

Three-Dimensional π -Electron Molecules

Research Center of Integrative Molecular Systems
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Organic molecules possessing three-dimensional (3D) curved π -conjugated structures are attractive research targets in organic synthesis, physical organic chemistry, and organic material science. My research interest is the creation of new 3D π -conjugated organic molecules, the elucidation of properties, and the application in material science.

1. Butterfly- and Bowl-Shaped Molecules

We succeeded to create new butterfly-shaped¹⁾ (Figure 1) and bowl-shaped²⁾ (Figure 2) π -conjugated molecules with embedded hydrazine structure. The butterfly-shaped molecules were synthesized by dimerization of heterocycles (dimethyl-acridine, phenothiazine, acridone). The bowl-shaped molecule with bicarbazole structure was synthesized by desulfurization of butterfly-shaped biphenothiazine. The bowl-shaped molecule was found to undergo reversible two-electron oxidation,

in which the shape of molecule was transformed between bowl and planar geometries (Figure 2).

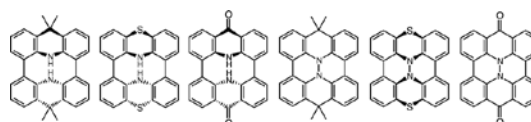


Figure 1. Butterfly- and bowl-shaped molecules.

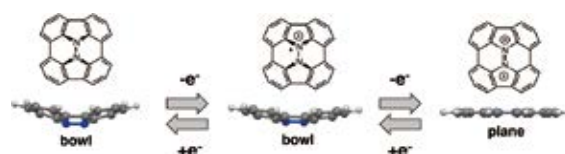


Figure 2. Butterfly- and bowl-shaped molecules.

References

- 1) K. Yamamoto and S. Higashibayashi, *Chem. –Eur. J.* **22**, 663–671 (2016).
- 2) S. Higashibayashi, P. Pandit, R. Haruki, S. Adachi and R. Kumai, *Angew. Chem., Int. Ed.* **55**, 10830–10834 (2016).

Coordination Behavior of Heteroarenes to Palladium Centers

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The coordination behavior of heteroarenes to palladium centers has attracted much attention since their coordination has been involved in Pd-catalyzed functionalization reactions of heteroarenes. However, heteroarene–palladium complexes have rarely been isolated, due to the labile nature of heteroarene–Pd complexes. In this project, synthesis and structural characterization of heteroarene–Pd complexes have been studied.^{1,2)}

1. σ - π Continuum in Indole–Pd^{II} Complexes

It has been proven that there is a σ - π continuum in heteroarene–metal complexes through isolation and systematic structural analysis of σ - and π -modes in indole–Pd^{II} complexes, while σ -mode has been assumed as the dominant mode for heteroarene–Pd interaction. The insight into the hetero-

arene–Pd interaction will provide a structural aspect on the key catalytic intermediates of palladium-catalyzed heteroarene transformations. Further study to verify the reactivity of σ -, σ/π -intermediate-, and π -complexes of indole is now underway.

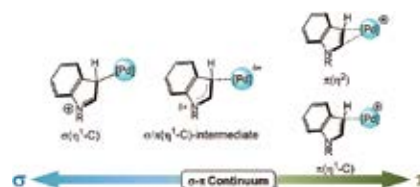


Figure 1. σ - π Continuum in indole–Pd complexes.

References

- 1) K. Yamamoto, S. Kimura and T. Murahashi, *Angew. Chem., Int. Ed.* **55**, 5322–5326 (2016).
- 2) K. Yamamoto, Y. Ishikawa, S. Kimura and T. Murahashi, *C. R. Chim.* **18**, 785–789 (2015).