Press Release

Chromium-Centered Cycloparaphenylene Rings as New Tools for Making Functionalized Nanocarbons

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A team of chemists at Nagoya University has synthesized novel transition metal-complexed **c**yclo**p**ara**p**henylenes (CPPs) that enable selective monofunctionalization of CPPs for the first time, opening doors to the construction of unprecedented nanocarbons.

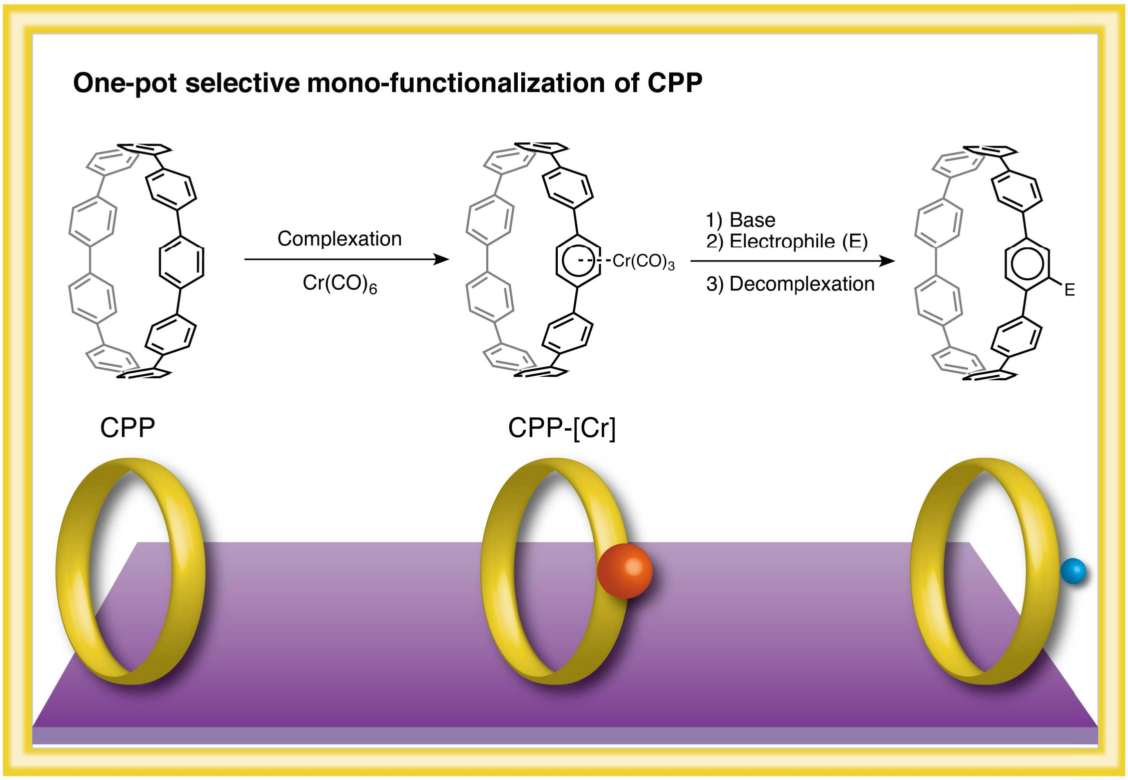

Figure 1. One-pot selective monofunctionalization of CPP via a chromium complex

Nagoya, Japan – Professor Kenichiro Itami, Yasutomo Segawa and Natsumi Kubota of the JST-ERATO Itami Molecular Nanocarbon Project and the Institute of Transformative Bio-Molecules (ITbM), Nagoya University have synthesized novel cycloparaphenylene (CPP) chromium complexes and demonstrated their utility in obtaining monofunctionalized CPPs, which could become useful precursors for making carbon nanotubes with unprecedented structures. CPPs consist of a chain of benzene rings and are the shortest segment of carbon nanotubes. Since their first synthesis and isolation in 2008, CPPs have attracted wide attention in the fields of materials science and supramolecular chemistry. Applying the basic concepts of chromium arene chemistry, Itami and his coworkers have performed the first selective installation of a functional group on CPP, which has previously been difficult due to multiple reactive arene sites on the CPP ring. By being able to selectively install and tune the functional groups on CPPs, it is envisaged that carbon nanotubes with new properties can be constructed by this method. The study, published online on January 12, 2015 in the *Journal of the American Chemical Society*, illustrates the first synthesis, isolation and analysis of a CPP chromium complex, which enables a one-pot access to monofunctionalized CPPs. This outcome is believed to be a significant advance in the fields of both CPP chemistry and organometallic chemistry.

