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Multicavity halloysite-amphiphilic cyclodextrin hybrids for co-delivery of natural drugs into thyroid cancer cell

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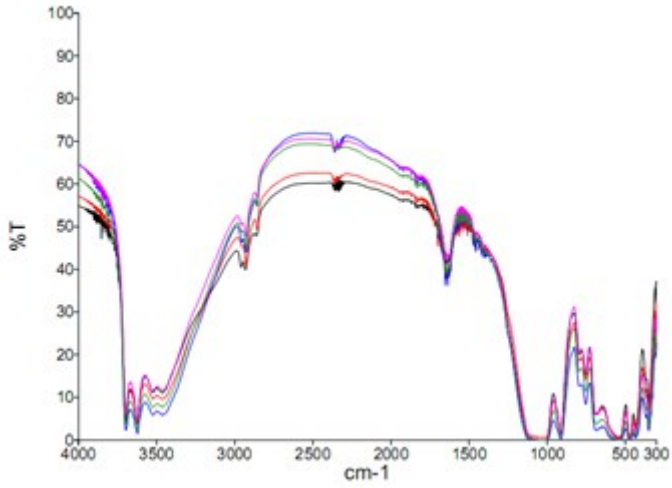

Figure S.1. FT-IR spectra of compounds **3a-d**.

We recorded the UV–vis spectra of dispersion of p-HNT/Sil in aqueous solution, at 25 °C and at a fixed concentration of silibinin (1×10^{-4} M) in the presence of increasing amounts of p-HNT (0–1×10^{-3} g/mL). The occurrence of the interaction was evaluated by measuring the absorbance at the maximum absorption wavelength of the silibinin (325 nm). Typical trends are depicted in Fig. S.2. The absorbance value decreases on increasing of p-HNT concentration. Moreover, after interaction with p-HNT, the p-HNT/Sil has a peak at the same absorption wavelength as free silibinin. These findings suggest that silibinin has been successfully encapsulated into the HNT lumen

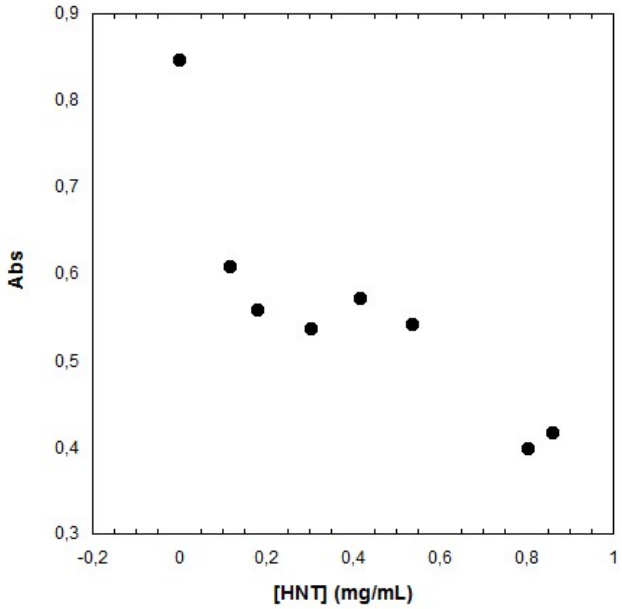

Figure S.2. Trend of the absorbance of the silibinin (1×10^{-4} M) as function of p-HNT concentration (0–1×10^{-3} g/mL).

It is interesting to observe from TGA data that the silibinin encapsulated in p-HNT shows a higher degradation temperature (314 °C) as compared to the pure compound (294 °C). This striking enhancement of the thermal stability can be due to encapsulation of the degradation products into the nanotube lumen (Figure S.3).

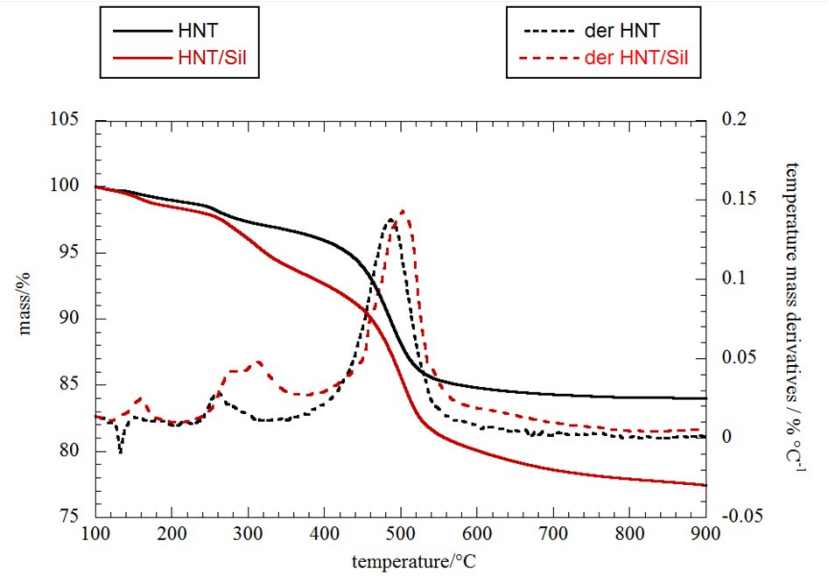

Figure S.3. Thermoanalytical curves for p-HNT and p-HNT/sil complex.

