

Self-Assembly of Tetraazamacrocyclic Compounds on Single-Walled Carbon Nanotubes: Experimental and Theoretical Studies

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ABSTRACT

To explore the possibility of reversible modification of carbon nanotube (CNT) sidewalls with aromatic ligands and their metal complexes employing aromatic stacking phenomena, we studied (experimentally and theoretically) interaction of a series of tetraazamacrocyclic compounds tetraazaannulene, *meso*-tetraphenylporphine, Ni(II) and Cu(II) complexes of tetramethyltetraazaannulene with single-walled carbon nanotubes. All of them are conjugated systems with a high degree of aromaticity. Molecular mechanics modeling was used to estimate what kind of arrangements can form. In some cases HRTEM results were obtained consistent with theoretical results. Adsorption of aromatic molecules, having a bent shape and/or hydrophobic substituents, allows to reversibly attach modifying chemical species. The latter stick strongly to the nanotube walls due to π - π and hydrophobic interactions and remain stable in aqueous solutions, but can be removed by washing with non-polar solvents.

Keywords: carbon nanotubes, tetraazamacrocyclic, porphines, metal complexes, molecular mechanics

1 INTRODUCTION

All the existing methods of chemical modification of carbon nanotubes (CNTs) can be divided in two groups, depending on whether functionalizing moieties are introduced onto the nanotube tips or sidewalls. The latter approach [1-3] offers wider opportunities to change CNT properties, since it allows high coverages with modifying groups. It can rely upon either covalent bond formation, or simple adsorption on CNTs *via* non-covalent interactions (hydrophobic, π -stacking, etc.).

To explore the possibility of reversible modification of CNT sidewalls with aromatic ligands and their metal complexes employing similar stacking phenomena, we studied (experimentally and theoretically) interaction of a

series of tetraazamacrocyclic compounds tetraazaannulene (H₂TAA), *meso*-tetraphenylporphine (H₂TPP), Ni(II) and Cu(II) complexes of tetramethyltetraazaannulene (H₂TMTAA) (see structures in Figure 1) with single-walled carbon nanotubes (SWNTs). All of them are conjugated systems with a high degree of aromaticity.

2 EXPERIMENTAL

We used open-end SWNTs commercially available from Iljin Nanotech Co., Ltd., Korea (by arc-discharge process, 95%+ purified by thermal oxidation and chemical treatment). H₂TPP ligand and the macrocyclic complexes NiTMTAA and CuTMTAA were synthesized according to the procedures described elsewhere [4-7].

Typically, H₂TPP, NiTMTAA or CuTMTAA was dissolved in benzene (for H₂TPP) or ethanol (for the complexes), then SWNTs were added to the resulting solution and left overnight. After centrifugation of the product, it was additionally washed with a small amount of the corresponding solvent, then centrifuged again and dried under ambient conditions. Upon washing, the solvent acquired only a pale green (for NiTMTAA) or red-brownish (for CuTMTAA and H₂TPP) coloration, indicating a relatively strong adsorption of the tetraazamacrocyclic compounds on SWNTs.

The NiTMTAA—SWNT adduct had a noticeable dark-greenish color and metallic luster, common for NiTMTAA; the CuTMTAA—SWNT product was more alike the starting nanotube material in appearance. The amount of adsorbed tetraazamacrocyclic compound was calculated by measuring UV-Vis absorption of the solution before and after the adsorption. It was about 80% in both cases. This percentage corresponds to a SWNT:tetraazamacrocyclic complex mass ratio of about 5:4. The H₂TPP—SWNT adduct also had a strong metallic luster. The amount adsorbed calculated from the UV-Vis absorption differences, was about 50%, which is lower as compared to

