



Revisit of polystyrene-modified fullerene core stars: A computational study



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ABSTRACT

Density functional theory (DFT) calculations have been used to clarify the number of poly(styryl) lithium anions that are grafted onto C_{60} fullerene. The computational results suggest that 6-arm-grafted C_{60} fullerene is the most thermodynamically favorable, and the grafted C_{60} fullerene with arms more than 6 is only achievable under certain circumstances. This observation is consistent with the previous experiments [Macromolecules 2013; 46:7451–57.]. Both electronic effect and steric effect have been thoroughly examined and they are found to play different roles in the arm-grafted C_{60} fullerene. The current study will pave a way for the future architecture of polymers on C_{60} fullerene and the like.

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1. Introduction

Since C_{60} fullerene was first detected in 1985 [1], its physical and chemical properties have been extensively investigated [2]. It is particularly interesting to incorporate C_{60} fullerene with a polymer matrix because it combines both the unique electronic properties of C_{60} fullerene and the well-known advantages of polymers in a single material. However, the poor solubility and incompatibility of C_{60} fullerene in polymers make such materials difficult to have practical applications.

As a multifunctional core molecule, C_{60} fullerenes have been used for the preparation of star-shaped polymers by grafting polymer or copolymer chains, in order to overcome the incompatibility between C_{60} and most polymers [3–7]. In 1992, Samulski and co-workers reported the reaction of poly(styryl) lithium (PSLi) with C_{60} fullerenes [3]. The experiments suggested that with the ratio of PSLi to C_{60} growing, the molecular weight of the product also increased, and the maximum number of arms is somewhere between 4 and 10. However, it had also been pointed out in the meantime by the authors that the Size Exclusion Chromatography (SEC) had the inherent limitations to characterize branched materials. Years later,

Ederle and Mathis produced narrow monomodal C_{60} core stars under the high purity conditions when C_{60} was reacted with either PSLi or poly(isoprenyl) lithium (PILi) in nonpolar solvents, such as toluene [4]. Determined by SEC coupled with Light Scattering (LS), the maximum number of grafted chains per C_{60} core was found to be six for both PSLi and PILi. The limitation to six grafted arms is attributed to the charge delocalization of the six carbanions on the six pyracyclene units of the C_{60} core, resulting in the less favorable addition of more than six arms owing to the strong Coulombic repulsion between negative charges on the same pyracyclene unit [6]. However, very recent experiments by temperature gradient interaction chromatography (TGIC) [8–14] observed the C_{60} core stars with greater than six arms [15].

Although there have been plentiful studies on the arm-grafted C_{60} fullerene both experimentally and theoretically [3–8,15–17], several questions still remain: why 6-arm-grafted C_{60} core star is observed in every experiments with the most abundance; why greater than 6-arm-grafted C_{60} core star is only observed by the latest experiments; how the arms are grafted on C_{60} fullerene. In this work, we aim to systematically study the relationships between the grafted arms and C_{60} fullerene by DFT calculations. Different strategies will be adopted to build the arm-grafted C_{60} core star model. Thermodynamic results, alongside molecular orbital correlation, will be discussed for a thorough explanation on the experimental observations, in hope for providing guidance for future utilization of arm-grafted C_{60} core star.

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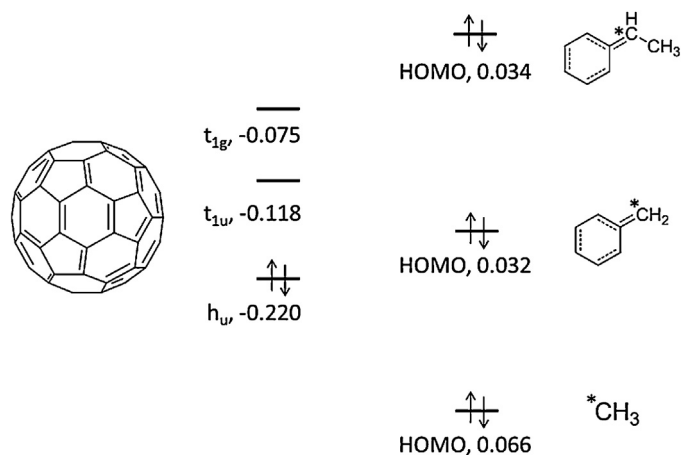


Fig. 1. HOMO, LUMO, and LUMO+1 of C₆₀ calculated at the B3LYP/6-31G(d) level of theory using Gaussian 09 [26], and HOMO of different model arms with orbital energy (a.u.) calculated at the B3LYP/6-31++G(d,p) level of theory; asterisk indicates where the lone pair electrons (HOMO) mainly locate.

2. Methods

DFT calculations were performed using the Vienna *ab initio* simulation package (VASP) [18–21], unless stated otherwise. The Kohn–Sham equations were solved using the projector-augmented wave (PAW) method [22,23] with the Perdew–Burke–Ernzerhof (PBE) exchange and correlation functional [24,25] within the generalized gradient approximation. Each structure was enclosed in a supercell with a size of $30 \times 30 \times 30 \text{ \AA}^3$, large enough to ensure a separation from its periodic image by at least 10 \AA . A kinetic energy cutoff of 400 eV was used for the plane-wave basis set. The Γ -point only sampling was used to describe the wave functions. The convergence criterion for the electronic self-consistent loop was set to 10^{-5} eV. During the structural optimizations, the lattice vectors of the supercell were fixed while all atoms were fully relaxed until the Hellmann–Feynman forces acting on them were smaller than 0.01 eV/\AA . The above computational setups have been validated in our previous work [15]. The final energies of the ion–electronic systems were used to calculate the total binding energies (TBEs) and the differential binding energies (DBEs) according to:

