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Immobilization of tetra-*tert*-butylphthalocyanines on carbon nanotubes: a first step towards the development of new nanomaterials

Xianbao Wang, Yunqi Liu,* Wenfeng Qiu and Daoben Zhu*

Center for Molecular Science, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, P. R. China. E-mail: liuyq@infoc3.icas.ac.cn

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Non-covalent functionalization of carbon nanotubes (CNTs) is of paramount importance for developing new nanomaterials without destruction of the electrical properties of the CNTs. In this paper, we report a simple approach to immobilize tetra-*tert*-butylphthalocyanines (*t*BuPcs) on CNTs. The immobilization results from the π–π interaction, rather than a covalent interaction, between the CNTs and the conjugated *t*BuPc molecules. It is found that CNTs can fade the color of chloroform solutions of *t*BuPcs. There is an adsorption threshold of the CNTs for *t*BuPcs in our case. The more the relative weight of *t*BuPcs as compared with CNTs, the more slowly CNTs fade the solution, and the bluish green color of the *t*BuPcs cannot be decolorized when the weight ratio of *t*BuPcs to CNTs is larger than 1.5. The versatility of this simple method can be extended to other members, with the desired properties, of the Pc family, and constitutes a first step in the development of new Pc-based nanomaterials.

Introduction

Phthalocyanines (Pcs) are of enormous commercial and industrial importance for the manufacture of blue and green pigments for paints, textiles, plastics, and metal surfaces.[1] Besides their outstanding thermal and chemical stability, Pcs also possess some interesting photophysical and conducting properties that render them suitable for a number of "high-tech" applications. Examples are their use as charge carriers in photocopiers, as dyes in laser printing[2a] and as laser light absorbers for optical data storage systems.[2b] Others are promising candidates for exploitation in devices such as solar cells,[3a] gas sensors[3b] and optical limiters[3c] and, in medicine, as singlet oxygen photosensitizers for photodynamic therapy[3d] and as a therapy for transmissible spongiform encephalopathies.[3e] Since most of these potential applications need the Pcs to be in the solid state, preparations of Pc-based thin films or materials are prerequisites for carrying out these researches and applications.

Carbon nanotubes (CNTs), discovered by Iijima,[4] are attractive candidates for use as nanomaterials and nanodevices on account of their novel structural characteristics and promising electronic and mechanical properties.[5] The ability to immobilize biomolecules[6] and organic compounds[7] on CNTs can put the strategy into effect. Unlike the chemical modification[8] of CNTs with the risk of their partial destruction, the immobilization is carried out by means of noncovalent functionalization, which preserves the π-networks of CNTs and thus their electronic characteristics. The electronic properties of nanotubes coupled with the photophysical and conducting properties of the immobilized Pc molecules would make novel nanomaterials and nanodevices. In this paper, we report a simple approach to immobilize tetra-*tert*-butylphthalocyanines (*t*BuPcs) on CNTs. The π–π interaction between the CNTs and the conjugated *t*BuPc molecules, which is responsible for the immobilization, is discussed in detail.

Experimental

The preparation of *t*BuPcs was carried out according to the method reported in the earlier literature.[9] We have successfully synthesized great quantities of CNTs by pyrolysis of metal phthalocyanines under an Ar–H_2 flow at 900 °C.[10] The purified CNTs can be simply obtained by treatment with HCl because there are few nanoparticles in our products. For the *t*BuPc/CNT complex, 2 mg of the purified CNTs were dispersed in 40 mL $CHCl_3$ by ultrasonication for 15 min prior to the addition of 2 mg of *t*BuPcs. The resulting bluish green suspension was allowed to stand at room temperature for 72 h. When the color had faded, the resulting suspension was filtered and washed three times with pure $CHCl_3$. The *t*BuPc/CNT complex was then allowed to dry under vacuum at room temperature overnight.

The resulting *t*BuPc/CNT complex was characterized by transmission electron microscopy (TEM, JEOL 2010F, 100 KV), atomic force microscopy (AFM, SPI 3800, non-contact mode), UV–Vis spectroscopy (Hitachi, Model U-3010), infrared spectroscopy (IR, Bruker EQUINOX55), thermogravimetric analysis (TGA, N_2, 20 °C min^{-1}) and X-ray photoelectron spectroscopy (XPS, VG Escalab 220-ixl, Al-Kα X-ray source, 1486.6 eV).

Results and discussion

The purified CNTs were added to a chloroform solution to form the suspended CNT solution after ultrasonication. The turquoise suspension was observed immediately on the addition of *t*BuPcs. The resulting sample was incubated at room temperature. It is interesting that after 72 h the turquoise suspension was decolorized and thus became clear, while the flocculent CNTs were visible in the transparent $CHCl_3$ solution. The following experiment indicated that the *t*BuPcs were adsorbed on the CNTs. We firstly separated the solid CNTs from the liquid $CHCl_3$ solution by filtration, followed by rinsing three times with pure $CHCl_3$. The UV–Vis measurements of the clear filtrate suggested that no signal for *t*BuPc was detected in the $CHCl_3$ solution.

