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Hydrogenation of Fullerene C$_{60}$: Material Design of Organic Semiconductors by Computation

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1. Introduction

1.1. Motivation

Carrier mobility [1] in organic semiconductors is one of the most important properties in the performance of organic light-emitting diodes (OLEDs), organic field-effect transistors (OFETs), and organic solar cells, which are expected to be used in next-generation technologies [2]. Organic semiconductors have the advantages of lightness, flexibility, and low cost. Therefore, research and development of new materials with chemical and thermal stability has recently been very active [3–6]. However, the wide variety of organic materials, which is generally a major advantage of these materials, has hindered the systematic research and development of novel materials. Thus, the establishment of design guidelines for new organic materials is a matter of great urgency.

Up till now, much effort has been made to understand theoretically the relationship between the structure and the carrier-transport properties of these materials [7–10]. Theoretical investigations can give reliable guidelines for the development of such new organic semiconductors. We have also been studying the quantum-chemical design of organic semiconductors based on fullerenes from both scientific and technological viewpoints [11–19]. C$_{60}$ derivatives (Figure 1) are very interesting from the viewpoint of practical use. Some types of C$_{60}$ derivatives are shown in the figure, and C$_{60}$ derivatives of types (a) and (b) have already been studied in our research group [11–19].

It is well known that C$_{60}$ is chemically and thermally stable, and its method of synthesis is also established. Carrier mobility of amorphous silicon is about $1\,\mathrm{cm^2 V^{-1} s^{-1}}$, so that a mobility above this value is desirable for organic semiconductors. However, hole mobility in C$_{60}$ film is in the order of $10^{-5}\,\mathrm{cm^2 V^{-1} s^{-1}}$ [20], so that C$_{60}$ has not been used as a hole-transport material (p-channel semiconductor). Thus, the main purpose of our previous studies [11–14, 17–19] was to improve the hole mobility of C$_{60}$ by chemical methods. There is the possibility
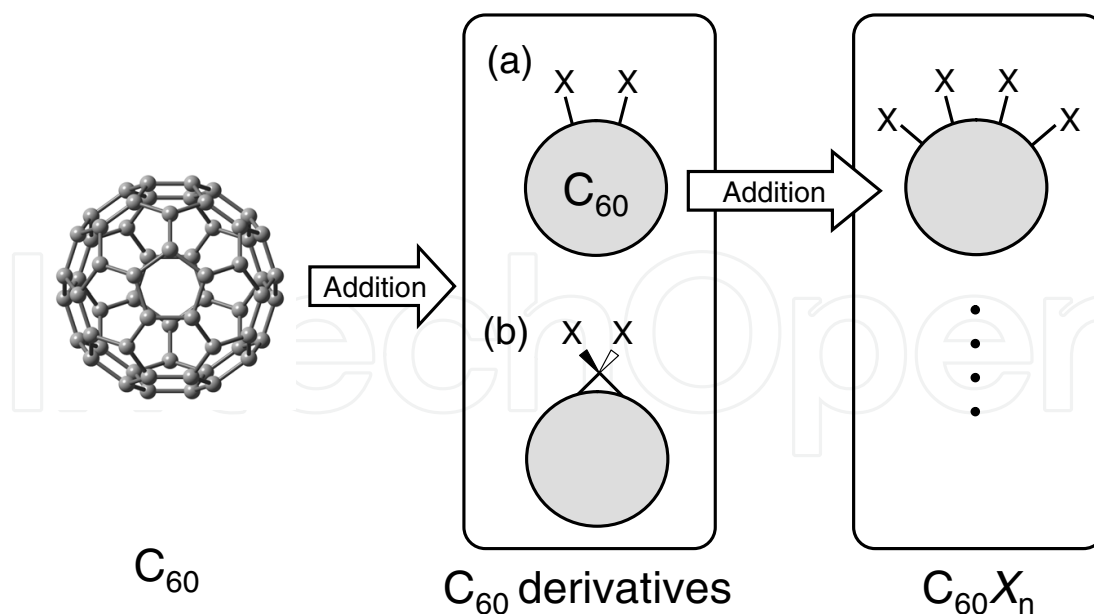
Figure 1. Fullerene C_{60} and some examples of C_{60} derivatives.

that the addition of hydrogen to C_{60} would result in a considerable modification of the C_{60} materials. This possibility originates from the fact that C_{60} has an electronic degeneracy in its cationic state because of its high symmetry I_h [21, 22], but C_{60} hydrides usually do not because of the reduction in symmetry by the addition of hydrogen. Electron mobility in C_{60} film is about $1\,cm^2V^{-1}s^{-1}$ [20, 23, 24] so that C_{60} is one of the most useful electron-transport materials. However, to achieve low-cost production and large-area devices, it is necessary for C_{60} materials to have a solution-processable form, such as [6,6]-phenyl C_{61}-butyric acid methyl ester (PCBM) [25]. Therefore, in organic electronics, the electronic properties of C_{60} derivatives rather than those of the original C_{60} are of much interest and importance.

Although ambipolar transport in [6,6]-phenyl-C_{71}-butyric acid methyl ester ([70]PCBM) was reported recently, its hole mobility ($2 \times 10^{-5}\,cm^2V^{-1}s^{-1}$) is much smaller than its electron mobility ($2 \times 10^{-3}\,cm^2V^{-1}s^{-1}$) [26]. Therefore, the enhancement of hole mobility is necessary for the practical use of fullerene derivatives as ambipolar transistor materials. Very recently, conduction-type control of fullerene C_{60} films from n- to p-type by doping with molybdenum(VI) oxide (MoO_3) was demonstrated [27]. Thus, analysis of the hole-transport properties of C_{60} derivatives is very important for the practical use of C_{60} materials.

