## Electronic Supplementary information: Controlling the noncovalent functionalization of carbon nanotubes using sub-cmc dilutions in a co-surfactant environment.

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Study of the solubilisation of  $H_2$ TPP in surfactants.

The goal of the study is to reach a full functionalization of carbon nanotubes with H<sub>2</sub>TPP molecules without the help of sonication. Therefore, we choose a protocol consisting simply in mixing a micellar suspension of  $H_2$ TPP with a micellar suspension of nanotubes and let the functionalization process to occur. The first step was to prepare a micellar suspension of  $H_2$ TPP. The most evident choice was to use the same surfactant as the one of nanotubes. Sodium cholate is known to be one of the best surfactant for single wall carbon nanotubes.[1, 2]Its use leads to suspensions of well individualized nanotubes, stable for months. First, we test the solubilization of  $H_2$ TPP in SC aqueous suspension by using the micelle swelling method. [3] We prepare a 2 wt% $(c_{SC} = 46 \text{ mmol.L}^{-1})$  SC suspension in a 10 % pH= 8  $(10^{-2} \text{ mol.L}^{-1})$  sodium borate buffer. Shortly, a solution of  $H_2$ TPP in dichloromethane (DCM) is added with a 10 % DCM/water ratio, and sonicated with a tip during 90 minutes. Then, the aqueous phase is separated from the organic phase. By performing experiments as a function of the  $H_2$ TPP concentration in DCM, we monitor the ability of molecules to pass from the organic phase to the aqueous phase. In the following, we define the maximal concentration as the theoretical concentration that could pass into the micelle suspension if the transfer from the DCM phase was 100% efficient. The quantity of molecules in the micellar suspension is measured by means of optical absorption spectroscopy. Figure S1 displays the optical absorption spectrum of  $H_2$ TPP in SC (red) and in sodium dodecyl sulfate (SDS, black) in the spectral domain of Q bands.[4] Figure S1 (insert) shows the optical density on the  $Q_y(0-0)$  band of H<sub>2</sub>TPP as a function of the maximal concentration.

It shows a saturation of the Q band optical density in the SC medium. Above a maximal concentration of about 100  $\mu$ mol.L<sup>-1</sup>, almost no H<sub>2</sub>TPP monomer can be added to the aqueous suspension of SC without the creation of large H<sub>2</sub>TPP aggregates, visible on the optical absorption spectrum.[5, 6] In order to increase the maximal concentration of H<sub>2</sub>TPP in water, we tested another surfactant: SDS. The choice of SDS was guided by the



FIG. S1: Optical absorption spectra of porphyrin in SC (red) and in SDS (blac) for a maximal concentration of 390  $\mu$ mol.L<sup>-1</sup>. (insert) Optical density of H<sub>2</sub>TPP Q<sub>y</sub>(1, 0) band in SC (red) and SDS (black) as a function of maximal concentration.

idea that we needed spherical micelles with large aggregation numbers to isolate hydrophobic porphyrin in water. [7] Furthermore, the chosen surfactant from molecules had to be also a good one for nanotubes. Even if SDS is not as good as bilt salts to solubilise small nanotubes, it is known to work well. Historically, the use of SDS unveiled the observation of the intrinsic photoluminescence of carbon nanotubes.[8, 9] Moreover, SDS and SC are known to mix very well and this mixture has been used extensively for separation of carbon nanotubes by density gradient ultracentrifugation, [10] gel chromatography or aqueous two phase methods.[11–13] Figure S1 (black) displays the evolution of  $Q_u(0-0)$  band optical density of  $H_2$ TPP in a SDS (2 wt%,  $c_{SDS} = 70$  mmol.L<sup>-1</sup>) micellar suspension. It shows a linear dependence with the maximal concentration in DCM up to 400  $\mu$ mol.L<sup>-1</sup>, leading to highly concentrated aqueous suspensions of H<sub>2</sub>TPP in the aqueous phase. The estimated concentration in the final sample is around 300  $\mu$ mol.L<sup>-1</sup>, which is close to the maximal value. In comparison, direct inclusion of porphyrin in micelles by a simple stirring method enables to reach concentration of  $\simeq 1 \mu \text{mol.L}^{-1}$ .[14] This proves

the efficiency of the swelling method[3] to force a large quantity of molecules into a micelle environment.

To test the degree of isolation of the molecules in micelles, we performed time resolved photoluminescence (TR-PL). When porphyrin are well isolated (as in DCM), the fluorescence exhibits a monoexponential relaxation decay with a time constant of  $\simeq 12$  ns. When molecules form aggregates in micelles, their decay time decrease due to self quenching effects. [5] Our functionalization method aims at mixing a suspension of nanotubes with a one of  $H_2$ TPP and letting the mix evolve. Therefore, we need to prevent the self aggregation of molecules that may compete with the stacking reaction. Figure S2 shows the TR-PL response of porphyrin both in SC and in SDS for concentration of respectively 95  $\mu$ mol.L<sup>-1</sup> and 108  $\mu$ mol.L<sup>-1</sup>. While on SDS, the curve is mainly exponential, the SC/H<sub>2</sub>TPP TR-PL decay is non-exponential with the appearance of a short component characteristic of the presence of aggregates.



FIG. S2: Time-resolved photoluminescence of  $H_2$ TPP in SDS (black) at 108  $\mu$ mol.L<sup>-1</sup> and in SC (red) at 95  $\mu$ mol.L<sup>-1</sup>, just after preparation of the suspensions.

