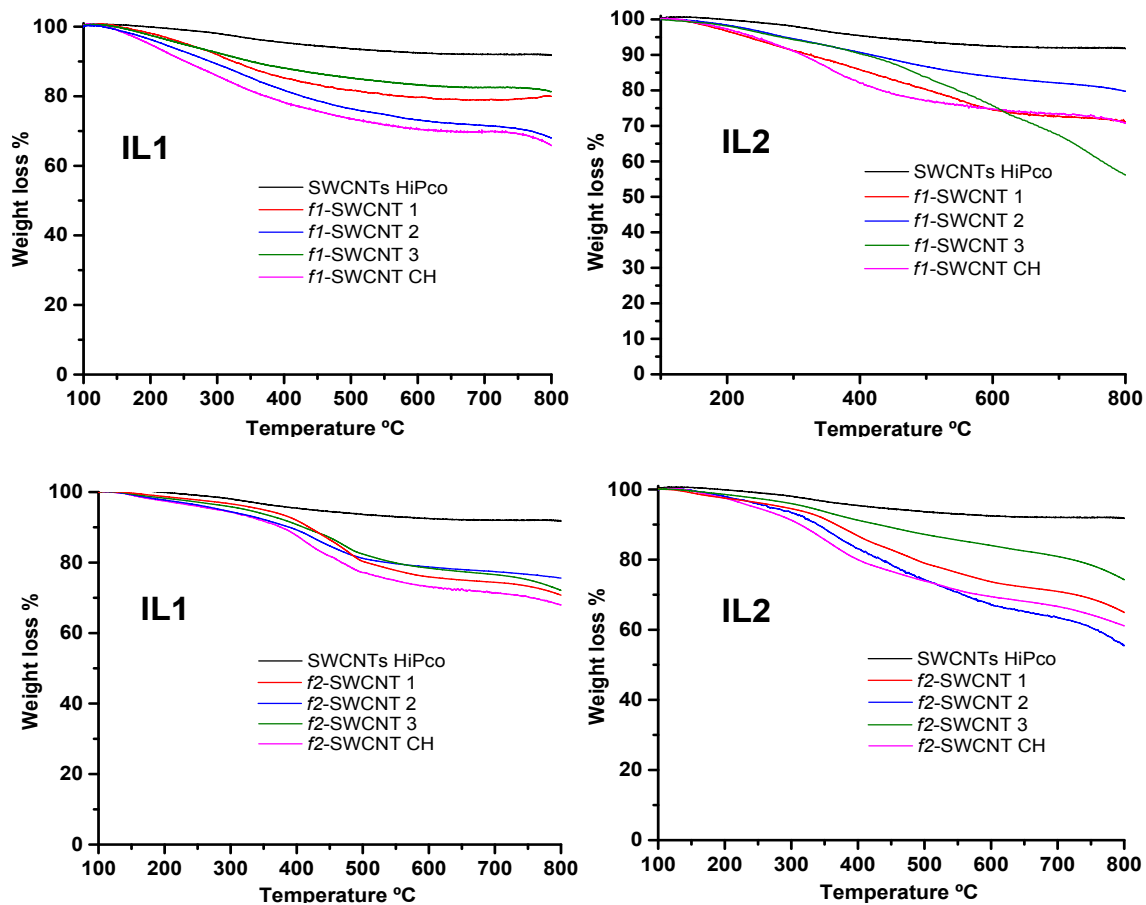


Figure S2. TGA studies IL-1/Salt-1 (top-left); IL-2/Salt 1 (Top-Right); IL-1/S2 (Bottom-Left) and IL-2/S2 (Bottom-right).

