# Multistate Photochromism of 1-PhenyInaphthalene-Bridged Imidazole Dimer That Has Three Colorless Isomers and Two Colored Isomers

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**Supporting Information** 

**ABSTRACT:** A new type of the bridged imidazole dimer with a 1-phenylnaphthalene moiety that bridges two diphenylimidazole units at the 2- and 2'-positions was synthesized and the photochemical and thermochemical properties were investigated. This molecule shows unique multistate photochromism, in which the stable colorless 1,2'-isomers A and B photochemically isomerize to the colorless 2,2'-isomer through the short-lived biradical with a half-life of 180 ns at 25 °C. The 2,2'-isomer thermally returns to the 1,2'-isomers A and B through the colored isomer at elevated temperatures. The 1,2'isomers A and B, the 2,2'-isomer, and the colored isomer were



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isolated, and their molecular structures were determined by X-ray crystallographic analysis. These isomers are stable at room temperature and can be almost fully converted to the 2,2'-isomer by light irradiation. This study serves the useful strategy for the molecular design of a new type of negative photochromic molecules applicable to switch molecular properties by visible light irradiation.

# INTRODUCTION

Hexaarylbiimidazole (HABI) is a photochromic molecule that shows photochemical color change from the colorless imidazole dimer to the colored imidazolyl radical (Scheme 1a).<sup>1-19</sup> This coloration is attributed to the photogeneration of triphenylimidazolyl radical (TPIR) by homolytic cleavage of the C-N bond between the imidazole rings. The decoloration reaction proceeds only thermally by the radical recombination reaction of TPIRs to form the imidazole dimer. However, the radical recombination reaction forms several different kinds of imidazole dimers with different binding manners between two imidazole rings depending on temperature (Scheme 1b). The diversity of the bond formation between the imidazole rings makes the imidazole dimer attractive to develop a new type of photoresponsive material. It was reported that the 1,2'-isomer and the 1,4'-isomer show photochromism, whereas the 2,2'isomer and the 2,4'-isomer exhibit piezochromism and thermochromism, respectively.<sup>2-8</sup> The radical recombination reaction of TPIRs takes several minutes at room temperature due to the diffusion of TPIRs into the medium.

We have developed two types of the bridged imidazole dimers with a [2.2]paracyclophane ([2.2]PC) moiety<sup>20-32</sup> and a naphthalene (NP) moiety<sup>33-38</sup> that bridge a set of diphenylimidazole (DPI) and triphenylimidazole (TPI) units,

respectively, to accelerate the radical recombination reaction by suppressing the diffusion of the imidazolyl radicals into the medium. The colorless [2.2]PC-bridged imidazole dimers show instantaneous coloration upon exposure to UV light and rapid fading in the dark. Upon UV light irradiation, the C-N bond between the two imidazole rings is homolytically cleaved to give a pair of the imidazolyl radicals, and the solution of the [2.2]PC-bridged imidazole dimer is colored. In contrast to any other currently available photochromic molecules, the [2.2]PCbridged imidazole dimers have high quantum yields close to unity for the bond-cleavage reactions, enabling the visible inspection of the coloration upon UV light irradiation, even with their fast thermal bleaching rate. The molecular structures of the colorless form of the [2.2]PC-bridged imidazole dimers were revealed by X-ray crystallographic analysis to have the C-N bond between the two imidazole rings to form the 1,2'isomer.<sup>20,21</sup> The formation of the 1,2'-isomer by the radical recombination reaction between the imidazolyl radical is also the case for the NP-bridged imidazole dimers except for the unique NP-bridged imidazole dimer in which two imidazole

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Scheme 1. Photochromism of (a) HABI, (c) [2.2]PC-Bridged Imidazole Dimer, and (d) NP-Bridged Imidazole Dimer and (b) Molecular Structures for Possible HABI Isomers



rings are constrained to an anticonformation leading to the formation of the 1,4'-isomer.<sup>38</sup>

