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Light harvesting with non covalent carbon nanotube/porphyrin compounds

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ABSTRACT

We present recent developments in the synthesis and in the functional study of non covalently bound porphyrin/carbon nanotube compounds. The issue of the chemical stability of non covalent compounds is tackled by means of micelle assisted chemistry. The non covalent functionalization allows to preserve the electronic integrity of the nanotubes that display bright NIR luminescence. In the same time, the coupling between the subunits is very strong and leads to efficient energy transfer and PL quenching of the chromophore. This transfer occurs on a subpicosecond time-scale and leads to a near 100% efficiency. It allows to uniformly excite a whole set of chiral species with a single wavelength excitation. Insight into the transfer mechanism is gained by means of transient absorption spectroscopy.

1. Introduction

Single Wall Carbon Nanotubes (SWNTs) are famous for their many fascinating physical properties opening the way to promising applications. In the same time, they appear as unique prototypes of quasi one dimensional objects allowing unprecedented testing of basic physical effects. However, it appeared rapidly that the structure of nanotubes with all atoms at the surface, leads to strong interactions with the environment that can possibly induce a drastic alteration of their properties. For instance, the interaction of nanotubes with a substrate can lead to a full quenching of their luminescence [1,2] or to an important degradation of their electronic transport properties [3,4]. Several strategies were proposed to overcome these effects such as the encapsulation of nanotubes in micelles of surfactant [5,6] or in various polymers [7], or such as the use of suspended nanotubes [1,8]. On the other hand, the ability of SWNTs to interact with their environment can be used favorably as a way to create new functional materials. This is the field of functionalized nanotubes, where the general philosophy is to put together organic molecules and carbon nanotubes in order to combine their specific properties and possibly create new ones due to the interaction between the two species. The approach turned out to be highly valuable in many fields including optoelectronics, chemistry or biology [9,10]. In this quest, a general compromise has to be found between the robustness of the compound and the preservation of the properties of the tube. In fact, covalent functionalization leads to the most stable compounds but also significantly alters the transport and optical properties of the nanotubes [11,12]. In contrast, non covalent compounds allow to preserve these intrinsic properties, which is highly valuable for many applications, but at the cost of the chemical stability.

In this paper, we report on a new approach based on micelle assisted chemistry that allows to obtain non covalent compounds that show at the same time a remarkable stability and an excellent coupling between the molecule and the nanotube. This coupling between the chromophore and the nanotube gives rise to an extremely efficient energy transfer that allows to enhance considerably the effective absorption cross section of the nanotube in the visible range, while preserving its emitting properties in the near infrared (NIR) range. This kind of compounds may be of interest for long term applications such as light harvesting and bio labeling. In the latter case for instance, the NIR emission of nanotubes could be profitable since it matches the window of relative transparency of biological tissues. Therefore, the preservation of the luminescence properties of nanotubes is essential, while the molecules could be used to bind the compound with specific targets allowing functional imaging of biological tissues. Regarding photo-voltaic applications, carbon nanotubes are known to be good electron acceptors and allow to separate the photo generated electron–hole pairs when associated to various organic materials and polymers [13–16,10,17]. In this case, the use of non covalent functionalization allows to preserve the electronic mobility of the nanotubes and therefore allows to reduce the losses in the device.

Although these investigations are motivated by possible long term applications, this paper is devoted to a basic investigation of the microscopic mechanisms leading to the efficient electronic coupling in non covalent compounds. In this perspective, we focus on the properties of a non-covalently bound porphyrin/nanotube compound (H_2TPP@SWNT) showing efficient energy transfer, which allows a full optical investigation of the coupling including time-resolved studies. These compounds are made of a layer of free

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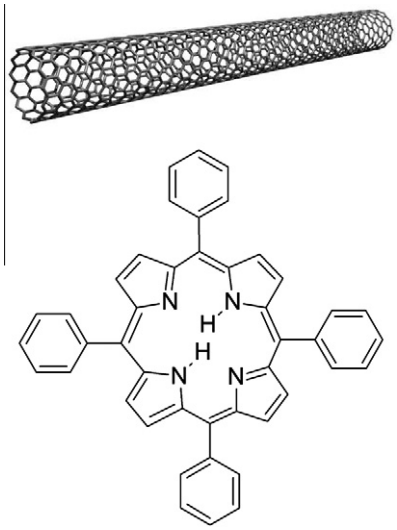

Fig. 1. Schematic representation of a SWNT and of the H_2TPP molecule.

base tetraphenyl porphyrin molecules (H_2TPP) π-stacked on the wall of the nanotubes (CoMoCat SG65) (Fig. 1). Porphyrin is a major building block in bio-chemistry. It stands for the backbone in chlorophylls and hemoglobin molecules. It is also well known for its photo-physical properties especially in the photosynthesis cycle and was previously used as sensitizer for organic photovoltaic cells [18].

