Supplementary Information

Multivariate Analysis Applied to Raman Mapping of dye-functionalized Carbon nanotubes: a novel approach to support the rational design of functional nanostructures

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Raman measurements and Principal Component Analysis

Subtle differences can be identified in the Raman spectra acquired at different positions of the same sample. Figure S1 shows two spectra obtained at different points on the powder sample of oxidized CNTs treated with cyanine.

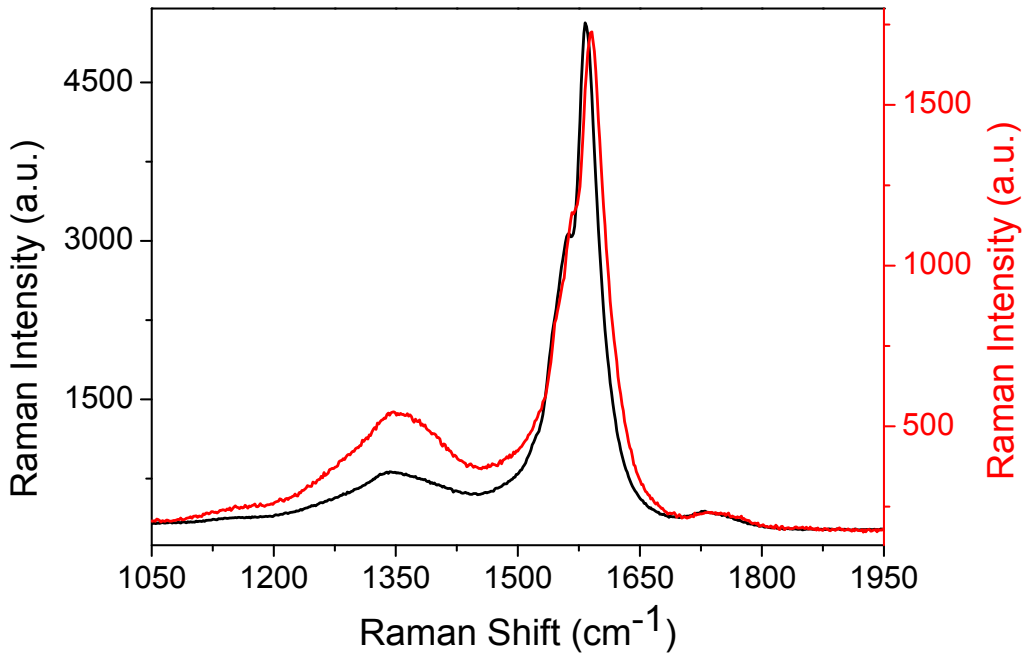

Figure S1

Figure S2 presents the results of the Lorentzian fit performed on the curves shown in figure 1 of the main text (pristine CNTs on the left, oxidized CNTs on the right). The fits allowed to obtain the D and G band intensities, calculated as the area of the respective spectroscopic features located at about 1330 and 1590 cm^{-1}. The ratio R between the D and G band intensities has been then calculated to estimate the CNT structural disordering induced by the oxidation procedure. The Raman spectrum collected on pristine CNTs is associated to an R value of (0.21 ± 0.02), which rises to (1.7 ± 0.1) after the chemical treatment.

