JACS
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
Article
pubs.acs.org/JACS

Unusual Negative Photochromism via a Short-Lived Imidazolyl Radical of 1,1′-Binaphthyl-Bridged Imidazole Dimer

Sayaka Hatano,[†] Takeru Horino,[‡] Atsuhiro Tokita,[‡] Toyoji Oshima,[‡] and Jiro Abe*[,†,§]

[†]Department of Chemistry, School of Science and Engineering, Aoyama Gakuin University, 5-10-1 Fuchinobe, Chuo-ku, Sagamihara, Kanagawa 252-5258, Japan

[‡]Tokyo Research Laboratory, Mitsubishi Gas Chemical Company, Inc., 6-1-1 Niijuku, Katsushika, Tokyo 125-0051, Japan

[§]CREST, Japan Science and Technology Agency, K's Gobancho, 7 Gobancho, Chiyoda-ku, Tokyo 102-0076, Japan

Ⓢ *Supporting Information*

ABSTRACT: We have synthesized a new photochromic compound that exhibits unusual negative photochromism, in which the stable colored species photochemically converts into the metastable colorless species via a short-lived radical. This compound has a 1,1′-binaphthyl moiety bridging the two diphenylimidazole units. Its photochemical properties were investigated by nanosecond laser flash photolysis. The colored species isomerizes to the colorless species upon exposure to visible light and thermally returns to the original colored species within 20 min at room temperature. Moreover, the photodecoloration reaction proceeds via a short-lived radical with a half-life of 9.4 μs in benzene at room temperature. Both the colored and colorless species show the photoinduced homolytic bond cleavage reaction of the C−N bond between the nitrogen atom of the imidazole ring and the carbon atom of the 1-position of the 1,1′-binaphthyl moiety and that of the C−C bond between each of the carbon atoms of the 2-position of the imidazole ring, respectively, followed by their formation by rapid radical coupling.

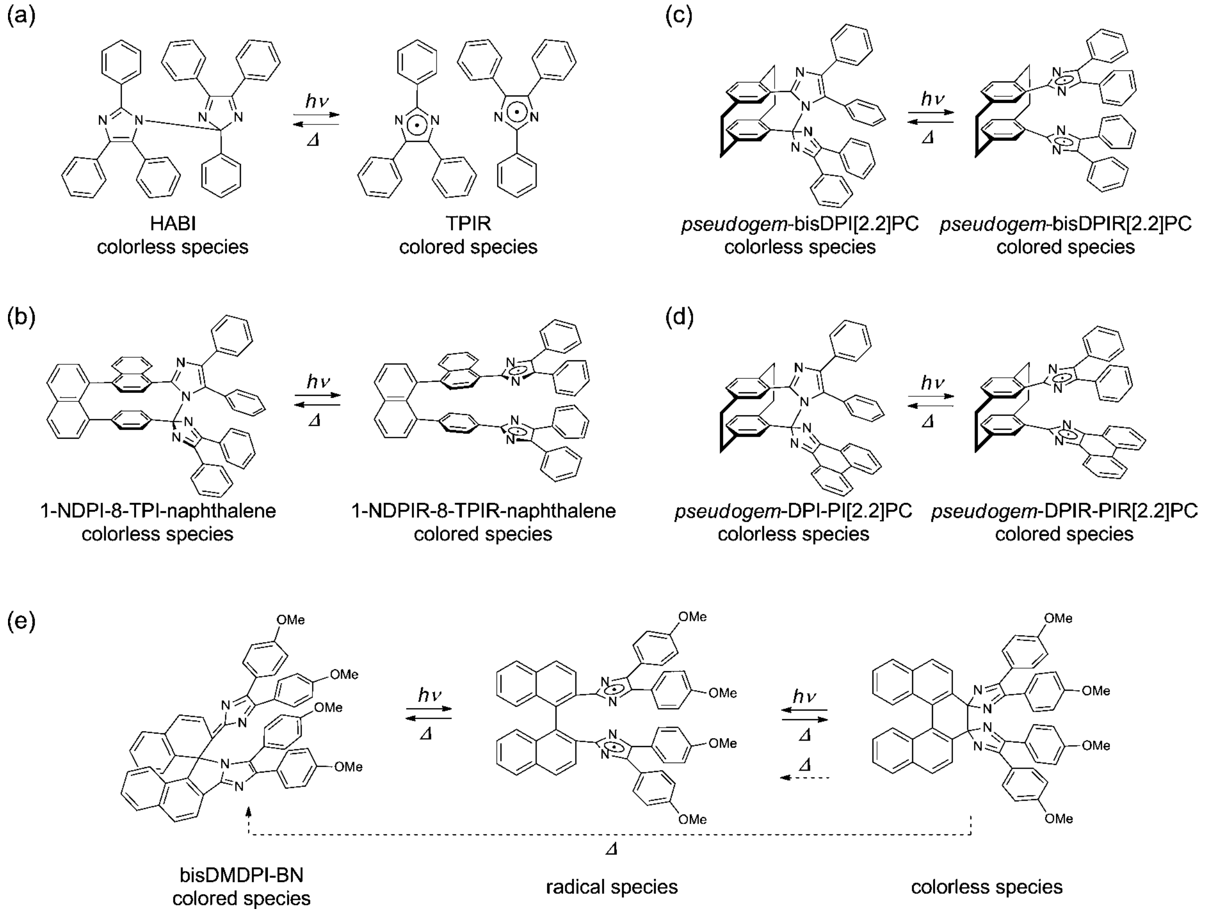
INTRODUCTION

The reversible rearrangements of a chemical species between two forms induced in one or both directions by light absorption that causes changes in the absorption spectra is known as photochromism.[1] Photochromic materials change their color upon irradiation; the photogenerated species can be reversed to the original species either thermally or by subsequent irradiation with a specific light wavelength. For example, azobenzene shows a photochemically and thermally responsive transformation between the *cis* and *trans* isomers. Diarylethene and fulgide derivatives photochemically undergo reversible cyclization and cycloreversion reactions. Most of the photochromic compounds change from a thermally stable colorless state to a metastable colored state upon UV light irradiation. On the other hand, there are a few reports on "negative photochromism" that is observed with several photochromic molecules where the absorption spectrum of the compound after irradiation is blue-shifted relative to that before irradiation.[2,3] The colored species of a negative photochromic compound is more stable than the colorless species, and the colored species becomes colorless upon exposure to visible light. For example, in a highly polar environment, several spiropyrans,[2] especially those with free hydroxy, carboxy or nitro groups, exhibit negative photochromism because of the stabilization of the colored zwitterionic merocyanine (MC) form. Factors such as hydrogen bonding,[2n] combination with crown ether[2f,o,q] or a polypeptide,[2e,k,p] and complexation with a metal[2g−i,l] can also lead to the stabilization of the MC form. Hence, it is important for the negative photochromism of spiropyran to produce a suitable environment that stabilizes the MC form. Thus, negative photochromism can be seen only under the above-mentioned specific conditions. The development of a unique photochromic compound with negative photochromism would open a new avenue for the design of advanced photoresponsive materials. Herein, we report a new photochromic compound exhibiting unusual negative photochromism, in which a stable colored species photochemically converts to a metastable colorless species via a short-lived radical. The isomerization mechanism from the colored to the colorless species is completely different from those reported for the negative photochromic compounds.

