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A Fast Photochromic Molecule That Colors Only under UV Light

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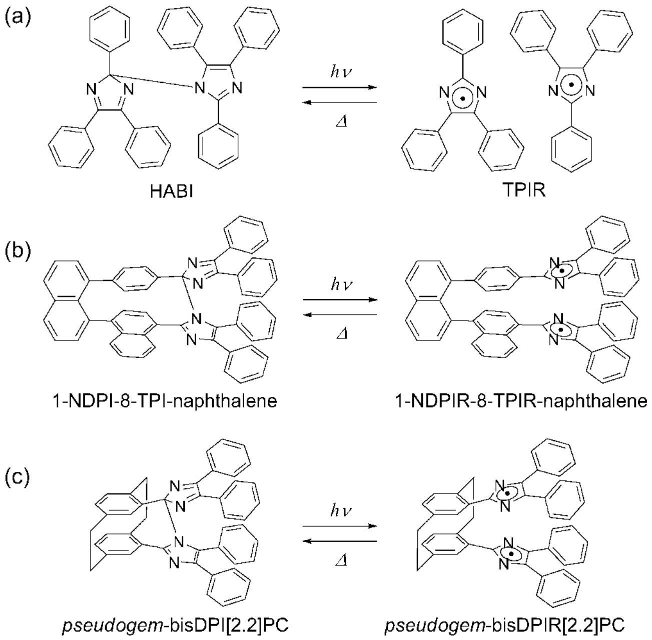
Photochromic materials are a well-known class of molecules that change color upon irradiation with light; the photogenerated species can be converted back to the initial species either thermally or by subsequent irradiation with a specific wavelength of light. The main interest in photochromic materials has been in their applications, including optical waveguides and shutters, optical data storage, and ophthalmic plastic lenses.[1] There is also increasing interest in the use of photochromic materials to modulate conductivity, fluorescence, magnetism, and shape at the bulk level.[2] Increasing switching rates, particularly the thermal bleaching rate, is indispensable for certain applications, such as optical data processing and light modulators. For application to real-time image processing at video frame rates,[3] the return to the initial state should be accomplished within tens of milliseconds; however, the thermal back-reaction of a colored species to its colorless form is generally on the time scale of tens of seconds to hours, which precludes their practical use in certain applications. In this work, we demonstrate that photochromism based on light-driven reversible bond cleavage can enable rapid coloration with UV light irradiation and successive fast thermal bleaching within tens of milliseconds at room temperature. Photochromic materials showing such intense photocoloration and fast thermal bleaching performance could be promising materials for possible fast light modulator applications.

Hexaarylbiimidazole (HABI), shown in Scheme 1a, was discovered in the early 1960s by Hayashi and Maeda, and it has subsequently attracted significant interest because of its unusual physical properties.[4] Various stimuli, such as heat, light, and pressure, readily cleave HABI into a pair of 2,4,5-triphenylimidazolyl radicals (TPIRs), which thermally recombine to reproduce their original imidazole dimer. The solution of HABI changes from colorless to purple under UV irradiation. Indeed, this photochromic behavior can be attributed to the photoinduced homolytic bond cleavage of the C−N bond between the imidazole rings. The dissociation of HABI into the geminate radical pair occurs with a time constant of 80 fs along the repulsive potential energy surface of the first excited singlet state.[4i] The thermal bleaching process, however, is relatively slow. In organic solvents, the thermal transformation of the TPIRs to HABI requires several minutes at room temperature.

We recently developed a unique photochromic molecule, 1-NDPI-8-TPI-naphthalene (Scheme 1b), that exhibits improved photochromic performance in coloration and thermal bleaching rates as well as a greater optical density in the colored state.[4f] 1-NDPI-8-TPI-naphthalene is a HABI derivative containing a naphthalene moiety that tethers two triarylimidazole units. 1-NDPI-8-TPI-naphthalene cleaves photochemically into 1-NDPIR-8-TPIR-naphthalene in a manner similar to HABI derivatives, and the solution changes from colorless to green. However, unlike conventional HABI derivatives, the photogenerated radical pair in 1-NDPIR-8-TPIR-naphthalene cannot diffuse into the medium to yield free radicals. A kinetic study of the thermal back-reaction of the colored species showed that the thermal bleaching process obeys first-order kinetics with a half-life of 179 ms in benzene at 25 °C. This thermal bleaching rate is fast enough to be utilized in ophthalmic lenses. Although this development was noteworthy in that the thermal back-reaction was drastically accelerated while the optical density in the colored state was maintained, it was not satisfactory for application to real-time image processing at video frame rates. We were able to make a green spot move quickly and follow the movement of UV light irradiation in solution, but an afterimage could be recognized for 1 s or less with the naked eye.[4f]

