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Chapter 2

Rational Synthesis of Fullerenes

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Abstract

Fullerenes are a unique family of carbon-based cage molecules, which attract interest because of their remarkable properties and potential applications. Most effort so far has been focused on the study of C_{60} and C_{70}, whereas other members of the huge fullerene family remain poorly explored. One of the main challenges in this field is the developing of the synthetic methods, which are suitable for the production of these unique materials in isomer-pure form in macroscopic amounts. Here, we review studies toward the rational synthesis of fullerenes from molecular precursors that have been published to date. The scope and limitation of the zipping strategy are discussed. The relevance and prospects for construction of the fullerene cages and related carbon-based nanostructures via cyclodehydrofluorination (C—F bond activation) are highlighted.

Keywords: fullerenes, bottom-up synthesis, zipping approach, C—F bond activation

1. Introduction

Fullerenes represent a unique class of sp^2-carbon-based compounds with a spherical π-system, displaying intriguing physical and chemical properties [1, 2]. The conventional methods of fullerene production are based on various graphite evaporation techniques which result in the heterogeneous fullerene containing soot [1, 2]. Unfortunately, none of the existing techniques provide access to fullerenes in isomer-pure form, which is crucial for their possible applications. The random nature of the fullerene formation results in a highly heterogeneous mixture containing mainly the most stable C_{60}-I_h and C_{70}-D_{5h} cages. Both fullerenes can be rather easily obtained in pure form by single-step HPLC separation of the fullerene soot extract (**Figure 1**). So far, only these two fullerenes have been the subject of in-depth investigations although the fullerene family represents a huge class of carbon-cage molecules. As soon as C_{60} became available in bulk amounts, a number of unique properties such as superconductivity [3], ferromagnetism [4, 5],

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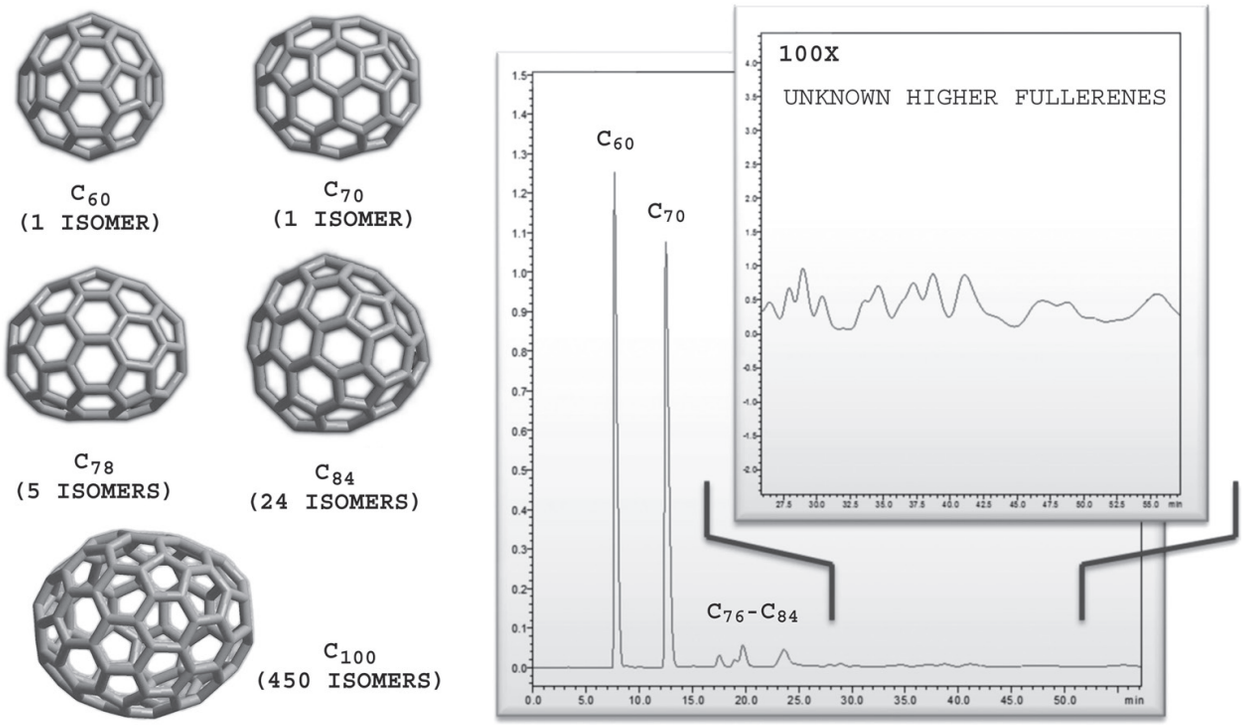


Figure 1. (Left) Several members of the fullerene family and the number of possible IPR isomers. (Right) Typical HPLC profile of the fullerene soot extract (Buckyprep column, toluene as eluent, UV detection). Two strong signals at 8 and 10 min correspond to C_{60}-I_h and C_{70}-D_{5h} fullerenes, which can be easily isolated. The fraction eluting between 17 and 25 min corresponds to abundant higher fullerenes—C_{76}-C_{84} (mixture of about 30 fullerene species). The huge number of small overlapping peaks (t_R > 28 min) corresponds to the mixture of a large number of unknown higher fullerenes.

and high electron affinity [6] have been disclosed. C_{60} and C_{70} fullerenes were found to be ideal material for the development of solar-energy conversion systems, in which the fullerene plays the role of effective electron acceptor [7]. Besides these two fullerene members, the fullerene soot typically contains about 1% of the so-called higher fullerenes (C2n with n > 35). In contrast to C_{60} and C_{70}, the higher fullerenes have several structural isomers obeying the isolated pentagon rule (IPR), stating that all pentagons have to be completely surrounded by hexagons [8]. Some of isomers of C_{76}-C_{84} can be obtained in small amounts by multi-step HPLC using recycling HPLC. However, the HPLC technique reaches its limit already on the separation of individual isomers of C_{84}. The separation of isomers of higher fullerenes with more than 84 carbon atoms is extremely complicated and these fullerenes remain highly unexplored (**Figure 1**). Moreover, the number of possible IPR isomers surges exponentially with increasing number of carbon atoms in the cage, which make the separation of higher fullerenes practically impossible. For example, C_{100} has 450 IPR isomers whereas for C_{200} the number of possible IPR isomers is 15.655.672. Furthermore, fullerenes that satisfy the IPR rule represent only a tiny fraction of possible carbon cages that in principle can be formed. Thus, C_{60} has 1811 non-IPR isomers whereas C_{200} has already more than 214 millions of isomers [8]. The non-IPR cages are remarkably less stable than IPR fullerenes, since adjacency of two pentagons resulted in high local strain and therefore high reactivity of these species. Nevertheless, it has been demonstrated that non-IPR cages exist and can be isolated at least in the form of exohedral or endohedral derivatives [9]. Furthermore, the possibility to introduce heteroatoms (heterofullerenes) [10], and/or to incorporate rings of

different sizes (non-classical fullerenes) into the carbon cage [11], provides virtually unlimited number of possible fullerene structures. Each individual fullerene molecule possesses its own set of unique properties such as HOMO-LUMO gap, electron affinity, optical and magnetic characteristics. Despite intense research in the fullerene field during last decades, only a small fraction of possible fullerenes has been isolated in pure form and characterized. The higher fullerenes, as well as non-IPR and non-classical cages remain poorly explored due to the extremely low content in the soot and difficulties connected with purification. Further development in this field requires alternative synthetic methods which are suitable for the macroscopic production of desired fullerenes in isomer-pure form.

