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Photo-controlled Uptake and Release of Zinc Metal Ions by Spiropyran receptors anchored to Single-Walled Carbon Nanotubes

*Elisa Del Canto, Manuel Natali, Dania Movia and Silvia Giordani**

School of Chemistry / Centre for Research on Adaptive Nanostructures and
Nanodevices (CRANN), University of Dublin, Trinity College, Dublin 2, Ireland.

*e-mail: giordans@tcd.ie

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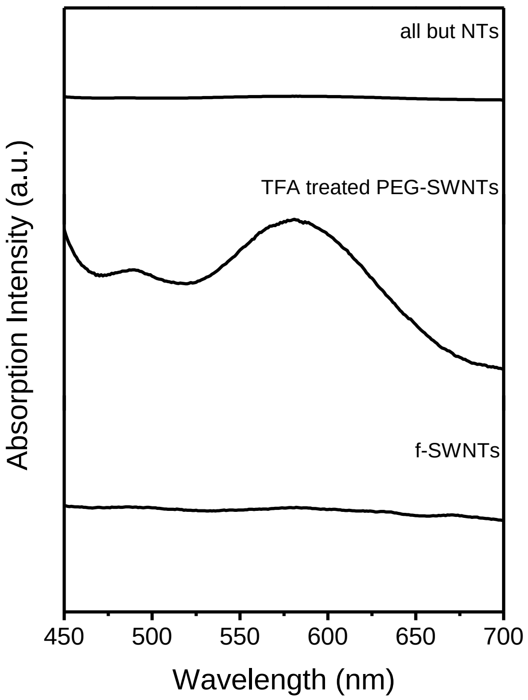

Fig. S1: UV-Vis absorption profiles of TFA treated PEG functionalized SWNTs and SP functionalized f-SWNTs compared with a blank solution (all but nanotubes) which has been treated in the same way. The amine loading was calculates as 383 μmol/g of material for TFA treated PEG functionalized SWNTs and as 134 μmol/g for SP functionalized f-SWNTs, therefore the difference of 249 μmol/g constituted the amino groups that reacted with the SP derivative. SP loading: 249μmol/g x 424.45 μg/μmol=105.7 μg SP/mg SWNTs.

