Highlight Review

Approaches to Size-selective Formation of Fullerenes by Cyclization of Highly Reactive Polyyne Chains

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Abstract

As an approach to size-selective formation of fullerenes, we developed a method based on the cyclization of reactive cyclic polyynes which were generated by [2 + 2] cycloreversion of [4.3.2]propellatriene units. This method was proven to work successfully for the first time for the formation of fullerene ions C_{60}^{+} and C_{60}^{-} in the gas phase. This protocol is useful for generation of a small three-dimensional carbon cluster ion C_{36}^{-} and a large fullerene C_{78}^{-}, as well.

◆ Introduction

Since the discovery of fullerene[1] and its preparative scale production,[2] the chemistry of fullerenes has been extensively developed. In contrast to the production methods based on vaporization of graphite by resistive heating,[2] arc discharge,[3] and laser irradiation,[4] nowadays fullerene mixture can be produced in a tons/year scale on a commercial basis by combustion of hydrocarbons in fuel-rich flames.[5] Although fullerenes with almost unlimited size and diverse symmetry properties are possible,[6] only a limited numbers of them have been isolated and even fewer have been characterized. Since large fullerenes are of interest in view of their small band gaps and their possible chiroptical properties, they are expected to fill the gap between fullerenes and nanotubes. Therefore, it is still important to develop rational synthetic methods of fullerenes which allow construction of the carbon cages in a size- and shape-selective manner. In addition, the total synthesis of fullerenes has been regarded as one of the greatest challenges in synthetic organic chemistry. The first attempt to the total synthesis of C_{60} fullerene was set up by Chapman's school as early as 1981, a time well before the first observation of C_{60},[1] and was documented in four Ph.D. theses.[7] One of their approaches is based on the ring closure by the McMurry coupling reaction of two molecules of triketone **1** containing 6 of the required 12 five-membered rings of C_{60}. Also, Rassat reported the synthesis of C_{45} fragment **2** possessing the partial framework of the C_{60} surface by the acid-catalyzed trimerization of a triindanone derivative.[8a] However, further transformation of **2** to C_{60} was not successful. Recently, Ferrier proposed a similar approach to construct C_{60} from a C_{45} fragment analogous to **2** (Chart 1).[8b]

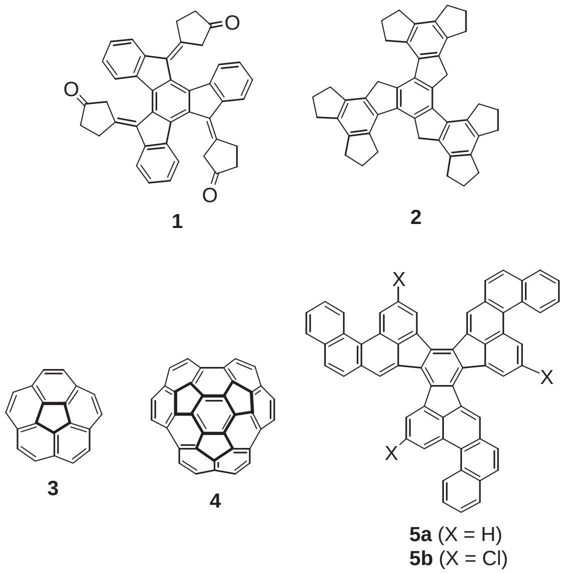

Chart 1.

As a conceptually similar but practically different approach to build up six-membered rings around five-membered rings by intramolecular C–C bond formation, Scott, Rabideau, and others have synthesized a number of bowl-shaped molecules called "bucky-bowls" or "fullerene fragments," of which the smallest unit is corannulene (**3**).[9] To date, the largest known fullerene fragment is $C_{36}H_{12}$ (**4**) synthesized by Scott under the condition of flash vacuum pyrolysis (FVP).[10] As a goal of this approach, synthesis of the molecules possessing 60 carbon atoms, a twisted $C_{60}H_{30}$ hydrocarbon **5a** and its derivative which represent an unfolded diagram of C_{60}, and their conversion into C_{60} were attempted.[11,12] In the event, Scott's group has shown that upon laser irradiation the threefold symmetric hydrocarbon **5a** converts into the C_{60}^{+} ion selectively in the gas phase by C–C bond formation accompanying dehydrogenation.[12a] Finally, they succeeded for the first time in the size-selective preparation of C_{60} by FVP of the related chlorohydrocarbon $C_{60}H_{27}Cl_3$ (**5b**).[12b] Even though the new synthesis provides C_{60} in no more than 1% yield, this achievement marked a milestone toward the size- and shape-selective synthesis of fullerenes.[13]