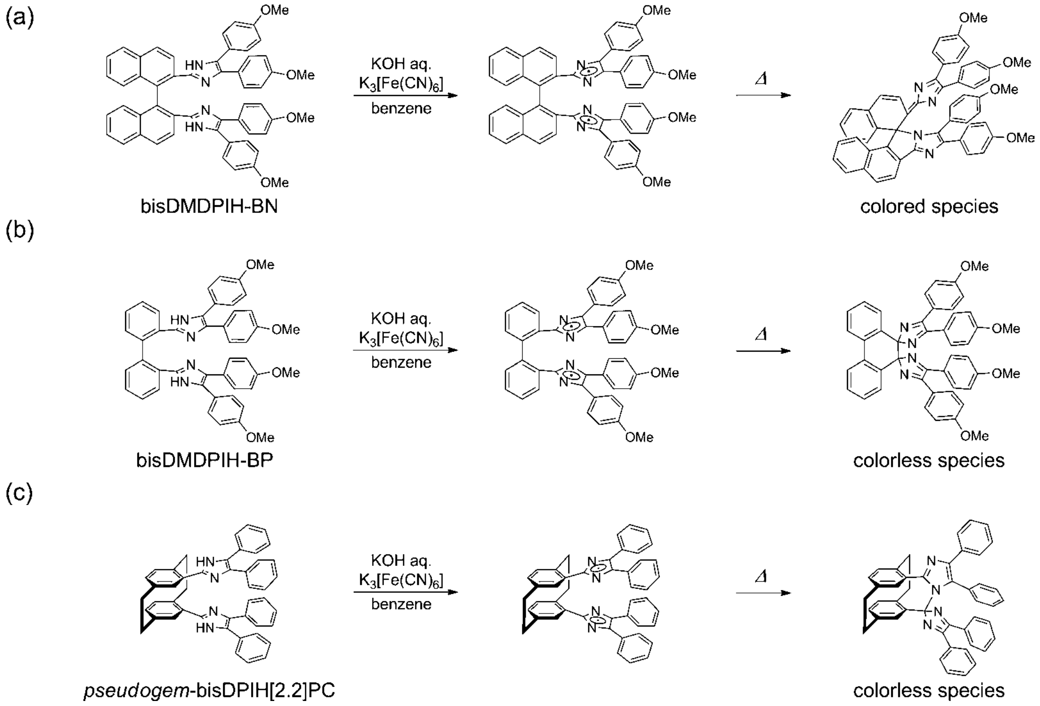
Hexaarylbiimidazole (HABI) is a photochromic compound that shows photochemical color change from colorless imidazole dimer to colored imidazolyl radical (Scheme 1a).[4] This behavior of HABI can be attributed to the photogenerated homolytic cleavage of the C−N bond between the imidazole rings, resulting in the formation of the colored triphenylimidazolyl radical (TPIR). The decoloration reaction proceeds only thermally by the radical recombination reaction of TPIRs to form the original C−N bond. However, this reaction takes several minutes at room temperature because of the TPIR diffusion into the medium. To increase the thermal bleaching rate, the TPIR diffusion should be suppressed. Thus, we have

Received: November 19, 2012
Published: February 12, 2013

Scheme 1. Photochromism of (a) HABI, (b) 1-NDPI-8-TPI-naphthalene, (c) *pseudogem*-bisDPI[2.2]PC, (d) *pseudogem*-DPI-PI[2.2]PC, and (e) bisDMDPI-BN



Scheme 2. Preparations of (a) bisDMDPI-BN, (b) bisDMDPI-BP, and (c) *pseudogem*-bisDPI[2.2]PC



designed and synthesized several HABI derivatives with a naphthalene or a [2.2]paracyclophane ([2.2]PC) moiety that bridges two triphenylimidazole (TPI) or diphenylimidazole (DPI) units.[5,6] We have also succeeded in the acceleration of the thermal decoloration rate. The half-lives of the colored species of naphthalene-bridged imidazole dimer, 1-NDPI-8-TPI-naphthalene,[5b] and [2.2]PC-bridged imidazole dimer, *Pseudogem*-bisDPI[2.2]PC,[6a] in solution are 170 and 33 ms at 298 K, respectively. *pseudogem*-DPI-PI[2.2]PC, containing a phenanthroimidazole (PI) group, shows the fastest thermal back-reaction, with a half-life of 35 μs in solution at 298 K.[6b] The original colorless state is fully restored within 200 μs at 298 K.

In this study, we synthesized a novel HABI derivative, (2,2′-dimethoxydiphenylimidazole)-1,1′-binaphthyl (bisDMDPI-BN), with a flexible linker, 1,1′-binaphthyl (BN) moiety, that bridges two DPI units (Scheme 1e). We found that this molecule has a unique molecular structure compared with the known photochromic imidazole dimers. This newly developed imidazole dimer shows unusual negative photochromism with a complicated photochemical reaction.

■ RESULTS AND DISCUSSION

Molecular Structure of the Colored Species. As shown in Scheme 2c, generally, HABI derivatives can be obtained in a colorless form with the C−N bond between the imidazole rings by oxidizing the lophine precursor with potassium ferricyanide under basic conditions. Upon the oxidation of the imidazole anion, the radical species is generated and the C−N bond is formed between the two imidazole rings by radical−radical coupling, resulting in the formation of an imidazole dimer as the colorless species. On the other hand, the oxidation of bisDMDPIH-BN under basic conditions leads to the formation of a deep-red-colored species in powder form.

The recrystallization of the compound with the exclusion of light from a benzene/acetonitrile mixture gave deep-red blocks. The molecular structure of the colored species revealed by X-ray crystallographic analysis is shown in Figure 1. This structure obtained by the oxidation of bisDMDPIH-BN is completely different from that obtained by the oxidation of the triarylimidazole derivatives. The colored species has the C−N bond between the nitrogen atom N(1) of the imidazole ring and the carbon atom C(8) at the 1-positon of the BN moiety. This bond formation results in a five-membered ring structure. The C−N bond length (1.487(2) Å) is approximately equal to that of other bridged imidazole dimers. The colored species has a spiro carbon at the BN moiety. The C(9)−C(10) bond length (1.372(2) Å) is slightly longer than that typical C=C bond length (1.339 Å), and the N(2)−C(11) and N(3)−C(24) bond lengths in the imidazole ring are 1.313(2) and 1.311(2) Å, respectively. They are also shorter than the respective C(10)−N(2) and C(10)−N(3) bond lengths of 1.394(2) and 1.413(2) Å. These results indicate that a part of the structure including one imidazole ring forms the diazafulvene structure.[6e]

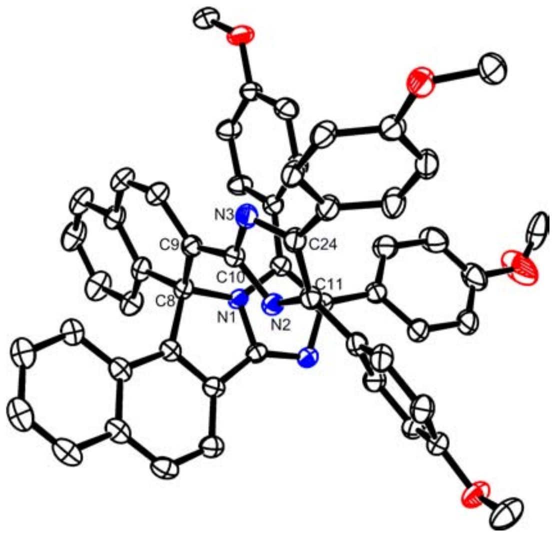


Figure 1. ORTEP representations of the colored species of bisDMDPI-BN with thermal ellipsoids (50% probability), where nitrogen atoms are highlighted in blue and oxygen atoms are highlighted in red. Hydrogen atoms are omitted for clarity.

Recently, we reported a unique photochromic [2.2]PC-bridged imidazole derivative with the C−N bond between the [2.2]PC moiety and the imidazole ring, which yields a monoradical on either UV or visible light irradiation.[6e] This imidazolyl radical cannot form the C−N bond between the imidazole rings because of the strong steric repulsion, and a unique radical−radical coupling was observed. This exemplifies the feasibility of the specific reaction of the imidazolyl radical. Furthermore, the imidazolyl radical with the BN moiety also reacts with the carbon atom of the 1-positon of the BN moiety. In this molecule, due to the structural flexibility of the BN moiety in arranging an orthogonal conformation, it is considered that the two imidazole rings are very far apart to form the C−N bond between the imidazole rings. As a result, the carbon atom at the 1-position of the BN moiety is attacked by the imidazolyl radical.