2. The concept of the rational synthesis of fullerenes

Rational synthesis of fullerenes is of practical interest as a promising method for the synthesis of isomer-pure fullerenes, including fullerenes which cannot be obtained by conventional techniques. One of the first attempts of the "rational synthesis" of fullerenes was undertaken in 1993 [12]. It has been proposed that C_{60}-I_h fullerene cage can be constructed by the fusion of six naphthalene moieties. Indeed, small amounts of C_{60} were detected in the pyrolysis products of the naphthalene performed in the argon atmosphere at 1000°C [12]. The proposed mechanism suggests a step-by-step assembly of naphthalene molecules via cyclodehydrogenation leading to various oligo-naphthalenes. Some of hexamers with defined orientation of naphthalene fragments possess the required for C_{60} connectivity, and thus can act as a precursor of C_{60}. The intramolecular cyclization of such precursors should unambiguously lead to the C_{60} cage formation. One of the possible naphthalene hexamers ($C_{60}H_{28}$), which is likely to form C_{60} trough intramolecular condensation, is shown in **Figure 2**. The low yield of C_{60} in this case might be explained by the low probability of the formation of the naphthalene hexamer with required orientation of subunits during accidental condensation. Indeed, as it was shown later, the pyrolysis of properly connected oligo-naphthalene improves the C_{60} yield [13]. In spite of the fact that this hypothesis does not explain the simultaneous formation of C_{70}, which was also observed in the pyrolysis products (direct assembly of C_{70} from naphthalene fragments is impossible), the given mechanism suggests that fullerenes can be built from well-defined aromatic fragments—the so-called fullerene precursors. These polycyclic aromatic hydrocarbons (PAHs), already containing required carbon connectivity, appear to be the key intermediates which exhaustive cyclization should lead to the strictly predefined carbon cage. In 2001, this methodology was successfully employed by Scott et al. for C_{60} fullerene synthesis under laser ablation conditions [14]. The rigid C_{60} fullerene precursor, containing all 60 carbon atoms at required positions, was obtained through a multi-step organic synthesis and subjected to the LDI-induced "pyrolysis" (laser desorption ionization). According to MS analysis the LDI-induced cyclization led the formation of C_{60} (**Figure 2**) [14]. Although the cyclization was found to be rather inefficient, the demonstrated principal transformation of the preprogrammed PAH precursor to the desired carbon cage paves the way for the rational construction of the fullerenes and other related carbon-based nanostructures.

The general strategy of the rational synthesis of fullerenes is based on the synthesis of specially "designed" PAH-precursor molecules containing the carbon framework required for

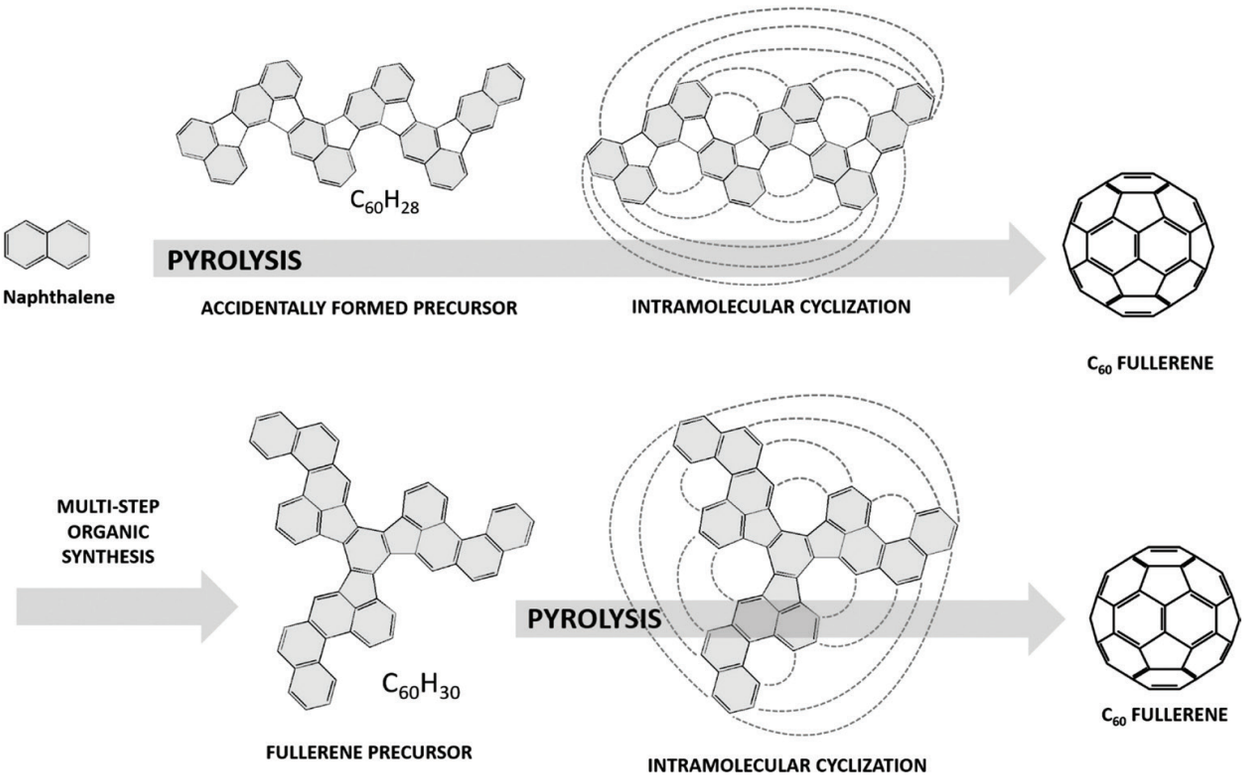


Figure 2. (Top) Schematic presentation of the C_{60} fullerene formation during naphthalene pyrolysis showing formation of the naphthalene hexamer as a key intermediate. (Bottom) Synthesis of C_{60} fullerene by zipping of the rigid atomically precise precursor under LDI conditions. The new C—C bond, which forms during cyclization, is coded by dashed lines.

the formation of the target fullerene cage. The respective precursor can be "zipped" to the desired fullerene by the tandem intramolecular Aryl—Aryl coupling. The characteristic feature of this approach is a zipper mechanism of cyclization in the final synthetic step. Since the regiospecificity of each condensation step can be strictly predefined by the precursor design, the cyclization will lead to the preprogrammed isomer of fullerene exclusively. This final cyclization step represents the key transformation in the rational synthesis of fullerenes by the zipping approach.