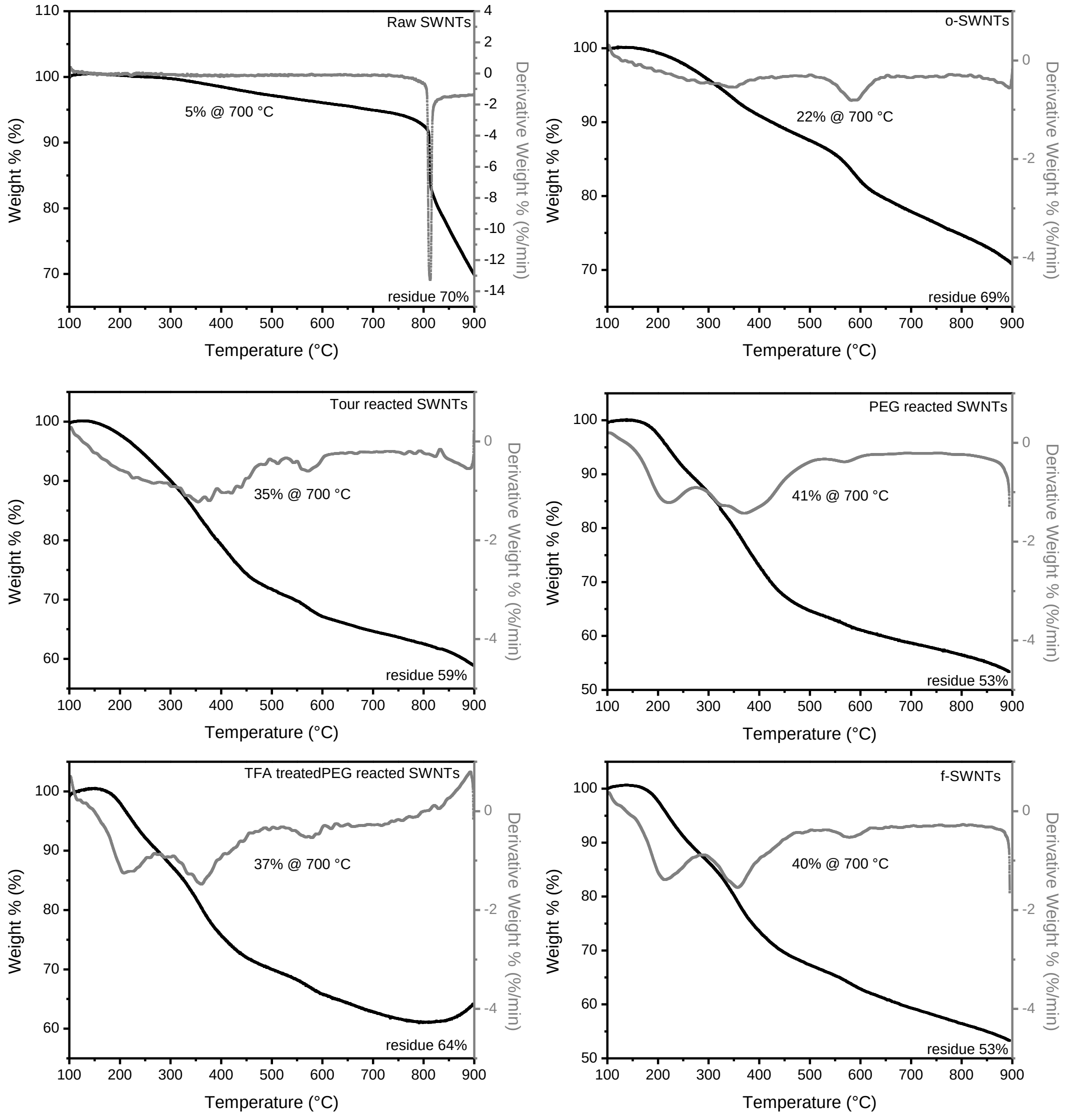

Fig. S2: TGA traces of raw SWNTs, o-SWNTs, Tour reacted SWNTs, PEG reacted SWNTs, TFA treated PEG reacted SWNTs, and SP functionalized f-SWNTs. The weight losses % at 700 °C attributed to the decomposition of organic groups in the nanotube samples are reported. All the experiments have been run in N_2 atmosphere with a temperature rate of 10 °C min^{-1}.

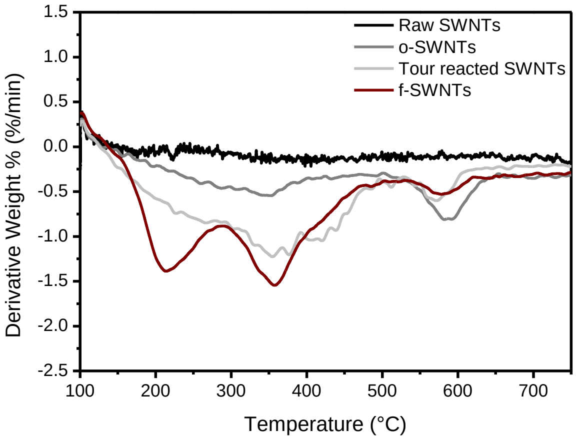

Fig. S3: TGA first derivative traces in the 100-750 °C range of raw, purified, Tour reacted SWNTs and SP functionalized f-SWNTs recorded under nitrogen flow.

As already reported,[1] SP derivative almost completely decomposed at 400 °C displaying two temperature maximum weight loss rates around 180 °C and 240 °C. Two maxima appeared for f-SWNTs, and were again shifted to higher values of 214 °C and 357 °C, indicating the presence of SP enriched PEGylated linkers in the nanotube material.