1.2. Our previous publication: $C_{60}X_n$ (n = 2, 4, and 6)

In our previous publication [11], the effect on carrier-transport properties of chemical addition of X (X=H, R, R-COOH, and R-SH, where R is an alkyl chain) to C_{60} was systematically discussed from the viewpoint of reorganization energy (λ) using Marcus theory [28]. We focused on the C_{60} derivatives of type (a) in Figure 1, $C_{60}X_n$, where X is the added group and n is the number of added X. There are many isomers for $C_{60}X_n$, so that the position of X was also a subject of investigation. The dependence of carrier-transport properties on the type or chemical nature of X was discussed from the results of $C_{60}X_2$. The dependence of carrier-transport properties on the number of added groups was discussed from the results
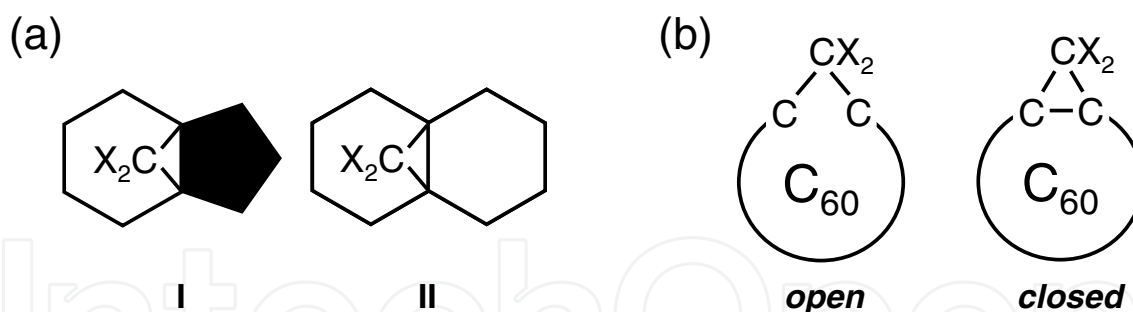
Figure 2. (a) Two addition patterns of CX_2. (b) Open and closed structures of C$_{60}$CX_2.

of C$_{60}$H$_n$ (n = 2, 4, and 6). From these discussions, guidelines for effective design of carrier-transport materials were proposed:

- Carrier-transport properties of C$_{60}$X$_2$ are quite different from those of C$_{60}$ [13–15, 18].

- Chemical addition can improve hole mobility of C$_{60}$ for some isomers [13, 14, 18]. Conversely, electron mobility of C$_{60}$ is not influenced or is decreased by the chemical addition [15].

- The values of reorganization energies of both hole transport and electron transport are almost independent of the type (chemical nature) of addition group X, but are strongly dependent on the position and the number of addition groups [15]. Therefore, reorganization energies of other types of C$_{60}$X$_2$ will be approximately estimated from the results of C$_{60}$H$_2$ [15].

- Hole and electron mobilities are closely related to the distribution patterns of the HOMO (highest occupied molecular orbital) and the LUMO (lowest unoccupied molecular orbital), respectively [13–15]. Delocalized orbitals give high carrier mobility (small reorganization energy) and localized molecular orbitals produce a low carrier mobility (large reorganization energy).

- There is a clear linear relationship between the reorganization energy and the geometrical relaxation upon carrier injection.

These results will also be applied to other types of X, and give us a guideline for efficient design of novel materials based on C$_{60}$ from both experimental and theoretical approaches. For example, in the experimental viewpoint, we can freely select an X that is appropriate for thin-film formation and is easily synthesized without considering the influence of X on the electronic properties. From the theoretical viewpoint, this result enables us to save computation time and resources in the material design because various types of C$_{60}$X$_2$ can be simplified to C$_{60}$H$_2$ in the prediction and discussion of these properties.

1.3. Our previous publication: C$_{60}$CX_2

In another of our publications [12], the effect of methylene bridging of C$_{60}$ by –CX_2 (X = H, halogen, R, R-COOH, and R-SH, where R is an alkyl chain) on carrier-transport properties was systematically discussed. There are two isomers for C$_{60}$CX_2, **I** and **II** (Figure 2). Systematic

analyses of reorganization energies of methylene-bridged fullerenes $C_{60}CX_2$ give us very important knowledge for the efficient design of useful C_{60} materials:

- Hole mobility of C_{60} is strongly influenced by methylene bridging. $C_{60}CBr_2$ (**II**) has the smallest reorganization energy (93 meV). On the other hand, $C_{60}CX_2$ (**I**) isomers with R, R-COOH, and R-SH chains have very large reorganization energies of about 500 meV.

- Electron mobility of C_{60} is not influenced or is decreased by methylene bridging [16].

- Values of reorganization energies of both hole transport and electron transport are dependent on the type (chemical nature) of X. Therefore, especially for the case of hole transport, reorganization energies of other types of $C_{60}CX_2$ will not be easily predicted from the results of $C_{60}CH_2$. This result is quite different from the case of $C_{60}H_2$ and $C_{60}X_2$.

- There is a clear linear relationship between the reorganization energy and the change in the distance between bridged $C\cdots C$ atoms.

- Hole and electron mobilities are closely related to the distribution patterns of the HOMO and the LUMO between bridged carbon atoms, respectively [16]. Small carrier mobility and large reorganization energy result from strong antibonding character between bridged carbon atoms.

One of the important findings in this work is that the properties of $C_{60}CX_2$ are dependent on the type (chemical nature) of X. This is because CX_2 addition directly changes the carbon network around the addition position. The possibility of a transformation between a *closed* structure and an *open* structure upon carrier injection is one of the reasons why the reorganization energy of $C_{60}CX_2$ is strongly dependent on the type of X. Therefore, the molecular design of type (b) molecules is a little more difficult compared with the molecular design of type (a) molecules, $C_{60}X_2$.

We also found that electron-transport properties are little influenced by the methylene bridging, so that we can freely select an X that is appropriate for thin-film formation and is easily synthesized without considering the effect of X on the electronic properties. On the other hand, when constructing high-mobility hole-transport materials, the use of isomer **I** of $C_{60}CX_2$, which includes an alkyl chain with -CH$_3$ and -COOH terminals, should be avoided.

1.4. This chapter

In this chapter, the effect of further hydrogenation of C_{60} on hole-transport properties is systematically discussed from the viewpoint of reorganization energy. We again focus on the C_{60} derivatives of type (a) in Figure 1. The dependence of hole-transport properties on the number and the position of hydrogen atoms is discussed from the results of $C_{60}H_n$ (n = 2, 4, 6, 8, 52, 54, 56, 58, and 60). From these discussions, guidelines for the effective design of high-performance carrier-transport materials of type (a) are proposed.

