

Stability and Electronic Properties of C₆₀Chain Polymer: DFT Study

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Abstract

Interfullerene C₆₀ cages polymers have been investigated by density functional theory in general gradient approximation PBE calculations based on DZP basis set. The electronic spectra of these systems are carried out by using TDDFT (PBE/DZP) method. The heat of formation, electronic levels and electronic density of states are explored. The integrated polymer (polymer-A) has a high heat of formation and a very low band gap (like a semi-metallic), while the inter-bonded cyclo addition polymer (polymer-B) has moderate heat of formation and a semiconductor band gap. C₆₀ polymers have strong electron correlation, which increases the localization of electrons. The electron excitations have two peaks for polymer-A, one is strong and the other is weak. Polymer-B has a single band of absorption with higher energy than that of polymer-A.

Keywords: C₆₀ chain polymer, fullerene molecules, electronic properties, DFT

1. Introduction

Since the discovery of fullerene molecules C₆₀ (Kroto *et al* 1985, Kratschmer *et al* 1990) considerable effort has been devoted to understand the properties of this new molecule (Beu 2006, Kato *et al* 2011, Garcia-Hernandez *et al* 2013). Studies by IR, NMR and Raman spectroscopy showed the lowering in symmetry of the fullerene molecules and the presence of *sp*³ intermolecular bonds in the polymerized C₆₀ structures (Iwasa *et al* 1995, Nunez-Regueiro *et al* 1995, Oszlanyi & Forro 1995). The molecules C₆₀ are linked with each other by [2+2] cycloaddition mechanism forming a four membered ring between the neighbors (Sundqvist 1999, Jung *et al*. 2008, Or Rashid *et al* 2010, Liu *et al* 2011, Onone *et al* 2012). Strong covalent bonding between the cages and, as a consequence, the reduction of number of π -electrons in C₆₀ change the electronic properties of the fullerite. So, the bands in the photoemission spectrum of polymerized C₆₀ film are shifted toward the Fermi level (Ito *et al*. 1993) decreasing the energy gap relative to that for the fullerite. At present, the techniques of producing the polymeric phase in the pure form, sufficient for experimental researches such electronic properties, are still developing. In this connection, a study of the electronic structure of polymers by quantum chemistry is very important for the prediction of their possible properties and applications. From tight-binding calculation, a linear C₆₀ chain has been found to be semiconductive with a finite band gap 1.148 eV and almost pure σ -type of intermolecular bonding (Tanaka *et al* 1995).

A family of novel carbon materials with remarkable physical and mechanical properties may be obtained via polymerization of the fullerenes (Burgos *et al* 2000, Wood *et al* 2002). High pressure and high temperature treatment of C₆₀ under certain P, T conditions resulted in the formation of polymerized phases of the fullerene with one- and two-dimensional polymerization motif. These 1D and 2D polymers were extensively characterized by means of X-ray diffraction, Raman and IR-spectroscopy (Nunez-Regueiro *et al* 1995, Senyavin *et al* 1999, Davydov *et al* 2000). This paper presents an *ab initio* calculation of C₆₀ with one dimensional polymer, by using all electron mixed-basis formalism. The calculation of the electronic structure of solid C₆₀ is carried out for two cases, in case one, the molecules integrated and fused to each other while in case two, the molecules have the cycloaddition between each cages. Comparison between each cases will be discussed.

2. Computational Details

Two C₆₀ polymer segments containing four C₆₀ cages of the perimeter carbons were selected as the polymer model. The following segments were studied by fully optimizing the geometry of the corresponding products: (i) the polymer model C₆₀-A of the newly formed as showed in figure 1; (ii) cycloaddition model of C₆₀-B which presented in figure 1. Polymer-A losses 18-atoms from three of these four cages, 6-atoms by one cage, and it shares 6-atoms between each two cages. While, polymer-B, has all cage member atoms. All calculations were performed using density functional theory (DFT) with a general gradient approximation PBE and a DZ basis set. The present level of calculation, DFT(UPBE)/DZ, is used to predict electronic transition states over 30 allowed transitions. The computations were carried out using the DFT quantum mechanics package, Amsterdam density functional (ADF 2012.01) software (ADF 2012).