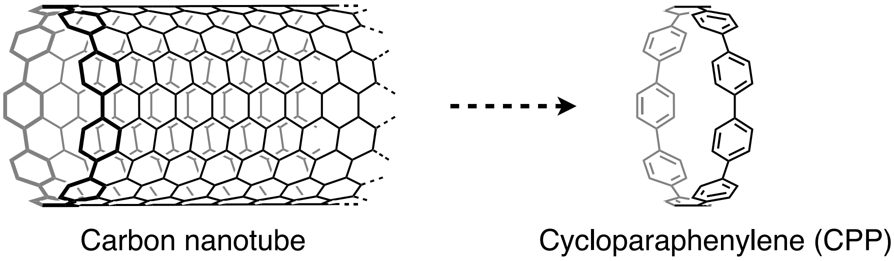

Figure 2. Cycloparaphenylene and carbon nanotube

Arenes are known to coordinate to transition metals and the corresponding metal complexes exhibit different reactivities relative to the free arene. CPPs, which consist of a chain of arenes, also reacted with chromium carbonyl to successfully generate the first chromium complex of CPP. Interestingly, the main product was a CPP with one chromium moiety complexed to one arene on the outer side of the ring, as confirmed by ^{1}H NMR (nuclear magnetic resonance) spectroscopy, high-resolution mass spectrometry and X-ray crystallography.

“Chromium arene chemistry is a well-established area and we decided to apply this organometallic method to synthesize the first CPP chromium complex,” says Itami, the Director of the JST-ERATO project and the Institute of Transformative Bio-Molecules. “As CPPs have a number of arene rings, we initially expected that chromium would form a complex with each arene ring,” says Segawa, a group leader of the JST-ERATO project. “However, we were surprised to see that CPP reacted with chromium in a 1:1 ratio in all the conditions that we tried. Simulation of the molecular structure suggested that the first equivalent of chromium complexed to CPP lowers its reactivity, thus preventing the reaction with a second chromium moiety.”

Upon finding that a monometallic CPP complex could be obtained, Itami’s team explored the possibility of obtaining monofunctionalized CPPs from this complex. Itami and Segawa describe the steps in achieving this. “This was not an easy task as chromium arene complexes are usually air and light sensitive, and CPP chromium complexes were no exception. But Natsumi worked persistently to obtain a pure crystal of the first CPP chromium complex,” says Itami. “We then performed the subsequent reactions in one-pot, to synthesize monofunctionalized CPPs after addition of base/electrophiles and removal of the metal from the CPP chromium complex,” says Segawa.

