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Lithium Adsorption at the C_{20} Fullerene-Like Cage: DFT Approach

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ABSTRACT. Adsorption of neutral and cationic forms of lithium (Li) atom have been examined at the surface of pristine C_{20} and boron/nitrogen doped ($C_{12}B_8$ and $C_{12}N_8$) fullerene-like cages by density functional theory (DFT) calculations. All of singular cages have been first optimized and their complex formations with each of Li or Li^+ atoms have been examined, subsequently. The spherical structures of all three cages have been approved and the surfaces have been adequate for Li/Li^+ adsorption processes. The $C_{12}N_8$ cage has been seen the most proper one for the purpose based on adsorption distances and the corresponding values of binding energy. Generally, the neutral Li atom has been seen to be better adsorbed at the surface of all three cages in comparison with cationic Li^+ atom. Examining the electronic orbitals of models indicated that the cages could yield a sensing behavior for differential diagnosis of Li/Li^+ adsorptions based on recording the changes of electronic orbitals at the cage structures as an advantage further than containing capability. Finally, based on the obtained computer-based data, C_{20} fullerene-like cage could be considered for the case of Li adsorption problem in further studies.

Keywords: Lithium; Adsorption; Fullerene; DFT; Nano.

INTRODUCTION

Since the days of nanotechnology innovation, so many researchers have been focused on opening new windows to expected applications of nano-based structures and technologies.[1] Although the pioneering work of Iijima has made the carbon nanotube (CNT) very much well known for the science world, but the already found fullerene (C_{60}) had been introduced some years before the CNT.[2, 3] The original nature of the nanostructures are mostly inorganic; however, considerable efforts have been devoted to invent biological applications for the novel nanostructures.4, 5 In addition to pristine materials, the doped models of nanostructures have been also seen very much useful for evaluating specific applications.[6-10] Boron and nitrogen atoms are those favorite atomic dopants for carbon nanostructures based on their valence electrons lower and upper than the valence electrons of carbon atom, respectively.[11, 12] Since the carbon nanostructures are expected to show semiconducting behavior, such dopants could modify such behavior for the pristine nanostructures.[13] Moreover, the surface of carbon nanostructures could detect different environments based on each of boron/nitrogen doped systems.[14] It is worth to note that the combination of boron and nitrogen atoms yields single standing boron nitride (BN) nanostructures, which are among the most important non-carbon based nanostructures.[15] Among various applications of nanostructures, they are expected to adsorb other atoms or molecules through adsorption mechanisms.[16] To this aim, this work has been performed to investigate the electronic and structural properties of lithium (Li) adsorption process at the surface of a representative fullerene-like nanostructure (C_{20}) as shown in Figs. 1 and 2. Li atom is very much important regarding the technology of batteries for modern electrical systems power sources.[17] Because of the alkaline nature, it is not really easy of keep and contain Li for batteries in conventional

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systems; therefore, nanostructures are expected to have such role of Li-containers for batteries power sources.[18] Earlier works have indicated that the nanostructures could play such role in addition to other organic molecules.[19-22] Although considerable efforts have been dedicated to find a global solution for employing nanostructures for Li batteries, but the problem has been yet remained unsolved and further analyses are required.[23]

Within this work, capability of C_{20} fullerene-like cage for adsorbing Li atom has been investigated based on quantum chemical density functional theory (DFT) calculations. To this aim, adsorption of neutral and cationic forms of Li atom has been considered at the surface of pristine and boron/nitrogen doped structures including C_{20}, $C_{12}B_8$ and $C_{12}N_8$ cages. The obtained results various optimized properties and graphical representations (Table 1, Figs. 1-3) to be discussed in next parts of this paper. It is noted that the computational works could provide insightful information about details of chemical processes in atomic and molecular scales to make more careful decisions on applications of matters for specific purposes.[24-32]

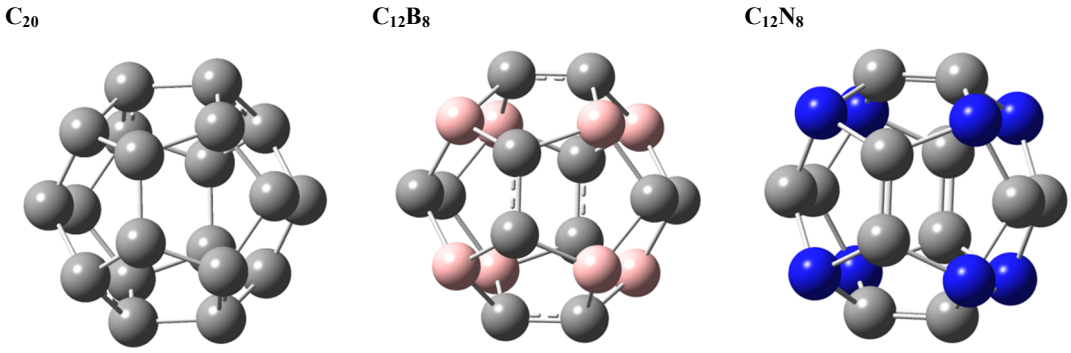

Fig. 1: Models of fullerene-like structures.