Almost all photochromic molecules including HABI derivatives change their molecular structures from a thermally stable colorless isomer to a thermally metastable colored isomer upon UV light irradiation. The metastable colored isomer can be reversed to the original colorless isomer either by thermal means or by subsequent irradiation with a specific light wavelength. On the other hand, only a few molecules have been reported to show negative photochromism that is observed with several photochromic molecules where the absorption spectrum of the molecule after irradiation is blue-shifted relative to that before irradiation.<sup>39–66</sup> The colored isomer of a negative photochromic molecule is more stable than the colorless isomer, and the colored isomer becomes colorless upon exposure to visible light. By changing the bridging unit with a 1,1'-binaphthyl moiety, we have recently developed the 1,1'binaphthyl-bridged imidazole dimer (bisDMDPI-BN) that shows unusual negative photochromism (Scheme 2a), in which the stable colored isomer photochemically converts into the metastable colorless isomer through the short-lived biradical.<sup>67</sup> Although the usual bridged imidazole dimers are

obtained as the colorless 1,2'-isomers by oxidizing the corresponding lophine precursor, bisDMDPI-BN is obtained as the colored isomer that has the C-N bond between the nitrogen atom of the imidazole ring and the carbon atom at the 1-position of the 1,1'-binaphthyl moiety to have the diazafulvene substructure. The thermally stable colored isomer shows decoloration from reddish orange to colorless by visible light irradiation and the <sup>13</sup>C NMR spectral analysis revealed that the colorless isomer is the 2,2'-isomer. The colorless 2,2'isomer in benzene thermally returns to the initial colored isomer within 20 min in the dark at 25 °C. Both the 2,2'-isomer and the colored isomer photochemically generate the common biradical with a half-life of 9.4  $\mu$ s in benzene at 25 °C. That is, bisDMDPI-BN has three kinds of isomers, i.e., the 2,2'-isomer, the colored isomer, and the biradical. On the other hand, the biphenyl-bridged imidazole dimer (bisDMDPI-BP) is obtained as the colorless photochromic 2,2'-isomer (Scheme 2b) that does not show the photochromic color change at room temperature. Moreover, the formation of the biradical of bisDMDPI-BP could not be detected by using a nanosecond leaser flash photolysis setup.67

Thus we expected that negative photochromism of the biarylbridged imidazole dimers could be controlled by changing the bridging unit. Herein, we report the unique photochromic and thermochromic behavior of the 1-phenylnaphthalene-bridged imidazole dimer (bisDPI-PN) shown in Scheme 2c. We found that this molecule has three kinds of colorless isomers and one colored isomer other than the short-lived colored biradical and successfully isolated four kinds of isomers, i.e., the 1,2'-isomer A, the 1,2'-isomer B, the 2,2'-isomer, and the colored isomer, leading to the determination of the molecular structures by Xray crystallographic analysis.

## EXPERIMENTAL SECTION

**Synthesis.** Commercially available reagents and solvents for syntheses were of reagent grade and used without further purification. All reactions were monitored by thin-layer chromatography carried out on 0.2 mm E. Merck silica gel plates (60F-254). Column chromatography was performed on silica gel (Silica Gel 60N (spherical, neutral),  $40-50 \mu$ m, Kanto Chemical Co., Inc.). <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded with a NMR spectrometer (Bruker, Avance III 400 NanoBay). DMSO-*d*<sub>6</sub> (0.03% TMS) and CDCl<sub>3</sub> (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 (Hz). ESI-TOF MS spectra were recorded on a Bruker Daltonics micrOTOFII-AGA1 instrument using positive-ion mode.

BisDPI-PN was prepared as shown in Scheme 3.

1-(Formylphenyl)-2-naphthaldehyde (1).<sup>72</sup> Under a N<sub>2</sub> atmosphere, 1-bromo-2-naphthaldehyde (202 mg, 0.86 mmol) and 2-formyl-1-phenylboronic acid (202 mg, 1.35 mmol) were added to degassed DME (3 mL), EtOH (2 mL), and 2 M Na<sub>2</sub>CO<sub>3</sub> aq (3.8 mL). The reaction mixture was stirred at 60 °C, and tetrakis(triphenylphosphine)palladium (0) (112 mg, 0.097 mmol) was added. The mixture was stirred at 80 °C for 28 h. After cooling to room temperature, the resulting mixture was washed with water and extracted with CH<sub>2</sub>Cl<sub>2</sub>. The crude sample was purified by silica gel column chromatography using CH<sub>2</sub>Cl<sub>2</sub>/hexane = 2/1 as eluent to give a white powder of 1. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>),  $\delta$ : 9.84 (s, 1H), 9.57 (s, 1H), 8.18 (d, 1H, *J* = 7.67 Hz), 8.12 (d, 1H, *J* = 8.52 Hz), 8.03 (d, 1H, *J* = 8.94 Hz), 7.97 (d, 1H, *J* = 8.52 Hz), 7.78 (t, 1H, *J* =

