Hydrogen storage of Li$_4$&B$_{36}$ cluster

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The Saturn-like charge-transfer complex Li$_4$&B$_{36}$, which was recently predicted with extensive first-principles theory calculations, were studied as a candidate for hydrogen storage material in the present work. The bonding characters of Li–B, B–B and Li–H bonds were revealed by the quantum theory of atoms in molecules (QTAIM). Each Li atom in Li$_4$&B$_{36}$ cluster can bind six H$_2$ molecules at most, which results into the gravimetric density of 10.4%. The adsorption energies of H$_2$ molecules on Li$_4$&B$_{36}$ cluster are predicted in the range of 0.08–0.14 eV at the wB97x level of theory.

The hydrogen storage is an important issue not being solved up to now. Hydrogen can be adsorbed on a material through three different manners. For chemisorption, the materials bind the dissociated hydrogen atoms with high binding energy of 2–4 eV, like metal hydrides and light complex hydrides. The desorption occurs at high temperatures for the case of chemisorption. On the other hand, the materials, like nanostructured carbon, attached hydrogen molecules weakly with a binding energy in the meV range, which was regarded as physisorption. The strength of third form of binding is in the 0.1–0.8 eV range, and is intermediate between physisorption and chemisorption. Metal-decorated carbon-based nanomaterials and even their derivatives, in which the metal atoms bind hydrogen in molecular form with intermediate binding energy, belong to the third form of binding. For example, the Li$_2$C$_{60}$ cluster was theoretically predicted to bind 60H$_2$ at most, resulting in high gravimetric density. Yoon et al. have indicated that Ca can functionalize carbon fullerenes into high hydrogen storage capacity with a gravimetric density $>$8.4 wt%. In experiments, a lithium-doped fullerene with a Li:C$_{60}$ mole ratio of 6:1 can reversibly desorb up to 5 wt % H$_2$ with an onset temperature of ~270 °C. Deuteration of Li$_{12}$C$_{60}$ was determined in experiment, and the results indicated that up to 9.5 wt % deuterium (D$_2$) are absorbed in Li$_{12}$C$_{60}$.

Highly stable clusters were generally designed in theory for the hydrogen storage. For example, Ba Tai et al. have found that the B$_2$Li$_4$ cluster is a promising candidate for hydrogen storage media, which corresponds to a hydrogen uptake of 24% and adsorption energy of 0.099 eV estimated at the DFT level. Our previous work indicated that the C$_{17}$Ti$^{2+}$ cluster can bind 20 H$_2$ molecules at most with adsorption energy of 0.24 eV, which can result into the gravimetric density of 19%. However, an ideal system is yet to be synthesized in experiment.

Boron fullerenes are also seen as efficient hydrogen storage media due to the light weight and capability to bind with metal adatoms. Many works reported the hydrogen storage of doped cage-like B$_{80}$ with alkali-metal and alkaline-earth metal and transitional metal. In fact, B$_{36}$ favors a core-shell (stuffed fullerene) structure in energy, not a cage-like configuration. Therefore, the applications of B$_{36}$ as hydrogen storage materials may be unrealistic. Recently, a combined experimental and theoretical study observed the first borospherenes (B$_{36}$) with a cube-like cage structure, which brings the development of borospherene chemistry. Bai et al. have investigated the hydrogen storage of the lithium-decorated borospherene B$_{36}$ and found the potential utilization of Li-B$_{36}$ complexes as a novel nanomaterial for hydrogen storage. The Ti-decorated borospherene also theoretically studied as a promising hydrogen storage material, and the evaluated reversible storage capacity is 6.1 wt% for Ti-B$_{36}$ complexes.

A high-symmetry C$_{60}$ quasi-planar structure with dual π aromaticity was predicted as the ground state of B$_{36}$. Nevertheless, by introducing four Li$^+$ counterions into the B$_{36}^{4-}$ system, the neutral Saturn-like charge-transfer Li$_4$&B$_{36}$ complex with D$_{3h}$ symmetry can be highly stabilized. In the present work, we will pay attention to the hydrogen storage capability of Li$_4$&B$_{36}$ system.