This chapter is organized as follows: In Section 2, the definition of λ and computational details of λ are presented. Synthesis methods of hydrogenated C_{60} are reviewed in Section 3. Structures of hydrogenated C_{60} molecules studied in this chapter are shown in Section 4. In Section 5, calculated results of λ for hole transport are shown. λ for electron transport is not
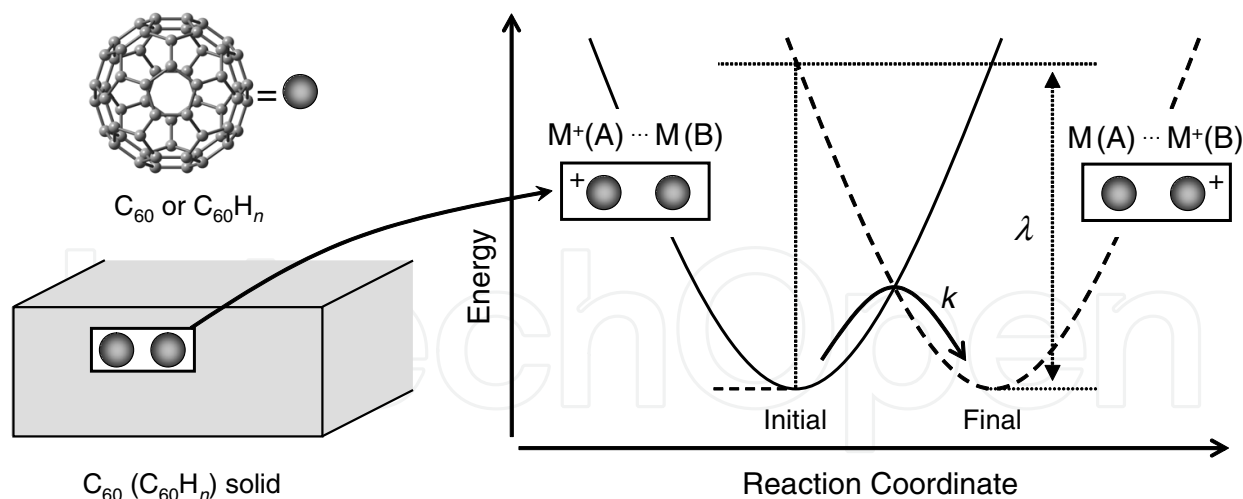
Figure 3. Schematic reaction diagram of a hole-transfer reaction $M^+(A) \cdots M(B) \rightarrow M(A) \cdots M^+(B)$.

discussed because it is expected that λ for electron transport is independent of the position and the number of hydrogen atoms. From the systematic discussion of these results, the dependence of λ on the position and the number of hydrogen atoms is shown in Section 6. Summarizing these discussions, simple guidelines for the efficient design of useful $C_{60}H_n$ semiconductors are proposed in Section 7.

2. Hole-transport mechanism

2.1. Hopping mechanism

The hole mobility of single-crystal C_{60} is around $10^{-5}\,\mathrm{cm^2V^{-1}s^{-1}}$ at a maximum. Materials having a mobility of $0.1-1\,\mathrm{cm^2V^{-1}s^{-1}}$ are categorized in the boundary region between the hopping and the band-transport mechanisms [29–31]. Therefore, in this chapter, only the hopping mechanism is considered because the hole mobility of C_{60} is much smaller than $0.1\,\mathrm{cm^2V^{-1}s^{-1}}$.

A schematic picture of hole hopping in an organic solid is shown in Figure 3. C_{60} and $C_{60}H_n$ molecules are represented by spheres in Figure 3. In the treatment of the hopping mechanism, two neighboring molecules are chosen from the solid. Then, a hole hopping between these two molecules, that is, the hole-transfer reaction, is considered. Repeating such a hopping between neighboring molecules, a carrier travels from one edge to the other edge of the organic solid. The initial and final states of a hole-transfer reaction are represented as $M^+(A) \cdots M(B)$ and $M(A) \cdots M^+(B)$. The system is fluctuating around the bottom of the potential curve as a result of molecular vibrations in its initial state. When the system occasionally reaches the transition state at which energies of the initial state and the final state are the same, the system jumps from the initial state to the final state with a rate constant k. This reaction is written as

$$M^+(A) \cdots M(B) \xrightarrow{k} M(A) \cdots M^+(B). \tag{1}$$
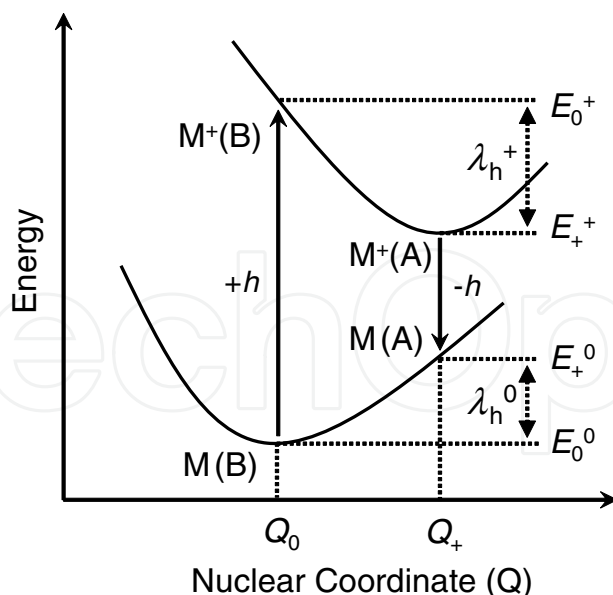
Figure 4. Schematic potential energy surfaces of molecules related to the hole-transfer reaction. Q_0 and Q_+ mean the nuclear coordinates of stable structures in neutral and cationic states, respectively. Subscripts on the right-hand side of E mean the geometrical structure of the molecule and superscripts on the right-hand side of E mean the charge on the molecule.

A localized hole on one molecule (A) jumps to the neighboring molecule (B). From the Marcus theory [28], the hole-transfer rate constant k of a homogeneous carrier-transfer reaction can be estimated from two parameters, the reorganization energy (λ), and the electronic coupling element (H) between adjacent molecules:

$$k = \frac{4\pi^2}{h} \frac{H^2}{\sqrt{4\pi\lambda k_B T}} \exp\left(-\frac{\lambda}{4k_B T}\right), \tag{2}$$

where k_B is the Boltzmann constant, h is the Planck constant, and T is the temperature of the system. We can see that a small λ, large H, and high temperature T result in a fast hole hopping.

