

Development of Novel Blackened and Near-Infrared Light Responsive Dyes Based on N-Confused Hexaphyrins

王, 越

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氏 名 : 王 越

論 文 名 : Development of Novel Blackened and Near-Infrared Light Responsive Dyes Based on N-Confused Hexaphyrins (N-混乱ヘキサフィリンを基盤とした近赤外光応答色素および黒色色素の開発)

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論 文 内 容 の 要 旨

Panchromatic dyes exhibiting efficient photon collecting capability have attracted attention due to the application in dye-sensitized solar cells. Moreover, near-infrared (NIR) dyes with NIR light response have been widely investigated owing to the application potential of diagnosing and therapy. Despite massive effort on achieving the desired optical features, simple strategy resulting in panchromatic and/or NIR light-harvesting dyes with robust photostability is still rarely proposed.

In this thesis, the author describes a molecular orbital (MO) engineering approach to achieve the blackened and/or NIR absorption based on the N-confusion modification and carefully selected metalation on hexaphyrin, a hexapyrrolic expanded porphyrin. The desired dyes were synthesized and the relationship between the structure and optical features were studied in detail. MO engineering was demonstrated with the aid of computational study. Furthermore, for illustrating the diagnostic and therapeutic application potential of the developed dyes, the capability of converting light energy into other forms, such as thermal and acoustic ones, was examined.

In Chapter 1, an overview of the chemistry of porphyrinoids, including the essential structures, optical properties, modifications, metalations are given. Hexaphyrin, a NIR absorbing expanded porphyrin, is an ideal platform for development functional dyes. However, the metalation on regular hexaphyrin is limited. Regarding this, Chapter 1 introduces one approach that is affording a structural stable hexaphyrin analog as ligands for various coordination. The core modification of hexaphyrin skeleton by altering the linkage of pyrrole units, namely, N-confusion, is proposed to provide distinct cores with more nitrogen atoms in the cores with decreased metalation difficulty.

In Chapter 2, the author describes the synthesis and characterization of a hetro-metallohexaphyrin-based “black dye” Au-Pd oxohexaphyrin with absorption capabilities across the visible-to-NIR range. DFT calculation suggests the orbital interactions between metal (d)-ligand (π) molecular orbitals, resulting in a broadened and bathochromically shifted absorption. The bis-metallohexaphyrin possesses efficient light-harvesting, photostability, and superior photothermal (PT) conversion abilities. The one step forward encapsulation of the black dye affords a water-soluble nanoscale structure demonstrating intense photoacoustic (PA) properties in the NIR region in water. The unique photophysical properties of the compound indicate the potential of therapeutic and/or diagnostic applications.

In Chapter 3, the author describes the synthesis and characterization of bis-Pd(II) and bis-Pt(II) complexes of doubly N-confused non-oxo hexaphyrin. The obtained complexes are fully characterized, revealing the third NIR (NIR-III) absorption and emission capabilities. The theoretical studies demonstrate that symmetry alteration of the frontier molecular orbitals of bis-Pd(II) and bis-Pt(II) complexes of hexaphyrin via N-confusion modification led to substantial metal $d\pi$ - $p\pi$ interactions. This MO mixing results in a significantly narrower HOMO–LUMO energy gap leading a significant red-shifted NIR-III absorption beyond 1700 nm of bis-Pt(II) hexaphyrin. Bis-Pd(II) complex exhibits unusual NIR-III emission beyond 1500 nm. Furthermore, the bis-Pt(II) complex intensely responds in the NIR-III region. Benefitting the NIR-III emission and PA property, the bis-metal complexes show the potential to be utilized as bio-imaging agents working in deep tissue.

In Chapter 4, the author describes the synthesis of a series of silicon-incorporated complexes of the N-confused hexaphyrin. The Au(II)Si(IV) complex exhibits unexpected antiaromaticity, which is the first time observed in N-confused hexaphyrin systems. The bis-Si(IV) complex of doubly N-confused dioxohexaphyrin shows red-shifted absorption and emission compared with the parent free-base hexaphyrin. According to this observation, the axial phenyl group on the silicon is critical for forming of stable siliconized hexaphyrin complexes.

In Chapter 5, the author summarizes the findings and perspectives of future works. These bis-metal complexes of hexaphyrin analogs obtained by the N-confusion modification can be utilized for bio-imaging, and/or therapeutic applications.

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