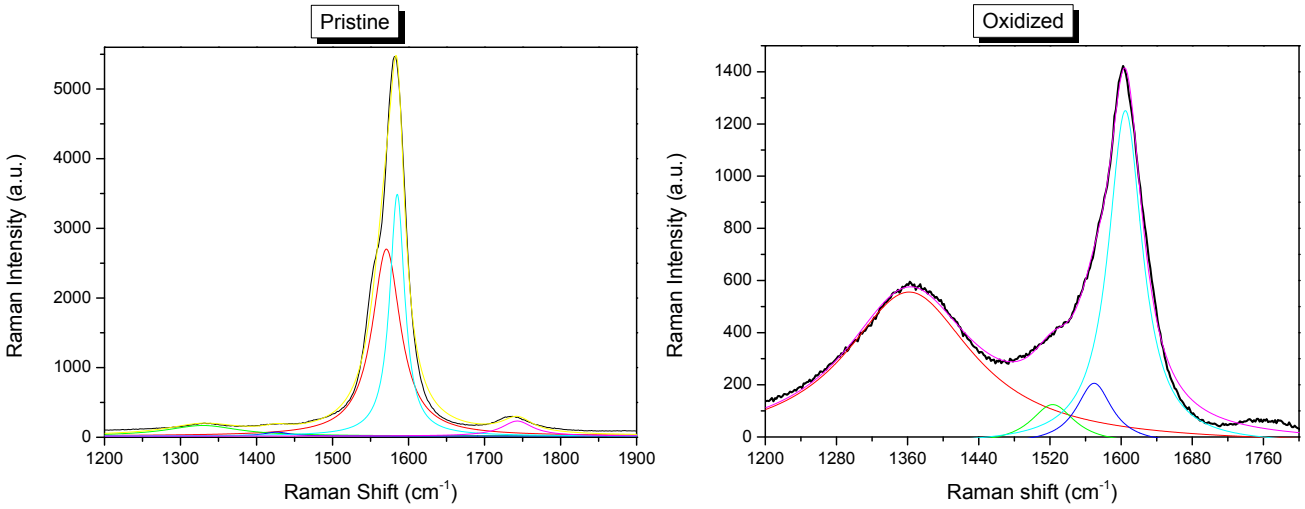

Figure S2

Figure S3 presents the results of Principal Component Analysis obtained when considering maps collected on pristine CNTs (black circles), on pristine CNTs treated with rhodamine (grey down-triangles), on oxidized CNTs (magenta squares) and in two different areas of the powder sample of oxidized CNTs treated with rhodamine (red up-triangles and orange diamonds). The last two maps are almost superposed.

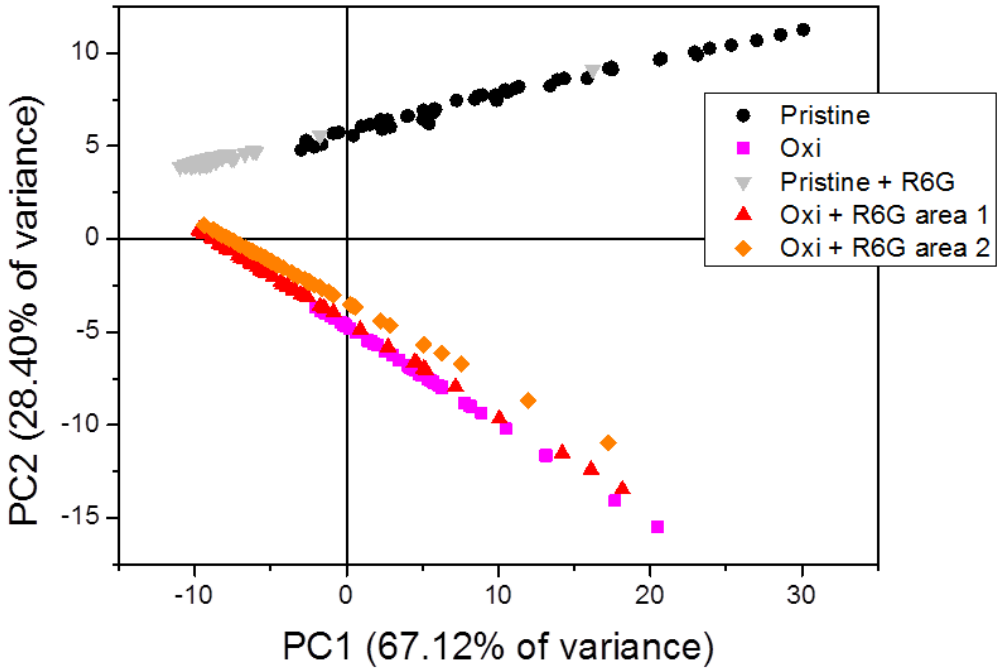

Figure S3.

Figure S4 shows the comparison between the results obtained with Principal Component Analysis applied to Raman maps collected on differently treated CNTs when using the Covariance matrix (left side) and the Correlation matrix (right side).

