

# Chemistry of Bowl-Shaped Aromatic Compounds and Metal Nanocluster Catalysts

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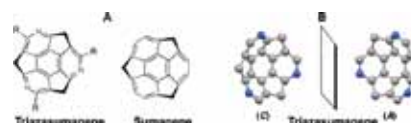
Bowl-shaped  $\pi$ -conjugated compounds including partial structures of the fullerenes, which are called “buckybowls,” are of importance not only as model compounds of fullerenes but also as their own chemical and physical properties. For example, in solution they show the characteristic dynamic behavior such as bowl-to-bowl inversion. On the other hand, they sometimes favor stacking structure in a concave-convex fashion in the solid state, giving excellent electron conductivity. Furthermore, some buckybowls are conceivable to possess the bowl-chirality if the racemization process, as equal as bowl-to-bowl inversion, is slow enough to be isolated. Very few buckybowls has been achieved for preparation mainly due to their strained structure, and no report on the preparation of chiral bowls has appeared. In this project, we develop the rational route to the various buckybowls with perfect chirality control using the organic synthesis approach.

We also investigate to develop novel catalytic properties of metal nanoclusters. We focus on the following projects: Preparation of size-selective gold nanoclusters supported by hydrophilic polymers and its application to aerobic oxidation catalysts; Synthetic application using metal nanocluster catalyst: Development of designer metal nanocluster catalyst using the highly-functionalized protective polymers.

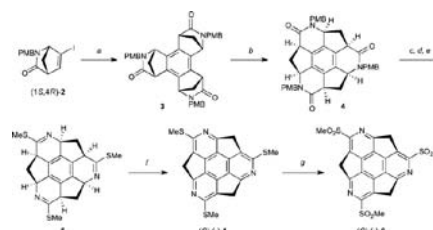
## 1. Enantioselective Synthesis of a Chiral Nitrogen-Doped Buckybowl<sup>1)</sup>

Bowl-shaped aromatic compounds, buckybowls, constitute a family of curved polycyclic aromatic carbons along with fullerenes and carbon nanotubes (CNTs). Doping of heteroatoms to the carbon frameworks of such aromatic compounds drastically modulates their physical and chemical properties. In contrast to nitrogen-doped azafullerenes or CNTs, synthesis

of azabuckybowls, nitrogen-doped buckybowls, remains an unsolved challenging task. Accordingly, we have achieved the first enantioselective synthesis of a chiral azabuckybowl, triazasumanene. X-ray crystallographic analysis confirmed that the doping of nitrogen induces a more curved and deeper bowl structure than in all-carbon buckybowls. As a result of the deeper bowl structure, the activation energy for the bowl inversion (thermal flipping of the bowl structure) reaches an extraordinarily high value (42.2 kcal/mol). Since the bowl inversion corresponds to the racemization process for chiral buckybowls, this high bowl inversion energy leads to very stable chirality of triazasumanene.



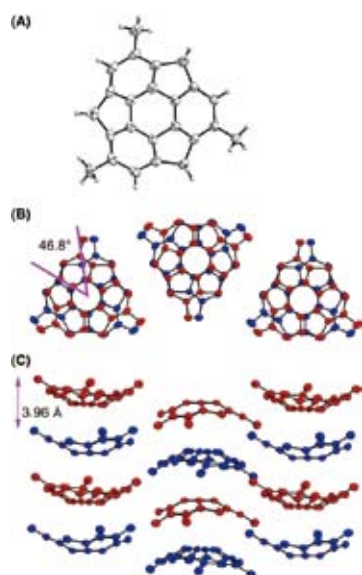
**Figure 1.** (A) Triazasumanene and sumanene; (B) Enantiomers of triazasumanene.



**Figure 2.** Conditions: (a)  $\text{Pd}(\text{OAc})_2$ ,  $\text{PPh}_3$ ,  $\text{Bu}_4\text{NOAc}$ ,  $\text{Na}_2\text{CO}_3$ , molecular sieve 4 Å, 1,4-dioxane, 100 °C, 2 h, 57%; (b) i) 12 M HCl, AcOH, 60 °C, 3 h; ii)  $\text{C}_6\text{F}_5\text{OP}(=\text{O})\text{Ph}_2$ , DIPEA, DMF, 0 °C to 60 °C, 59% (two steps); (c) Lawesson's reagent, dichloroethane, microwave, 160 °C, 40 min, 92%; (d) Trifluoroacetic acid, microwave, 100 °C, 2 h, 88%; (e) MeI,  $\text{K}_2\text{CO}_3$ , DMF, 30 °C, 3 h, 79%; (f)  $\text{Ph}_3\text{CBF}_4$ , DTBMP,  $\text{CH}_2\text{Cl}_2$ , 25 °C, 3 d, 73%; (g) *m*-CPBA,  $\text{CH}_2\text{Cl}_2$ , 25 °C, 5 h, 90%.

