

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

Research Center for Molecular Scale Nanoscience  
Division of Molecular Nanoscience



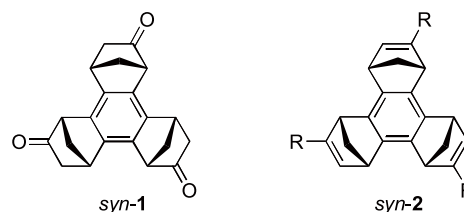
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Bowl-shaped  $\pi$ -conjugated compounds including partial structures of the fullerenes, which are called “buckybowls,” are of importance not only as model compounds of fullerenes but also as their own chemical and physical properties. Heteroatom-containing buckybowls (heterobuckybowls) have also been expected to exhibit unique physical characters. 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. However, very few buckybowls/heterobuckybowls has been achieved for preparation mainly due to their strained structure, and no report on the preparation of chiralbowls has appeared. In the present project, we develop the rational route to the various kinds of buckybowls/heterobuckybowls with perfect chirality control using the organic synthesis approach.

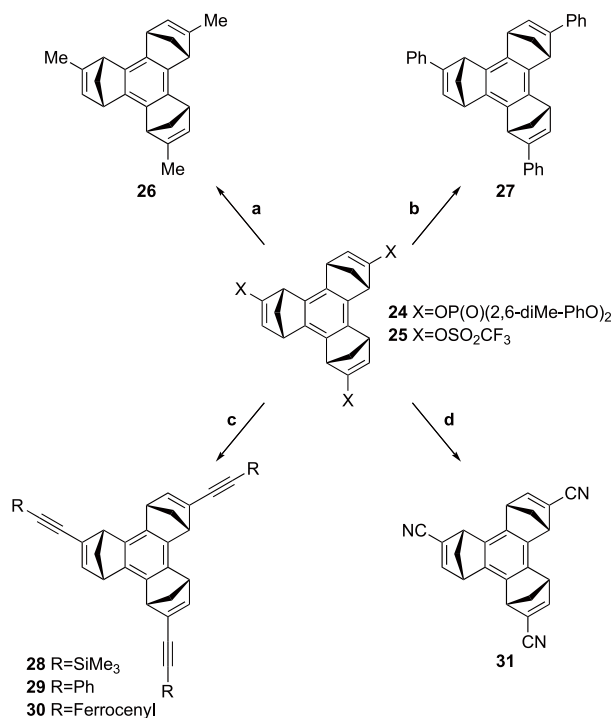
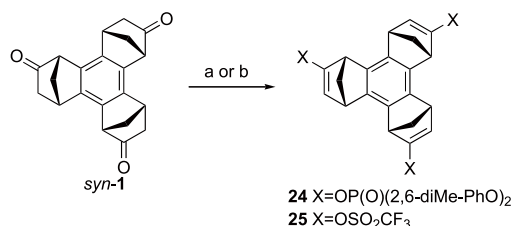
We also investigate to develop novel catalytic properties of metal nanoclusters. We focus on the following projects: Preparation of size-selective gold nanoclusters supported by hydrophilic polymers and its application to aerobic oxidation catalysts: Synthetic application using metal nanocluster catalyst: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

## 1. Preparation of $C_3$ Symmetric Homochiral *syn*-Trisnorbornabenzenes through Regio-Selective Cyclotrimerization of Enantiopure Iodonorbornenes<sup>1)</sup>

$C_3$  symmetric homochiral (-)-*syn*-trisoxonorbornabenzene **1** possessing a rigid cup-shaped structure was synthesized through a novel regio-selective cyclotrimerization of enantiopure iodonorbornenes catalyzed by palladium nanoclusters. The yield of the cyclotrimerization was dependent on the stability of the palladium clusters, which was ascertained from the appearance and TEM images of the reaction mixtures. The efficient preparation of (-)-*syn*-**1** was established in short steps including the newly developed cyclotrimerization reaction.