Molecular Structures of the Colorless Species. The colored species was found to reversibly isomerize to the colorless species upon exposure to visible light. Though the details of the photochromic behavior of the colored species will be discussed later, the negative photochromism of the colored species was confirmed by measuring the UV−vis absorption spectra. However, it is difficult to obtain crystals for the colorless species of bisDMDPI-BN because of its thermal instability. The colored species is restored from the colorless species within 20 min at room temperature in the dark. Therefore, we attempted to determine the molecular structure of the colorless species using ^{13}C NMR by comparison with that of the colorless 1,1′-biphenyl-bridged imidazole dimer (bisDMDPI-BP).

The preparation of bisDMDPI-BP is shown in Scheme 2b. Following the oxidation of bisDMDPIH-BP with potassium ferricyanide under basic conditions, bisDMDPI-BP is obtained in a colorless form. The recrystallization of the compound from an acetonitrile/ethanol mixture gave colorless blocks. The molecular structure of bisDMDPI-BP was determined by X-ray crystallographic analysis as shown in Figure 2. A remarkable fact is the formation of a 2,2′-imidazole dimer with the C−C bond (1.5619(16) Å) between the imidazole rings, whereas all of other bridged imidazole dimers previously reported by our group have the C−N bond between the imidazole rings. Thus, bisDMDPI-BP has a couple of equivalent sp^3 carbon atoms at the 2-position of each imidazole ring. This compound does not exhibit photochromic properties as observed in the 1,2′-imidazole dimers. The colorless species of bisDMDPI-BN can be also expected to have a molecular structure similar to bisDMDPI-BP.

The ^{13}C NMR spectra of the colored and colorless species of bisDMDPI-BN and bisDMDPI-BP in CDCl$_3$ are shown in Figure 3. As previously described, the colorless species of bisDMDPI-BN thermally isomerizes to the colored species,

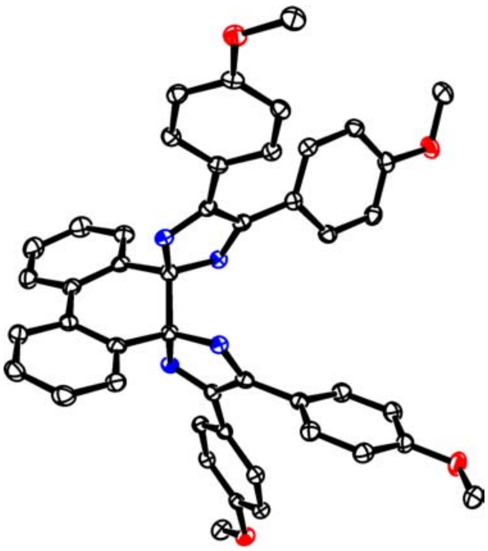


Figure 2. ORTEP representations of the colorless species of bisDMDPI-BP with thermal ellipsoids (50% probability), where nitrogen atoms are highlighted in blue and oxygen atoms are highlighted in red. Hydrogen atoms and solvent molecules are omitted for clarity.

which is completely restored within 20 min in the dark at room temperature. To decelerate the rate of the thermal back reaction of the colorless species, the NMR measurements of the colorless species were carried out at 223 K after forming sufficient amounts of the colorless species with visible light irradiation. The spectrum of the colorless species (Figure 3b) is similar to that of bisDMDPI-BP (Figure 3c). The NMR spectrum of the colored species of bisDMDPI-BN exhibits four characteristic peaks assignable to four different methoxy groups, whereas only two peaks are observed around 55 ppm in the spectrum of bisDMDPI-BP. The colorless species of bisDMDPI-BN also shows only two peaks corresponding to methoxy groups. The NMR spectra suggest that the colorless species of bisDMDPI-BN has also a symmetric structure similar to that formed in bisDMDPI-BP. The symmetric feature of the molecular structures for bisDMDPI-BN and bisDMDPI-BP is also supported by the ^{1}H NMR spectra (Figures S5 and S9). Moreover, the colorless bisDMDPI-BP shows a single characteristic peak at 105 ppm assignable to the sp^3 carbon of the imidazole ring. The spectrum of the colorless species of bisDMDPI-BN also shows peaks with almost the same chemical shifts of bisDMDPI-BP. Thus, from the analogy of the molecular structure of bisDMDPI-BP, the molecular structure of the colorless species of bisDMDPI-BN can be unambiguously determined to be the 2,2′-isomer, where the C−C bond is formed between the imidazole rings.

Photochromism. Generally, HABI derivatives show photochromic behavior changing from the colorless imidazole dimer to the colored imidazolyl radicals upon UV light irradiation. The colored species recombines to form the original imidazole dimer. Thus, the colorless species of HABI is more stable than the colored species. In contrast, the oxidation of the precursor bisDMDPIH-BN gives bisDMDPI-BN as the stable colored species, as shown in Scheme 2a. The solution color of the colored species changes from pale orange to colorless upon visible light irradiation at room temperature, followed by the back reaction to that thermally restores the colored species. By taking advantage of 1,2-bis(2-methylbenzo[*b*]thiophene-3-yl)-perfluorocyclopentene[7] (DAE) as a standard, the photochemical conversion efficiency from the colored species to the colorless species was estimated by nanosecond laser flash photolysis. The colorless open-ring isomer of DAE can undergo cyclization in a conrotatory fashion to the colored closed-ring isomer upon UV light irradiation. The thermal back-reaction is symmetry-forbidden, giving excellent thermal stability to the closed-ring isomer. The cycloreversion reaction from the closed-ring isomer to the open-ring isomer occurs only by irradiating with a visible light. Solutions of the colored species of bisDMDPI-BN in benzene and the closed-ring isomer of DAE in hexane with matched absorbances at the excitation wavelength of 517 nm were irradiated at various laser energies.

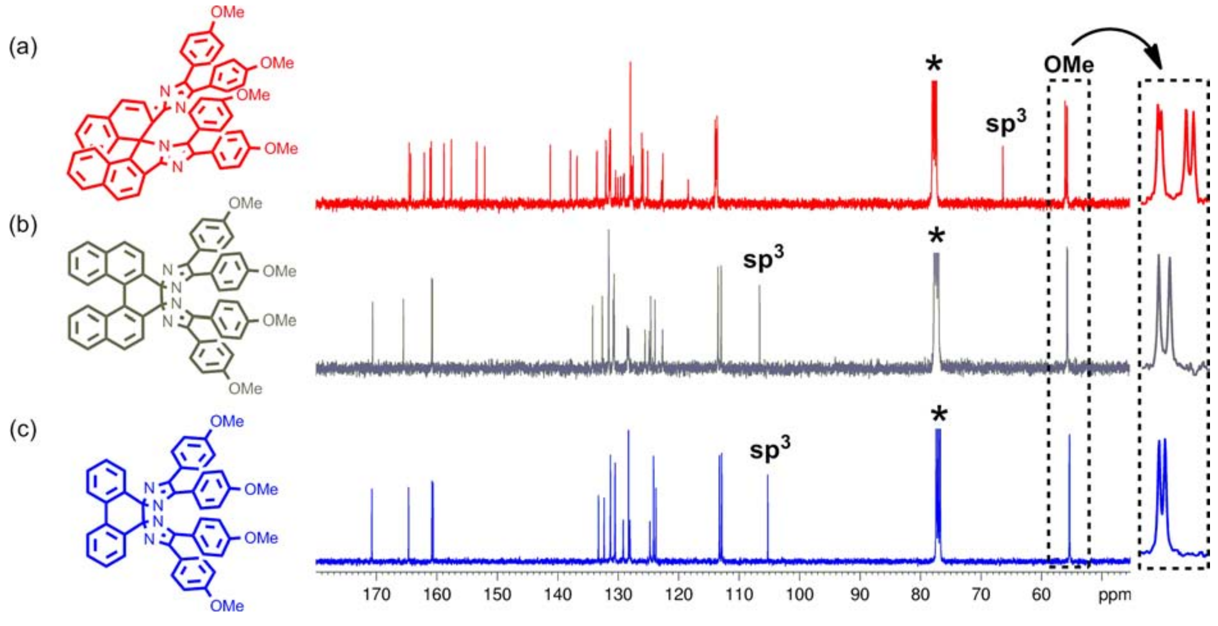


Figure 3. ^{13}C NMR spectra of (a) the colored species of bisDMDPI-BN, (b) the colorless species of bisDMDPI-BN, and (c) the colorless species of bisDMDPI-BP in $CDCl_3$ at 223 K (* = solvent peaks).