$$\begin{aligned} n\text{PS}^- (\text{arm}) + \text{C}_{60} (\text{core}) &\rightarrow (\text{PS})_n\text{C}_{60}^{n-} (\text{n-arm star}), \\ \text{TBE} &= E(\text{n-arm star}) - nE(\text{arm}) - E(\text{core}) \end{aligned} \quad (1)$$

$$\begin{aligned} \text{PS}^- (\text{arm}) + (\text{PS})_{n-1}\text{C}_{60}^{(n-1)-} ((n-1)\text{-arm star}) \\ \rightarrow (\text{PS})_n\text{C}_{60}^{n-} (\text{n-arm star}), \end{aligned} \quad (2)$$

$$\text{DBE} = E(\text{n-arm star}) - E(\text{arm}) - E((n-1)\text{-arm star})$$

3. Results and Discussion

The real system is (PS)_nC₆₀Li_n, which is formed upon each subsequent addition of PSLi to C₆₀. However, the real system is too large to perform *ab initio* calculations. To this end, we adopted similar simplifications as those in our previous work [15]. Briefly speaking, the arms (PS) are modeled by small organic groups, such as methyl (Me), C(C₆H₅)H₂ (also as CPhH₂), and CPhMeH. It should be noted that these organic groups are all mono-anionic. These organic groups and C₆₀ are shown in Fig. 1, along with the relevant orbitals (HOMO: highest occupied molecular orbital; LUMO: lowest unoccupied molecular orbital). On the other hand, Li⁺ counterions are treated implicitly by adopting a homogeneous background charge

(+n) in the calculation, depending on the magnitude of the negative charge (−n) present on the anionic species, (PS)_nC₆₀^{n−}. The implicit treatment of counterions is a reasonable choice in light of the salt nature of the core star anions which may remain dissociated as an electrolyte.

It is the central issue which carbon atoms of C₆₀ the arms will attach. Two strategies will be discussed in the following. The first one is called “Consecutive”, short as “C”, and the other is called “Rearrangeable”, short as “R”. The basic assumption for both ideas is that the arms tend to minimize the steric repulsion from each other. Even though relatively small organic groups were used in our current study, it should be noted that the real arms (PS) are long chains, and thus steric constraint is quite significant. The difference between the two ideas is that for “C”, the N-th arm attaches the position with the minimum steric repulsion from all the previous N-1 arms, and will not move once it has bound to C₆₀; while for “R”, all the N arms will be allowed to adjust to minimize the steric repulsion. In mathematics, this comes to the aim of maximizing the distance between the attached carbon atoms of C₆₀. We also assume that C₆₀ maintains I_h symmetry during the model building, which avoids the complexity caused by the arms, and makes the modeling more straightforward.

Figs. 2 and 3 show the position/positions of C₆₀, labeled in red, which the arm/arms will attach for “C” and “R”, respectively. Since carbon atoms of C₆₀ are all identical, we just simply select one of them to start with. Considering the center of C₆₀ buckyball, the 2nd carbon atom is in the opposite position to the 1st one, like a linear molecule. “C” and “R” begin to be different from N=3. For “C”, these three carbon atoms form T-shape geometry, while for “R”, they are nearly trigonal planar. It should be reminded that C₆₀ buckyball is not a perfect sphere, so carbon atoms are not always in the ideal positions in geometry. When N=4, the four carbon atoms are almost square planar for “C”, but tetrahedral for “R”. For “C” at N=5, the five carbon atoms form square based pyramidal geometry, as the 1st - 4th carbon atoms on the same equatorial plane, and the 5th atom sitting on the polar point. For “R”, on the other hand, the five carbon atoms could be seen in two ways: either pseudo trigonal bipyramid if taking **a/b** or **c/d** in the axial positions and leaving the other three on the equatorial plane, or more distorted square based pyramid than in “C” if taking **e** in the apical position. “R” and “C” happen to be the same at N=6, as octahedral geometry. It is easy to understand the way to build those of N>6 for “C” from the octahedral geometry of N=6. It is mono-capped octahedral geometry for N=7, up to quadruple-capped octahedral geometry for N=10. The even-numbered carbon atoms are always in the opposite position to its precedent odd-numbered atom. It is interesting at N=12: one set of six carbon atoms comes from an outer conjunct circle of one six-membered ring, and anti-symmetric to the other respective set. For “R” at N=7, the seven carbon atoms form pseudo pentagonal bipyramid, as the **a/b** carbon atoms in the axial positions, and the other five atoms approximately on the equatorial plane. For N=8, it is a distorted square antiprismatic geometry: **a/b/c/d** on the same plane, and **e/f/g/h** on the other plane. For N=9, it is close to capped square antiprismatic geometry, derived from N=8 with the **i** carbon atom in the apical position. Similarly, it is biccapped square antiprismatic geometry for N=10, with the **i/j** carbon atom in the apical position. It is a distorted icosahedron for N=12, while for N=11, it is the combination of half of N=10 (**a/b/c/d/j**) and half of N=12 (**e/f/g/h/i/k**).

Based on the strategies discussed above, different arm-grafted C₆₀ core stars have been fully optimized, as shown in Supporting Information. Following Eqs. (1) and (2), the TBEs and DBEs were calculated from the total energies of the ion–electronic systems including mono-anionic arms (Me, CPhH₂, and CPhMeH), C₆₀, and (arm)_nC₆₀^{n−} where n ranges from 1 to 12, as seen in Fig. 4 (the

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