2.2. Reorganization energy

From Figure 3, we can see that the reorganization energy is the difference between "the energy in the final state of the system with a stable nuclear configuration in the *final* state" and "the energy in the final state of the system with a stable nuclear configuration in the *initial* state". For the calculation of λ, potential energy diagrams of the hole-transfer reaction are shown in Figure 4. The values of λ are obtained by the following procedure: First, the geometries of neutral C_{60} and $C_{60}H_n$ were fully optimized, giving a nuclear coordinate Q_0 and energy E_0^0. At Q_0, single-point energy calculations of cations give E_0^+. Next, the structures were fully optimized in their cationic states, giving Q_+ and E_+^+. Single-point energy calculations of the neutral states with geometry Q_+ give E_+^0. The reorganization energy of the hole-transfer reaction (λ_h) is defined as the sum of λ_h^+ and λ_h^0:

$$\lambda_h = \lambda_h^+ + \lambda_h^0, \tag{3}$$

where λ_h^+ and λ_h^0 are relaxation energies in the cationic and neutral states, respectively, estimated from

$$\lambda_h^+ = E_0^+ - E_+^+, \tag{4}$$

$$\lambda_h^0 = E_+^0 - E_0^0. \tag{5}$$

2.3. Rate constant

In this chapter, the calculation and analysis of λ_h are focused on. The electronic-coupling element for hole transport (H_h) can be approximated by one half of the molecular orbital energy splitting between the HOMO and the next HOMO of the neutral dimer [3, 32]. However, the values of H_h are dependent on both the distance and the relative orientation between the two molecules. Therefore, H_h is assumed to be the same for C_{60} and all $C_{60}H_n$ for ease of discussion in this work [33]. Therefore, we cannot know the numerical values of the rate constants k_h. Instead, we define k_h' as a ratio of the rate constant of $C_{60}H_n$ to that of C_{60} at $T = 300$ K. The values of k_h' for hole transport are calculated as

$$
\begin{aligned}
k_h' &= \frac{k_h^{C_{60}H_n}}{k_h^{C_{60}}} \\
&= \left(\frac{H_h^{C_{60}H_n}}{H_h^{C_{60}}}\right)^2 \cdot \sqrt{\frac{\lambda_h^{C_{60}}}{\lambda_h^{C_{60}H_n}}} \cdot \exp\left(-\frac{\lambda_h^{C_{60}H_n} - \lambda_h^{C_{60}}}{4k_B T}\right) \\
&\approx \sqrt{\frac{\lambda_h^{C_{60}}}{\lambda_h^{C_{60}H_n}}} \cdot \exp\left(-\frac{\lambda_h^{C_{60}H_n} - \lambda_h^{C_{60}}}{4k_B T}\right)
\end{aligned}
\tag{6}
$$

on the supposition that $H_h^{C_{60}H_n} \approx H_h^{C_{60}}$. Hereafter, we regard k_h' as the hole mobility. The values of k_h' are usually calculated using Equation 6 in this chapter.

All calculations (geometrical optimizations and self-consistent field (SCF) energy calculations) necessary to obtain the values of the energies in Figure 4 were performed by a quantum-chemical method, namely, density functional theory (DFT) using the B3LYP functional. For the calculation of λ_h, the 6-311G(d, p) basis set was adopted. All neutral (ionic) systems were calculated in singlet (doublet) states. Calculations were performed using the GAUSSIAN 03 [34] program package.

3. Hydrogenation of fullerene

Although the main topic of this chapter is a theoretical discussion of hydrogenated fullerenes, synthesis methods of hydrogenated fullerenes are also important for practical use. Up to now, many types of hydrogenated fullerenes have been synthesized. Hydrogenated fullerenes, $C_{60}H_2$, $C_{60}H_4$, and $C_{60}H_6$, have been prepared by hydroboration [35, 36], hydrozirconation [37], rhodium-catalyzed hydrogenation [38], diimide [39] and hydrazine [40] reduction, dissolving metal reduction [41, 42], photoinduced-electron-transfer

reduction with 10-methyl-9,10-dihydroacridine [43, 44], and ultrasonic irradiation in decahydronaphthalene [45]. In many cases, a mixture of C_{60}, $C_{60}H_2$, and $C_{60}H_n$ ($n > 2$) is obtained [46]. Birch reduction [47] and transfer hydrogenation [48] of C_{60} produce $C_{60}H_{18}$ and $C_{60}H_{36}$. In the ruthenium-catalyzed hydrogenation, other types of $C_{60}H_n$ ($n = 10$, 12, 34, 36, 38, and 40) were observed using a field-desorption (FD) mass spectrometer [49]. Direct hydrogenation of C_{60} was achieved without the use of a catalyst by exposing solid-phase fullerenes to high-pressure hydrogen gas, and many types of $C_{60}H_n$ ($n = 2-18$) were identified by laser-desorption Fourier-transform mass spectrometry [50]. Unfortunately, highly hydrogenated fullerenes discussed in this chapter, $C_{60}H_{52} - C_{60}H_{60}$, have not been synthesized.

4. Isomers of hydrogenated fullerenes

4.1. Low hydrogenation: $C_{60}H_2 - C_{60}H_8$

There are 23 isomers for $C_{60}H_2$ [51]. 11 isomers of Figure 5(a) with a small formation energy were selected to consider the possibility of synthesis. The ground state of these isomers is the singlet state. Other isomers that are not considered in this chapter have triplet ground states in semiempirical calculations [51]. The initial hydrogen atom of $C_{60}H_2$ is already shown in the figure. The second hydrogen atom is added to one of the carbon atoms labeled 1–11. These isomers are named **1–11** in boldface. As predicted by Matsuzawa *et al*. [51] from quantum-chemical calculations, two isomers, **1** from 1,2-addition and **5** from 1,4-addition, have been synthesized [35, 39]. Furthermore, isomer **1** has been synthesized by many different methods [52].

Although there are a total of 4190 isomers for $C_{60}H_4$ [53], we consider eight isomers originating from two H_2 additions to [6,6]-ring fusions (see Figure 5 (b)) [54]. In other words, these isomers result from 1,2-addition to $C_{60}H_2$-**1**. In Figure 5 (b), the second H_2 pair is added to one of the carbon atom pairs labeled 1–8 and these isomers are named **1–8**. Experimentally, some of the eight isomers have been synthesized, and four isomers (**1**, **4**, **6**, and **8**) among them were identified [36, 39–41, 55–57].

