**B₃₆ bowl-like structure as nanocarrier for sulfonamides: a theoretical study**

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**Abstract**

Density functional theory method used to investigate the interaction of the simplest sulfonamide with the B₃₆ nanocluster. The obtained results indicate that although sulfonamide weakly interacts with convex and concave sides of the nanocluster, the B atom at the edge of B₃₆ nanocluster is favorable position for adsorbing. The interactions have been also studied in terms of natural bond order charges analysis. The electronic properties of the nanocluster are significantly altered once the sulfonamide molecule is adsorbed. Thus, the energy gap between HOMO and LUMO orbitals is reduced which could be applied as a chemical signal. Moreover, the relative high dipole moments obtained for B₃₆/sulfonamide configurations suggest that these structures could be solubilized or dispersed in polar mediums like water. According to the results obtained, the B₃₆ nanostructure could be a potential carrier for delivering sulfonamides in nanomedicine applications.

**Graphic abstract**

**Keywords** Sulfonamide molecule · B₃₆ structure · Nanocarrier · Theoretical study

**Introduction**

Nanomedicine is a branch of medicine that applies the knowledge and tools of nanotechnology to the prevention and treatment of disease by using nanoscale materials for delivery, diagnosis, sensing, or actuation purposes in a living organism. Although nanomedicine is a hot topic today, nanoparticles started their use in medicine long time ago (e.g., nanosilver for bacterial infections, colloidal gold for treating rheumatoid arthritis, alum as adjuvant in vaccines, ...). As above mentioned, one application of nanotechnology in medicine involves employing nanoparticles to deliver drugs, heat, light, or other substances to specific types of cells. These nanoparticles are attracted to diseased cells which allow direct treatment of those cells. This technique reduces damage to healthy cells in the body and allows for earlier detection to disease. Thus, one of the major goals of nanomedicine is the design of materials capable of delivery and targeting of pharmaceutical, therapeutic, and diagnostic agents (i.e., nanocarriers).

Since the mid-1980s, the development of nanocarriers, incorporating specific receptors for the target cells, has
Certainly been the most promising strategy as demonstrated by the theoretical and experimental studies published up to date [1–7]. Carbon-based and boron-based nanostructures have been proposed as nanocarriers [8–12]. Boron is an electron deficient element which has a rather fascinating chemistry [13]. In contrast to the covalent, ionic, van der Waals, and metallic bonds, it has a variety of crystal structures containing multicenter bonds, which is a result of an electron deficiency [14, 15]. Boron is possibly the second element that can possess multiple low-dimensional allotropes. Recently, the quasiplanar boron clusters (B_{36}) with sixfold symmetry and a central hexagonal hole has been synthesized [16]. The strongly bound atoms of B_{36} enhance its resistance to mechanical impact. This nanostructure exhibits potential to have an important role in future thin film technology and two-dimensional materials research. Moreover, these structures can serve as well as potential chemical sensors and two-dimensional materials research. Moreover, these structures can serve as potential chemical sensors and two-dimensional materials research. Moreover, these structures can serve as potential chemical sensors.

Sulfonamide (SA) is a functional group (Fig. 1) present in several groups of drugs called sulfonamides, sulfa drugs or sulpha drugs that were the first successfully synthesized selectively toxic antimicrobial drugs [23, 24]. Figure 1 represents SAs’ general structure where R^1, R^2, and R^3 may be alkyl, aryl, or heteroaryl groups, although R^2, R^3 may be also hydrogen atoms. After SA discovery and up to now, more than twenty thousand SA derivatives, analogs and related compounds have been synthesized although the best therapeutic results are obtained by replacing one hydrogen atom within the –SO2NH2 group by one heterocyclic ring [29]. Obviously, these syntheses have resulted in the discovery of new compounds with diverse pharmacological properties [25]. SAs can be classified in different ways although one of the most comprehensive classifications [26] is into topical and oral SAs. In addition, oral SAs classify in those that can be absorbed or not. Several drugs containing SA group are being used in clinical therapies (e.g., antibacterial and antifungal drugs [27, 28], carbonic anhydrase inhibitors [29–31], anti-inflammatory agents [32], anticonvulsant agents [33], antimigraine agents [34], hypoglycemic, protease inhibitors [35], agents acting against diabetic mellitus [36], cancer chemotherapy [37, 38], among others).

