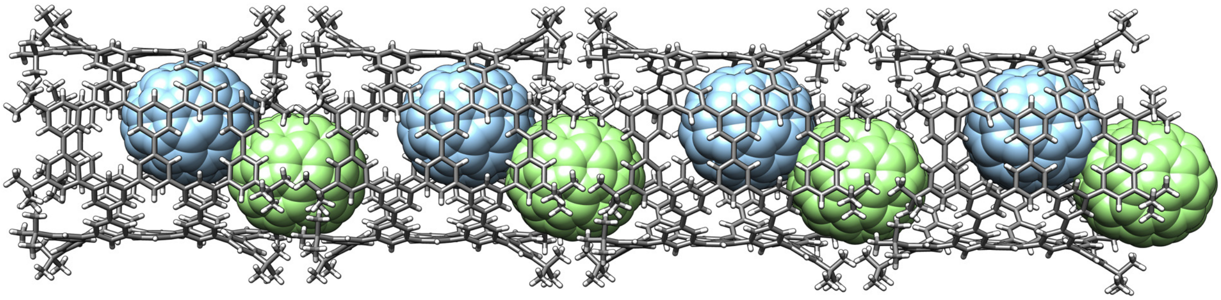

Fig. 2. Nanometer-sized pNT cylinder containing fullerene C_{70} molecules.

Isobe says the team has fallen in love with the perfect cylindrical structure and symmetry of their nanotubes. They are now working on creating nanotubes of different widths and lengths, as well as helical and zigzag forms of pNT.

"We hope that the beauty of our molecule also points to unique properties and useful functions waiting to be discovered," Isobe told *Nano Today*. "With these new structural variants, we hope to open a new interdisciplinary field connecting neighboring fields such as materials science."

The researchers hope to explore some of these possibilities in the near future, as well as improving on the synthesis process.

César Moreno of the Catalan Institute of Nanoscience and Nanotechnology (ICN2) believes the approach is interesting.

"As in architecture, mastering the void is a challenging task beyond the control of the matter. Isobe's work demonstrates how it is possible to control the void with exquisite precision," he comments.

The team's efforts expand on previous demonstrations of top-down synthesis of porous carbon nanotubes and Roman Fasel's pioneering on-surface synthesis approach to creating atomically precise graphene nanoribbons.

"If Isobe's approach demonstrates the ability to functionalize these pores, then we will be able to artificially mimic biomembranes," points out Moreno. "Another important aspect will be to explore the thermoelectric performance of phenine nanotubes and explore if there is room to perform pore engineering."

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Nanographenes 'zip-up' on nonmetallic surfaces

Cordelia Sealy

Carbon nanomaterials like nanotubes and graphene nanoribbons promise a new generation of electronic devices. But in order to realize this potential, practical means of fabricating these nanomaterials on different substrates are needed. Now researchers have managed to synthesize nanographenes successfully on the surface of the metal oxide, titania (TiO_2) [Kolmer et al., *Science* **363** (2019) 57–60, https://doi.org/10.1126/science.aav4954].

"For the first time, [we have] accomplished the rational synthesis of nanographenes on a non-metallic substrate, using rutile TiO_2 as the example," says first author of the study, Marek Kolmer from Jagiellonian University in Poland, currently affiliated to Oak Ridge National Laboratory.

While it has been possible to fabricate carbon nanotubes, graphenes, and graphene nanoribbons on metallic substrates for some time, reproducing this on non-metallic surfaces has proved more elusive. The growth process typically involves heating a metal substrate to catalyze the cyclodehydrogenation of polycyclic aromatic hydrocarbon (PAH) precursors, effectively driving off hydrogen to form carbon structures held together by C—C bonds. Recreating this process on non-metallic surfaces requires such high temperatures that selectivity is lost.

