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One Step Closer to Isomerically Pure Fullerenes and Heterofullerenes: Harnessing the Potential of Catalytic Surfaces**

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The power of synthetic organic chemistry is perhaps best appreciated by surveying the spectacular syntheses of complex natural products that nowadays adorn the pages of journals with impressive regularity. These successes feed the myth that "we can now make anything!". Practitioners in the art of organic synthesis, however, are the first to point out just how far short of that goal we still stand. How, for example, could one synthesize a fullerene ("buckyball") in which three of the carbon atoms are replaced by nitrogen atoms at preselected positions? Molecules like this bear little structural resemblance to traditional natural products, but a recent breakthrough may pave the way to such synthetic targets.[1]

Otero et al. began their work by depositing the $C_{60}H_{30}$ polycyclic aromatic hydrocarbon **1** onto a platinum (111) surface by vacuum thermal evaporation. Scanning tunneling microscopy (STM) analysis of the partially covered surface (ca. 0.2 monolayers) clearly showed the individual molecules as triangular images with a width of approximately 2.2 nm. Upon heating to 750 K, the fullerene precursors all close up by sequential surface-catalyzed cyclodehydrogenation reactions to produce C_{60} balls on the surface. STM analysis confirmed that the resulting molecules are round, as well as narrower and taller than the $C_{60}H_{30}$ precursors, as expected for fullerenes. The STM images of the newly formed molecules are also indistinguishable from those of authentic C_{60} balls deposited onto an identical surface by vacuum thermal evaporation. The same experiments were then performed with the $C_{57}N_3H_{33}$ polycyclic aromatic compound **2** to give the previously unknown heterofullerene $C_{57}N_3$. The structures of compounds **1** and **2** can be seen in Figure 1, along with STM images of the $C_{57}N_3H_{33}$ triazafullerene precursor before and after cyclization.

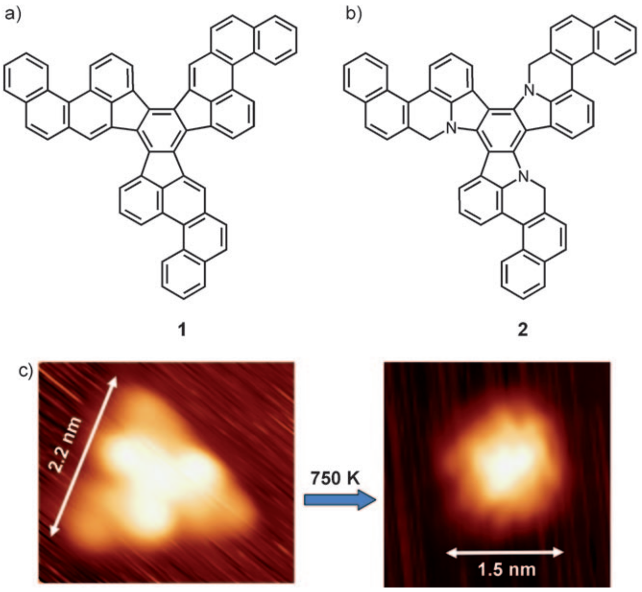

Figure 1. a) Aromatic precursor to fullerene C_{60} ($C_{60}H_{30}$, **1**) and b) aromatic precursor to triazafullerene $C_{57}N_3$ ($C_{57}N_3H_{33}$, **2**). c) STM image of $C_{57}N_3H_{33}$ (**2**) on a Pt (111) surface before heating (left) and STM image of triazafullerene $C_{57}N_3$ on a Pt (111) surface after heating **2** to 750 K (right).

From the full STM analysis, it is clear that none of the aromatic precursor molecules remain in their original state after having been heated to 750 K and that essentially 100 % of the molecules are converted to fullerenes. This finding contrasts sharply with the results of previous work on the cyclodehydrogenation of **1** to C_{60} with a UV laser[2] and the cyclization of a trichloro derivative of **1** to C_{60} by flash vacuum pyrolysis.[3] In the latter study, C_{60} was obtained in quantities sufficient for isolation and characterization by chromatographic and spectroscopic methods, but the yield was only about 1 %. Whether or not the Pt-catalyzed cyclodehydrogenation route can be scaled up from its present state, which is suitable only for subfemtogram amounts, to become a preparatively useful method remains to be seen. Otero et al. have initiated experiments toward that objective and report mass spectrometric detection of C_{60} that was formed by depositing hydrocarbon **1** from solution onto a platinum nanopowder and heating the resulting mixture at 700 K under

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vacuum (10^{-4} mbar). The ultimate goal is to produce isolable quantities of isomerically pure fullerenes and heterofullerenes.

Surface-catalyzed cyclodehydrogenation reactions of polycyclic aromatic compounds are relatively new, but they are not unprecedented. Nuckolls and colleagues recently reported cyclodehydrogenation of the $C_{48}H_{24}$ hydrocarbon **3** to produce the surface-bound nanotube end cap **4** (Figure 2).[4] Until now, however, no research group had ever succeeded in stitching up an aromatic precursor all the way to a fullerene on the surface of a cyclodehydrogenation catalyst.

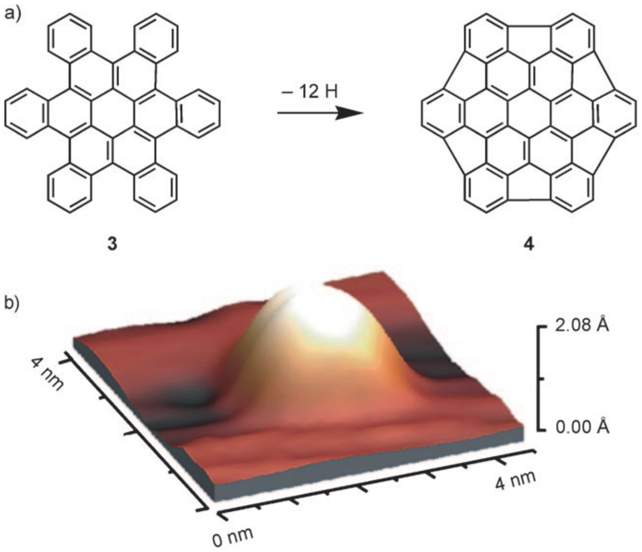

Figure 2. a) Cyclodehydrogenation of $C_{48}H_{24}$ hydrocarbon **3** to produce the nanotube end cap **4**. b) STM image of the surface-bound nanotube end cap **4** on Ru (0001).

The world of fullerenes begins with C_{60}, for which only the familiar I_h isomer is stable, but many stable isomers are expected for the vast majority of higher fullerenes; for example, 24 isomers for C_{84}, 450 isomers for C_{100}, and thousands of isomers for even larger fullerenes.[5] From the production of fullerenes by graphite vaporization, fewer than a dozen of these carbon allotropes are formed in sufficient quantities to permit chemical investigation. To open up this branch of materials science, researchers require access to all the fullerenes and to heterofullerenes on a "made-to-order" basis. Synthetic methods are needed that will produce a single isomer of a fullerene, uncontaminated by other isomers or by fullerenes of different sizes. Quite recently, the flash vacuum pyrolysis method has been successfully applied to the directed synthesis of C_{78} that is uncontaminated by other fullerenes; however, the isomeric purity of the product remains to be established.[6] In the work by Otero et al. the isomeric purity of the $C_{57}N_3$ produced likewise remains unconfirmed.

Many challenges still lie ahead on the long road to isomerically pure fullerenes and heterofullerenes by chemical synthesis, but a new milestone has now been passed, and the goal no longer seems so far away.

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