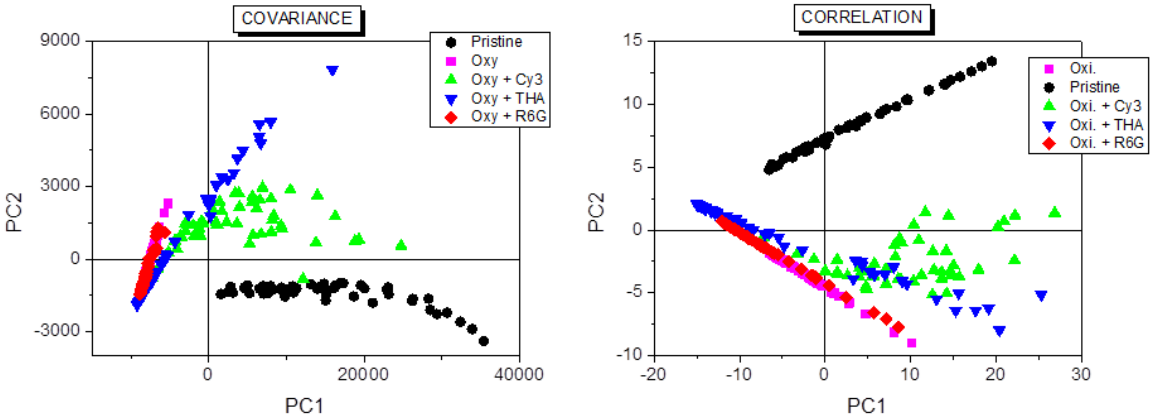

Figure S4

Table S1 contains the complete list of the Raman shifts used for the Principal Components Analysis. The wavenumbers are chosen in the spectral ranges corresponding to the RBM, D, G, M and G' bands, as indicated in the Table.

Table S1

Spectral Band	Wavenumbers (cm^{-1})	Spectral Band	Wavenumbers (cm^{-1})	Spectral Band	Wavenumbers (cm^{-1})	Spectral Band	Wavenumbers (cm^{-1})	Spectral Band	Wavenumbers (cm^{-1})
R B M	109.12454	D	1239.74	G	1470.1949	M	1700.123	G '	2403.2261
	120.7914		1249.9067		1480.0563		1709.6799		2413.293
	130.5045		1260.0598		1489.9047		1720.8156		2423.344
	140.2053		1270.1992		1499.74		1730.3458		2433.3813
	149.8940		1280.3251		1509.5623		1739.8636		2441.9712
	159.5746		1290.4374		1519.3716		1750.9512		2443.4011
	169.2431		1300.5361		1530.8003		1760.4424		2453.4075
	180.8309		1310.6232		1540.5819		1771.4996		2463.3962
	190.4752		1320.6949		1550.3506		1780.9628		2473.3716
	200.1096		1330.7551		1560.1064		1790.4137		2483.3313
	209.7320		1339.1261		1561.7311		1801.4232		2493.2739
	219.3464		1350.8334		1564.9794				2503.2029
	230.8677		1360.8514		1568.2264				2513.1167
	240.4561		1370.858		1571.4705				2523.0151
			1380.8512		1574.7151				2534.3074
			1390.8312		1577.9585				2544.1736
			1400.7979		1581.1989				2554.0247
			1410.7513		1584.438				2563.8589
			1420.6915		1587.6777				2573.6797
			1430.6185		1589.2953				2582.0845
			1440.5323		1590.9144				2590.4775
			1450.433		1600.6154				2591.8767
			1460.3206		1610.3055				2603.0483
					1621.5925				2612.8088
					1631.2537				2623.9436
					1640.9038				2633.6709
					1650.5397				2643.3835
					1660.1627				2653.0813
					1671.3738				2662.7642

1680.97	2672.4324
1690.5519	2682.0842
	2691.7229
	2702.7192
	2713.6973
	2723.2871
	2732.8608

Figures S5 and S6 present the loading plots corresponding, respectively, to the results of the principal component analysis reported in Figures 3A and 3B.