The absorbance changes, $\Delta OD(DAE)$, before and after a laser pulse irradiation at 517 nm for the closed-ring isomer of DAE were plotted against those for the colored species of bisDMDPI-BN, $\Delta OD(s)$ (Figure S15). The conversion efficiency was estimated from the slope of the fit of the data to the following equation,[8]

$$\Delta OD(DAE) = \frac{\varphi_{DAE}\varepsilon_{DAE}}{\varphi_s\varepsilon_s}\Delta OD(s) \tag{1}$$

where φ_{DAE} (0.35) is the quantum yield of cycloreversion reaction of DAE excited at 517 nm,[9] φ_s is the conversion efficiency from the colored species to the colorless species of bisDMDPI-BN, and ε_{DAE} (0.91×10^4 M^{-1} cm^{-1}) and ε_s (2.53×10^4 M^{-1} cm^{-1}) are the absorptivity coefficients of DAE[9] and the colored species of bisDMDPI-BN at 517 nm, respectively. As shown in Figure S15, φ_s is obtained from the slope of the fit of the data to eq 1 and was determined to be 0.03. The full experimental data are shown in the Supporting Information.

As will be discussed below, this photodecoloration reaction of the colored species proceeds via the unstable radical species. That is, the C−N bond of the colored species is homolytically cleaved to generate the imidazolyl radical upon visible light irradiation, followed by the radical coupling to form the colorless species with the C−C bond between the imidazole rings in the dark. Finally, the colorless species thermally changes to the colored species.

Figure 4a shows the transient UV−vis absorption spectrum of the benzene solution of the colorless species of bisDMDPI-BN standing at 298 K in the dark. The measurement of the transient UV−vis absorption spectrum started immediately after ceasing the visible light irradiation at the photo-stationary state at 298 K. The UV−vis absorption spectrum before the visible light irradiation clearly corresponds to that of the colored species with a characteristic absorption band ranging from 400 to 550 nm. As it can be seen in Figure 4a, the colorless species possesses no absorption bands at wavelengths longer than 400 nm. The intensity of the characteristic of the colored species absorption band at 490 nm gradually increases in association with the spectrum change and isosbestic points at 300 and 355 nm after ceasing the visible light irradiation. Finally, the UV−vis absorption spectrum becomes identical to the spectrum of the colored species. From the time profile of the absorbance at 490 nm in the dark, shown in Figure 4b, it is found that the time taken to thermally restore the colored species is approximately 20 min at 298 K. This coloration process obeys first-order kinetics with a rate constant of 5.16×10^{-3} s^{-1} at 298 K. The first-order rate constant, k, was determined by fitting the experimental data to the following equation,[10]

$$\ln\left(\frac{A_\infty - A_t}{A_\infty - A_0}\right) = -kt \tag{2}$$

where A_t, A_0, and A_∞ are the absorbances at time t, time zero, and infinite time, respectively. As shown in the inset of Figure 4b, the first-order plot according to eq 2 gives a good straight line. The rate constant was obtained from the slope of the first-order plot.

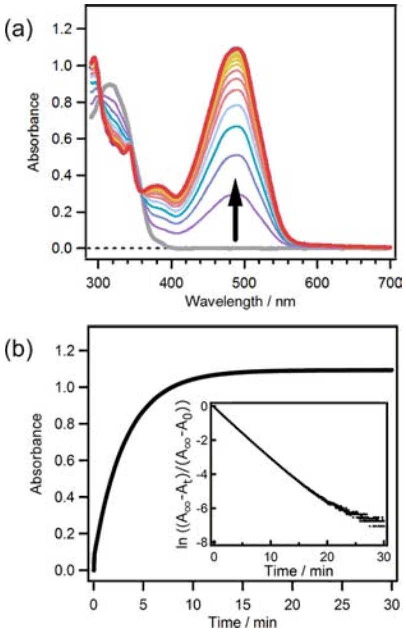


Figure 4. (a) Transient UV−vis absorption spectra of bisDMDPI-BN in deaerated benzene (2.9×10^{-5} M) at 298 K. Each of the spectra was recorded at 1 min intervals after irradiation with visible light. The spectrum of the colored species is shown in red and that of the colorless species is shown in gray. (b) Time profile of the colorless species generated from the colored species upon irradiation with visible light (400−700 nm), monitored at 490 nm in deaerated benzene at 298 K. The inset is a first-order plot according to eq 2.

Two different thermal reaction paths can be considered for the coloration process as indicated in Scheme 1e in broken lines: stepwise isomerization via the radical species formed by the homolytic bond cleavage of the C−C bond between the imidazole rings and the one-step rearrangement. Although an electron spin resonance (ESR) measurement was conducted to detect the radical species in the course of the thermal transformation from the colorless species to the colored species, no significant ESR signal could be detected for the solution of the colorless species. This result never neglects the possibility for the stepwise isomerization path via the radical species in view of the fact that the radical species with an extremely short half-life would not be accumulated enough to be detected by a conventional continuous-wave ESR apparatus. Though the mechanism for the thermal back reaction to form the colored species from the colorless species is not presently clear, the photodecoloration phenomenon of the colored species of bisDMDPI-BN is exactly negative photochromism.

Laser Flash Photolysis. As described above, the colorless species of bisDMDPI-BN thermally isomerizes to the colored species, whereas the colored species photochemically isomerizes to the colorless species upon visible light irradiation. We have investigated the possible presence of the unstable imidazolyl radical in the photochemical process of bisDMDPI-BN by nanosecond laser flash photolysis. Figure 5a shows the transient vis−NIR absorption spectra of the colored species of bisDMDPI-BN in benzene at 298 K, excited by a nanosecond laser pulse at 355 nm. The identical transient absorption spectrum was also obtained by using a 500 nm laser pulse as the excitation light source. A sharp absorption band at 400 nm and a broad absorption band ranging from 500 to 1000 nm can be ascribed to the radical species with two parts of the imidazolyl radicals because its spectrum shape is similar to that of the colored radical species observed for the bridged imidazole dimers. Figure 5b shows the decay profile of the transient absorbance of the radical species in benzene at 750