Results and Discussion

Structures and bonding characters of Li$_4$&B$_{36}$ cluster. In previous work, the extensive structural search has found that the most stable structure of Li$_4$&B$_{36}$ cluster is one high-symmetry Saturn-like geometry. As shown in Fig. 1, our calculation also obtained a high-symmetry structure corresponding to a closed-shell electronic state (ES) ($^{1}A_g$). As Table 1 shows, the average Li–B and B–B bond lengths are 2.306 Å and 1.687 Å, respectively, predicted with wB97x functional in conjunction with 6-31g
(d, p) basis set, and the calculated bond lengths are excellent in agreement with previous results. Natural population analysis (NPA) charge (shown in Table 1) indicate that each face-capping Li atom donating about one electron to the electron-deficient B core acts as electron donor, resulting into the \((\text{Li}^+)\text{B}_{36}^4\) charge-transfer complex. From the electron configuration of Li atoms \((\text{C}_{\text{Li}})\) in Li-\&B_{36} cluster, one can find that the charge transfer from Li to B atoms result into the empty occupancy of 2 s valence shell. The sphere aromaticity of Li-\&B_{36} is revealed by the huge negative nucleus-independent chemical shifts (NICS) of -44.6 ppm at the cage centers. The lowest vibrational frequency is 203 cm\(^{-1}\) at the wB97x/6-31 G(d, p) level of theory, which is sufficiently large to meet a stability criterion suggested by Hoffmann et al. Our calculated values at the wB97x/6-31 G(d, p) level of theory. The high binding energy of 4.09 eV per Li atom also confirms the high stability of Li-\&B_{36} cluster.

The bonding nature of Li-\&B_{36} cluster will be revealed with QTAIM method, the molecular graphs and corresponding topological parameters are given in Fig. 2 and Table 2, respectively. Different (3, -1) bond critical points (BCPs) relative to B-B bonds and the bond critical points (BCPs) between Li atoms and two neighboring B atoms are found. For the traditional topological criterion, the covalent interaction corresponds to a negative Laplacian of electron density \((\nabla^2\rho(r) < 0)\) at the BCP. Another property, the total energy density \(H(r)\) (defined as the sum of local kinetic energy density \(G(r)\) and local potential energy density \(V(r)\)) proposed by Cremer and Kraka was proven to be very appropriate to characterize the degree of covalency of a bond. The negative \(H(r)\)
are the total energy of Li$_4$&B$_{36}$ cluster, H$_2$, and H$_2$-adsorbed Li$_4$&B$_{36}$ cluster. Therefore, the H$_2$ adsorptions do not result into the high structure distortion of Li$_4$&B$_{36}$ (0.774 Å). It is obvious that the H-H bonds are not broken after being adsorbed on Li$_4$&B$_{36}$ cluster. The Li–H$_2$ bonds are more elongated in Li$_4$&B$_{36}$-4H$_2$ (4 H$_2$ coadsorption on one Li atom) than those in (Li-H$_2$)$_4$&B$_{36}$ which corresponds to uniform adsorption on 4 Li atoms. Moreover, the adsorption energy of (Li-H$_2$)$_4$&B$_{36}$ is significantly larger than that of Li$_4$&B$_{36}$-4H$_2$. This indicates that the hydrogen molecules tend to uniformly be attached to the Li$_4$&B$_{36}$ cluster. The bond lengths of adsorbed H$_2$ molecules are elongated by only 0.7% relative to the isolate H$_2$ molecule. The largest elongation of 0.025 Å is found for the sixth H$_2$ adsorbed by one Li atom is 0.04 eV. Therefore, we can conclude that each Li atom can at most attach six H$_2$ molecules in stable state. We note that a Li atom in Li-decorated nanomaterials. The adsorption of H$_2$ is difficult if the adsorption energy is less than −4.22 eV, i.e., the potential energy of H$_2$ molecule.

