

## 【Grant-in-Aid for Scientific Research (S)】

### Broad Section E



#### Title of Project : Creative Research and Development of Incoherent Nonlinear Photoswitchable Molecules

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Research Project Number : 18H05263 Researcher Number : 70211703

Keyword : Photochromism, Photochemistry, Nonlinear Optical response

#### 【Purpose and Background of the Research】

Photochromic molecules, which can reversibly interconvert between stable and metastable isomers upon exposure to light, are key elements for the development of photo-responsive systems that offer promising perspectives in the materials and life sciences. However, traditional photochromic molecules require the use of high-energy UV light for isomerizing in at least one direction. The use of UV light comes with inherent limitations for a range of applications that arise from irreversible chemical damage and limited penetration depth in many materials. Moreover, background light causes an undesired photochromic reaction because a linear absorption of light would occur even for one photon irradiation.

Recently, we have developed novel fast photochromic molecules which involve the stepwise two-photon reaction. These photochromic molecules show unique nonlinear photo-response. Only the short-lived transient colored species are formed by illumination with weak light, whereas the excitation with high power CW light generates the long-lived transient colored species. Although high power pulse lasers were necessary to induce conventional simultaneous and stepwise two-photon absorption processes, the stepwise two-photon absorption process with the fast photochromic compound can be initiated by extremely weak continuous wave (CW) LEDs.

We will develop nonlinear visible-light responsive photochromic molecules that can work only under high-power CW light and exclude the influence of background light.

#### 【Research Methods】

In this research project, we will focus on the development of the innovative photochromic molecules capable of visible-light excitation and wavelength selective excitation by combining the fast photochromism, the stepwise photochromism, and the stepwise photochromism via higher excited state. The first objective is to realize the nonlinear photochromic reaction upon the excitation with visible light between 400 and 600 nm, and the final

goal is set to achieve the stepwise photochromic reaction with visible light longer than 650 nm or near infrared pulse light.

#### 【Expected Research Achievements and Scientific Significance】

A reverse saturable absorber (RSA) is a material whose absorption coefficient would increase with increasing the excitation light intensity. On the other hand, a material whose absorption coefficient would decrease when the excitation light intensity increases is known as a saturable absorber (SA). Nonlinear photo-responsive photochromic molecules changing their color from colorless to colored (positive photochromism) upon high-power UV LED can be considered as RSAs. On the other hand, those changing their color from colored to colorless (negative photochromism) can be regarded as SAs. We expect the RSA and SA properties induced without the use of high power laser source can be applied to unique optical shutters and optical filters.

#### 【Publications Relevant to the Project】

- Y. Kobayashi, T. Katayama, T. Yamane, K. Setoura, S. Ito, H. Miyasaka, J. Abe, "Stepwise two-photon induced fast photoswitching via electron transfer in higher excited states of photochromic imidazole dimer", *J. Am. Chem. Soc.*, **138**, 5930-5938 (2016).
- K. Mutoh, Y. Nakagawa, A. Sakamoto, Y. Kobayashi, J. Abe, "Stepwise two-photon-gated photochemical reaction in photochromic [2.2]paracyclophane-bridged bis(imidazole dimer)", *J. Am. Chem. Soc.*, **137**, 5674-5677, (2015).

【Term of Project】 FY2018-2022

【Budget Allocation】 149,700 Thousand Yen

#### 【Homepage Address and Other Contact Information】

<http://www.chem.aoyama.ac.jp/Chem/ChemHP/phys3/top/abe.html>