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Controlling the kinetics of the noncovalent functionalization of carbon nanotubes using sub-cmc dilutions in a co-surfactant environment.[†]

Géraud Delport,^a Lucile Orcin-Chaix,^{a,b} Stéphane Campidelli,^b Christophe Voisin,^c and Jean Sébastien Lauret^a

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We investigate the origin of the slow kinetics of functionalization processes in micellar environments. We show that the ionic nature of the surfactants used to solubilize small molecules and nanoobjects plays a central role in the slowness of the kinetics. In order to solve this issue, we have developed an innovative method that we apply to the hybrid compound porphyrin molecule/carbon nanotube. We use two ionic surfactants to solubilize the molecules and the nanotubes respectively. Passing the molecule suspension below the cmc allows to circumvent the stability of the ionic surfactant while keeping the benefit of working with highly concentrated solutions. This method allows to finely control the functionalization reaction and to tune the kinetics characteristic time over more than two orders of magnitude.

Introduction

Colloidal nano-objects have attracted much attention for several decades. They are studied in a number of fields of research including biolabeling, drug delivery, photonics, photovoltaics. This class of materials covers many different type of objects: semiconducting or metallic nanoparticles, carbon nanotubes, fullerenes etc... A key issue concerns the solubility of those objects, in particular in water. Indeed, most nanoobjects tend to aggregate thereby blurring their intrinsic properties. In order to overcome this bottleneck, many strategies have been developed. For instance, covalent chemistry has been employed to add ligands at the surface of the nanoparticles in order to help their solubility in water.^{1–4} Another example is the use of surfactants in order to embed nanoobjects inside water soluble micelles. This approach has been, for instance, particularly efficient to solubilize carbon nanotubes.^{5–8}

In the same time, an important field regards the functionalization of these nanoobjects. For instance, one may enhance their optical properties by coupling them to chromophores in the con-

text of energy transfer processes.^{9,10} Once again, it is crucial to be able to perform the chemical reactions on properly dispersed objects to preserve their original properties. In this framework, chemistry on nanoobjects using micelles as nanoreactors is an interesting route. In the particular case of carbon nanotubes, several groups have recently developed a functionalization method of nanotubes in micellar environments.^{9,11–13} For instance, our groups have shown that it is possible to non covalently functionalize nanotubes with porphyrin molecules simply by mixing a suspension of molecules in micelle with a micellar suspension of single carbon nanotubes.¹⁴ Interestingly, these hybrid objects show an almost 100% energy transfer from the molecules to the nanotubes.^{15,16}

Ionic surfactants are known to lead to more stable micelles than neutral ones^{17,18}. Therefore, they are used to solubilize small molecules and nanoobjects.^{5,6,19–22} For example, ionic bile salts such as sodium cholate are known to be among the best surfactant for carbon nanotubes, leading to suspensions stable for months,⁶ and their interaction with nanotubes is still investigated.²⁰ Yet, as far as functionalization processes are concerned, a too high stability of the micelles will prevent them to merge, preventing the reactants to come across each other. The consequence is that many reactions in ionic surfactant environment have limited yields and present very long kinetic timescales (days, weeks).^{23–26} Therefore, a major challenge of chemistry in micelles is to find a balance between the ability of reactants to come across each other and the long term stability of the micelle embedded products.

In this paper, we report on the understanding of the microscopic mechanisms at the origin of these very slow kinetics. The

^a Laboratoire Aimé Cotton, CNRS, Univ. Paris-Sud, ENS Cachan, Université Paris-Saclay, 91405 Orsay Cedex, France; Tel: +33 1 69 35 21 32; E-mail: jean-sebastien.lauret@lac.u-psud.fr

^b LICSEN, NIMBE, CEA, CNRS, Université Paris-Saclay, CEA Saclay 91191 Gif-sur-Yvette Cedex, France.

^c Laboratoire Pierre Aigrain, Ecole Normale Supérieure, CNRS, UPMC, Université Paris Diderot, Paris, France.

