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Photochromism of a Radical Diffusion-Inhibited Hexaarylbiimidazole Derivative with Intense Coloration and Fast Decoloration Performance

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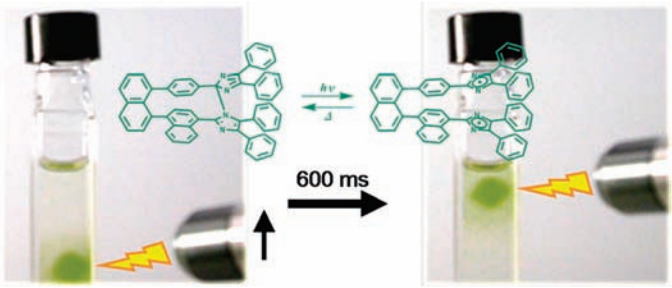
ABSTRACT



We report the synthesis and the photochromic behavior of a newly designed, photochromic, radical diffusion-inhibited hexaarylbiimidazole (HABI) derivative with markedly improved photochromic performance in coloration and decoloration rates as well as greater optical density in the colored state. The thermal bleaching rate ($\tau_{1/2}$ = 260 ms at 295 K) is the fastest among the reported ones for HABI derivatives.

Switching of the physical and chemical properties of materials by photochromic compounds has been the subject of considerable research. There is increasing interest in the use of organic photochromic compounds to modulate conductivity, fluorescence, magnetism, and shape at the bulk level.[1] Another important application of photochromic compounds lies in their use in photochromic lenses that darken in sunlight.[2] The ideal conditions for photochromic lenses are satisfied with molecules that can be stimulated by sunlight, rapidly developing an intense coloration in a wide range of visible light and returning to the initial state with fast fading kinetics in addition to fatigue resistivity for many coloring−decoloring cycles. Herein, we describe the synthesis and the photochromic behavior of a newly designed, photochromic, radical diffusion-inhibited hexaarylbiimidazole (HABI) derivative with markedly improved photochromic performance in coloration and decoloration rates as well as greater optical density in the colored state.

HABI is readily cleaved, both thermally and photochemically, into a pair of 2,4,5-triphenylimidazolyl radicals (TPIRs), which thermally recombine to reproduce its dimer.[3] The dimer is abbreviated as TPID and is identical to HABI. The photochromic behavior of HABI derivatives can be

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(1) (a) Kawai, T.; Kunitake, T.; Irie, M. *Chem. Lett.* **1999**, *28*, 905. (b) Kawai, T.; Nakashima, Y.; Irie, M. *Adv. Mater.* **2005**, *17*, 309. (c) Fernandez-Acebes, A.; Lehn, J.-M. *Adv. Mater.* **1998**, *10*, 1519. (d) Kawai, T.; Sasaki, T.; Irie, M. *Chem. Commun.* **2001**, 711. (e) Irie, M.; Fukaminato, T.; Sasaki, T.; Tamai, N.; Kawai, T. *Nature* **2002**, *420*, 759. (f) Lim, S.-J.; Seo, J.; Park, S. Y. *J. Am. Chem. Soc.* **2006**, *128*, 14542. (g) Matsuda, K.; Irie, M. *J. Am. Chem. Soc.* **2000**, *122*, 7195. (h) *Molecular Switches*; Feringa, B. L., Ed.; Wiley-VCH: Weinheim, Germany, 2001. (i) Irie, M. *Chem. Rev.* **2000**, *100*, 1683. (j) Yu, Y.; Nakano, M.; Ikeda, T. *Nature* **2003**, *425*, 145. (k) Kobatake, S.; Takami, S.; Muto, H.; Ishikawa, T.; Irie, M. *Nature* **2007**, *446*, 778.

(2) (a) Crano, J. C.; Guglielmetti, R. J. *Organic Photochromic and Thermochromic Compounds*; Plenum Press: New York, 1999. (b) Duerr, H.; Bouas-Laurent, H. *Photochromism: Molecules and Systems*; Elsevier: Amsterdam, 2003.