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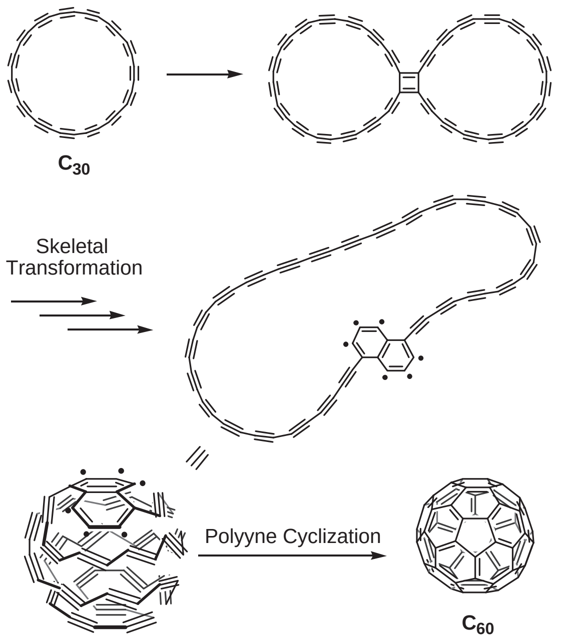
♦ Formation of C_{60} Fullerene by Polyyne Cyclization

Besides the total-synthetic approach, mechanism-based syntheses of C_{60} fullerene are conceivable. Though the mechanism that leads to formation of fullerenes is not well understood,[14] cyclic polyynes are regarded as most viable precursors of fullerenes on the basis of the mass spectrometric experiments for small- to medium-sized carbon clusters.[15] Diederich and co-workers observed the size-selective formation of fullerene C_{60}^{+} through the gas-phase coalescence of the cyclic polyyne C_{30}^{+}, which was produced size-selectively from a well-defined precursor by laser desorption (LD) mass spectrometry.[16] Roskamp and Jarrold proposed a fascinating mechanism for the C_{60} fullerene formation from two molecules of C_{30}, which was based on the ring formation between spiraling polyyne chains at the final stage (Scheme 1).[15b] It should be pointed out that they also predicted that the polyyne cyclization of some appropriate precursors would form larger fullerenes as well through similar cyclization pathways illustrated in Scheme 1.



Scheme 1. A speculated mechanism based on cyclization of polyyne chains leading to C_{60}.

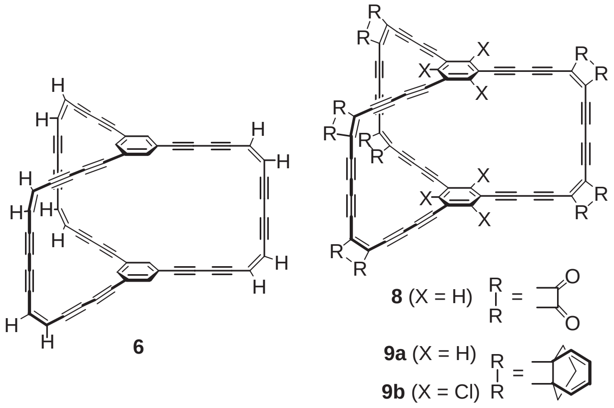
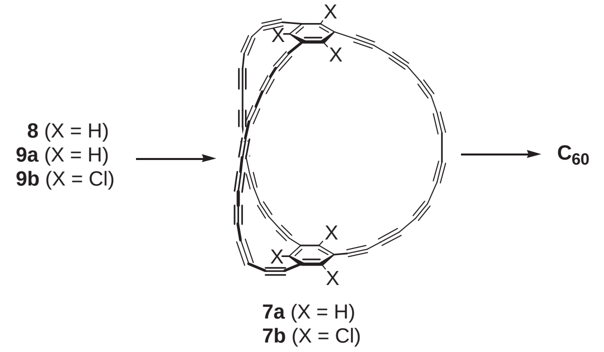


Chart 2.