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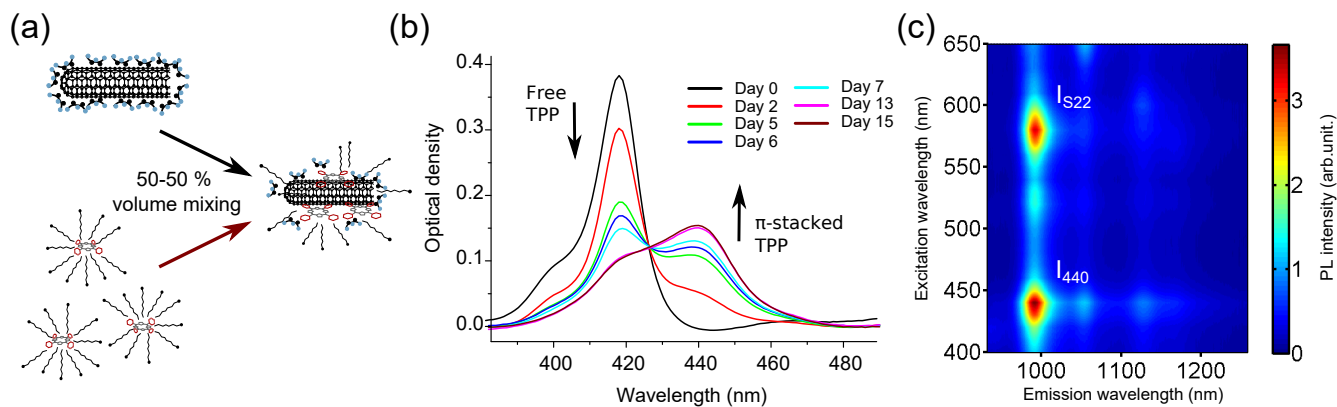


Fig. 1 (a) Scheme of the reaction. (b) Optical absorption spectra of the suspension performed at different delay after the mixing. (c) PLE map of the suspension. The initial concentration of H_2TPP is $20 \mu\text{mol.L}^{-1}$ and the initial S_{11} optical density of (6,5) nanotubes is 0.15

insight into the micellar processes allows us to develop an original strategy to control and speed-up the kinetics using sub-cmc co-surfactant mix. This study was conducted using porphyrin/carbon nanotube compounds as a model system. Indeed, our previous studies on the photophysics of these hybrid objects give us precise spectroscopic tools to monitor the reaction.^{9,14,15,27} A fine control of the kinetics of the π -stacking reaction is achieved by passing the concentration of the surfactant wrapping the porphyrin under the cmc, whereas the one wrapping the nanotubes remains well above the cmc. We show that the reaction rate can be tuned over several orders of magnitudes by this means.

Experimental

Carbon nanotubes are (6,5) enriched CoMoCat purchased from Sigma-Aldrich. The nanotubes suspension is prepared by means of tip sonication (1h30) of a 0.07 mg.mL^{-1} aqueous suspension with 2%wt of sodium cholate. Then the suspension is centrifuged at 120,000g during one hour to remove residual bundles. H_2TPP are tetraphenylporphyrin synthesized by common method²⁸ and purified twice by column chromatography. Sodium dodecyl sulfate and sodium cholate are purchased from Sigma-Aldrich. H_2TPP is solubilized first in dichloromethane. Then the micelle swelling method is used to include monomers in micelles, followed by a centrifugation step.⁹ Both optical absorption spectroscopy and time-resolved PL are used to ensure that no porphyrin aggregates are in solution (see ESI).

Optical absorption spectroscopy is performed with a lambda900 UV/VIS/NIR spectrophotometer (Perkin Elmer). A 1000 W Xenon lamp filtered with a monochromator is used as an excitation source for photoluminescence excitation experiments. The luminescence is then analysed with an Acton SP2500i spectrometer. A PIXIS100B CCD is used to detect the porphyrin fluorescence whereas an OMAV InGaAs diode array is used for the emission of carbon nanotubes. Time-resolved photoluminescence (TR-PL) were performed using the Time-correlated single Photon counting TimeHarp 260 system from PicoQuant. The excitation was the second harmonic of a pulse from a Ti:Sapphire laser (Mai Tai, Spectra-Physics). The emission was detected with a single photon avalanche diode (IDQuantique

ID150).