MATERIALS AND METHODS

First, 3D models of fullerene-like cages including C_{20}, $C_{12}B_8$ and $C_{12}N_8$ (Fig. 1) have been drawn and they have been optimized to reach the minimum level of structural energy. Next, adsorption of each of Li and Li^+ as the neutral and cationic atoms have been examined at the surface of each already optimized cage to reach the best complex Li@Cage systems (Fig. 2). By these processes, optimized properties including adsorption distance (D_{Ads}), binding energy (E_B), dipole moment (D_M), energies of the highest occupied and the lowest unoccupied molecular orbitals (HOMO and LUMO), and energy gap (E_G) have been evaluated (Table 1). HOMO and LUMO distribution patterns have been also exhibited for the investigated model systems (Fig. 3). Values of E_B and E_G have been evaluated using eqs. (1) and (2), other values have been directly obtained from the output files.

$$E_B = E_{Li/Li+@Cage} - E_{Li/Li+} - E_{Cage} \quad (1)$$

$$E_G = LUMO - HOMO \quad (2)$$

All calculations of this work have been done at the B3LYP/6-31+G* level of DFT as implemented in the Gaussian 09 program.[33] Dispersion corrections have been considered for the for complex systems by assigning IOp(3/124=30) for the calculations.[34] It is here noted that the computer-based methodologies could provide *in silico* environment for careful examining the materials and processes at the molecular scale to reveal insightful information about the investigated systems.[35-42]

RESULTS AND DISCUSSION

Adsorption processes of Li and Li^+ atoms at the surface of C_{20}, $C_{12}B_8$ and $C_{12}N_8$ fullerene-like cages have been investigated based on the obtained results from DFT calculations (Table 1, Figs. 1-3). A quick look at the panels of Fig. 1 reveals that the structures of pristine and doped cages are spherical enough to be similar to the leading C_{60} fullerene in smaller scales. The graphical formations of cages are reasonable according to provide surfaces for Li/Li^+ adsorption processes. Analyses of Fig. 2 indicates that the mechanism of adsorption action is almost specified for each cage separately, in which the position of localized Li atom is different especially for the $C_{12}N_8$ cage. Numerical values of Table 1 could reveal more information to show the significant adsorption distances for each of Li and Li^+ atoms at the surface of $C_{12}N_8$ cage in comparison with two other

cages. The obtained trend of interacting distances could be very well approved by the values of binding energies, in which the best stabilization energies could be found for the $C_{12}N_8$ cage related complexes. In all cases, neutral Li atom could be adsorbed better than cationic Li^+ atom at the surface of each of cages, in which the adsorption distance is shorter for the Li atom in comparison with the Li^+ atom. Distance itself is not maybe so much important, but it could correspond to energy. Generally, Li atom could be better adsorbed at the surface of cages with more tendency to the doped cages in comparison with pristine cage. For Li^+ atom, pristine cage is also a favorite surface for taking place the adsorption process. The spherical features of investigated cages could be very well designated by the almost zero-value of dipole moments. Comparing the results of this work by those have been obtained by previous works could indicate that the C_{20} fullerene-like cage could compete to adsorb LI/Li^+ atoms for possible applications in the battery power sources, in which boron/nitrogen doping could improve the chance of such competition especially for $C_{12}N_8$ cage.[43-46]

Table 1: Optimized properties.

Model	D_{Ads} Å	E_B eV	D_M Debye	HOMO eV	LUMO eV	E_G eV
C_{20}	N/A	N/A	0.00	-5.52	-3.67	1.85
$C_{12}B_8$	N/A	N/A	0.01	-6.48	-3.62	2.86
$C_{12}N_8$	N/A	N/A	0.01	-6.11	-3.59	2.51
Li@C_{20}	2.14	-1.72	7.42	-4.97	-3.17	1.81
Li^+@C_{20}	2.27	-1.55	8.98	-9.41	-7.45	1.96
Li@$C_{12}B_8$	2.13	-2.04	5.89	-5.02	-3.45	1.56
Li^+@$C_{12}B_8$	2.32	-1.38	8.21	-10.23	-7.46	2.77
Li@$C_{12}N_8$	1.91	-2.26	6.76	-5.31	-3.06	2.25
Li^+@$C_{12}N_8$	1.99	-2.18	7.36	-9.86	-7.77	2.09

See Figs. 1-3 for models representations.

