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Comparison of noncovalent interactions of zigzag and armchair carbon nanotubes with heterocyclic and aromatic compounds: Imidazole and benzene, imidazophenazines, and tetracene

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ABSTRACT

We study non-covalent functionalization of SWCNT by linear heterocyclic compounds such as imidazophenazine (**F1**) and its derivatives (**F2**–**F4**). MP2 and DFT/M05-2X quantum-chemical methods are used to determine the structures and the interaction energies of complexes formed by **F1**–**F4** with the zigzag(10,10) and armchair(6,6) nanotubes. The calculations show that for small diameter nanotubes the binding energies with zigzag nanotubes are stronger than with armchair nanotubes. But above the diameter of 1.4 nm the interaction energies for the armchair nanotubes become larger than for the zigzag nanotubes. Experimental measurements demonstrates that the ratio of the integral intensity of the resonance Raman bands assigned to the RBM modes of semiconducting nanotubes to the integral intensity of the metallic nanotubes increases for supernatant of SWCNT:**F4** (1,2,3-triazole-[4,5-*d*]-phenazine) hybrids solved in 1-Methyl-2-pyrrolidone as compared to this ratio in sediment samples. It demonstrates that the linear heterocyclic compounds can be used for separating SWCNTs with different electron-conduction types.

1. Introduction

Non-covalent functionalization of carbon nanotubes opens new possibilities for effectively exploiting the unusual properties of these nanomaterials for numerous applications in electronics, optics, in elaboration of effective energy conversion devices, for reinforcement of composite materials, as active element in sensors, etc., as well as for various biological applications [1–3]. The non-covalent functionalization of nanotubes has some advantages over the covalent functionalization, as it does not disrupt the π-conjugation network of the nanotubes allowing for these systems to retain their extraordinary properties. Another feature that makes the non-covalent functionalization very attractive is its reversibility which enables to regenerate quickly the bare nanotubes from the dispersant-coated material both in aqueous and organic solvents.

The nanotube non-covalent functionalization usually involves π-π-stacking interaction of an organic molecule/polymer with the surface of a single-walled carbon nanotube (SWCNT) [4–8].

To maximize the interaction, the attaching molecule should also have an extended π-electron system of aromatic carbon rings or heterocycles. Among heterocyclic compounds nitrogen bases [9–14] and porphyrins [2,15–18] have attracted special attention due to their very important biological and photophysical applications. A number of experimental and theoretical studies have been devoted to the analysis of these hybrid structures and of the interaction between various carbon nanotubes and different aromatic hydrocarbons, such as benzene [19–23], naphthalene [22–25] anthracene [23,26], phenanthrene, tetracene [23,27], pentacene [25], and pyrene [23,28,29]. It was established that these flat molecules bind to the nanotube surface in the planar stack orientation with the interaction energy which increases with the increasing intermolecular contact area (see, for example, [16,30]).

It was established that structural alteration of the benzene molecule involving replacement of some carbon atoms by nitrogen atoms leads to an increase of the binding energy [31–33]. In should be noted that substitution of some carbon atoms by nitrogen atoms in π-π cyclic molecules has high biological significance, as this results in the formation of nitrogen bases. These nitroaromatic compounds are usually polar due to their nonzero dipole moments [34]. Therefore, in the complexes formed by these nitroaromatic

systems with SWCNTs, in addition to the dominant dispersion forces, electrostatic forces are also present and enhance the interaction energy. This increase is however less significant than the increase resulting from addition of functional groups in back sites of the adsorbed systems. In most cases, the influence of the added functional groups on the binding of organic compounds with carbon nanotubes/graphene surfaces is determined by the electron-donor-acceptor (EDA) π-π interaction [31]. As carbon nanotubes can act as either electron-donors or acceptors relative to the adsorbed functionalized compound (group) (for example, for nitroaromatics in ref 31 nanotubes are electron acceptors while for 2,3-dichloro-5,6-dicyano-1,4-benzoquinone they are strong electron donors [35]) the adsorption of the benzene-functionalized aromatics on nanotubes is stronger than the adsorption of benzene [24,30]. Previous studies have shown that electrostatic forces between σ–π quadrupoles of the interacting rings constitute the major contribution to the π–π EDA interaction. The strength of the interaction depends on the difference of the quadrupole moments of the interacting systems, which, in turn, depends on ring substituents that either donate or withdraw electrons and polarize the donor π cloud [36,37].

The relative role of the electrostatic and dispersion interactions in these π-π stacked complexes was studied in detail by Wheeler and Houk who considered substituent effects in sandwich dimmers formed by a benzene dimer with substituted benzenes [32]. It was shown that substituent effects are better described as arising from local, direct interactions of the substituent with the proximal vertexes of the rings of the other system when compared to the conventional model based on π-polarization. Therefore, it seems reasonable to also apply this better model to study more complex π systems including carbon nanotubes and graphenes [38].