Scheme 2.

Inspired by the polyyne cyclization mechanism, Rubin's and our groups embarked independently a project to synthesize C_{60} fullerene from appropriate three-dimensional (3D) polyynes. First, Rubin and co-workers prepared $C_{60}H_{18}$ (**6**), made up from two benzene rings and three C_{16} enyne bridges (Chart 2).[17] In the MALDI FT (matrix assisted laser desorption ionization Fourier transform) negative-ion mass spectra of **6**, partial dehydrogenation down to $C_{60}H_{14}^{-}$ was observed, suggesting the possibility of complete dehydrogenation to C_{60} from precursors of higher degree of unsaturation. Another precursor $C_{60}H_6$ (**7a**), with three C_{16} polyyne chains, was deemed too reactive for isolation. Rubin and co-workers, therefore, prepared relatively stable 3D cyclophane **8**, possessing cyclobutenedione units, to generate **7a** by multiple decarbonylation. As expected, in the negative mode LD ICR (ion cyclotron resonance) mass spectrum of **8**, not only $C_{60}H_6^{-}$ (**7a$^-$**) but also a strong peak due to C_{60}^{-} were observed, suggesting that cyclization of the polyyne chains accompanied by dehydrogenation had taken place efficiently to form the fullerene cage.[18] On the other hand, our route to **7a** made use of the [2 + 2] cycloreversion strategy, which was employed successfully for the generation of highly reactive polyynes like cyclo[*n*]carbons.[19] Thus, we prepared 3D cyclophanes **9a** and its hexachloro derivative **9b** as precursors of **7a** and **7b**, respectively (Scheme 2).[20] Gratifyingly, the positive mode LD time-of-flight (TOF) mass spectrum of **9a** exhibited a peak due to C_{60}^{+} formed by extrusion of six indane fragments and six hydrogen atoms. Moreover, the LD TOF mass spectrum of hexachloro derivative **9b** exhibited a very strong peak due to C_{60}^{+} without any signal due to $C_{60}Cl_6^{+}$ (Figure 1a). It also showed weak peaks due to C_2-loss down to C_{50}^{+} and those up to C_{120}^{+}, the latter being formed by an ion-molecule reaction of C_{60}^{+} and the subsequent fragmentation of the dimeric cluster ion. Although the molecular structure of the C_{60}^{+} fragments under the present experimental condition has not yet been clarified in any spectroscopic measurement, the observation of the C_2-loss fragmentation as being frequently quoted as evidence for the closed carbon-cage structure is suggestive of the icosahedral (I_h) structure for the C_{60}^{+} ions. The formation of C_{60}^{+} is facilitated by the donation of an electron to a chlorine atom, as supported by the observation of a strong Cl^{-} peak in the negative mode spectrum of hexachloro derivative **9b** as described below (Figure 1b). The negative mode LD TOF mass spectrum of **9a**, in contrast with the positive mode spectrum, showed a peak due to $C_{60}H_6^{-}$ (**7a$^-$**), formed by extrusion of all indane units. The mass spec-

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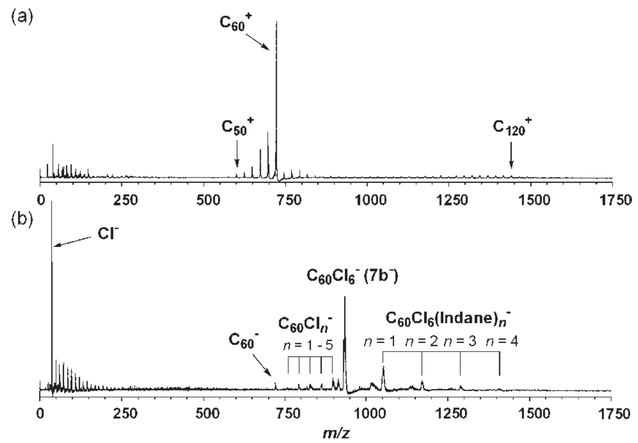
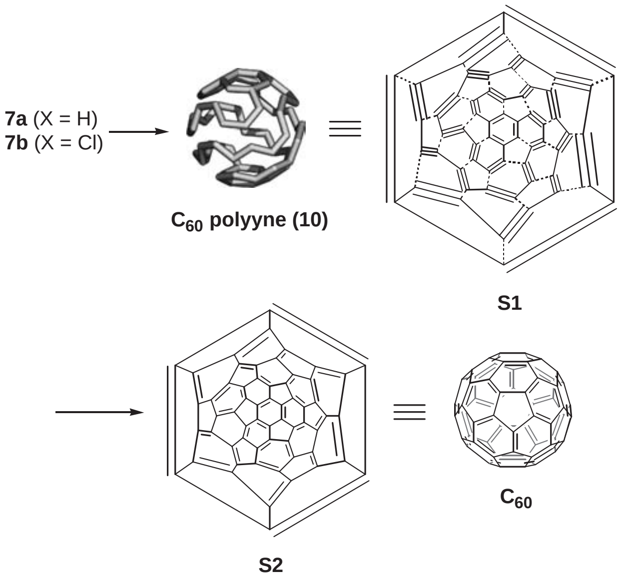