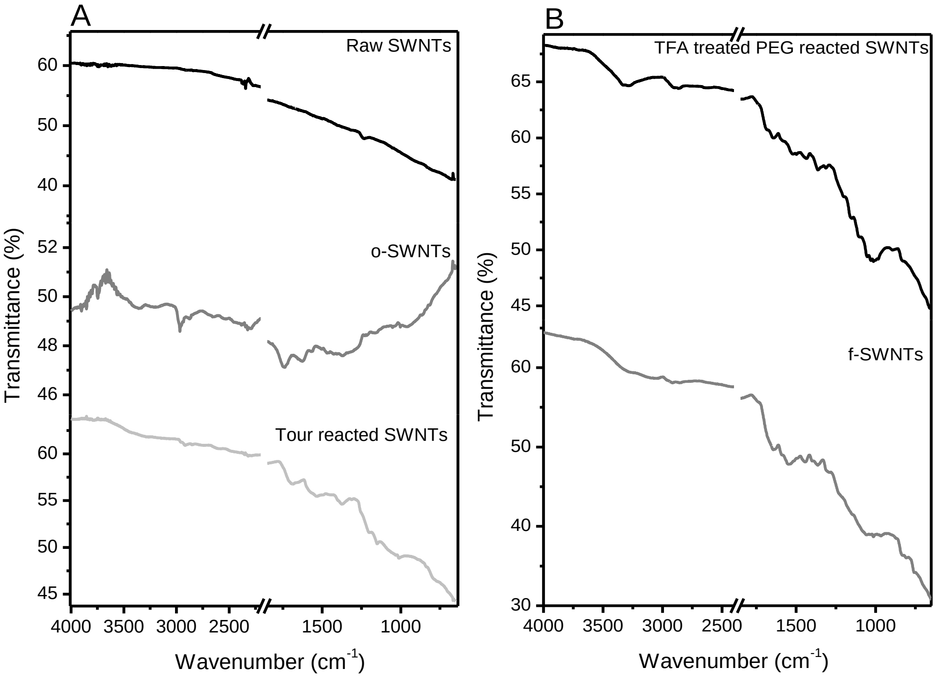

Fig. S4: ATR/FT-IR spectra of A] raw SWNTs), purified (o-SWNTs) and Tour reacted SWNTs, B] TFA treated PEG reacted SWNTs and f-SWNTs.

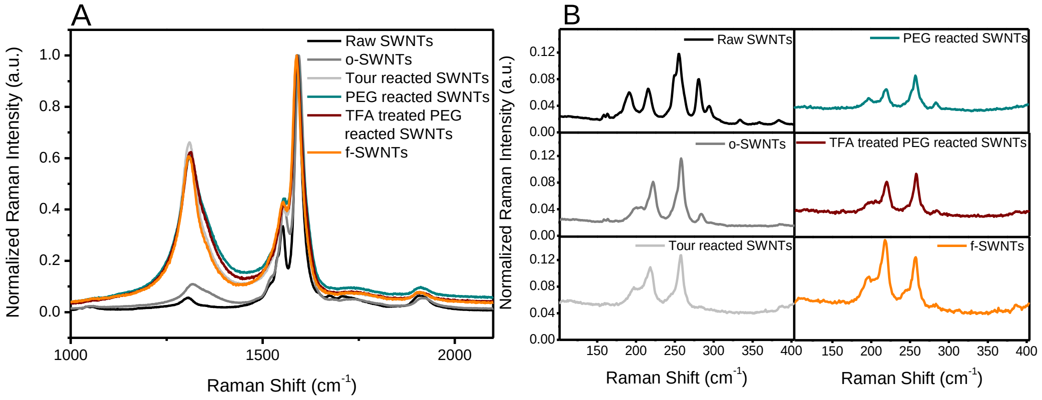

Fig. S5. Raman analyses (λ_{exc}= 633 nm) of enlarged A] D- and G- bands, and B] RBM bands of raw, purified and functionalized SWNTs. Spectra normalized on the G-band.

