Unveiling electronic structures of biradicaloids using fast switchable photochromism

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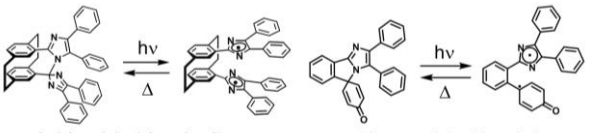
Biradicaloids have been extensively studied for their characteristic features. Besides, the study of the chemical and the physical properties of biradicaloids is expected to provide fundamental insight into the nature of chemical bonds.

Scheme 1 Photochromic reactions of the fast photochromic molecules.



bridged-imidazole dimer (ImD) Phenoxyl-imidazolyl radical complex (PIC)

One of the objectives of this study is to elucidate the relationship between the electronic structure and the reactivity of the singlet biradicaloid in which an open-shell biradical and a closed-shell quinoid exist as thermally equilibrated states. To answer this fundamental question, it is essential to provide a new molecular design that can (i) be applied an external stimulus to perturb the thermal equilibrium state and (ii) allow experimental evaluation of the open-shell character and the dynamic spin-spin interaction from the reactivity of the biradicals. We have recently developed photochromic bridged imidazole dimer (ImD) and phenoxyl-imidazolyl radical complex (PIC). The bridged imidazole dimer generates a transient biradical upon UV light irradiation. The transient biradical thermally goes back to the initial imidazole dimer. We have developed novel biphotochromic molecules consisting of the two photochromic units. The key feature of the stepwise two-photon induced photochromism is an effective electronic interaction between the photogenerated transient chromophores. The time evolution of the dynamic spin-spin interaction along with the molecular structural change is observed as a π-bond formation by combining biradical-quinoidal thermal isomerization with the stepwise two-photon induced photochromism.

In addition, the development of the biradical species on helical polycyclic aromatic structures has been also of interest as a novel platform for organic biradicals. We have designed and synthesized a photochromic bridged imidazole dimer with a helical structure. The helical imidazole dimer can be also expected as a novel family of fast photochromic molecules.