Figure 1. (a) Positive mode and (b) negative mode LD TOF mass spectra of $C_{60}Cl_6(Indane)_6$ (**9b**).

trum of **9a** also showed a small peak due to C_{60} anion formed by spontaneous removal of all hydrogen atoms from $C_{60}H_6^-$ (**7a⁻**), as judged from the isotope distribution of the spectrum. The negative mode spectrum of **9b** exhibited also a peak due to $C_{60}Cl_6^-$ (**7b⁻**), from which stepwise loss of chlorine atoms was observed, leading to C_{60}^- (Figure 1b). For considerations of a hypothetical mechanism of the cyclization reaction leading from the macrocyclic polyyne cage to the compact fullerene cage, the use of Schlegel diagram in Scheme 3 is helpful. When the macrocyclic polyyne **7a** or **7b** is twisted and folded so closely as to be forming new C–C bonds between the polyyne chains, the atoms in the molecule should have a spherical arrangement in space as C_{60} polyyne **10** in Scheme 3. The dotted lines in the Schlegel diagram **S1** are the C–C bonds to be formed to accomplish the formation of an I_h C_{60} cage. The donation of a pair of electrons from two triple bonds locating on different polyyne chains makes a C–C bond which bridges between the two sp-carbon chains. The successive formation of such bridging bonds (at the position of the dotted lines in **S1**) would result in the complete closure of the carbon cage into an all-sp^2-carbon cage of the fullerene structure as indicated in the Schlegel diagram **S2**. Even though neither we nor Rubin has yet succeed in the preparative scale synthesis of C_{60} by, for example, FVP of **8** or **9a** and **9b**, this method can be applied to the size-selective formation of small carbon clusters and large fullerenes, because the structure of the 3D polyynes, such as the length of the sp-carbon chains and their position of attachment to the benzene ring, can be modified. Moreover, the same method could be applied to the generation of $C_{58}N_2^-$ from a pyridine analog of **9a**, although the efficiency was low.[21]

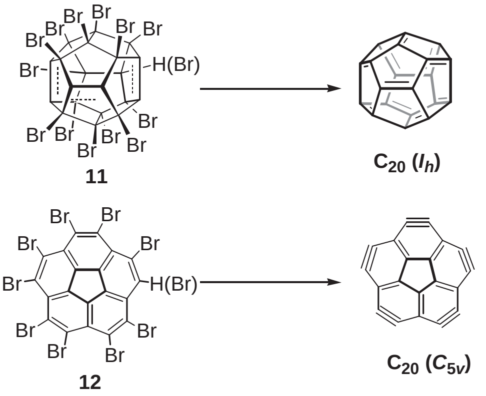


Scheme 3.