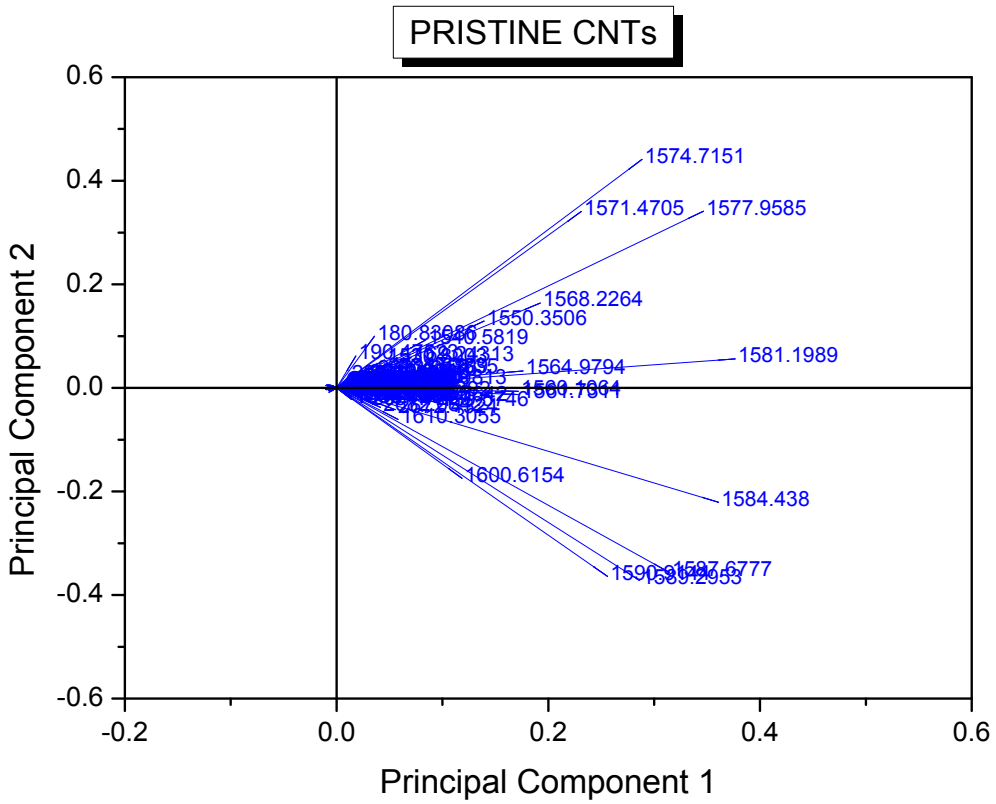

Figure S5

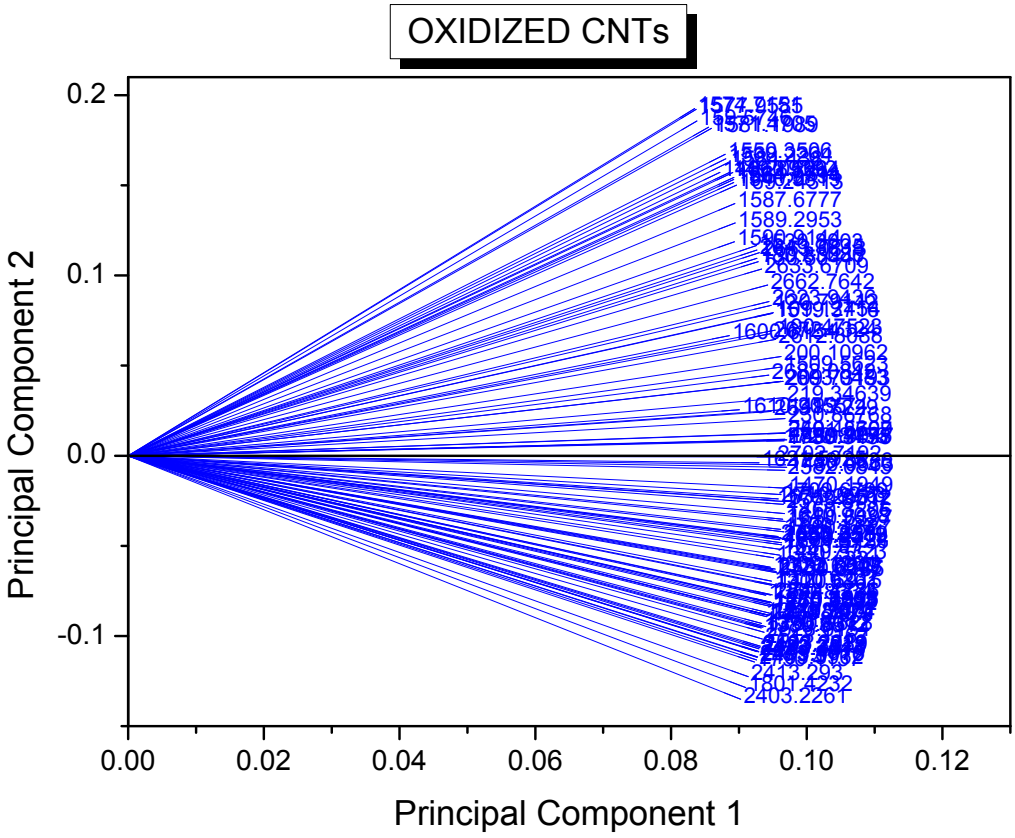

Figure S6

Oxidation procedure of pristine SWCNTs

Pristine SWCNTs, purchased from Sigma Aldrich have been oxidized by acid treatment as following: the SWCNT containing powder was ultrasonicated at 40°C in a highly acidic 3:1 mixture of H_2SO_4 and HNO_3 for 3 hours. The as collected filtered powder (oxidized SWCNTs) was then characterized.

Spectrochemical titration

In Figure S7, panel a), fluorescence spectra of THA at different concentrations are shown