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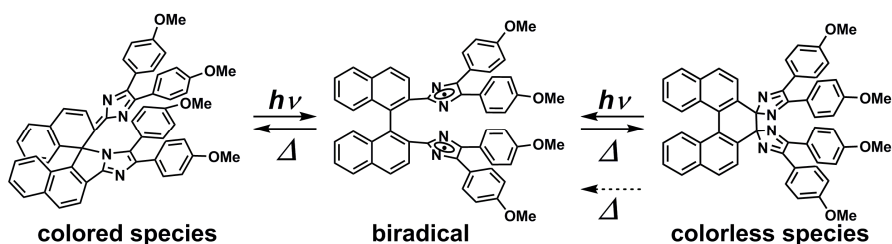
Unique Photochromism of 1,1'-Binaphthyl-bridged Imidazole Dimer

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Hexaarylbiimidazole (HABI) is one of the photochromic molecules, which is thermally or photochemically cleaved into a pair of triphenylimidazolyl radicals (TPIRs) that thermally recombine to form the original imidazole dimer. The solution of HABI changes from colorless to purple under UV irradiation, and the thermal transformation of TPIR to HABI requires several minutes to hours at room temperature. Recently our group developed a new type of HABI derivative (bridged imidazole dimer) containing a naphthalene moiety or a [2.2]paracyclophane moiety that tightly couples two TPIR units for suppressing the diffusion of the TPIRs into the medium to increase in the thermal recombination rate. Although we have been investigating the photochromism of various kinds of HABI derivatives to increase the thermal recombination rate, there has been no study for the investigation for the effect of the linker unit binding two TPIR units.

In this study, therefore, we designed a novel HABI derivative, (2,2'-bisDMDPI)-1,1'-BN^[1] with 1,1'-binaphthyl moiety which possessed flexible structure as a bridging part and investigated the chemical reactivity of the imidazolyl radicals. HABI derivatives generally show photochromic behavior, changing from colorless to colored species upon UV light irradiation. It means that the colorless species is more stable than the colored species. On the other hand, the colored species of (2,2'-bisDMDPI)-1,1'-BN is obtained as a most stable structure and the benzene solution changes from pale orange to the colorless gradually upon visible light irradiation at room temperature. The colored species of (2,2'-bisDMDPI)-1,1'-BN have the C–N bond between a nitrogen atom of one imidazole ring and a carbon atom of the bridged moiety, while the traditional imidazole dimers form the C–N bond between the two imidazole rings. Although the photochemical properties of a large number of HABI derivatives have been extensively investigated, there are no reports about such unique molecular structures. Indeed, these unique molecular structures gave both interesting information and a novel photochromic mechanism which could not be observed for the traditional HABI derivatives.

Scheme 1: Photochromism of (2,2'-bisDMDPI)-1,1'-BN



[1] Hatano, S.; Horino, T.; Tokita, A.; Oshima, T.; Abe, J. *J. Am. Chem. Soc.* **2013**, *135*, 3164.