Among a total of 418470 isomers of $C_{60}H_6$ [53], we consider only 16 isomers in Figure 5 (c) originating from one H_2 addition to $C_{60}H_4$-**1** at a [6,6]-ring fusion. One hydrogen pair is added to one of the carbon atom pairs labeled 1–16 and these isomers are named **1–16**.

We consider only six isomers of $C_{60}H_8$ in Figure 5 (d) originating from H_2 addition to $C_{60}H_6$-**1** at a [6,6]-ring fusion. One hydrogen pair is added to one of the carbon atom pairs labeled 1–6 and these isomers are named **1–6**.

4.2. High hydrogenation: $C_{60}H_{52} - C_{60}H_{60}$

As highly hydrogenated fullerenes, we consider $C_{60}H_{52}$, $C_{60}H_{54}$, $C_{60}H_{56}$, $C_{60}H_{58}$, and $C_{60}H_{60}$. $C_{60}H_{60}$ has I_h symmetry. We consider 11, 8, 16, and 6 isomers for $C_{60}H_{58}$, $C_{60}H_{56}$, $C_{60}H_{54}$, and $C_{60}H_{52}$, respectively. For these highly hydrogenated isomers, hydrogenated carbon atoms in Figure 5 are to be considered the nonhydrogenated carbon atoms.
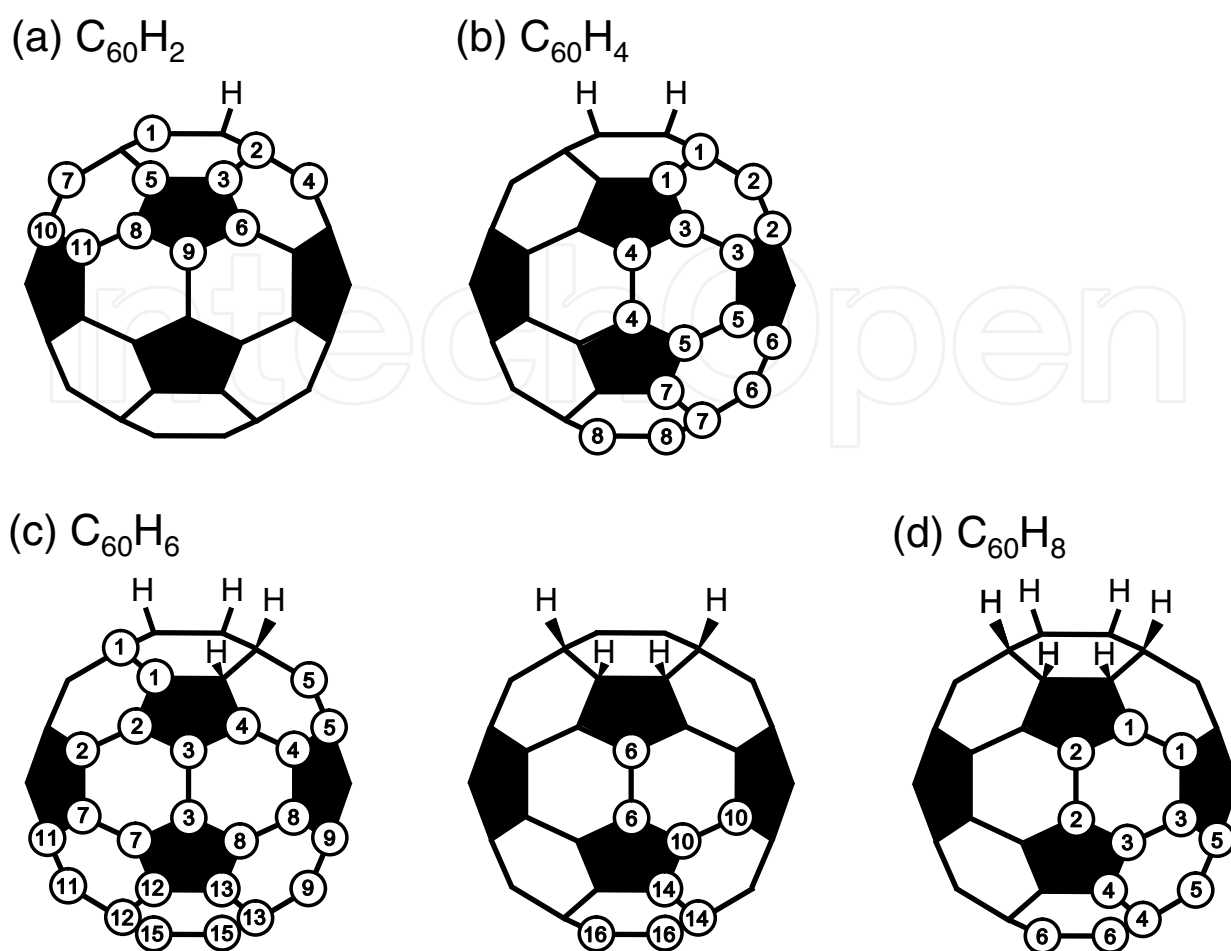
Figure 5. Isomers of (a) $C_{60}H_2$, (b) $C_{60}H_4$, (c) $C_{60}H_6$ (2 figures), and (d) $C_{60}H_8$. Hydrogen atoms are bonded to the labeled carbon atoms. Figures (a), (b), (c), and (d) also correspond to isomers of $C_{60}H_{58}$, $C_{60}H_{56}$, $C_{60}H_{54}$, and $C_{60}H_{52}$, respectively.

5. Reorganization energies and rate constants

5.1. C_{60}

The electronic structure of C_{60}^+ has been investigated both experimentally and theoretically because of its electronic degeneracy [58, 59]. C_{60}^+ has an H_u degenerate electronic state so that symmetry lowering because of the Jahn–Teller effect [21] stabilizes C_{60}^+. The most stable structure of C_{60}^+ was calculated as having D_{5d} symmetry, and its λ_h^+ is 95 meV in our calculation. The result of λ_h^+ is qualitatively consistent with previous works based on the static Jahn–Teller effect [60–62] in which the values of λ_h^+ were calculated as 351 [60], 35 [61], and 71 meV [62]. The value of λ_h^0 of $C_{60}^+(D_{5d})$ was calculated as 74 meV. Thus, the reorganization energy of the hole transport, λ_h, is 169 meV. It should be noted that the value of λ_h^+ is much larger than that of λ_h^0. This result comes from the fact that geometrical relaxation in the ionic state is very large because of Jahn–Teller distortion [21]. The potential curves of the ionic states are expected to have larger curvature around the minima than that of the neutral state.