In fact, we successfully observed immobilization of *t*BuPcs onto CNTs by TEM and AFM. Fig. 1a shows a TEM image of pristine CNTs, with a diameter range from 20 to 80 nm, without any anchored nanoparticles. However, after treatment with *t*BuPcs, a few nanoparticles of *t*BuPc with a diameter from several to tens of nanometres are clearly resolved on CNT

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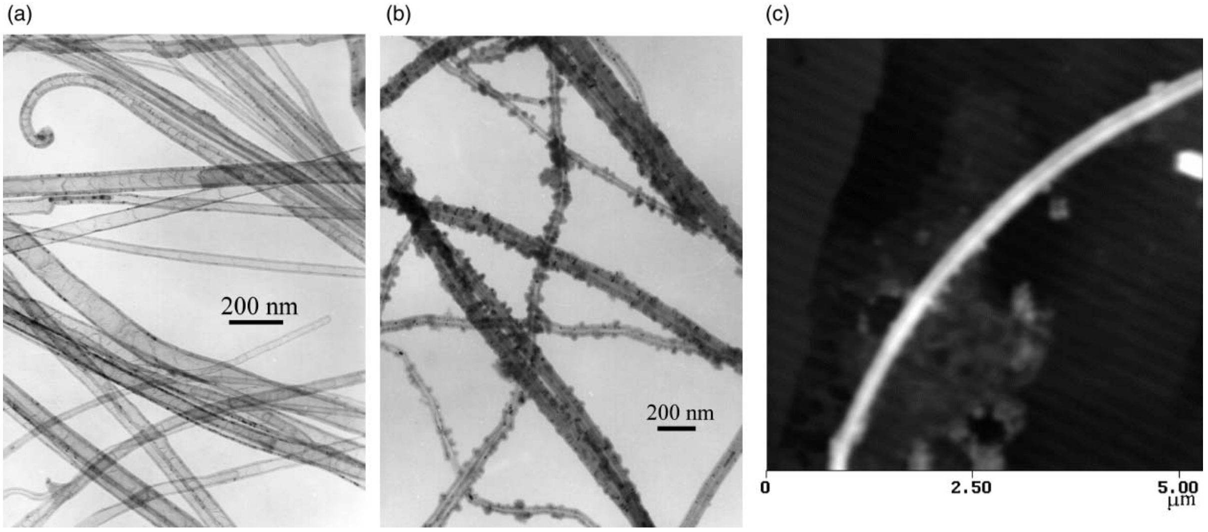

Fig. 1 (a) A TEM image of pristine CNTs without any nanoparticles before treatment; (b) typical TEM image of *t*BuPcs densely anchored on CNT surfaces after treatment; (c) AFM image of a CNT with attached *t*BuPc particles after treatment.

surfaces from a typical image of the *t*BuPc/CNT complex (Fig. 1b). This can be confirmed by an AFM image (Fig. 1c) of a CNT with attached *t*BuPc particles. To determine the strength of anchorage of the *t*BuPcs on the CNTs, again, we added the *t*BuPc/CNT complex to $CHCl_3$ solution and ultrasonicated for 3 h at a temperature of 40 °C. No color change of $CHCl_3$ solution was observed, suggesting that the *t*BuPcs can attach strongly to the tube walls. The immobilization of *t*BuPcs on the CNTs was efficient in a wide range of test conditions including various temperatures, solvents and CNT contents. We noticed that the higher the relative weight of *t*BuPcs as compared with CNTs, the more slowly CNTs fade the solution, and the bluish green of the *t*BuPcs cannot be decolorized when the weight of *t*BuPcs is one and a half times larger than that of the CNTs. This indicates that there is an adsorption threshold of CNTs for *t*BuPcs in our case.

