



Full Length Article

Interaction of metal phthalocyanines with carbon *zigzag* and *armchair* nanotubes with different diametersPavel O. Krasnov^{a,b,*}, Tamara V. Basova^{c,d}, Aseel Hassan^e^a Institute of Nanotechnology, Spectroscopy and Quantum Chemistry, Siberian Federal University, Krasnoyarsk 660041, Russia^b Reshetnev Siberian State University of Science and Technology, Krasnoyarsk 660049, Russia^c Nikolaev Institute of Inorganic Chemistry SB RAS, Novosibirsk 630090, Russia^d Novosibirsk State University, Novosibirsk 630090, Russia^e Material and Engineering Research Institute, Sheffield Hallam University, Sheffield, UK

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ABSTRACT

Quantum-chemical calculations of the association of metal free, cobalt, copper and zinc phthalocyanines (MPc) with carbon *zigzag* and *armchair* nanotubes (CNTs) with diameters in the range of 7–14 Å were carried out by the DFT method with the use of BH van der Waals density functional and DZP atomic basis set. It was shown that interaction energy between the phthalocyanine molecules and the CNTs, as a whole, increases with an increase of the diameter of carbon nanotubes. However, in the case of CNT(*n*,0) the energy reaches its maximal value at *n* = 16 or 17 depending on the central metal atom and phthalocyanine orientation on the carbon nanotubes surface. Up to diameter of 10.5 Å of the CNTs, stronger binding of the considered MPc macrocyclic molecules is observed with carbon *armchair* nanotubes. However, in the case of higher diameters the phthalocyanines are associated more strongly with the *zigzag* CNTs.

1. Introduction

Hybrid materials nowadays are well known materials studied and used for the development of photovoltaic devices as well as several other technological applications. As an example of such materials are those consisting of an inorganic part represented by carbon nanostructures such as fullerenes or carbon nanotubes (CNTs), and an organic part, e.g. phthalocyanine or porphyrin or their metal complexes. Over the last 10 years several tens of reviews [1–12] have been written summarizing numerous original works carried out and are devoted to the study of these hybrid materials and their practical applications. In these materials the macrocyclic molecules play the role of electron donors whereas carbon nanostructures are electron acceptors. The light adsorption leads to electrons transfer from the organic component to the inorganic part, with the formation of systems with separated charges. This phenomenon is useful for the operation of the solar cells. Apart from photovoltaic applications, these materials can also be used in different technological areas such as chemical and biological sensors, nanoelectronic devices, fuel cells, and so on [13,14].

Porphyrins or phthalocyanines can bind with fullerenes and carbon nanotubes via either covalent or non-covalent interactions [11], where in the last case, π - π -stacking arises between the aromatic rings. This

type of interaction is one of the examples of supramolecular interaction which plays an important role in materials science because it plays a role of driving force in such processes as molecular self-assembly.

It is necessary to mention that in the case of formation of hybrids of carbon nanotubes with the above mentioned macrocyclic molecules, the CNT size and its type of chirality as well as the nature of the central metal atoms and substituents in the phthalocyanine and porphyrin molecules have a significant effect on the strength of bonding between these two components [15,16].

DFT quantum-chemical calculations, performed by Zhao and Ding [17], have demonstrated that the strongest binding energy was observed in the case of semiconducting carbon nanotubes than in the case of metallic ones. The authors have compared the interaction of CNT(6,6) and CNT(10,0) with the cobalt, zinc, nickel and copper porphyrins (CoP, ZnP, NiP and CuP, respectively). At the same time, Alvarez *et al.* have concluded that the electronic properties of carbon nanotubes do not play a significant role in the interaction with phthalocyanines molecules [18]. According to their study, the diameter of CNTs has more significant effect, leading to an increase of the distortion of the macrocyclic plane with decreasing carbon nanotubes diameter. A strong distortion of metal free phthalocyanine (H_2Pc) interacting with CNT(5,5) and CNT(10,0) was observed by Chávez-Colorado and Basiuk

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[19]. According to their study this phenomenon allows H_2Pc to increase its contact area with the carbon nanotube sidewalls. Correa and Orellana have also observed a distortion of the macrocyclic molecules upon adsorption of metal free porphyrin and phthalocyanine as well as their Zn complexes onto the surface of CNT(14,0) [20]. The strong interaction of copper and zinc phthalocyanines with CNT(5,5) and CNT(10,0) was also demonstrated by Basiuk et al. [21], where the binding energies are in diapason from 1.41 eV (32.46 kcal/mol) to 1.61 eV (37.12 kcal/mol).

In addition, porphyrins and phthalocyanines as well as their metal complexes can have different orientations on the carbon nanotube surface [20,22]. The energy difference between the two types of macromolecules depends both on the nature of the central metal atom and the nature of macrocyclic molecule. If a porphyrin or a phthalocyanine molecule possesses an electric charge, being a cation, it binds to the carbon nanotube stronger than those in the neutral form [23]. Zhao and Ding have demonstrated that the binding energy of CoP with CNT(6,6) and CNT(10,0) is higher compared to ZnP, NiP and CuP. In the case of CNT(10,0) the interaction strengths with the zinc, nickel and copper porphyrins are almost equal [17]. At the same time, the binding energy of CNT(6,6) with NiP is a little bit higher than that with ZnP and CuP. Correa and Orellana have shown that the binding energy of

phthalocyanines with CNT(14,0) is higher than in the case of the corresponding porphyrins, and the interaction between carbon nanotubes and their zinc complexes is stronger than with metal-free molecules [20].