In this study, the ability of B_{16} nanocluster to adsorb the simplest SA molecule (i.e. R^1=R^2=R^3=H) has been investigated by means of electronic structure calculations. We select this molecule as a model for more complex SA drugs because it includes the common part of SA drugs but reducing the computational cost. In addition, this molecule is also important since it can act as a carbonic anhydrase inhibitor [31]. Up to now, based on our knowledge, this is the first study focused on using the B_{16} nanocluster as a SA nanocarrier. The results obtained may provide new insights in the progress of nanomedicine domain.

Results and discussions

Pristine B_{36} nanocluster and SA molecule geometry optimizations in gas phase and water medium

The optimized structures of pristine B_{36} and SA molecule as well as bond distances using the M06-2X/6-31G(d,p) level of theory in the gas phase, are shown in Fig. 2a, b, respectively. The bowl-shaped B_{36} nanocluster with a central hexagonal hole, exhibits different B–B bond lengths. This structure is exactly accordance with some previous studies [16, 20, 22, 39]. They indicated that the length of 1.6 Å is related to the shortest bond, while the other B–B bonds are slightly longer (1.7 Å). Figure 2c represents the B_{36} TDOS with an energy gap of 3.42 eV. Our results have a little difference with their results due to differences in the method used. Rostami et al. show that the HOMO, LUMO, and energy gap depend strongly on the type of density functional used [22]. But they confirmed our method in their investigation. Other values obtained from the TDOS analysis are listed in Table 1. Also, the acquired results for SA molecule (see Fig. 2b) are in agreement with previous studies [40, 41]. The electrostatic potential (ESP) distribution is also shown in Fig. 2d and its shape will be discussed later. Moreover, the solvent effect (i.e., water medium) on B_{36} and SA structures has been analyzed by means of a polarizable continuum model (PCM). The optimized structures along with the most representative bond distances are shown in Fig. 3a, b proving only insignificant differences in some distances between the structures in gas phase and in water medium. Table 1 also indicates the electronic properties of B_{36} nanocluster in presence of water solvent derived from TDOS plotted in Fig. 3c.
It confirms the small effects also derived from the presence of the water medium.