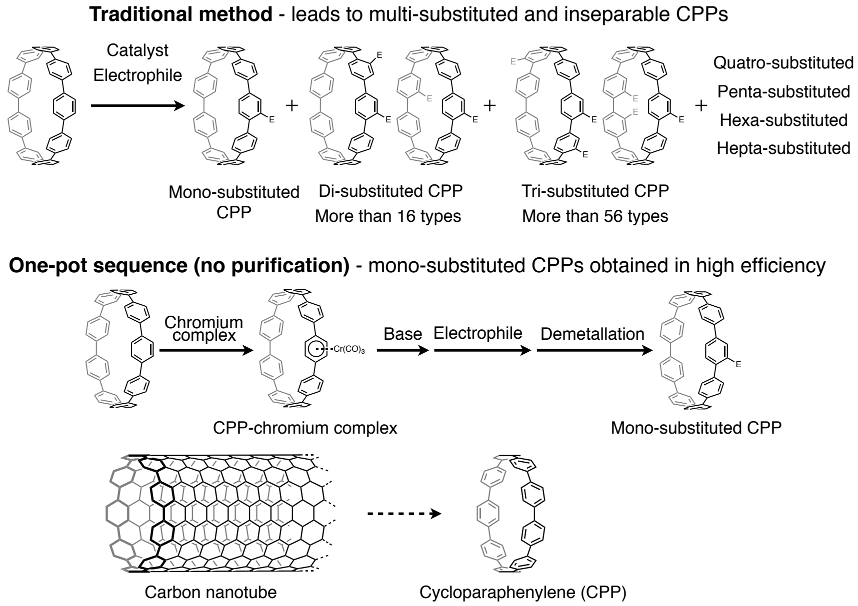

Figure 3. Obtaining substituted CPPs – traditional method and one-pot sequence (this work)

Selective monofunctionalizations of CPPs i.e. installation of one functional group at a single position on the arene ring, are difficult to achieve as all carbon-hydrogen bonds on the arene rings are chemically equivalent. Direct functionalization of metal-free CPPs usually leads to multiple substitutions on the arene rings in an uncontrolled manner. Despite CPPs being desirable components for carbon nanotubes, there has been no efficient method to obtain directly functionalized CPPs up to now.

"We were pleased to see that a functional group could be selectively installed on one arene ring via chromium coordination of CPPs," says Segawa. "As electrophiles, we utilized silyl, boryl and ester groups, which act as handles that can be easily transformed to other useful functionalities," he continues. Itami says, "We hope that this new approach evolves to become a valuable method to construct carbon nanotubes with unique structures and properties."

This article "η^6-Cycloparaphenylene Transition Metal Complexes: Synthesis, Structure, Photophysical Properties, and Application to the Selective Monofunctionalization of Cycloparaphenylenes" by Natsumi Kubota, Yasutomo Segawa, and Kenichiro Itami is published online on January 12, 2015 in the *Journal of the American Chemical Society*.
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About WPI-ITbM (http://www.itbm.nagoya-u.ac.jp/)
The World Premier International Research Center Initiative (WPI) for the Institute of Transformative Bio-Molecules (ITbM) at Nagoya University in Japan is committed to advance the integration of synthetic chemistry, plant/animal biology and theoretical science, all of which are traditionally strong fields in the university. As part of the Japanese science ministry's MEXT program, ITbM aims to develop transformative bio-molecules, innovative functional molecules capable of bringing about fundamental change to biological science and technology. Research at ITbM is carried out in a "Mix-Lab" style, where international young researchers from multidisciplinary fields work together side-by-side in the same lab. Through these endeavors, ITbM will create "transformative bio-molecules" that will dramatically change the way of research in chemistry, biology and other related fields to solve urgent problems, such as environmental issues, food production and medical technology that have a significant impact on the society.

About JST-ERATO Itami Molecular Nanocarbon Project(http://www.jst.go.jp/erato/itami/index.html)
This project entails the design and synthesis of as-yet largely unexplored nanocarbons as structurally well-defined molecules, and the development of novel, highly functional materials based on these nanocarbons. Through the combination of chemical and physical methods, the project aims to achieve the controlled synthesis of well-defined uniquely structured nanocarbon materials. Interdisciplinary research is conducted to encompass the control of molecular arrangement and orientation, structural and functional analysis, and applications in devices and biology.

About JST-ERATO (http://www.jst.go.jp/erato/en/about/index.html)
ERATO (The Exploratory Research for Advanced Technology), one of the Strategic Basic Research Program, aims to form a headstream of science and technology, and ultimately contribute to science, technology, and innovation that will change society and the economy in the future. In ERATO, a Research Director, a principal investigator of ERATO research project, establishes a new research base in Japan and recruits young researchers to implement his or her challenging research project within a limited time frame.

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