5.2. $C_{60}H_2 - C_{60}H_8$

On average, λ_h^+ of $C_{60}H_2$ is 84 meV, which is smaller than that of C_{60} by 11 meV and λ_h^0 of $C_{60}H_2$ is 90 meV, which is larger than that of C_{60} by 16 meV [12, 13]. The average value of λ_h of $C_{60}H_2$ (174 meV) is almost as large as that of C_{60} (169 meV). However, only the addition of two H atoms leads to the large difference in λ_h, 101–257 meV. It is interesting that six isomers of $C_{60}H_2$ (**1**, **4**, **5**, **6**, **8**, and **9**) have a smaller λ_h than C_{60}. In particular, isomer **6** has the smallest λ_h (101 meV), which is over 40% less than that of C_{60}. In addition, the k_h' of **6** is about 2.5 times as large as that of C_{60}. From the viewpoint of practical use, it should be noted that the values of λ_h for the two synthesized isomers, **1** and **5**, are 133 and 142 meV, respectively, which are about 20% smaller than that of C_{60}. The values of k_h' for these isomers are about 1.5 times as large as that of C_{60}. These results indicate that hydrogenation can be an effective method for modifying the hole-transport properties of C_{60}. Two synthesized isomers of $C_{60}H_2$, **1** and **5**, have potential utility as hole-transport materials. For almost all isomers of $C_{60}H_2$, λ_h^+ is almost equal to λ_h^0. This means that the potential curves of the ionic and neutral states have almost the same curvature around the minima because the hydrogenation removes the electronic degeneracy in ionic states of C_{60}.

On average, λ_h^+ of $C_{60}H_4$ is 65 meV, which is smaller than that of C_{60} by 30 meV and λ_h^0 of $C_{60}H_4$ is 68 meV, which is smaller than that of C_{60} by 6 meV [12, 14]. The average value of λ_h of $C_{60}H_4$ (134 meV) is much smaller than that of C_{60} (169 meV) and is almost as large as that of $C_{60}H_2$-**1** (133 meV). The addition of two H atoms to $C_{60}H_2$-**1** results in the large difference in λ_h, 83–183 meV. Seven isomers of $C_{60}H_4$ (**1**, **3**, **4**, **5**, **6**, **7**, and **8**) have smaller λ_h than C_{60}. Remarkably, the major product **1** has the smallest λ_h (83 meV), which is over 50% less than that of C_{60}. In addition, k_h' of **1** is 3.28 times as large as that of C_{60}, and more than twice as large as that of the synthesized $C_{60}H_2$-**1** [13]. Isomer **7** with the second smallest λ_h has a value for k_h' that is 2.83 times as large as that of C_{60}. Other identified isomers **4**, **6**, and **8** also have small λ_h (138, 150, and 126 meV, respectively), and k_h' of these isomers are respectively 1.49, 1.26, and 1.74 times larger than that of C_{60}. Synthesized isomers of $C_{60}H_4$, especially the major product **1**, have potential utility as useful hole-transport materials.

On average, λ_h^+ of $C_{60}H_6$ is 61 meV, which is much smaller than that of C_{60} by 34 meV and λ_h^0 of $C_{60}H_6$ is 66 meV, which is smaller than that of C_{60} by 8 meV [12]. The average value of λ_h for $C_{60}H_6$ (127 meV) is much smaller than that for C_{60} (169 meV); however, it is much larger than that for $C_{60}H_4$-**1** (83 meV). Further addition of two H atoms to $C_{60}H_4$-**1** leads to a large difference in λ_h, 71–182 meV. 14 of the 16 isomers have smaller λ_h than C_{60}. Isomer **1** has the smallest λ_h (71 meV), which is about 60% less than that of C_{60}. In addition, k_h' of **1** is 3.94 times as large as that of C_{60}. Isomer **4** with the second smallest λ_h has a value of k_h' that is 3.22 times as large as that of C_{60}.

λ_h and k_h' of $C_{60}H_8$ are shown in Table 1. On average, λ_h^+ of $C_{60}H_8$ is 51 meV, which is much smaller than that of C_{60} by 44 meV, and λ_h^0 of $C_{60}H_8$ is 62 meV, which is smaller than that of C_{60} by 12 meV. The average value of λ_h for $C_{60}H_8$ (113 meV) is much smaller than that for C_{60} (169 meV); however, it is much larger than that for $C_{60}H_6$-**1** (71 meV). Further addition of two H atoms to $C_{60}H_6$-**1** leads to a large difference in λ_h, 81–175 meV. Five of the six isomers have smaller λ_h than C_{60}. Isomer **5** has the smallest λ_h (81 meV), and k_h' of **5** is 3.39 times as large

$C_{60}H_8$	λ_h^+	λ_h^0	λ_h	k_h'
(C_{60})	95	74	169	1.00
1	57	72	128	1.69
2	37	50	86	3.09
3	81	94	175	0.92
4	55	68	123	1.82
5	36	45	81	3.39
6	41	42	84	3.23
Average	51	62	113	2.09

Table 1. Reorganization energies (λ_h in meV) and rate constants (k_h') for hole transport in $C_{60}H_8$. Values for the original C_{60} and an averaged value over the six $C_{60}H_8$ isomers are also shown.

as that of C_{60}. Isomer **6** with the second smallest λ_h has a value of k_h' that is 3.23 times as large as that of C_{60}.

5.3. $C_{60}H_{52} - C_{60}H_{58}$

λ_h and k_h' of $C_{60}H_{52}$ are shown in Table 2. On average, λ_h^+ of $C_{60}H_{52}$ is 122 meV, which is much larger than that of C_{60} by 27 meV, and λ_h^0 of $C_{60}H_{52}$ is 132 meV, which is much larger than that of C_{60} by 58 meV. The average value of λ_h of $C_{60}H_{52}$ (254 meV) is much larger than that of C_{60} (169 meV). Hydrogenation leads to a large difference in λ_h, 175–441 meV. Isomer **6** has λ_h as large as C_{60}.

