Materials Physics and Mechanics 18 (2013) 63-69 Received: November 6, 2013

MODELING AND INVESTIGATIONS OF THE HETEROFULLERENES $C_{59}X$ (X=Na, Li, Mg, Be)

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Abstract. Geometric and electronic structure of the heterofullerenes $C_{59}X$ (X=Na, Li, Mg, Be) has been theoretically studied. The main emphasis has been given to the stability of the heterofullerenes and their both HOMO and LUMO energies and ability to stabilize negative charge. Obtained results prove the possibility of use investigated heterofullerenes as components for solar cells.

1. Introduction

In various fields of science and technology growing interest of researchers is dedicated to the variety of unusual physical and chemical properties of fullerenes and promising prospects of their possible applications [1, 2].

In the more than 20 years organic solar cells have undergone a gradual evolution that has led to energy conversion efficiencies of about 5 % [3-6]. Efforts to optimize the performance of organic solar cells should find their basis in the fundamental mechanism of operation. It is known, that the energy conversion process has four fundamental steps in the commonly accepted mechanism [7]: 1) Absorption of light and generation of excitons, 2) diffusion of the excitons, 3) dissociation of the excitons with generation of charge, and 4) charge transport and charge collection.In organic materials, the optical energy gap is defined as HOMO-LUMO energy gap and excitation of electrons from HOMO to LUMO in these materials forms tightly bound excitons instead of free electron-hole pair [8]. It is also found that energy difference between the HOMO of the donor and the LUMO of the acceptor is closely correlate with open circuit voltage value [9, 10]. It is therefore apparent that the choice of the components in the active layer as well as its morphology, which governs the physical interaction between the donor and acceptor, are the primary factors affecting the performance of the device.

Fullerenes are currently considered to be the ideal acceptors for organic solar cells for several reasons: an energetically deep-lying LUMO, i.e. affinity of the molecule is very high relative to the numerous potential organic donors [11]; the degenerate LUMO of the high symmetry fullerenes allows the molecules to be reversibly reduced with up to two electrons, thus illustrating its ability to stabilize negative charge. It is necessary to mention, a number of conjugated polymer–fullerene blends are known to exhibit ultrafast photoinduced charge transfer (ca. 45 fs), with a back transfer that is orders of magnitude slower [12]. Furthermore, T. B. Singh and et al exhibited that C_{60} have a very high electron mobility of up to 1 $cm^2V^{-1}s^{-1}$ in field-effect transistors [13].

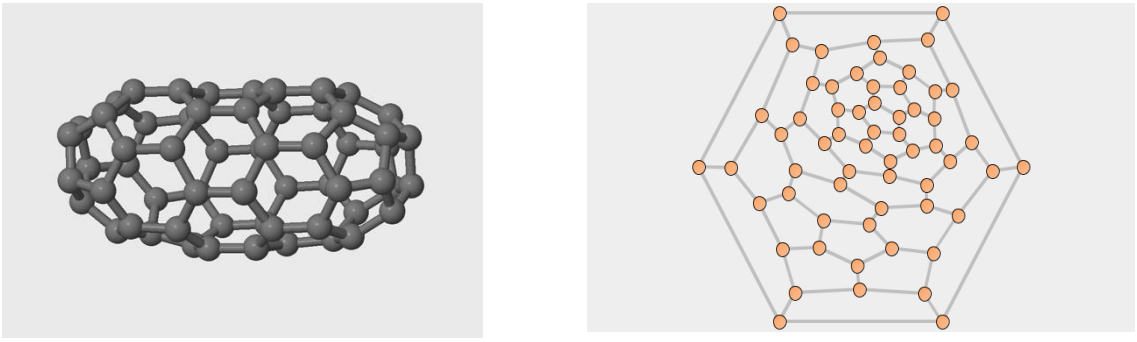
Currentlly, heterofullerenes (the type of fullerenes) attrack great attention because of their various interesting features associated with quasi-two-dimensional structure, high

anisotropy and acceptor properties. So far successful heterofullerenes, containing the elements of B, N, Si, O, P, As and Ge etc., have been reported. Remarkable structural, electronic, optical, and magnetic properties were shown during the experimental and theoretical investigation of this material.