On the other hand, the Li–B bonds are gradually elongated as the numbers of adsorbed H$_2$ molecules increase due to the increased interaction between Li atoms and H$_2$ molecules. The largest elongation of 0.025 Å is found for the sixth H$_2$ adsorbed by one Li atom is 0.04 eV. Therefore, we can conclude that each Li atom can at most attach six H$_2$ molecules in stable state. We note that a Li atom in Li-decorated B$_{40}$ also attach six H$_2$ molecules at most in previous work. The adsorption of 24 H$_2$ on the present system is the indicator of a covalent bond. As Table 2 shows, all bond critical points relative to Li–B bonds correspond to positive Laplacian of electron density $\nabla^2 \rho(r)$ and $H(r)$ value. This indicates that the Li–B bonds show typical closed-shell character corresponding to ionic bonds. The Li–B bond critical point between Li atom and H$_2$ molecule is localized. The corresponding electron density, and other topological parameters ($\nabla^2 \rho$, $H(r)$) of Li–H$_2$ BCP suggest that the Li–H$_2$ interaction shows weak noncovalent characteristic. In addition, we note that the topological parameter of bond critical points relative to Li–B and B–B bonds in H$_2$-adsorbed species are almost the same to those of isolated Li$_4$&B$_{36}$ cluster. This further demonstrates that the structure of host cluster was not distorted after H$_2$ was adsorbed.

### Table 2. Topological parameters of isolated H$_2$ molecule and Li$_4$&B$_{36}$ cluster and H$_2$-adsorbed Li$_4$&B$_{36}$-$n$H$_2$ complex.

| Species       | BCP         | $\rho$   | $\nabla^2 \rho$ | $H(r)$ | FBO | ELF |
|---------------|-------------|----------|-----------------|--------|-----|-----|
| H$_2$         | H-H         | 0.270    | -1.219          | -0.305 | 1.00| 1.00|
| Li$_4$&B$_{36}$ | B-Li       | 0.026    | 0.113           | 0.001  | 0.23| 0.05|
|               | B-B         | 0.127 (0.151) | -0.090 (-0.271) | -0.073 (-0.115) | 0.56 (0.87) | 0.69 (0.87) |
| Li$_4$&B$_{36}$-H$_2$ | B-Li       | 0.026    | 0.113           | 0.001  | 0.23| 0.05|
|               | B-B         | 0.127 (0.151) | -0.090 (-0.271) | -0.073 (-0.115) | 0.56 (0.87) | 0.69 (0.87) |
| Li$_4$&B$_{36}$-2H$_2$ | Li-H$_2$   | 0.008    | 0.043           | 0.002  | 0.21| 0.01|
| Li$_4$&B$_{36}$-3H$_2$ | H-H       | 0.267    | -1.190          | -0.299 | 0.76| 1.00|

H$_2$ adsorption on Li$_4$&B$_{36}$ cluster. In this section, we will pay attention to the hydrogen storage stability of Li$_4$&B$_{36}$ cluster. The bond length of free H$_2$ molecule is predicted as 0.744 Å at the wB97x-6-31 g (d, p) level of theory, and is in agreement with the experimental value of 0.741 Å. The free and adsorbed H$_2$ molecules in Li$_4$&B$_{36}$ show almost the same topological parameter as shown in Table 2. This indicates that the hydrogen is attached by the cluster in molecule form. The geometry of Li$_4$&B$_{36}$ cluster is maintained after H$_2$ being attached comparing with isolated one. The molecular graph of Li$_4$&B$_{36}$-H$_2$ is also shown in Fig. 2, from which one can find that one bond critical point Li atom and H$_2$ molecule is localized. The corresponding electron density, and other topological parameters ($\nabla^2 \rho$, $H(r)$) of Li–H$_2$ BCP suggest that the Li–H$_2$ interaction shows weak noncovalent characteristic. In addition, we note that the topological parameter of bond critical points relative to Li–B and B–B bonds in H$_2$-adsorbed species are almost the same to those of isolated Li$_4$&B$_{36}$ cluster. This further demonstrates that the structure of host cluster was not distorted after H$_2$ was attached.