2.1. Wet-chemical synthesis

Since a big number of new C—C bonds have to be established during precursor zipping, the efficiency of each condensation has to be very high in order to achieve reasonable conversion. Unfortunately, methods developed for the synthesis of the planar PAHs via intramolecular Aryl–Aryl coupling are usually uneffective in the case of highly strained fullerenes. The strain energy of the fullerenes stems mainly due to pyramidalization of carbon atoms, as a result of deviation from energetically ideal values observed in graphene lattice. The perturbation of the π-system causes enormous enhancement of the energy, which has to be overcome during cyclization. Thus for example, various polyphenylenes can readily undergo an intramolecular cyclization under UV irradiation in the presence of an oxidant [15]. The photocyclization is an effective and frequently used technique for the synthesis of large planar polycyclic systems.

Alternatively, oxidative intramolecular cyclodehydrogenation can be carried out under Scholl condition [16]. Recently, this approach has become of high practical interest for the synthesis of large PAHs such as nanographenes and nanoribbons [17, 18]. Although both cyclodehydrogenation methods show excellent efficiency in the case of planar PAHs, these techniques appear to be not effective for the synthesis of bowl-shaped PAHs and fullerenes. Several alternative intermolecular aryl–aryl coupling techniques have been developed to overcome these disadvantages. Here the palladium(0)-catalyzed direct arylation utilizing bromo and chloro derivatives has been found to be effective for the synthesis of small fullerene fragments [19]. The largest fullerene fragments obtained so far contain 50 carbon atoms and formally represent more than 83% of the C_{60} fullerene surface (**Figure 3**) [20].

Although the largest synthesized C_{50} bowl is more curved than C_{60} [20], the rational synthesis of fullerene following this route still remains a challenge. This is mainly connected with difficulties to perform the Pd-catalyzed cyclization in a domino fashion. Secondly, the reaction conditions appear to be aggressive with respect to fullerene species. The recent discovery of effective intramolecular aryl–aryl coupling via C-F bond activation under transition-metal free conditions might be a solution to this problem. Recently, Siegel et al. [21], Ichikawa et al. [22], and Amsharov et al. [23, 24] have demonstrated the efficiency of the C—F bond activation strategy for the synthesis of various bowl-shaped PAHs via formal HF elimination step (cyclodehydrofluorination). In the last case, the effective cyclization was achieved utilizing easily accessible aluminum oxide, which makes the approach highly attractive for preparative-scale synthesis. Moreover, it has been found that intramolecular Aryl-Aryl coupling of fluoroarenes via γ-aluminum oxide-mediated C—F bond activation can be realized under mild conditions with unprecedentedly high chemoselectivity [25, 26]. Using this technique an extended bowl-shaped PAHs representing more than 75% of the C_{60} fullerene connectivity was obtained with close to quantitative yield (**Figure 4**) [24], demonstrating high potential for generating extended nonplanar carbon-based nanostructures including fullerenes. Although the rather big fullerene fragments can be successfully produced by wet-chemical methods, the solution-synthesis of fullerenes remains a challenge.

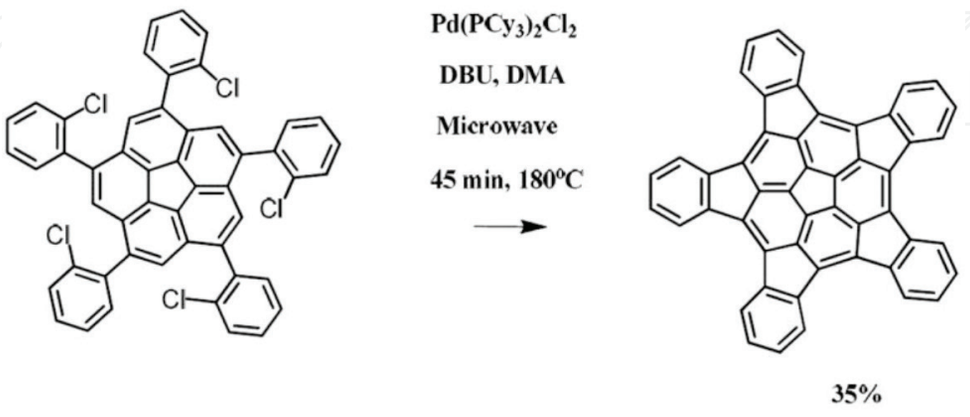


Figure 3. The synthesis of bowl-shaped PAH (C_{60} fullerene fragment) by Pd-catalyzed microwave-assisted intramolecular arylations.

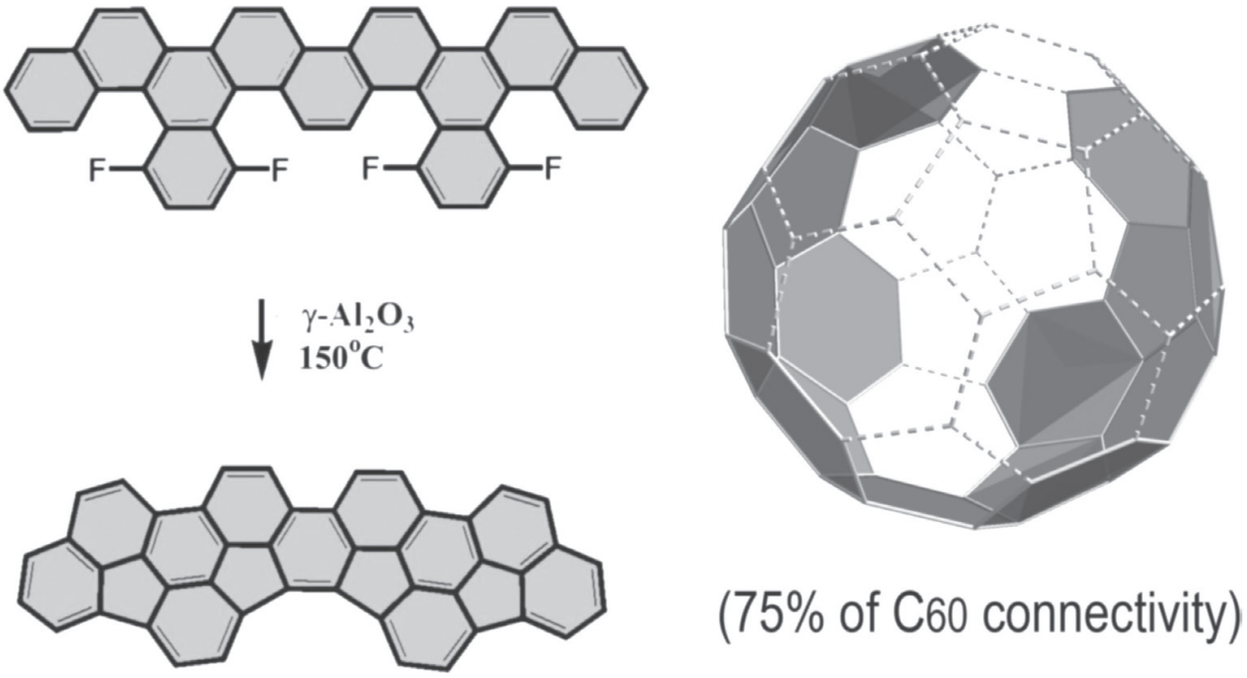


Figure 4. (Left) Synthesis of the extended fullerene fragments via alumina-assisted cyclodehydrofluorination. (Right) Superposition of C_{60} fullerene (dashed lines) and buckybowl (highlighted by gray) structures showing the same atom topology.

