Journal Club 2013.9.26

Yuki ITABASHI

A Grossly Warped Nanographene and The Consequences of Multiple Odd-membered-ring Defects

Katsuaki Kawasumi, Qianyan Zhang, Yasutomo Segawa, Lawrence T. Scott and Kenichiro Itami

Nature Chemistry. DOI:10.1038/nchem.1704

1. Introduction

1.1 The structure of nanocarbon

-Three nanocarbons, ball-like fullerene, cylindrical carbon nanotube, and planar graphene, have been previously identified. Discoveries of fullerene and graphene were awarded Nobel Prizes in 1996 and 2010, respectively.

-Some of them are used as a mixture because the purification is difficult.

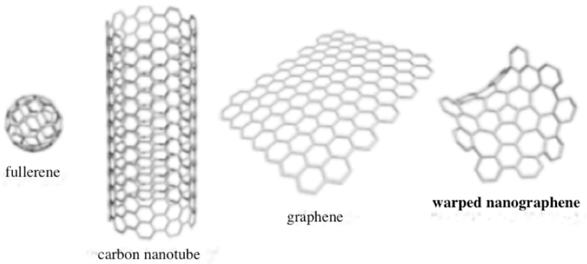


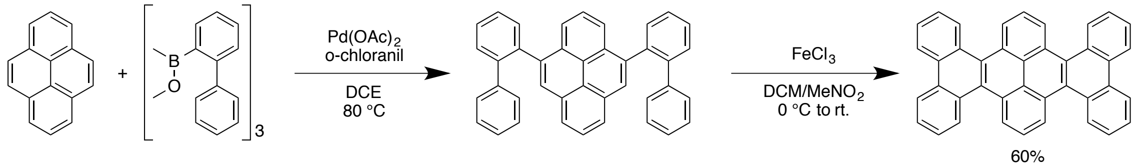
Figure 1. The structure of nanocarbon

=>a convenient and versatile method to synthesize nanocarbon is desired.

1.2 Previous work by author: palladium catalyst system for nanographene

-Nanographene is a part structure of graphene but it has different physical properties (for example semiconductivity, magnetism).

-The properties of nanographene depend on its structure. Therefore, the synthesis of nanographene is desired.



Scheme 1. Direct arylation and annulation

-The authors developed direct arylation of polycyclic aromatic hydrocarbons through palladium catalysis. (***Scheme 1***)[1]

-This reaction and oxidation can give a variety kind of nanographene.
Problem; They are hard to handle due to poor solubility.
=> It is necessary to improve their solubility.

=> If their Van der Waals interaction is suppressed, the solubility of nanographene can be improved?

1.3 This work: warped nanographene

-The authors succeeded in synthesizing a novel nanocarbon, warped nanographene, by combining planar graphene and a five-membered ring and five seven-membered rings using the previously developed catalyst.

-It has also shown the effectiveness of the previously developed coupling reaction.

-Warped nanographene (like *Pringles*) cannot be categorized as one of the three existing nanocarbons, and therefore, it must be declared as a fourth nanocarbon.

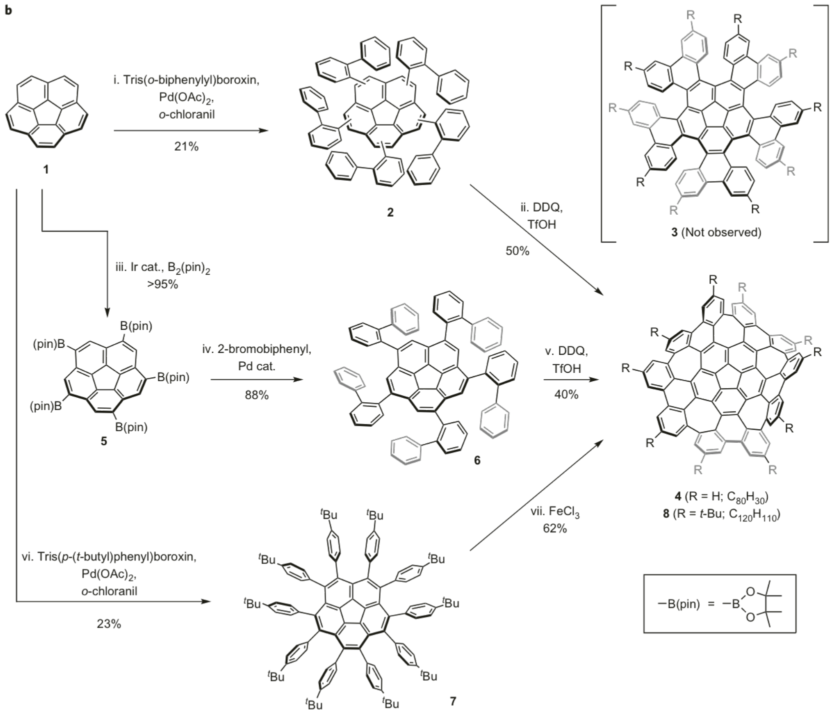
-Since warped nanographene has a curved structure, it is more soluble than nanographene and can be widely used in chemical reactions.
(Warped nanographene **8** is freely soluble even in hexane!)

