Electronic Supplementary Material (ESI) for Nanoscale.

Supplementary Information for : Diameter-selective non-covalent functionalization of carbon nanotubes with porphyrin monomers.

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Evaluation of the $(6,5)$ concentration

In the commercial enriched solution (purchased from NanoIntegris), the $(6,5)$ nanotubes represents roughly 80% of the material, as expected from similarly enriched suspensions.[1] The absorbance spectrum confirms the presence of minor chiral species (Figure S-1). In order to evaluate the equivalent total length of nanotube in the suspension, we need to extract the intrinsic (6,5) absorption at the E_{22} resonance. To this end, we subtracted the background absorption arising from other minority species and impurities by using PLE measurements.[2] Finally, the (6,5) nanotube concentration is obtained by dividing this intrinsic absorbance at the E_{22} resonance by the absorption cross section reported in the literature.[3,4]

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Fit to the experimental titration data

Using the Hill formalism, the chemical equilibrium reads :

$$X_{n,m} = \frac{(K_{n,m}[TPP]_{eq})^{h_{n,m}}}{1 + (K_{n,m}[TPP]_{eq})^{h_{n,m}}} \tag{1}$$

where $X_{n,m}$ is the reaction extent evaluated from resonant PL intensities ($X_{n,m} = 0$ from pristine tubes and $X_{n,m} = 1$ for completely functionalized tubes) and $[TPP]_{eq}$ is the TPP monomers concentration in solution at equilibrium. This model allows us to evaluate $K_{n,m}$ and $h_{n,m}$ from PLE measurements of HiPCO nanotubes solutions with different initial TPP concentrations (Figure **??**d). In the case where only one species is present in solution (here the $(6,5)$ nanotubes), we can assess the absolute coverage on the sidewall (Figure 3b). Using again the Hill formalism, we can express the initial TPP concentration ($[TPP]_0$) as a function of the equilibrium concentration and the initial $(6,5)$ nanotube binding sites concentration $[CS]_0$:

$$[TPP]_0 = \frac{[TPP]_{eq} + (K_{6,5}[TPP]_{eq})^{h_{6,5}}([CS]_0 + [TPP]_{eq})}{1 + (K_{6,5}[TPP]_{eq})^{h_{6,5}}} \tag{2}$$

Practically, $[TPP]_{eq}$ is deduced from luminescence intensity measurements at the wavelength of the Q bands of the TPP, knowing that this luminescence is completely quenched for monomers stacked on a nanotube.[5] This luminescence was carefully calibrated against the TPP concentration in reference samples. The fit to the data of Figure 3b allowed us to extract the concentration of binding sites $[CS]_0$ and therefore the number of TPP monomer stacked per unit length of nanotube, knowing the nanotube concentration from absorbance measurements (see above). Interestingly, Eq. 2 has an asymptotic expression for large TPP concentration : $[TPP]_{eq} \simeq [TPP]_0 - [CS]_0$ which simply reflects the conservation of matter when all carbon sites are filled. This allows to explain the linear asymptotic behavior and alternatively, to deduce the absolute number of binding site from the intercept of the asymptote with the baseline.

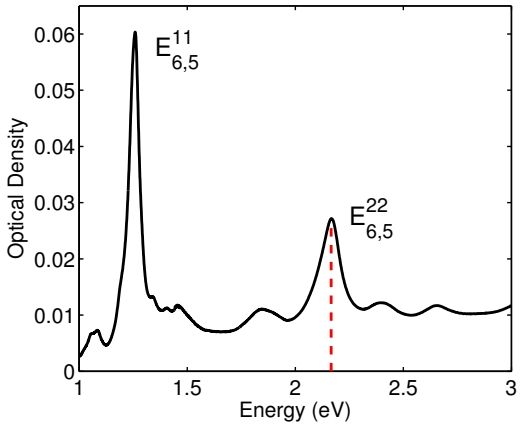

Figure S-1: Absorbance spectrum (1 mm thick cuvette) of the commercial $(6,5)$ enriched suspension used for the coverage evaluation.

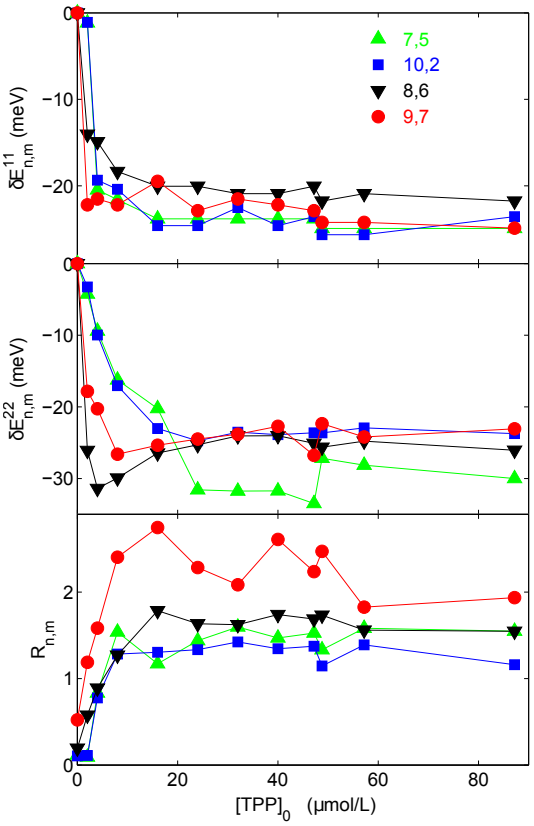

Figure S-2: Energy shifts of the E^{11} and E^{22} resonances, and transfer ratio $R_{n,m}$ (see definition in text) as a function of the initial monomer concentration, evaluated for 4 different NT species in HiPCO suspensions. The saturation brings evidence for the monolayer completion on the nanotube sidewalls.