2.2. Surface-assisted synthesis

The direct on-surface synthesis of nanostructures is a highly promising strategy. The on-surface studies are usually conducted on single-crystal surfaces under ultra-high vacuum conditions that offer extraordinary degree of control in the experiments [27]. Moreover, the usage of atomically clean and flat crystal surfaces allows the observation of the reaction process at the single molecule level by means of scanning tunneling microscopy (STM) [28]. Recent progress in this field demonstrates a high potential for the synthesis of complex architectures via Aryl-Aryl coupling of organic precursors on single-crystal metal surfaces [29, 30]. In the case of planar PAHs, the intramolecular cyclodehydrogenation can be performed effectively on Cu(111), Ag(111), and Au(111) surfaces. Intramolecular cyclization on Au(111) surfaces typically occurs at around 400°C [31]. On the more reactive copper surfaces, cyclization takes place earlier at 200°C [32]. However, attempts to perform a similar cyclization to form non-planar PAHs were unsuccessful because of the intermolecular merging of the precursor molecules. Therefore, the synthesis of fullerenes requires harder conditions, including using more reactive Pt-group metal surfaces and applying higher temperatures of 450–600°C [33]. The first surface-assisted synthesis of the bowl-shaped PAH was reported by Rim et al. on the example of the hemispherical PAH C_{48}, which was generated on the Ru(0001) surface via exhaustive cyclodehydrogenation of hexabenzocoronene precursor (**Figure 5**) [34]. The six-fold cyclodehydrogenation on the periphery of precursor was achieved by annealing of the precursor molecule at 600°C. Note that Ru surface serves not only as a catalyst for the cyclodehydrogenation it also prevents intermolecular coupling due to efficient bonding to the surface. Finally, the Ru surface acts as a support for precursors and products enabling STM investigation. The STM analysis has

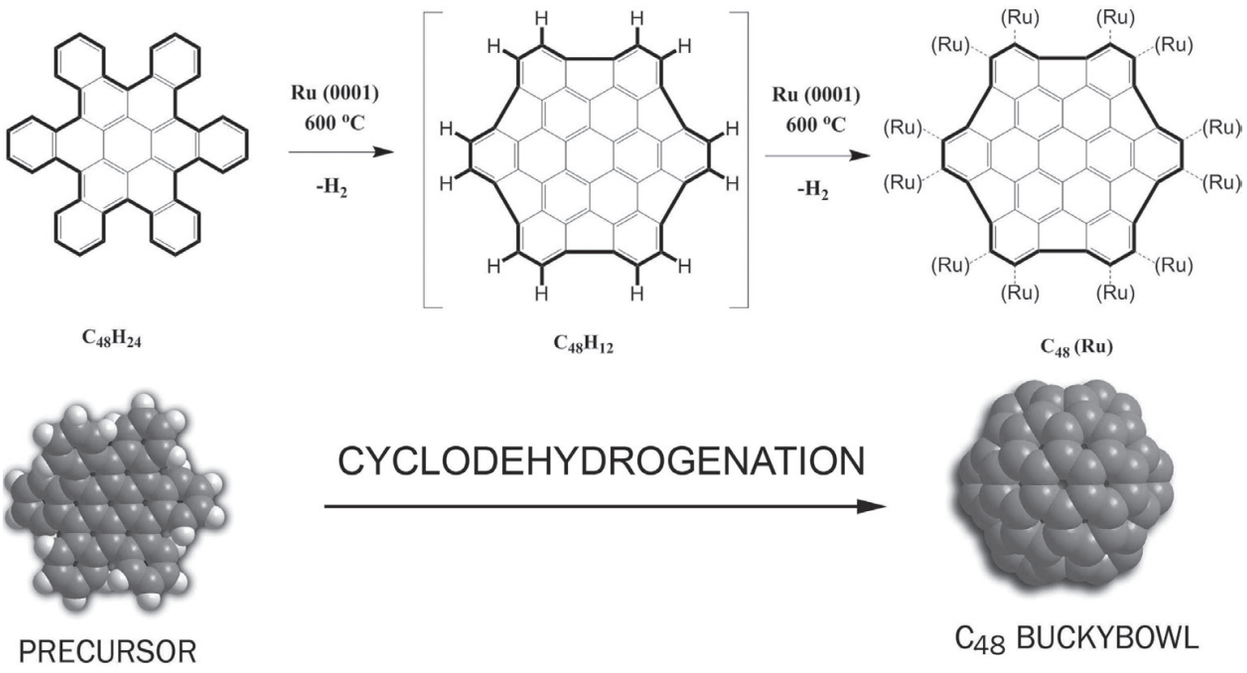


Figure 5. Surface-assisted synthesis of the hemispherical C_{48} buckybowl via exhaustive cyclodehydrogenation of hexabenzocoronene on Ru surface at 600°C.

revealed a high selectivity and exceptionally high conversion ratio of the deposited precursors into non-planar PAH structure (**Figure 5**). However, due to high reactivity of the Ru surface and high temperature applied, the dehydrogenation process does not stop on the formation of the $C_{48}H_{12}$ bowl. The bowl-shaped PAH undergoes further dehydrogenation resulting in all-carbon C_{48} bowl covalently bonded to the Ru surface by 12 C—Ru bonds (**Figure 5**) [34].

Soon after, the efficiency of the surface-assisted approach has been demonstrated by Otero et al. on the synthesis of C_{60} fullerene on Pt surface [35]. In their study, $C_{60}H_{30}$ fullerene precursor molecules (**Figure 6**, precursor A) were deposited onto a Pt(111) surface and annealed at around 480°C. The annealing step led to the formation of C_{60} cages with an efficiency close to 100%. The STM analysis shows that the molecular coverage does not change during temperature-induced reaction, and all of the precursor molecules converted into fullerenes [35]. Later it was shown that the process is highly selective in nature and is not accomplished by skeletal rearrangements. This important question has been addressed by the investigation of surface-catalyzed cyclodehydrogenation of a specifically designed precursor molecule (**Figure 6**, precursor B) "preprogrammed" to the formation of the C_{60}-bowl-shaped PAH with unique triangular shape [36]. The on-surface cyclodehydrogenation of two isomeric $C_{60}H_{30}$ precursors (**Figure 7**) gave convincing evidence that the reaction occurs in a highly selective manner [36]. In contrast to the condensation of the precursor A whose cyclodehydrogenation leads to the spherical C_{60}, the zipping of the precursor B resulted in a triangular-shaped C_{60}-bowls whose formation was distinguished by the STM analysis.

Those works demonstrated that the surface-assisted cyclodehydrogenation on Pt-group metal surfaces is highly selective and can be used for fabrication of various specifically designed carbon-based nanostructures including fullerenes.