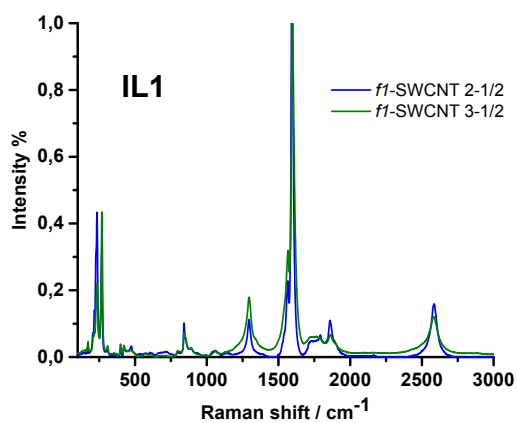


Figure S3. Raman plot for IL-1/Salt-1 in the presence of half amount of salt-1.

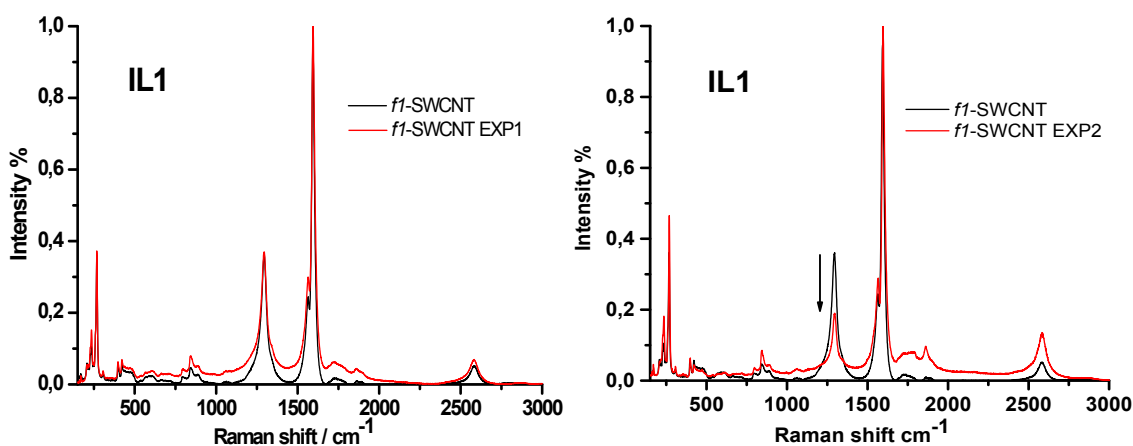


Figure S4. Control experiments about the retro-functionalization mechanism under MW irradiation in the presence on the IL (left), and in the presence of the IL plus the salt (right).

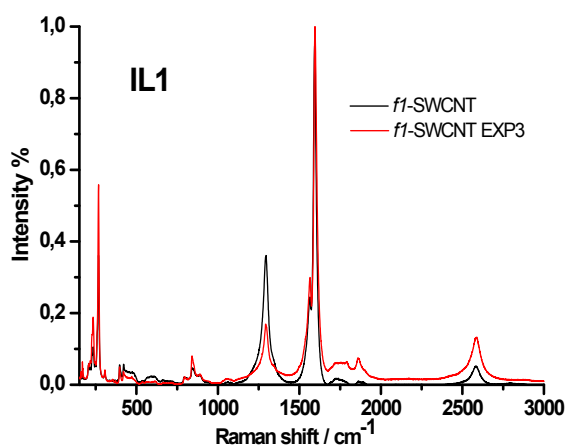


Figure S5. Control experiment in the presence of the phenyl radical scavenger CBr_4 .