3.Results and Discussion

At first, we studied the possible combination products of C_{60} polymer by four C_{60} fullerene cages to integrate and fuse to each other, as illustrated in figure 1 (polymer-A). Strong covalent bonding between the cages is a possible case and so, four C_{60} cages are linked to each other by forming a four membered ring between the neighbors as shown in figure 1 (polymer-B). The stability of these two segments is very different, where polymer-A has heat of formation of about 0.666eV/atom, and polymer-B has value of 0.277eV/atom, see table I. The high value in the case of polymer-A is due to that each cage will be in nearest distances from two of other cages, and so this causes an increase in the electron correlation energy of the system. Some of carbon atoms at each two cages have short distance among them, so the repulsion energy increased among their nuclei. The cycloaddition product has less correlation and repulsion energies, thus it will be easier to synthesize and perhaps to be more stable, and this agrees with experimental results which indicated that cycloaddition synthesized under high temperature and pressure and by increasing the pressure integrated polymer is produced. The frontier electronic states and their separations are presented at table I. The higher occupied state (HOMO) of C_{60} cage is pushed toward higher energies in two polymer morphs. This pushing in energy may be related to the electronic correlation energy which increased by small packing of C_{60} polymers, where HOMO level is a bonding π -state and a raising in electron correlation state will weaken the bonding states. LUMO level in C_{60} cage is an anti-bonding π -state which is enhanced by increasing the electron correlation energy that is induced by a polymerization operation. So LUMO state in polymer-A is shifted for lower value, while the polymer-B has a very small difference in LUMO level as compared with a fullerene. The unaffected electronic state of polymer-B may be related to a change that occurs in a type of LUMO state under cycloaddition structure. The LUMO state of this polymorph may be almost a pure σ -type of molecular anti-bonding. The energy band gap of fullerene C_{60} is large as observed experimentally (experimental value is 1.9 eV)(Weaver et al 1991). The polymerization makes significant changes in band gap values, as shown in table I, the close packing of polymer-A reduces the difference between HOMO and LUMO levels and so it has the lowest E_g as compare with polymer-B.

To investigate the fundamental electronic properties of fullerene polymers it has performed the electronic density of states (DOS) for two polymorphs of C_{60} as depicted in Fig. 2. It is clearly shown that the two polymers have wide valence and conduction bands that reflect a semiconductor indication. Furthermore, it is noted that both the polymorphs have the same valence band structure, but they have a little difference in the style of conduction band. The origin of the occupied peaks is mainly due to the p -states of the C atoms with little contributions from the carbon s -orbitals. Near the Fermi level, polymer-A has shallow occupied (which are induced at the intermolecular bonding space) and unoccupied states (which are placed at cages centers) as shown in figure 3-a,b. Figure 3-c,d shows the spatial distribution of HOMO and LUMO states over the two polymers. The interconnection regions bring the higher energy electrons, while the unoccupied states spread over fullerenes surfaces. For narrow bands, localization is expected to occur.

Theoretical spectra of electronic transitions for two kinds of polymorphs are depicted in Figure 2. Polymer-A has absorption offset (0.78eV) which is related to electron excitation with a major contribution from HOMO to LUMO+4 transition, that is higher than the band gap of HOMO-LUMO difference in table I. Also, it has another weak peak which occurs by a transition from HOMO to LUMO+8 with a magnitude of energy about 1.036eV. Polymer-B has a single weak transition from HOMO-4 to LUMO with excitation energy of 1.416 eV. The cycloaddition polymerization produces a passive material for optical response because the frontier orbitals localized over balls of C_{60} cages at the same atoms space. This localization is induced because the one-electron band width that is narrow and these bands have low density of states near Fermi energy level. This parameter, however, is sensitive to the packing of the molecules, and it may be further narrowed by electron-phonon (polaronic) effects.

Conclusions

DFT study has been carried out for two kinds of interfullerene C_{60} cages polymers. The heat of formation, electronic levels, electronic density of states and electronic excitation are explored. The integrated polymer has a high heat of formation and a very low band gap, while the inter-bonded cycloaddition polymer has moderate heat of formation and a semiconductor band gap. C_{60} polymers have localization of electrons which is induced by increasing of electron correlation. The electron excitations have two peaks for polymer-A, one is strong and the other is weak. Polymer-B has a single band of absorption with higher energy than that of polymer-A.