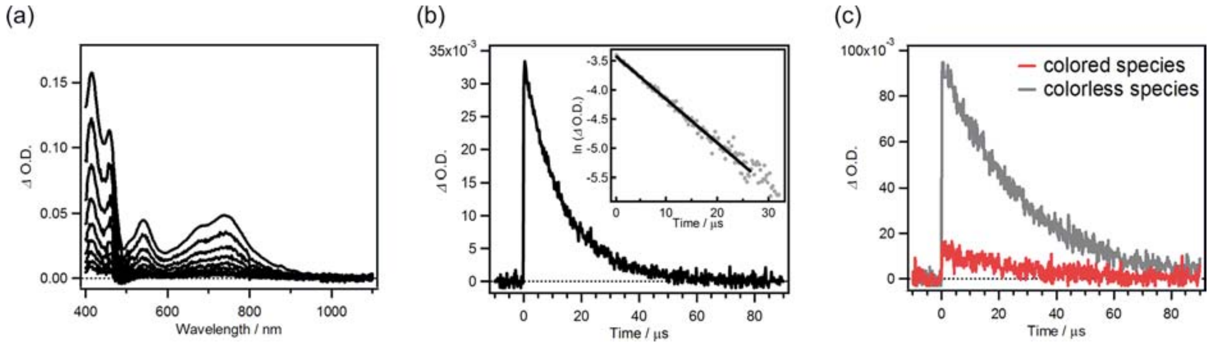


Figure 5. (a) Transient vis−NIR absorption spectra of the colored bisDMDPI-BN in deaerated benzene (1.1×10^{-4} M) at 298 K. Each of the spectra was recorded at 5 μs intervals after excitation with a nanosecond laser pulse (excitation wavelength, 355 nm; pulse width, 5 ns; power, 4 mJ/pulse). (b) Decay profile of the radical species generated from the colored species of bisDMDPI-BN monitored at 750 nm in deaerated benzene (6.0×10^{-5} M) at 298 K (excitation wavelength, 500 nm; pulse width, 5 ns; power, 4 mJ/pulse). (c) Decay profiles of the radical species generated from the colored species (red line) and the colorless species (gray line) of bisDMDPI-BN monitored at 750 nm in deaerated benzene (3.4×10^{-5} M) at 281 K (excitation wavelength, 355 nm; pulse width, 5 ns; power, 4 mJ/pulse).

nm measured at 298 K with excitation light of 500 nm. The decay profile of the radical species obeys first-order kinetics with a half-life of 9.4 μs at 298 K, which is the fastest among the reported half-lives of the radicals of HABI derivatives.

As described above, the half-life of the colored species of *pseudogem*-DPI-PI[2.2]PC, shown in Scheme 1d, is 35 μs at 298 K.[6b] We considered that the change in Gibbs energy (ΔG^0) of the thermal back reaction would increase by destabilizing the colored species. According to Marcus theory, the thermal back reaction would accelerate with increasing ΔG^0, which is closely linked to decreasing the free energy of activation $\Delta G^{\ddagger}$. The steric repulsion between the rigid phenanthroimidazole group and the phenyl rings facing each other should destabilize the radical, whereas the rotational motion along the C−C single bond between the imidazole group and the phenyl ring in the radical of *pseudogem*-bisDPI[2.2]PC should relax the steric hindrance between the phenyl rings facing each other. Therefore, the radicals of bisDMDPI-BN and *pseudogem*-DPI-PI[2.2]PC are anticipated to be less labile.

Though no transient species of the colorless bisDMDPI-BP could be detected by laser flash photolysis excited by a nanosecond laser pulse at 355 nm, the laser excitation of the colorless species of bisDMDPI-BN was found to give a colored transient species. We compared the photochemical reaction between the colored and colorless species in benzene solutions with same concentration of bisDMDPI-BN at 281 K. First, the laser flash photolysis was carried out for the solution of the colored species. Then, the measurement for the colorless species was performed immediately after the colored species fully converted to the colorless species by prolonged irradiation with visible light at 281 K. The negligibly low concentration of the colored species for the light-irradiated solution was confirmed by the UV−vis absorption spectrum, where the absorbance at 490 nm attributed to the colored species was almost negligible. As shown in Figure 5c, the decay profile of the transient species formed from the colorless species is almost identical to that of the radical species formed from the photolysis of the colored species, except the magnitude of the ΔOD value immediately after laser excitation. Thus, the transient species formed by the photolysis of the colorless species could be assigned to the identical radical species formed from the colored species. The difference in the ΔOD value in Figure 5c can be attributed to the difference in the quantum yield for the bond cleavage reaction between the C−N bond of the colored species and the C−C bond of the colorless species, because the molar absorptivity at 355 nm of these species is almost similar to that seen in Figure 4a.

The decay profiles of the absorbance in Figure 5c were monitored at 750 nm, at which wavelength only the radical species absorbs. On the other hand, as shown in Figure 6, the remaining absorbance attributable to the formation of the colored species is confirmed by the photolysis of the colorless species by monitoring at 490 nm, at which wavelength both the colored species and the radical species absorb. Thus the colorless species is also converted to the colored species via the short-lived radical species upon UV light irradiation at room temperature. That is, the C−C bond between the imidazole rings of the colorless species would be homolytically cleaved into the imidazolyl radicals upon UV light irradiation as well as the photochemical bond cleavage of the C−N bond between the imidazole rings of the colored bisDMDPI-BN. The photochemical properties of HABI derivatives have been extensively investigated since the discovery of the photochromic behavior of HABI. It is noteworthy that no reports have suggested the photochemical C−C bond cleavage between two imidazole rings for the photochromism of imidazole dimers.

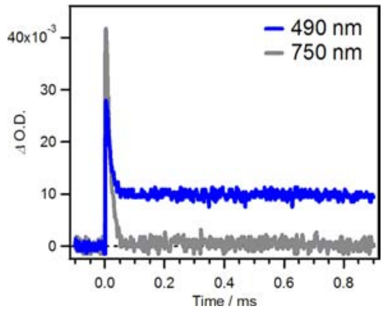
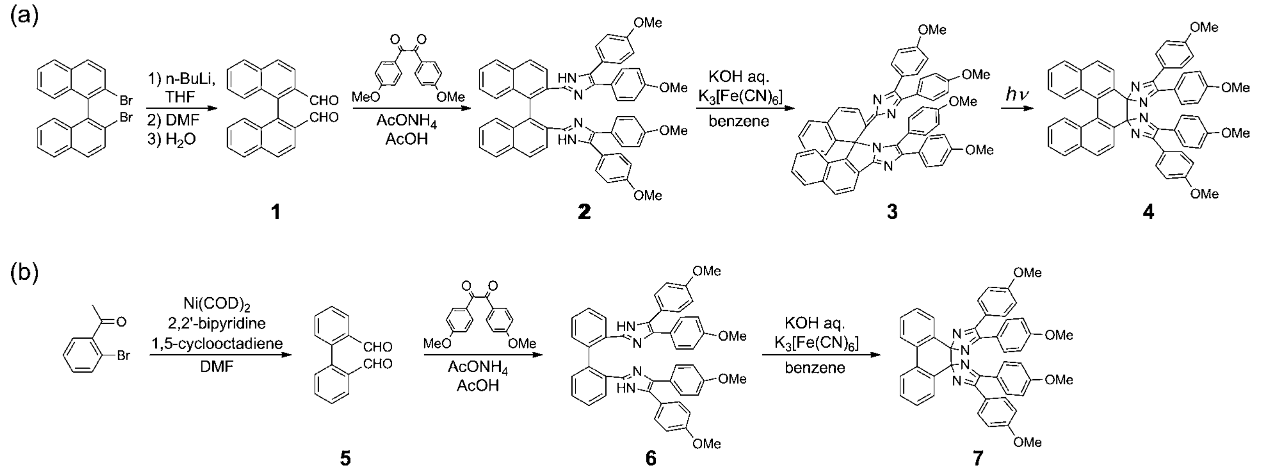


Figure 6. Decay profiles of transient absorbance of the colorless species of bisDMDPI-BN in deaerated benzene (1.6×10^{-5} M) at 281 K monitored at 490 and 750 nm in wide time region (excitation wavelength, 355 nm; pulse width, 5 ns; power, 4 mJ/pulse).

