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Photochromic Phenoxyl-Imidazolyl Radical Complex via Homolytic C–O Bond Cleavage

Various radical-dissociation-type photochromic molecules have been reported so far, such as hexaarylbimidazole (HABI), bridged imidazole dimers, and phenoxyl-imidazolyl radical complexes (PIC).[1)] All of them undergo homolytic cleavage of C–C or C–N bonds upon photoirradiation, resulting in the formation of biradicals. On the other hand, Photochromic molecules that undergo C–O bond cleavage include well-known systems such as benzopyrans, naphthopyrans, and spiropyrans. However, all of them generate closed-shell colored species upon bond dissociation, and no molecular systems are known to produce open-shell biradical species.

In this study, we develop a photochromic molecule (1) capable of C–O bond cleavage by light irradiation by altering the substitution position of the phenoxyl moiety in PIC (Figure 1a). Time-resolved infrared spectra and density functional theory calculations reveal that the photogenerated transient species exhibit biradical character, demonstrating the photoinduced homolytic bond cleavage in this system. Whole photochromic reaction pathways are described in Figure 1b.

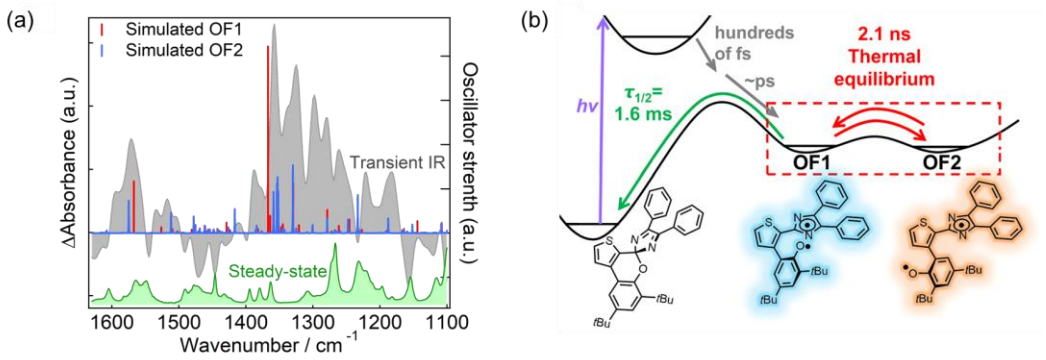

Figure.1 (a) Time-resolved transient IR spectra of 1 (b) photochromic reaction of 1.

1) Yamashita, H.; Ikezawa, T.; Kobayashi, Y.; Abe, J. *J. Am. Chem. Soc.* **137**, 4952 (2015).