Results and Discussion

Our functionalization protocol simply consists in mixing a micellar suspension of H_2TPP with a micellar suspension of single wall carbon nanotubes and in letting it evolve spontaneously (see figure 1(a)). We use sodium cholate (SC) as the surfactant for nanotubes, and sodium dodecyl sulfate (SDS) to solubilize H_2TPP molecules in water, as it creates spherical micelles that are more efficient to solubilize small molecules (see ESI).²⁹ The final suspension is obtained by mixing a volume V_{sds} of a 2 wt% SDS suspension of H_2TPP with a volume V_{sc} of a (6,5) enriched CoMoCat carbon nanotubes suspension in SC at 2 wt%. The relative amount of SDS in the final sample is quantified through the volume ratio:

$$r_{sds} = \frac{V_{sds}}{V_{sc} + V_{sds}} \quad (1)$$

Figure 1(b) displays the optical absorption spectra of the suspension, for a ratio $r_{sds} = 50\%$. On the timescale of a few days, the free porphyrin signature at 420 nm decreases while the one of the porphyrin attached to the nanotube increases at 440 nm.^{9,30} Moreover, a fingerprint of the functionalization of the nanotubes by H_2TPP molecules is the observation of a strong energy transfer from the molecules to the nanotube.^{9,15} This is observed on the photoluminescence map (figure 1(c)) which shows the characteristic energy transfer resonance for an excitation at 440 nm on the Soret band of the H_2TPP and an emission at 995 nm on the excitonic transition of the nanotubes.^{9,27} In this configuration, the equilibrium of the functionalization reaction is reached on the timescale of a week.

This functionalization reaction is very slow in comparison with standard micellar reorganisation processes. As an example, surfactant monomers exchanges usually occur on timescales of μs to ms, depending on the surfactant and the experimental conditions.³¹ Therefore, more complex processes have to be invoked to explain the kinetics reported here. A parallel can be drawn with the exchange of dye molecules between micelles. Those processes have been widely investigated.^{17,18,32} For instance, Y. Rharbi *et al* reported on the exchange of pyrene dyes in diverse micellar environments.¹⁸ According to their studies, two kinds of

micellar processes allow the exchange of hydrophobic molecules between micelles. The first one is a simple collision where an empty micelle merges with a micelle containing more than one dye molecule resulting in a larger micelle. This latter eventually splits in two micelles, each containing dye molecules. The second process consists in the fission of the molecule's micelle into unstable submicelles, that will eventually merge with empty micelles. For non-ionic surfactants (such as Triton X100), the timescale of these two processes is close to a second. For the ionic SDS, the authors showed that such exchanges occur on the timescale of a day, similarly to the dynamics observed for the functionalization reaction reported here.¹⁸ This slow rate for SDS surfactant is interpreted as a consequence of the higher stability of the micelle structure. In fact, the coulombic repulsion from the anionic heads of dodecyl sulfate molecules stabilizes the micelles. This limits the ability of SDS monomers to leave the micelle, and concomitantly provides a stabilizing interaction between adjacent micelles. This last assumption was confirmed by a study from Patist and coworkers that exhibited a correlation between the demicellization time and the mean distance between SDS micelles.³³

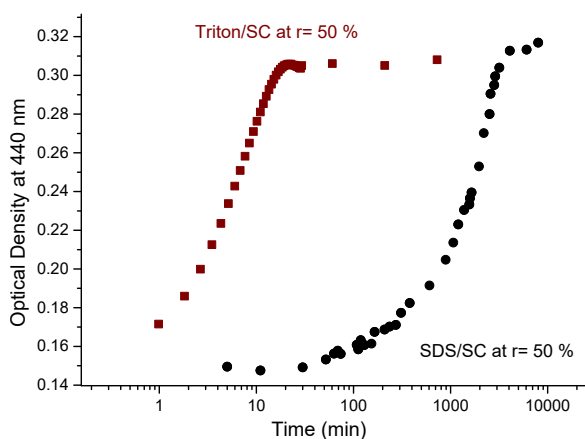


Fig. 2 Optical density of the π -stacked porphyrins on nanotubes (at 440 nm) as a function of time for a starting suspension of H_2 TPP in TritonX100 micelles (red) and in SDS (black) for a dilution ratio of 50%. Nanotubes are in suspension in SC. H_2 TPP concentration is $20 \mu\text{mol.L}^{-1}$.