2. Results and Discussion

2.1 Synthesis of warped nanographene

•Synthesis of warped graphene

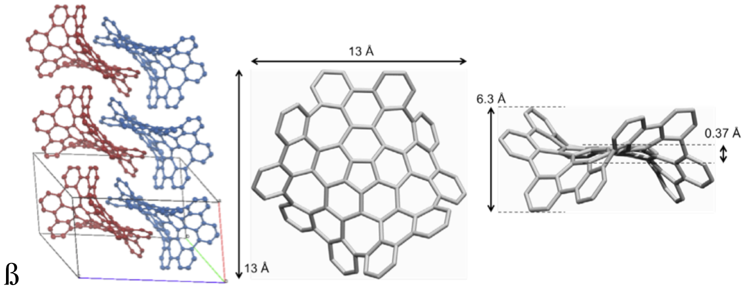
By using the previously developed coupling reaction and oxidation reactions, warped nanographene was reduced in two or three steps from corannulene ,which is commercially available.



Scheme 2. Sythesis of warped nanographenes

2.2 Structure of warped nanographene

-Synthesized nanographene was caracterized by X-ray crystallography. It was grossly warped molecule.



-The presence of five helical hexa[7]circulene moieties, each with *M* or *P* chirality around the seven-membered ring, makes **4** a chiral molecule with enantiomers of *MPMPM* and *PMPMP* configuration.

-Because warped structure suppresses Van der Waals interaction, the solubility is improved.

2.3 **Conformationnal flexibility of grossly warped nanographene**

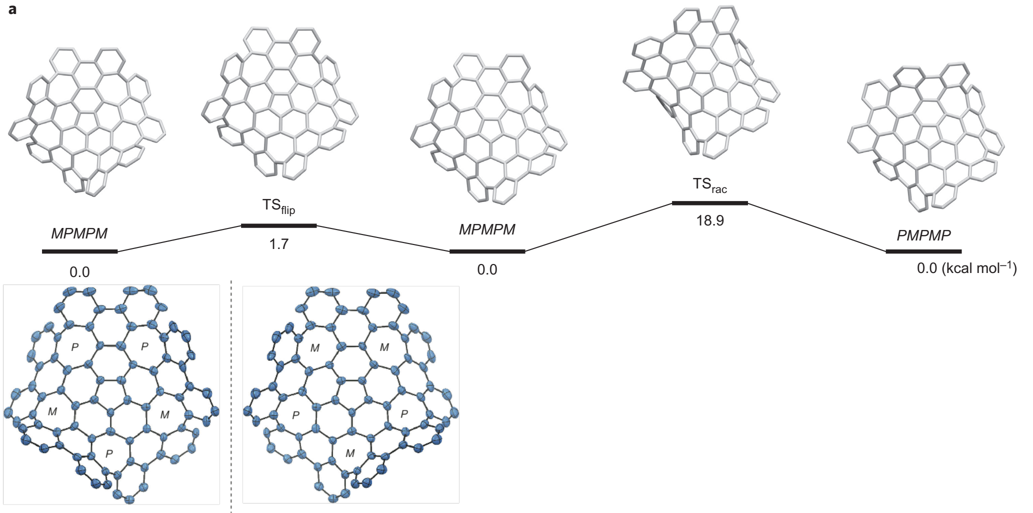


Figure 3. DFT calculation of warped nanographene

- Bowl-to-bowl inversion (left, *MPMPM* ⇔ TSflip ⇔ *MPMPM*) and racemization (right, *MPMPM* ⇔ TSrac ⇔ *PMPMP*) pathways of **4** determined by DFT calculation.

- The activation energies of bowl-to-bowl inversion and racemization of **4** are predicted to be 1.7 and 18.9 kcal mol^{-1}, respectively. The bowl-to-bowl inversion barrier of **4** is considerably lower than that of corannulene . (TS of corannulene is 10.4 kcal mol^{-1})

- Evidence for rapid equalization of the ten benzo groups on the perimeter can be seen from the ^{1}H NMR spectrum of **4**

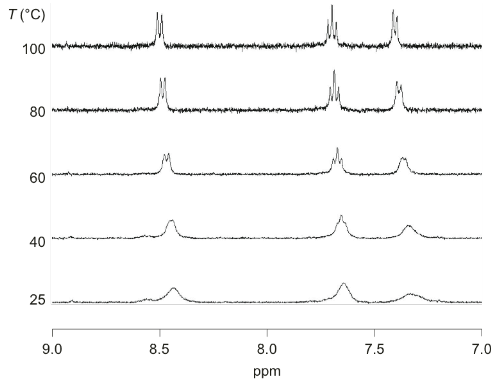
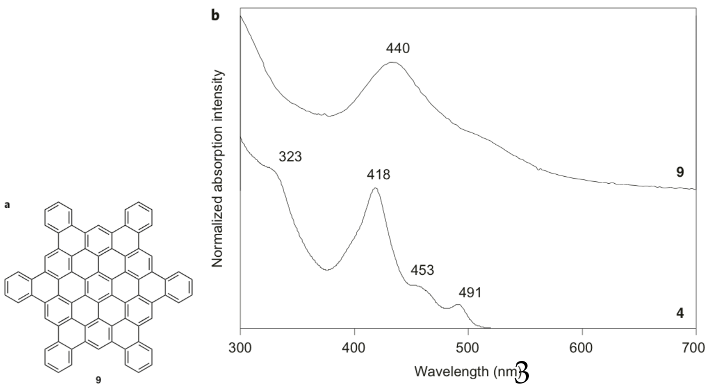