Scheme 1. Photochromism of (a) HABI, (b) 1-NDPI-8-TPI-naphthalene and (c) *pseudogem*-BisDPI[2.2]PC



In order to increase the thermal bleaching rate, the photogenerated radical pairs should be more closely spaced. Thus, we have designed and synthesized a novel HABI derivative, *pseudogem*-bisDPI[2.2]PC, which has a paracyclophane (PC) moiety that tightly couples two TPIR units (Scheme 1c). The molecular structure of *pseudogem*-bisDPI[2.2]PC was determined by X-ray crystallographic analysis and is shown in Figure 1a, along with that of 1-NDPI-8-TPI-naphthalene in Figure 1b. The C−N bond length connecting the two imidazole rings in *pseudogem*-bisDPI[2.2]PC [1.4876(15) Å] is approximately equal to that in 1-NDPI-8-TPI-naphthalene [1.488(2) Å]. *pseudogem*-BisDPI[2.2]PC undergoes a photochromic reaction involving a color change from colorless to blue upon UV irradiation both in the solid form and in solution at

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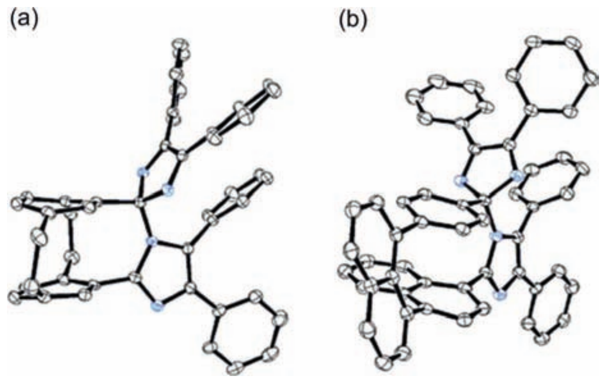

Figure 1. Crystal structures of (a) *pseudogem*-bisDPI[2.2]PC and (b) 1-NDPI-8-TPI-naphthalene[4f] with thermal ellipsoids at 50% probability. Hydrogen atoms and solvent molecules have been omitted, and nitrogen atoms are highlighted in blue.

room temperature. Under continuous irradiation, the solution of *pseudogem*-bisDPI[2.2]PC reaches photostationary equilibrium very quickly, and after irradiation ceases, the absorption decreases very rapidly according to monoexponential thermal bleaching kinetics. It is worth noting that complete bleaching is achieved within 200 ms in benzene at 25 °C. Figure 2a shows transient vis−NIR absorption spectra of *pseudogem*-bisDPI[2.2]PC in benzene at 25 °C measured by a nanosecond laser flash photolysis experiment. A sharp absorption band at 400 nm and a broad absorption band ranging from 500 to 900 nm can be ascribed to the colored species, *pseudogem*-bisDPIR[2.2]PC. All of the absorption bands decay with the same time constant, indicating the presence of a single conformation for the colored species. The half-life of the colored species is 33 ms at 25 °C. Figure 2b shows the time profile of the transient absorbance at 400 nm measured over the temperature range from 5 to 40 °C. The thermal bleaching process obeys first-order kinetics, and the half-life of the colored species varies from 198 ms at 5 °C to 10 ms at 40 °C, as shown in Figure 2c. The enthalpies and entropies of activation ($\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, respectively) for the thermal back-reaction were estimated from an Eyring plot over the temperature range from 5 to 40 °C. The Eyring plot produced an excellent straight line (Figure S5 in the Supporting Information), and the $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values estimated from standard least-squares analysis of the Eyring plot are 59.8 kJ mol^{-1} and −19.1 J K^{-1} mol^{-1}, respectively. The free energy barrier ($\Delta G^{\ddagger} = \Delta H^{\ddagger} - \mathrm{T}\Delta S^{\ddagger}$) is 65.5 kJ mol^{-1} at 25 °C.