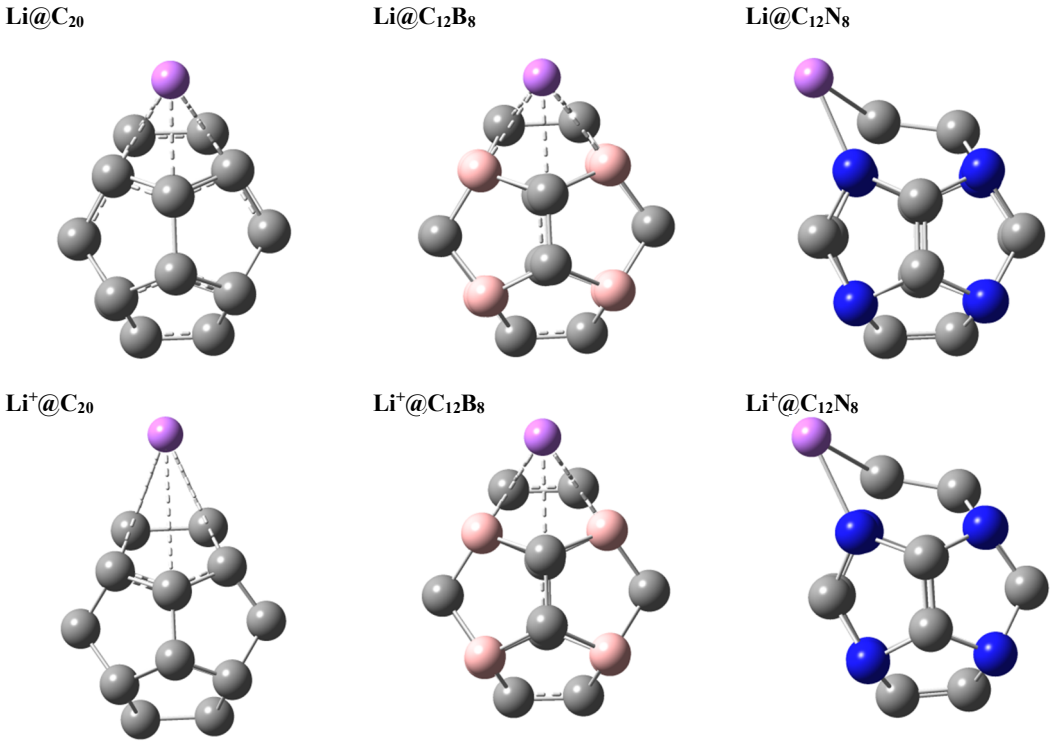

Fig. 2: Models of Li/Li^+ adsorption at the fullerene-like surfaces.

The values of HOMO and LUMO are shown to be sensitive to the type of fullerene-like cage and also the type of adsorbent, in which different values have been evaluated for the investigated models. As an important note of such electronic differences, it is to diagnose the adsorption process by recording the E_G signals. Considerable differences of values of E_G for pristine and doped models and also for adsorption of Li and Li^+

reveal that the investigated cages could be very well used for Li/Li^+ adsorption diagnosis, like a sensor or detector. In addition to original idea of employing C_{20} fullerene-like cages for battery power sources, diagnosis is a further capability for such molecular-scale systems. Distribution patterns (Fig. 3) also indicate different effects of each of boron/nitrogen dopants at the electronic orbital properties of the pristine cage in addition to different effects of Li/Li^+ adsorption at the corresponding cage surfaces. Moreover, the orbitals are localized at the cages but detecting the effects of adsorbed Li/Li^+ atom. The trend could help the idea of diagnosis, in which the changes of cage could be recorded for the purpose.

