Direct Synthesis of Fullerenes

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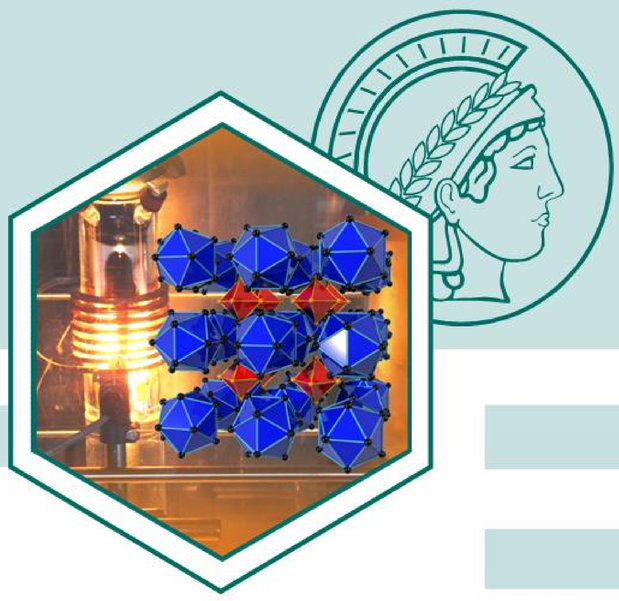
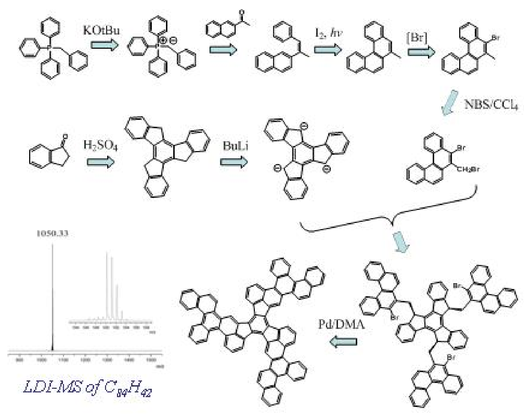


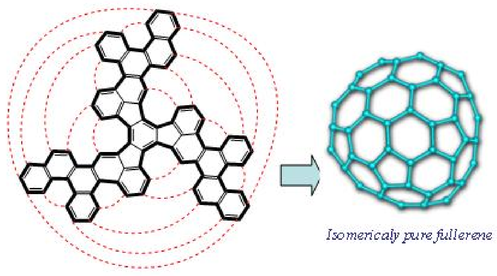
The Strategy of Direct Fullerene Synthesis



LDI-MS of $C_{84}H_{42}$

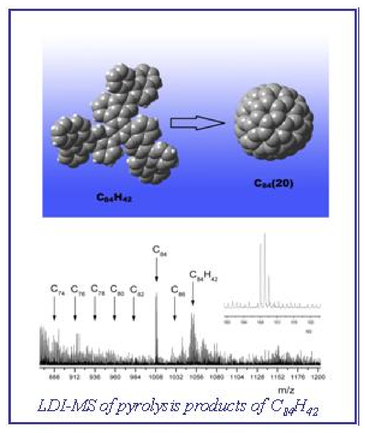
The synthetic route to C_{84} fullerene precursor

Direct synthesis of fullerenes is of considerable interest as a method to access new fullerenes which can not be obtained in the uncontrolled process of graphite evaporation or forms in low yields as a hard-to-isolate mixture. The general strategy of the direct approach to fullerenes is based on the synthesis of polycyclic aromatic hydrocarbons (PAH) that already contain the required carbon framework. Such "unrolled" molecules can be "rolled up" to form fullerenes under flash vacuum pyrolysis (FVP) conditions. The presence of chlorine or bromine in the initial precursor has been found to be essential for effective cyclization via free radical mechanism. Although the FVP approach has proven to be prolific for the synthesis of many small non-planar PAHs, high-yield synthesis of isomerically pure fullerenes has remained a challenge. The possibility of selective fullerene cage formation through FVP has been demonstrated by the examples of C_{60},[1-3] C_{78},[4] and C_{84}.[5] However, the rates of conversion to the target molecules have remained disappointingly low because of lack of efficient promoters of intramolecular condensation. The usually employed bromine or chlorine functionalizations reach their limits in the case of large molecules due to decomposition of such halogenated precursors during sublimation. The molar masses will generally be high, since the large numbers of new C-C bonds that need to be formed in the fullerene precursor necessitate the introduction of a considerable number of promoter groups. Moreover, the radical nature of the condensation drastically affects the selectivity of the process.