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Table I: Difference in heat of formation, frontier electronic states and energy gap of C60 cage and its polymers.

| property | C ₆₀ cage | Poly.-A | Poly.-B |
|----------------------|----------------------|---------------|---------------|
| $\Delta H.F.eV/atom$ | ----- | 0.666 | 0.277 |
| HOMO eV | -7.626 | -6.703 | -7.153 |
| LUMO Ev | -6.094 | -6.634 | -6.097 |
| EgeV | 1.532 | 0.069 | 1.056 |

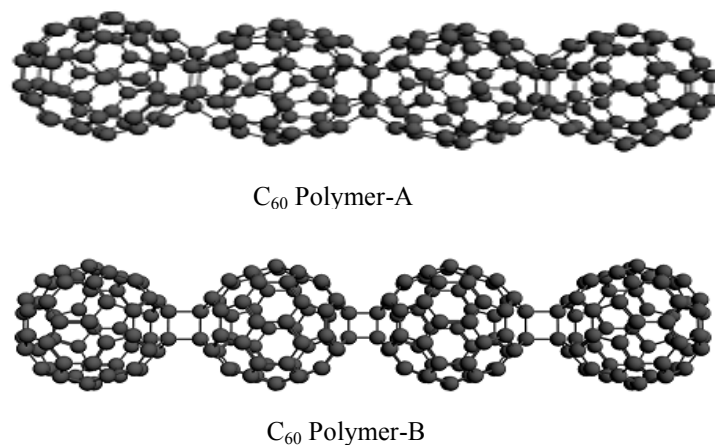


Figure 1: Two models of C_{60} polymer.

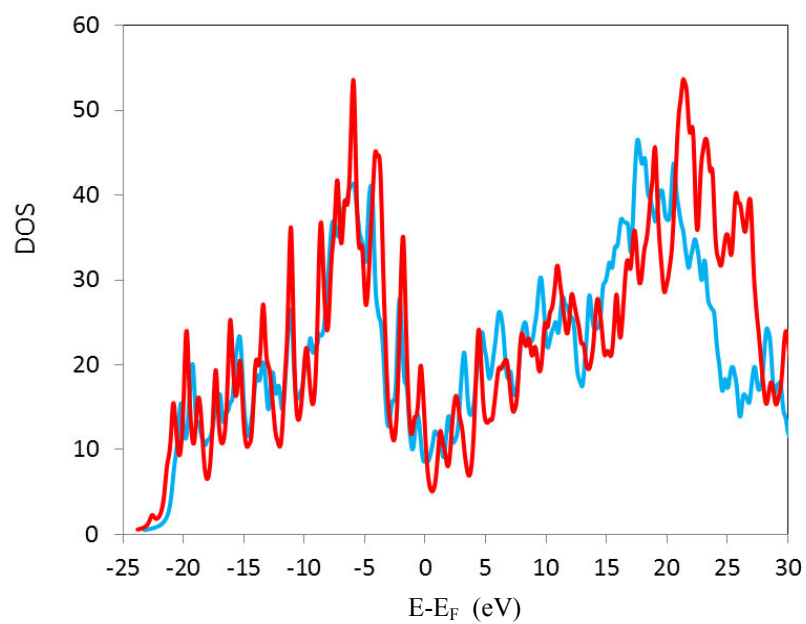


Figure 2: Density of state of C_{60} polymer-A (blue) and polymer-B (red).