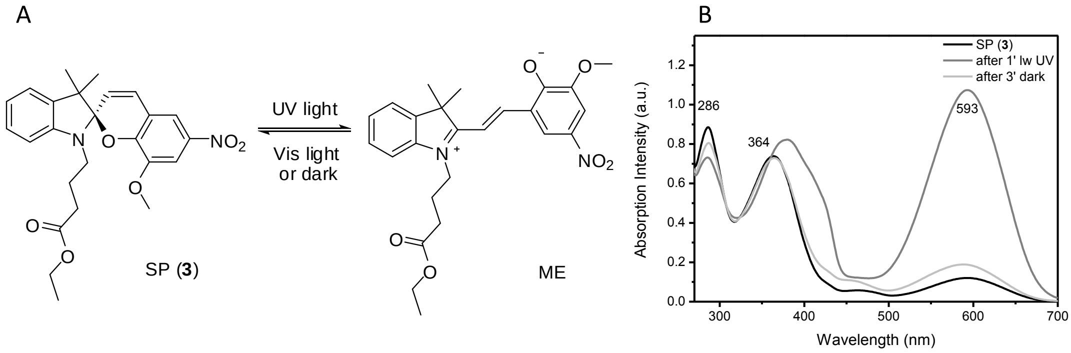

Fig. S6: A] Photo interconversion of the closed SP (**3**) into the ME open form. B] Absorption spectra of SP (**3**) 10^{-4} M in DMF after 1 min UV illumination (365 nm) and after 3 min storage in the dark. SP (**3**), which is the ethyl ester form of SP (**2**), was specifically chosen as it better resemble the features of that bounded to the SWNTs scaffold.

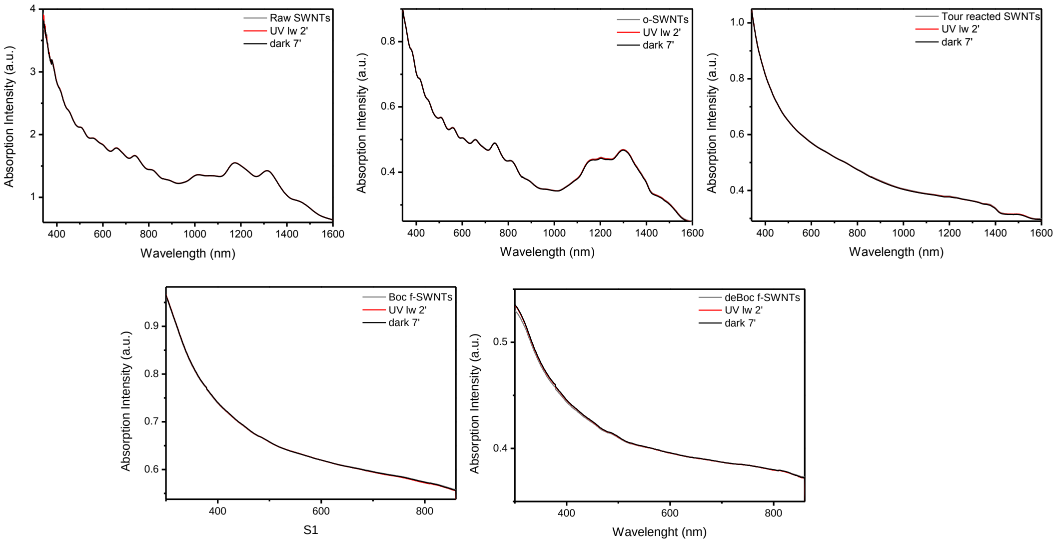

Fig. S7: UV-Vis absorption spectra of raw SWNTs, o-SWNTs and functionalized SWNTs after UV illumination for 2 min and storage in the dark for 7 min.