Scheme 2. (a) Photochromism of bisDMDPI-BN and Molecular Structures of (b) bisDMDPI-BP and (c) bisDPI-PN



Scheme 3. Synthesis of bisDPI-PN



7.51 Hz), 7.72 (t, 1H, J = 7.51 Hz), 7.65 (t, 1H, J = 7.51 Hz), 7.51–7.42 (m, 2H), 7.38 (d, 1H, J = 8.51 Hz).

*bisDPIH-PN* (2). Compound 1 (30 mg, 0.115 mmol), benzil (54 mg, 0.260 mmol), and ammonium acetate (118 mg, 1.34 mmol) were dissolved in CHCl<sub>3</sub> (0.6 mL). The mixture was refluxed at 110 °C for 2 days. After cooling to room temperature, the resulting mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> and washed with water. The crude mixture was purified by silica gel column chromatography using AcOEt/hexane = 1/2 as eluent to give white powder of 2. <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ ),  $\delta$ : 13.83 (s, 1H), 13.66 (s, 1H), 8.07 (d, 1H, *J* = 7.99 Hz), 7.99 (d, 1H, *J* = 8.31 Hz), 7.92 (d, 1H, *J* = 8.63 Hz), 7.87 (d, 1H, *J* = 7.35 Hz), 7.61 (t, 1H, *J* = 7.70 Hz), 7.50 (d, 1H, *J* = 7.34 Hz), 7.43–7.06 (m, 23H). ESI-TOF-MS, *m/z*: calcd, 640.263 (C<sub>46</sub>H<sub>32</sub>N<sub>4</sub>); found, 663.3150 [M + Na]<sup>+</sup>.

*bisDPI-PN*. All manipulations were carried out with exclusion of light. Compound **2** (25 mg, 0.039 mmol) was dissolved in degassed benzene (12 mL) and  $K_3$ [Fe(CN)<sub>6</sub>] (627 mg, 2.33 mmol) aqueous solution containing KOH bilayer, and the solution was stirred for 18 h. After the reaction was completed, the reaction product was extracted with benzene, and washed

with water. The crude mixture was purified by silica gel column chromatography using AcOEt/hexane = 1/2 as eluent to give reddish white powder. The slow evaporation of an acetonitrile solution of bisDPI-PN gave colorless, plate single crystal suitable for X-ray crystallographic analysis. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>),  $\delta$ : 8.79 (d, 1H, J = 8.42 Hz), 8.26 (d, 1H, J = 7.73 Hz), 7.86 (d, 1H, J = 7.73 Hz), 7.69 (d, 1H, J = 8.42 Hz), 7.56–7.38 (m, 14H), 7.38–7.14 (m, 11H), 7.00 (d, 1H, J = 8.42 Hz). HR-ESI-TOF-MS, m/z: calcd, 638.247 (C<sub>46</sub>H<sub>30</sub>N<sub>4</sub>); found, 661.239 [M+Na]<sup>+</sup>.

**HPLC Analysis.** HPLC analysis was carried out on a ODS reversed phase column (Mightysil RP-18 GP, Kanto Chemical Co., Inc.). The HPLC system consists of a pump unit (PU-2080 plus, JASCO), a photodiode array (PDA) detector (MD-2018 plus, JASCO), and a control unit (LC-NetII/ADC, JASCO).

**X-ray Crystallographic Analysis.** The diffraction data of the single crystals were collected on the Bruker APEX II CCD area detector (Mo Ka,  $\lambda = 0.71073$  nm). During the data collection, the lead glass doors of the diffractometer were covered to exclude the room light. The data refinement was

carried out by the Bruker APEXII software package with SHELXT program<sup>73,74</sup> All non-hydrogen atoms were aniso-tropically refined.

Laser Flash Photolysis. The laser flash photolysis experiments 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, 3 mJ/pulse) was employed for the excitation light. Excitation pulses at 510 and 550 nm (pulse width, 5 ns; power, 3 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 (R2929, Hamamatsu Photonics K.K.) through a spectrometer (MD2000, Unisoku Co., Ltd.). Sample solutions were deaerated by argon bubbling prior to the laser flash photolysis experiments.