A second important point is the stability of the suspension over time. Figure S3 displays TR-PL experiments performed both on SC/H<sub>2</sub>TPP and SDS/H<sub>2</sub>TPP suspension at low concentration over time. Within seven days, the SC/H<sub>2</sub>TPP TR-PL decay becomes non-exponential while no major changes is observed in SDS. All of these features proves that the stability of isolated porphyrin is improved in SDS with respect to SC. The ability to transfer molecules in large quantities, in a controlled manner, into the micelle phase is of great interest to develop a facile route to properly functionnalize nanotubes.

## Comparison of the kinetics between anionic and cationic surfactant

The TPP have been suspended in a 2%w.t. suspension of the cationic surfactant CTAB. Figure S4 shows the ki-



FIG. S3: Time-resolved photoluminescence of  $H_2$ TPP in SDS and in SC at low concentration, 1 day and 7 days after the preparation of the suspensions.

netics of the reaction at 50% ratio at which the dilution process does not destabilize the CTAB micelles. The characteristic time of the kinetics in CTAB is of 40 minutes, which is two orders of magnitudes faster than the same experiments performed with SDS micelles. Here, the decrease of the timescale with respect to SDS/SC samples may be explained by the presence of attractive forces between the TPP/CTAB micelles and the Nt/SC ones.



FIG. S4: Optical density of the  $\pi$ -stacked porphyrins on nanotubes (at 440 nm) as a function of time for a starting suspension of H<sub>2</sub>TPP in CTAB micelles (red) and in SDS (black) for a dilution ratio of 50%. Nanotubes are in suspension in SC. H<sub>2</sub>TPP concentration is 20  $\mu$ mol.L<sup>-1</sup>.

## Thermodynamic study of the reaction

Here, the aim is to extract the thermodynamical parameters of the reaction. For this purpose, several samples have been prepared, at  $r_{sds} = 10$  %, with different

porphyrin concentrations. Then, the final equilibrium of the reaction was monitored. Following a procedure reported in a previous paper,[15] we evaluate the reaction extent X through the increase of the energy transfer ratio  $R(c_{tpp})$  as a function of the porphyrin concentration  $c_{tpp}$ :

$$X = \frac{R(c_{tpp}) - R(c=0)}{R(c=\infty) - R(c=0)}$$
(1)

where R(c=0) is the ratio without porphyrins, due to the natural absorption of nanotubes at 440 nm. From Figure S5, we see that the reaction extent follows a saturation behaviour with respect to the equilibrium porphyrin concentration [TPP]<sub>eq</sub>.



FIG. S5: Evolution of the equilibrium reaction extent  $X_{eq}$  with final free H<sub>2</sub>TPP concentration for an  $r_{sds}$  dilution ratio of 10%.

This allows to extract the thermodynamical parameters of the reaction, from a Hill adsorption model:

$$X = \frac{\left(K\left[\text{TPP}\right]_{eq}\right)^n}{1 + \left(K\left[\text{TPP}\right]_{eq}\right)^n} \tag{2}$$

A reaction constant of  $K = 5.10^5$  and a cooperativity parameter of n = 4 are extracted. This leads to a reaction Gibbs energy of  $\Delta rG = -33$  kJ.mol<sup>-1</sup> in good agreement with a previous report in full SC suspensions. That shows that the SDS molecules do not perturb the thermodynamics of the adsorption process.

## Influence of the variation of micelles occupation probability on the reaction rate above and below SDS cmc

Another parameter varying during the dilution is the proportion of micelles filled with porphyrin molecules in the initial suspension. To study the impact of such effect, we calculate the number of molecules per micelles in the SDS phase before dilution. Under the used conditions, the aggregation number of SDS micelles is close to  $N_a = 60.[7]$  From a simple model,[7] the concentration of SDS micelles can be written as:

$$c_{mic-sds} = \frac{c_{sds} - cmc}{N_a} \tag{3}$$

For a SDS solution at 2 wt% w.t., the concentration of micelles is 1000  $\mu$ mol.L<sup>-1</sup>. Maiti *et al.* suggested to evaluate the proportion p of micelles containing n molecules by a poissonian law:[14]

$$p(n) = \frac{x^n e^{-x}}{n!} \tag{4}$$

where  $x = c_{H_2TPP}/c_{micelles}$ . This method is used to



FIG. S6: Plot of  $k = 1/\tau$  as a function of the proportion of micelles containing porphyrin in the sds phase.

evaluate the proportion of empty and filled micelles in the SDS phase before mixing with the nanotubes. The inset of figure S6 shows the variation of p(n>0) as a function of  $r_{SDS}$ . One observes that the probability of having one or several molecules per micelle is large for the  $r_{sds} \leq 10$  %. For the other ratios, the proportion of empty micelles is predominant, with an increasing importance as r<sub>sds</sub> grows from 10% to 50%. Figure S6 displays the evolution of  $1/\tau$  as a function of the probability to have one or more H<sub>2</sub>TPP molecules per micelle. For high occupation probabilities,  $1/\tau$  depends linearly on the proportion of filled micelles p(n > 0) in the SDS phase. This indicates that the proportion of filled versus empty micelles can influence the kinetics of the reaction for  $r_{sds} < 10$  %. However for lower occupation probabilities, the curve shift away from the linear tendency. Hence, the empty/filled micelle competition is not a relevant effect for samples with a final SDS concentration above the cmc. In this region, the porphyrin/SDS micelles remain stable, and the TPP

diffusion occur through a slow micellar exchange process described in the main text, involving fission/growth or collision fusion events. Between these two stages, there seems to be a concentration threshold, that is very close from cmc of SDS, demonstrating a change of regime. Below the cmc, micelles are destabilized. Then, the more the intial micelle contains  $H_2TPP$  molecules the fastest is the reaction.

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