**SA adsorption on pristine B_{36} nanocluster in gas phase**

The adsorption of the SA molecule on both convex and concave sides of the B_{36} nanocluster has been examined. The electrostatic potential (ESP) distribution helps to determine the electrophilic and nucleophilic sites within a molecule. The regions with low ESP are characterized by the negative charge and are shown in red color in a typical ESP map. Conversely, the regions with high ESP, the positive charge, are shown with blue color. Figure 2d shows that the electron density (red color) is localized on the O atoms of SA molecule. According to this, and to the fact that B_{36} nanocluster is nucleophile, SA molecule should approach to the nanocluster through the O atom. Thus, we have searched for the appropriate adsorption configuration of the SA molecule on the B_{36} nanocluster in gas phase. After the full optimization of various initial structures, eight stable adsorption configurations are obtained (labeled with letters A–H). These relaxed structures and their corresponding binding distances are given in Fig. 4. The calculated $E_{\text{ads}}$ values for
these configurations are listed in Table 2. According to the results of this table, adsorption energies for these configurations are between $−37.79$ and $−64.74$ kJ/mol. Among them, A configuration implies the strong physisorption process of the SA molecule onto B36 surface by appreciable adsorption energies. Actually, the SA molecule does not adsorb efficiently neither on convex nor concave surfaces of the B36 nanocluster. This fact is confirmed by the great interaction distances (2.6–3.6 Å) and small $E_{\text{ads}}$ value (see Fig. 4 and Table 2). In the most stable configuration (A), the oxygen atom of SA (the negative region in the ESP map) approaches the B atom at the edge of B36 nanocluster with an interaction distance of 1.5 Å and $E_{\text{ads}} = −64.74$ kJ/mol. It is straightforward that boron atoms at the edge of B36 are more reactive toward the nucleophilic attack of the SA molecule. It is noticeable that the SA adsorption distorts significantly the B36 nanocluster (see Fig. 4). Also, S–O bond in SA molecule is elongated from 1.444 Å to 1.524 Å after adsorption at the edge of B36 nanocluster (see Table 3). The obtained charge transfer, changes of enthalpies ($\Delta H_{\text{ads}}$) and Gibbs free energies ($\Delta G_{\text{ads}}$) of these configurations were also calculated and their values are listed in Table 2. These results confirm the strong physisorption of SA on the surface of B36 nanocluster in A configuration. The calculated NBO charge indicates that remarkable charge transfer (388 $|\text{me}|$) occurs from SA to B36 nanocluster, implying the electrostatic interaction between SA and B36 nanocluster. Indeed, the SA molecule acts as a Lewis acid; whereas the nanocluster plays the role of a Lewis base. As shown in Fig. 6a, the calculated ESP demonstrates that the positive charge (blue color) is located on the SA molecule after the adsorption process, confirming donation of charge from SA to B36 nanocluster. Actually, the dipole moments of the considered systems in gas phase, which are important since the B36 may be used for a carrier of drugs in biological systems, are also reported in Table 2. The polarity of isolated B36 and SA molecule is found to be 2.63 and 4.85 Debye, respectively. On the other hand, the high polarity of A configuration (i.e., 7.09 Debye) indicates that this structure could be solubilized or dispersed in polar mediums, like water making B36 nanocluster a promising candidate for drug delivering.

### SA adsorption on pristine B36 nanocluster in water medium

Stable configurations for the interacting system in the gas phase, obtained in previous sections, are reoptimized in water medium (see Fig. 5). In these configurations, interaction distance between the SA molecule and surface of B36 nanocluster is about 1.5–3.5 Å. The range of calculated $E_{\text{ads}}$ value for these configurations is between $−22.31$ to $−64.62$ kJ/mol (see Table 2). This result reveals that SA molecule physisorbes onto B36 nanocluster in water medium. As can be seen in Table 2, like the gas phase only A configuration adsorbed B atom at the edge of B36 nanocluster. It confirmed strong physisorption with amount of $−64.62$ kJ/mol for adsorption energy. In this configuration, interaction distance between O atom of SA and B atom of nanocluster is 1.5 Å which is shorter than in gas phase. It should be noted; the adsorption process leads to a local structural deformation in both fragments (see Fig. 5). Also, S–O bond of SA molecule is elongated from 1.444 Å to 1.524 Å after adsorption at the edge of B36 nanocluster (see Table 3). The obtained charge transfer, changes of enthalpies ($\Delta H_{\text{ads}}$) and Gibbs free energies ($\Delta G_{\text{ads}}$) of these configurations were also calculated and their values are listed in Table 2. These results confirm the strong physisorption of SA on the surface of B36 nanocluster in A configuration. The calculated NBO charge indicates that remarkable charge transfer (388 $|\text{me}|$) occurs from SA to B36 nanocluster, implying the electrostatic interaction between SA and B36 nanocluster. Indeed, the SA molecule acts as a Lewis acid; whereas the nanocluster plays the role of a Lewis base. As shown in Fig. 6a, the calculated ESP demonstrates that the positive charge (blue color) is located on the SA molecule after the adsorption process, confirming donation of charge from SA to B36 nanocluster.
to 1.524 Å after adsorption at the edge of B$_{36}$ nanocluster (see Table 3). On the other hand, in B–H configurations, SA molecule adsorbed on the both convex and concave surfaces of the B$_{36}$ nanocluster through weekly physisorption process (see Fig. 5 and Table 2). Therefore, these configurations are not interested. The obtained changes of enthalpies ($\Delta H_{\text{ads}}$) and Gibbs free energies ($\Delta G_{\text{ads}}$) of these configurations were also calculated and their values are listed in Table 2. These results confirm the strong physisorption of SA on the surface of B$_{36}$ nanocluster in A configuration.