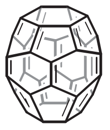
◆ *Application to Small Carbon Clusters*

There has been longstanding interest in relatively small carbon clusters in the field of spectroscopy and theoretical chemistry because of their structure and bonding and of their possible astrophysical significance.[22] From the extensive theoretical and spectroscopic studies, it has become apparent that the properties of the isomers of carbon clusters with a linear-, a cyclic-, or a caged form vary as a function of the cluster size.[23] As one of the experimental approaches to study the isomer-dependent properties, the small carbon clusters produced from an appropriate series of organic precursors of a well-defined structure have been utilized for spectroscopic investigations further. For example, Prinzbach demonstrated that cage- and bowl-shaped carbon cluster ions C_{20}^- (I_h) and C_{20}^- (C_{5v}), respectively, were selectively generated from the corresponding polybrominated precursors **11** and **12** (Scheme 4).[24] The structure of the cluster anions was characterized by UPS (ultraviolet photoelectron spectroscopy) in combination with the molecular orbital (MO) calculations. Piskoti et al. reported that C_{36} formed by arc discharged of graphite possess a cage structure with D_{6h} symmetry (Chart 3), which turned out to exist as a polymeric form in the solid state.[25] Soon after, Shinohara and co-workers succeeded in the isolation of C_{36} hydrides such as $C_{36}H_6$ that are produced by high-temperature laser ablation of metal-doped graphite.[26]

We attempted to form C_{36} in a size-selective manner from the polyyne precursors **14a** and **14b** under the mass spectrometric condition. Just as in the case of proposed transformation of multicyclic polyynes $C_{60}H_6$ and/or $C_{60}Cl_6$ into C_{60} fullerene, we envisioned that a similar cyclization of polyyne chains and subsequent dehydrogenation or dechlorination of polyyne-bridged paracyclophanes **13a** and **13b** would give D_{6h}-symmetric C_{36} (Scheme 5).[27] Polyynes **13a** and **13b** would be generated by laser irradiation of the corresponding cyclophanes **14a** and **14b**

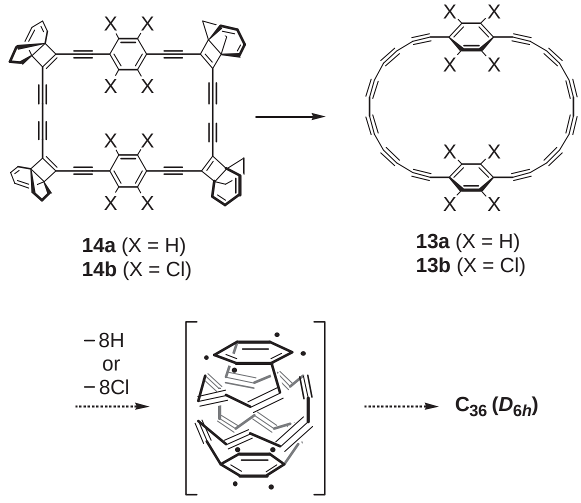


Scheme 4.



C_{36} (D_{6h})

Chart 3.



Scheme 5.

having the propellane units. Indeed, in the negative mode of LD TOF mass spectrum of **14a**, the [2 + 2] cycloreversion took place cleanly to form **13a$^-$**. Unlike the case of $C_{60}H_6^-$ (**7a$^-$**),[18,20] however, subsequent dehydrogenation to afford C_{36}^- was not observed, which can be ascribed to both thermodynamic and kinetic reasons. In contrast, the mass spectrum of the octachloro derivative **14b** exhibits not only the peaks due to $C_{36}Cl_6^-$ (**13b$^-$**) as shown in Figure 2 but also those due to the stepwise loss of chlorine atoms down to C_{36}^- analogously to the degradation of $C_{60}Cl_6^-$ (**7b$^-$**).[20] One might consider the extreme case that the cleavage of the C–H or C–Cl bonds is followed by the cage formation complete. We rather conceive of a dynamical picture that the H or Cl atom leaves off concertedly with the formation of a bridging C–C bond, i.e. cleavage on the sewing-up site. Since the intensity of the C_{36}^- signal is considerably larger than those of $C_{36}Cl^-$, $C_{36}Cl_2^-$, and $C_{36}Cl_3^-$, we conjecture that the dechlorination is accompanied by drastic skeletal rearrangement, which affords C_{36}^- with a cage structure.