Isomericaly pure fullerene

The strategy starts with the synthesis of a planar polycyclic aromatic hydrocarbon (PAH) that already contains the carbon framework required for the formation of the target fullerene molecule. Such "unrolled" molecules can be "rolled up" to form fullerenes via cyclodehydrogenation process.

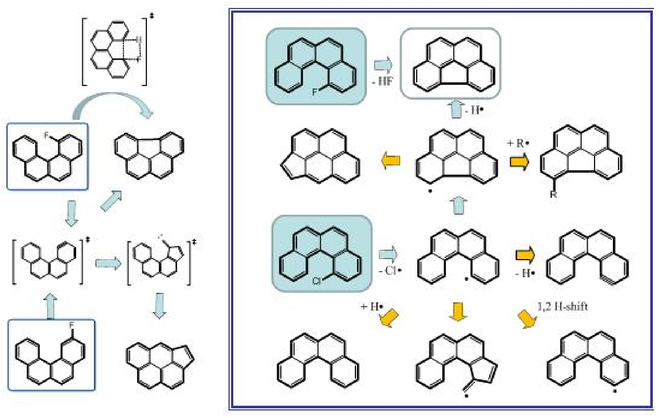


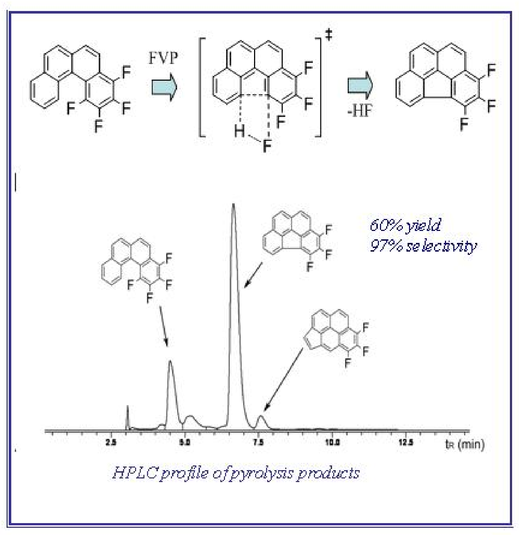
LDI-MS of pyrolysis products of $C_{84}H_{42}$

The selective formation of C_{84} fullerene by tandem cyclodehydrogenation of $C_{84}H_{42}$ precursor

Homo elimination of HF - an efficient approach for intramolecular Aryl-Aryl coupling

Recently we reported on an efficient intramolecular fluorine promoted ring closure in benzo[c]phenanthrenes under FVP conditions via HF elimination, and have shown that HF elimination is a synchronous process leading directly to the target molecule without any intermediates, thus producing no side products.[6] 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 rational fullerene synthesis.

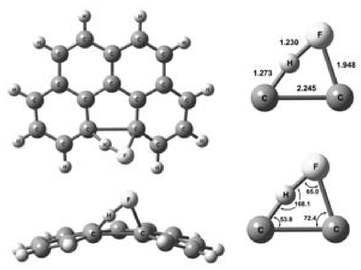




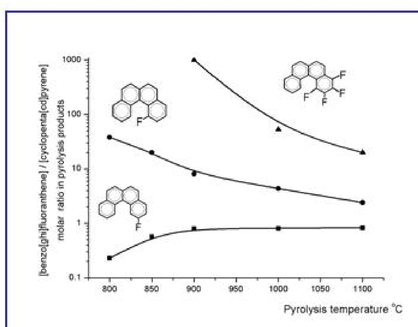
HPLC profile of pyrolysis products

C_{sp2}-H and C_{sp2}-F groups can interact directly through space whereas the rest of the molecule is not involved in the process but is just interconnecting the reacting atoms. This interaction finally results in formation of a new C_{sp2}-C_{sp2} bond and elimination of HF.

The through-the-space fluorine activation of benzo[c]phenanthrene condensation was examined experimentally. The HF homo-elimination mechanism was identified and confirmed by quantum chemical calculations. The activation energies found are qualitatively in a good accordance with FVP experiments data. Taking into consideration that fluorine can promote the desired ring closure only if hydrogen is placed neighboring in space in the precursor structure, it seems to be possible to fully control the direction of the condensation. According to our results the highly efficient intramolecular condensation of appropriately functionalized PAH to non-planar PAHs via homo- HF elimination can be achieved.[7] Using fluorine as an activating group solves the problem of selectivity in FVP and should provide an effective conversion of respective planar PAH precursors to the desired fullerene cage.

