Stepwise Two-Photon-Gated Photochromic Reaction of Bis([2,2]Paracyclophane-Bridged Imidazole Dimer)

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The two-photon absorption process exhibits a nonlinear photoresponse, which is important not only for promising for 3D fabrication and two-photon microscopies but also for developing attractive photo-responsive materials. Recently, we have achieved to develop the fast-switchable photochromic system, [2.2]PC-bridged bis(imidazole dimer), which shows the stepwise two-photon absorption reaction.[1,2] The one-photon reaction generates the short-lived biradical species through a chemical bond breaking, which shows the further photochemical reaction to generate the long-lived quinoid species. This smart photosystem has different coloration response as a function of the intensity and duration of incident light.

In this study, we designed a new type of a stepwise photochromic compound, bis([2,2]PC-bridged imidazole dimer) (**1**), and investigated the two-photon induced photochromic property of **1**. The transient vis-NIR absorption spectra of **1** were measured by nanosecond laser flash photolysis measurements. We observed a broad transient absorption spectrum **1** upon 355 nm laser irradiation with 200 μJ, which is attributable to the biradical species. On the other hand, the irradiation with high power at 6.5 mJ leads to the increase of the absorbance at 630 nm. This result suggests that the long-lived quinoid species is produced by the stepwise two-photon excitation process via the intermediate biradical species.

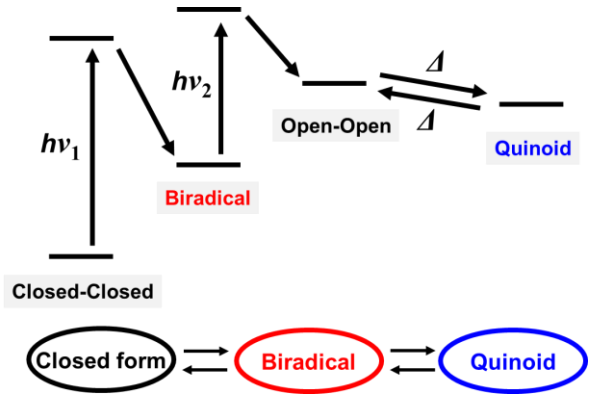

Figure 1. Schematic image of the stepwise biphotochromic systems.

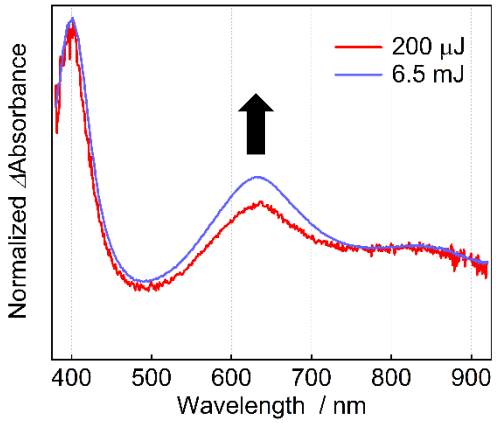

Figure 2. Normalized transient vis-NIR absorption spectrum of **1** excited at 355 nm in benzene at 298 K.

References:

[1] Y. Kobayashi, K. Mutoh, J. Abe, *J. Phys. Chem. Lett.*, **2016**, 7, 3666

[2] K. Mutoh, Y. Nakagawa, A. Sakamoto, Y. Kobayashi, J. Abe, *J. Am. Chem. Soc.*, **2015,** 137, 5674