As explained above, collision/fusion and fission/growth processes are faster in non-ionic surfactants.¹⁸ Therefore, experiments with the non-ionic surfactant TritonX100 have been performed in order to test the influence of the micelle stability on the kinetics of the functionalization. Figure 2 shows the kinetics of the reaction for H_2 TPP in TritonX100 and nanotubes in SC. The characteristic time of the kinetics is 8 minutes (rate constant of 0.125 min^{-1}), which is more than two orders of magnitude shorter than for SDS micelles in the same conditions (\sim one week). This result strongly suggests that internal and external coulombic repulsion is the limiting factor of the kinetics when SDS micelles are used (an experiment performed with the cationic CTAB is described in ESI and confirms the interpretation). Therefore, a scheme of the microscopic mechanisms of the functionalization can be proposed, inspired by chromophore exchange experiments (see figure 3). Unfortunately, non-ionic surfactants such as TritonX100 are not as efficient as SDS for dis-

persing molecules. Moreover, they are not useful to solubilize nanotubes, as the suspensions flocculates rapidly. Therefore, non-ionic surfactants can not be used to obtain stable suspensions of functionalized nanotubes. We are once again faced with the paradox that ionic micelles are needed to get stable suspensions, but that their stability hinders the functionalization process.

In the following, we describe an original way to overcome the stability of SDS micelles and at the same time to use their ability to disperse H_2 TPP molecules while keeping nanotubes in a good surfactant (SC). First, a highly concentrated solution of H_2 TPP in SDS micelle is prepared. Then a mix with the nanotube/SC suspension is performed in a proportion such that the final concentration of SDS is under its cmc. We speculate that this will force the fission of the SDS micelles and then favour the interaction with the nanotubes. To test this assumption, we studied systematically the kinetics of the reaction as a function of the dilution ratio r_{sds} below and above the cmc concentration of SDS in the final suspension (see figure 4(a)). For all the samples, the H_2 TPP concentration in the final suspension was set to $20 \mu\text{mol.L}^{-1}$ and the nanotube concentration was also fixed with an optical density at the S_{11} transition of 0.07.

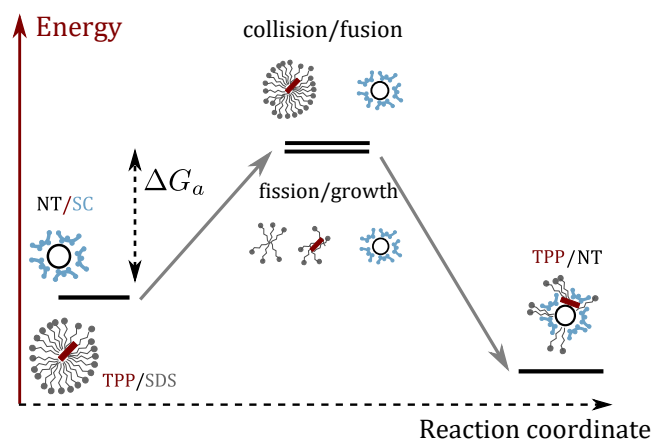


Fig. 3 Possible energy levels diagram according to the observed kinetic evolution, inspired from Rharbi's work.¹⁸

Whatever the values of r_{sds} (from 2 to 50 %), an exponential kinetic behavior is always observed. For each sample, the reaction time constant τ was extracted. The variation of the reaction rate $1/\tau$ as a function of r_{sds} is displayed in figure 4(b). A decrease of the rate is observed when the r_{sds} increases. From $r_{sds} = 2\%$ to 50%, the rate of the reaction is tuned over several orders of magnitudes from 0.05 min^{-1} ($\tau = 20$ minutes) to approximately $1.5 \times 10^{-4} \text{ min}^{-1}$ ($\tau = 3$ days and 6 hours). This demonstrates that such surfactant mixing techniques offer a fine control on the kinetics that may open the way to the design of more complex chemical reactions.

