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

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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 calculated as 383 \( \mu \text{mol/g} \) of material for TFA treated PEG functionalized SWNTs and as 134 \( \mu \text{mol/g} \) for SP functionalized f-SWNTs, therefore the difference of 249 \( \mu \text{mol/g} \) constituted the amino groups that reacted with the SP derivative. SP loading: 249\( \mu \text{mol/g} \times 424.45 \mu \text{g/\mu mol}=105.7 \mu \text{g SP/mg SWNTs.} \)
**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 N₂ 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 ($\lambda_{ex} = 633$ 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 ($\lambda_{\text{exc}} = 593$ 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 ($\lambda_{exc} = 593$ 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 ($\lambda_{exc} = 440$ 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$_2$O, 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$_2$Bz/CH$_3$CN 9:1.

**References**