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学位論文題目 Synthesis and Supramolecular Assembly of Highly
Planar Amphiphilic Porphyrin Complexes

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The supramolecular integration of porphyrin and its derivatives has attracted great attention because of the relevance to natural photosynthetic systems. In order to obtain well-defined porphyrin aggregates, not only covalent bonding but also metal coordination, hydrogen-bonding and van der Waals interactions have been utilized and the obtained integrated structures have been employed for applications in various fields of materials science and technology. The author has focused on the supramolecules of amphiphilic motives with rigid π -conjugated cores, which have been well employed to obtain excellent optoelectronic properties associated with the characteristic nanostructures. In this study, he has developed an asymmetrically β -substituted amphiphilic porphyrin, which is designed to be much planar and less bulky with an aim to accomplish densely packed nanostructures and induce strong intermolecular interactions between the metal centers.

The triethyleneglycol(TEG)-tethered and alkyl-tethered dipyrromethanes have been prepared, and then the synthesis of the target porphyrin has been accomplished by the condensation reaction of these dipyrromethanes. In contrast to the synthesis of *meso*-aryl-type porphyrin, that of asymmetrically substituted β -alkyl-type porphyrin has not been well explored. Several conditions were examined for the condensation reaction of two different dipyrromethanes and finally, the target zinc porphyrin was successfully obtained by condensation of TEG-tethered dipyrromethane and an alkyl-tethered α,α' -dipropylimino-dipyrromethane in refluxing cyclohexane in the presence of $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ as a template. In this procedure, an isomerization reaction of porphyrin derivatives, so-called scrambling reaction, was suppressed under lower reaction temperature or in less polar solvents by hampering the pathway of this side-reaction. For the optimized synthesis, 44.8 mg of the porphyrin mixture was obtained in 18% yield and the ratio of the target compound and the isomer (isomer/target) was 0.03. The isolation of the target porphyrin 1-Zn from the isomeric mixture was accomplished by repeated recrystallizations from the solution in a CH_2Cl_2 -MeOH mixed solvent. As a result, the isomeric mixture of 44.8 mg afforded 22.5 mg of the target 1-Zn to be pure at NMR level. The characterization of the target porphyrin has been carried out by ^1H and ^{13}C NMR spectroscopies and HR FAB-MS spectrometry. The central zinc atom was demetallated under the acidic condition with TFA in CH_2Cl_2 and the freebase porphyrin 1- H_2 was obtained in 98% yield. The insertion of copper ions was carried out by refluxing the solution of 1- H_2 in the presence of $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$, which resulted in target compound 1-Cu quantitatively.

The supramolecular integration of the obtained porphyrins 1- H_2 and 1-Cu has been examined in some polar solvents by taking advantage of the amphiphilic properties of the porphyrins. The UV-Vis spectral changes were observed on adding H_2O to the solution of the freebase 1- H_2 in THF. The Soret absorption band of 1- H_2 shows red

shift by 42 nm. Similar behaviors were observed for the absorption experiments of 1-H₂ upon cooling the hot MeOH solution. On the other hand, when H₂O was added to the solution of 1-Cu in THF, the Soret band of 1-Cu at 397 nm displayed clear blue shifts with a peak (λ_{max}) at 392 nm in THF : H₂O = 1 : 9 mixed solvent. In general, Kasha's exciton theory predicts that a blue shift observed in the optical absorption indicates a face-to-face H-aggregation of the chromophores.

The shapes of the nanostructures of the integrated porphyrin assemblies have been confirmed by the SEM and TEM observations. When the suspension of freebase porphyrin 1-H₂ precipitated from the hot MeOH solution was casted on a substrate, the TEM image revealed a rod structure that consists of the bundles of wires with the diameter of about 25 nm. The precipitate of 1-Cu obtained from THF-H₂O showed short rod-like structures with the diameter of around 11 nm and the length in the range of 140–310 nm as estimated from the SEM and TEM observations. The SEM image of the precipitate of 1-Cu obtained from a hot MeOH solution afforded a helical ribbon-structure without chiral selectivity.

The XRD analysis of the precipitate of 1-Cu from THF-H₂O solution revealed that the molecules are packed in a *monoclinic* unit cell with the dimensions of $a = 67.71(4)$, $b = 3.546(3)$ and $c = 24.62(2)$ Å and $\beta = 96.72(7)^\circ$ and the π -stacked 1-D chains are aligned to the b -axis with the π -stacking distance of 3.55 Å.