Figure 5(a) displays the kinetics of the reaction for $r_{sds} = 10\%$. A sigmoid shape is observed which is characteristic of autocatalytic reactions.^{34,35} These processes can be divided in two steps. The first step consists in an incubation process. Here, for $r_{sds} = 10\%$, the incubation time is of the order of 5 minutes. Note that the exact value of the incubation time varies from one to ten minutes when reproducing the experiment, which is also

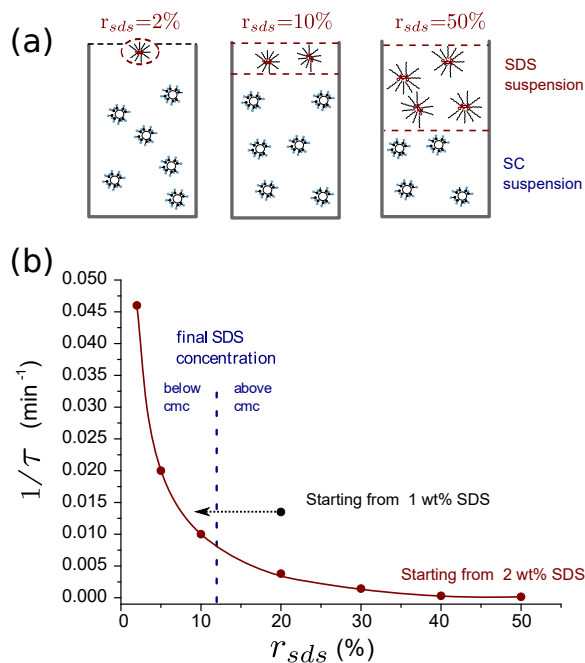


Fig. 4 (a) Scheme of the dilution procedure. (b) Evolution of the reaction rate $\frac{1}{\tau}$ as a function of the dilution ratio r_{SDS} (see main text for details). The H_2TPP concentration is fixed at $20 \mu\text{mol.L}^{-1}$.

characteristic of auto-catalytic processes.^{34,35} The second part of the kinetics is exponential and corresponds to the functionalization reaction itself. At this dilution ratio, the time constant is $\tau \simeq 60$ minutes (rate constant of $\sim 0.017 \text{ min}^{-1}$).

The effect of the dilution process on the stability of the SDS micelles during the mixing procedure is now discussed. During the dilution, the SDS final concentration varies in a wide proportion. Indeed, the initial suspension of H_2TPP is made at 2 wt% of SDS, corresponding to approximately 9 times the cmc of SDS ($\text{cmc}_{SDS} = 8 \text{ mmol.L}^{-1}$).³⁶ Therefore, at $r_{sds} = 50\%$, the final concentration of SDS is about 4 times the cmc, while it is just above the cmc for $r_{sds} = 20\%$ (see figure 4(b)). Then, for lower r_{sds} , the final SDS concentration falls below the cmc, which means that SDS micelles are no longer stable and will break into small submicellar structures (see figure 3). It is noteworthy that the speed of the reaction greatly increases for final SDS concentrations below the cmc. In order to verify if the SDS concentration is indeed the relevant parameter, the amount of SDS before dilution has been divided by two at 1 wt%. Then, we repeated the $r_{sds} = 20\%$ dilution experiment (black dot on figure 4(b)). Here, the final SDS concentration after dilution is 7 mmol.L^{-1} , below the cmc. The corresponding reaction rate is approximately four times higher than for the 2 wt% initial suspension with the same volume ratio. Moreover, it is actually quite close to the SDS 2 wt% experiment for $r_{sds} = 10\%$. As these two dilutions provide the same quantity of SDS to the final sample, we may assume that the c_{sds}/cmc ratio after mixing is the key parameter to understand the kinetics of such reaction. This strongly supports that passing below the SDS cmc during the dilution destabilizes the micelles containing the molecule promoting the fission/growth reaction pathway (see figure 3).

