Photosynergetic Responses in Molecules: Multiphoton-Gated Photochromic Reactions

Hiroshi Miyasaka

Division of Frontier Materials Science and Center for Promotion of Advanced Interdisciplinary Research, Graduate School of Engineering Science, Osaka University,
Toyonaka, Osaka, Japan
miyasaka@chem.es.osaka-u.ac.jp

Molecules in the electronic excited state take important roles in various photo-functional processes. For molecules in condensed phase, however, three general restrictions limit the efficient utilization of light energies. First, molecules in higher excited states usually very rapidly relax to lower electronic states (Kasha's rule) and some portion of the absorbed photon energy is diminished in this relaxation. Second, a large number of the molecules excited in assemblies undergo fast annihilation and only a small number of excited state molecules can remain, leading to the loss of the number of photons absorbed in the system. In addition, the electronic state accessible through the one- photon absorption is limited by the optical selection rule and we cannot access various dark electronic excited states of molecules. These three restrictions have been limiting the photochemistry in "one-photon one-molecule responses in the lowest electronic state".

Research outcomes beyond these restrictions, however, have been recently reported by several groups including us in the field of photochemistry, such as specific photochemical reactions in higher excited state attained by multiple excitation and multiphoton absorption, cooperative responses of multiple excitons/excited states in molecular assemblies, modulation of electronic states via the strong-coupling between light and matters, and so on. Based on these backgrounds, we have started a new project, "Photosynergetics"[1], as a research program supported by the Ministry of Education, Culture, Sports, Science and Technology, Japan (MEXT). Since 2014, we have been conducting this project through the collaborative investigations so as to develop and advance excitation methods and molecules/molecular assemblies that can overcome these three restrictions.

In the present talk, we will introduce several topics relating to Photosynergetic project, such as multiple and multiphoton excitation responses in photochromic molecules [2-8], one-color control of both reactions in photochromic systems [9,10] and so forth.

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