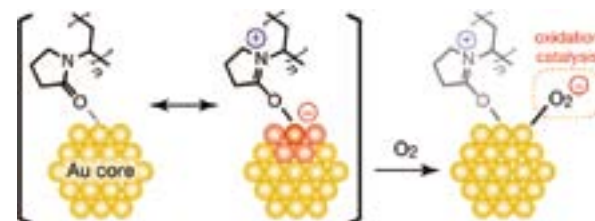


The thus-prepared homochiral (-)-*syn*-**1** can serve as a key intermediate for the synthesis of  $C_3$  symmetric homochiral cup-shaped molecules with a helical arrangement of substituents. Introduction of several types of substituents was well demonstrated through palladium-catalyzed coupling reactions with the corresponding phosphate and triflate of (-)-*syn*-**1**.



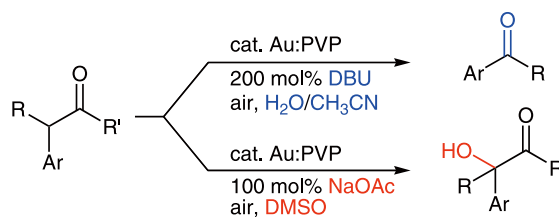
## 2. Effect of Electronic Structures of Au Clusters Stabilized by Poly (*N*-vinyl-2-pyrrolidone) on Aerobic Oxidation Catalysis<sup>2)</sup>

Au clusters smaller than 1.5 nm and stabilized by poly (*N*-vinyl-2-pyrrolidone) (PVP) showed higher activity for aerobic oxidation of alcohol than those of larger size or stabilized by poly(allylamine) (PAA). X-ray photoelectron spectroscopy, Fourier transform infrared spectroscopy of adsorbed CO, and X-ray absorption near edge structure measurements revealed that the catalytically active Au clusters are negatively charged by electron donation from PVP, and the catalytic activity is enhanced with increasing electron density on the Au core. Based on similar observations of Au cluster anions in the gas phase, we propose that electron transfer from the anionic Au cores of Au:PVP into the LUMO ( $\pi^*$ ) of O<sub>2</sub> generates superoxo or peroxy-like species, which plays a key role in the oxidation of alcohol. On the basis of these results, a simple principle is presented for the synthesis of Au oxidation catalysts stabilized by organic molecules.



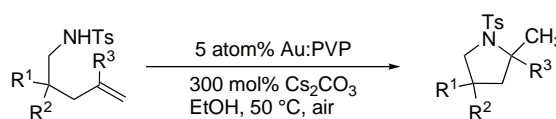
## 3. Aerobic Oxygenation of Benzylic Ketones Promoted by Gold Nanocluster Catalyst<sup>3)</sup>

Au:PVP promoted the oxidation of benzylic ketones, including auto-oxidation-type bond cleavage reactions and  $\alpha$ -hydroxylation, under ambient conditions. The catalyst accelerates the formation of an  $\alpha$ -peroxide intermediate, from which bond cleavage spontaneously proceeds in aqueous solvent to give the auto-oxidation products. In contrast, the  $\alpha$ -hydroxylation product is obtained predominantly in DMSO solvent.



## 4. Intramolecular Addition of Toluene-Sulfonamide to Unactivated Alkenes Catalyzed by Gold Nanoclusters under Aerobic Conditions<sup>4)</sup>

Au:PVP catalyzed the intramolecular addition of tosyl amides to unactivated alkenes in EtOH under aerobic conditions.



## References

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- 2) H. Tsunoyama, N. Ichikuni, H. Sakurai and T. Tsukuda, *J. Am. Chem. Soc.* **131**, 7086–7093 (2009).
- 3) H. Sakurai, I. Kamiya, H. Kitahara, H. Tsunoyama and T. Tsukuda, *Synlett* 245–248 (2009).
- 4) H. Kitahara, I. Kamiya and H. Sakurai, *Chem. Lett.* **38**, 908–909 (2009).