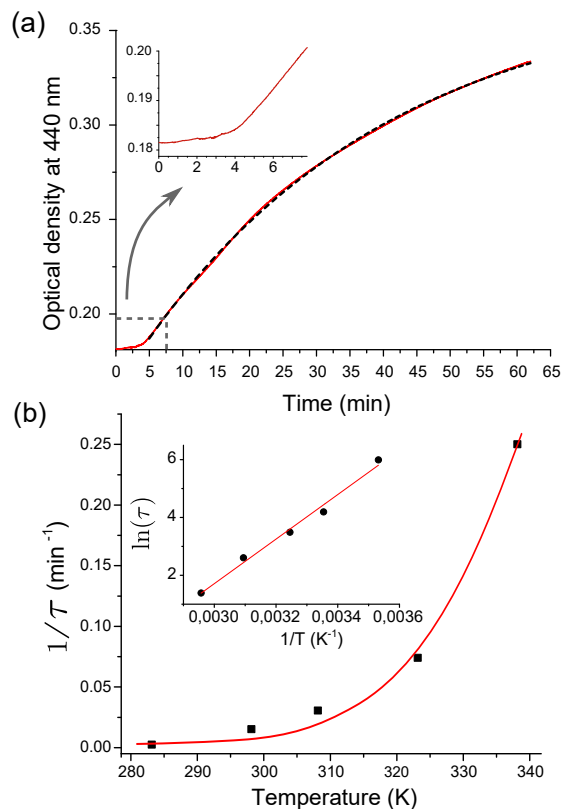


Fig. 5 (a) Kinetics of the reaction for a dilution ratio $r_{SDS}=10\%$. (b) Reaction rate as a function of temperature for a dilution ratio $r_{SDS}=10\%$. The H_2TPP concentration is fixed at $20 \mu\text{mol.L}^{-1}$.

Finally, the reaction scheme displayed on figure 3 is associated to an energy barrier ΔG_a . Here, the energy barrier is expressed with a Gibbs energy to account for a probable variation of the entropy of the system during the functionalization.³⁷ For instance, the micelle ordering is likely to change during the reaction. Therefore, experiments as a function of temperature were performed to test this description. Figure 5(b) shows an increase of the reaction rate $1/\tau$ when the temperature increases. The variation of the reaction rate as a function of temperature is well described with an Arrhenius law $k = 1/\tau \propto \exp\left(\frac{-\Delta G_a}{RT}\right)$ with an activation Gibbs energy of $80 \pm 10 \text{ kJ.mol}^{-1}$. This value is of the same order of magnitude than other first order reactions involving micelles suspended nanotubes,^{24,38} where the authors showed that the involved kinetic are driven by the surfactant desorption from the nanotube's surface. Likewise, this activation energy is quite close to the one found for the exchange of pyrene molecules between TritonX100 micelles.¹⁸ These experiments confirm that the functionalization reaction is thermally activated with an activation energy that is likely to be ruled by a micellar processes.

Conclusions

To summarize, we present an efficient method to non-covalently functionalize carbon nanotubes with porphyrin molecules, using mixed surfactants. We bring evidence that the stability of the micelles containing the molecules plays a key role in the reaction velocity. We show that this stability can be overcome by a simple method based on an appropriate dilution of one of the surfac-

tants. In particular, when the SDS concentration falls below its cmc, the kinetics is more than two orders of magnitude faster than above cmc experiments. This new co-surfactant functionalization technique protects the nanotubes surface and allows the desired reactants to rapidly break in. As it can be easily adapted to others chemical reactions involving nanotubes in micelles, or other nanoparticles, this technique opens the way to the design of more complex functionalization reactions.

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