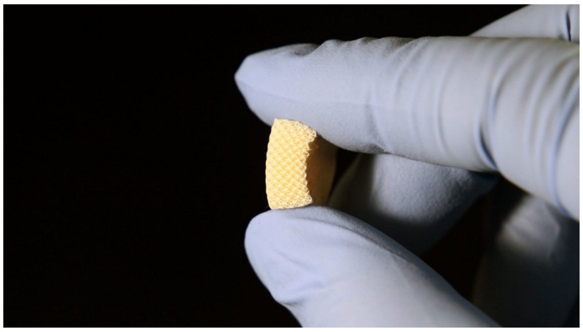

Fig. 2. 3D printed, flexible energy harvester. (Photo courtesy of H. Cui, Zheng Lab.)

He is confident that the approach will allow engineers to custom design and print transducers and flexible energy harvesting devices without the need for expensive cleanroom facilities (Fig. 2). The researchers are now working on improving the process so that fully functional devices can be fabricated using a desktop printer.

Zhong Lin Wang of Georgia Tech, one of the pioneers of piezoelectric technology, comments:

"This paper introduces 3D printing to fabricate piezoelectric materials with designed anisotropy and directional response. This is a new approach toward building multiple function sensors using composites of piezoelectric materials in any shape or even any dimension."

He believes the work will be important for guiding sensor systems for soft robotics, intelligent actuators, and new mechanical triggering structures.

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New nanotube comes with built-in holes

Cordelia Sealy

Researchers have synthesized a new type of carbon-based nanotube using benzene rings as building blocks [Sun et al., *Science* **363** (2019) 151–155, https://doi.org/10.1126/science.aau5441]. Instead of carbon atoms in a regular carbon nanotube, the new chemical structure is composed of hexagonal six-membered benzene rings. Because of the way in which the rings bond together, the resulting cylinder contains regular defects in the form of gaps or holes. If many of these cylindrical molecules could be linked together, the resulting carbon nanotubes would have properties defined by these vacancies.

The team from the University of Tokyo, Japan Science and Technology Agency (JST), Center for Emergent Matter Science at RIKEN, and Tohoku University synthesized the phenine nanotube (pNT) molecules, which have the chemical formula $C_{304}H_{264}$, in a nine-step process. Despite the complexity of the multi-step process, it is relatively efficient say the researchers.

"The benzene rings are synthetically stitched together by 52 covalent bonds with a high average efficiency of 91%," explains Hiroyuki Isobe of the University of Tokyo, who led the study.

The process begins with six molecules of benzene, which are combined into a larger ring called cyclo-meta-phenylene (CMP). In the presence of Pt, four CMP molecules form an open-ended cube. When the Pt atoms are removed, the cube closes up to form a cylinder (Fig. 1). The resulting pNT molecule is just 2 nm in size.

"From a chemistry perspective, our demonstration of concise synthesis of a large rigid cylinder is novel," says Isobe. "We believe no one had ever imagined that one could synthesize a 2-nm $C_{304}H_{264}$ molecule with a molecular weight of 4 kDa from benzene in nine steps."

The molecules themselves are uniquely interesting, but they can also be fused together to form highly porous nanostructures.

"The pNT molecules are aligned and packed in a lattice rich with pores and voids," he adds. "These nanopores can encapsulate various substances which imbue the pNT crystal with properties useful in electronic applications."

As an example, the researchers embedded fullerene C_{70} molecules into the pNT pores (Fig. 2). The porous nature of the new molecule could form the basis of novel composite materials, which might be of particular interest as high capacity electrode materials for solid-state lithium ion batteries.

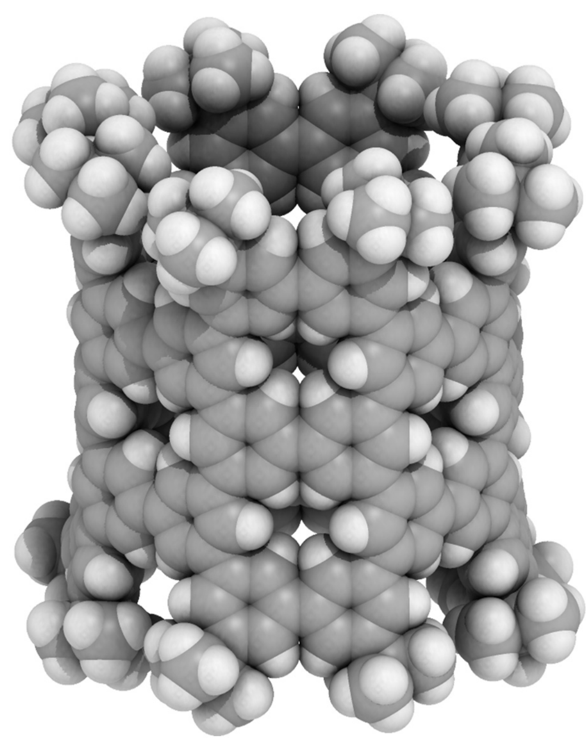

Fig. 1. Nanometer-sized pNT cylinder made of 40 benzene units.

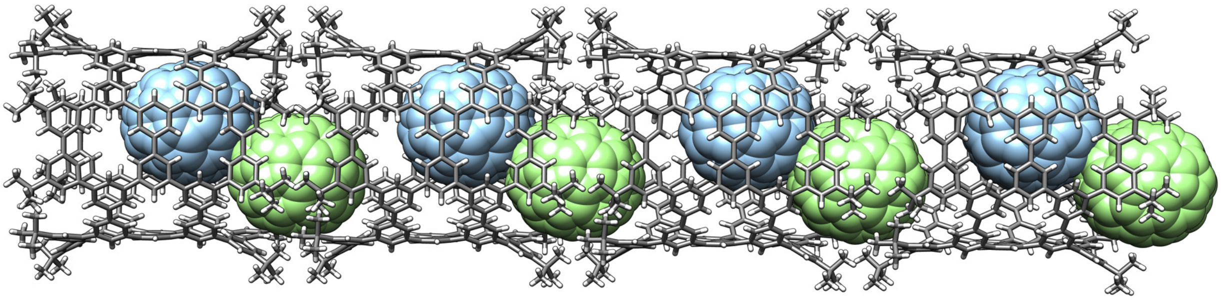

Fig. 2. Nanometer-sized pNT cylinder containing fullerene C_{70} molecules.

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.