Hence, the objects of our study were structures based on C_{60} fullerene, so-called heterofullerene $C_{59}X$ (where X - the alkali metal Na, Li, Be and Mg). We predict that these system could offer new possibilities to generate photocurrent, particularly because HOMO-LUMO gap may be smaller or large than that of pure fullerenes they could be able to stabilize negative charge such as C_{60} fullerenes. These band gap and stabilization of the negative charge indicate that low/high-energy light could be used when the above described heterofullerenes would be used to generate photocurrent. It implies to increase effectiveness of the photovoltaic devices.

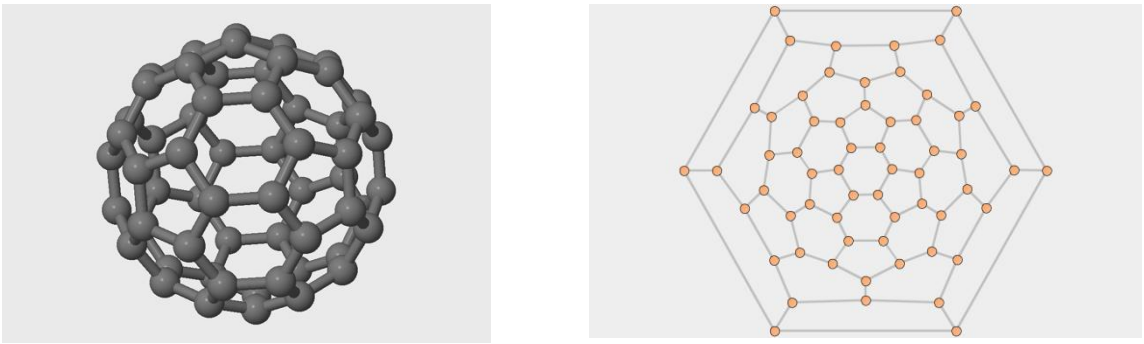
2. Metod of investigations

In order to determine the implant atom influence to stability of the fullerenes, the highest I_h and lowest C_1 symmetry of C_{60} fullerene were chosen. Heterofullerene structures of C_1 and I_h symmetries with numbered atoms are shown on Figs. 1 and 2, respectively.



(a) (b)

Fig. 1. 3D (a) and 2D (b) structures of C_{60} fullerene with C_1 symmetry.



(a) (b)

Fig. 2. 3D (a) and 2D (b) structures of C_{60} fullerene with I_h symmetry.

Using spiral algorithm, all the C_{60} fullerenes composed of pentagons and hexagons were generated by means of FULLGEN program [14]. The program package GAUSSIAN version 03 was used as a modeling tool [15]. Fullerene optimization was carried out with the help of program GAUSSIAN using 6-31G basis set by means of density functional theory

(DFT). B3LYP (Becke-3- Lee-Yang-Parr) exchange – correlation hybrid functional [16-18] was used.

Orbitals with different shapes were add to split valence basis set by using 6-31G basis set. This basis set implies that each atomic orbital is represented by six Gaussians, while the valence orbitals are splitted into two parts that are described by three and one Gaussian [15]. It is necessary to split valence atomic orbitals into two parts aiming to allow anisotropy in the valence shell. For carbon atom there will be nine basis functions of the form;

$$\varphi_{1s}(r) = \sum_{k=1}^{N_1} d_{1s,k}\, g_s(\alpha_{1k}, r), \tag{1}$$

$$\varphi'_{2s}(1,r) = \sum_{k=1}^{N'_2} d_{2s,k'}\, g_s(\alpha_{2k'}, r), \tag{2}$$

$$\varphi'_{2p_x}(1,r) = \sum_{k=1}^{N'_2} d_{2p,k'}\, g_{2p_x}(\alpha_{2k'}, r), \tag{3}$$

$$\varphi''_{2s}(1,r) = \sum_{k=1}^{N''_2} d_{2s,k'}\, 'g_s(\alpha_{2k''}, r), \tag{4}$$

$$\varphi''_{2p_x}(1,r) = \sum_{k=1}^{N''_2} d_{2p,k''}\, g_{2p_x}(\alpha_{2k''}, r). \tag{5}$$

Where the function φ'' and φ' (Eqs. 1–5) represent outer and inner parts of the valence shell where $\alpha_{2k''}<\alpha_{2k'}$. In the 6-31G basis set for heavy atoms, the N_1, N_2'and N_2'' are equal to 6, 3 and 1, respectively. These numbers are chosen on the basis of the compromise between the needs for accuracy and efficiency. The 6-31G basis is used in many calculations of medium/large sized systems, because it's often needs to multiplythe size of a basis set by increasingthe number of basis functions per atom.

