

Abstract of Doctoral Thesis

Title : Synthesis, Reactivity and Physical Property of Diketonated Chlorophyll Derivatives

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Chlorophyll (Chl) pigments play important roles in photosynthesis and possess various substitutions at the peripheral position of cyclic tetrapyrrole ring. Chls have two characteristic absorption bands, Q and Soret bands in longer and shorter wavelengths, respectively. The absorption bands are strongly affected by the peripheral substitutions. Therefore a lot of synthetic Chl derivatives are available in literature and utilized as dye sensitizers and chemical sensors. 1,3-Dioxopropane analogs, β -diketone compounds are readily prepared and highly reactive. Typically, they are synthesized by Claisen condensation and tautomerized to their diketonate forms. β -Diketone compounds are reacted with amines to afford mono-adducts. In coordination chemistry, diketonate compounds are frequently used as ligands to form metal complexes. In this study I synthesized chlorophyll derivatives possessing a trifluoroacetylacetonate moiety at the C3 position and investigated their reactivities and physical property.

Chlorophyll-*a* derivatives possessing a trifluoroacetylacetonate moiety at the C3 position were prepared by Claisen condensation. The resulting Claisen condensation products took exclusively diketonate forms in a CDCl_3 solution and the single crystal, and gave red-shifted and broadened Qx/Qy absorption bands in the visible to near-infrared region.

The terminal trifluoroacetyl moiety in a β -diketonate group at the C3 position of the synthetic chlorophyll derivative was reacted with butylamine in dichloromethane to give the hemiaminal-type adduct. Electronic absorption spectra showed the keto carbonyl group at the C3 position of the adduct was converted into the enol type under the basic conditions.

The peripheral diketonate group in chlorophyll derivatives coordinated ruthenium bisbipyridine to give direct conjugates of the chlorin ring with Ru(II) complex. Since the diketonate group at the C3 position of chlorophyll derivatives coordinated to bulky $\text{Ru}(\text{bpy})_2^{2+}$, the plane of the diketonate group was twisted from the chlorin π ring. The coordination to ruthenium complex moiety at the peripheral position shifted the electrochemical reduction of the chlorin part in acetonitrile to a negative potential.