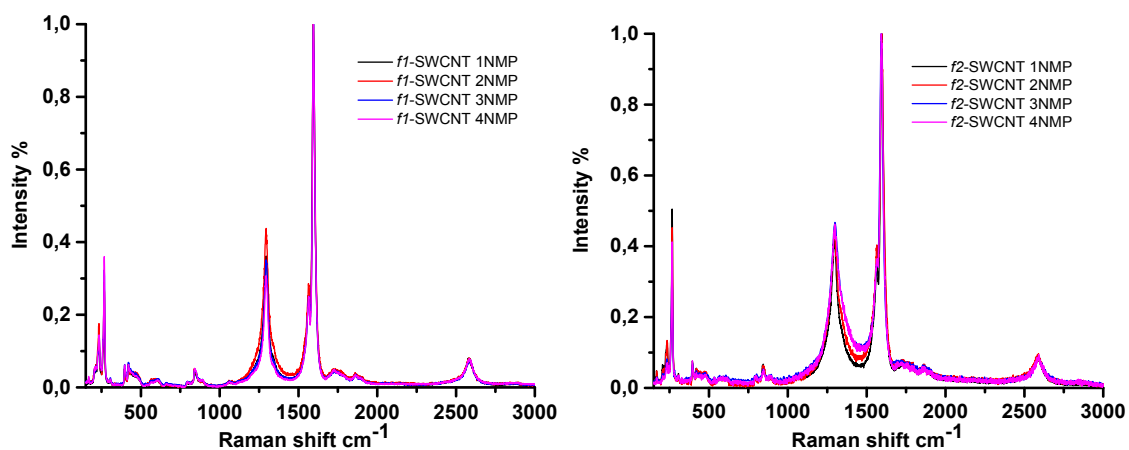


Figure S6. Control experiments in NMP under MW irradiation for different reaction times.

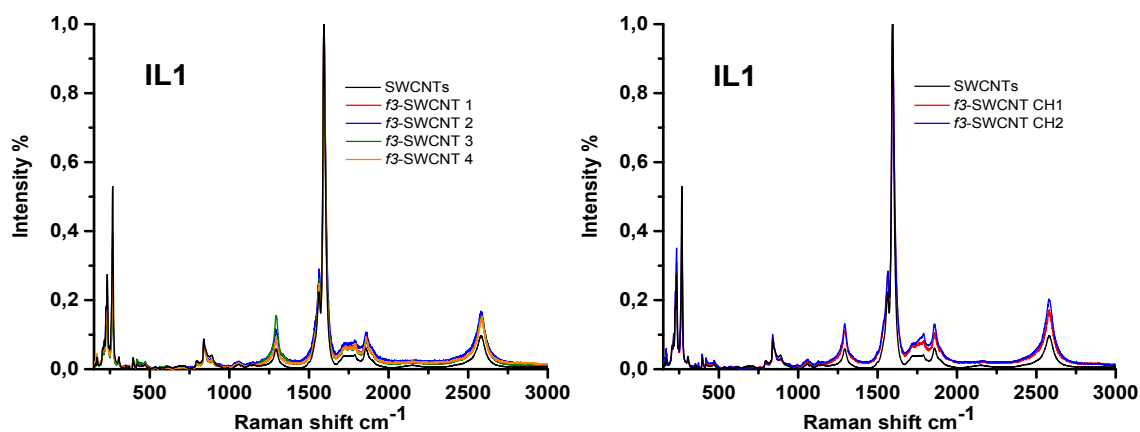


Figure S7. Raman plots for the 1,3-dipolar cycloaddition of azomethine ylides to CNTs under MW irradiation (left) and under classical heating (right).

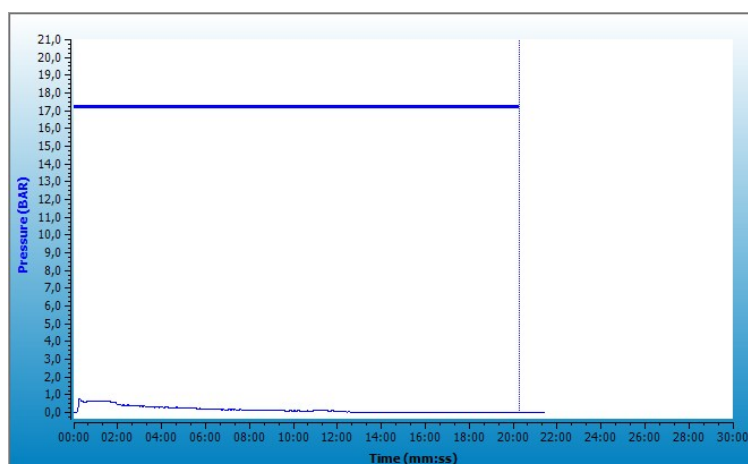


Figure S8. Pressure profile for *f1*-SWCNT 2 where is observable the maximum pressure value reached during the reactions under MW irradiation.