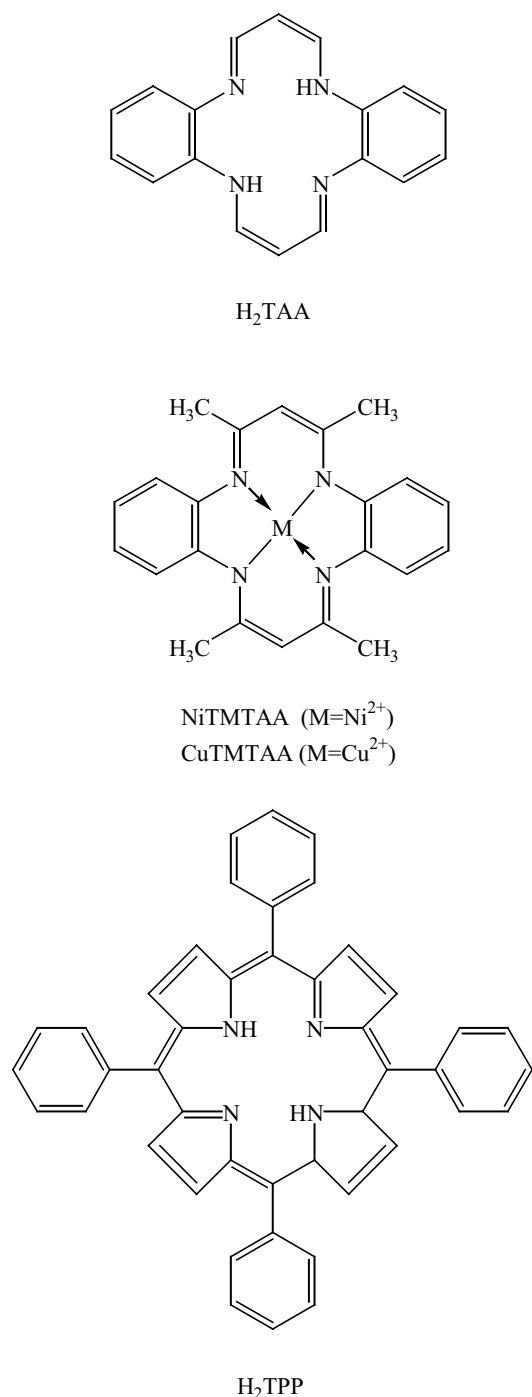


Figure 1. Chemical structures of the tetraazaannulene (H₂TAA), metal complexes of tetramethyltetraazaannulene (H₂TMTAA) with Ni(II) and Cu(II), and *meso*-tetraphenylporphine (H₂TPP).

the previous case. This corresponds to a SWNT:H₂TPP mass ratio of ca. 10:3.

Infrared spectra were recorded on a Nicolet 55X FTIR spectrometer (in KBr); UV-Vis spectra, on a Shimadzu UV-160U spectrophotometer. Microscopic measurements were

performed on a JEOL 100CX transmission electron microscope (TEM) and a JEOL 4000EX high-resolution transmission electron microscope (HRTEM).

In our theoretical simulations, we used universal force fields UFF and MM+, included into Gaussian 98W [8] and HyperChem version 5.1 (by HyperCube Inc., Canada) packages, respectively. For geometry optimizations with Gaussian 98W, the default convergence criteria were applied. When HyperChem 5.1 was used, the optimizations were performed with the Polak-Ribiere conjugate gradient algorithm and a root mean square gradient of 0.001 kcal Å⁻¹ mol⁻¹. Both methods produce essentially similar results.

3 RESULTS AND DISCUSSION

In the case of TMTAA complexes (for a preliminary report, see [9]), their geometry is distorted from the plane due to the presence of four methyl substituents interfering with the benzene rings. As a result, the molecules of NiTMTAA and CuTMTAA adopt a saddle shape conformation, with the CH₃ groups and benzene rings turned to opposite sides of the MN₄ coordination plane. This geometry was especially attractive for our purpose, since it matches the curvature of SWNT sidewalls. One can expect that preferable mutual orientation of the metal complexes and the nanotube is 'saddle-on-horseback', increasing the contact area and thus adsorption strength.