The calculated NBO charges indicate that the charge transfer of 425 |me| is occurred from SA molecule to B$_{36}$ nanocluster, confirming strong physisorption. The main interaction between the B$_{36}$ nanocluster and SA in water medium is due to charge transfer from the lone pair orbital of the O atom in SA to the empty p orbital over the B atom of the nanocluster. Hence, SA molecule acts as Lewis acid; in contrast the nanocluster plays the role of a Lewis base. As shown in Fig. 6b, the calculated ESP demonstrate that the positive charge (blue color) is located on the SA molecule after the adsorption process, positive, confirming donation of charge from SA to B$_{36}$.
Fig. 4 Optimized structures of the B₃₆/SA configurations in the gas phase (bonds are in Å)
nanocluster. Moreover, the calculated dipole moment for this configuration achieved about 12.98 Debye in contrast to 4.10 and 6.31 for isolated B_{36} and SA molecule, respectively, in water medium. These results indicate that this configuration could be solubilized or dispersed in polar mediums, like water. As mentioned above, the occurred large charge transfer in water medium would be depend on the polarity environment [42]. These features and the high polarity recommend that these systems are promising candidate for drug delivery because of their high solubility.

**TDOS and NCI into A complex in gas and water medium**

Previous section showed how perturbation in the electronic properties can be an important aspect of the adsorption

### Table 2

Dipole moment, charge polarization transfer from SA to B_{36} (Q_T), adsorption energy (E_{ads}), and calculated thermodynamic properties at 298 K and 1 atm (\Delta H_{ads} and \Delta G_{ads}) for pristine B_{36} and for the SA adsorbed on the nanostructure at different sites (from A to H) in the gas phase and water medium.

| Configuration | Dipole moment/D | Q_T/me | E_{ads}/kJ mol^{-1} | \Delta H_{ads}/kJ mol^{-1} | \Delta G_{ads}/kJ mol^{-1} |
|---------------|-----------------|--------|---------------------|--------------------------|--------------------------|
| **Gas phase** |                 |        |                     |                          |                          |
| B_{36}        | 2.63            | -      | -                   | -                        | -                        |
| A             | 7.09            | 388    | -64.74              | -59.26                   | -7.80                    |
| B             | 4.78            | 5      | -45.43              | -39.84                   | 1.81                     |
| C             | 4.31            | 4      | -44.92              | -39.32                   | -0.97                    |
| D             | 4.42            | 4      | -45.36              | -40.23                   | -1.34                    |
| E             | 5.47            | 8      | -46.56              | -41.50                   | -0.93                    |
| F             | 4.80            | 37     | -47.53              | -45.10                   | -0.43                    |
| G             | 7.33            | 39     | -37.79              | -31.99                   | 6.26                     |
| H             | 1.54            | 24     | -38.02              | -32.32                   | 5.70                     |
| **Water medium** |                 |        |                     |                          |                          |
| B_{36}        | 4.10            | -      | -                   |                          |                          |
| A             | 12.98           | 425    | -64.62              | -59.88                   | -12.16                   |
| B             | 7.83            | 4      | -26.97              | -22.28                   | 16.57                    |
| C             | 7.16            | 5      | -26.55              | -20.95                   | 15.59                    |
| D             | 7.24            | 4      | -26.77              | -22.10                   | 15.97                    |
| E             | 8.73            | 4      | -29.88              | -25.19                   | 18.16                    |
| F             | 7.44            | 41     | -24.68              | -19.12                   | 22.18                    |
| G             | 10.60           | 47     | -30.61              | -25.24                   | 13.21                    |
| H             | 3.13            | 21     | -22.31              | -17.22                   | 19.67                    |

### Table 3

Bond distances (in Å) and angles (in °) in SA molecule free and adsorbed onto B_{36} nanostructure in the gas phase and in water medium.