$C_{60}H_{52}$	λ_h^+	λ_h^0	λ_h	k_h'
1	163	174	337	0.14
2	204	237	441	0.04
3	100	104	204	0.65
4	86	94	180	0.87
5	92	96	188	0.78
6	86	89	175	0.92
Average	122	132	254	0.36

Table 2. Reorganization energies (λ_h in meV) and rate constants (k_h') for hole transport in $C_{60}H_{52}$. The average value over six $C_{60}H_{52}$ isomers is also shown.

Values of λ_h and k_h' for $C_{60}H_{54}$ isomers are shown in Table 3. On average, λ_h^+ of $C_{60}H_{54}$ is 176 meV, which is much larger than that of C_{60} by 81 meV, and λ_h^0 of $C_{60}H_{54}$ is 181 meV, which is much larger than that of C_{60} by 107 meV. The average value of λ_h of $C_{60}H_{54}$ (357 meV) is much larger than that of C_{60}. It is interesting that the values of λ_h are in the range 254–397 meV and there is not so large a difference.

Values of λ_h and k_h' for $C_{60}H_{56}$ isomers are shown in Table 4. On average, λ_h^+ of $C_{60}H_{56}$ is 140 meV, which is much larger than that of C_{60} by 45 meV, and λ_h^0 of $C_{60}H_{56}$ is 154 meV, which is much larger than that of C_{60} by 80 meV. The average value of λ_h for $C_{60}H_{56}$ (294 meV) is

$C_{60}H_{54}$	λ_h^+	λ_h^0	λ_h	k_h'
1	122	132	254	0.36
2	182	190	372	0.09
3	192	196	388	0.08
4	187	177	363	0.10
5	182	187	368	0.10
6	214	184	397	0.07
7	174	186	360	0.11
8	176	180	356	0.11
9	158	170	328	0.15
10	188	194	382	0.08
11	183	187	369	0.10
12	178	187	364	0.10
13	164	174	338	0.14
14	160	185	345	0.13
15	184	179	363	0.10
16	179	188	367	0.10
Average	176	181	357	0.12

Table 3. Reorganization energies (λ_h in meV) and rate constants (k_h') for hole transport in $C_{60}H_{54}$. The average value over 16 $C_{60}H_{54}$ isomers is also shown.

much larger than that for C_{60}. The values of λ_h are in the range 230–501 meV. Isomer **2** has the largest λ_h of more than 500 meV.

$C_{60}H_{56}$	λ_h^+	λ_h^0	λ_h	k_h'
1	180	186	366	0.10
2	217	284	501	0.02
3	126	141	267	0.31
4	128	121	249	0.38
5	119	123	242	0.41
6	123	129	252	0.37
7	107	123	230	0.47
8	118	124	242	0.41
Average	140	154	294	0.23

Table 4. Reorganization energies (λ_h) and rate constants (k_h') for hole transport in $C_{60}H_{56}$. The average value over eight $C_{60}H_{56}$ isomers is also shown.

λ_h and k_h' of $C_{60}H_{58}$ are shown in Table 5. On average, λ_h^+ of $C_{60}H_{58}$ is 606 meV, which is much larger than that of C_{60} by 511 meV and λ_h^0 of $C_{60}H_{58}$ is 468 meV, which is much larger than that of C_{60} by 394 meV. The average value of λ_h of $C_{60}H_{58}$ (1074 meV) is much larger than that of C_{60}. It is interesting that the values of λ_h are in the range 392–2411 meV. Isomers **1**, **2**, and **4** have smaller λ_h.

C$_{60}$H$_{58}$	λ_h^+	λ_h^0	λ_h	k'_h
1	205	263	467	0.03
2	196	214	409	0.06
3	1323	1089	2411	0.00
4	184	208	392	0.08
5	1235	607	1842	0.00
6	704	478	1182	0.00
7	693	513	1206	0.00
8	585	463	1049	0.00
9	543	458	1001	0.00
10	444	366	810	0.00
11	556	488	1044	0.00
Average	606	468	1074	0.00

Table 5. Reorganization energies (λ_h) and rate constants (k'_h) for hole transport in C$_{60}$H$_{58}$. The average value over 16 C$_{60}$H$_{58}$ isomers is also shown.

These results mean that highly hydrogenated C$_{60}$H$_{52}$ − C$_{60}$H$_{58}$ are generally not suited for hole-transport materials.

5.4. C$_{60}$H$_{60}$

C$_{60}$H$_{60}^+$ has nine electrons in fivefold degenerate h_u orbitals. Thus, C$_{60}$H$_{60}^+$ has an H_u degenerate electronic state, and symmetry lowering because of the Jahn–Teller effect [21] stabilizes C$_{60}$H$_{60}^+$. The most stable structure of C$_{60}^+$ was calculated as having D_{3d} symmetry, and its λ_h^+ is 101 meV in our calculation. The value of λ_h^0 for C$_{60}^+$(D_{3d}) was calculated as 40 meV. Thus, the reorganization energy for hole transport, λ_h, is 140 meV. Similar to C$_{60}$, λ_h^+ is much larger than λ_h^0 because of the Jahn–Teller effect. k'_h of C$_{60}$H$_{60}^+$ is 1.44 times as large as that of C$_{60}$.