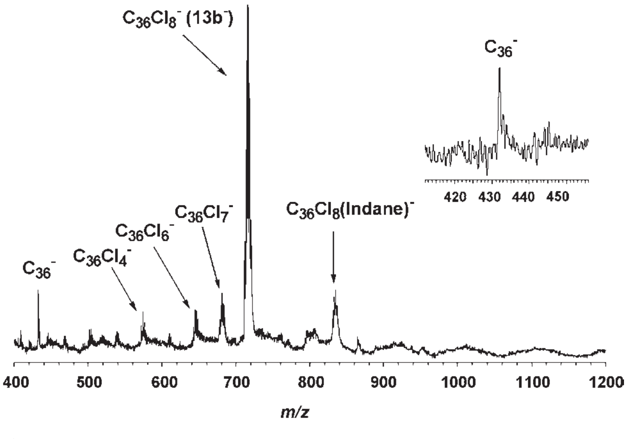
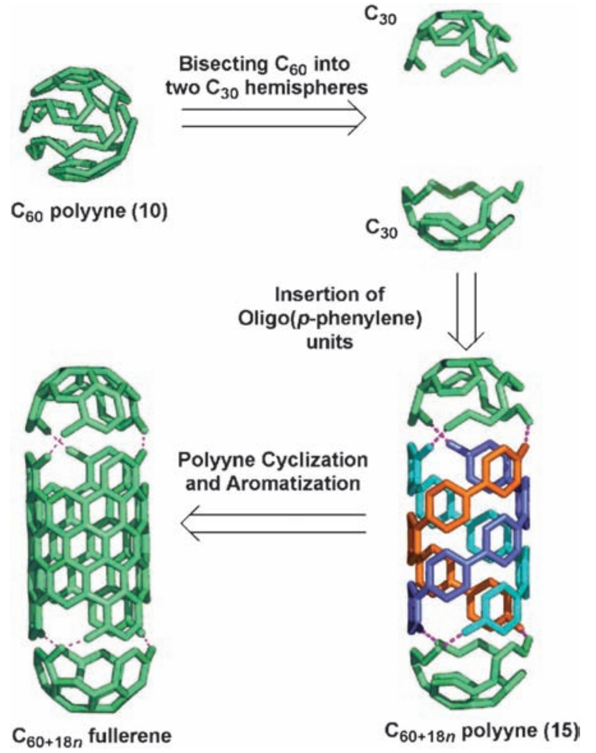


Figure 2. Negative mode LD TOF mass spectrum of $C_{36}Cl_8$-(Indane)$_4$ (**14b**). Inset: Expansion of the spectrum for C_{36}^-.

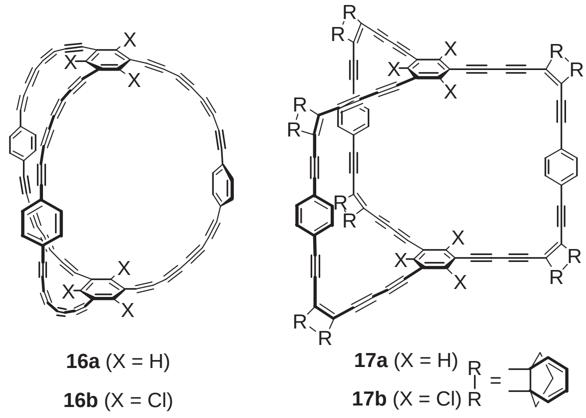
◆ *Application to Large Fullerenes*

In the conventional methods for the production of macroscopic amount of fullerenes,[2–5] fullerenes C_n larger than C_{70} form in relatively low yields and since they are obtained as hard-to-isolate mixtures of various isomers, the size-selective and isomer-selective formation of the large fullerenes are one of the most challenging issues. In this context, we planned to extend our polyyne cyclization approach to the size-selective formation of large fullerenes. We envisioned C_{60} polyyne **10** shown in Scheme 3 can be bisected into two hemispheres, namely, top and bottom (Scheme 6). The insertion of three oligo(*p*-phenylene) units between the two C_{30} hemispheres would result in C_{60+18n} polyyne **15** which would form C_{60+18n} fullerene by triggering cyclization at the reactive polyyne chains in the hemispheres as shown in Scheme 6 for $n = 5$. In order to prove this working hypothesis, we examined, as an initial step, the formation of C_{78} fullerene from the corresponding polyynes **16a** and **16b** having three benzene rings between the C_{30} hemispheres (Chart 4).[28] One of the possible cyclization modes is shown in Scheme 7 as a Schlegel diagram.