To determine the interaction between *t*BuPcs and CNTs, we carried out an analysis of the UV–Vis absorption spectrum. The UV–Vis absorption spectra (Fig. 2) were obtained from a dilute solution (0.01 mg mL^{-1}) of the *t*BuPcs, and suspensions (0.01 mg mL^{-1}) of the CNTs and the *t*BuPc/CNT complex in $CHCl_3$. Two major absorption bands with λ_{max} values at 664 and 701 nm were observed for the *t*BuPcs, which were broadened in the complex (Fig. 2, inset). The other significant variation of the *t*BuPc/CNT complex spectrum comes from the broadening of the bands with λ_{max} values at 241 and 259 nm as compared with that of the CNTs. Presumably, this results from π–π interaction between the CNTs and the conjugated *t*BuPc backbone.[11,12] The isoindolyl group of the *t*BuPcs, being highly aromatic in nature, is known to interact strongly with the basal plane of graphite *via* π-stacking,[13] and is also found here to strongly interact with the CNTs in a similar manner.[6d] The interaction between the *t*BuPcs and the CNTs can be indicated from the analysis of IR spectra (Fig. 3) as well. The IR spectrum (KBr pressed pellet) of the *t*BuPc/CNT complex shows peaks at 2921.6 and 2852.2 cm^{-1}, which are due to the C–H stretching modes in the *tert*-butyl group (appearing at 2957.3 and 2865.4 cm^{-1} in the *t*BuPcs). The shifts to lower wavenumbers may result from the electron delocalization due to the π–π interactions. The sharp peak at 3293.2 cm^{-1} is from the N–H stretching modes in the *t*BuPcs, which cannot be resolved in the spectrum of the *t*BuPc/CNT complex. We carried out contrast experiments, in which pyrrole and pyridine were used instead of *t*BuPc. The IR and UV–Vis spectra demonstrated that pyrrole could be adsorbed on CNTs while pyridine could not be. Therefore, this means that not all aromatic molecules, which fit the Hückel Rule ($4n + 2$ π-electrons), can attach to CNTs due to π–π interaction, though more experiments are necessary.

The π–π interactions could disrupt the van der Waals interactions that cause CNTs to aggregate into bundles, which is confirmed by the fact that the CNTs with attached *t*BuPc molecules can be dispersed in $CHCl_3$ more easily than the

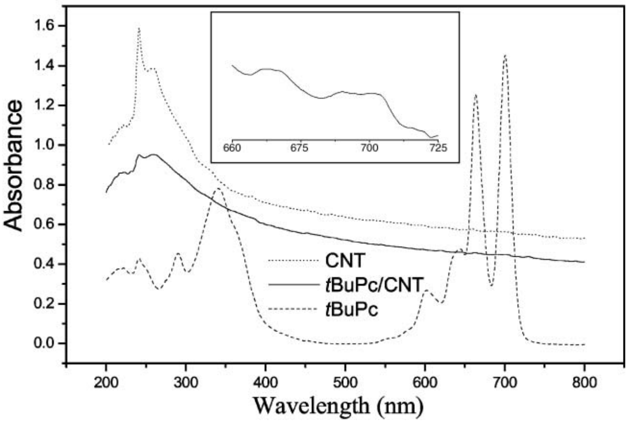

Fig. 2 UV–Vis spectra (quartz cell, light path 10 mm) of the CNTs (dotted line), the *t*BuPc/CNT complex (solid line), and the *t*BuPcs (dashed line). The concentration of all the samples in $CHCl_3$ was 0.01 mg mL^{-1}.

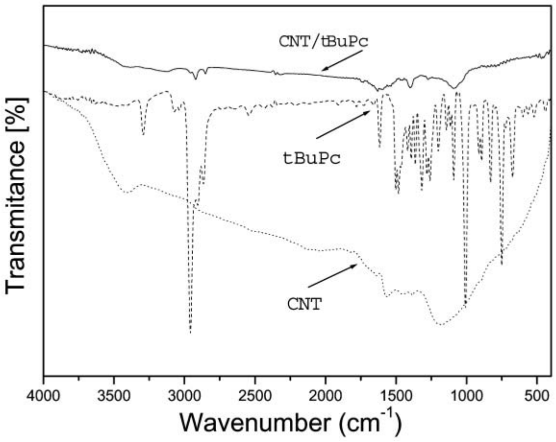

Fig. 3 IR spectra (KBr pellet, Bruker EQUINOX55) of the CNTs (dotted line), *t*BuPcs (dotted dashed line) and *t*BuPc/CNT complex (solid line).

purified CNTs. This may be because the ropes or bundles of CNTs have been exfoliated by ultrasonication prior to treatment with *t*BuPcs, in which case the adsorption of the *t*BuPcs could indeed inhibit aggregation of CNTs.

The experiment using copper(II) tetra-*tert*-butylphthalocyanines[9] (*t*BuCuPcs) instead of *t*BuPcs shows that the color of the solution, regardless of the content of *t*BuCuPcs relative to CNTs, cannot be faded. It is quite evident that the formation of a coordinate bond between copper and nitrogen destroys the aromaticity of the conjugated *t*BuCuPc backbone and thus prevents the π–π interaction between CNTs and *t*BuCuPcs. Besides this, other aspects could be responsible for the observed difference, for example the destruction of metal free Pcs upon reaction with the CNTs could take place whereas the metalated system is more stable. However, if this were true no effective binding would take place, since *t*BuCuPcs do not react with CNTs.