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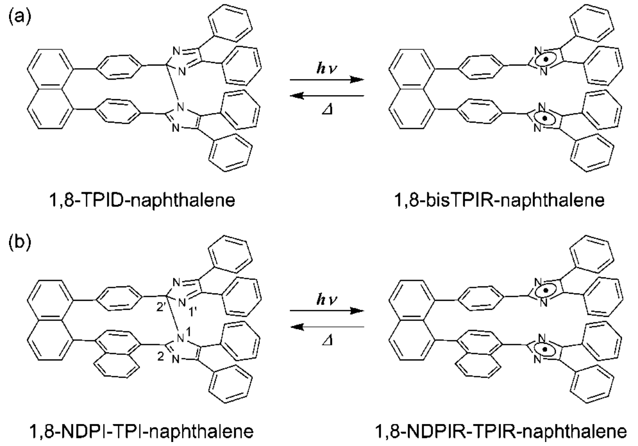
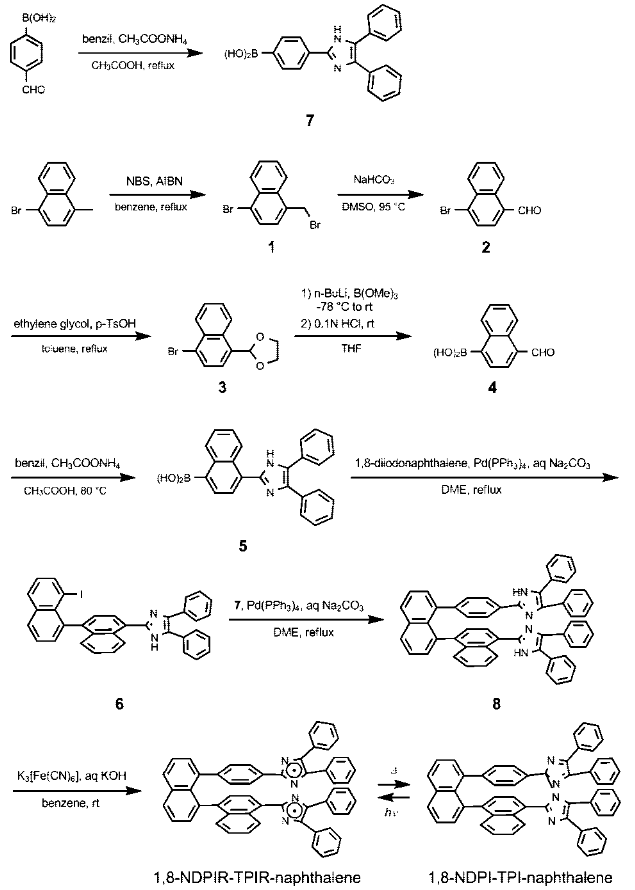
attributed to the photoinduced homolytic reversible cleavage of the C−N bond between the imidazole rings. We have been investigating the photochromism of various kinds of HABI derivatives.[4] Recently, we have developed a new class of radical diffusion-inhibited HABI, 1,8-TPID-naphthalene, with the aid of a naphthalene linker as a radical diffusion inhibition unit, as shown in Scheme 1a.[4a] 1,8-TPID-naphthalene cleaves photochemically into 1,8-bisTPIR-naphthalene, and the solution changes from colorless to green. Unlike conventional HABI derivatives, the photoinduced radical pair in 1,8-bisTPIR-naphthalene cannot diffuse into the medium to yield free radicals. A kinetic study of the thermal back-reaction from the diradical to the dimerized product showed that the reaction obeys first-order kinetics with a 730 ms half-lifetime in degassed benzene at 298 K.

Scheme 1. Photochromism of (a) 1,8-TPID-naphthalene and (b) 1,8-NDPI-TPI-naphthalene



In this study, we have developed a new type of radical diffusion-inhibited HABI derivative, 1,8-NDPI-TPI-naphthalene (Scheme 1b), which consists of two different TPIR units, i.e., 2-(1-naphthyl)-4,5-diphenylimidazolyl radical (NDPIR) and TPIR units. The colored species (1,8-NDPIR-TPIR-naphthalene) of 1,8-NDPI-TPI-naphthalene can be expected to give a superposed absorption spectrum in the visible region for the corresponding NDPIR and TPIR. Thus, a wide range of visible light would be absorbed by 1,8-NDPIR-TPIR-naphthalene because TPIR and NDPIR absorb light between 500 and 600 nm and 550 and 900 nm in addition to a sharp band at around 460 nm, respectively (Figure S1, Supporting Information).

