

氏名	山本 智史
学位の種類	博士 (工学)
学位記番号	甲 第 669 号
学位授与の日付	平成 2 9 年 3 月 2 0 日
学位授与の要件	信州大学学位規程第 5 条第 1 項該当
学位論文題目	Design of metallophthalocyanines for enhancing photo-conversion efficiency in the near-infrared region (近赤外領域の光変換効率向上のためのフタロシアニン錯体の分子技術に関する研究)
論文審査委員	主査 教授 木村 睦 教授 太田 和親 教授 浅尾 直樹 准教授 西井 良典 教授 内山 真伸 (東京大学)

論 文 内 容 の 要 旨

Capturing solar energy and converting it to usable forms such as electricity or chemical fuels remains a huge challenge. Recently, the photovoltaic devices using organic compounds such as organic thin film photovoltaic (OPV) and dye-sensitized solar cells (DSSCs) have been intensely investigated as a promising candidate for low-cost, lightweight, and scalable solar cells. However OPVs have achieved high conversion efficiencies, their organic semiconductors mainly absorb the light in visible range. To enhance their efficiency, the expansion of light-harvesting range is a key issue in this field.

Phthalocyanines (Pcs) and their metal complexes (MPcs), synthetic porphyrin analogues, have been widely investigated as near-IR absorbing dyes because of their intense Q band (600-700 nm), high molar extinction coefficients ($\epsilon > 100000 \text{ M}^{-1} \text{ cm}^{-1}$), and excellent thermal, chemical, and photolytic stabilities. The electronic structure and properties of MPcs can be tailored by modifying the macrocyclic ligands and changing the central metals.

This thesis gives a detailed description of the design and synthesis of new near-IR (NIR) sensitizing metallophthalocyanines for solar-energy conversion applications. It is divided in 7 chapters, where **Chapter 1** gives an introduction to the field of metallophthalocyanines and the organic material based solar cells including OPVs and DSSCs. **Chapter 2** provides an overall insight on the general experimental including the syntheses, the characterization analyses, the fabrication methods of organic based solar cells, and the analyses of organic devices. **Chapter 3 to 6** deal with the work of the author, starting with the first publication and the other following in chronological order. The thesis is completed with some concluding remarks (**Chapter 7**).

Chapter 3 describes the design, syntheses, and characterization of novel ring-expanded phthalocyanines. Fusing fluorene rings with the porphyrazine core resulted in narrower band gap and tuning of both the HOMO and LUMO energy levels compared with unsubstituted ZnPcs. The synthesized ring-expanded phthalocyanines **1-3** were incorporated into bulk-heterojunction solar cells based on P3HT and PCBM. The addition of **3** having eight alkyl chains resulted in improved device performance with a 16 % enhancement of the short circuit current compared with that of reference cell without **3**.

Chapter 4 describes the potential of the novel ring-expanded phthalocyanines as a photosensitizer in dye-sensitized solar cells (DSSCs) because of their suitable HOMO levels and the red-shifted Q band. In this chapter, a ring-expanded near-IR absorbing sensitizer (**FcS1**), in which three fluorene rings are fused with a porphyrazine core, was synthesized from 9,9-diarylfuorene precursor and methyl 3,4-dicyanobenzoate. The fusion of fluorene rings with a porphyrazine ring provides suitable HOMO and LUMO energy levels for efficient operation of DSSCs. Furthermore, the attachment of hexylphenyl groups at the C9 position of the fluorene rings enables the formation of suitable packing that have a tilted orientation of adsorbed dyes on the TiO₂ surface. When used as a light-harvesting sensitizer in DSSCs, **FcS1** based cells gave a PCE value of 3.2 %. The light-harvesting region of the **FcS1** extends close to 900 nm though the formation of suitable packing on the TiO₂ surface.

In Chapter 5, a novel covalently linked zinc phthalocyanine - zinc porphyrin dyad is reported. The phthalocyanines and porphyrins are considered as important molecular components in the molecular arrays due to their complementary absorption regions in visible light. Moreover, intramolecular energy transfer from the porphyrin to phthalocyanine occurs very efficiently in most phthalocyanine-porphyrin dyads because the Q band absorption of phthalocyanine almost overlaps fluorescence wavelength of porphyrin. Thus, a new phthalocyanine – porphyrin dyad was designed and synthesized for the photosensitizer of DSSCs. UV-Vis absorption and fluorescence spectral studies demonstrated that the energy harvested from the zinc porphyrin moiety can be efficiently transferred to the zinc phthalocyanine unit through the Förster resonance energy transfer. While the dyad gave an energy conversion efficiency of 2.7 %, the dyad could convert the whole visible light region between 300 to 800 nm to electronic energy.

Chapter 6 describes effect of substitution of thiophene at the α or β position on optical property of phthalocyanine. Since α -substituted ZnPc showed a larger red shift of the Q band, the two new hybrid chromophoric systems were designed and synthesized, in which a π -conjugated side chain with an adsorption site was introduced at an α position of the MPC to act as the photosensitizer for DSSCs.

Chapter 7 concludes this thesis providing final summary and strategy for future work. It is also worth mention that each chapter contains a short introduction, experimental methods, followed results and discussion, and a final conclusion section.