Various approaches exist to perform the exchange and correlation energy using DFT calculation methods. These approaches differ in using either only the electron density (local methods) or the electron density, and its gradients (gradient corrected methods or generalized gradient approximation, GGA). Aside from these DFT methods, another group of hybrid functional exists, in which mixtures of DFT and Hartree-Fock exchange energies are used. This approach was abandoned by Lee, Yang and Parr in 1988, who turned to the Helium atom instead. Lee, Yang and Parr turned correlation energy formula for the Helium atom in terms of the second order HF density matrix into a functional of the density, gradient and Laplacian [19, 20]. BLYP geometries are of a standard comparable to HF theory (however, BLYP tends to overestimate bond lengths, whereas HF underestimates), and atomization energies, ionization energies, electron affinities and proton affinities are usually accurate to within 20 kJ mol^{-1} of experiment [21]. BLYP predicts harmonic frequencies that are of an accuracy similar to that of MP2 theory -- a noticeable improvement over HF. The basic idea behind the hybrid functionals is to mix exchange energies calculated in an exact (Hartree-Fock-like) manner with those obtained from DFT methods in order to improve performance. B3LYP uses a different mixing scheme involving three different mixing parameters.

In this case, the gradient-corrected exchange energy functional is in the form:

$$\Delta E_x = -\beta \int \rho(r)^{4/3} \frac{x_\sigma^2}{1 + 6\mathrm{x}_\sigma \sinh^{-1} x_\sigma} d^3 r, \tag{6}$$

where *b* is an easily determined parameter with the least-square satisfying the exact atomic HF data and

$$x_\sigma = \frac{|\rho_\sigma(r)|}{\rho_\sigma^{4/3}}. \tag{7}$$

And the correlation energy is calculated by the following formula:

$$E_c = -a\int \frac{\rho(r)+b\rho(r)^{-2/3}\left[t_{HF}(r)-2t_w(r)e^{-c\rho(r)^{-1/3}}\right]}{1+d\rho(r)^{-1/3}}d^3r, \quad (8)$$

where

$$t_w(r)=\frac{1}{8}\left(\frac{|\nabla\rho(r)|^2}{\rho(r)}-\nabla^2\rho(r)\right) \quad (9)$$

is the Weirsacher kinetic energy density and

$$t_{HF}(r)=\frac{1}{8}\sum\left(\frac{|\nabla\rho_i(r)|^2}{\rho_i(r)}-\nabla^2\rho(r)\right) \quad (10)$$

is the Hartree Fock kinetic energy density.

The density functional methods are derived for obtaining total energies, for examples, such as the functional of the structure within 6-31G basis set.

This is one of the most commonly used approximation to the exchange-correlation energy functional that incorporate exact exchange from Hartree-Fock theory with exchange and correlation from *ab initio* theory. This approach was chosen as the most effective between adequacy and duration of computer calculations.

Each position of the atoms in heterofullerene with symmetry C_1 is unique, that's why we have checked all the possible positions of implanted atoms, while in heterofullerene with symmetry I_h only four positions were checked.

To analize stability of the heterofullerenes, the binding energy (energy per atom)was determined using following Eq. 11:

$$E=\frac{\left|E_{C_{59}X}-(59E_c+E_X)\right|}{60}, \quad (11)$$

where E_c, E_x - total energy of carbon and the implanted atom (Li, Be, Na, and Mg), respectively (eV); E_{C59X} - total energy of the heterofullerene, eV. This way, the greater total energy for one electron means the more stability of the whole heterofullerene structure.