5.5. Summary

Figure 6 shows minimum and average values of λ_h for C$_{60}$H$_n$. C$_{60}$ and C$_{60}$H$_{60}$ have only one isomer so that the minimum values are equal to the average values. From the systematic discussion through C$_{60}$H$_n$ (n = 2, 4, 6, and 8), it was found that hydrogenation has a large effect on the improvement of hole-transport properties (λ_h). The minimum values of λ_h decrease as the number of hydrogen atoms increases: C$_{60}$ (169 meV) → C$_{60}$H$_2$-**6** (101 meV) → C$_{60}$H$_4$-**1** (83 meV) → C$_{60}$H$_6$-**1** (71 meV). However, λ_h increases for C$_{60}$H$_8$-**5** (81 meV). The average values of λ_h change as C$_{60}$ (169 meV) → C$_{60}$H$_2$ (174 meV) → C$_{60}$H$_4$ (134 meV) → C$_{60}$H$_6$ (127 meV) → C$_{60}$H$_8$ (113 meV). The average λ_h of C$_{60}$H$_4$ (134 meV) is almost as large as that of C$_{60}$H$_2$-**1** (133 meV), but the average λ_h of C$_{60}$H$_6$ (127 meV) is much larger than that of C$_{60}$H$_4$-**1** (83 meV), and the average λ_h of C$_{60}$H$_8$ (113 meV) is much larger than that of C$_{60}$H$_6$-**1** (71 meV). Highly hydrogenated C$_{60}$H$_n$ generally has large λ_h. The average λ_h is C$_{60}$H$_{52}$ (254 meV), C$_{60}$H$_{54}$ (357 meV), C$_{60}$H$_{56}$ (294 meV), C$_{60}$H$_{58}$ (1074 meV), and C$_{60}$H$_{60}$ (140 meV). Only C$_{60}$H$_{60}$ has a smaller λ_h than C$_{60}$.
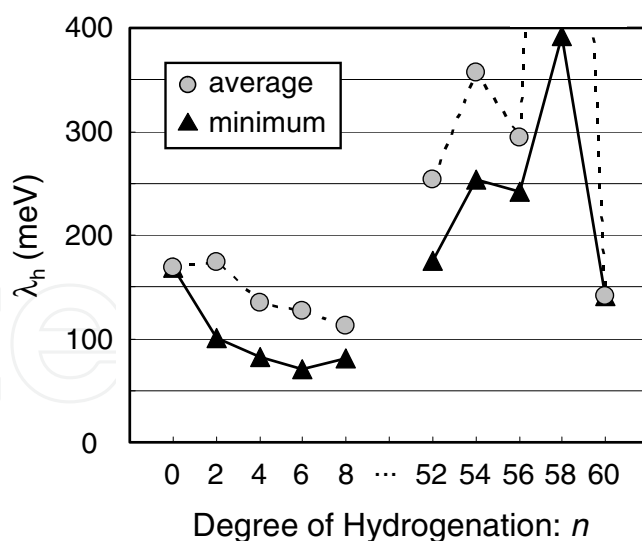
Figure 6. Dependence of minimum and average values of λ_h on the degree of hydrogenation. The average value of λ_h for $C_{60}H_{58}$ is very large (1074 meV), therefore it is not shown in the figure.

6. Analysis for molecular design

6.1. Geometrical relaxation

The reorganization energy is a stabilization energy by geometrical relaxation originating from the change in electronic structure [64–66]. The strong forces on the nuclei generally result in large λ and geometrical relaxation. In our previous publications, we defined parameters Δr that characterize the geometrical relaxation as

$$\Delta r = \sum_i |\Delta r_i|, \tag{7}$$

where Δr_i is the difference in the ith bond length between neutral and cationic states. The summation is taken over all bonds. It has already been shown that there is an almost linear relationship between Δr and λ_h for $C_{60}H_n$ (n = 2, 4, and 6) [11]. Figure 7 shows the relationship between λ and Δr for hole transport in $C_{60}H_8$, $C_{60}H_{52}$, $C_{60}H_{54}$, $C_{60}H_{56}$, $C_{60}H_{58}$, and $C_{60}H_{60}$. A linear relationship between Δr and λ_h is observed for $C_{60}H_8$ and $C_{60}H_{58}$. A clear linear relationship is not found for $C_{60}H_{52}$, $C_{60}H_{54}$, and $C_{60}H_{56}$ because the values of the reorganization energy for these species are almost the same. When the values of Δr are the same, $C_{60}H_8$ has a smaller reorganization energy but $C_{60}H_{58}$ has a larger reorganization energy.

6.2. Molecular orbital pattern

It is well known that the electronic properties of the HOMO have a close relation to hole-transport properties. Therefore, we focus on the distribution of the HOMOs of $C_{60}H_n$. The HOMO of C_{60}, which is originally fivefold degenerate, splits because of the interaction between C_{60} and the H atoms. The distribution of the HOMO easily changes depending on the interaction between C_{60} and the H atoms.

Figure 7. Relationship between reorganization energy (λ) and geometrical relaxation (Δr) for hole transport in $C_{60}H_n$ ($n = 8, 52, 54, 56, 58,$ and 60).

The HOMOs of isomer-**1** of $C_{60}H_n$ are shown in Figure 8. The HOMOs of $C_{60}H_8$-**1** and other lowly hydrogenated fullerenes [11, 13, 14] are distributed over the whole molecule. In

Figure 8. HOMOs of isomer-**1** of $C_{60}H_n$.

contrast, the HOMOs of $C_{60}H_{52}$-**1**, $C_{60}H_{54}$-**1**, $C_{60}H_{56}$-**1**, and $C_{60}H_{58}$-**1** are localized around the nonhydrogenated C atoms. Therefore, highly hydrogenated C_{60} has a large reorganization energy. In particular, the HOMO of $C_{60}H_{58}$-**1** is localized on two carbon atoms, therefore the reorganization energy is very large. The HOMO of $C_{60}H_{60}$ is delocalized over the whole molecule because $C_{60}H_{60}$ has high symmetry, so that the value of λ_h is smaller than that for other highly hydrogenated fullerenes.

7. Summary

Systematic analyses of reorganization energies of hydrogenated fullerenes $C_{60}H_n$ (n = 2, 4, 6, 8, 52, 54, 56, 58, and 60) give us very important knowledge for efficient design of useful C_{60} materials:

- Considering only 1,2-addition, $C_{60}H_6$-**1** has the smallest reorganization energy (71 meV). Further hydrogenation does not reduce the reorganization energy.

- Highly hydrogenated fullerenes, especially $C_{60}H_{58}$, have very large reorganization energies because the HOMOs are localized around nonhydrogenated carbon atoms. Therefore, these C_{60} derivatives are not suited for hole-transport materials.

- However, $C_{60}H_{60}$ has a smaller reorganization energy than other highly hydrogenated fullerenes and C_{60} because the HOMO of $C_{60}H_{60}$ is distributed over the whole molecule.

- There is a linear relationship between the reorganization energy and the geometrical relaxation. When the values of Δr are the same, lowly hydrogenated fullerenes have smaller reorganization energies than highly hydrogenated fullerenes.

Acknowledgments

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