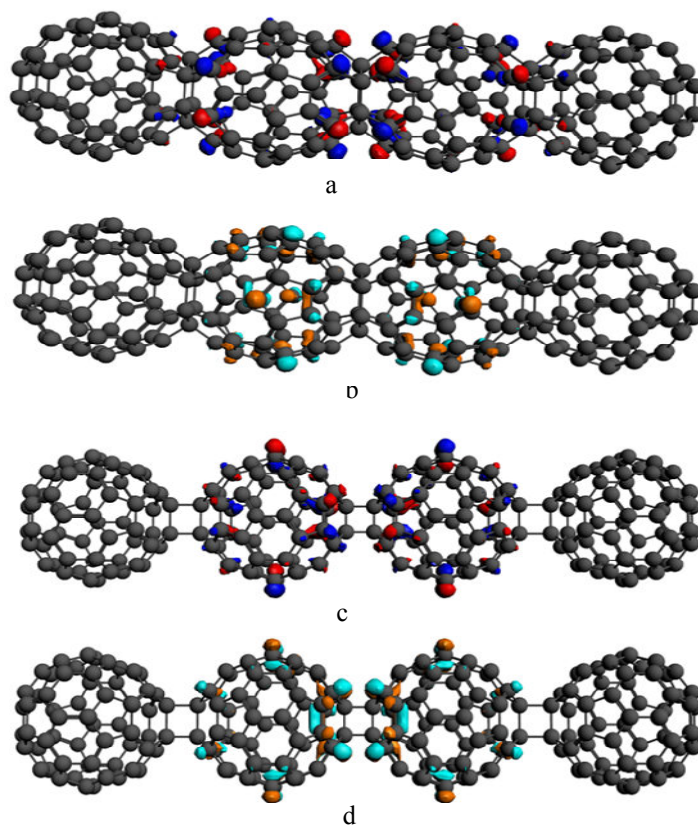


Figure 3: Frontier electronic states of C60 models. Polymer-A (a-HOMO, b-LUMO) and polymer-B (c-HOMO, d-LUMO).

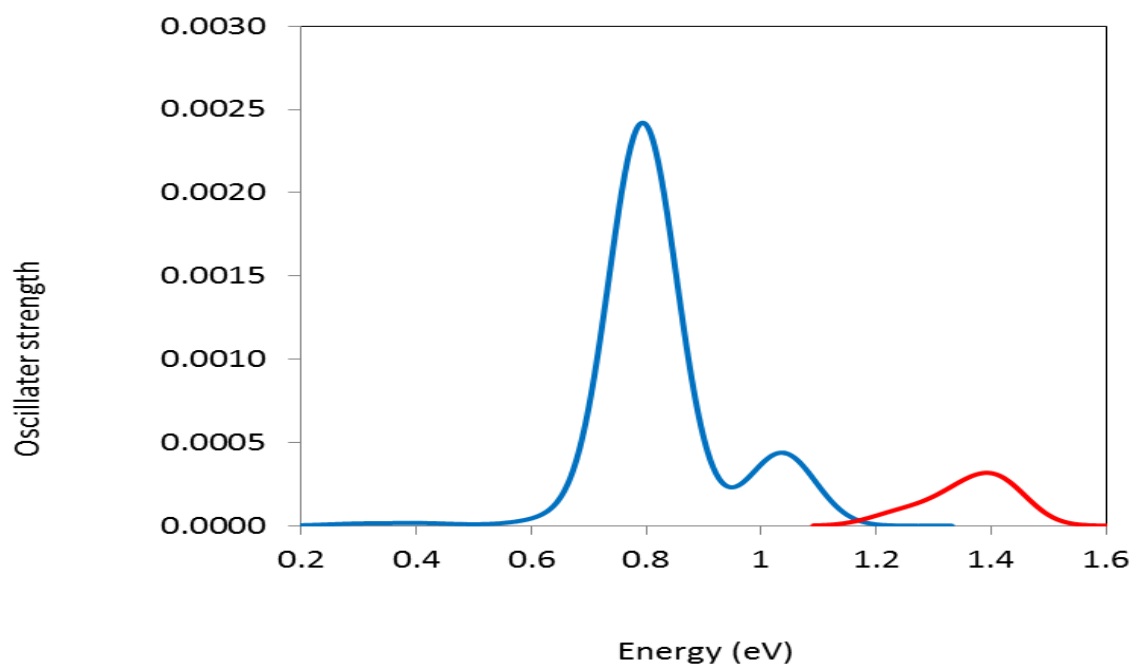


Figure 4: The electronic excitation of C60 polymers. Polymer-A (blue) and polymer-B (red).