Despite of the above-described work, it still remains unclear how the interaction between the phthalocyanines and carbon nanotubes depends on the size and chirality of the latter, and which orientation of the macrocyclic molecules on CNT surface is more favorable.

In this work, we use DFT quantum-chemical calculations to study the interaction between metal phthalocyanines (MPc, where $M = H_2, Co, Cu$ and Zn) and carbon *zigzag* and *armchair* nanotubes with diameters in the range 7–14 Å.

2. Computational details

Metal free phthalocyanine (H_2Pc) and its complexes with cobalt, copper and zinc (MPc, where $Me = Co, Cu$ and Zn) were chosen to study the effect of the central atom on the interaction with *zigzag* and *armchair* nanotubes with diameter (d) in the range 7–14 Å, i.e. CNT($n,0$), where $n = 9–18$, and CNT(m,m), where $m = 5–10$, respectively.

In a similar manner to the case of metal free phthalocyanine

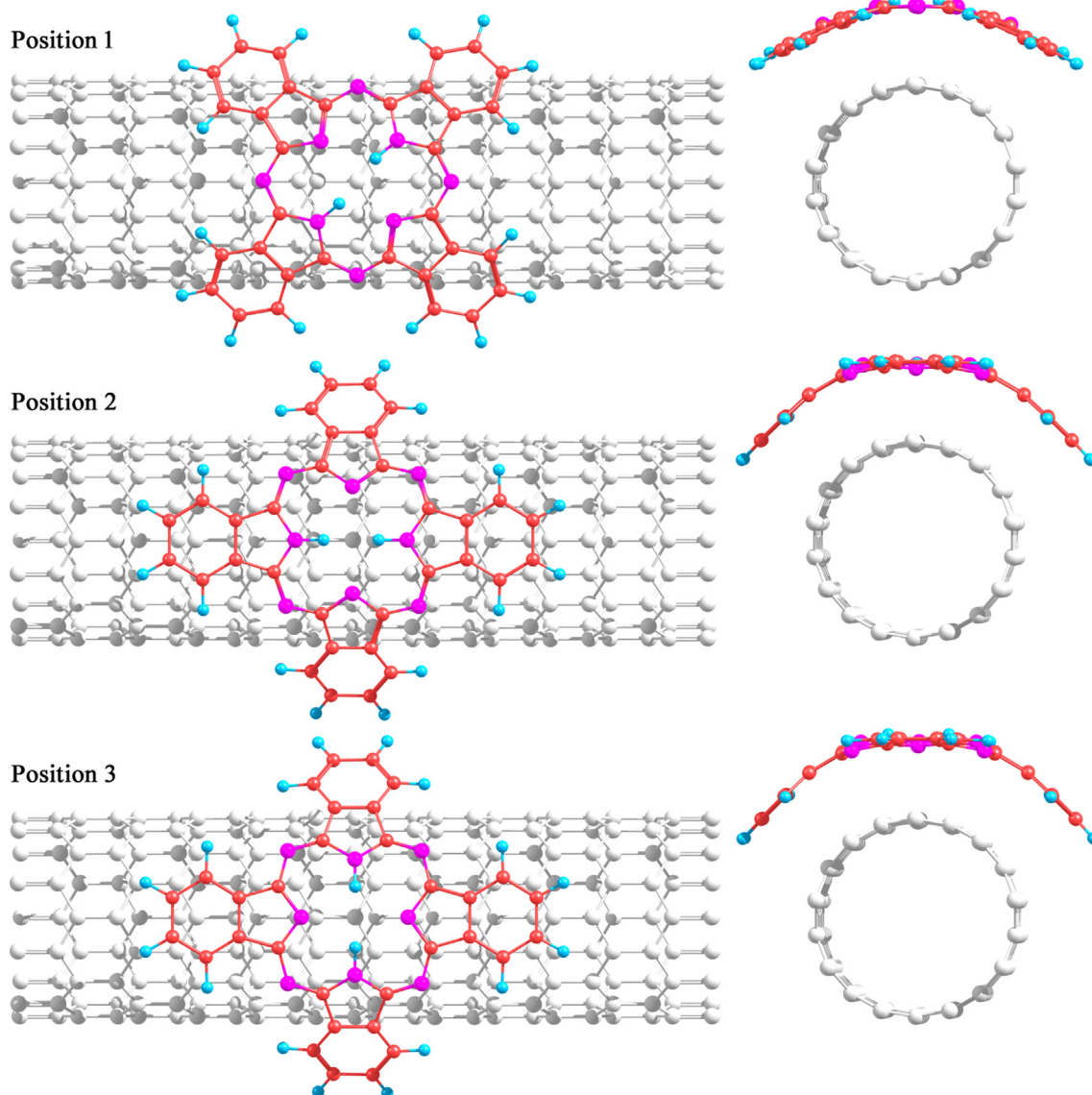


Fig. 1. Three possible positions of H_2Pc on the CNT(9,0) surface.

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