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論 文 内 容 要 旨

The essence of this doctoral thesis is the synthesis and spectroscopic and electrochemical elucidation of novel core-modified phthalocyanines and related compounds, including subphthalocyanine and phthalocyanine dimers, which contain internal six-membered or seven-membered ring units instead of pyrrolic five-membered ring units. The main content is showed as follows.

In Chapter 2, a general method which produces core-modified phthalocyanines (APPcs) containing one or two internal six-membered ring units instead of pyrrolic five-membered ring units by utilizing 1, 8-naphthalenedicarbonitrile as a key starting material has been developed, and these novel phthalocyanine analogues were investigated by means of spectroscopic and electrochemical measurements. All of the APPcs retain a similar aromaticity to that of phthalocyanine, while the spectroscopic and electrochemical properties are strongly altered depending on the number and positions of the incorporated six-membered ring units. Mono-substituted APPc shows red-shifted and split Q bands, and the red-shift is enhanced upon increasing the number of incorporated six-membered rings. *adj*-AP₂Pc shows non-split Q band, while *opp*-AP₂Pc shows strongly split Q bands, depending on the relative positions of the two six-membered rings. The first oxidation potentials of APPcs shift to the negative side upon increasing the number of incorporated six-membered rings, while the first reduction potentials remain almost unchanged. Accordingly, destabilization of the HOMOs of APPcs is found, and the extent of the changes of the LUMOs is small. The decreased HOMO-LUMO gaps are consistent in turn with the red-shifts of the lower-energy Q bands and decreased potential differences.

In Chapter 3, the method employed in Chapter 2 has been further developed to produce a novel core-modified phthalocyanine (AZPPc) containing one seven-membered ring unit instead of a pyrrolic five-membered ring unit, by utilizing biphenyl-2, 2'-dicarbonitrile as a key starting material. The two cyano groups

in the biphenyl-2,2'-dicarbonitrile are further away from each other than those in 1,8-naphthalenedicarbonitrile. In this case, a further-expanded seven-membered ring is incorporated into the phthalocyanine skeleton. Crystallographic analysis on AZPPc unambiguously shows a severely distorted conformation, where the biphenyl part is almost perpendicular to the remainder of the molecule. A large splitting of Q bands is observed in the absorption spectrum, and the Q bands are situated in the higher and lower energy regions of the corresponding phthalocyanine. The first oxidation potential of AZPPc shows a large shift to the negative, while the first reduction potential shifts slightly to the positive side. These changes in potentials result in a lowering of the potential difference between the first oxidation potential and the first reduction potential. Theoretical calculations reveal that coefficients are not displayed on the biphenyl unit owing to the orthogonal arrangement. This kind of localization destabilized the HOMO and LUMO+1 to a large degree, resulting in a small HOMO-LUMO gap and a large HOMO-LUMO+1 gap. The electronic structure of AZPPc can thus be better understood in the form of tetraazachlorin rather than phthalocyanine. The influence of the seven-membered ring in AZPPc system is quite distinct compared with that of the six-membered rings in APPcs. The difference can be attributed to their unique conformations.

In Chapter 4, the method used to produce core-modified phthalocyanine has been developed for the synthesis of the core-modified subphthalocyanine analogue (SubAPPc) containing a six-membered ring unit instead of a pyrrolic five-membered ring unit, by utilizing 1,8-naphthalenedicarbonitrile as a key starting material. This novel subphthalocyanine analogue has been intensively investigated by means of spectroscopic and electrochemical measurements. The absorption spectrum shows a red-shifted and strongly split Q band by over 1000 cm^{-1} , indicating a considerable change in the electronic structure due to the expansion of the π -conjugation system by incorporation of the six-membered ring. Electrochemical measurements show a negative shift of the first oxidation potential, while maintaining the first reduction potential. A decreased potential difference is obtained with respect to that of general subphthalocyanines. Theoretical calculations reveal a high-lying HOMO and LUMO+1 due to the additional distribution on the electron-rich naphthalene units. A small HOMO-LUMO gap and considerable energy splitting of the frontier LUMOs are thus reproduced. The incorporation of the six-membered ring gives rise to a significant alteration of the electronic structure.