| Configuration | Configuration | d(SO)  | d(SH)  | d(SN)  | d(NH)  | \alpha(OSO) | \alpha(HSO) | \alpha(HNH) | \alpha(HNS) |
|---------------|---------------|--------|--------|--------|--------|-------------|-------------|-------------|-------------|
| **Gas phase** | Free          | 1.444  | 1.359  | 1.638  | 1.010  | 124.245     | 106.407     | 117.997     | 117.077     |
| A             | 1.524         | 1.357  | 1.615  | 1.023  | 116.135| 101.777     | 116.182     | 115.679     |             |
| B             | 1.451         | 1.364  | 1.635  | 1.015  | 123.302| 106.057     | 116.821     | 115.752     |             |
| C             | 1.452         | 1.363  | 1.638  | 1.016  | 123.116| 105.595     | 116.036     | 115.322     |             |
| D             | 1.453         | 1.361  | 1.635  | 1.016  | 123.265| 105.711     | 116.862     | 116.750     |             |
| E             | 1.451         | 1.361  | 1.634  | 1.014  | 123.439| 106.122     | 117.967     | 118.129     |             |
| F             | 1.452         | 1.352  | 1.652  | 1.017  | 122.489| 107.122     | 112.957     | 117.878     |             |
| G             | 1.457         | 1.358  | 1.641  | 1.015  | 123.683| 106.464     | 116.912     | 116.366     |             |
| H             | 1.451         | 1.363  | 1.637  | 1.016  | 123.256| 105.661     | 116.093     | 114.969     |             |
| **Water medium** | Free          | 1.452  | 1.353  | 1.638  | 1.015  | 121.429     | 107.158     | 113.100     | 113.787     |
| A             | 1.539         | 1.354  | 1.608  | 1.020  | 114.940| 102.477     | 114.342     | 114.949     |             |
| B             | 1.454         | 1.359  | 1.634  | 1.017  | 121.488| 106.815     | 114.100     | 113.982     |             |
| C             | 1.456         | 1.358  | 1.637  | 1.018  | 121.313| 106.341     | 113.243     | 113.367     |             |
| D             | 1.456         | 1.357  | 1.636  | 1.018  | 121.349| 106.519     | 113.674     | 114.241     |             |
| E             | 1.454         | 1.360  | 1.633  | 1.016  | 121.493| 106.721     | 115.173     | 116.009     |             |
| F             | 1.457         | 1.347  | 1.639  | 1.015  | 121.128| 107.318     | 114.860     | 113.776     |             |
| G             | 1.453         | 1.352  | 1.642  | 1.016  | 121.299| 107.040     | 112.952     | 113.481     |             |
| H             | 1.456         | 1.358  | 1.636  | 1.018  | 121.250| 106.479     | 113.288     | 113.396     |             |
Fig. 5 Optimized structures of the B$_{36}$/SA configurations in water medium (bonds are in Å)
We study the effects of SA molecular adsorption on the electronic properties of the B$_{36}$ nanocluster in gas phase (see Table 1). Looking at the results of Table 1, we can see that the energy gap values of B–H configurations remain invariant and no distinct change of $E_g$ is observed by the SA adsorption for these configurations. The percentage of energy gap variation ($\% \Delta E_g$) decrease in the range of 0.16–1.13%. Therefore, it seems that the SA molecule just floats on the surface of nanocluster and there is no evidence for chemisorption or strong physisorption of this molecule. On the other hand, through the adsorption process of SA at the edge of B$_{36}$ nanocluster, the energy gap of the A configuration is found to be 3.15 eV. Based on the HOMO, LUMO, and TDOS visualizations for this configuration (presented in Fig. 7a), HOMO is more located on nanocluster in A configuration and slightly on SA molecule, while LUMO in this interacting system is remained over the B$_{36}$ nanocluster. Table 1 also confirms that the adsorption of SA molecule is accompanied by a significant change near the valance and conduction level compared to pristine B$_{36}$. In addition, the band gap of the A configuration decreases by 8.09%, and consequently, the conductivity of the system changes. Based on the reported results, the B$_{36}$ nanocluster is expected to be sensitive enough to act as a sensor for SA molecule.