Fast thermal bleaching kinetics enables a solution to change color only where the solution is irradiated with UV light, because the thermal bleaching rate is much faster than the diffusion rate of the colored species at room temperature (a movie showing this is available). It should be noted that the afterimage seen in the photochromic reaction of 1-NDPI-8-TPI-naphthalene is not visible to the naked eye for *pseudogem*-bisDPI[2.2]PC system. In view of the thermal bleaching rate, the fast photochromism of *pseudogem*-bisDPI[2.2]PC is applicable to real-time image processing at video frame rates. In addition, the photogeneration of paramagnetic radical species attributable to the homolytic bond cleavage is one of the important features of the photochromism of HABI derivatives. From the viewpoint of spin state, the photochromic reaction of *pseudogem*-bisDPI[2.2]PC can be regarded as a transformation from the diamagnetic colorless state to a paramagnetic colored state. Thus, in addition to the optical properties, the magnetic properties can also be switched reversibly between the two states simply by turning the optical stimulation on and off. The fast optical switching in both color and spin states cannot be realized by any other currently available photochromic system.

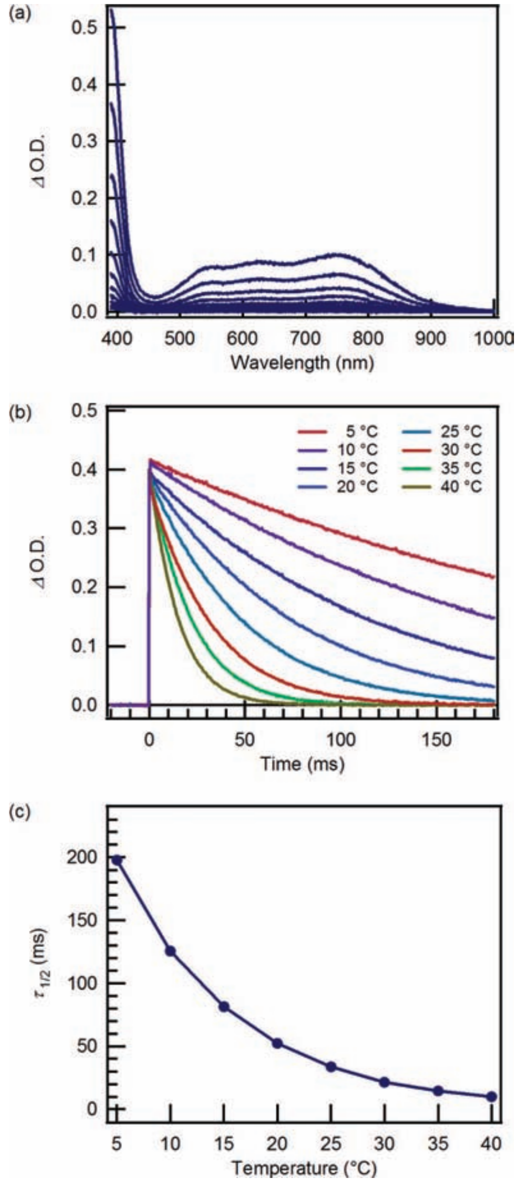

Figure 2. (a) Transient vis−NIR absorption spectra of *pseudogem*-bisDPI[2.2]PC in degassed benzene at 25 °C (2.1×10^{-4} M, 10 mm light-path length). Each of the spectra was recorded at 20 ms intervals after excitation with a nanosecond laser pulse (excitation wavelength, 355 nm; pulse width, 5 ns; power, 8 mJ/pulse). (b) Decay profiles of the colored species generated from *pseudogem*-bisDPI[2.2]PC, monitored at 400 nm in degassed benzene (1.5×10^{-4} M). The measurements were performed over the temperature range from 5 to 40 °C. (c) Temperature dependence of the half-life of the colored species in degassed benzene determined from the measurements of the nanosecond laser flash photolysis experiment.