■ CONCLUSION

We developed a novel photochromic compound, bisDMDPI-BN, that exhibits unusual negative photochromism, in which

Scheme 3. Synthesis of (a) (2,2′-bisDMDPI)-1,1′-BN (3) and (b) (2,2′-bisDMDPI)-1,1′-BP (7)



the stable colored species converts to the metastable colorless species via short-lived radical species. The colored species has the C−N bond between the nitrogen atom of the imidazole ring and the carbon atom of the 1-positon of the 1,1′-binaphthyl moiety. The C−N bond formation gives a five-membered ring structure, whereas the other imidazole ring forms a diazafulvene structure. The colored species isomerizes to the colorless species upon visible light irradiation at room temperature, followed by back reaction to thermally restore the colored species. This photodecoloration reaction of the colored species upon visible light irradiation is negative photochromism. The colorless species forms the 2,2′-imidazole dimer with the C−C bond between each of the carbon atoms of the 2-position of the imidazole ring. Both the colored and colorless species show the photoinduced homolytic bond cleavage reaction of the C−N and C−C bonds, respectively, that produces the short-lived radical species with a half-life of 9.4 μs at 298 K. The rapid radical coupling reactions lead to the formation of the colored and colorless species. This unusual negative photochromism has not been reported to date and may open new avenues in the development of advanced photoresponsive materials.

■ EXPERIMENTAL SECTION

Synthesis. Commercially available reagents and solvents for syntheses were of reagent grade and used without further purification. ^{1}H and ^{13}C NMR spectra were recorded with a NMR spectrometer (Bruker, Avance III 400NanoBay). DMSO-d_6 (0.03% TMS), CD_2Cl_2, and $CDCl_3$ (0.03% TMS) were used as deuterated solvents. Chemical shifts are reported in parts per million (ppm) relative to tetramethylsilane, and the coupling constants (J) are reported in Hertz. ESI-TOF MS spectra were recorded on a Bruker Daltonics micrOTOFII-AGA1 instrument using positive-ion mode.

bisDMDPI-BN (**3**) and bisDMDPI-BP (**6**) were prepared as shown in Scheme 3.

*[1,1′-Binaphthalene]-2,2′-dicarboxaldehyde (**1**).* [1,1′-Binaphthalene]-2,2′-dicarboxaldehyde (**1**) was prepared according to a literature procedure[11a]

*bisDMDPIH-BN (**2**).* **1** (940 mg, 3.03 mmol), 4,4′-dimethoxybenzil (1.77 g, 6.55 mmol), and ammonium acetate (6.88 g, 89.2 mmol) were refluxed in acetic acid (30 mL) for 18 h. After cooling to room temperature, the reaction mixture was neutralized with aqueous NH_3. The slurry precipitate formed by neutralization was filtered off, washed with water, and then dried. This residue was purified with silica gel column chromatography using AcOEt/hexane =1/2 to 1/1 as eluent to give a yellow powder (1.72 g, 70.0%). ^{1}H NMR (400 MHz, 296 K, DMSO-d_6): δ 3.67 (s, 3H × 2, −OMe), 3.71 (s, 3H × 2, −OMe), 6.72 (d, J = 8.0 Hz, 2H × 2), 6.83 (d, J = 8.0 Hz, 2H × 2), 6.89 (d, J = 10.0 Hz, 1H × 2), 7.10 (d, J = 8.0 Hz, 2H × 2), 7.14 (d, J = 8.0 Hz, 2H × 2), 7.26 (t, J = 10.0 Hz, 1H × 2), 7.46 (t, J = 10.0 Hz, 1H × 2), 7.99 (d, J = 10.0 Hz, 1H × 2), 8.02 (d, J = 10.0 Hz, 1H × 2), 8.17 (d, J = 10.0 Hz, 1H × 2), 13.82 (s, 1H × 2, −NH). ^{13}C NMR (100 MHz, 296 K, DMSO-d_6): δ 54.97, 55.11, 113.62, 114.14, 123.08, 125.66, 126.50, 126.93, 127.13, 127.93, 128.22, 128.69, 130.21, 132.47, 133.01, 134.38, 135.26, 146.46, 157.92, 158.58. ESI-MS (m/z): $[M+H]^+$ 811.35, $[M+Na]^+$ 833.33.

*bisDMDPI-BN Colored Species (**3**).* All manipulations were carried out with the exclusion of light. Under nitrogen, to a solution of **2** (1.55 g, 1.91 mmol) in benzene (200 mL) was added a solution of potassium ferricyanide (36.2 g, 144 mmol) and KOH (16.1 g, 287 mmol) in water (150 mL), and the reaction mixture was vigorously stirred for 2 h. The organic layer was separated, exhaustively washed with water, and concentrated; 1.48 g of a dark red powder was obtained. 80 mg of this residue was purified by recrystallization from CH_2Cl_2/hexane to give dark red crystals (59.5 mg, 71.4%). Slow evaporation of benzene/CH_3CN of bisDMDPI-BN gave deep red, block single crystals suitable for the X-ray crystallographic analysis. ^{1}H NMR (400 MHz, 296 K, CD_2Cl_2): δ 3.64 (s, 3H, −OMe), 3.66 (s, 3H, −OMe), 3.72 (s, 3H, −OMe), 3.74 (s, 3H, −OMe), 6.37 (d, J = 8.9 Hz, 2H), 6.50 (d, J = 8.9 Hz, 2H), 6.64 (d, J = 8.9 Hz, 2H), 6.75 (d, J = 8.9 Hz, 2H), 6.78 (d, J = 8.9 Hz, 2H) 6.82 (d, J = 7.9 Hz, 1H), 6.85 (d, J = 9.8 Hz, 1H), 7.01 (ddd, J = 7.9, 6.1, 2.1 Hz, 1H), 7.13−7.25 (m, 4H), 7.33 (d, J = 8.9 Hz, 2H), 7.34−7.39 (m, 1H), 7.38 (d, J = 8.9 Hz, 2H), 7.41 (d, J = 8.9 Hz, 2H), 7.74 (d, J = 7.9 Hz, 1H), 7.82 (d, J = 9.8 Hz, 1H), 7.88 (d, J = 8.4 Hz, 1H), 8.10 (d, J = 8.4 Hz, 1H). ^{13}C NMR (100 MHz, 223 K, $CDCl_3$): δ 55.05, 55.13, 55.39, 55.42, 65.74, 113.12, 113.22, 113.32, 113.46, 117.90, 122.10, 122.32, 124.62, 125.39, 125.46, 125.59, 127.03, 127.25, 127.49, 128.53, 128.64, 129.11, 129.58, 129.95, 130.80, 130.90, 131.03, 131.55, 133.03, 136.36, 137.45, 140.78, 151.64, 152.99, 157.19, 158.39, 160.52, 160.72, 161.69, 163.92, 164.19. ESI-MS (m/z): $[M+H]^+$ 809.33.

*bisDMDPI-BN Colorless Species (**4**).* ^{1}H NMR (400 MHz, 223 K, $CDCl_3$): δ 3.79 (s, 3H × 2, −OMe), 3.88 (s, 3H × 2, −OMe), 6.74 (d, J = 8.8 Hz, 2H × 2), 6.90 (d, J = 8.8 Hz, 2H × 2), 7.24 (d, J = 8.1 Hz, 1H × 2), 7.39 (t, J = 8.1 Hz, 1H × 2), 7.42 (d, J = 8.8 Hz, 2H × 2), 7.46 (d, J = 8.8 Hz, 2H × 2), 7.57 (t, J = 10.0 Hz, 1H × 2), 7.82 (d, J = 10.0 Hz, 1H × 2), 7.88 (d, J = 10.0 Hz, 1H × 2), 7.98 (d, J = 10.0 Hz, 1H × 2). ^{13}C NMR (100 MHz, 223 K, $CDCl_3$): δ 55.31, 55.42, 106.38, 112.77, 113.28, 122.50, 123.75, 124.46, 124.68, 125.39, 128.10, 128.22, 128.34, 130.54, 130.66, 131.43, 132.49, 134.08, 160.65, 160.76, 165.49, 170.58.