3. Results

It is not surprise, that stability of the heterofullerenes are depended on the position of the alcali metal. It is very well known that head place among the fullerenes takes C_{60} molecule, which is characterized by its high symmetry and, as a result, the highest stability. However, implementation of the alkali metal atoms to fullerene change dramatically (lowered) initial symmetry of the pure fullerenes. It allows us to predict that in some cases the stability of the heterofullerenes arised from C_{60} cage of I_h and C_1 symmetry could be similar. Thus, we performed investigation of the two type heterofullerenes; i. arised from C_{60} of the I_h symmetry; ii. arised from C_{60} of the C_1 symmetry.

Obtained results showed the stability of the heterofullerenes arise from C_{60} with symmetry I_h higher than that arise from the fullerene of C_1 symmetry. However, the results of our calculations exhibited the energy of the $C_{60}I_h$ is lower than that of C_{60} C_1 by 3.35 eV, while this difference in the case of the most stable heterofullerenes arisen from different symmetry of C_{60} become perceptible larger (Fig. 3). It implies, that implantation of the alkali

metal atom to the lowest symmetry C_{60} fullerene leads to the lower stability of these compounds, thus presence of the heterofullerenes arise from the highest symmetry fullerenes is more probable. Therefore we present below results only on the investigations of the most stable heterofullerenes (Fig. 3).

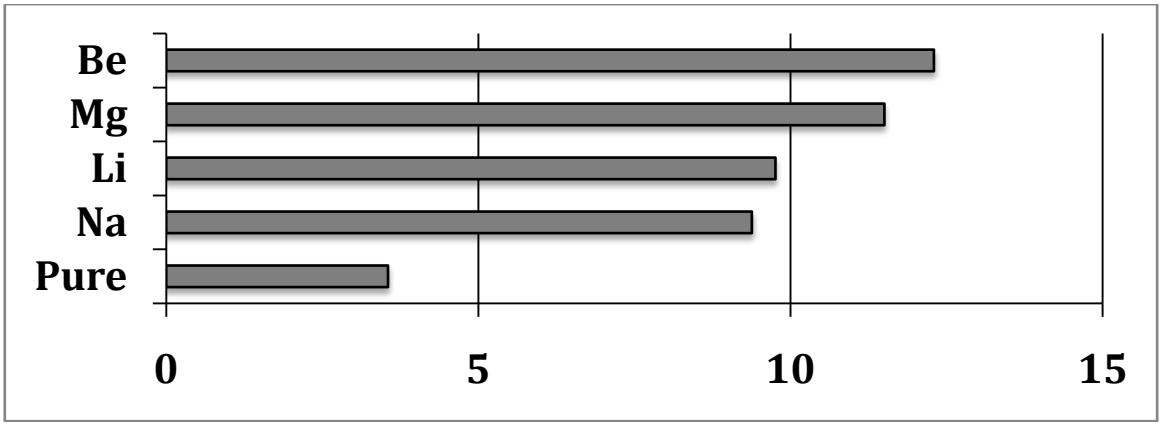


Fig. 3. The difference of the energies (eV, Ox axis) of the pure C_{60} fullerene with I_h and C_1 symetry (pure) and that of the most stable heterofullerenes.

More deeper analysis of the binding energy per atoms of the heterofullerenes indicates insertion of Mg and Na as imposible because$|E_{C59X}|<|59E_c+E_x|$, while binding energies per atom obtained indicate the C_{59}Li and C_{59}Be heterofullerenes as more stable than C_{60} I_h.It is necessary to mention that implemented atoms located in the vertice of the pentagon and two hextagon rings. The results coincide with other author presented results for other types of fullerene.

Table 1. The HOMO and LUMO of the investigated heterofullerenes (named as Li and Be) and pure fullerene (named as C).

Fullerene	HOMO, eV	LUMO, eV	HOMO-LUMO gap, eV
C	6.46	3.85	2.61
Li	5.54	3.97	1.57
Be	5.99	4.35	1.64