In the first half of Chapter 5, the method used in Chapter 2 has been further developed for the synthesis of a core-modified dimer containing internal six-membered rings instead of pyrrolic five-membered rings, by utilizing 1,4,5,8-naphthalenetetracarbonitrile as a key starting material. The synthesis and preliminary purification are described, and preliminary spectroscopic and theoretical results reported. In the second half of Chapter 5, the synthesis of novel core-modified naphthalocyanines is described.

In summary, a general synthetic method has been developed by utilizing starting materials bearing two cyano groups at the 1,3- or 1,4-positions of aromatic units in the chemistry of phthalocyanine. Several novel core-modified phthalocyanines and related compounds with six- or seven-membered rings have been prepared and intensively investigated. All of these compounds retain the aromaticity, while the spectroscopic and electrochemical properties are strongly altered. Studies on these compounds suggest that core-modification is a promising modification method for exploring new properties in the chemistry of phthalocyanines.

論文審査の結果の要旨

フタロシアニン (Pc) は年間 5 万トン以上生産され、特許も 2000 以上出されている機能分子である。今迄合成された Pc は環中央部に 4 つ或は時に 3 つのピロール環を含むもの (サブフタロシアニン、SubPc) であり、構造を変える場合も全てピロール環の外側だけであった。朱华提出の論文では、ピロール環の一つ或は 2 つを 6 員環、或は 7 員環に換えた Pc および SubPc の合成と分光学的・電気化学的性質について報告している。

第 1 章では今迄の Pc 類の代表的構造、合成法、分光学的性質について概説した。

第 2 章で 1,8-ジシアノナフタレン (1,8Np) と種々のフタロニトリル (PN) の混合縮合法によるアザフェナレン型 Pc の合成と分離精製、性質について述べている。1,8Np 単位の導入により、中心金属配位圏で 6 員のピリジン型になる。この単位の導入により Pc 面が歪み、導入単位が一つの時吸収スペクトルの最長波長は通常のものより 140nm も長波長移動した。この単位が 2 つ導入されるとシス形とトランス型があるが、骨格の平面性は通常の Pc から遥かに歪み、前者では C_{2v} 型に、後者ではサドル型になった。吸収波長は前者で通常の Pc のそれより 200nm 長波長移動し、後者では 2 つに分裂した長波長側のピークは 990nm に達した。

第 3 章では 2 章での 1,8Np の代わりにビフェニル-2,2'-ジカルボニトリルを合成し、種々の PN 類と混合縮合によりビフェニル単位が一つ導入された Pc 誘導体を合成した。X 線結晶解析からビフェニル部分は中央金属に 7 員環で配位しており、しかも Pc 面からは垂直に近い構造を持つ非常に特異的な構造を有することを証明した。

第 4 章ではピロール単位 3 つの SubPc のピロール環の一つを、1,8Np を出発物質の一つとして用いて 6 員環に換えた。この化合物は X 線結晶解析からお椀型をしており、 π 共役系が伸び色が変わる程性質が変化した。

第 5 章では 1,4,5,8-テトラシアノナフタレンを架橋単位とした Pc 平面 2 量体について、その合成と分光学的性質について記述した。この 2 量体は 1100-700nm に幅広い吸収 (ピーク位置 928nm) を示し、新規近赤外吸収色素として極めて有望であることを示した。

第 1 ~ 7 章の分光学的・電気化学的性質は理論計算によっても支持された。

第 7 章では著者の研究成果を総括した。

以上、本研究は機能色素材料の分野に画期的な貢献をするもので、著者が自立して研究活動を行うに必要な研究能力と学識を有することを示している。従って、朱华提出の論文は、博士 (理学) の学位論文として合格と認める。