*[1,1′-Biphenyl]-2,2′-dicarboxaldehyde (**5**).* [1,1′-Biphenyl]-2,2′-dicarboxaldehyde (**5**) was prepared according to a literature procedure[11b]

bisDMDPIH-BP (**6**). **5** (49.5 mg, 0.235 mmol), 4,4′-dimethoxybenzil (174 mg, 0.643 mmol), and ammonium acetate (662 mg, 8.59 mmol) were refluxed in acetic acid (3 mL) for 24 h. After cooling to room temperature, the reaction mixture was neutralized with aqueous NH_3. The slurry precipitate formed by neutralization was filtered off, washed with water, and then dried. This residue was purified with silica gel column chromatography using AcOEt/hexane = 1/3 to 1/1 as eluent to give a yellow powder, 136 mg (80.4%). ^{1}H NMR (400 MHz, 296 K, DMSO-d_6): δ 3.69 (s, 3H × 2, −OMe), 3.73 (s, 3H × 2, −OMe), 6.75 (d, J = 8.4 Hz, 2H × 2), 6.85 (d, J = 8.8 Hz, 2H × 2), 7.05 (dd, J = 7.6, 1.0 Hz, 1H × 2), 7.13 (d, J = 8.8 Hz, 2H × 2), 7.19 (d, J = 8.4 Hz, 2H × 2), 7.38 (td, J = 7.6, 1.0 Hz, 1H × 2), 7.47 (td, J = 7.6, 1.0 Hz, 1H × 2), 7.72 (td, J = 7.6, 1.0 Hz, 1H × 2), 13.23 (s, 1H × 2, −NH). ^{13}C NMR (100 MHz, 296 K, DMSO-d_6): δ 54.98, 55.11, 113.62, 114.12, 123.27, 126.20, 127.36, 127.42, 127.96, 128.23, 128.76, 129.39, 130.30, 130.64, 135.20, 140.86, 146.04, 157.88, 158.54. ESI-MS (m/z): [M+H]$^+$ 711.31.

bisDMDPI-BP (**7**). All manipulations were carried out with the exclusion of light. Under nitrogen, to a solution of **6** (40.0 mg, 0.0563 mmol) in benzene (15 mL) was added the solution of potassium ferricyanide (1.53 g, 6.07 mmol) and KOH (650 mg, 11.6 mmol) in water (10 mL), and the reaction mixture was vigorously stirred for 2 h. The organic layer was separated, exhaustively washed with water, and concentrated; 27.8 mg of a white powder was obtained. This residue was purified by recrystallization from CH_3CN/EtOH to give colorless, block crystals suitable for the X-ray crystallographic analysis (19.8 mg , 49.6%). ^{1}H NMR (400 MHz, 223 K, $CDCl_3$): δ 3.82 (s, 3H × 2, −OMe), 3.86 (s, 3H × 2, −OMe), 6.80 (d, J = 8.1 Hz, 2H × 2), 6.88 (d, J = 8.1 Hz, 2H × 2), 7.04 (d, J = 7.6 Hz, 1H × 2), 7.26 (t, J = 7.6 Hz, 1H × 2), 7.43 (d, J = 8.1 Hz, 2H × 2), 7.45 (d, J = 8.1 Hz, 2H × 2), 7.52 (t, J = 7.6 Hz, 1H × 2), 8.12 (d, J = 7.6 Hz, 1H × 2). ^{13}C NMR (100 MHz, 223 K, $CDCl_3$): δ 55.35, 55.41, 105.28, 112.90, 113.28, 123.80, 124.18, 124.77, 128.08, 129.19, 130.55, 131.31, 132.36, 133.30, 160.62, 160.81, 164.67, 170.74. ESI-MS (m/z): [M+H]$^+$ 709.30.

X-ray Crystallographic Analysis. The diffraction data of the single crystals were collected on a Bruker APEX II CCD area detector (Mo Kα, λ = 0.71073 nm). During the data collection, the lead glass doors of the diffractometer were covered to exclude room light. Data refinement was carried out by the Bruker APEXII software package with SHELXT program[12] All non-hydrogen atoms were anisotropically refined.

Time-Resolved UV−Vis Absorption Spectra. Time-resolved UV−vis absorption spectra shown in Figure 4 were recorded on a spectrophotometer (USB4000, Ocean Optics, Inc.) over a 200−700 nm range in a 10 mm × 10 mm quartz cell cooled to the desired temperature in a single-cell Peltier-controlled cuvette holder (CUV-QPOD, Ocean Optics, Inc.) and a temperature controller (TC 125, Quantum Northwest Inc.). UV irradiation was carried out using a UV-400 series UV-LED (UV-50H type, Keyence Co., Japan), equipped with a UV-L6 lens unit (365 nm, irradiation power 5.4 mW/cm^2), and that for visible light (400−700 nm) was performed by a xenon lamp (LAX-100, Asahi Spectra Co., Ltd.). Sample solutions were deaerated by argon bubbling prior to the experiments.

Laser Flash Photolysis. The laser flash photolysis experiments shown in Figure 5 were carried out with a time-resolved spectrophotometer (TSP-1000, Unisoku Co., Ltd.). A Continuum Minilite II Q-switched Nd:YAG laser with the third harmonic at 355 nm (pulse width, 5 ns; power, 4 mJ/pulse) was employed for the excitation light. Excitation pulses at 500 and 517 nm (pulse width, 5 ns; power, 4 mJ/pulse) were provided by a Continuum Surelite II Q-Switched Nd:YAG coupled to a Continuum Panther EX OPO. The probe beam from a halogen lamp (HLX64623, OSRAM GmbH) was guided with an optical fiber scope to be arranged in an orientation perpendicular to the exciting laser beam. The probe beam was monitored with a photomultiplier tube (R2949, Hamamatsu Photonics K.K.) through a spectrometer (MD200, Unisoku Co., Ltd.). Sample solutions were deaerated by argon bubbling prior to the laser flash photolysis experiments and cooled to the desired temperature using a liquid nitrogen cryostat (USP-203-A, Unisoku Co., Ltd.).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray crystallographic analysis data, HPLC chromatograms, and ^{1}H and ^{13}C NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

jiro_abe@chem.aoyama.ac.jp

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was partially supported by the Core Research for Evolutional Science and Technology (CREST) program of the Japan Science and Technology Agency (JST), a Grant-in-Aid for Scientific Research (A) (22245025) from the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan, and NAIST Advanced Research Partnership Project.

■ REFERENCES

(1) (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.

(2) (a) Shimizu, I.; Kokado, H.; Inoue, E. *Bull. Chem. Soc. Jpn.* **1969**, *42*, 1730. (b) Inoue, E.; Kokado, H.; Shimizu, I.; Kobayashi, H. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 1951. (c) Namba, K.; Shimizu, I. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 1323. (d) Sunamoto, J.; Iwamoto, K.; Akutagawa, M.; Nagase, M.; Kondo, H. *J. Am. Chem. Soc.* **1982**, *104*, 4904. (e) Ciardelli, F.; Fabbri, D.; Pieroni, O.; Fissi, A. *J. Am. Chem. Soc.* **1989**, *111*, 3470. (f) Inouye, M.; Ueno, M.; kitao, T. *J. Am. Chem. Soc.* **1990**, *112*, 8977. (g) Hirano, M.; Miyashita, A.; Shitara, H.; Nohira, H. *Chem. Lett.* **1991**, *20*, 1873. (h) Takagi, K.; Kurematsu, T.; Sawaki, Y. *J. Chem. Soc., Perkin Trans. 2* **1991**, *10*, 1517. (i) Nakano, S.; Miyashita, A.; Nohira, H. *Chem. Lett.* **1993**, *22*, 13. (j) Yokoyama, Y.; Shiroyama, T. *Chem. Lett.* **1995**, *24*, 71. (k) Fissi, A.; Pieroni, O.; Ruggeri, G.; Ciardelli, F. *Macromolecules* **1995**, *28*, 302. (l) Takagi, K.; Kurematsu, T.; Sawaki, Y. *J. Chem. Soc., Perkin Trans. 2* **1995**, *8*, 1667. (m) Minami, M.; Taguchi, N. *Chem. Lett.* **1996**, *25*, 429. (n) Suzuki, T.; Lin, F.-T.; Priyadashy, S.; Weber, S. G. *Chem. Commun.* **1998**, *24*, 2685. (o) Tanaka, M.; Nakamura, M.; Salhin, M. A. A.; Ikeda, T.; Kamada, K.; Ando, H.; Shibutani, Y.; Kimura, K. *J. Org. Chem.* **2001**, *66*, 1533. (p) Pieroni, O.; Fissi, A.; Angelini, N.; Lenci, F. *Acc. Chem. Res.* **2001**, *34*, 9. (q) Tanaka, M.; Ikeda, T.; Xu, Q.; Ando, H.; Shibutani, Y.; Nakamura, M.; Sakamoto, H.; Yajima, S.; Kimura, K. *J. Org. Chem.* **2002**, *67*, 2223. (r) Yokoyama,_, Y.; Hara, W.; Inoue, T.; Ubukata, T.; Sakomura, M.; Tukada, H. *Chem. Lett.* **2005**, *34*, 1622. (s) Keum, S.-R.; Roh, S.-J.; Kim, S.-E.; Lee, S.-H.; Cho, C.-H.; Kim, S.-H.; Koh, K.-N. *Bull. Korean Chem. Soc.* **2006**, *27*, 187. (t) Tomasulo, M.; Yildiz, I.; Raymo, F. M. *Inorg. Chim. Acta* **2007**, *360*, 938. (u) Zhang, C.; Zhang, Z.; Fan, M.; Yan, W. *Dyes Pigm.* **2008**, *76*, 832. (v) Sakai, K.; Imaizumi, Y.; Oguchi, T.; Sakai, H.; Abe, M. *Langmuir* **2010**, *26*, 9283.