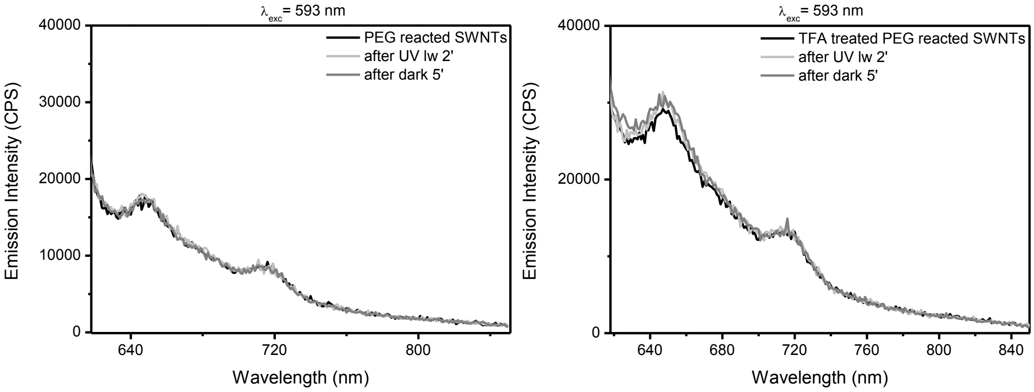

Fig. S8: Emission profiles (λ_{exc}= 593 nm) of PEG reacted SWNTs before and after removal of the Boc protecting group by TFA recorded after UV illumination for 2 min and storage in the dark for 5 min. The bands at 650 nm and 715 nm in all the nanotube samples are associated to the emitting behaviour of SWNTs in the visible region when excited at 593 nm.[2]

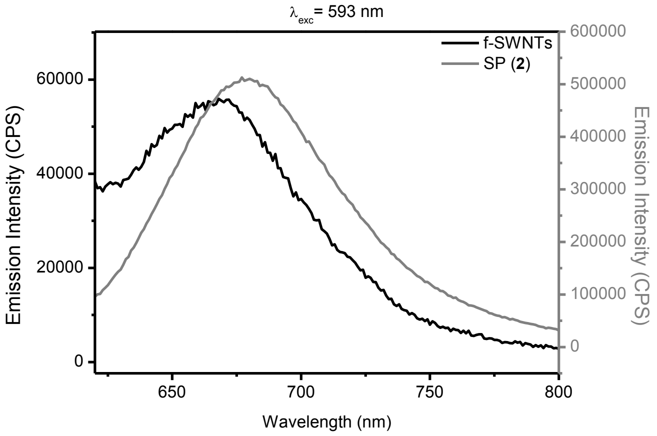

Fig. S9: Comparison of emission profiles (λ_{exc}= 593 nm) of f-SWNTs and SP (**2**) after UV illumination (365 nm) for 2 min in DMF. [SWNTs] = supernatant of initial 0.1 mg/mL, [SP] = 10^{-5} M.

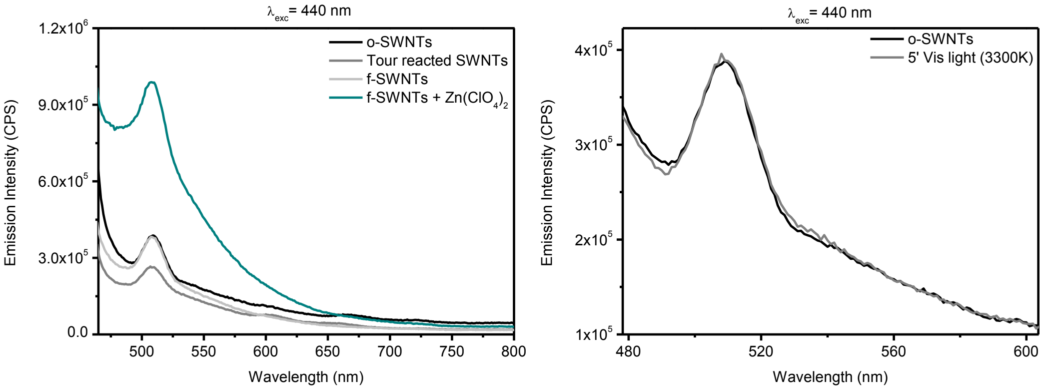

Fig. S10: Emission spectra (λ_{exc}= 440 nm) of A] o-SWNTs, Tour reacted SWNTs and f-SWNTs before and after the addition of $Zn(ClO_4)_2$ (10^{-1} M, H_2O, 1μl/mL of NTs), B] o-SWNTs before and after irradiation with Vis light (3300K) for 5 min. Spectra collected on the supernatant of initial 0.1 mg/mL nanotubes in Cl_2Bz/CH_3CN 9:1.

References

1. E. Del Canto, K. Flavin, M. Natali, T. Perova and S. Giordani, *Carbon*, 2010, **48**, 2815-2824
2. D. Movia, E. Del Canto and S. Giordani, *The Journal of Physical Chemistry C*, 2010, **114**, 18407-18413.