**DFT Calculations.** All DFT calculations were carried out using the Gaussian 09 program (Revision D.01).<sup>75</sup> The molecular geometries were fully optimized at the MPW1PW91/6-31G(d) level of the theory, and analytical second derivatives were computed using vibrational analysis to confirm each stationary point to be a minimum. Zero-point energy (ZPE) corrections were adopted to compare the relative energies for the isomers.

## RESULTS AND DISCUSSION

**Photochromic and Thermochromic Behavior.** Colorless crystals are formed from the acetonitrile solution of the reddish white powder of bisDPI-PN. Though the oxidation of the lophine precursor of bisDMDPI-BN gives only the colored isomer, the major oxidation product of the lophine precursor of bisDPI-PN is colorless isomer as well as the oxidation of the lophine precursor of bisDMDPI-BP. The molecular structure of the colorless isomer of bisDPI-PN was determined by X-ray crystallographic analysis as shown in Figure 1a. It is revealed that the colorless isomer is the 2,2'-isomer with the C–C bond (1.5775(18) Å) between the imidazole rings as well as bisDMDPI-BP. The 2,2'-isomer of bisDPI-PN is stable at room temperature contrary to that of bisDMDPI-BN that



Figure 1. ORTEP representations of the molecular structures of (a) the 2,2'-isomer, (b) the colored isomer, (c) the 1,2'-isomer A, and (d) the 1,2'-isomer B of bisDPI-PN with thermal ellipsoid. The hydrogen atoms and the solvent molecule are omitted. Nitrogen atoms are highlighted in blue.

thermally returns to the colored isomer within 20 min in benzene at room temperature. Though the 2,2'-isomers of the classical HABI derivatives show piezochromism, the 2,2'-isomer of bisDPI-PN does not show the color change by grinding at room temperature The solution of the 2,2'-isomer of bisDPI-PN changes its color from colorless to yellow by UV light irradiation and returns to the original colorless state by visible light irradiation. This reversible color change can be repeated many times by alternating UV and visible light irradiation. This photoisomerization behavior was followed by HPLC analysis. As shown in Figure 2, the UV light irradiation to the benzene



**Figure 2.** HPLC chromatograms of the benzene solution of the 2,2'isomer of bisDPI-PN (a) before and (b) after UV irradiation. The HPLC analysis was performed using a reverse phase column (eluent, H<sub>2</sub>O/acetonitrile = 1/9; flow rate, 1 mL/min;  $\lambda_{obs}$  = 344 nm).

solution of the 2,2'-isomer results in the appearance of a small peak other than the peak of the 2,2'-isomer. Upon visible light irradiation to the yellow solution, the small peak completely disappears and the solution color returns to colorless. The UV-vis absorption spectrum of the fraction of the small peak has an intense absorption band in visible light region, suggesting that the fraction of the small peak is the colored isomer in analogy with bisDMDPI-BN. The colored fraction is stable at room temperature to allow for recrystallization. The Xray crystallographic analysis of the single crystal of the colored fraction revealed the molecular structure as shown in Figure 1b. As would be expected, the colored isomer forms the structure similar to the colored isomer of bisDMDPI-BN. The photostationary state of the benzene solution was reached after 1 min of irradiation at 365 nm at room temperature and the fraction of the colored isomer at the photostationary state is 0.01, indicating low conversion efficiency from the 2,2'-isomer to the colored isomer upon UV light irradiation.

The thermal stability at room temperature of the colored isomer and the colorless 2,2'-isomer of bisDPI-PN makes it possible to isolate these isomers, whereas the thermal coloration of the 2,2'-isomer is observed at elevated temperatures. The heated colorless solution of the 2,2'-isomer once becomes yellow, and the color of the solution subsequently changes to colorless very slowly with time. These color changes take longer in benzene as compared with those in cyclohexane (Figure S7, Supporting Information). Therefore, we carried out the thermal isomerization experiment for the cyclohexane solution of the 2,2'-isomer. Figure 3b shows the HPLC chromatograms for the cyclohexane solution of the 2,2'-isomer kept at  $70~^\circ C$  for 3 days in the dark. The HPLC peak of the 2,2'-isomer decreases and that of the colored isomer increases by heating. Thus the 2,2'-isomer is thermally converted to the colored isomer. The rate of disappearance of the 2,2'-isomer follows the first-order kinetics, and the rate constant is 2.70  $\times$  $10^{-5}\ s^{-1}$  at 70  $\ ^{\circ}C$  in cyclohexane (Figures S10 and S11,



**Figure 3.** HPLC chromatograms of the cyclohexane solution of bisDPI-PN: (a) the 2,2'-isomer, (b) the solution after kept 3 days at 70 °C, (c) the solution after kept 18 days at 70 °C, and (d) the solution after visible light (400–700 nm) irradiation. HPLC analysis was performed using reversed phase column (eluent, H<sub>2</sub>O/acetonitrile = 9/1; flow rate, 1 mL/min;  $\lambda_{obs}$  = 344 nm).