Scheme 2. Synthesis of 1,8-NDPI-TPI-naphthalene



The synthesis was performed according to Scheme 2. The molecular structure revealed by X-ray crystallographic analysis is shown in Figure 1. 1,8-NDPI-TPI-naphthalene

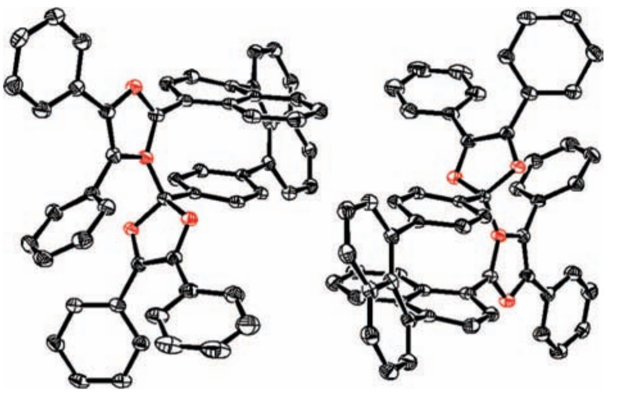


Figure 1. Crystal structure of 1,8-NDPI-TPI-naphthalene with thermal ellipsoids (50% probability). The hydrogen atoms and the solvents are omitted. Nitrogen atoms are highlighted in red.

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(3) (a) Hayashi, T.; Maeda, K. *Bull. Chem. Soc. Jpn.* **1960**, *33*, 565. (b) White, D. M.; Sonnenberg, J. *J. Am. Chem. Soc.* **1966**, *88*, 3825. (c) Cohen, R. *J. Org. Chem.* **1971**, *36*, 2280. (d) Riem, R. H.; MacLachlan, A.; Coraor, G. R.; Urban, E. J. *J. Org. Chem.* **1971**, *36*, 2272. (e) Cescon, L. A.; Coraor, G. R.; Dessauer, R.; Silversmith, E. F.; Urban, E. J. *J. Org. Chem.* **1971**, *36*, 2262.

(4) (a) Iwahori, F.; Hatano, S.; Abe, J. *J. Phys. Org. Chem.* **2007**, *20*, 857. (b) Satoh, Y.; Ishibashi, Y.; Ito, S.; Nagasawa, Y.; Miyasaka, H.; Chosrowjan, H.; Taniguchi, S.; Mataga, N.; Kato, D.; Kikuchi, A.; Abe, J *Chem. Phys. Lett.* **2007**, *448*, 228. (c) Miyamoto, Y.; Kikuchi, A.; Iwahori, F.; Abe, J. *J. Phys. Chem. A* **2005**, *109*, 10183. (d) Nakahara, I.; Kikuchi, A.; Iwahori, F.; Abe, J. *Chem. Phys. Lett.* **2005**, *402*, 107. (e) Kikuchi, A.; Iwahori, F.; Abe, J. *J. Am. Chem. Soc.* **2004**, *126*, 6526. (f) Kikuchi, A.; Iyoda, T.; Abe, J. *Chem. Commun.* **2002**, 1484. (g) Abe, J.; Sano, T.; Kawano, M.; Ohashi, Y.; Matsushita, M. M.; Iyoda, T. *Angew. Chem., Int. Ed.* **2001**, *40*, 580. (h) Kawano, M.; Sano, T.; Abe, J.; Ohashi, Y. *Chem. Lett.* **2000**, *29*, 1372. (i) Kawano, M.; Sano, T.; Abe, J.; Ohashi, Y. *J. Am. Chem. Soc.* **1999**, *121*, 8106.

