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Green chemical functionalization of single-wall carbon nanotube with methylimidazolium dicyanamid ionic liquid: A first principle computational exploration

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ABSTRACT

The study of the structural and electronic properties of ionic liquid functionalized carbon nanotubes can lead to the development of the applications of CNTs, such as chemical and biological sensors. In this work, chemical functionalization of (4,4) zigzag single-walled CNT via cycloaddition reaction of [MIM][$N(CN)_2$] ionic liquid is explored at the B3LYP/6–31 + G(d) level of theory. The position of [MIM^+] cation on top of the tube plays a significant role in the CNT—[MIM] interaction. Four types functionalized CNTs (E, **S1–3**, **P1–3** and **V1–3**) were found on the potential energy surface of the reaction between [MIM^+] and CNT. The HOMO–LUMO gap, electronic chemical potential μ, hardness η, softness S and electrophilicity index ω for CNT and different configurations of functionalized CNT were calculated. These results show that the functionalization of (4,4) armchair CNT results in significant changes in the electronic and structural properties of CNT. The results also show that functionalization by IL makes the CNT soluble in water.

1. Introduction

Single-walled carbon nanotubes (SWCNTs) synthesized by Iijima in 1991 [1]. They have unique electrical and mechanical properties such as exceptionally high tensile strength [2], high thermal conductivity [3], high current carrying density [4], high current mobility [5] and electronic properties ranging from metallic to semiconducting [6]. The SWCNTs have been used as multifunctional materials such as efficient gas storage elements, sensors in medicine, electromechanical systems in nanoelectronics and in battery devices which have recently attracted considerable attention [7]. Many of these applications require modifications to pristine nanotubes. To optimize the use of nanotubes, in most cases there is a need to attach the functional groups to their surface and then assemble the nanotubes into structures or attach other nanostructures to the nanotubes [8]. In particular, chemical functionalizations have been shown to be an attractive method to modify some of electronic and mechanical properties [9]. The functionalization of pristine SWCNTs dramatically changes their chemical, electronic and transport properties [10]. To functionalize carbon nanotubes, different functional groups are attached to the nanotube by covalent and non-covalent interactions. The various chemical groups can be used to functionalize nanotubes such as drugs [11], biomolecules [12], organic molecules [13], surfactants [14,15], polymers [16,17], metal nanoparticles [18,19] and small functional groups as amine ($-NH_2$), carboxylic acid ($-COOH$) [20], hydroxyl ($-OH$) and ($-CHO$) [21] that are often studied because they are highly reactive.

Room temperature ionic liquids, which are composed of organic cation and inorganic anion have melting points below room temperature. Ionic liquids (ILs) have attracted an increased interest in recent years after the identification of their unique properties [22]. ILs are suitable solvents for a wide range of inorganic and organic materials. In addition, because their non-volatility prevents environmental pollution, ILs have been proposed as environmentally and human friendly solvents for "green" chemistry [22]. On the basis of these characteristics, ILs are able to disperse CNTs, affording readily processable gelatinous substances. For that reason, ILs provide an excellent way to increase CNT dispersibility without the need for solid substances or organic solvents [23,24].

Modification of CNTs with ionic liquids not only improve their compatibility and stability but also creates more opportunity for applications of MWCNTs in sensors and actuators by improving the electrical contact with chemical species. There are some experimental reports that ILs have been used as media for functionalization reactions or as functionalizing agents for the covalent binding of CNTs. Chen and coworkers [25] studied functionalization of carbon nanotubes by an ionic liquid polymer. They have shown that the polymerized ionic liquid (PIL) film on the CNTs creates a distribution of ionic species with

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positive charge that prevents aggregation of the CNTs and induces stable nanotube suspensions in water, which serves as the medium to stabilize and anchor metal nanoparticles. Niu et al. used CNTs covalently modified with ILs to support Au nanoparticles [26]. Based on the excellent physicochemical properties of ILs, gold nanoparticle/CNT-IL nanohybrids showed good electrocatalytic behavior toward oxygen reduction. Liu et al. [27] were the first to prepare poly(urethane–IL)/MWCNT (PUIL/MWCNT) composites by inserting MWCNTs into a novel type of PIL [poly(urethane-IL)]. Hong et al. [28] reported a new practical route for synthesizing SWCNT-polymeric IL gels by noncovalent functionalization of oxidized SWCNT surfaces with imidazolium-based PILs based on in-situ radical polymerization. Yang et al. [29] developed a green chemical process for functionalizing MWCNTs in water and [Bmim][BF_4] IL. Tung et al. [30] accomplished the surface modification of CNTs by using poly(1-vinyl-3-ethylimidazolium).

Although, as mentioned above, experimental methods have provided a lot of information about the chemical functionalization of CNTs by ionic liquid, but it is still a great challenge to understand the behaviors of these functionalizations at molecular levels. To the best of our knowledge, functionalization of CNTs by methyl imidazolium dicyanamid ionic liquid [MIM][$N(CN)_2$] has not been reported. The main aims of this work are to find the structural and electronic properties of (4,4) armchair single-walled carbon nanotube functionalized with [MIM][$N(CN)_2$] ionic liquid including bond lengths, bond angles, tip diameters, dipole moments, energies and energy gaps ($E_{LUMO–HOMO}$), by using DFT method. Furthermore, we investigate the quantum molecular descriptors [31,32] including electronic chemical potential (μ), global hardness (η), electrophilicity index (ω) [33], energy gap, global softness (S) and electronegativity (χ) [34] and solubility of functionalized CNTs.