Table S1. Quantitative data of the amount of diazonium salt consumed during the reaction procedure for each reaction step.

	IL1+S1 (mmol)	IL1+S2 (mmol)	IL2+S1 (mmol)	IL2+S2 (mmol)
<i>f1</i>	$1.01 \cdot 10^{-3}$	$9.32 \cdot 10^{-4}$	$1.20 \cdot 10^{-3}$	$8.61 \cdot 10^{-4}$
<i>f2</i>	$1.44 \cdot 10^{-3}$	$8.29 \cdot 10^{-4}$	$1.06 \cdot 10^{-3}$	$1.24 \cdot 10^{-3}$
<i>f3</i>	$6.61 \cdot 10^{-4}$	$7.39 \cdot 10^{-4}$	$1.08 \cdot 10^{-3}$	$3.92 \cdot 10^{-4}$
CH	$1.63 \cdot 10^{-3}$	$1.07 \cdot 10^{-3}$	$1.38 \cdot 10^{-3}$	$1.32 \cdot 10^{-3}$

Experimental section

General: All the chemicals and solvents were purchased from Sigma Aldrich and used without any further purification. SWCNTs HiPco were purchased from nanointegris (Bath HP27-078). Raman spectra were obtained on Renishaw inVia Raman microscope

at room temperature with exciting laser sources ($\lambda = 785 \text{ cm}^{-1}$). Measurements were taken with 10 s of exposure time at varying numbers of accumulations. The laser spot was focused on the sample using a 50x objective and the spectra were collected on numerous spots on the sample. Thermogravimetric analyses were performed with a TGA Q500 (TA Instruments) at 10 °C/min under N₂. UV-Vis-NIR measurements were carried out on a Cary 5000 Spectrometer (Varian), using 1 cm path quartz cuvettes using NMP as solvent. Continuous microwave irradiation was carried out in a CEM-Discover monomode microwave apparatus, with simultaneous monitoring of irradiation power, pressure, and temperature. Pressure was monitored for all the runs being always lower than 1 bar as clearly observed in the profile in figure S6. Compressed air was applied to improve the temperature control of the reaction mixtures. DFT calculations for dipole moment estimation were performed on the Wavefunction Spartan '14 with a B3LYP hybrid functional and a 6-311 + G** basis set.

General procedure for the modification of SWCNT with aryl diazonium salts through MW irradiation in ILs

Pristine HiPco SWCNTs (5 mg) were dispersed in the appropriate ionic liquid (IL1 or IL2) (0,5 mL) by means of an ultrasound bath sonicator for 10 minutes. Then the corresponding diazonium salt (1 mmol per mequiv of carbon) was added. The mixture was subjected to MW irradiation (5 W, 120 °C) at different reaction times (10, 20 and 30 min). After cooling to room temperature, the suspension was filtered through a polytetrafluoroethylene (PTFE) (0,1 µm) membrane and washed repeatedly with N,N-dimethylformamide (DMF) and methanol (MeOH), until the filtrate solution remained colorless; finally, the material was dried overnight under reduced pressure affording the *functionalized* materials **f1-SWCNT 1-3** and **f2-SWCNT 1-3**.

General procedure for the modification of SWCNT with aryl diazonium salts through classical heating in ILs

Pristine HiPco SWCNTs (5 mg) were dispersed in the appropriate ionic liquid (IL1 or IL2) (0,5 mL) by means of an ultrasound bath sonicator for 10 minutes. Then the corresponding diazonium salt (1 mmol per mequiv of carbon) was added. The reaction mixture was heated at 120 °C for 24 hours. After cooling to room temperature, the suspension was filtered through a polytetrafluoroethylene (PTFE) (0,1 µm) membrane and washed repeatedly with DMF and MeOH, until the filtrate solution remained

colorless; finally, the material was dried overnight under reduced pressure affording the *functionalized* materials ***f1-SWCNT CH*** and ***f2-SWCNT CH***.