as an example of spectrochemical titration. Panel b) presents the calibration curves for THA, R6G and Cy3 (three to five points from 9.7 x 10^{-8} to 2.4 x 10^{-7}; mother solution 9.7 x 10^{-5}) done by using the fluorimetric method described in the experimental section of the paper ($R^2 = 0.999$).

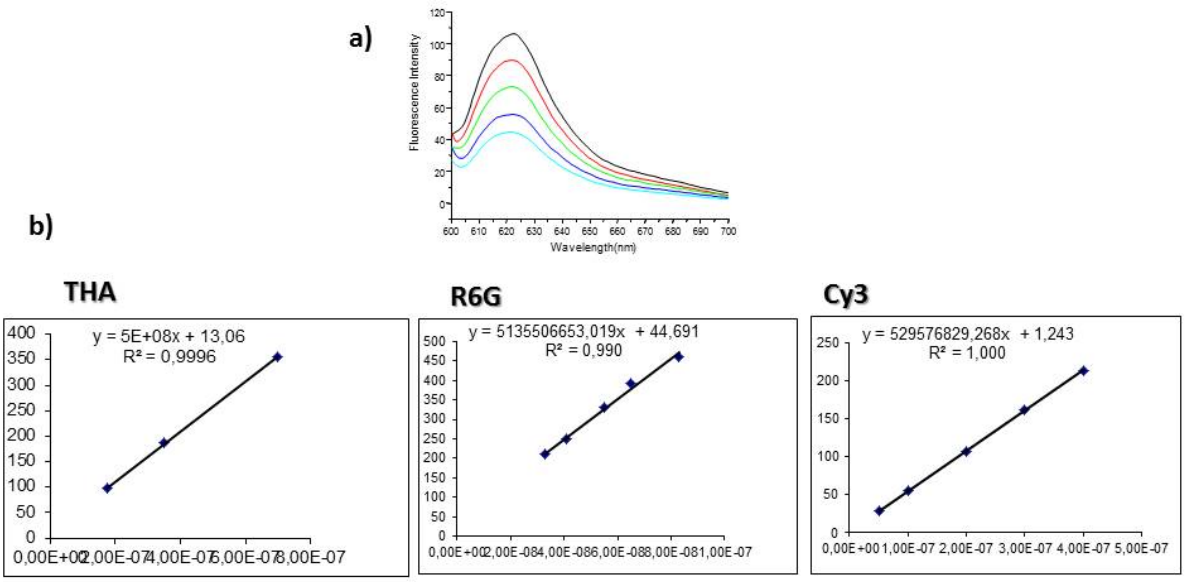

Figure S7

Figure S8 shows examples of fluorescent spectra of dyes reacted with pristine SWCNTs (p-SW) and oxidized SWCNTs (f-SWCNTs). For non oxidized nanotubes the resulting dye solution was diluted 400 times.