(3) (a) Mitchell, R. H.; Ward, T. R.; Chen, Y.; Wang, Y.; Weerawarna, S. A.; Dibble, P. W.; Marsella, M. J.; Almutairi, A.; Wang, Z.-Q. *J. Am. Chem. Soc.* **2003**, *125*, 2974. (b) Kobayashi, M.; Takashima, A.; Ishii, T.; Naka, H.; Uchiyama, M.; Yamaguchi, K. *Inorg. Chem.* **2007**, *46*, 1039. (c) Irie, M.; Fukaminato, T.; Tanaka, M. Japan Patent JP 2009-062344 A, 2009. (d) Fukaminato, T.; Doi, T.; Tanaka, M.; Irie, M. *J. Phys. Chem. C* **2009**, *113*, 11623. (e) Ayub, K.; Li, R.; Bohne, C.; Williams, R. V.; Mitchell, R. H. *J. Am. Chem. Soc.* **2011**, *133*, 4040. (f) Peng, P.; Strohecker, D.; Liao, Y. *Chem. Commun.* **2011**, *47*, 8575.

(4) (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. (f) Qin, X. -Z.; Liu, A.; Trifunac, A. D.; Krongauz, V. V. *J. Phys. Chem.* **1991**, *95*, 5822. (g) Kawano, M.; Sano, T.; Abe, J.; Ohashi, Y. *J. Am. Chem. Soc.* **1999**, *121*, 8106. (h) Abe, J.; Sano, T.; Kawano, M.; Ohashi, Y.; Matsushita, M. M.; Iyoda, T. *Angew. Chem., Int. Ed.* **2001**, *40*, 580. (i) Kikuchi, A.; Iyoda, T.; Abe, J. *Chem. Commun.* **2002**, *38*, 1484. (j) Kikuchi, A.; Iwahori, F.; Abe, J. *J. Am. Chem. Soc.* **2004**, *126*, 6526. (k) Miyamoto, Y.; Kikuchi, A.; Iwahori, F.; Abe, J. *J. Phys. Chem. A* **2005**, *109*, 10183. (l) Miyasaka, H.; Satoh, Y.; Ishibashi, Y.; Ito, S.; Nagasawa, Y.; Taniguchi, S.; Chosrowjan, H.; Mataga, N.; Kato, D.; Kikuchi, A.; Abe, J. *J. Am. Chem. Soc.* **2009**, *131*, 7256. (m) Kimoto, A.; Niitsu, A.; Iwahori, F.; Abe, J. *New J. Chem.* **2009**, *33*, 1339. (n) Kikuchi, A.; Harada, Y.; Yagi, M.; Ubukata, T.; Yokoyama, Y.; Abe, J. *Chem. Commun.* **2010**, *46*, 2262.

(5) (a) Iwahori, F.; Hatano, S.; Abe, J. *J. Phys. Org. Chem.* **2007**, *20*, 857. (b) Fujita, K.; Hatano, S.; Kato, D.; Abe, J. *Org. Lett.* **2008**, *10*, 3105. (c) Hatano, S.; Abe, J. *J. Phys. Chem. A* **2008**, *112*, 6098. (d) Hatano, S.; Fujita, K.; Tamaoki, N.; Kaneko, T.; Nakashima, T.; Naito, M.; Kawai, T.; Abe, J. *J. Phys. Chem. Lett.* **2011**, *2*, 2680. (e) Hatano, S.; Abe, J. *Phys. Chem. Chem. Phys.* **2012**, *14*, 5855.

(6) (a) Kishimoto, Y.; Abe, J. *J. Am. Chem. Soc.* **2009**, *131*, 4227. (b) Harada, Y.; Hatano, S.; Kimoto, A.; Abe, J. *J. Phys. Chem. Lett.* **2010**, *1*, 1112. (c) Kimoto, A.; Tokita, A.; Horino, T.; Oshima, T.; Abe, J. *Macromolecules* **2010**, *43*, 3764. (d) Mutoh, K.; Hatano, S.; Abe, J. *J. Photopolym. Sci. Technol.* **2010**, *23*, 301. (e) Hatano, S.; Sakai, K.; Abe, J. *Org. Lett.* **2010**, *12*, 4152. (f) Takizawa, M.; Kimoto, A.; Abe, J. *Dyes Pigm.* **2011**, *89*, 254. (g) Mutoh, K.; Abe, J. *J. Phys. Chem. A* **2011**, *115*, 4650. (h) Mutoh, K.; Abe, J. *Chem. Commun.* **2011**, *47*, 8868. (i) Yamashita, H.; Abe, J. *J. Phys. Chem. A* **2011**, *115*, 13332. (j) Mutoh, K.; Nakano, E.; Abe, J. *J. Phys. Chem. A* **2011**, *116*, 6792. (k) Ishii, N.; Kato, T.; Abe, J. *Sci. Rep.* **2012**, *2*, 819. (l) Kawai, S.; Yamaguchi, T.; Kato, T.; Hatano, S.; Abe, J. *Dyes Pigm.* **2012**, *92*, 872.

(7) Hanazawa, M.; Sumiya, R.; Horikawa, Y.; Irie, M. *J. Chem. Soc., Chem. Commun.* **1992**, 206.

(8) (a) Wintgens, V.; Johnston, L. J.; Scaiano, J. C. *J. Am. Chem. Soc.* **1988**, *110*, 511. (b) Sheepwash, M. A. L.; Ward, T. R.; Wang, Y.; Bandyopadhyay, S.; Mitchell, R. H.; Bohne, C. *Photochem. Photobiol. Sci.* **2003**, *2*, 104.

(9) Yamaguchi, T.; Uchida, K.; Irie, M. *Bull. Chem. Soc. Jpn.* **2008**, *81*, 644.

(10) Sasaki, T.; Ikeda, T.; Ichimura, K. *Macromolecules* **1993**, *26*, 151.

(11) (a) Dubois, F.; Gingras, M. *Tetrahedron Lett.* **1998**, *39*, 5039. (b) Reisch, H. A.; Enkelmann, V.; Scherf, U. *J. Org. Chem.* **1999**, *64*, 655.

(12) (a) Sheldrick, G. M. *SHELXS-97* and *SHELXL-97*; University of Gottingen, Germany, 1997. (b) Sheldrick, G. M. *SADABS*; University of Gottingen, Germany, 1996.