In order to obtain additional information on the π–π interaction and thermal stability of the *t*BuPc/CNT complex, TGA was performed under a nitrogen atmosphere. As can be seen in Fig. 4, the onset pyrolysis temperature (213.7 °C) of the *t*BuPc/CNT complex is remarkably lower than that of the *t*BuPcs (465.8 °C), while a *t*BuPc/CNT sample that is prepared by a physical treatment—simply grinding two materials into fine power in an agate mortar—begins to be pyrolysed at a temperature of 433.6 °C, slightly lower than that of the *t*BuPcs. The lower decomposition temperature indicates that the stability of the *t*BuPc molecules anchored on CNTs is lower than that of the bulk *t*BuPc molecules, that is to say, the internal energy of the adsorbed *t*BuPc molecules increases because of its π–π interaction with the CNTs. We attribute the phenomenon to the twist of the molecular configuration of the *t*BuPcs, to a certain extent, to match well with the cylinder structure of the CNTs and thus firmly immobilize the *t*BuPcs on the surface of the tubes. It is the only structural twist that results in increasing the internal energy of the adsorbed *t*BuPc molecules and thus decreasing the pyrolysis temperature.

Apart from the structures, XPS was employed to determine the elemental composition and bonding character of the *t*BuPc/CNT complex. Fig. 5 shows the C 1s, N 1s, and O 1s signals, corresponding to the main peaks centered at 284.6, 398.2, and 533.7 eV, respectively. The peak at 533.7 eV arises from oxygen absorbed on the surface of the CNTs.[10a] A Gaussian fit of the π^*-type peak of the N 1s spectrum (Fig. 5, inset) reveals the presence of two peaks at 398.2 and 399.9 eV, which correspond to the "pyridinic" and "pyrrolic" nitrogens of the *t*BuPc molecules.[14] it should be pointed out that the terms pyridinic and pyrrolic are used in a rather broad sense; the first one is used to refer to N atoms which contribute to the π system with one p-electron, whereas the second refers to N atoms with two p-electrons in the π system, although not necessarily in a five-membered ring as in pyrrole. The measurement further demonstrates that the immobilization of *t*BuPc onto CNTs is efficient.

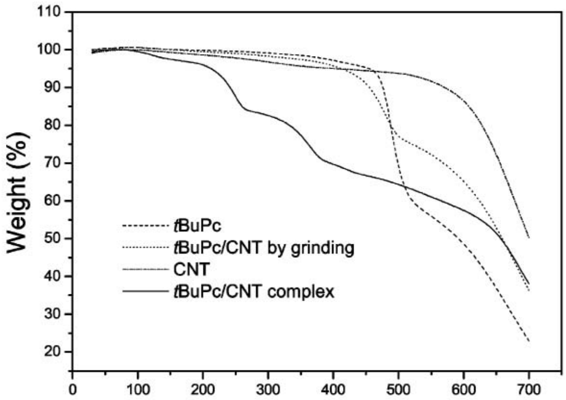

Fig. 4 TGA of the *t*BuPcs (– – –), the *t*BuPc/CNT compositions by grinding (···), the CNTs (· – ·), and the *t*BuPc/CNT complexes (——).

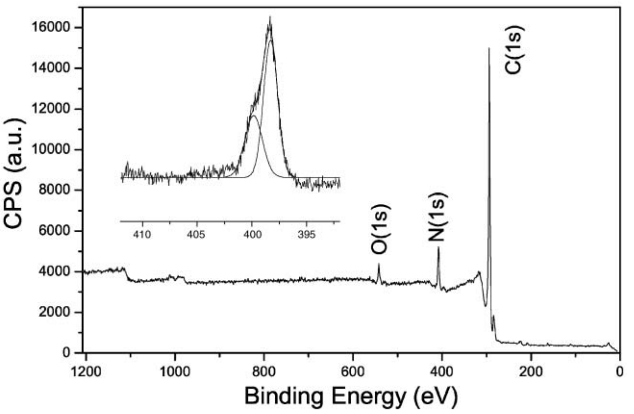

Fig. 5 A wide survey XPS spectrum of the *t*BuPc/CNT complex. Inset, a Gaussian fit of the π^*-type peak of the N 1s spectrum reveals the presence of two peaks at 398.2 and 399.9 eV.

In summary, we successfully immobilized *t*BuPcs onto CNTs with a simple approach. The resulting complex would possess the outstanding properties of *t*BuPcs without any destruction the of electrical properties and structures of the CNTs. The versatility of this simple method can be extended to other members, with the desired properties, of the Pc family. The method constitutes the first step in the development of new Pc-based nanomaterials.

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