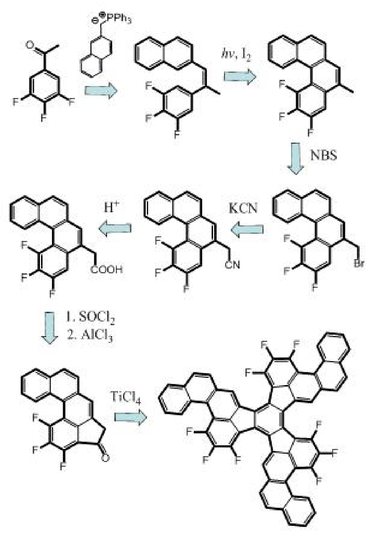


Transition state geometry for HF homo-elimination predicted with the DFT B3LYP/6-311G(d,p) method.

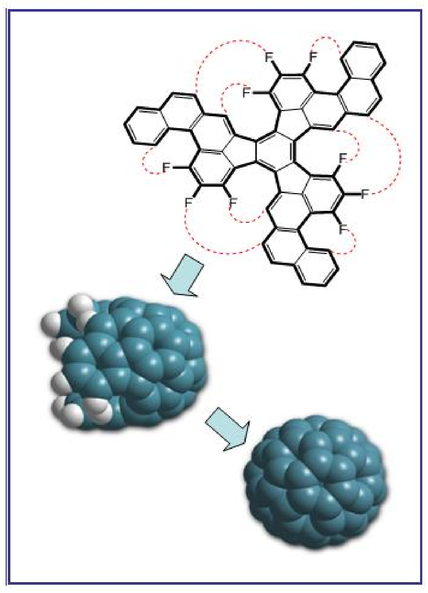


*Temperature dependent dynamic of benzo[ghi]fluoranthene / cyclopenta[cd]pyrene molar ratio in FVP of fluorinated benzo[c]phenanthrenes **1**, **2** and **3**. The molar ratios are obtained from HPLC data of the pyrolysis product. * - the concentration of trifluoro-cyclopenta[cd]pyrene are estimated on the assumption of equal sorption with unsubstituted cyclopenta[cd]pyrene.*

C_{60} Fullerene Precursors with Fluorine in Key Positions



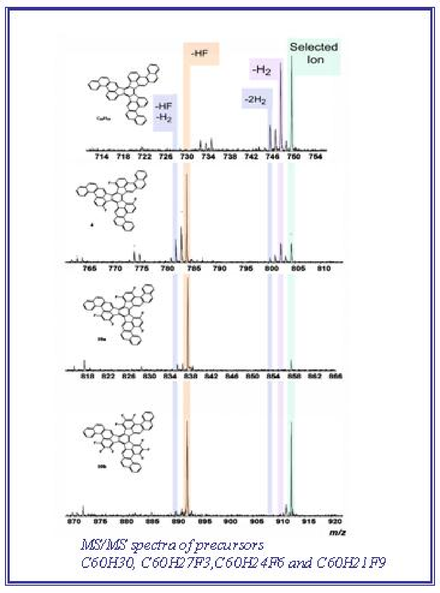
The synthetic route to C_{60} fullerene precursor containing 9 fluorine atoms in the key positions.