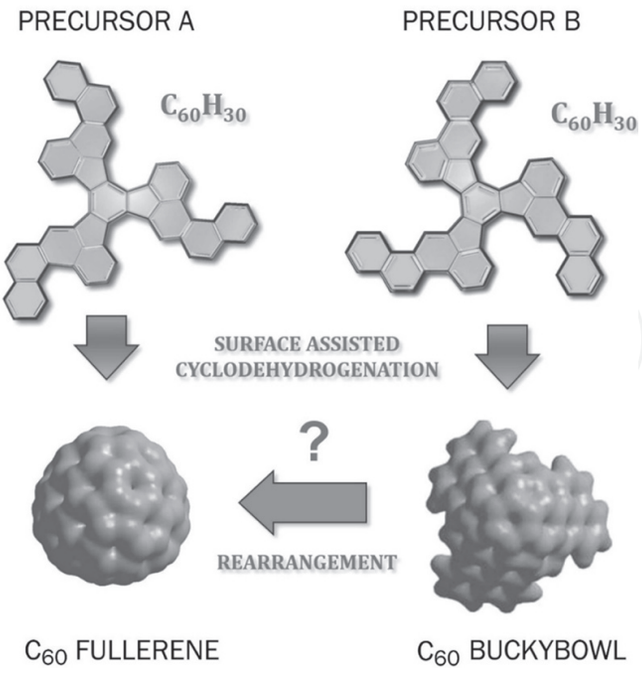


Figure 6. Structures of the C_{60} fullerene precursor (A and the C_{60} buckybowl precursor (B) molecules and their cyclodehydrogenation products.

Finally, the approach was successfully applied for the first rational synthesis of isomer-pure higher fullerene C_{84}(20) [36]. Upon annealing of specially designed $C_{84}H_{42}$ precursor at 550°C on Pt(111) surface, the shape of all of precursor molecules changed and all species became spherical with a lateral size expected for C_{84} fullerene (**Figure 8**). The formation of the C_{84} fullerene cages was additionally confirmed by MS analysis [36]. Moreover, the approach was found to be suitable for the synthesis of highly interesting hetero fullerenes. The fabrication of an azafullerene by surface-assisted approach has been demonstrated by Otero et al. on the example of $C_{57}N_3$ synthesis. In this study, a structurally related precursor with three incorporated nitrogen atoms was quantitatively converted to the hetero fullerene $C_{57}N_3$ upon annealing on Pt(111) surface at 477°C [35].

Although the technique allows to perform effective zipping to the target carbon nanostructures [37, 38], the resulting nano-carbons are covalently bonded to the metal surface and cannot be desorbed without decomposition. Those difficulties could be probably overcome by using less active metal oxide surfaces. Since the metal oxides show low activity in cyclodehydrogenation, the cyclization on such surfaces would require much higher temperatures leading to loss of selectivity. However, introduction of "activating" groups into the precursor structures could significantly reduce the activation barriers. In particular, it has been found that fluorine functionality appears to be an excellent ring-closure promoter, which has demonstrated unexpectedly high efficiency. It has been found that coupling can be realized in fluoroarenes on thermally activated aluminum oxide at very mild conditions [23–26]. Moreover, the alumina-supported cyclodehydrofluorination (cyclization via formal HF elimination) has demonstrated unprecedentedly high chemoselectivity and regiospecificity. The intramolecular Aryl–Aryl coupling on aluminum oxide was achieved with close to quantitative yield even

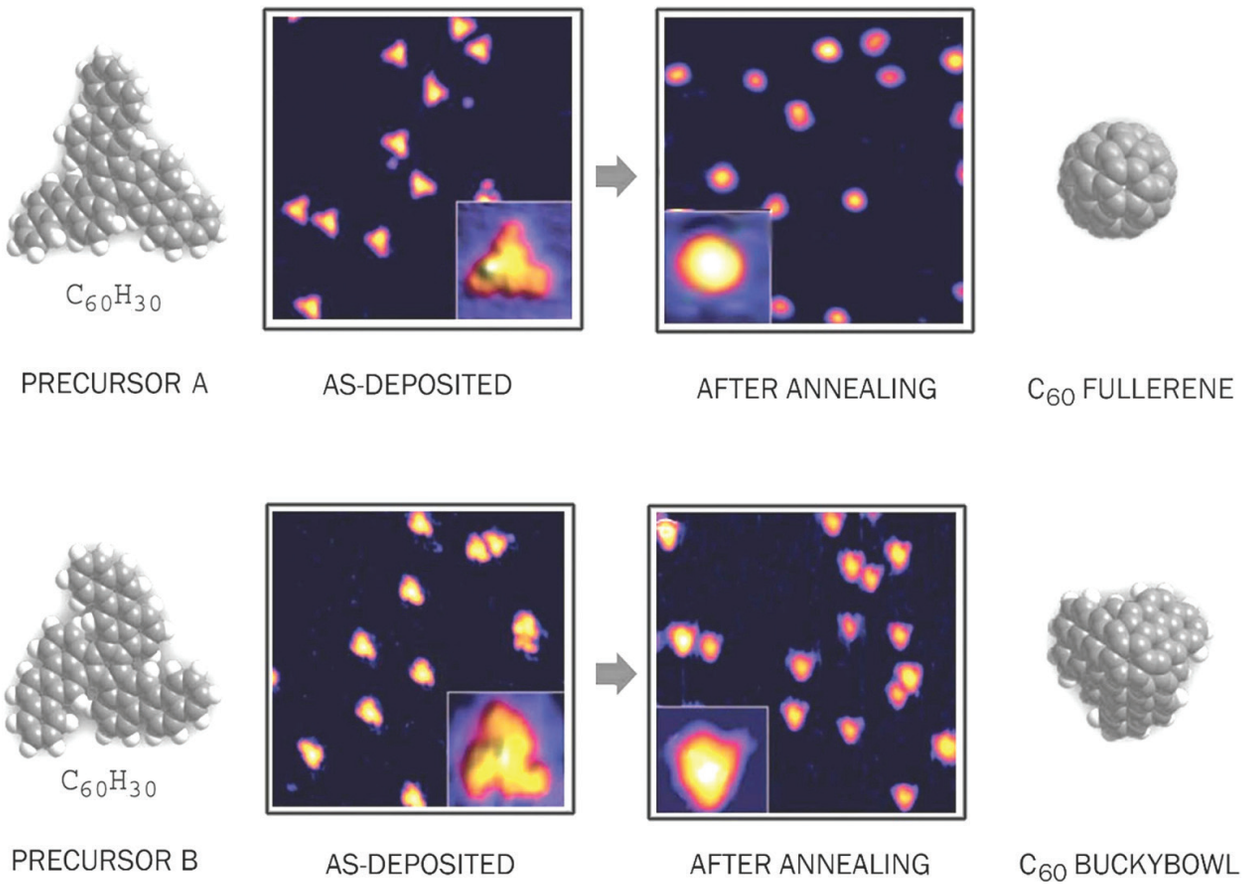


Figure 7. Surface-assisted synthesis of fullerene C_{60}-I_h (top) and C_{60} buckybowl (bottom) via cyclodehydrogenation of respective precursors on Pt(111) surface. STM images of the precursor before and after annealing at 480°C (reprint with permission from Ref [36]).

in the case of large bowl-shaped PAHs. Since fluorine can promote the ring closure only if hydrogen is placed neighboring in space in the precursor structure, it was possible to perform the cyclization in domino fashion. This makes the cyclodehydrofluorination more attractive in comparison to cyclodehydrogenation where the selectivity must be predefined by the rigid structure of precursor. Further, it was found that metal oxides of II, III and IV groups are active in the cyclodehydrofluorination of fluoroarenes. In particular, zirconium, titanium and indium oxides were found to be effective for cyclization via C─F bond activation [39]. These results point the way for fabrication of higher fullerenes and other related carbon-based nanostructures in a fully controllable manner directly on metal oxide surfaces.