Supporting Information). Other than the peak for the colored isomer, new peaks (peak A and peak B) are observed with a retention time of 17-19 min, as shown in Figure 3b. These fractions are not detected for the light irradiated solution of the 2,2'-isomer or the colored isomer. After another 15 days at 70 °C, the peaks for the 2,2'-isomer and the colored isomer completely disappeared and the peaks A and B increased (Figure 3c). Taking into account the thermal conversion from the colorless 2,2'-isomer to the colored isomer of bisDMDPI-BN at room temperature, it is plausible to assume that the 2,2'isomer of bisDPI-PN is thermally converted to the colored isomer and the resultant colored isomer also thermally isomerizes to the two new constituents of peaks A and B. These two constituents are also stable at room temperature and can be isolated by preparative HPLC. The single crystals were grown from the solution of the constituent of peak A in the CH<sub>2</sub>Cl<sub>2</sub>/MeOH mixture and that of peak B in CH<sub>2</sub>CN. The Xray crystallographic analysis revealed that the constituents of peak A and peak B are the 1,2'-isomer A and the 1,2'-isomer B, respectively (Figure 1c,d). The 1,2'-isomer has two types of imidazole rings, Im1 and Im2, as indicated in Figure 1c,d.<sup>23,26</sup> Im1 is a resonant planar structure that has a typical bond length for a  $6\pi$ -electron system with an electron-donating characteristic, whereas Im2 has two localized C=N double bonds and one sp<sup>3</sup> carbon atom connecting Im1, consistent with a  $4\pi$ electron system with an electron-withdrawing characteristic. Thus the 1,2'-dimer A and the 1,2'-dimer B can be distinguished in a bonding manner between the imidazole ring and the aryl moiety. Im1 of the 1,2'-dimer A is bonded to a naphthyl ring whereas that of the 1,2'-dimer B is bonded to a phenyl ring. The bond lengths of the C-N bonds between two imidazole rings of 1,2'-isomers A and B are 1.478(2) and 1.486(2) Å, respectively. These bond lengths are approximately equal to that of 1,2'-isomers of the other bridged imidazole dimers.

Moreover, we found that the 1,2'-isomers A and B are converted to the 2,2'-isomer not only by UV light irradiation but also by visible light irradiation. The UV light irradiation to the solution of 1,2'-isomers forms both the 2,2'-isomer and the colored isomer and causes the color change of the solution from colorless to yellow, whereas the visible light irradiation does not change the color of the solution and forms only the 2,2'- isomer, as shown in Figure 3d. As will be described below, this behavior can be attributable to the photoconversion of the colored isomer to the 2,2'-isomer through the biradical with the irradiation of visible light that is not absorbed by the 2,2'isomer. As shown in Figure 4, the absorption tails of the 1,2'-



**Figure 4.** UV-vis absorption spectra of each isomer of bisDPI-PN in benzene at 25  $^{\circ}$ C. The inset is the enlargement of the spectra.

isomers A and B extending into the visible light region of the spectra as well as the other 1,2'-dimers including the classical HABI derivatives<sup>9</sup> make it possible to form the biradical by visible light irradiation. The mechanism of this unique photoisomerization will be discussed later.

Laser Flash Photolysis. Because all bridged imidazole dimers except for bisDMDPI-BP have been reported to generate biradicals by light irradiation, the four kinds of structural isomers of bisDPI-PN could be also expected to generate the biradical by light irradiation. We investigated the possible presence of the short-lived biradical in the photochemical process of bisDPI-PN by nanosecond laser flash photolysis. Figure 5a shows the transient vis–NIR absorption



