【Grant-in-Aid for Scientific Research(S)】
Science and Engineering (Chemistry)

Title of Project : Supraporphyrin Chemistry:Explorations of Novel π-systems

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Research Area : Organic chemistry
Keyword : Structural organic chemistry

【Purpose and Background of the Research】

Porphyrins have been extensively studied in a wide range of research fields for long years owing to their favorable optical and electrochemical properties as well as remarkable catalytic abilities of metal complexes. In this project, we expand our own porphyrin chemistry that includes mono-disperse giant porphyrin arrays, extremely π-extended porphyrin tapes, ring-expanded porphyrins, ring-contracted porphyrins (subporphyrins), which can be regarded as supraporphyrins. Möbius aromatic and antiaromatic molecules will be also studied. A real goal will be to find novel π-conjugated electronic systems that lead to innovation of organic, inorganic, photochemical, and material chemistry.

【Research Methods】

As a new highly conjugated system, directly *meso-meso* linked porphyrin-hexaphyrin hybrids will be explored. A porphyrin-hexaphyrin-porphyrin triad has been already prepared and has been transformed into corresponding triply linked hybrid tape. Surprisingly, this molecule displays a Q-like band at 1924 nm, which is more red-shifted than the previously synthesized zinc porphyrin tape (1852 nm). Synthetic method to connect a porphyrin and a hexaphyrin will be improved and repeated oxidative dimerization reactions will provide longer hybrid arrays. Final oxidative fusion reaction will give hybrid porphyrin tapes.

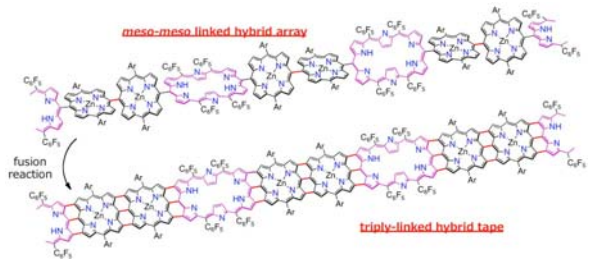

Figure 1 Hybrid porphyrin-hexaphyrin

A concept of dual aromaticity will be examined by synthesizing internally 1,3-phenylene-, 2,5-thiophenylene- or 2,5-pyrrolylene-bridged hexaphyrins. In these molecules, both [18]porphyrin and [26]hexaphyrin conjugation pathways are conceivable. Detailed structural and electronic studies on these molecules will give useful information on the dual aromaticity.

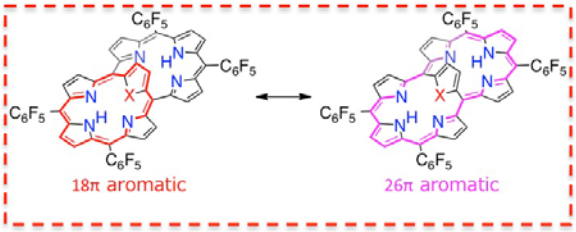

Figure 2 Annulenoannulene

Recently, a *meso-meso* linked subporphyrin dimer and subporphyrin-porphyrin dyad have been successfully obtained via reductive coupling and cross-coupling, respectively. By utilizing this strategy, we'll produce novel subporphyrins such as fused subporphyrin dimers.

【Expected Research Achievements and Scientific Significance】

So far, we have explored various aspects of porphyrinoids that are structurally and electronically flexible. Through these studies on supraporphyrins, a class of novel π-conjugated systems is expected to emerge, which will have strong impacts on organic chemistry, inorganic chemistry, coordination chemistry, physical chemistry, and material chemistry.

【Publications Relevant to the Project】

- Masaaki Kitano, Atsuhiro Osuka *et al.* "Effective *meso*-Fabrications of Subporphyrins" *Angew. Chem. Int. Ed.* **51**, 5593-5597 (2012).
- Hirotaka Mori, Atsuhiro Osuka *et al.* "Fused porphyrinoids as promising near-infrared absorbing dyes" *J. Mat. Chem. C* **1**, 2500-2519. (2013)

【Term of Project】 FY2013-2017

【Budget Allocation】 97,400 Thousand Yen

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