2. Computational methods

In the present work, calculation of the geometrical and electronic properties of [Mim][$N(CN)_2$]–functionalized (4,4) CNT were carried out using B3LYP hybrid density functional method. We have carried out all calculation by using Gaussian 03 [35] and GAMESS [36] program packages. The geometry optimization of complexes was performed at ONIOM(B3LYP/6–31 + G(d):PM6) level of theory. All structures were optimized without symmetric constraints. The effect of polar solvent on the property of functionalized CNT was investigated by using the method of Polarizable Continuum Model (PCM) [37].

In an N-electron system having total energy (E), the electronegativity (χ) is given by:

$$\chi = -\left(\frac{\partial E}{\partial N}\right)_{v(r)} = -\mu \tag{1}$$

where μ is the chemical potential of the species and is defined as the negative value of the electronegativity. Similarly, the global hardness (η) is expressed in terms of the second derivative of energy with respect to the external potential of $\nu(r)$ [38–41]:

$$\eta = \frac{1}{2}\left(\frac{\partial^2 E}{\partial N^2}\right)_{v(r)}. \tag{2}$$

In finite difference approach, chemical potential and global hardness can be approximated as: [42]

$$\mu = -\chi = -\frac{1}{2}(I + A)$$
$$\eta = \frac{1}{2}(I - A) \tag{3}$$

where I is the ionization potential and A is the electron affinity of the molecule. The Frontier orbital approach as proposed by Koopmans' theorem [39,43] for closed shell system is totally appropriate in explaining stability and chemical reactivity of the molecules based on HOMO and LUMO orbitals. The energy corresponding to HOMO represents the ionization potential of the molecule and the LUMO corresponds to electron affinity value. Using Koopmans' theorem, I and A values can be correlated with the Frontier orbitals by the following relation:

$$I = -E_{HOMO}, \quad A = -E_{LUMO}. \tag{4}$$

The global softness (S) is the inverse of global hardness [44]:

$$S = \frac{1}{\eta}. \tag{5}$$

The electrophilicity index is a measure of the electrophilic power of a molecule and the electrophilicity index as defined by Parr et al. [33] is given by the expression:

$$\omega = \mu^2/2\eta. \tag{6}$$

3. Results and discussion

3.1. Energies and geometries

It is predicted that [MIM][$N(CN)_2$] IL can be connected to exterior sidewall of (4,4) armchair SWCNT through C═C bond of MIM ring. Three different types of functionalized CNT (f-CNT) were found from interaction between IL and the exterior sidewall of (4,4) armchair SWCNT with diameter (5.66 Å) and length (12.36 Å). Selected structural parameters of IL and CNT are given in Fig. 1. The possible configurations (**E**, **S1–3**, **P1–3** and **V1–3**) are given in Fig. 2 and S1 (Supplementary data file). As can be seen in Fig. 2, [MIM][$N(CN)_2$] ionic liquid is connected to the exterior sidewall of the nanotube through C═C bond of MIM ring. The C═C bond of MIM ring can be located parallel to the tube axis (P series), slanted to the tube axis (S series) and in edges of NT (**E** complex). Accordingly, seven structures namely **S1**, **S2**, **S3**, **P1**, **P2**, **P3** and **E** are predicted. For the structure **E**, the imidazolium ring is located at the edge site of open-ended SWCNT, which is quite different in binding from the other structures. In addition, when C═C bond of IMI ring locates perpendicular to the tube axis, **V1–V3** f-CNTs can be expected to be formed. Since, these complexes are less stable than **S** and **P** series (~80.0 kcal/mol); we have not discussed **V1–V3** f-CNTs in this manuscript. However, the structures of **V1–V3** complexes are given in Fig. S1 of Supplementary data file.

In both series of f-CNT, C atoms of CNT at the fused point move outward from the tube surface. The curvature leads to a modification of the molecular orbitals of the carbon atoms and a shift of the electronic density toward the outside of the tube, corresponding to an enhanced reactivity of the outer surface. Here, we have defined the angle ($\Phi_P = 120 - \Phi$), where Φ is the average value of three angles around the fused C atoms. The Φ_P of two C atoms in fused points are 0.3° (edge carbon) and 1.9° in pristine CNT, 11.4° and 9.6°(edge carbon) in **S1**, 11.2° and 12.8° in **S2** and 11.5° and 11.5° in **S3**, 11.6° and 9.6° (edge carbon) in **P1**, 11.7° and 12.0° in **P2** and 11.3° and 11.8° in **P3**. As can be seen, Φ_P increases upon functionalization of CNT, so that the average values of Φ_P for **S1** in the **S** series and **P1** in the **P** series are the smallest values. Therefore, the structural changes of CNT upon functionalization in **S1** and **P1** are expected to be smaller than those of **S1** and **S2** in **S** series and **P2** and **P3** in **P** series, respectively.

For **P** and **S** structures, two new C_{IM}–C_{NT} bonds are formed between imidazolium and CNT. As shown in Fig. 2, two newly C_{IM}–C_{NT} chemical bonds formed between imidazolium and CNT make two six-membered rings in **S** complexes. The lengths of newly created C_{IM}–C_{NT} bonds in