In our previous study we compared the interaction of such chromophores as imidazo-[4,5-*d*]-phenazine (**F1**) and its deriviatives (2-methylimidazo-[4,5-*d*]-phenazine (**F2**), 2-trifluoridemethylimidazo-[4,5-*d*]-phenazine (**F3**), and 1,2,3-triazole-[4,5-*d*]-phenazine (**F4**)) (Fig. S1) with graphene employing quantum-chemical calculations [39]. To estimate the contribution to the binding energy of these linear molecules with graphene from separate rings the interaction of benzene and imidazole with graphene was also studied. The interaction energies and structures of **F1**–**F4** were compared with those determined for graphene hybridized with tetracene (**TET**). The study revealed that tetracene, being a symmetric molecule, shows a small difference in the binding energy with graphene along the two distinct directions, i.e. the zigzag and armchair directions. On the contrary, the calculations performed for the **F1**–**F4** compounds demonstrated a substantial difference in the binding energy for the zigzag and armchair directions. The calculations also showed that in the binding of linear cyclic hydrocarbons and their derivatives with graphene the back-side groups can noticeably contribute to the interaction energy.

The imidazophenazine derivatives considered in this work were synthesized earlier [40] in the DNA study focusing mainly on their spectral properties [41]. The study revealed that the fluorescence of these dyes is very pH sensitive [42] and can be used in fluorometric sensors. In the study we also analyzed in detail the vibrational structure of these compounds employing the pre-resonance Raman and IR absorption spectroscopy [43,44].

In this work, we study the noncovalent functionalization of single-walled carbon nanotubes with imidazophenazine derivatives. The study focuses on the energetic and structural aspects of the interaction. In particular, the adsorption of the derivatives on nanotubes with extremes chiralities, i.e. zigzag and armchair, is considered and the influence of the asymmetry of the studied molecules on the binding energy and on the structure of the complex is investigated. We also pay attention to the influence of

substitution of some carbon atoms with nitrogen atoms in the studied molecules and to the role played by back-side groups (specifically CH_3 and CF_3) and to the arrangement of the imidazophenazine deriviatives on the nanotube surface on the binding energy. A comparison of the results obtained for nanotubes with different radii and with graphene enables to investigate the role of the surface curvature of these systems on the strength of the interaction with the adsorbed molecules. The study also involves an analysis of the changes of the charge density of the SWCNT surface induced by adsorption of symmetrical and asymmetrical linear molecules. In the calculations the DFT method is used. It allows to determine the interaction energies and to calculate the structures of the nanohybrids. We also use Raman spectroscopy to investigate the interaction of one of the imidazophenazine derivates (**F4**) with metallic and semiconductive nanotubes.

2. Methods

2.1. Experimental

2.1.1. Sample preparation

Purified SWCNTs produced by HIPCO® method are purchased from Unidym (USA) and used without additional purification. 1,2,3-triazole-[4,5-*d*]-phenazine (**F4**) is synthesized by method described in Ref. [45]. SWCNTs (0.6 mg) are added to 4 mL solution of **F4** (0.6 mg) in 1-Methyl-2-pyrrolidone (NMP) (Sigma-Aldrich, Europe) and sonicated (1 W, 44 kHz) for 30 min to increase the selectivity of the adsorption. The complex is centrifuged at 10,000g for 20 min. The supernatant and sediment are selected and deposited on quartz substrates by the drop coating method and dried by warm air.

2.1.2. Experimental method

The Raman experiments are performed in the 90° scattering configuration relative to the laser beam using the 632.8 nm (1.96 eV) light from a He-Ne laser. The laser beam is focused onto a stripe ($\sim$0.1 mm $\times$ 1 mm) to yield the laser power density of $100\ W/cm^2$. The spectra are analyzed using a Raman double monochromator with the reverse dispersion of 3 Å/mm and detected with a thermocooled CCD camera. The peak positions of the bands corresponding to the radial breathing mode (RBM) (200–320 cm^{-1}) in the nanotube film is determined with the accuracy not worse than 0.5 cm^{-1}. This level of accuracy is achieved because the frequency positions of the plasma lines from the He–Ne laser in the vicinity of the RBM bands are used in the internal calibration of the spectrometer. Intensity of RBM bands in each recorded spectrum is normalized to the most intense G^+ band located around 1590 cm^{-1}.

2.2. Calculations

The geometries of the complexes formed by SWCNTs with tetracene and imidazophenazine and its derivatives are optimized at the DFT level of theory. The M05-2X functional [46] is used. As shown before, the M05-2X functional is capable of predicting the structures and interaction energies of noncovalent complexes formed by carbon nanotubes in close agreement with the MP2 results [9]. In this work, we use the SLDB (same level different basis) approach to lower the total number of basis functions in the calculations. For the nanotube carbon atoms and for all atoms of the studied molecules the standard 6-31G(d) and 6-31++G(d,p) basis sets, respectively, are used. The standard STO-3G basis is employed for the terminal hydrogen atoms of the carbon surface.

The calculations are performed for complexes formed by the studied molecules with fragments of the SWCNTs with different