A visualization analysis of the non-covalent interactions has been made to understand the nature of non-bonding interactions in A configuration. According to Yang et al., large negative values of the term $[\text{sign} (\lambda \rho)]$ in the two dimensional RDG plots represents attractive interactions (e.g., hydrogen bonding) whereas large positive values means steric repulsions. On the other hand, the values close to zero (in the low-density region) represent van der Waals interactions. Figure 7b shows the scatter graph of A configuration in gas phase. According to the data plotted, disperse spikes near $[\text{sign} (\lambda \rho)] = -0.01$ a.u. can be settled within the regions of the isosurface with deep blue equivalent to stabilizing interactions, viz., O–B, reflective attractions. While, a red space corresponding to the scatter plots with more than $-0.01$ a.u. for $[\text{sign} (\lambda \rho)]$ indicates a weak repulsive interaction between the SA molecule and B atom at the edge of B$_{36}$ nanocluster.

Upon the adsorption process in water medium, $E_g$ of A configuration is found to be 3.16 eV (Fig. 7c). The HOMO, LUMO, and TDOS calculations are also performed for this configuration, Fig. 7c. According to this figure, the HOMO is located more on nanocluster and slightly over SA molecule in the A configuration while the LUMO is remained on the nanocluster. It can be seen that after adsorption process in water medium, the valance level and conduction level are closed together compared to that of the pristine B$_{36}$. These alterations occur closed to the Fermi energy, and therefore can alter the electronic properties of B$_{36}$. For this reason, the band gap of the A configuration shows 7.73% decrement, and the conductivity of the system is changed. Based on the mention results, this nanocluster is sensitive enough for adsorption and sensing of SA molecule.

RDG scatter graph of in A configuration in water medium is also shown in Fig. 7d. The spikes with values near 0.01 a.u. arise from the relatively strong interaction between the oxygen atom in the SA molecule and B atom at the edge of B$_{36}$ nanocluster. In addition, the spikes with values near $-0.01$ a.u. arise from the weak repulsive interaction between the SA and B$_{36}$ nanocluster.

In the end, based on the DFT calculations, we have found that the electronic properties of B$_{36}$ nanocluster interacting with SA molecule are changed significantly. Our study indicates that the adsorption energy of SA in the exothermic process is negative. Also, based on achieved results, B atom at the edge of B$_{36}$ nanocluster is the best position for adsorbing SA molecule. The reported results in the previous study for the adsorption of fluorouracil molecule on the B$_{36}$ nanocluster are in consistence with the present results.

Fig. 6 Molecular electrostatic potential surface of A configuration in the gas phase and b in water medium. The surfaces are defined by the 0.0004 electron/bohr$^3$ contour of the electronic density (all distances are in Å and color ranges in a.u.) (color figure online)
Therefore, \( B_{36} \) nanocluster is proposed a promising candidate for drug delivery.

**Conclusion**

In the present research, DFT calculations are performed to scrutinize the interactions between SA and \( B_{36} \) nanocluster. It is found that the SA molecule remarkably tends to adsorb via its oxygen atoms at the edge of \( B_{36} \) nanocluster with appreciable adsorption energy. The results illustrate that the edge B atoms are more reactive than the inner atoms toward the SA molecule. Indeed, the SA interaction via this nanocluster affected its electronic nature. The energy gaps of the most stable configuration in the gas phase reduce by 8.09%. The \( B_{36}/SA \) systems are also investigated in water medium. The electrical conductance of \( B_{36} \) is affected via interaction between \( B_{36} \) and SA in water medium. These features and the high polarity recommend that these systems are promising candidate for drug delivery. Thereby, this system might be an innovative candidate as nanovehicle in nanomedicine domain, which is due to its solubility in water medium. The results might open a new perspective for designing novel drug delivery systems based on boron-based nanomaterials.