has the chirality resulting from the 1,1′-binaphthyl unit, and the two enantiomeric forms of the molecule are found to make up the racemic crystal. The C−N bond connecting two imidazolyl rings is formed between N1 of the NDPI unit and C2′ of the TPI unit (1,2′-isomer), and the bond length (1.488(2) Å) is approximately equal to that (1.494(3) Å) of 1,8-TPID-naphthalene. Another possibility for the C−N bond formation between N1′ of the TPI unit and C2 of the NDPI unit (2,1′-isomer) was suggested by the B3LYP/6-31G(d) level density functional theory (DFT) calculations (Figure 2). However, the zero-point corrected electronic energy of the latter conformation is 2.2 kcal/mol higher than that corresponding to the observed conformation. This energy difference is attributable to the steric repulsion between the H atom in the naphthalene ring of NDPI unit and the N atom in the later conformation. The 2,1′-isomer is not formed even after photolysis. This may be due to the difference in the reaction rate to form the imidazole dimer from the radical species. What this means is that the free energy barrier ($\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger}$) for the radical−radical reaction leading to the 2,1′-isomer is larger than that for the 1,2′-isomer.

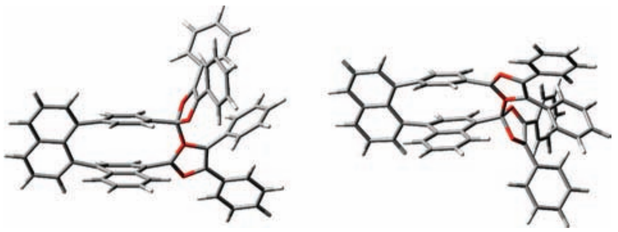

Figure 2. Optimized structures of the 1,2′-isomer (left) and the 2,1′-isomer (right) by the DFT Beck3LYP/6-31G(d) method. Nitrogen atoms are highlighted in red.

1,8-NDPI-TPI-naphthalene shows photochromic reaction changing its color from colorless to moss green on UV irradiation in both solid and solution. Under continuous irradiation, the degassed toluene solution of 1,8-NDPI-TPI-naphthalene reaches the photostationary equilibrium very quickly, and the absorption decreases very rapidly following monoexponential thermal bleaching kinetics after ceasing the irradiation. The complete bleaching is achieved within 1 s at 295 K. Figure 3 shows the transient vis−NIR absorption spectra of 1,8-NDPI-TPI-naphthalene in degassed toluene solution at 253 K. The measurement of the transient absorption spectra was started immediately after ceasing the irradiation when a photostationary state was reached on UV irradiation. The colored species absorbs the whole range of visible light, which is attributed to the NDPIR and TPIR chromophores of 1,8-NDPIR-TPIR-naphthalene. Figure 4a shows the transient absorption decay at 450 nm measured by the nanosecond laser flash photolysis experiment (355 nm excitation, 5 ns pulsewidth). The thermal back-reaction obeys first-order kinetics, and the half-lifetime at 295 K is 260 ms. This thermal bleaching rate is the fastest among the reported one for HABI derivatives. The fast fading kinetics makes it possible to change the color of the solution

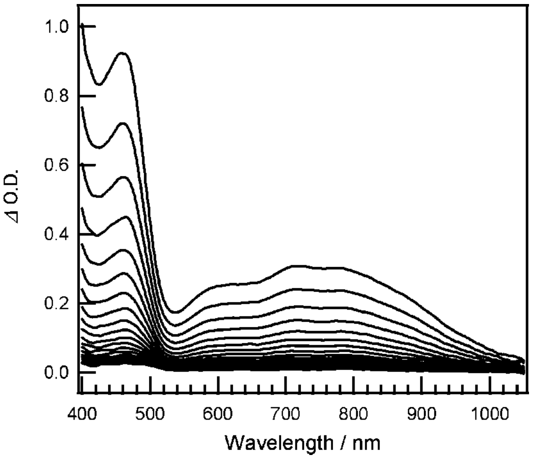

Figure 3. Transient vis−NIR absorption spectra of 1,8-NDPI-TPI-naphthalene in degassed toluene solution (1.2×10^{-4} M) at 253 K after irradiation with 365 nm of UV light in a well-stirred quartz cell (light-path length: 10 mm). Each of the spectra was recorded at 3 s intervals over a 1 min period.