The HOMO of the heterofullerenes lies higher than that of the most symmetrical C_{60} fullerene (Table 1). It proves that implement of the Li or Be atoms to fullerene leads to acceptor- property degradation in respect of that of the pure fullerene. However, it is necessary take into account the HOMO energy of the ideal donor polymer for the fullerene. This HOMO energy is determined by considering the band-gap of thepolymer, and hence the absorption of light, as well as theinfluence on the open circuit voltage. A compromise isfound by considering that a band-gap of about 1.5 eV is anoptimal value for a polymer absorber [22]. This gives an idealpolymer HOMO energy of about 5.4 eV [7]. The HOMOs of the both our investigated heterofullerenes lie lower than that of the ideal polymers, and the difference between the HOMOSs of the two components (HOMOs of donor and acceptor) is 0.14 and 0.59 eV, i.e. these heterofullerenes are acceptors in respect of the ideal polymers. It implies that the heterofullerenes to be the acceptors for the polymers used to produce solar cells. Comparison of the position of the HOMO and LUMO of the heterofullerenes allows us to conclude that the using of the C_{59}Be is more promising due to deeper lying HOMO than those of the C_{59}Li.

Let us to remember, that fullerenes are currently considered to be the ideal acceptors for organic solar cells due to an energetically deep-lying degenerated LUMO. The results of our investigation prove, that the LUMO of our investigated heterofullerenes lies deeper than pure fullerenes, i.e. the affinity of the molecules is higher than that of C_{60} relative to the numerous potential organic donors (Table 1). The experimental studies published in the past few years demonstrate that open-circuit voltage increase as the gap of the LUMO (aceptor) and HOMO (donor) widen [23]. Hence, we may predict the increasing of the open-circuit voltage when the $C_{59}Li$ and $C_{59}Be$ will be used and as consequence increasing the power conversion efficiences of the nanostructured donor/aceptor photovoltaics utilizing small molecule organics or conjugated polymers [24]. On the other hand, the energy differences between LUMOs of the donor and acceptor must be taken into account because the energy differences larger than minimum value obtained (0.3 eV) results in wasted energy that does not contribute to device performance [7]. Thus, the deeper lying LUMOs of the heterofullerenes indicate that polymers which LUMOs reside deeper than those of the ideal polymer for the fullerenes (such as PCMB) could be applied for solar cells.

Second very important property of the fullerenes that make them to be very useful composite of solar cell is the degenerate LUMO that allows the molecules to be reversibly reduced with up to two electrons, thus illustrating its ability to stabilize negative charge. Of course, the implementation of the alkali atom to fullerene dramatically lowered symmetry of the compounds, i.e. the symmetry of the described heterofullerenes is C_1 and it is the main reason of the LUMO degeneration disappearance. Indeed the LUMOs of the both our investigated heterofullerenes are not degenerated, however the quasi-degeneration of LUMO+1 is obtained in the case of the $C_{59}Be$. It is notable, that these quasi-degenerated orbitals lie deeper than LUMO of the pure fullerene, but it is not deeper than that of the ideal polymer. Hence, implementation of the Li and Be to the fullerene could lead to lower ability to stabilize negative charge if the stability is related only with the LUMO degeneration, but the heterofullerene bond structure is differ from the fullerene: in the fullerene each carbon atom can share electrons with up to four different atoms, i.e form the C atom that could make four covalent bonds, while Li and Be atoms may form one and two covalent bonds respectively. Hence implement of the alkali atoms leads to insufficiency of the electrons to form covalent bonds and we speculate that it could be a reason to stabilize negative charge as well as better charge separation.

4. Conclusions

In the work we present our first results on the investigations of the different types of the heterofulerenes. Results of uor investigations show that the stability of the heterofullerenes arise from C_{60} with symmetry I_h higher than that arise from the fullerene of C_1 symmetry and implantation of the alkali metal atom to the lowest symmetry C_{60} fullerene leads to the lower stability of these compounds. The results allow us to conclude the presence of the heterofullerenes arise from the highest symmetry fullerenes as more probable.

It is important, that $C_{59}Li$ and $C_{59}Be$ are acceptors with the energetically deep-lying LUMO. The afinity of these heterofulerenes is higher than that of the C_{60} those they could be better component for solar cells although it is not clear do the heterofulerenes stabilize negative charge due to their unique chemical bond structure and what donor could be used to avoid solar energy waste.

Acknowledgments

The authors would like to thank InSpire and NGI.LT projects for provided resources and technical support. The work was performed under the project funded by Education Exchanges Support Foundation and Belarussian goverment project "Informatics and Space", subprogram 1.6.06 "Nanomaterials and Nanotechnology".

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