The nH$_2$-adsorbed configurations were extensively optimized to probe into the hydrogen storage stability. Vibrational frequency calculations confirmed that all the relaxed nH$_2$-adsorbed structures are to be local stable, and the Cartesian coordinates of these species are listed in Table S1 of supporting information. The relaxed configurations are depicted in Fig. 3. Our calculations indicate that each Li atom in Li$_4$&B$_{36}$ cluster can attach six H$_2$ molecules at most. The average Li–B and B–B bond lengths of nH$_2$-adsorbed species are collected in Table 3, from which one can see that the B–B bond lengths in adsorbed species are not changed relative to the isolated cluster. On the other hand, the Li–B bonds are gradually elongated as the numbers of adsorbed H$_2$ molecules increase due to the increased interaction between Li atoms and H$_2$ molecules. The largest elongation of 0.025 Å is found for (Li-$6$H$_2$)$_2$&B$_{36}$ species. Therefore, the H$_2$ adsorptions do not result into the high structure distortion of Li$_4$&B$_{36}$ cluster. The bond lengths of adsorbed H$_2$ molecules are elongated by only 0.7% relative to the isolate H$_2$ molecule (0.774 Å). It is obvious that the H–H bonds are not broken after being adsorbed on Li$_4$&B$_{36}$ cluster. The Li–H$_2$ distances are in a rather wide range from 2.207 Å to 3.080 Å as shown in Table 3. It is observable that there is an abrupt increase in the Li–H$_2$ bond lengths from Li$_4$&B$_{36}$-4H$_2$ to Li$_4$&B$_{36}$-5H$_2$, so that the first four H$_2$ molecules are closer to the Li site than the next one. By comparing Li$_4$&B$_{36}$-4H$_2$ and (Li-H$_2$)$_4$&B$_{36}$, one can find that the Li–B bonds are more elongated in Li$_4$&B$_{36}$-4H$_2$ (4 H$_2$ coadsorption on one Li atom) than those in (Li-H$_2$)$_4$&B$_{36}$ which corresponds to uniform adsorption on 4 Li atoms. Moreover, the adsorption energy of (Li-H$_2$)$_4$&B$_{36}$ is significantly larger than that of Li$_4$&B$_{36}$-4H$_2$. This indicates that the hydrogen molecules tend to uniformly be attached by 4 Li atoms.

We calculated consecutive adsorption energy ($E_r$) as the energy gained by successive additions of H$_2$ molecules to evaluate the reversibility for storage of H$_2$ molecules. The average adsorption energy ($E_{ads}$) was calculated to evaluate the adsorption capability of the Li$_4$&B$_{36}$ cluster. They are defined as follows:

