

Fully Conjugated Azacorannulene Dimer as Large Diaza[80]fullerene Fragment

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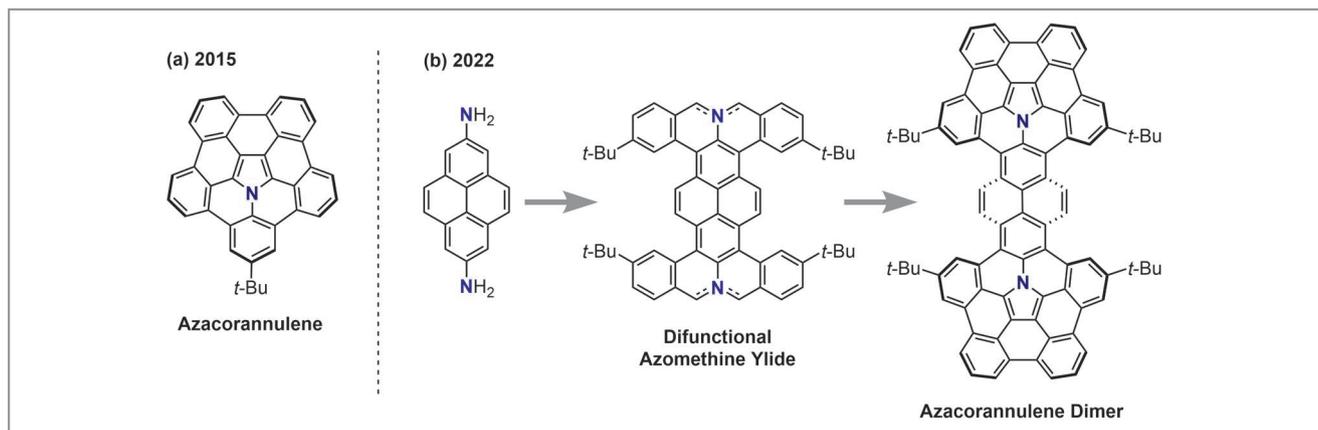
Since their discovery in the 1980s, fullerenes have attracted much attention as a molecular form of carbon allotrope. Owing to their curved structure and rich π -electron density, fullerenes exhibit a wealth of interesting phenomena and properties and thus have been studied and tested for applications in various research fields such as electronics, catalysis, and gas storage. Fullerenes have also been an important target of bottom-up synthesis for synthetic chemists. Although the synthesis of C_{60} from small polycyclic aromatic precursors was achieved,¹ fullerenes of different shapes and sizes are still difficult to synthesize selectively. The group of Professor Shingo Ito at Nanyang Technological University (Singapore) has been studying this synthetic challenge, leading to the title paper in *Nature Communications*.

“Aside from altering the size and shape of fullerenes, introducing one or more heteroatoms into the fullerene cage can be used as an alternative approach to tune its physicochemical properties, thus changing the photochemical and electronic character of the fullerene clusters,” explained Professor Ito. “However, in contrast to hydrocarbon-based fullerenes, the synthesis of heterofullerenes has been much more of a challenge. The successful example of solution-based synthesis thus far is Wudl’s synthesis of $C_{59}N$.² Despite this, the synthesis of multiple heteroatom-embedded fullerenes has not been achieved on a macroscopic scale. There are two major challenges for this synthesis,” continued Professor Ito: “Firstly, syn-

thetic methods for heteroatom-embedded polycyclic aromatic molecules with large π -surfaces are still lacking, compared to hydrocarbon molecules consisting of only carbon and hydrogen atoms. Secondly, the ‘isomeric problem’, whereby introducing multiple heteroatoms into fullerene skeletal structure could generate numerous possible isomers, is a serious issue. Hence, the synthesis and isolation of a single isomer becomes much more of a challenge.”

Encouraged by the above-mentioned bottom-up synthesis of C_{60} ,¹ researchers have shown tremendous interest in the bottom-up synthesis of multi-azafullerenes from polycyclic aromatic precursors. This synthetic approach allows for the controlled and selective introduction of nitrogen atoms into fullerenes. However, suitable synthetic protocols for nitrogen-embedded polycyclic aromatic molecules as large azafullerene fragments have not yet been developed.

Professor Ito said: “In 2015, we reported the efficient synthesis of aza-pentabenzocorannulene (Scheme 1; left), where the key to the successful synthesis is the use of a polycyclic aromatic azomethine ylide.³ This compound has attracted considerable attention from the community, as it represents the first example of a heteroatom-embedded corannulene. Additionally, the molecule can be regarded as a partial structure of mono-azafullerene $C_{79}N$. However, the surface area this compound covers is not large enough to be used as a precursor for azafullerene synthesis. Shinokubo et al. have reported



Scheme 1 (a) Azacorannulene reported in 2015. (b) Synthesis of azacorannulene dimer via difunctional azomethine ylide.

