

## 博士論文の内容の要旨

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論文題目	Studies on design and characterization of phthalocyanine-based liquid crystals and liquids (液晶および液体フタロシアニンの設計と評価に関する研究)

(博士論文の内容の要旨)

Intermolecular interactions play a key role in formation of aggregates in materials as well as physical state. Aggregation states are one of the factors to affect material's functions. In the field of material chemistry, controlling molecular interaction is one of the crucial factor to develop novel functional material and enhance performance of molecule-based devices.

Phthalocyanines (Pcs) have attracted much attention for their near-infrared (NIR) absorption and potential application to luminous dyes. In general, Pcs tend to form face-to-face (H-) aggregate in condensed state due to their planar and rigid structure. The organizational property is attractive for applications as semiconductor. However, formation of H-aggregate leads to lose of their NIR luminous property.

The main objective of the present thesis is to reveal relationship between molecular structure and aggregation property of Pcs in liquid crystalline and solvent-free liquid states. Combination of flexible units and rigid  $\pi$ -conjugated units can not only provide enhanced solubility to organic solvents but also control intermolecular interactions. In addition, introduction of flexible units to  $\pi$ -conjugated units can induce soft molecular assemble such as liquid crystals and molecular liquids. In this thesis, the author has been adopted the methodology to achieve the research objective. The positions of alkyl chains on phenyl ether groups have been changed from *m*-position (**Chapter 3**) to *o*-position (**Chapter 4**), leading to reduction of  $\pi$ - $\pi$  interactions between Pcs. Detailed analyses have been conducted for the Pc's aggregates in columnar liquid crystalline (**Chapter 3**) and solvent-free liquid states (**Chapter 4**). Moreover, the author has focused on the structures of bulky yet flexible units, and the bulky unit's position on Pc ring (**Chapter 5**). The relationship between the molecular structures and aggregation property has been investigated. These works are summarized in the following section.

**Chapter 3** describes the synthesis, characterization, mesomorphism of novel octa(*m*-alkoxyphenylthio)PcCu. The structure of  $\pi$ - $\pi$  stacks and liquid crystalline phase depended on the ether linkers (O in previous work, S in this work) and length of alkyl chains. Each of the present longer alkoxy-substituted *phenylthio* derivatives (*m*-C<sub>*n*</sub>OPhS)<sub>8</sub>PcCu (*n* = 4~16) showed only rectangular columnar (Col<sub>ro</sub> (P2m)) phase (tilted  $\pi$ - $\pi$  stack), whereas each of the previous longer alkoxy-substituted *phenoxy* derivatives (*m*-C<sub>*n*</sub>OPhO)<sub>8</sub>PcCu (*n* = 10~20) showed only a hexagonal columnar (Col<sub>ho</sub>) phase (face-to-face  $\pi$ - $\pi$  stack). The different mesophase appearance may be originated from the difference in interaction among the Pc cores having steric hindrance of the peripheral substituents (PhO and PhS).

**Chapter 4** investigates the detailed liquid properties of octa(*o*-dodecyloxyphenoxy) copper phthalocyanine and the metal-free derivative. The result of absorption spectra in liquid film indicated that face-to-face (H-) aggregates were formed in the solvent-free liquid state. Polarizing optical microscopic and rheological experiments suggested the presence of nano-sized rod-like cluster, and the clusters collapsed in response to external inputs of temperature and shear force.

In **Chapter 5**, the synthesis and relationship between the molecular structures and aggregation properties for novel liquid Pcs **1** and **2** are reported. **1** formed H-aggregates in the solvent-free liquid state. On the other hand, **2** remained monomeric non-aggregated state in the solvent-free state, which contributes to NIR-fluorescence emission in the liquid state. In addition, enhanced photostability in relative to the control sample is found in **2** due to steric wrapping effect of the branched alkyl chains.