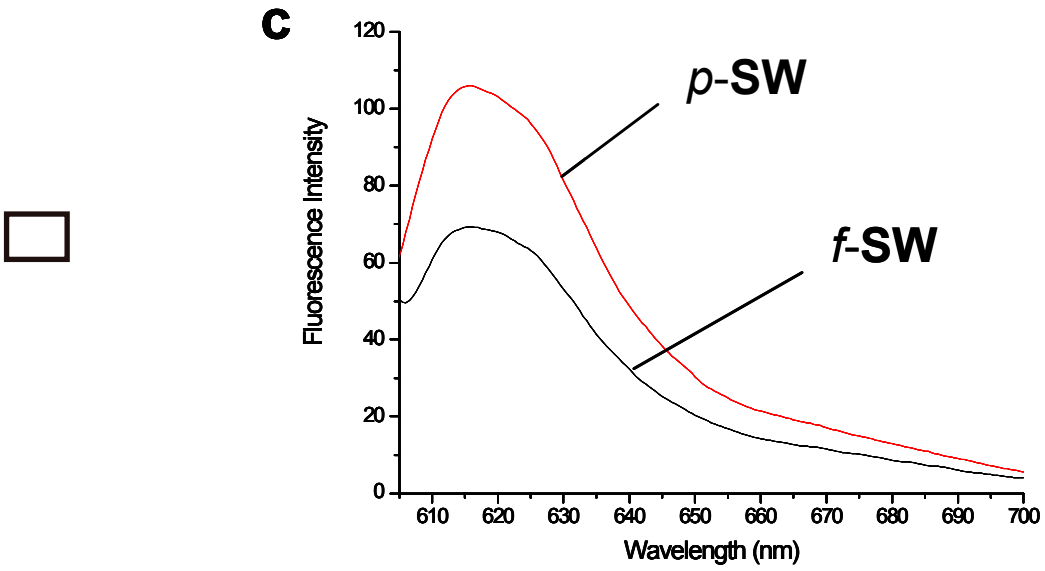

Figure S8

Figure S9 shows the difference of dye concentration calculated in the presence of oxidized SWCNTs and pristine SWCNTs (see paragraph 3.4 of the text).

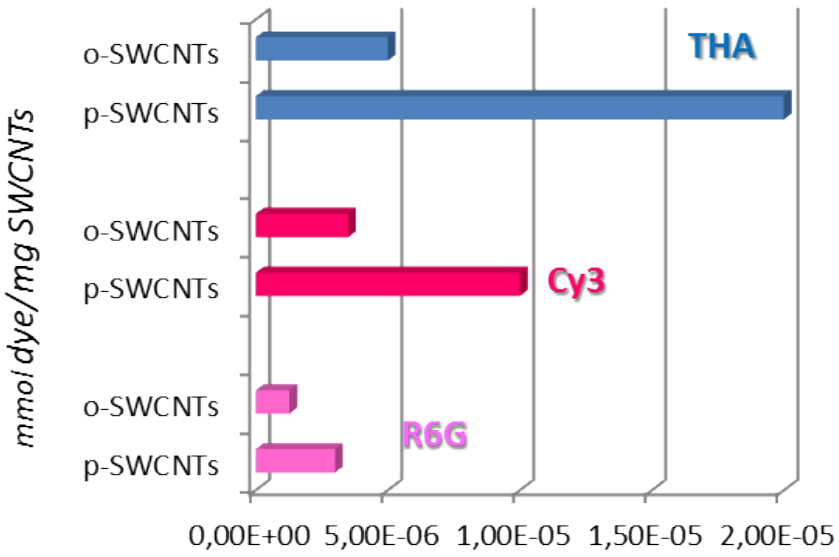

Figure S9