Procedure for the retro-functionalization control experiment 1

f1-SWCNT (3mg) were dispersed in IL1 (0,3 mL) by means of an ultrasound bath sonicator for 10 minutes. The resulting suspension was subjected to MW heating at 120 °C for 1 hour. After cooling to room temperature, the suspension was filtered through a polytetrafluoroethylene (PTFE) (0,1 µm) membrane and washed repeatedly with DMF and MeOH and dried overnight yielding ***f1-SWCNT EXP1***.

Procedure for the retro-functionalization control experiment 2

f1-SWCNT (3mg) were dispersed in IL1 (0,3 mL) by means of an ultrasound bath sonicator for 10 minutes and salt 1 (1 mmol per mequiv of carbon) was added. The resulting suspension was subjected to MW heating at 120 °C for 1 hour. After cooling to room temperature, the suspension was filtered through a polytetrafluoroethylene (PTFE) (0,1 µm) membrane and washed repeatedly with DMF and MeOH and dried overnight yielding ***f1-SWCNT EXP2***.

Procedure for the retro-functionalization control experiment 3

f1-SWCNT (3mg) were dispersed in IL1 (0,3 mL) by means of an ultrasound bath sonicator for 10 minutes and CBr₄ (0,1 mmol) was added. The resulting suspension was subjected to MW heating at 120 °C for 1 hour. After cooling to room temperature, the suspension was filtered through a polytetrafluoroethylene (PTFE) (0,1 µm) membrane and washed repeatedly with DMF and MeOH and dried overnight yielding ***f1-SWCNT EXP3***.

General procedure for the modification of SWCNT with aryl diazonium salts through MW irradiation in NMP

Pristine HiPco SWCNTs (5 mg) were dispersed in NMP (0,5 mL) in the sonic bath for 10 minutes. Then the corresponding diazonium salt (1 mmol per mequiv of carbon) was added and the mixture was subjected to MW irradiation (5 W, 120 °C) at different reaction times (10, 20, 30 and 40 min). After cooling to room temperature, the suspension was filtered through a polytetrafluoroethylene (PTFE) (0,1 µm) membrane and washed repeatedly with DMF and MeOH, until the filtrate solution remained colorless; finally,

the material was dried overnight under reduced pressure affording the *functionalized* materials **f1-SWCNT 1-4NMP** and **f2-SWCNT 1-4NMP**.

General procedure for the 1,3-dipolar cycloaddition of azomethine ylides to SWCNTs through MW irradiation

Sarcosine (37 mg, 0.42 mmol) and the heptanal (94,8mg, 0,83 mmol) were added to a dispersion of SWCNTs (5 mg, 0.42 mmol) in IL1(0,5 mL). The reaction mixture was subjected to MW irradiation (5W, 120 °C) at different reaction times (10, 20, 30 and 40 min). After cooling to room temperature, the suspension was filtered through a polytetrafluoroethylene (PTFE) (0,1 µm) membrane and washed repeatedly with DMF and MeOH, until the filtrate solution remained colorless; finally, the material was dried overnight under reduced pressure yielding the products **f3-SWCNT 1-4**.

General procedure for the 1,3-dipolar cycloaddition of azomethine ylides to SWCNTs through classical heating

Sarcosine (37 mg, 0.42 mmol) and the heptanal (94,8mg, 0,83 mmol) were added to a dispersion of SWCNTs (5 mg, 0.42 mmol) in IL1 (0,5 mL). The reaction mixture was heated at 120 °C for 24 hours. After cooling to room temperature, the suspension was filtered through a polytetrafluoroethylene (PTFE) (0,1 µm) membrane and washed repeatedly with DMF and MeOH, until the filtrate solution remained colorless; finally, the material was dried overnight under reduced pressure yielding the products **f3-SWCNT 1CH** and **f3-SWCNT 2CH**.