2.3. Gas phase synthesis

The rational construction of fullerenes in the gas phase seems to be very logic, since in all conventional techniques the cage fabrication occurs in the gas phase. First of all, fullerenes, including higher, non-IPR and heterofullerenes, are stable in the gas phase. Second, the undesired intermolecular interactions can be effectively suppressed in the gas phase, providing excellent conditions for intramolecular processes. Not surprising that gas-phase synthesis appears to be the most promising approach.

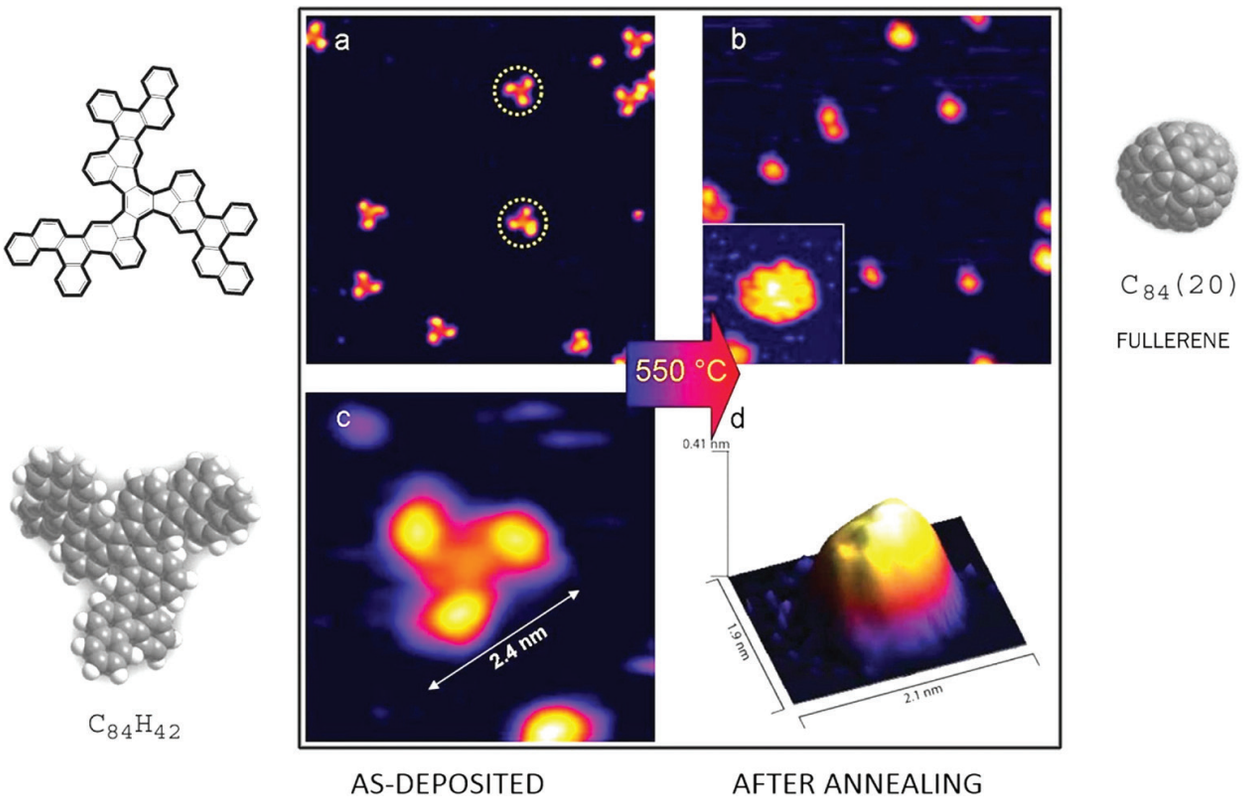


Figure 8. Surface-assisted synthesis of fullerene $C_{84}(20)$ via cyclodehydrogenation of $C_{84}H_{42}$ precursors on Pt(111) surface. STM images of the precursor before and after annealing at 550°C (reprint with permission from Ref. [36]).

The flash vacuum pyrolysis (FVP) represents one of the most powerful techniques for the synthesis of highly strained architectures via intramolecular cyclization. It consists in the heating of precursor molecules in the gas phase to a very high temperature for a very short time. The high temperature applied in FVP causes hemolytic cleavage of C—H bonds leading to the formation of radicals possessing enough energy to cause intramolecular cyclization yielding highly strained products. Pioneering by Scott et al., variety of small bowl-shaped PAHs (fullerene fragments) have been successfully synthesized in macroscopic amounts via intramolecular cyclization of quasi-planar PAH precursors under FVP conditions [40–42]. It was found that introduction of chlorine or bromine functionalities into the initial precursor is essential to facilitate the cyclization via free radical mechanism (**Figure 9**). Finally, this methodology has been successfully applied for the first rational synthesis of C_{60} utilizing partially chlorinated C_{60} fullerene precursor (**Figure 9**) [43]. Despite the low yield of C_{60} (0.1–1%) the power of the strategy has been clearly demonstrated.

The possibility of the synthesis of higher fullerenes by FVP has been shown on the examples of C_{78} [44] and C_{84} [45] by pyrolysis of specially programmed precursors. In both cases the size-selective formation of fullerenes was observed as indicated by the MS analysis (**Figure 10**). However, the rates of conversion to the target molecules have remained disappointingly low because of the low efficiency of intramolecular condensation of non-activated precursors. The usually employed for activation chlorine reach their limits in the case of large molecules because of decomposition of precursors during sublimation. The molar masses will generally