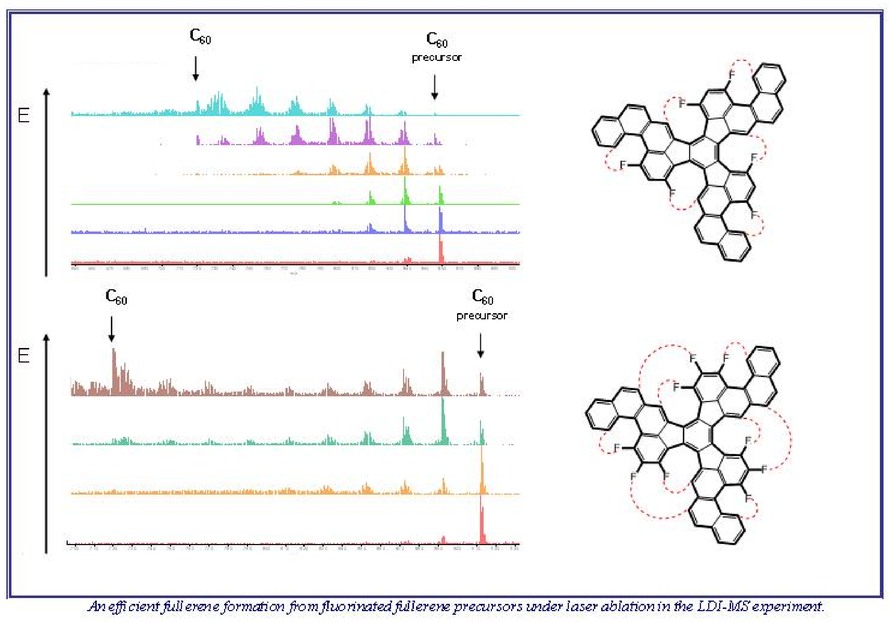
Several C_{60} fullerene - related structures containing a various number of fluorine atoms in the key positions have been synthesized. The fluorinated PAHs obtained represent attractive precursor molecules for rational fullerene synthesis by flash vacuum pyrolysis.[8] Taking into consideration that fluorine can promote the ring closure only if hydrogen is placed in a neighboring position in the precursor structure it appears to be possible to fully control the direction of the process. Using fluorine as an activating group could solve the problem of selectivity in FVP and should provide an effective conversion of the planar PAH precursors to the desired fullerene cage.

The FVP experiments have shown selective fullerene formation from fluorinated precursor under FVP conditions via HF-homoelimination. Additionally it was found that laser ablation causes effective intramolecular C-C coupling via HF elimination as well. High effective fullerene formation have been observer in the LDI-MS experiment.

We are optimistic that optimization of the condensation process will increase the yield of the fullerene to preparative scale and new fullerenes could be obtained by this approach. The respective investigations are in progress.



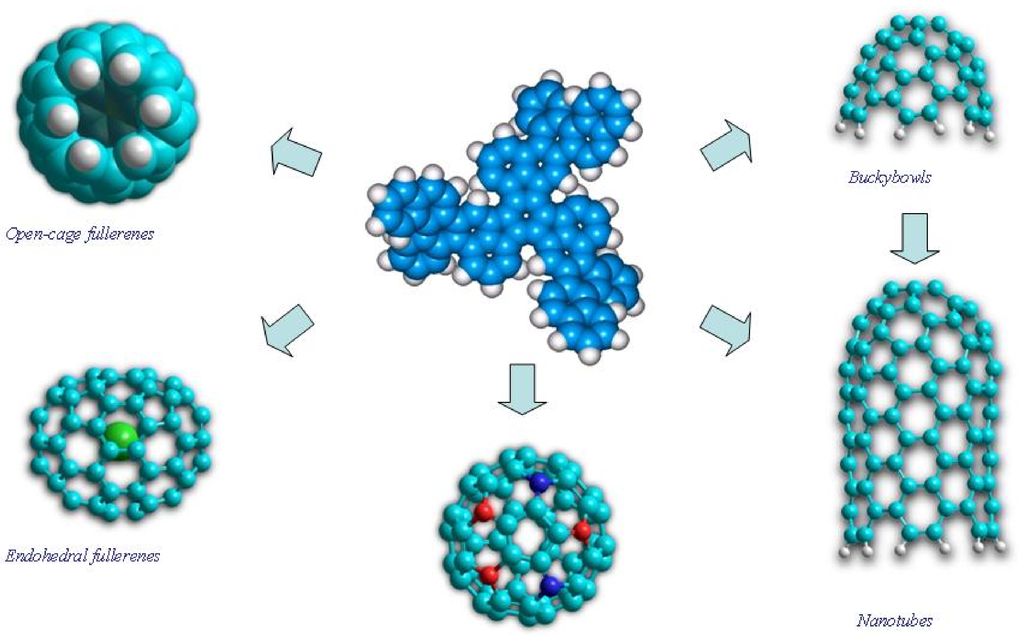
MS/MS spectra of precursors C60H30, C60H27F3, C60H24F6 and C60H21F9



An efficient fullerene formation from fluorinated fullerene precursors under laser ablation in the LDI-MS experiment.

Prospects of Direct Synthesis

The direct synthetic approach is not limited to the synthesis of fullerenes but can be extended for synthesis of many other carbon nanostructures including buckybowls, endohedral- and hetero- fullerenes as well as nanoribbons and nanotubes.



References

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