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研究成果の概要(和文)：本研究で、私たちは短波長から長波長までの光を吸収することが期待される金属錯体と有機化合物を設計・合成した。これらの新規光増感材を用いて、Multi-dye (UV-dye, VIS-dye and NIR-dye) sensitized dye sensitized solar cellsを作成することに成功した。

研究成果の概要(英文)：In this project, I have design and synthesized few potential new dyes covering a short and a long wavelength light based on metal complexes and metal-free organic dyes. Using these new sensitizers, I have successfully fabricated Multi-dye (UV-dye, VIS-dye and NIR-dye) sensitized dye sensitized solar cells with these novel new dyes. Optical and electrical investigation shows that small UV-dyes can suppressed strongly the TiO<sub>2</sub> injected electron recombination with the electrolyte(I<sup>3-</sup>). These triple dye co-sensitized solar cells showed a panchromatic response with an IPCE >70% over the entire visible spectrum extending to the NIR region, suggesting their usage in indoor applications. The research results are presented at 8 international scientific meetings and also published in 17 peer reviewed scientific journals.

研究分野：太陽電池

キーワード：色素増感 ペロブスカイト

## 1 . 研究開始当初の背景

Dye-sensitized solar cells (DSCs) are promising next-generation alternatives to conventional silicon-based photovoltaic devices owing to their low manufacturing cost and potentially high conversion efficiency. Traditional silicon based solar cells require high-purity silicon and skilled manufacturing techniques, which result in high costs, so their widespread use has been limited. This makes DSCs attractive as a replacement for existing technologies in applications. Until now, the certified champion efficiency of about 11% was achieved. To parallel the efficiencies of silicon-based solar cells for mass production, a high efficiency of >15% is desired. In the approach to improve conversion efficiency, much effort has been carried out to solve the problems that limit improvement, such as utilizing efficient single or multi-sensitizers (dye) with broad light absorption spectra that extend into the UV, VIS and IR regions). The light harvesting dye is clearly a crucial component of the cell design and needs to fulfill several criteria; adsorption onto nanocrystalline metal oxide (TiO<sub>2</sub>) surface, overlap effectively with solar spectrum, inject electrons efficiently into metal oxide and be stable for many million cycles. In contrast to inorganic absorbers, dyes for the DSCs have Gaussian-shaped absorption spectra. This restricts DSCs dyes to absorbing a broad wavelength range of light as inorganic absorbers do. Thus, the current generated by DSCs is determined to be lower than that generated by inorganic solar cells. Many attempts have been carried out to broaden the absorption spectra of the cells, including tandem DSCs, dye-multilayer and co-sensitized DSCs, with complementary absorption properties to enhance light harvesting to broad-wavelength-range (UV-VIS-NIR). Both tandem and dye-multilayer DSCs device structures are expensive and need complicated fabrication processes. In recent years, increasing attention has been paid to

the co-sensitization of TiO<sub>2</sub> films by mixed dyes, so-called “dye cocktails”, with complementary absorption properties like UV-dye, VIS-dye and NIR-dye. However, so far only a few combinations of dye cocktails have succeeded in improving the conversion efficiency of high efficiency DSCs. The selection or design of co-sensitizers remains a major challenge with regard to effectively preventing competitive adsorption and unfavorable aggregation of dyes that tend to result in a decrease of photocurrent or photovoltage in DSCs. Recently, we successfully enhanced the IPCE of black-dye (VIS-dye) in the UV region in a two-dye based co-sensitized DSC and achieved the highest certified conversion efficiency of 11.4%.

## 2 . 研究の目的

Utilization of different dye molecules with different absorption maxima (UV-dye, VIS-dye and NIR-dye) in one cell, such as a multi-dye (cocktail) structure adopted in compound semiconductor-based solar cell can construct an efficient DSCs with, **a high efficiency of >15%** for practical application. The goal of this research is molecular engineering of novel UV-dye, VIS-dye and NIR-dye to improve light harvesting efficiency to a wider range of wavelengths and also design and construction of multi-dye (UV-dye, VIS-dye and NIR-dye) based DSCs. This new **multi-dye sensitized DSCs** is expected to harvest light from UV-visible to near IR regions (300 nm to 1100). A feasible strategy for further improvement of the efficiency is therefore the development of new compounds like UV-dye, VIS-dye and NIR-dye that can be used as co-sensitizers in a multi-dye based DSCs with advantageous characteristics for overcoming the aforementioned problems.

