

Stepwise Two-Photon-Gated Photochromism of Bis(Reversed Phenoxyl-Imidazolyl Radical Complex)

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The study about a cooperative interaction between multiple photons and molecules, which is called “photosynergetic” effect, has been received much attention. To develop the photofunctional materials which show multiple photoresponses depending on the intensity and wavelength of excitation light, the mutual electronic and structural coupling between chromophores is fundamentally required. The key feature of the stepwise two-photon induced photochromic compound is the spin-spin interaction in the transient radical species.

In this study, we synthesized a stepwise photochromic compound (bisRPIC) which has two reversed phenoxyl-imidazolyl radical complex (RPIC^[1]) units. The stepwise photochromic reaction of bisRPIC was investigated by the two-pulse laser flash photolysis measurement. The absorption of the first photon leads to the formation of *o*-biradical species (Fig. 1) which thermally isomerizes to *o*-quinoid species. The absorption of the additional photon by *o*-biradical species leads to the formation of a couple of *o*-biradical units which quickly isomerizes to *p*-quinoid species via bis(*o*-quinoid species). In contrast, *o*-quinoid–*o*-biradical species, generated by the additional excitation of *o*-quinoid species, shows the relatively slow thermal isomerization to *p*-quinoid species. These results indicate the stepwise photochromism of bisRPIC involves the two thermal equilibrium, one is the equilibrium between *o*-biradical and *o*-quinoid species and the other is the equilibrium between *p*-biradical and *p*-quinoid species. The dynamic change in the spin-spin interaction between the radicals could be observed by perturbing the equilibrium state upon light irradiation.

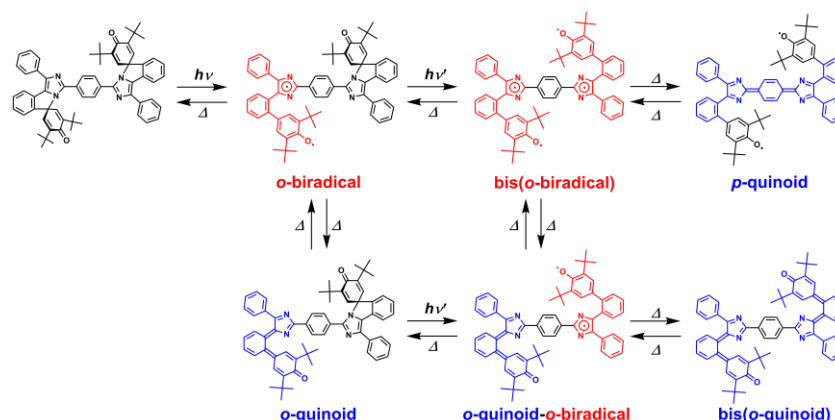


Figure 1. Photochromic reaction scheme of bisRPIC.

Reference

- [1] Y. Kobayashi, K. Shima, K. Mutoh, J. Abe, *J. Phys. Chem. Lett.*, **2016**, 7, 3067