He investigated the thermal magnetic behaviors of 1-Cu with SQUID measurements in order to confirm the intermolecular metal-metal interaction induced by the supramolecular integration. The magnetic susceptibility of the precipitate obtained from THF-H₂O solution shows a bent on decreasing temperature, which indicates a weak magnetic interaction between the Cu(II) centers. The Curie-Weiss plot of the susceptibility between 4–300 K affords the Weiss constant as -0.22 K. The induction of intermolecular magnetic interaction between metal centers with soft-material systems is rare.

The supramolecular integration of the porphyrin without any solvents has been also investigated by slow cooling from the melting state. The DSC measurement and the POM observation of 1-Cu showed that the melting point was *ca.* 130 °C and the porphyrin was thermally stable upto this temperature region. When 1-Cu was heated over 130 °C, fluid-like porphyrin was observed. After cooling to r. t., integrated 1-Cu was obtained easily and the UV-Vis spectrum and the XRD analysis of this aggregate suggested a similar supramolecular structure as 1-Cu precipitates obtained from the solution in polar solvents.

In summary, the author has succeeded in the syntheses of novel amphiphilic porphyrin complexes, investigated their self-assembly behaviors and the properties of the assembled nanostructures.

機能性ナノ物質の開拓は、分子デバイスの構築という観点から極めて重要な課題である。機能性物質を構築するには、分子の配列を精密制御し、その秩序を長距離にわたって保つことが鍵となる。本研究では、 π 電子系分子の配列制御に着眼し、超分子アプローチを用いて、新規な機能性物質の合成に挑戦した。具体的に、新規な高い平面性を有するポルフィリン錯体を設計し、両親媒性を付与することで、低次元機能性物質群を創出し、その構造に由来する特異な機能について検討した。

第一章は超分子自己組織化に関して、これまでの分子設計指針や超分子ナノ構造と機能について記述してある。第二章は両親媒性ポルフィリンを合成するため、その前駆体となる親水性鎖と疎水性鎖を有するジピロールメタン類の合成、精製、及び構造同定について述べてある。出発原料から13工程を経て作り上げるため、各工程における合成収率の向上を目指した。第三章は親水性鎖と疎水性鎖を有するジピロールメタン類を用いて、様々な反応条件下でポルフィリンの合成を試み、最適条件を突き止めた。また、異性体の生成機構を考察し、それを抑制するための反応条件の検討を行った。両親媒性ポルフィリンの精製、脱金属反応、及び銅錯体の錯形成反応、カラム精製、構造同定、両親媒性銅ポルフィリン錯体の合成について記述している。第四章は両親媒性ポルフィリン類を用いて、溶媒中における自己組織化、紫外・可視吸収スペクトルを用いた自己組織化過程の追跡、TEM、XRDを用いたナノ構造体の解析、分子配列構造の特定、及びナノ構造体の特異な磁氣的相互作用について記述している。第五章は固体状態において、加熱・冷却による自己組織化、構造体の構造変化、DSCを用いた自己組織化過程の追跡などについて記述されている。第六章は全体まとめと展望について記述している。

ポルフィリンを用いた自己組織化アプローチは、ポルフィリンの多彩な光機能や酸化還元、磁氣的な機能を活かすことができる。両親媒性ポルフィリンの合成は数多くの段階を要し、合成法も確立されていない中、ゼロからスタートした合成である。また、構造特異な低次元機能性ナノファイバーやロッドを構築することに成功し、これまでのアプローチで困難であったH会合体を形成することを見いだしている。このような低次元H会合体における磁氣的な相互作用を明らかにし、構造-機能の相関を突き止めた。本研究は、『高い平面性を有する両親媒性ポルフィリン』の初めての例として注目され、新しい光・電子機能性物質として大いに期待できる。

以上のように、本論文では、高い平面性を有する両親媒性ポルフィリン錯体を設計・合成し、新規な低次元ナノ構造体合成及び機能開拓に成功している。特に、両親媒性ポルフィリンの合成は極めて独創的である。審査において小田氏の研究に対するあくなき取組み

やたゆまぬ努力が伺われた。高い平面性を有する両親媒性ポルフィリン錯体の合成およびその機能開拓を通じて、新しい分子モチーフとなり得る物質を創出したことで、国際的にも高い水準の研究であると判定された。研究発表も内容、質疑応答ともにきちんとしており、審査委員会は出願論文が博士（理学）の授与に値すると全員一致で判断した。