**Figure 5.** (a) Transient vis–NIR absorption spectra of the 2,2'-isomer of bisDPI-PN in deaerated benzene  $(1.1 \times 10^{-4} \text{ M})$  at 25 °C. The spectrum was recorded at 100 ns after excitation with a nanosecond laser pulse (excitation wavelength, 355 nm; pulse width, 5 ns; power, 3 mJ/pulse). (b) Decay profile of the biradical monitored at 400 nm in deaerated benzene  $(1.1 \times 10^{-4} \text{ M})$  at 25 °C (excitation wavelength, 355 nm; pulse width, 5 ns; power, 3 mJ/pulse).

spectrum of the 2,2'-isomer of bisDPI-PN in benzene at room temperature, excited with a nanosecond laser pulse at 355 nm. The identical transient absorption spectra were also obtained for the other isomers. A sharp absorption band around at 400 nm and a broad absorption band ranging from 500 to 800 nm can be ascribed to the biradical because its spectrum shape is similar to those of the colored biradicals observed for the other bridged imidazole dimers. Figure 5b shows the decay profile of

the transient absorbance at 400 nm of the biradical. The decay profile of the biradical obeys first-order kinetics with a half-life of 180 ns at 25  $^{\circ}$ C, which is the fastest among the reported half-lives of the imidazolyl radicals of HABI derivatives. We also confirmed that the shape of the transient absorption spectra and the decay kinetics are not affected by the presence of molecular oxygen as shown in Figure S12 (Supporting Information).

Radical Recombination Reaction of the Biradical. The significant question to be solved as to the photochemical isomerizations is to elucidate the products formed by the radical recombination reaction of the photogenerated biradical. As already mentioned, the 2,2'-isomer is converted to the colored isomer by UV light irradiation, and the colored isomer mainly returns to the 2,2'-isomer by visible light irradiation. The 1,2'-isomers A and B mainly return to the 2,2'-isomer by UV or visible light irradiation. These observations can raise the assumption that the major product by the radical recombination reaction of the biradical is the 2,2'-isomer. The photochemical conversion of the colored isomer was investigated by HPLC analysis for the benzene solution irradiated with the laser pulses of the wavelength of 550 nm at 70 °C, at which temperature the experiment of the thermal conversion of the 2,2'-isomer shown in Figure 3 was conducted.

As shown in Figure 6, the peak intensity of the colored isomer with a retention time around 9 min decreases with



**Figure 6.** HPLC chromatograms of the benzene solutions of the colored isomer of bisDPI-PN. The solution was irradiated with the laser pulses (3 mJ/pulse) of the wavelength of 550 nm at 70 °C. HPLC analysis was performed using reverse phase column (eluent,  $H_2O$ /acetonitrile = 9/1; flow rate, 1 mL/min;  $\lambda_{obs}$  = 344 nm).

increasing the irradiation times of the visible laser pulses, whereas that of the 2,2'-isomer with a retention time around 8 min increases. It is worth noting that the HPLC peaks attributable to the 1,2'-isomers A and B do not appear after the light irradiation. Thus, it can be concluded that the radical recombination reaction of the biradical affords the 2,2'-isomer as a major product and the colored isomer as a minor product. The observation of the photochemical conversion from the 2,2'-isomer to the colored isomer by UV light irradiation as shown in Figure 2 would be the direct evidence for the formation of the biradical. It is considered that the activation energy barriers toward the formation of the 2,2'-isomer is smaller than those of the colored isomer and the 1,2'-isomers A and B.

**Photochemical Conversion Efficiency.** The photochemical conversion efficiency from the colored isomer to the 2,2'isomer was investigated with the intention to evaluate the negative photochromic property of bisDPI-PN. The conversion efficiency was estimated by nanosecond laser flash photolysis by using 1,2-bis(2-methylbenzo[b]thiophen-3-yl)perfluorocyclopentene (DAE) as a standard.<sup>67,68</sup> 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 symmetryforbidden, 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. The solutions of the colored isomer of bisDPI-PN 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 S13, Supporting Information). 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,  $\Delta OD(S)$ , for the colored isomer of bisDPI-PN. The conversion efficiency was estimated from the slope of the fit of the data to the following equation,69,70

$$\Delta OD(DAE) = \frac{\varphi_{DAE} \varepsilon_{DAE}}{\varphi_{s} \varepsilon_{s}} \Delta OD(S)$$
(1)