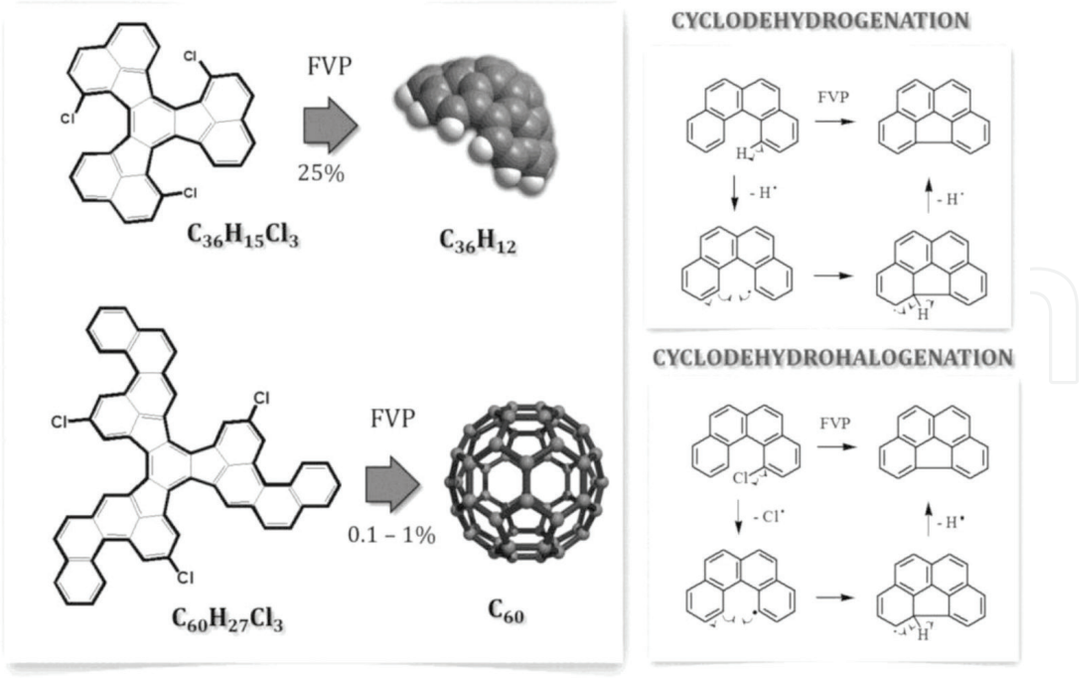


Figure 9. (Left) Synthesis of fullerenes and fullerene fragments by FVP approach from chlorinated PAH precursors. (Right) The cyclization mechanism under FVP condition for activated (chlorinated) and non-activated PAHs.

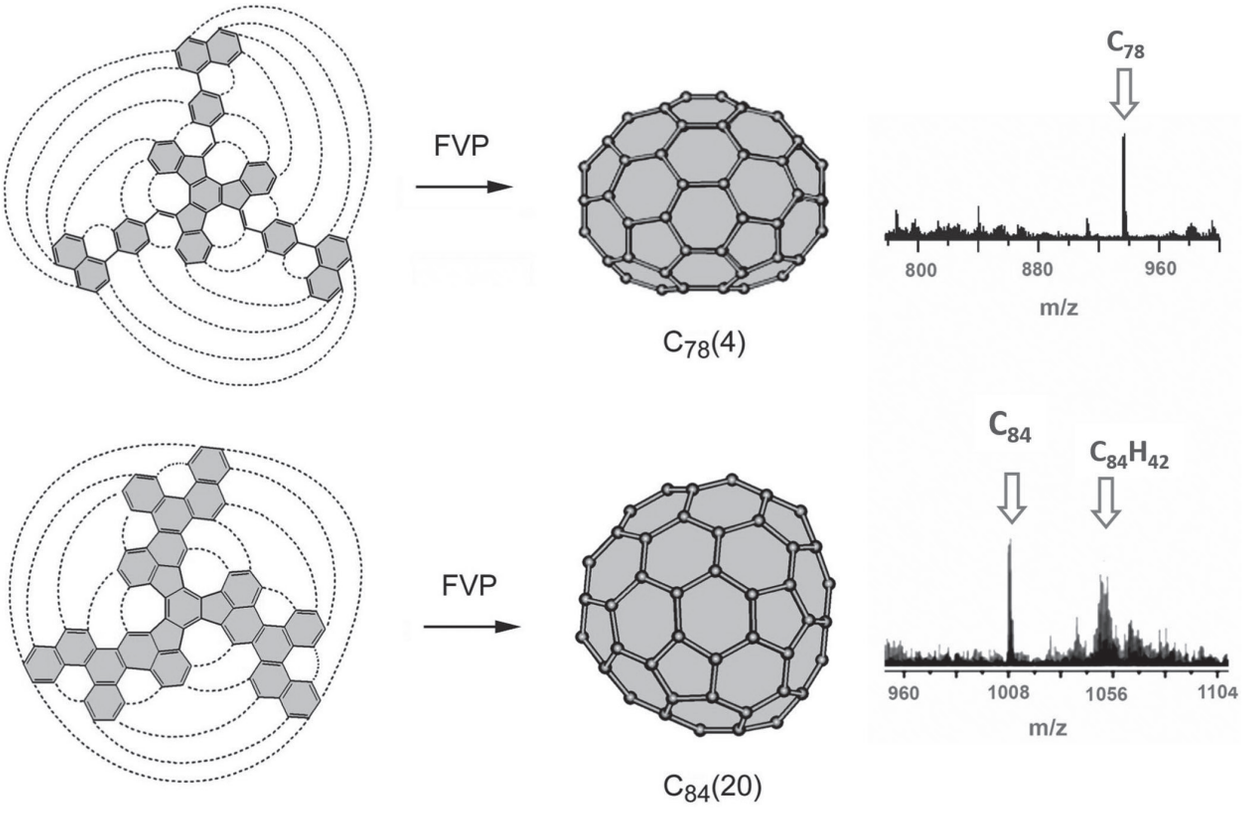


Figure 10. Schematic representation of the intramolecular cyclodehydrogenation of fullerene precursors to fullerenes C_{78}(4) and C_{84}(20). Dashed lines indicate where the new bonds have to be established in order to create a closed fullerene cage.

be high, since a large number of new C—C bonds that need to be formed necessitate the introduction of a big number of promoter groups. Moreover, the radical nature of the condensation could drastically affect the selectivity of the process.

Although the FVP approach has been proven to be very prolific for the synthesis of small non-planar PAHs, the high-yield synthesis of large bowls and isomerically pure fullerenes has remained challenging. Recently, an efficient intramolecular fluorine-promoted ring closure in benzo[c]phenanthrenes under FVP conditions via HF elimination has been reported [46]. It has been shown that HF elimination is a synchronous process leading directly to the C—C bond formation without any intermediates, thus producing no side products [46]. The small size and low molecular weight of fluorine, as well as high thermostability of the C—F bond make fluorine a perfect activating group for the rational synthesis of fullerene by zipping approach. The feasibility of the approach has been demonstrated on the successful synthesis of C_{60} fullerene from the respective fluorinated precursor which was effectively folded into the fullerene under laser ionization. The respective 15-fold cyclization was realized in a domino fashion via consecutive HF elimination without observation of side reactions or undesired fragmentations [47]. As it is shown in **Figure 11**, the precursor molecule undergoes highly selective HF loss (with simultaneous C—C bond formation) leading to the open-cage which

