

# Thermal-Photo Switching of the Selective Photochromism of a Biphotochromic Molecule

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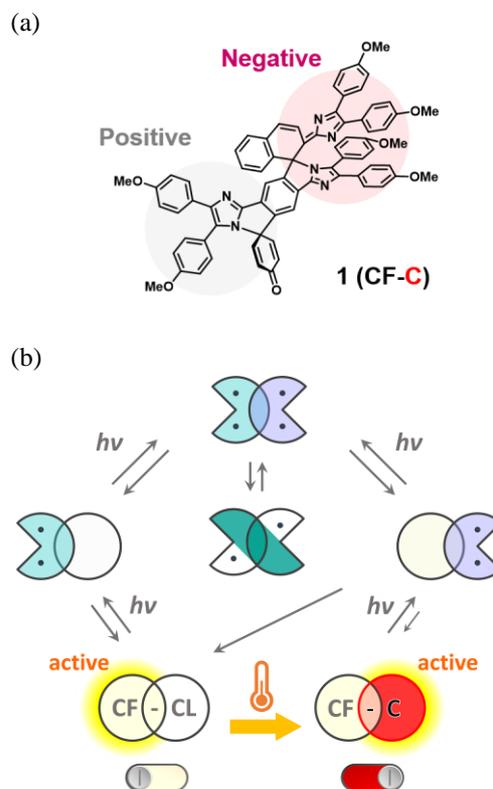
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One of the major challenges in the biphotochromic systems is orthogonality, that is, the possibility of selectively realizing a photochromic reaction of one photochromophore in the presence of others. However, there are several factors to be considered for achieving the selectivity. In general, it is difficult to choose two different photochromophores with almost no overlapping the absorption bands each other, even in both of the colored and colorless states. Furthermore, the energy transfer between the chromophores prevents the selective photoreaction. Feringa *et al.* reported the orthogonal photoswitching of the biphotochromic molecules by connecting two distinct types of photochromophores<sup>1</sup>.

Herein, we present a selective photochromic system with two different types of photochromophores. A newly developed compound, **1** (Figure 1a), is based on two photochromic units that generate stable radicals by light irradiation. The unit in one side is based on phenoxyl-imidazolyl radical complex (PIC)<sup>2</sup> and it shows positive photochromism. The colorless closed-ring isomer gives a short-lived biradical by UV light irradiation, which has the absorption band in visible light region. Another unit is based on 1-phenylnaphthalene-bridged imidazole dimer (bisDPI-PN)<sup>3</sup>. BisDPI-PN shows negative photochromism, where the color changes from red to colorless by visible light irradiation.

The clear color change is attributable to the isomerization between the red-colored closed-ring form and the colorless one via the photogenerated biradical species. Compound **1** has two closed-ring isomers, the colorless form (CF-CL) and the colored form (CF-C) in the same manner as bisDPI-PN. While the biradical of the PIC unit is selectively generated by UV light irradiation to CF-CL, the visible or UV light irradiation to CF-C induces the photochromism of the bisDPI-PN unit. This selective photochromism is based on switching of the energy level of the bisDPI-PN unit compared with that of the PIC unit, and the photoswitch can be achieved by heating (from CF-CL to CF-C) or visible light (from CF-C to CF-CL).

Furthermore, compound **1** shows a stepwise photochromism depending on the light intensity due to the strong electronic coupling between two photochromic sites. By the irradiation of the intense excitation light, the long-lived component, *p*-Quinoid (Figure 1b, in the center of the pentagon) is confirmed in the transient absorption spectra. The absorption of the second photon by the short-lived biradical species leads to the formation of bis(biradical), leading to the isomerization to the more stable *p*-Quinoid. This cooperative photochromism is achieved by the interaction between the two chromophores in the conjugated structure.



**Figure 1.** (a) The molecular design of compound **1**. (b) Thermal-photo switching of the selective photochromism of **1**.

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