## 2. Trimethylsumanene: Enantioselective Synthesis, Substituent Effect on Bowl Structure, Inversion Energy, and Electron Conductivity<sup>2)</sup>

$C_3$  symmetric chiral trimethylsumanene was enantioselectively synthesized through Pd-catalyzed *syn*-selective cyclotrimerization of an enantiomerically pure iodonorbornenone, ring-opening/closing olefin metathesis, and oxidative aromatization where the  $sp^3$  stereogenic center was transmitted to the bowl chirality. Chiral HPLC analysis/resolution of the derivatives were also achieved. Based on theoretical calculations, the columnar crystal packing structure of sumanene and trimethylsumanene was interpreted as due to attractive electrostatic or CH- $\pi$  interaction. According to the experimental and theoretical studies, the bowl depth and inversion energy were found to increase on methylation for sumanene in contrast to corannulene. Dissimilarities of the effect of methylation on the bowl structure and inversion energy of sumanene and corannulene were ascribed to differences in steric repulsion. A double-well potential model was fitted to the bowl structure-inversion energy correlation of substituted sumanenes, with a small deviation. The effects of various substituents on the sumanene structure and bowl inversion energy were analyzed by density functional theory calculations, and it was shown that the bowl rigidity is controlled by a combination of electronic and steric effects of the substituents. The electron conductivity of trimethylsumanene was investigated by time-resolved microwave conductivity method, compared with that of sumanene.



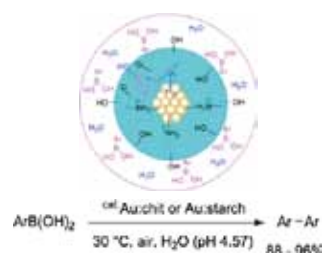
**Figure 3.** (A) ORTEP drawings of X-ray crystallographic analysis of (±)-3, (B) top view, (C) side view, shown at the 50% probability level.

### Awards

DHITAL, Raghu Nath; Young Scientist Award, International Conference on Advanced Materials and Nanotechnology (2011).  
 DHITAL, Raghu Nath; Young Oral Presentation Award, International Symposium on Catalysis and Fine Chemicals 2011 (2011).  
 TAN, Qi Tao; Outstanding Poster Presentation, International Symposium on Catalysis and Fine Chemicals 2011 (2011).

## 3. Dual Roles of Polyhydroxy Matrices for Homocoupling of Arylboronic Acid Catalysed by Gold Nanoclusters Under Acidic Conditions<sup>3)</sup>

Polyhydroxy biopolymers including chitosan and starch play the dual roles of stabilization of gold clusters as well as activation of arylboronic acids through reversible binding. In acidic pH of 4.57 the electronic state of boron is changed to the corresponding to that at pH 9 inside the vicinity of Au:chit or Au:starch which favours the transmetallation process *i.e.* why homo-coupling product was observed even under acidic solutions.



## 4. Anomalous Efficacy of Bimetallic Au/Pd Nanoclusters in C-Cl Bond Activation and Formal Metathesis-Type C-B Bond Activation at Room Temperature<sup>4)</sup>

Au/Pd alloy nanoclusters stabilized by poly (N-vinylpyrrolidone) catalyze two different reactions of phenylboronic acid with 4-chlorobenzoic acid at room temperature in a single reaction cycle, cross coupling and metathesis-type homocoupling that is normally inaccessible through conventional catalysis.



### References

- 1) Q.-T. Tan, S. Higashibayashi, S. Karanjit and H. Sakurai, *Nat. Commun.* 3:891 doi: 10.1038/ncomms1896 (2012).
- 2) S. Higashibayashi, R. Tsuruoka, Y. Soujanya, U. Purushotham, G. N. Sastry, S. Seki, T. Ishikawa, S. Toyota and H. Sakurai, *Bull. Chem. Soc. Jpn.* **85**, 450-467 (2012).
- 3) R. N. Dhital, A. Murugadoss and H. Sakurai, *Chem. -Asian J.* **7**, 55-59 (2012).
- 4) R. N. Dhital and H. Sakurai, *Chem. Lett.* **41**, 630-632 (2012).