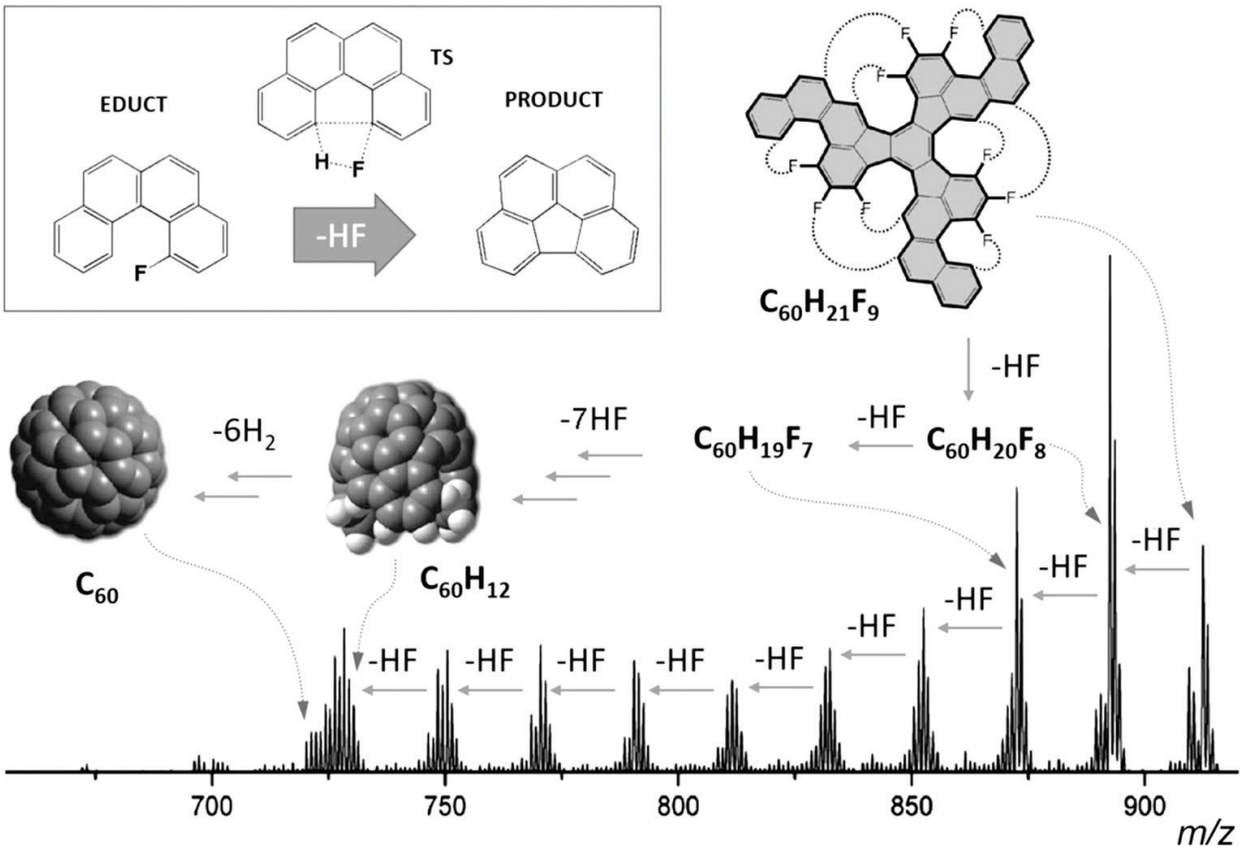


Figure 11. Mass spectrum of the C_{60} fullerene precursor ($C_{60}H_{21}F_9$) obtained under laser ablation (negative-ion mode) showing an effective domino-like HF elimination yielding C_{60} fullerene via 15 selective C—C bond formation steps. The mechanism of single cyclodehydrofluorination involving a four-centered transition state is shown in the insert on the example of benzo[c]phenanthrene model.

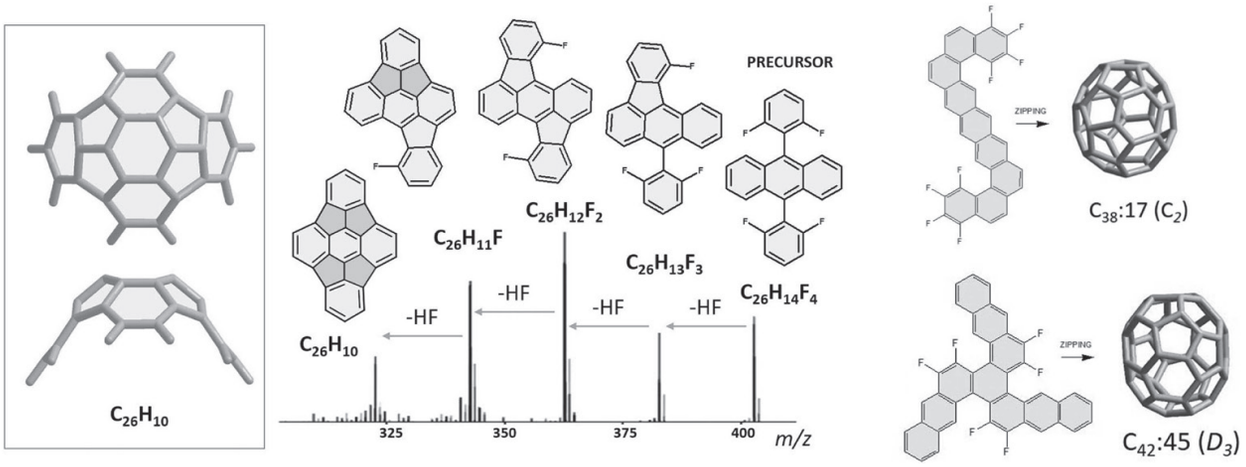


Figure 12. Mass spectrum of model precursor $C_{26}H_{14}F_4$ obtained under laser ablation showing tandem cyclodehydrofluorination yielding the non-IPR $C_{26}H_{10}$ fragment. The DFT optimized geometry of the non-IPR bowl (side and top views) is shown in the inset. (Right) Two examples of possible non-IPR fullerene precursor.

spontaneously collapses to the target C_{60} via H_2 loss. The regioselectivity of the domino-like cyclization and the formation of bowl-shaped intermediates and finally spherical C_{60}-I_h cage were recently confirmed by ion-mobility experiments [48].

Due to exceptionally high efficiency, it was assumed that the same approach can be extended to the synthesis of higher fullerenes as well as to the synthesis of highly attractive non-IPR cages. Recently, it has been demonstrated that non-IPR fragments can be indeed fabricated via cyclodehydrofluorination in the gas phase. It was shown that despite high strain the respective precursor undergoes rather smooth four-fold cyclodehydrofluorination, leading to the non-IPR fullerene fragment $C_{26}H_{10}$ (**Figure 12**) [49]. These results demonstrate the general possibility of rational fabrication of the non-IPR architectures via cyclodehydrofluorination of the specially preprogrammed fluoroarene-based precursors. Two possible precursors for generation of non-IPR fullerenes C_{38} and C_{42} are shown as example. Taking into account the present state-of-the-art of MS-based synthesis/deposition technique, which allows multilayer deposition of such compounds, the future scale-up appears to be feasible. Among non-IPR cages, the laser-induced cyclodehydrofluorination approach seems to be also applicable for the rational synthesis of higher and non-classical carbon cages.

3. Conclusion

The zipping strategy had been proved to be prolific for the rational synthesis of the fullerene fragments and the fullerene cages. The progress in this field shows the general possibility to fabricate elusive fullerenes in a fully controllable manner. Production of these unique materials in isomer-pure form in macroscopic amounts does no longer appear elusive, and there is promising prospect that such compounds will become available in the near future. Since there are virtually no limiting factors, there are no principle obstacles standing against extending the zipping approach to highly interesting related carbon-based architectures.

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