Figure 4. NMR of warped graphene

2.4 **Optical property of warped nanographene**



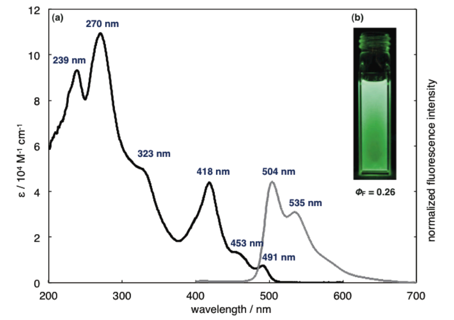


Fig. S8. (a) UV-Vis absorption (black line) and normalized fluorescence (gray line) spectra of $C_{80}H_{30}$ (**4**) in CH_2Cl_2 upon excitation at 418 nm. λ_{max} (ε) = 239 nm (9.3×10^4), 270 nm (1.1×10^5), 323 nm (5.0×10^4), 418 nm (4.4×10^4), 453 nm (1.3×10^4), 491 nm (7.5×10^3). (b) Green fluorescence emission of $C_{80}H_{30}$ (**4**) in CH_2Cl_2. Absolute fluorescence quantum yield determined by a calibrated integrating sphere system within ±3% error.

Figure 5. UV and FL of warped nanographene

The β band and the longest wavelength absorption maximum of **4** (418 nm and 491 nm, respectively) are located at shorter wavelengths than those of **9** (440 nm and ~525 nm, respectively), which indicates that the warped nanographene **4** has a wider band gap than the planar analogue **9**.

2.5 **Electric property of warped graphene**

-The sufficient solubility of deca-*t*-butyl derivative **8** enabled cyclic voltammetry measurements. In CH_2Cl_2, **8** displays two reversible oxidations with first and second oxidation potentials of $E_{ox,1} = +0.63$ V and $E_{ox,2} = +0.97$ V (versus Fc/Fc^+). In the negative potential region, reversible redox waves were observed at the first, second and third reduction potentials of $E_{red,1} = -1.59$ V, $E_{red,2} = -2.02$ V and $E_{red,3} = -2.31$ V (versus Fc/Fc^+).

-A comparison of these cyclic voltammetry data with those of a planar reference system is not possible because planar nanographenes such as **9** are extremely insoluble.

-Corannulene and fullerene are reduced easily, but are somewhat difficult to oxidize. In contrast, warped nanographenes can be oxidized easily as well as be reduced.

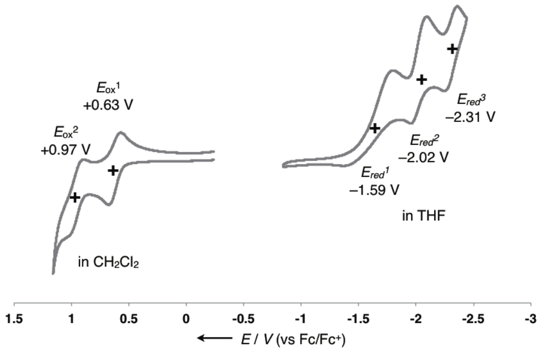


Fig S12. Cyclic voltammogram of $(t\text{-Bu})_{10}C_{80}H_{20}$ (**8**) in CH_2Cl_2 (1.0 mM) and THF (1.0 mM). Scan rate: 100 mV s^{-1}; working electrode: Pt; reference electrode: $Ag/AgNO_3$; electrolyte: $n\mathrm{Bu}_4\mathrm{NPF}_6$. Fc/Fc+ = ferrocene/ferrocenium.

Figure 6. CV of warped nanographene

3. Conclusion

•Unprecedented structure

-A grossly warped grapheme subunit

•Rapid synthesis

-These warped nanographene was synthesized in two or three steps from corannulene

-It has shown the effectiveness of a previously developed coupling reaction.

•Unique properties

Warped nanographene has these properties due to its structure.

-Soluble in common organic solvents

-UV absorption ($\lambda_{max} = 491$ nm)

-Green fluorescence ($\lambda_{max} = 504, 535$ nm)

-Relatively large HOMO-LUMO gap (3.06 eV)

4. Perspective

It will be useful in applications such as solar batteries, organic semiconductors, and bioimaging.

5. Reference

Mochida, K., Kawasumi, K., Segawa, Y. & Itami, K. *J. Am. Chem. Soc.* 133, 10716–10719 (2011).