Using molecular mechanics (MM) modeling, we tried to estimate what kind of arrangement can correspond to SWNT:complex mass ratios close to the one of 5:4 found experimentally. According to our results, given a uniform distribution of the macrocyclic molecules, an approximately monolayer coverage forms. A saddle-shaped conformation of the macrocyclic molecules helps their alignment along SWNT axis and better accommodation on the outer nanotube walls (Figure 2a), where the annulene complexes are arranged in a chess-like order (Figure 3a). No manifestations of the above molecular assembly can be distinguished by TEM. However HRTEM observations [9] revealed on SWNT bundles periodic transversal formations (period close to 1 nm), consistent with the MM results.

H₂TAA ligand molecules, due to the absence of methyl substituents in the macrocyclic ring, are flat. At the same time, their two benzene rings remain to be possible sites for π-π and hydrophobic interactions with SWNT walls, in addition to the annulene system. MM modeling showed that adsorption on the nanotube walls is more energetically preferable when H₂TAA molecules are oriented along SWNT axis (Figure 2b). Nevertheless, the difference for the longitudinal and transversal orientation is small, and in the case of many H₂TAA molecules adsorbed, they interfere the position of each other. As a result, no highly ordered molecular assembly was found (Figure 3b). Related experimental data have not been obtained so far.

In the case of H₂TPP, the orientational effect can be expected due to the existence of four C₆H₅ groups. Steric hindrance between the latter and the neighboring pyrrole

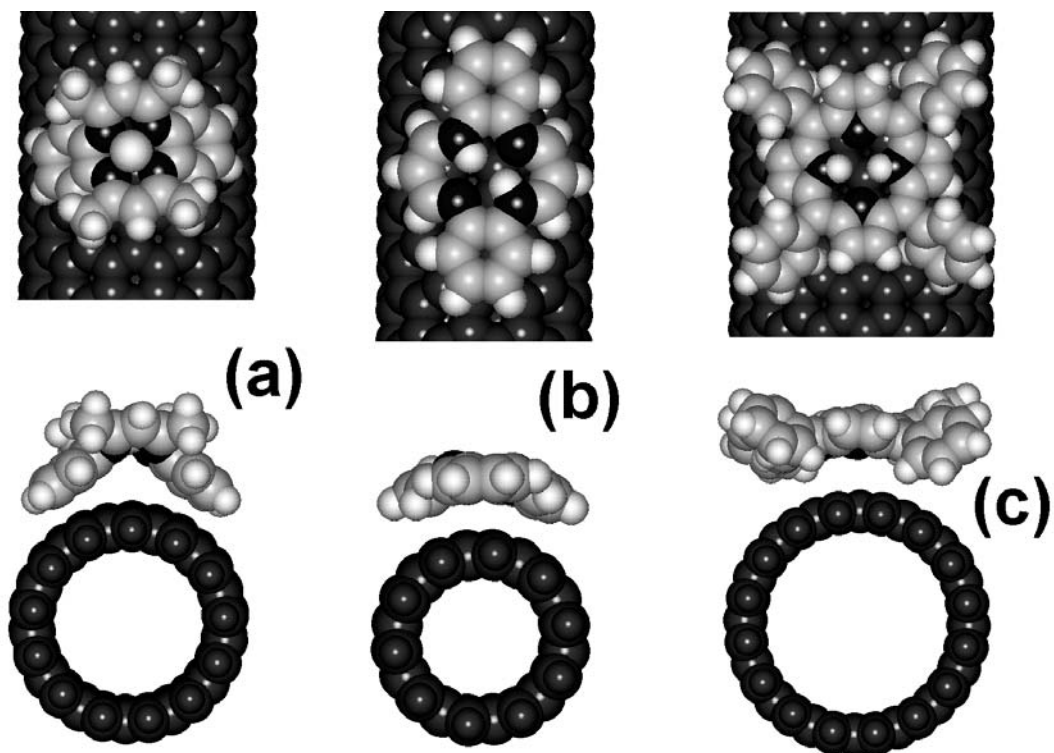


Figure 2. Energetically preferable orientation of adsorbed NiTMTAA (a), H₂TAA (b) and H₂TPP (c) molecules on SWNT walls, according to molecular mechanics simulation. Upper row, side views; lower row, cross sections.