where  $\varphi_{\text{DAE}}$  (0.35) is the quantum yield of cycloreversion reaction of DAE excited at 517 nm,<sup>71</sup>  $\varphi_{\rm s}$  is the conversion efficiency from the colored isomer to the 2,2'-isomer of bisDPI-PN, and  $\varepsilon_{\text{DAE}}$  (0.91 × 10<sup>4</sup> M<sup>-1</sup> cm<sup>-1</sup>) and  $\varepsilon_{\rm s}$  (0.98 × 10<sup>4</sup> M<sup>-1</sup> cm<sup>-1</sup>) are the absorptivity coefficients of DAE<sup>71</sup> and the colored isomer of bisDPI-PN at 517 nm, respectively. As shown in Figure S15 (Supporting Information),  $\varphi_{\rm s}$  was obtained from the slope of the fit of the data to eq 1 and was determined to be 0.14, which is about 5 times larger than that of bisDMDPI-BN reported in our previous paper.<sup>67</sup>

DFT Calculations for the Isomers. By comparing the photochemical and thermochemical properties of bisDMDPI-BP, bisDMDPI-BN, and bisDPI-PN, we found that the biaryl moiety that bridges a set of DPIs would have a significant effect on the stability of the isomers. BisDPI- PN has four kinds of stable isomers, i.e., the 2,2'-isomer, the colored isomer, and the 1,2'-isomers A and B, and a short-lived biradical, whereas bisDMDPI-BN has two kinds of stable isomers, i.e., the 2,2'isomer and the colored isomer, and a short-lived biradical. On the other hand, only the 2,2'-isomer is the stable form of bisDMDPI-BP. We carried out the DFT calculations to investigate the relative energies for the isomers of bisDMDPI-BP, bisDMDPI-BN, and bisDPI-PN. As shown in Figure 7, the most stable isomer for these biaryl-bridged imidazole dimers is the 1,2'-isomer. However, the 1,2'-isomers are not formed from the biradicals that is generated by the oxidation of the lophine precursors or by the photochemical reaction in the case of bisDMDPI-BN and bisDPI-PN. This incomprehensible behavior leads to the idea that the activation energy barriers toward the formation of the 1,2'-isomers from the biradicals are significantly higher than those toward the formation of the 2,2'isomers and the colored isomers. We considered that the major products of the radical recombination reaction of the biradicals are not the colored isomers but the 2,2'-isomers. This idea can be supported by the two experimental results. The first basis is that the 1,2'-isomers A and B of bisDPI-PN are converted to the 2,2'-isomer by UV light irradiation, and the second basis is that the oxidation of the lophine precursor of bisDMDPI-BN at room temperature initially forms the colorless solution that gradually changes to the red solution by forming the colored isomer.



Figure 7. Schematic drawing of the energy level diagrams of the isomers of bisDMDPI-BP, bisDMDPI-BN, and bisDPI-PN calculated by the DFT MPW1PW91/6-31G(d) level of the theory. The energy levels of the 1,2'-isomers of all the molecules are set to zero for comparing the energy differences for each molecule.

The stability of the colored isomers can be accounted for by the resonance energy of the phenyl ring in the biaryl-bridging moiety. Both the colored isomer of bisDMDPI-BP and the colored isomer B of bisDPI-PN described in Figure 7 are unstable due to the loss of aromaticity of the phenyl ring in the biaryl-bridging moiety. On the other hand, the colored isomer of bisDMDPI-BN and the colored isomer A of bisDPI-PN, which is identical to the colored isomer isolated in this work, have the same diazafulvene substructure connected to the naphthyl moiety. Thus it is considered that these colored isomers are relatively stable compared with the colored isomers that lose the aromaticity of the phenyl rings.

By combining the above-described considerations, we assume the thermal conversion from the 2,2'-isomers to the colored proceeds by the thermally generated biradical. The 2,2'-isomer of classical HABI is known to show thermochromism that gives triphenylimidazolyl radicals by homolytic cleavage of the C–C bond between the imidazole rings.<sup>3,4,7,12</sup> The oxidation of triphenylimidazole at lower than 5 °C gives the 2,2'-isomer,