A homogeneous amorphous film of *pseudogem*-bisDPI[2.2]PC can be readily prepared with concentrated solutions by spin-coating or dip-coating (Figures S6−S8 in the Supporting Information). The transparent amorphous film also shows fast thermal bleaching of the photochromic reaction even at room temperature (Figure S9 in the Supporting Information). Of course, the switching performance of photochromic molecules within polymeric matrices has been an important area of research in the development of optical solid-state devices. Thus, we investigated the photochromic properties of a poly(methyl methacrylate) (PMMA, MW = 3.5×10^5) film doped with 20 wt % *pseudogem*-bisDPI[2.2]PC. The dye-doped PMMA film also undergoes the photochromic reaction, as does the amorphous film. The transient absorption spectrum of the dye-doped

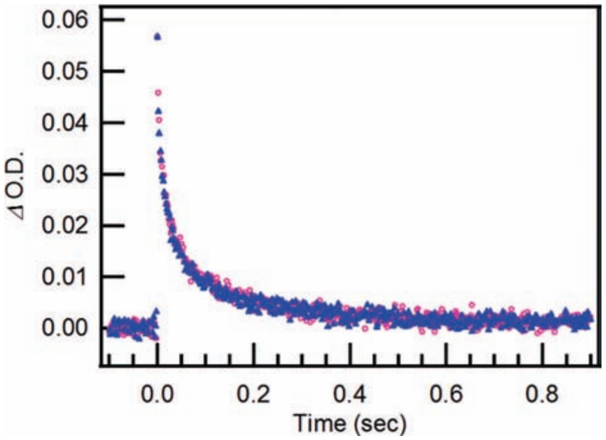

Figure 3. Time profiles of the transient absorbance at 400 nm of the PMMA film doped with 20 wt % *pseudogem*-bisDPI[2.2]PC, measured at 25 °C: (red ○) freshly prepared sample; (blue ▲) after irradiation with 10 000 laser pulses (excitation wavelength, 355 nm; pulse width, 5 ns; power, 4 mJ/pulse; repetition frequency, 1 Hz).

PMMA film is almost identical to that of the solution (Figure S11 in the Supporting Information). While the decay of transient absorbance at 400 nm does not obey simple first-order kinetics, the half-life of the colored species is roughly estimated to be shorter than 20 ms at 25 °C. This half-life is slightly shorter than that in a benzene solution at the same temperature. Moreover, thousands of switching cycles can be repeated consecutively without any sign of degradation, even in the presence of molecular oxygen. The traces in Figure 3 demonstrate the time profile of the transient absorbance at 400 nm measured at 25 °C after irradiation with 10 000 laser pulses, in order to evaluate the photochemical fatigue resistance. The time profiles for the freshly prepared film and the film after 10 000 laser pulses are indistinguishable, indicating that *pseudogem*-bisDPI[2.2]PC is indeed stable, making it attractive for practical applications in optical solid-state devices. The excellent fatigue resistance in PMMA matrices is particularly surprising in view of the fact that the photogenerated radical of HABI is an excellent hydrogen abstractor and has been used as an excellent initiator of free-radical polymerization in combination with proper co-initiators, such as hydrogen donors and efficient chain-transfer agents. The remarkable stability of the colored biradical generated from the photochromic reaction of *pseudogem*-bisDPI[2.2]PC can be attributed to the inhibition of diffusion into the PMMA matrix and the rapid geminate recombination of the nascent radical pair. Actually, the photochemical reactions between photoactive substituents in the pseudogeminal positions in [2.2]paracyclophane were reported by Hopf et al.[5] in 1995.

In general, the faster the thermal bleaching rate is, the lighter is the color of the photostationary equilibrium because of the fundamental difficulty in increasing the stationary concentration of colored species.[6] In contrast to any other currently available photochromic system, the high quantum yields (close to unity[4i]) of the bond-cleavage reactions of HABI derivatives can enable visual inspection of the coloration upon UV light irradiation in both solutions of *pseudogem*-bisDPI[2.2]PC and dye-doped PMMA films, even with their fast thermal bleaching rate. A moderate range of the thermal bleaching rate is also important for recognition by the human eye. It is difficult to detect a phenomenon that occurs in less than 10 ms by the human eye, but the colored species derived from *pseudogem*-bisDPI[2.2]PC has a half-life of tens of milliseconds, which is favorable to detection by the human eye. Thus, *pseudogem*-bisDPI[2.2]PC can potentially be applied to real-time image processing at video frame rates. Our molecular design can lead to the development of a new family of photochromic compounds with unprecedented switching speeds and remarkable stabilities, which could eventually evolve into solid-state photonic materials with unique photoresponsive characteristics.

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Supporting Information Available: Synthesis of *pseudogem*-bisDPI[2.2]PC, experimental details of the spectroscopic measurements, Eyring plots, transient absorption spectra of the dye-doped PMMA film, crystallographic data in CIF format, and a movie of the photochromic reaction in AVI format. This material is available free of charge via the Internet at http://pubs.acs.org.

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