$$E_r = [E(Li_4&B_{36} - (n - 1)H_2) + E(H_2) - E(Li_4&B_{36} - nH_2)]$$

$$E_{ads} = [E(Li_4&B_{36}) + nE(H_2) - E(Li_4&B_{36} - nH_2)]/n$$

where, $E(Li_4&B_{36})$, $E(H_2)$, $E(Li_4&B_{36} - nH_2)$ are the total energy of Li$_4$&B$_{36}$ cluster, H$_2$, Li$_4$&B$_{36}$-$n$H$_2$, and Li$_4$&B$_{36}$-(n-1)H$_2$, respectively. The $E_r$ is an important index for testing the continuous hydrogen adsorption capacity of nanomaterials. The adsorption of H$_2$ is difficult if the $E_r$ is negative, and the positive $E_r$ means the spontaneous adsorption can occur between the hydrogen molecule and the Li$_4$&B$_{36}$ structure. From Table 3, one can be found that the $E_r$ for the sixth H$_2$ adsorbed by one Li atom is 0.04 eV. Therefore, we can conclude that each Li atom can at most attach six H$_2$ molecules in stable state. We note that a Li atom in Li-decorated B$_{40}$ also attach six H$_2$ molecules at most in previous work. The adsorption of 24 H$_2$ on the present system
(Li₄&B₃₆-H₂) corresponds to a gravimetric density of 10.4%. It is obvious that the gravimetric density exceeds the 5.5 wt% at 2017 specified by the US department of energy (DOE). It can be seen from Table 3 that the E_ads are in the range of 0.08 eV–0.14 eV calculated at the wB97x/d-311+ +g(2d, 2p) level of theory. These values are very close to the average bonding energy for lithium coated fullerene Li₁₂C₆₀⁴, aromatic B₆Li₈⁵ complex, and lithium-decorated borospherene Li₆B₄₀²⁹.

It can be seen from Table 3 that the Li atoms in all nH₂-adsorbed species act as electron donor, and the charge transfer is decreased as the numbers of adsorbed H₂ molecules increase. In addition, the 2s→2p electron

Table 3. Calculated structural parameters, NPA charge (Q_Li) and electron configuration (C_Li) of Li atom, adsorption energy (E_ads) and consecutive adsorption energy (E_r) of H₂-adsorbed Li₄&B₃₆ species.

| Species            | R_Li-B(Å) | R_B-B(Å) | R_Li-H(Å) | Q_Li(e) | C_Li          | E_ads (eV) | E_r (eV) |
|--------------------|-----------|----------|-----------|---------|---------------|------------|----------|
| Li₄&B₃₆-H₂         | 2.306     | 1.687    | 0.748     | 2.207   | 0.74          | 1s²2s²2p⁰.20 | 0.14     | 0.14   |
| Li₄&B₃₆-2H₂        | 2.309     | 1.687    | 0.749     | 2.257   | 0.60          | 1s²2s²2p⁰.20 | 0.13     | 0.12   |
| Li₄&B₃₆-3H₂        | 2.311     | 1.687    | 0.749     | 2.407   | 0.54          | 1s²2s²2p⁰.20 | 0.11     | 0.07   |
| Li₄&B₃₆-4H₂        | 2.314     | 1.687    | 0.748     | 2.645   | 0.52          | 1s²2s²2p⁰.20 | 0.10     | 0.07   |
| Li₄&B₃₆-5H₂        | 2.314     | 1.687    | 0.748     | 2.914   | 0.52          | 1s²2s²2p⁰.20 | 0.09     | 0.04   |
| Li₄&B₃₆-6H₂        | 2.315     | 1.687    | 0.748     | 3.080   | 0.53          | 1s²2s²2p⁰.20 | 0.08     | 0.04   |
| (Li-H₃)₄&B₃₆       | 2.305     | 1.687    | 0.749     | 2.218   | 0.73          | 1s²2s²2p⁰.20 | 0.13     | —      |
| (Li-2H₂)₄&B₃₆     | 2.309     | 1.687    | 0.749     | 2.258   | 0.60          | 1s²2s²2p⁰.20 | 0.13     | —      |
| (Li-3H₂)₄&B₃₆     | 2.326     | 1.687    | 0.749     | 2.416   | 0.54          | 1s²2s²2p⁰.20 | 0.11     | —      |
| (Li-4H₂)₄&B₃₆     | 2.327     | 1.687    | 0.748     | 2.674   | 0.53          | 1s²2s²2p⁰.20 | 0.10     | —      |
| (Li-5H₂)₄&B₃₆     | 2.330     | 1.687    | 0.748     | 2.935   | 0.53          | 1s²2s²2p⁰.20 | 0.08     | —      |
| (Li-6H₂)₄&B₃₆     | 2.331     | 1.687    | 0.748     | 3.011   | 0.53          | 1s²2s²2p⁰.20 | 0.08     | —      |

Figure 3. Optimized structure of H₂ molecules adsorbed Li₄&B₃₆ cluster.
promotion occurs in the Li atoms after H₂ being adsorbed, which results into the non-empty occupancy in 2p orbital (0.20–0.37e) of Li atoms.