whereas the 1,2'-isomer is obtained at room temperature. This behavior can be accounted for by the difference in the activation energy barriers toward the formation of the imidazole dimers. That is, the activation energy barrier for the dimerization path to form the 2,2'-isomer is lower than that for the 1,2'-isomer. However, the 2,2'-isomer consisting of a couple of  $4\pi$ -electron imidazole rings is less stable than the 1,2'isomer consisted of a  $6\pi$ -electron imidazole ring and a  $4\pi$ electron imidazole ring because of the lack of resonance effect in imidazole ring for the 2,2'-isomer. Thus the thermochemical instability of the 2,2'-isomer causes the thermochromism by forming the thermally stable 1,2'-isomer through the biradical by increasing the temperature. We already reported the in situ direct observation of the thermal isomerization from the 2,2'isomer to the 1,2'-isomer of HABI in crystal by X-ray crystallographic analysis.<sup>73,74</sup> Therefore, it seems reasonable to assume that the 2,2'-isomer of bisDPI-PN also shows thermochromism at elevated temperature to form the biradical that would dimerize to form the more stable colored isomer A

than the 2,2'-isomer by overcoming the activation energy barrier toward the formation of the colored isomer A. However, an attempt to detect the biradical of bisDPI-PN at elevated temperature by EPR measurement was unsuccessful due to the low concentration of the biradical with extremely short half-life (180 ns at 25  $^{\circ}$ C) as described above.

On the other hand, it can be considered that the colored isomer of bisDPI-PN isomerizes to the 1,2-isomers A and B by a rearrangement reaction, whereas the large activation energy barrier for the rearrangement reaction of bisDMDPI-BN is presumed to prevent the thermal isomerization to form the 1,2'-isomer. If the biradical is formed in the thermal isomerization process, the radical recombination reaction of the biradical should give the 2,2'-isomer besides a small amount of the colored isomer, and the 1,2'-isomers will not be formed. As a whole, the photochemical and thermochemical transformations between the isomers of bisDPI-PN can be summarized as shown in Figure 8.



**Figure 8.** Schematic drawing of the potential energy surfaces for the excited state (upper) and the ground state (lower) of bisDPI-PN accounting for the photochemical and thermochemical transformation between the isomers.

## CONCLUSION

We investigated the photochemical and the thermochemical behavior of bisDPI-PN with a 1-phenylnaphthalene moiety that bridges two diphenylimidazole units at the 2- and 2'-positions. This molecule shows unique multistate photochromism, in which the stable colorless 1,2'-isomers A and B photochemically isomerize to the colorless 2,2'-isomer. Although the 2,2'-isomer is stable at room temperature, it thermally returns to the initial 1,2'-isomers A and B through the biradical and the colored isomer at elevated temperatures. The colored isomer consists of the diazafulvene structure formed by the C–N bond between the nitrogen atom of the imidazole ring bonded at the

2'-position and the carbon atom at the 2-position of the 1phenylnaphthalene moiety. The molecular structures of these four kinds of structural isomers were determined by X-ray crystallographic analysis. It should be emphasized that these isomers are stable at room temperature and can be almost fully converted to the 2,2'-isomer by light irradiation. The photochemical conversion can be accounted for by the radical recombination reaction of the short-lived biradical with a halflife of 180 ns at 25 °C that is generated from all isomers by light irradiation. The reason the 2,2'-isomer is mainly formed from the biradical would be attributable to the low activation energy barrier toward the formation of the 2.2'-isomer by comparing the activation energy barriers toward the formation of the other isomers. The theoretical considerations of the mechanisms for the thermal isomerization and the radical recombination reaction are important problems left for future study.

Thus the aryl-bridged imidazole dimers are attractive multistate photochromic molecules with negative and positive photochromic properties. As described at the beginning, only a few molecules have been reported to show negative photochromism.<sup>39-66</sup> The development of unique photochromic molecules with negative photochromism would open a new field in the photoresponsive materials. This study serves the useful strategy for the molecular design of a new type of negative photochromic molecules applicable to switch molecular properties by visible light irradiation. The rational molecular design to prevent the formation of the colorless 1,2'-dimer from the colored isomer and to destabilize the colorless 2,2'-isomer will lead to the development of an unknown fast negative photochromic molecule that enables us to change and reset the molecular properties by simply turning a visible light source on and off.

# ASSOCIATED CONTENT

#### **Supporting Information**

<sup>1</sup>H and <sup>13</sup>C NMR spectra, MS spectra, X-ray crystallographic analysis data, HPLC chromatograms, decay profiles, transient vis–NIR absorption spectra, conversion efficiency measurement (including laser intensity dependence of the time profiles and laser power dependence of the absorbance change), and DFT calculations (atomic coordinates and optimized structures). Complete refs 17 and 75. CIF files. This information is available free of charge via the Internet at http://pubs.acs.org.

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#### Notes

The authors declare no competing financial interest.

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