Studies on Synthesis, Structure, and Properties of Metal Coordinated N-Confused Calixphyrin Analogues.

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https://doi.org/10.15017/2534410

出版情報：Kyushu University, 2019, 博士（工学）, 課程博士
バージョン：
権利関係：

（様式２）

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論 文 名　：Studies on Synthesis, Structure, and Properties of Metal Coordinated N-Confused Calixphyrin Analogues.　(N-混乱カリックスフィリン類縁体金属錯体の合成及び構造、物性に関する研究)

区　　分　：甲

論文内容の要旨

Porphyrin is a well-known π-conjugated macrocycle composed of four pyrrole units bridged with a methine carbon at the meso-positions, which is abundant in the nature and plays some crucial roles in the sustenance of life as functional dyes. Various porphyrins and their homologues have been developed and utilized in wide-range research areas such as for renewable energy production (solar cell, hydrogen storage), medicinal chemistry (anticancer drugs, imaging techniques), catalysis (drug metabolism), and so forth. Among the analogues, the author focuses on calixphyrin, a class of porphyrin-related macrocycles which contains both sp^3- and sp^2- hybridized carbons in the meso-position. The disrupted π-conjugation in the calixphyrin leads to the unique optical profile and metal binding affinities at the bent NNNN core.

In this thesis, the author describes the wide scope of modified calixphyrin analogues as the photosensitizing material applications through an N-confusion approach. The implementation of the peculiar pyrrole subunits linking at the α– and β–pyrrole positions in the calixphyrin scaffold afforded specific organometallic environment at the core. Upon metal complexation of these N-confused calixphyrins, the resulting organometallic species stabilized by the strong σ-donating carbon moieties represents fascinating photophysical properties (e.g., red-shift of the energy) and photosensitizing abilities (e.g., singlet oxygen

generation). The findings presented in this thesis would provide an important basis for rational design of photosensitizers used for applications, such as bio-imaging, photodynamic therapy, etc. in the future.

Chapter 1 outlines a brief overview of the vast area of porphyrinoid analogue chemistry, mainly focusing on the fundamental structural properties, reactivity, and utility applications. In particular, the advanced chemistry of N-confused porphyrins and calixphyrin analogues has been discussed. This chapter also describes how the ring expansion modifications effect the photophysical properties of porphyrinoid macrocycle. In this aspect, core modification of the calixphyrin skeleton with N-confusion approach can provide new ligand platforms for various organometallic complexes, which should be the promising candidates for photosensitizers, emitters, and photocatalysis.

Chapter 2 describes the synthesis of novel singly and doubly N-confused calix[4]phyrin platinum(II) complexes as an unique class of photosensitizers for singlet oxygen generation. The structural effects on the metal coordination ability, optical/electrochemical properties and photosensitizing behavior were investigated by means of various spectroscopic techniques. As increasing the number of confused pyrrole rings embedded in the skeleton, the absorption and emission energies of the complexes were red-shifted. The reasonably high efficiency for the photosensitized singlet oxygen generation was realized by using N-confused calixphyrin platinum complexes under aerobic conditions.

Chapter 3 focused on further core modification of the N-confused calixphyrins by expansion of the core pyrrole numbers, being as doubly N-confused calix[6]phyrins. In fact, due to the π-extended structures, the resulting mono/bis-palladium(II) complexes of the calix[6]phyrins showed intense absorption profiles in the visible-to-NIR region (500–750 nm) depending on the number of central metals. With use of these complexes as the triplet photosensitizers, the efficient singlet oxygen generation was observed, particularly with the most photo-stable bis-palladium complexes.

In Chapter 4, the author summarized the findings in the works along with the future perspectives. According to the structural effect of the core modifications, the number and orientation of the confused pyrrole units embedded in the parent scaffold should be of importance for achieving the desirable optical properties so as to use for photosensitizers. This design principle opens the doors for promising materials in the photodynamic therapy and photocatalysis, and so on.

〔作成要領〕

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