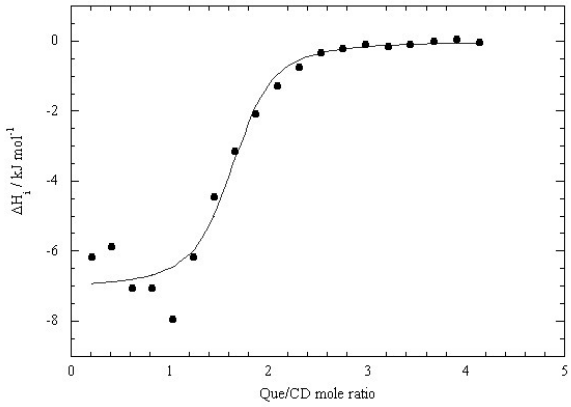

Figure S.4. ITC titration curve.

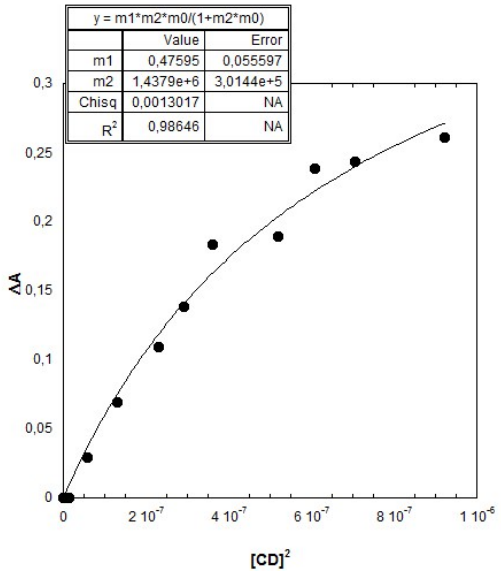

Figure S.5. Curve fitting analysis of UV-vis spectral titration of quercetin with amph-CD in phosphate buffer solution at pH 6.9.

In Figure S.6 is shown the trend of the fluorescence intensity of quercetin at 540 nm, as a function of pristine HNT concentration (0-1.5 mg/L).

The emission of quercetin, related to the supernatant solution, decreases on increasing of p-HNT concentration (Figure S.6.a). Moreover, after interaction with p-HNT, the p-HNT/Quer has a peak at the same emission wavelength as free quercetin. These findings suggest that quercetin has been successfully encapsulated into the HNT lumen, as we have previously reported for curcumin.

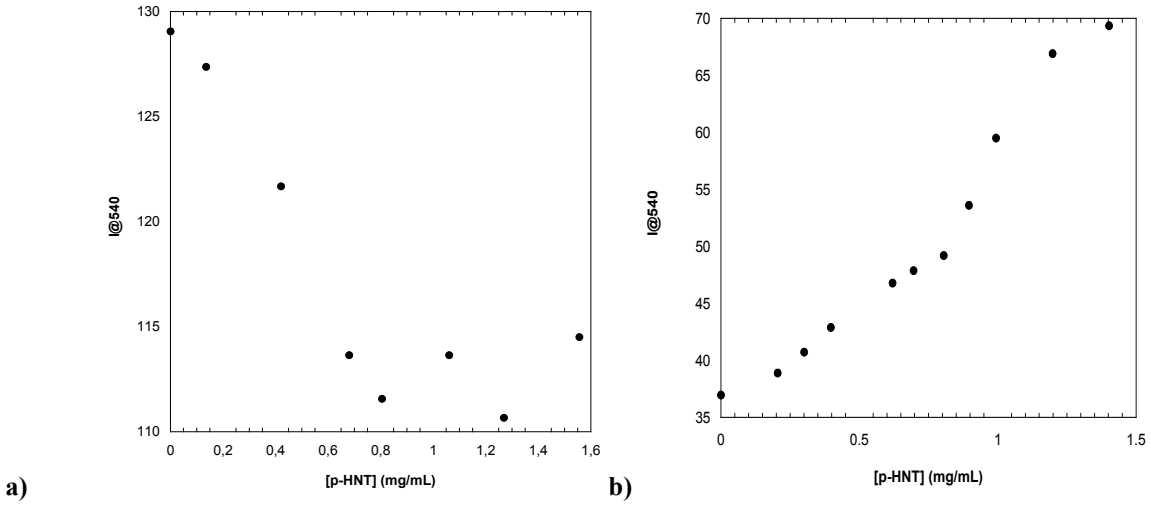

Figure S.6. Trends of the fluorescence intensity of quercetin, recorded at 540 nm, as a function of p-HNT concentration (0-1.5 mg/mL) related to a) supernatant solution; b) dispersions after sonication.

Recording the fluorescence intensity of the dispersions after sonication, we obtained the trend shown in Figure S.6.b. in this case as a consequence of the more hydrophobic inner HNT surface than the surrounding medium, we observed an increase in the emission of quercetin on increasing of HNT concentration.