The key to the success of the team from Jagiellonian University and Friedrich Alexander University Erlangen-Nuremberg (FAU) in Germany is the use of C—F bonds in organic precursor molecules to drive the formation of C—C bonds on non-metallic surfaces under ultrahigh vacuum conditions. The approach enables the very precise design of precursor molecules because only specifically 'chosen' C—F bonds, i.e. those that are close to C—H bonds, are activated. Heating a titania substrate drives the formation of C—C bonds and carbon nanomaterials (Fig. 1). The process works in a domino-like fashion, with the formation of each C—C bond triggering the activation of the next C—F bond. Since HF molecules are eliminated from the precursor during the intramolecular coupling, the researchers dub the process 'HF zipping'.

"We show that C—F bond activation in organic molecules may be a very efficient strategy to synthesize nanographene molecules on single crystal metal oxide surfaces via intramolecular C—C bond formation," says Konstantin Amsharov, who leads the organic chemistry group at FAU. "Our approach is unique because of the high selectivity of activated C—F bonds within the single molecule, which allows very flexible design of precursors and thus target molecules."

The researchers believe that their approach should open up an alternative route to forming carbon nanostructures on metal oxide substrates, which are more technologically useful than metals.

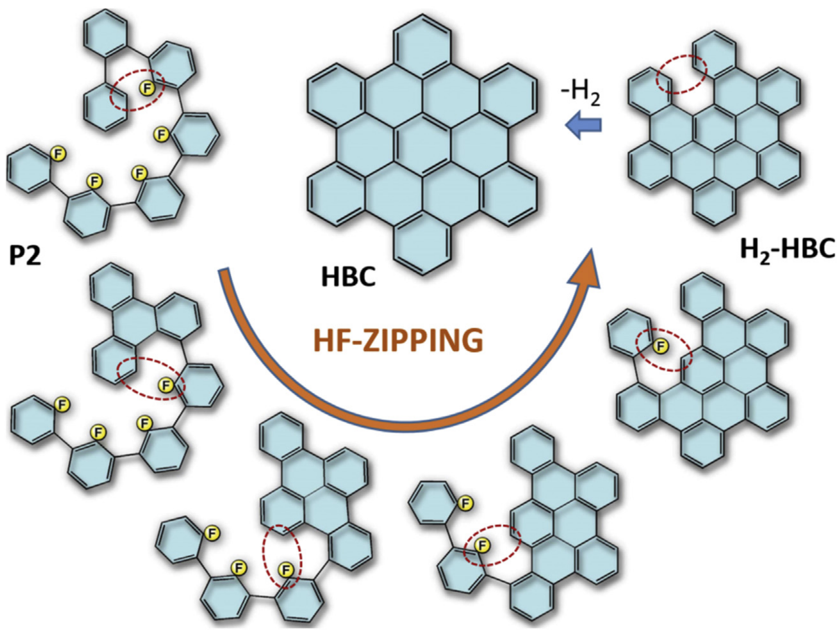

Fig. 1. Schematic of the formation of hexabenzocoronene (HBC).

"For future technological applications it is required to place atomically precise graphene moieties on non-metallic surfaces and our approach provides a new way for direct synthesis, without technically challenging transfer process from metals," explains Kolmer.

Moreover, the researchers are confident that their approach should work with other metal oxide surfaces, such as wide-band gap insulators like sapphire or silicon dioxide.

"Technological progress strongly relies on ways to prepare new materials designed with atomic scale precision," comments Pavel Jelinek of the Institute of Physics of the CAS in the Czech Republic. "One of the promising and fast developing fields to tackle this goal is 'on-surface chemistry', where reactions take place on a surface that imposes two-dimensional confinement."

The development of on-surface chemistry to produce controlled growth of graphene nanoribbons with desired structural and electronic properties on non-metallic surfaces is an exciting achievement, he believes.

"To achieve this goal, Kolmer et al., employed cleverly designed fluorinated oligophenylenes that selectively activate C—F bond in precursors," Jelinek explains. "This represents a new way to form covalent carbon-based nanostructures on insulator surfaces."

He cautions that characterizing these structures on insulating surfaces will be challenging with scanning probe microscopy (SPM), although other techniques could be used, but believes it will be interesting to see if this concept can be employed to create covalent organic frameworks of large sizes that are relevant for possible technological applications.

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