We first review the fabrication process and the structural characterization of the compound. Then, we propose a set of methods to evaluate the efficiency of the coupling between the chromophore and the nanotube including studies at the single nano-compound scale, that show the statistical distribution of the transfer yield and its correlations to other spectroscopic features. Finally, the dynamics of the transfer is investigated on a sub-picosecond time-scale and insight is given into the microscopic mechanism driving the energy transfer.

2. Synthesis and structural investigation

SWNTs are known to show strong π interactions between each other and to form strongly bound bundles. In these bundles, the electronic coupling between the tubes leads to efficient energy transfer between semi-conducting nanotubes [19,20]. For larger bundles where the presence of metallic nanotubes is very likely, this coupling eventually leads to an extremely strong quenching of the luminescence of semi-conducting nanotubes [21]. Therefore, in order to functionalize carbon nanotubes and benefit from their intrinsic properties, it is necessary to first split the bundles and obtain individualized nanotubes. A well known and wide spread strategy is the use of surfactants that leads to the creation of micelles containing individualized SWNTs [5,6]. In a first attempt to reach non covalent functionalization of SWNTs with porphyrin molecules, we tried to use hydrophilic porphyrins (TPPS) as a surfactant [22]. Other groups used similar approaches or tried for instance to substitute the surfactant by an amphiphilic chromophore in a micelle suspension of carbon nanotubes [23]. These approaches are interesting because they show unambiguously that the interaction between the porphyrin and the nanotubes through the "π stacking interaction" can be strong enough to allow the dissolution of carbon nanotubes in water. In addition, the first indications for an efficient coupling and energy transfer was demonstrated in this system [22]. However, the stability of the suspensions turned out to be poor with flocculation within a couple of days.

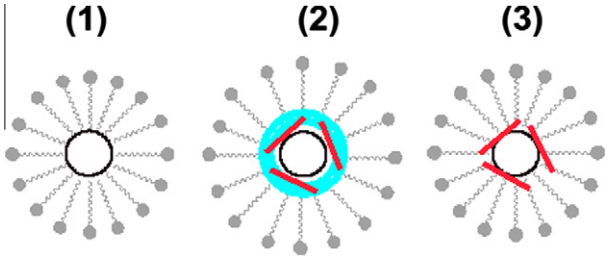

Fig. 2. Sketch of the micelle swelling method. An organic micro-environment is created around the nanotube by swelling the micelle with an organic solvent that brings the chromophore. After evaporation of the solvent a non-covalently functionalized nanotube remains in the core of the micelle.

The new approach that we developed is based on the idea that the stability of the nanotube/porphyrin compounds could be enhanced using hydrophobic porphyrins inserted in the core of regular micelles (sodium cholate) together with the nanotubes. However, it is not straightforward to drive the hydrophobic molecule through water into the micelle. The micelle swelling method allowed us to do so [24]. In this method, hydrophobic porphyrins are first dissolved in an organic solvent such as dichloro-methane (DCM) and mixed to a regular aqueous micellar suspension of carbon nanotubes by means of ultrasonic stirring. The fact that an organic solvent can penetrate the core of micelles with this method was demonstrated independently by Wang et al. [25] and later applied successfully to other compounds [26]. The scheme of the method is depicted in Fig. 2. As demonstrated below, the organic solvent serves as a vector to take the hydrophobic molecules to the core of the micelle.

Optical absorption spectroscopy is a powerful tool to monitor the functionalization process. Actually, the presence of porphyrin molecules on the wall of the nanotubes induces several clear spectroscopic features (Fig. 3). First the nanotube transitions show a sizable redshift which is mainly due to the screening of the Coulomb interactions in the nanotubes by the adsorbed molecules [2]. In addition, the appearance of a large absorption band in the blue part of the visible spectrum is the signature of the presence of porphyrin molecules in the micelles. This band corresponds to the Soret band of the porphyrin, but in the case of adsorbed molecules, its position is slightly red shifted because of conformational changes in the molecule [22]. Therefore a split Soret band is observed with one peak at 420 nm corresponding to porphyrin molecules alone in a micelle and another peak at 440 nm corresponding to the molecules adsorbed on the nanotube wall. Therefore, the intensity and the ratio of these peaks allow to monitor the

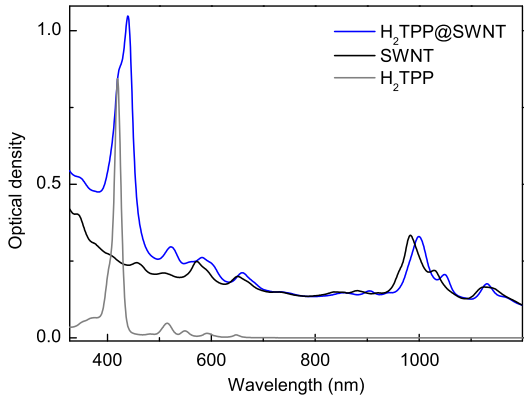

Fig. 3. Absorption spectrum of a micellar suspension of CoMoCat nanotubes (black line), a micellar suspension of H_2TPP (gray line) and a suspension of functionalized nanotubes (blue line). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)