To this end, we successfully prepared 3D cyclophanes $C_{78}H_{18}$(Indane)$_6$ (**17a**) and $C_{78}H_{12}Cl_6$(Indane)$_6$ (**17b**), as precursors of polyynes $C_{78}H_{18}$ (**16a**) and $C_{78}H_{12}Cl_6$ (**16b**), respectively. The negative mode LD TOF mass spectra of **17a** and **17b** are shown in Figure 3. Laser ionization/desorption of **17a** leads principally to the formation of the negative ion of $C_{78}H_{18}^-$

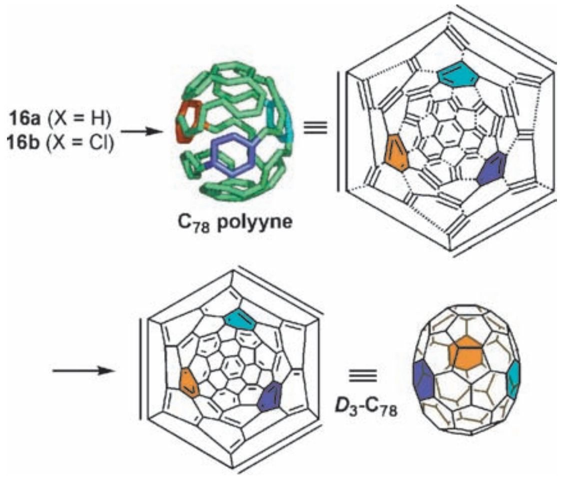


Scheme 6. A proposal for the formation of tubular fullerenes by triggering polyyne cyclization.



16a (X = H)
16b (X = Cl)
17a (X = H)
17b (X = Cl)

Chart 4.



Scheme 7. A speculation for the spiraling polyynes cyclization for $C_{78}H_{18}$ (**16a**) and $C_{78}H_{12}Cl_6$ (**16b**) to form C_{78}. The *p*-phenylene units inserted to the C_{30} hemispheres are indicated by shade.

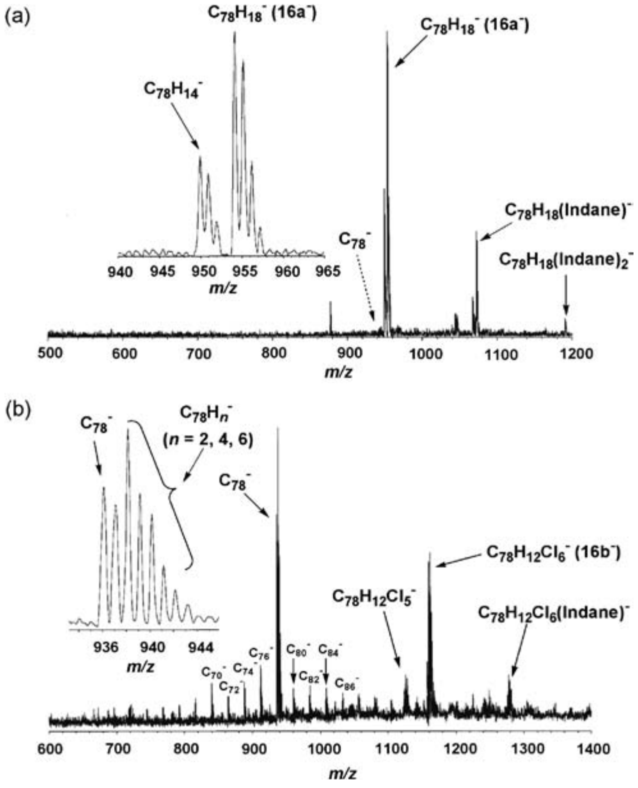
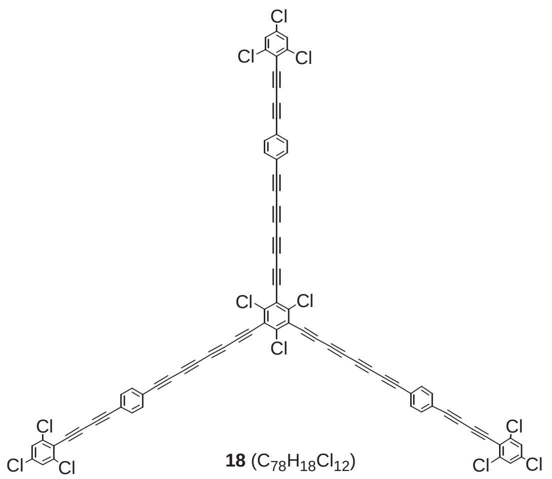