Partial density of states (PDOS) of free H₂ and Li₄&B₃₆ clusters were analyzed to understand the bonding characteristics of hydrogen adsorbed systems. The PDOS plots are depicted in Fig. 4. For Li₄&B₃₆ cluster, there exists very weak orbital overlaps between B and Li atoms, which is in agreement with the ionic characters revealed by aforementioned QTAIM analyses. Comparing to the free Li₄&B₃₆ cluster, there exists new peak around −15eV in the 20H₂-adsorbed complex, stemming from the 2p electron of Li atoms due to the 2s→2p electron promotion. Additionally, the new peak can participate into the orbital overlaps with H₂ molecules. This results into the physical interaction between H₂ molecules and Li₄&B₃₆ cluster.

Conclusion
The Saturn-like charge-transfer complexes Li₄&B₃₆ cluster were investigated as a candidate for hydrogen storage with density functional theory (DFT) methods. The bonding nature in bare and H₂-adsorbed Li₄&B₃₆ clusters was revealed with QTAIM analyses. Our results suggest that each face-capping Li atom donates about one electron to the electron-deficient B₃₆ core, resulting into the (Li⁺)₄B₃₆⁺ charge-transfer complex. The ionic characters of Li-B bonds and covalent characters of B-B bonds are understood for bare Li₄&B₃₆ cluster. Each Li atom in Li₄&B₃₆ cluster can at most attach five H₂ molecules, which results into the gravimetric density of 10.4%, exceeding the 5.5 wt% at 2017 specified by the US department of energy (DOE). The structure distortion of Li₄&B₃₆ cluster was not occurred after the H₂ molecules were attached. The adsorption energies of H₂ molecules on Li₄&B₃₆ cluster are in the range of 0.08–0.14 eV at the B97w/6-311g(2d, 2p) level of theory. These values are very close to the average bonding energy for lithium coated fullerene Li₁₂C₆₀, aromatic B₆Li₈ complex and lithium-decorated borospherene Li₄B₆. Our study indicates that the Li₄&B₃₆ cluster may be appropriate material for hydrogen storage, but also need further confirmation in experiment.

Method
All the calculations were carried out with G09 package. The molecular structures of bare and nH₂-adsorbed Li₄&B₃₆ species were fully relaxed without any symmetry constrains using wB97x functional. This functional has considered the long-rang corrections, and is proved to be reliable methods to predict non-covalent interactions. The classical extended basis set 6-31g (d, p) was utilized in the geometry optimization. By adding H₂ molecules around the Li atoms to construct the starting adsorption configurations of Li₄&B₃₆-nH₂ (n=1–20) which were then full relaxed at the wB97x/6-31 G(d, p) level of theory. The harmonic vibrational frequency calculations were carried out at the same level of theory to guarantee that the optimized structures correspond to local minima on the potential energy surface. The larger basis set, 6-311+++(2d, 2p), was employed in the single-point energy calculations to obtain the more reasonable adsorption energy.

To understand the bonding characters of the studied systems, the quantum theory of atoms in molecules (QTAIM) and natural population analyses (NPA) were performed with MULTIWFN program.

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Author Contributions
Jiguang Du conceived the main idea, analyzed the results and wrote the manuscript. Xiyuan Sun and Li Zhang performed all the calculation works. Chuanyu Zhang and Gang Jiang participated in the discussions and all authors contributed to revisions.

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