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Interaction of $B_{12}N_{12}$ nano-cage with cysteine through various functionalities: A DFT study

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ABSTRACT

The adsorption behavior of amino acid cysteine over the pure $B_{12}N_{12}$ nano-cluster has been investigated using density functional theory (DFT) and time-dependent density functional theory (TD-DFT) calculations. Interaction between the cluster and the amino acid has been explored through all the four functional groups; hydroxyl (-OH), carboxyl (-COOH), amine (-NH_2), and thiol (-SH) of the acid. The zwitterionic form of the amino acid has also been taken into consideration while studying the adsorption of amino acid on the cluster surface. The nature of interaction between the two has been exhaustively explored in terms of adsorption energy, nearest atom distance, optical and electronic properties as well as vibrational frequencies analysis. The affinity of cluster to bind more than one amino acid has been established for amino acids that are present as dippetide as well as for two distinct cysteine molecules.

1. Introduction

Amino acids, the fundamental building blocks of peptides and proteins, are the two major construction units in the living systems that reflect the chemical properties of complex biomolecules. Their conjugate structures with different nanomaterials are being widely explored as a new class of materials having fascinating applications in biosensors and other medical diagnosis [1–3]. The basic unit of amino acids constitutes of two functional groups i.e. amine and carboxyl groups that could act as linkers for their interaction with nanomaterials. L-cysteine ($SHCH_2CH(NH_2)COOH$), is one of the smallest σ-amino acid and is the only amino acid found in nature with potent thiol functional group in addition to amine and carboxyl groups. The ionic forms of L-cysteine in different phases are controlled by these three functional groups. In gas phase, L-cysteine is mainly present in its non-ionic form while in both aqueous and solid phases its zwitterionic state is the most stable. In bio-molecules, L-cysteine amino acid is mostly present on the border of large proteins as it can provide a link to anchor these proteins to inorganic supports [4–8]. Therefore, L-cysteine can be considered as the most distinguished member of the family of amino acids and is likely to be very crucial in understanding interactions between nanomaterials and biomolecules owing to the presence of three functional groups that render better control and flexibility in comparison to the rest of the amino acids [9,10].

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Smaller size, large number of functional groups and strong affinity of sulfur with different metals have expanded the applications of amino acids containing S atoms in developing new techniques [11,12]. The interactions of L-cysteine with various metals and metal oxides have already been investigated both experimentally and theoretically [13,14]. A variety of metals like Ag (111) [13], Au (111) [15], Pt-doped graphene etc. have proven to provide a suitable surface to L-cysteine to get adsorbed through a thiolate (R–S–M) linkage [16]. In addition, several metal oxides such as rutile and anatase forms of TiO_2 [17,18], quartz [19], kaolinite [20] etc. have also been critically examined by many researchers to investigate their interactions with L-cysteine. It has been observed from the theoretical studies that L-cysteine amino acid has strong affinity towards these metals and metal oxides and got chemically adsorbed mainly through –SH group rather than NH_2 and –COOH groups [21–25].

In the present era of nanotechnology, numerous nanomaterials have replaced the bulk materials in wide range of applications owing to their unprecedented properties. Out of several inorganic nanomaterials, boron nitride (BN) nano-clusters analogous of carbon nano-clusters have gained a great attention of researchers due to their wide range of excellent properties such as high temperature and oxidation stability, low dielectric constant, high thermal conductivity and the constant band gap with semiconductor nature in comparison to that of carbon [26–28]. Recent investigations on structures and stability of fullerene like cages of $(BN)_n$ nanostructures suggested the most stable cluster is where n = 12 i.e $B_{12}N_{12}$ consisting of six tetragon rings and eight hexagon rings [29,30]. In addition, BN nano-clusters exhibit excellent adsorbent properties which have been validated both experimentally and theoretically by numerous scientists [31–38]. The sensitivity of electronic properties of $B_{12}N_{12}$ nano-clusters towards adsorption of several toxic molecules like CO, HCN, SCN^- etc makes them a potential sensor towards them [39,40]. Moreover, the adsorption and decomposition of some aromatic molecules such as pyridine, methanol, methylamine, phenol etc [41–44], and the adsorption of common biomolecules including nucleobases; adenine, uracil and cytosine, drugs; caffeine, nicotine and amphetamine has also been studied over the surface of $B_{12}N_{12}$ nano-cluster in earlier reports [45–47]. The objective of the present study is to investigate the adsorption of cysteine over $B_{12}N_{12}$ nano-cluster's surface through theoretical calculations performed within the formalism of density functional theory (DFT).

2. Computational methods

The geometries of bare $B_{12}N_{12}$ nano-cluster, cysteine molecule and their adsorbed complexes with different orientations have been fully optimized by using Becke, 3-parameter, Lee-yang-Parr (B3LYP) level of theory in conjunction with 6-311 + G** basis set [48,49]. In addition, molecular electrostatic potential (MEP), frontier molecular orbital (FMO), density of states (DOS), and natural bond orbital (NBO) analysis have also been performed to evaluate other important parameters for critical investigation with Gaussian 03 software [50]. All optimization calculations have been carried out within DFT formalism implemented in GAMESS electronic structural package [51]. Incompleteness of basis set originates the basis set superposition errors (BSSE) during the investigation of weak intermolecular interactions in the present calculations which have been resolved by estimating the BSSE energy for all the complex systems using counter poise correction method [52]. Moreover, Time-dependent density functional theory (TD-DFT) has also been performed by incorporating M06-2X method with 6-311 + G** standard basis set [53]. The accuracy of calculations was further ascertained by reperforming the optimizations with another functional i.e. B3PW91 that yielded the same qualitative results. The adsorption energies (E_{ad}) of cysteine upon the pure BN nano-cages are represented by:

$$E_{ad} = E_{cluster\text{-}cysteine} - (E_{cluster} + E_{cysteine}) + E_{BSSE} \quad (1)$$

where $E_{cluster}$ is the total energy of the pure $B_{12}N_{12}$ nano-cluster. $E_{cluster\text{-}cysteine}$ is the total energy of cysteine adsorbed over the bare $B_{12}N_{12}$ cluster and $E_{Molecule}$ represents the total energy of an isolated cysteine molecule.

3. Results and discussion

The adsorption of cysteine amino acid on the surface of the $B_{12}N_{12}$ nano-cluster has been considered through four different interaction sites i.e. amine, thiol, carbonyl, and hydroxyl linkage with the cluster. It can be noted that cysteine amino acid exists as zwitterion in both aqueous and solid phase. Both O-centered and S-centered zwitterionic forms of cysteine amino acid in addition to its neutral form have been taken into consideration while investigating while interactions with the nanocluster. The optimized geometries of the bare $B_{12}N_{12}$ nano-cluster and cysteine amino acid along with their partial charges and their DOS plots are depicted in Fig. 1.

3.1. Adsorption via neutral functional groups

Four optimized geometries obtained while studying adsorption of neutral form of cysteine molecule on the cluster are shown in Fig. 2 along with the corresponding DOS and IR activity plots. Out of the four geometries that consider interaction through different functional groups of the amino acid, the most favorable interaction attributed in terms of adsorption energy and bond lengths (Table 1) is through amine functional group of cysteine with the B atom of the cluster. According to Eq. (1),