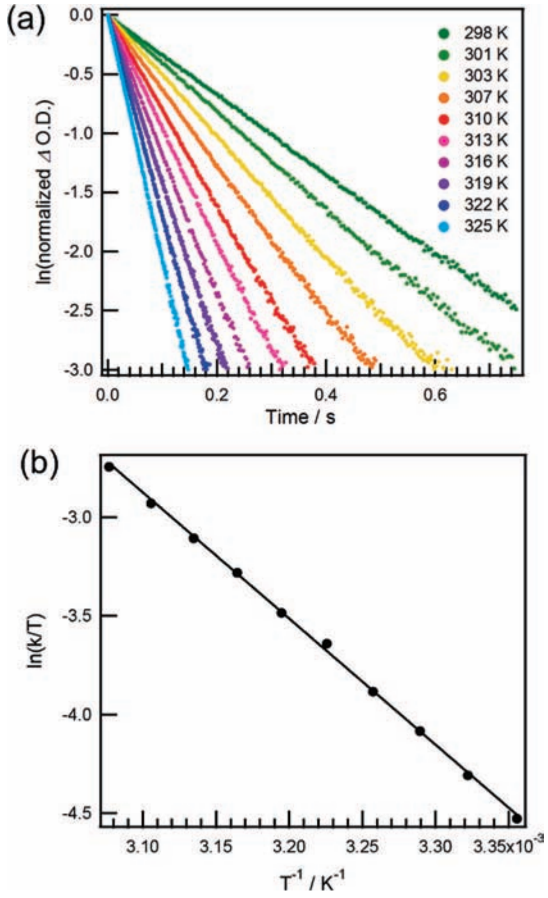

Figure 4. (a) Decay profiles of the colored species generated from 1,8-NDPI-TPI-naphthalene monitored at 450 nm in degassed toluene solution (1.2×10^{-4} M). The measurements were performed in the temperature range from 298 to 325 K. (b) Eyring plots for the thermal back-reaction over a temperature ranging from 298 to 325 K.

only where UV light is irradiated, because the diffusion rate of colored species is slower than the decoloration rate at room temperature (Movie S1, Supporting Information). The enthalpies and entropies of activation ($\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, respectively) for the thermal back-reaction were estimated from Eyring plots over a temperature ranging from 298 to 325 K. The Eyring plots give an excellent straight line (Figure 4b), and the $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values estimated from standard least-squares analysis of the Eyring plots are 53.0 kJ mol^{-1} and -57.1 J K^{-1} mol^{-1}, respectively.

In conclusion, we have developed a new type of radical diffusion-inhibited HABI derivative with intense coloration and fast decoloration performance. In the case of conventional HABI derivatives, the photoinduced homolytic cleavage of the C−N bond of a heterodimer of imidazolyl radicals yields a mixture of the homo- and heterodimers. However, the combination of different imidazolyl radicals is kept for the radical diffusion-inhibited HABI after many coloring−decoloring cycles, and the chemical and physical properties of each imidazolyl radical can be utilized to enhance the photochromic performance. Though the reason why the thermal bleaching rate of 1,8-NDPIR-TPIR-naphthalene is drastically accelerated compared to that of 1,8-bisTPIR-naphthalene is not clarified at the present stage, the steric or electronic effects resulting from the combination of different imidazolyl radicals probably play an important role in the photochromic performance. Thus, the present study demonstrated the advantage of the heterodimer of the imidazolyl radical incorporated in the radical diffusion-inhibited HABIs. We thus believe that this work may open an exciting new avenue for future development of the photochromic dyes.

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Supporting Information Available: Synthesis of 1,8-NDPI-TPI-naphthalene, experimental details of spectroscopic measurements, crystallographic data in CIF format, transient absorption spectra of the HABI and the NDPI dimer, DFT calculations, and movies for the fading process in MOV format. This material is available free of charge via the Internet at http://pubs.acs.org.

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