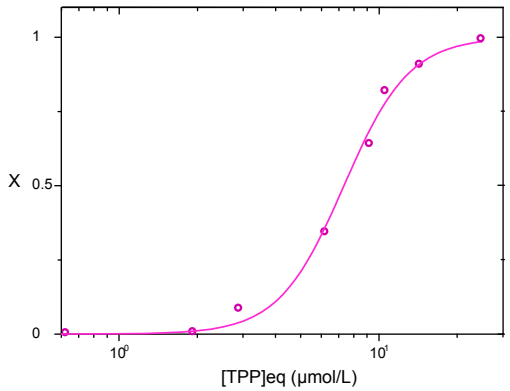

Figure S-3: Functionalization extent as a function of the TPP equilibrium concentration (log scale) for (6,5) CoMoCat nanotubes encapsulated in SDS surfactant. The solid line is a fit of the Hill equation to these data.

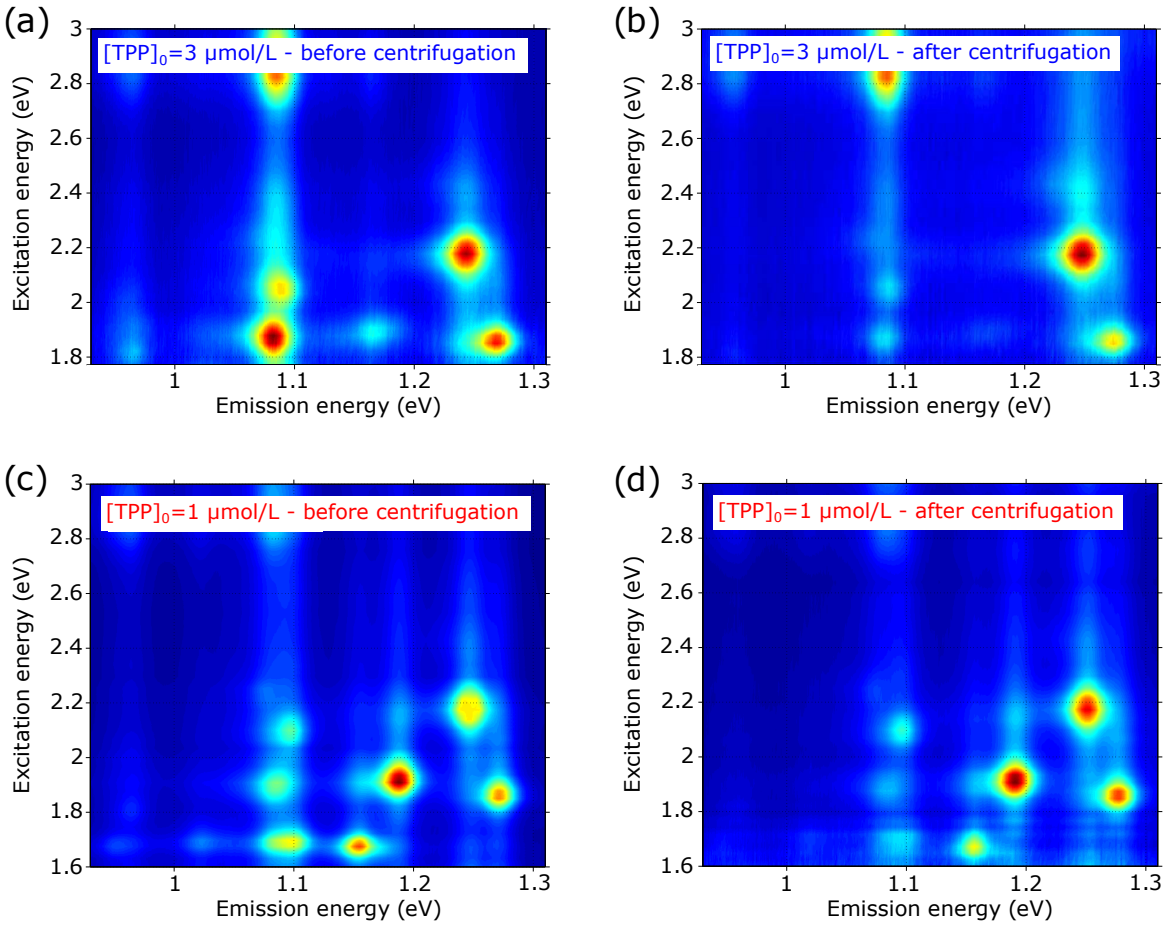

Figure S-4: Normalized PLE maps of partially functionalized HiPCO nanotubes with high (a,b) and low (c,d) TPP monomer concentrations, before (a,c) and after (b,d) the centrifugation process. The chiral enrichment of the surpernatants with low diameter tubes is assessed in the main text.

References

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