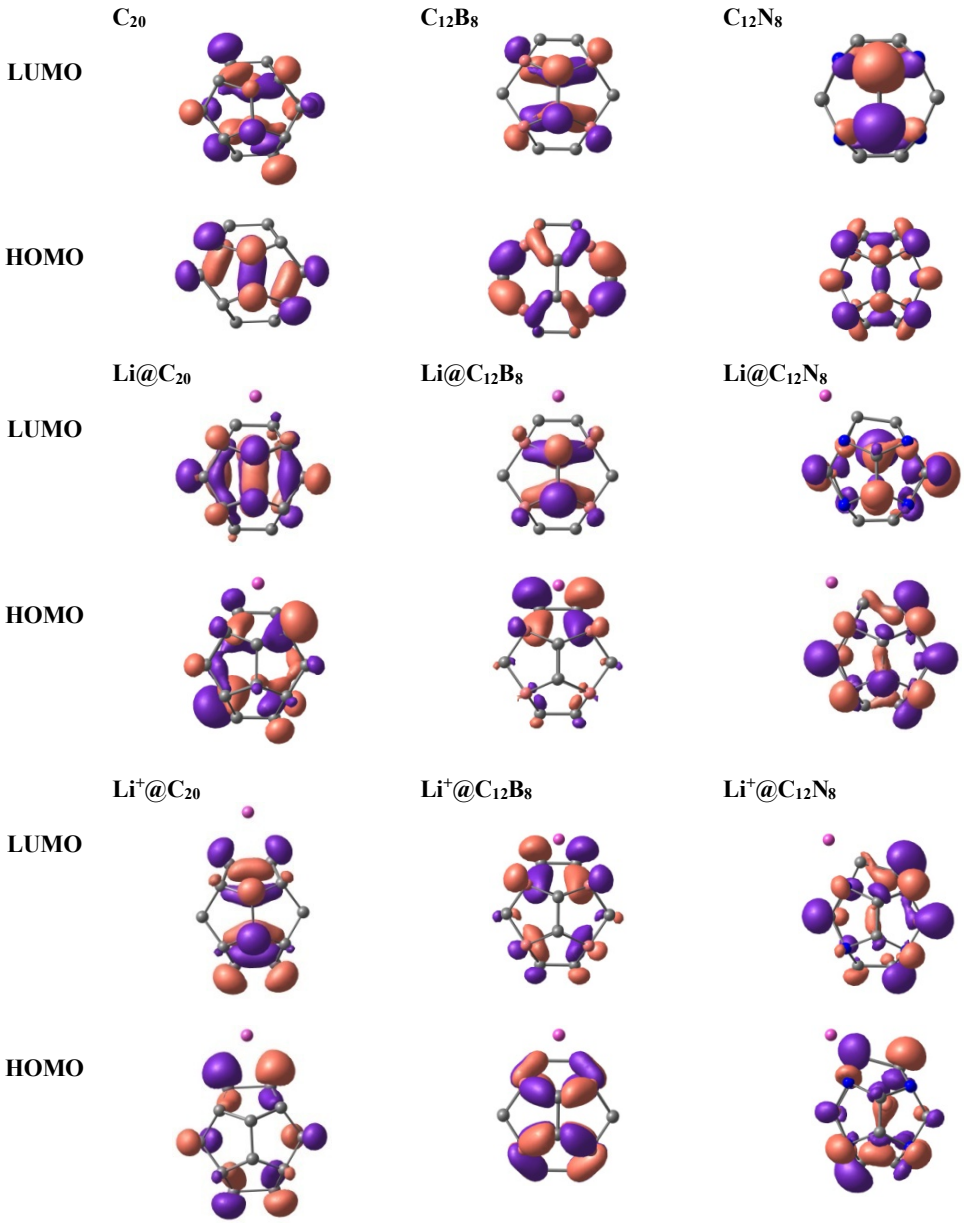

Fig. 3: HOMO and LUMO patterns.

CONCLUSION

Within this work, we have examined adsorption of neutral and cationic forms of Li at the surface of pristine C_{20} fullerene-like cage in addition to two of boron/nitrogen doped models ($C_{12}B_8$ and $C_{12}N_8$). The results indicated that spherical structures of all three cages are similar to the original C_{60} fullerene, in which the almost zero-values of dipole moment approved the achievement. Adsorption distances and the corresponding values of binding energy indicated that the $C_{12}N_8$ cage is the best surface for adsorption of both of Li and Li^+ atoms. Generally, neutral Li atom could be better adsorbed at the surface of all three cages in comparison with cationic Li^+ atom. In addition to containing capability of investigated cages for Li battery power sources, the values of HOMO and LUMO

and corresponding energy gap indicated that the investigated cages could yield a sensing behavior for differential diagnosis of Li/Li^+ adsorptions based on recording the changes of electronic orbitals at the cage structures. Finally, the obtained results indicated that the pristine and boron/nitrogen doped models of C_{20} fullerene-like cage could be considered for the case of Li adsorption problem in further studies.

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