In this project, a successful model for the design of efficient multi-dye sensitized DSCs device will be demonstrated. This research elucidates the directions to construct multiple dye sensitization, which

are crucial for harvesting light in a wide range of wavelengths and also open the possibility of significant improvement of existing DSCs by making multiple dye synthesized electrode in the future. A new multi-dye sensitized DSCs device complies with these new UV-dye, VIS-dye and NIR-dye developed in this research will achieved low cost and yet high efficient dye-sensitized solar cells in the near future. The results of this research will also help to propose the prediction on development the new materials and facilitate the modification of the cell structure.

### 3 . 研究の方法

This research was performed in the following three phases (Phase I, Phase II and Phase III).

Phase I – Conceptual development, synthesis/engineering and characterization of new UV-dyes and VIS-dyes and construction of prototype two-dye structure DSCs device with compact monolayer formation on nanocrystalline TiO<sub>2</sub>.

Phase-I-Task1: Brainstorming and conceptual development of the new UV-dyes, VIS-dyes and NIR-dyes and design of two-dye structure and multi-dye structure DSCs device. Phase-I-Task2: Design and synthesis of model UV-dyes and VIS-dyes. Characterization of new dyes. Phase-I-Task 3: Initial testing of two-dye structure DSCs prototype device with compact monolayer formation on nanocrystalline TiO<sub>2</sub>. Characterization of two-dye structure DSCs device performance (LHE, IV; IPCE, etc.).

Phase-II: Synthesis/engineering and characterization of new IR-dyes and construction of prototype multi-dye structure DSCs device with compact monolayer of UV-dyes, VIS-dyes and NIR-dyes (co-sensitize) on nanocrystalline TiO<sub>2</sub>. Phase II Task 1: Novel NIR-dyes with high molar extinction coefficient was developed in this phase for an efficient multi-dye based co-sensitized DSCs device with minimum TiO<sub>2</sub> film thickness.

Phase II Task 2: The objective was to construct a prototype multi-dye structure DSCs device utilizing the results generated in Phase I and Phase 2(1). Multi-dye structure DSCs device was constructed and performs initial performance evaluation in terms of: light harvesting efficiency (LHE) of novel dyes, current-voltage characteristic (I-V) and incident photon-to-current conversion efficiency (IPCE).

Phase II Task 3: New design and synthesis of more efficient UV-dyes, VIS-dyes and NIR-dyes was done based on the feedback of device performance especially spectral overlapping of the UV-dyes, VIS-dyes and NIR-dyes in the LHE and IPCE spectra of multi-dye system and thus a systematic development of device efficiency was done.

Phase III –Optimization of multi-dye based DSCs performance, summarized the factors that govern the efficiency of the device and proposals for future research directions.

Phase III Task 1: The objective was to optimize multi-dye structure DSCs device utilizing the results generated in Phase II specially new material develop in Phase II(2) and also using our high efficiency technology system and performs device performance evaluation.

Phase III Task 2: Different optical and electrical investigation will employ to understand inside the interfacial charge transfer dynamics. Electrochemical impedance spectroscopy (EIS) as a tool to scrutinize the salient factors governing the several interfacial charge-transfer and transport mechanisms occurring in in multi-dye based DSCs. The advanced characterization methods was used to determine the leakage current, carrier lifetimes, carrier diffusion lengths, etc. The conduction band positions of TiO<sub>2</sub> and electron lifetimes in TiO<sub>2</sub> film was investigated by charge extraction method (CEM) and intensity modulated photo voltage spectroscopy (IMVS) to understand the interfacial dynamics on TiO<sub>2</sub>/dye /electrolytes system and the compact

monolayer formation with UV-dyes, VIS-dyes and NIR-dyes (co-sensitize) on nanocrystalline TiO<sub>2</sub>.

Phase III Task 3: The proposed multi-dye structure DSCs device was further optimized to minimize the detected losses in Phase III (2). The key findings and the excellent results of this research will be patented and published. Finally, summarized the factors that govern the efficiency of the device and proposals for future research directions.

#### 4 . 研究成果

In this project, I have designed and synthesized few potential new dyes covering a short and a long wavelength light based on metal complexes and metal-free organic dyes. Using these new sensitizers, I have successfully fabricated Multi-dye (UV-dye, VIS-dye and NIR-dye) sensitized dye sensitized solar cells with these novel new dyes. Optical and electrical investigation shows that small UV-dyes can suppressed strongly the TiO<sub>2</sub> injected electron recombination with the electrolyte(I<sub>3</sub>). These triple dye co-sensitized solar cells showed a panchromatic response with an IPCE >70% over the entire visible spectrum extending to the NIR region, suggesting their usage in indoor applications. The research results are presented at 8 international scientific meetings and also published in 17 peer reviewed scientific journals.

#### 5 . 主な発表論文等

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〔 図書 〕 ( 計 件 )

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6 . 研究組織

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