Figure 3. (a) Negative mode LD TOF mass spectrum of $C_{78}H_{18}(Indane)_6$ (**17a**). Inset: Expansion of the spectrum for $C_{78}H_{18}^-$ (**16a$^-$**) and $C_{78}H_{14}^-$ and (b) Negative mode LD TOF mass spectrum of $C_{78}H_{12}Cl_6(Indane)_6$ (**17b**). Inset: Expansion of the spectrum for C_{78}^- and $C_{78}H_n^-$ ($n = 2, 4,$ and 6).

(**16a$^-$**) by extrusion of six indane fragments from the parent molecule (Figure 3a). As shown in the inset of Figure 3a, the loss of four hydrogen atoms down to $C_{78}H_{14}^-$ was observed. However, in contrast to the anion $C_{60}H_6^-$ (**7a$^-$**) which loses six hydrogen atoms to form C_{60}^-,[18,20] the anions $C_{78}H_{18}^-$ (**16a$^-$**) and $C_{78}H_{14}^-$ are resistant to further elimination of hydrogen, indicating that the polyyne cyclization accompanying hydrogen losses is not kinetically favorable. In contrast, expulsion of most of the hydrogen and chlorine atoms took place simultaneously from the chlorinated anion $C_{78}H_{12}Cl_6^-$ (**16b$^-$**) generated by laser irradiation of the chlorinated precursor **17b** (Figure 3b). As shown in the inset of Figure 3b, the distribution of the peaks at m/z 936–944 indicates the presence of C_{78}^- together with $C_{78}H_2^-$ and $C_{78}H_4^-$ in which two or four hydrogen atoms are still intact. It is rather surprising that the hydrogen-containing anions such as $C_{78}H_2^-$ and $C_{78}H_4^-$ are resistant to dehydrogenation in spite of their high degree of unsaturation. Introduction of chlorine atoms in the *p*-phenylene units of the precursor **17b**, as well as collision-induced dissociation (CID) of the ion **16b$^-$**, would facilitate the polyyne cyclization–elimination, leading to C_{78} ions more efficiently. Though the molecular structures of $C_{78}H_2^-$ and $C_{78}H_4^-$ are not clear, the C_{78} ion is likely to have a fullerene-cage structure, because of the small peaks down to C_{70} in Figure 3b due to the C_2-loss fragmentation, which is of characteristic for the fragmentation channel of fullerene-cage molecules. Moreover, highly unsaturated 2D polyyne precursor **18** (Chart 5), having 78 carbon atoms, generated by laser irradiation of the corresponding precursor having three propellane units did not give a trace of C_{78} ion, suggesting the crucial role of the 3D structure for the polyyne cyclization to occur. Thus, even though the spectroscopic proof of the molecular structure of C_{78}^- re-



18 ($C_{78}H_{18}Cl_{12}$)

Chart 5.

mains to be established, the above experiments indicate the viability of the polyyne cyclization pathway for the large fullerene formation. Further extension of this method to C_{96}, the next fullerene of the C_{60+18n} series, is currently underway in our laboratories.

Summary and Future Outlook

As an approach to size-selective formation of fullerenes C_{36}, C_{60}, and C_{78}, we developed a method based on the cyclization of reactive cyclic polyynes which were generated by [2 + 2] cycloreversion of [4.3.2]propellatriene units. The structure of the fullerenes, including their geometries, would be elucidated by measuring ultraviolet photoelectron spectra of the mass-selected negative ions. For further investigations of the molecular structure and the physical and chemical properties, the preparative scale synthesis of fullerene molecules by this method has not yet been achieved; apparently a technology for large scale laser ionization/vaporization of organic solids has to be developed. It should be pointed out that, in view of the possibility to construct well-defined polyyne precursors, this method would be applicable to the size-selective formation of even larger fullerenes than C_{78}.

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