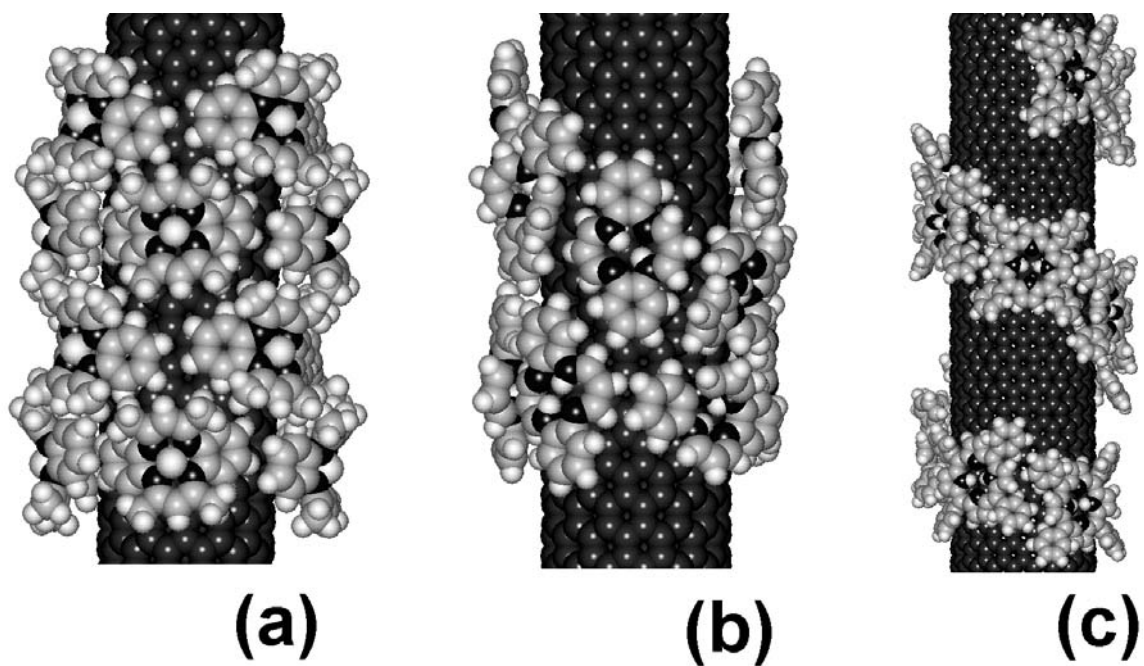


Figure 3. Assembly of the tetraazamacrocyclic compounds on SWNT walls, according to molecular mechanics simulation: (a) NiTMTAA, (b) H₂TAA, and (c) H₂TPP.

rings makes the C₆H₅ moieties turn with respect to the macrocyclic plane (Figure 2c). This can produce ordered molecular assemblies like 'staircase' or 'DNA strand' patterns (Figure 3c; according to MM), although TEM techniques were unable to detect such formations.

As a conclusion and further prospect, adsorption of aromatic molecules, having a bent shape and/or hydrophobic (in particular aromatic) substituents, can be useful in the modification of CNT materials. It allows to reversibly attach modifying chemical species. The latter stick strongly to the nanotube walls due to π - π and hydrophobic interactions and remain stable in aqueous solutions (and probably in some other polar media), but can be removed by washing with non-polar solvents.

ACKNOWLEDGEMENTS

The authors acknowledge financial support from the National Council of Science and Technology of Mexico (grant CONACYT-40399-Y) and from the National Autonomous University of Mexico (grants DGAPA-IN100402-3 and -100303). This work was supported in part by Tufts University Faculty Research Award (to ERA) and by the NSF (CHE 0111202). EPR facility at Tufts was supported in part by the NSF (CHE 9816557). The authors are grateful to Prof. Maria Stephanopoulos and Ms. Qi Fu for access to and help with SDR UV-Vis spectrophotometry.

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