**Fig. 7** a, c Total density of states (TDOS), b, d plot of the reduced density gradient (RDG) versus sign \((\lambda_2)\rho\) (isovalue = 0.5 a.u.) of A configuration in the gas phase and water medium (bonds are in Å)
Computational details

All the geometry optimizations for B_{36} nanocluster, SA molecule and the complex SA/B_{36} structure were performed using Gaussian09 package [43]. Molecular orbital calculations have been carried out using the hybrid meta-generalized gradient (GGA) M06-2X functional [44] and the 6-31G(d,p) basis set. M06-2X functional has been applied as an acceptable method in many nanoscale molecular systems due to the higher percentage of Hartree–Fock exchange (54%) [45, 46]. Moreover, M06-2X treats medium-range correlation effects more accurately than hybrid GGA functional through the inclusion of a spin kinetic energy density term (being a meta-GGA functional). The 6-31G(d,p) basis set is suitable for general calculations on medium to huge molecules [47–49]. The harmonic vibrational frequencies were computed to approve that an optimized geometry corresponds to a local minimum that has only real frequencies. The correlated S^2 values were zero, which confirms the pure singlet states. To analyze the solvation effects on the stabilities of the complex structures on water, a polarizable continuum model (PCM) [50, 51] with dielectric constant of 78.3553 has been used at the same level of theory. The charge between B_{36} and the SA molecule was calculated by using natural bond orbitals (NBO) analysis [52].

The energy gap (E_g), Fermi level (E_F), and adsorption energy (E_{ads}) values as quantum molecular descriptors [53] were computed. As usual, the energy gap was obtained as the difference in energy between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), Eq. (1).

\[ E_g = (E_{LUMO} - E_{HOMO}) \]  

Following the common convention, E_F stands approximately in the middle of the energy gap at 0 K. E_{ads} of SA over the surface of pristine B_{36} is defined as

\[ E_{ads} = E_{complex} - E_{SA} - E_{B_{36}} \]  

where E_{complex}, E_{SA}, and E_{B_{36}} are total energies of SA/B_{36} configuration, isolated SA, and pristine B_{36} nanocluster, respectively. According to Eq. (2), the more negative the adsorption energy leads to the more stable SA/B_{36} interacting complex.

In order to investigate the thermodynamic feasibility of the SA adsorption on the pristine B_{36} nanocluster, we have computed the changes of the free energies (\Delta G_{ads}) and enthalpies (\Delta H_{ads}) at 298.14 K and 1 atmosphere as defined by followings:

\[ \Delta G_{ads} = \Delta H_{ads} - T \Delta S_{ads} = \Delta H_{ads} - T(S_{complex} - S_{SA} - S_{B_{36}}) \]  

where H and S are thermal enthalpy and entropy, respectively.

Moreover, the total density of states (TDOS) analysis was performed on the pristine fragments and SA/B_{36} complex at the same level of theory by means of the GaussSum program [54]. Finally, the reduced density gradient (RDG) was also used here to characterize the non-covalent interactions. The dimensionless RDG(\rho) is evaluated as a function of the electron density (\rho) and its gradient [55], \( \delta = (1/(2(3\pi^2)^{1/3})) \langle(\nabla \rho/\rho^{2/3}) \rangle \). RDG values provide information about the strength of the non-covalent interaction (NCI) without giving a clear classification of this interaction neither attractive nor repulsive. For this purpose, the sign of the second eigenvalue of the electron density Hessian matrix (\lambda_2) is considered to distinguish among the different types of non-covalent interactions (i.e., hydrogen bonding, van der Waals interaction and steric repulsion). So, the electron density multiplied by the sign of \lambda_2 (i.e., \Omega = \text{sign}(\lambda_2)) is used as a descriptor of the nature of the interacting bonds. MULTIWFN [56] software was used here to draw the NCI plots (i.e., RDG vs. sign(\lambda_2))

Low-density and low-gradient spikes associated with electron density located between interacting paths are a signature of non-covalent interactions.

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