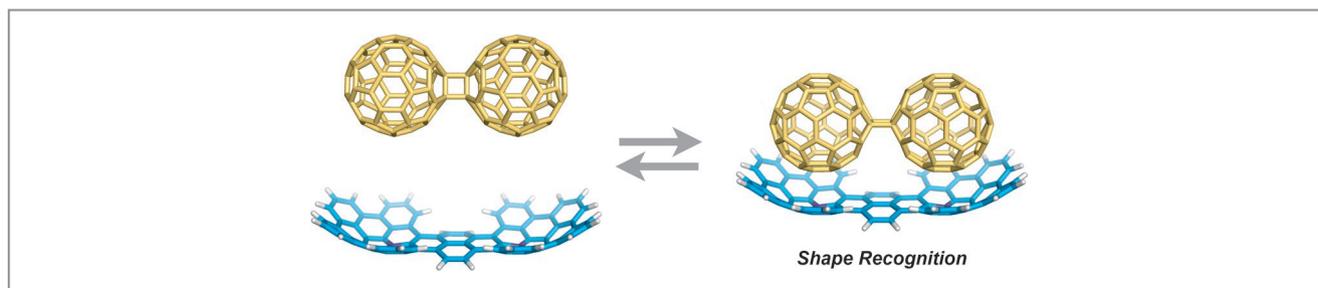


Figure 1 One of the possible modes of association between azacorannulene dimer and C_{120} determined by DFT calculations.

azacorannulene dimers linked via carbon–carbon single bonds;⁴ nevertheless, molecular fragments of azafullerene with larger π -surfaces are relatively rare, due to the limited number of synthetic approaches known.”

In the present study the group decided to synthesize a *fully conjugated* azacorannulene dimer (Scheme 1, right). “Towards the end, we employed a difunctional azomethine ylide derived from 2,7-diaminopyrene as a vital synthetic precursor,” revealed Professor Ito. He continued: “The first primary challenge we encountered was due to the low solubility of fully conjugated difunctional azomethine ylides. At the initial trial, we synthesized the compound without any bulky substituents, but it was found to have an extremely poor solubility, thus preventing us from performing basic structural characterization. Meanwhile, a drastic improvement in its solubility was observed following the introduction of multiple *tert*-butyl groups.

Professor Ito revealed that, following the first submission of this manuscript to *Nature Communications*, the authors received several critical comments and feedback from the reviewers. “One potential drawback raised by the reviewers was regarding the lack of any practical application,” said Professor Ito, continuing: “To address this issue, a reviewer suggested examining our molecule’s ability to act as a host molecule for selective association with C_{120} , which motivated us to investigate its intermolecular association with fullerenes, C_{60} and C_{120} . It was discovered that our azacorannulene dimer exhibits a higher association constant with C_{120} than with C_{60} . This indicates that the boat-shaped azacorannulene dimer has superior recognition of the dumbbell-like C_{120} molecule than of the spherical C_{60} (Figure 1). Thanks to this reviewer’s outstanding suggestion, we successfully managed to observe an interesting phenomenon that is difficult to achieve by other systems.”

“We believe that this method provides an important step towards the selective synthesis of diazafullerenes. The utilization of difunctional azomethine ylide provides a feasible

approach for the synthesis of large multi-azafullerene fragments,” said Professor Ito. He concluded: “In the future, we will be trying to further extend the π -surface of this azacorannulene dimer. Our ultimate goal is to synthesize azafullerene precursors that cover 100% of the atoms of multi-azafullerenes and to succeed in the total synthesis of multi-azafullerene.”

Mattes female

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About the authors



Dr. W. Wang

Weifan Wang was born in Yancheng, Jiangsu (P. R. of China). He received both his B.S. (2014) and Ph.D. (2019) degrees in chemical process engineering of forest products from Nanjing Forestry University (P. R. of China). His studies focused on synthesis and applications of low-valent magnesium complexes. In 2020, he joined Prof. S. Ito's group at Nanyang Technological University (Singapore) for post-doctoral research on the synthesis of heteroatom-containing π -functional molecules.



F. Hanindita

Fiona Hanindita was born in Jakarta (Indonesia). She received a bachelor's degree in chemistry from Nanyang Technological University (Singapore) in 2019. She has been pursuing her Ph.D. degree under the supervision of Professor S. Ito since 2019.



Y. Hamamoto

Yosuke Hamamoto was born in Hiroshima (Japan). He received his B.Sc. (2018) and M.Sc. (2020) in chemistry from Osaka University (Japan). He is currently pursuing his Ph.D. degree at Nanyang Technological University (Singapore) under the supervision of Prof. S. Ito. He works in the field of the synthesis and investigations of π -conjugated aromatic systems.



Dr. Y. Li

Yongxin Li was born in Nanyang, Henan (P. R. of China). He received his Ph.D. degree from the Chemistry Department at National University of Singapore (Singapore) in 2003. He has worked at Division of Chemistry and Biological Chemistry, School of Physical and Mathematical Sciences, Nanyang Technological University (Singapore), as a crystallographer since 2005.



Prof. S. Ito

Shingo Ito received his B.Sc. (2003), M.Sc. (2005), and Ph.D. (2008) degrees in chemistry from The University of Tokyo (Japan) under the supervision of Professor E. Nakamura. During that time, he joined the group of Professor S. E. Denmark at University of Illinois at Urbana-Champaign (USA) and the group of Professor M. Nakamura at Kyoto University (Japan) as a predoctoral researcher. In 2008, he was appointed as Assistant Professor in the group of Professor K. Nozaki at Department of Chemistry and Biotechnology, Graduate School of Engineering, The University of Tokyo (Japan), where he was promoted to Lecturer in 2017. Since 2018, he has been Assistant Professor at Division of Chemistry and Biological Chemistry, School of Physical and Mathematical Sciences, Nanyang Technological University (Singapore). His research interests include the synthesis and applications of novel π -conjugated molecules.