# Comprehensive Understanding of Structure- Photosensitivity Relationships of Photochromic [2.2]Paracyclophane-Bridged Imidazole Dimers

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### Supporting Information



The photochromic [2.2]paracyclophane-bridged imidazole dimers show instantaneous coloration upon exposure to UV light and rapid fading in the dark. Experimental details for the enhancement of the photosensitivity and the unique photoisomerization of newly designed [2.2]paracyclophane-bridged imidazole dimers are demonstrated. We explored the structure—property relation-ships and demonstrated an efficient strategy for designing high-performance fast-photochromic molecules with increased photosensitivity to solar UVA radiation. The [2.2]paracyclophane-bridged imidazole dimer consists of two types of imidazole rings, Im1 and Im2. Im1 is characterized by a  $6\pi$  electron system with an electron-donating characteristic, whereas Im2 is distinguished by a  $4\pi$  electron system with an electron-withdrawing characteristic. The introduction of electron-donating substituents into the phenyl rings attached to the electron-withdrawing Im2 was proved to enhance the photosensitivity with the aid of the intramolecular charge transfer transitions. The unique photoisomerization resulting from the changes in the bonding manner between two imidazole rings was also investigated in detail.

# **1. INTRODUCTION**

Photochromic materials are a well-known class of molecules that change their color upon UV light irradiation. The colored species goes back to the original state either thermally or photochemically. Thermally reversible photochromic molecules offer the opportunity to change and reset the molecular properties by simply turning a light source on and off, and have attracted great attention due to their potential applications in smart windows and ophthalmic glasses.<sup>1</sup> The development of thermally reversible photochromic dyes with different switching kinetics, thermal stabilities and coloration is important for the development of new switching devices and applications.<sup>2</sup> We recently designed and synthesized a unique photochromic molecule, pseudogem-bisDPI[2.2]PC, which is one of the [2.2]paracyclophane-bridged imidazole dimers showing instantaneous coloration upon UV light irradiation and rapid fading in the dark.<sup>3</sup> The [2.2] paracyclophane-bridged imidazole dimer has a [2.2] paracyclophane ([2.2]PC) moiety that tightly couples two imidazole rings. The [2.2]PC-bridged imidazole dimer shows photoinduced

homolytic bond cleavage of the C–N bond between the imidazole rings and successive fast C–N bond formation. Fast thermalbleaching kinetics enable a solution color change only where it is irradiated with light, because the thermal-bleaching rate is much faster than the diffusion rate of the colored species at room temperature. Furthermore, we could achieve a remarkable acceleration for the thermal back-reaction ( $\tau_{1/2} = 35 \,\mu s$  in the benzene solution at room temperature) by applying Marcus theory.<sup>3b</sup> Though the large optical density in the visible light region is necessary when [2.2]PC-bridged imidazole dimers are applied to fast-color changing ophthalmic lenses, fast bleaching rate causes the decrease in the optical density in the photostationary state. One possible approach to increase the optical density for the colored state is to enhance the photosensitivity to solar radiation. Unfortunately the photosensitivity of the earliest [2.2]PC-bridged

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Scheme 1. Photochromic Reaction of [2.2]Paracyclophane-Bridged Imidazole Dimers



imidazole dimer is poor because it does not have an efficient absorption band in the UVA radiation region. To improve the photosensitivity to sunlight, we recently developed a novel [2.2]PCbridged imidazole dimer derivative, pseudogem-bisTMDPI[2.2]PC, which shows excellent photochromic color change even under sunlight.<sup>3d</sup> The [2.2]PC-bridged imidazole dimer has two types of imidazole rings-Im1 and Im2-as shown in Scheme 1. It should be noted that the two imidazole rings are not equivalent in their electronic environment. Im1 is a resonant planar structure that has a typical bond distance for a  $6\pi$  electron system with an electrondonating characteristic, whereas Im2 has two localized C=N double bonds and one sp<sup>3</sup> carbon connecting Im1, consistent with a  $4\pi$ electron system with an electron-withdrawing characteristic. The absorption band in the UVA radiation region of pseudogembisTMDPI[2.2]PC was assigned to the intramolecular chargetransfer (CT) transition from the electron-donating dimethoxysubstituted phenyl rings to the electron-withdrawing Im2 based on the TDDFT calculation. However, the presence of the intramolecular CT transition was not proved by the definitive experimental evidence. In this study, we investigated the CT characteristics and the photochromic properties of two novel photochromic molecules, pseudogem-DPI-TMDPI[2.2]PC (4) and pseudogem-TMDPI-DPI-[2.2]PC (5). Moreover, we revealed that 4 and 5 would isomerize each other through an identical transient colored species upon UV light irradiation.

# 2. EXPERIMENTAL SECTION

**2.1. Synthesis.** 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 (Wakogel C-300). <sup>1</sup>H NMR spectra were recorded at 500 MHz on a JEOL JNM-ECP500A. DMSO- $d_6$  and CDCl<sub>3</sub> (1% TMS) were used as deuterated solvents. Mass spectra (FAB–MS) were measured by using a JEOL MStation MS700. *m*-Dinitrobenzilalcohol was used as a MASS matrix. All glasswares were washed





with distilled water and dried. Unless otherwise noted, all reagents and reaction solvents except acetic acid were purchased from TCI, Wako Co. Ltd., Aldrich Chemical Co., Inc., and ACROS Oraganics, and were used without further purification. Acetic acid was purified by adding 5 wt % KMnO<sub>4</sub>, boiling under reflux for 2 h and then fractionally distilling to remove acetaldehyde.

pseudogem-DPI-TMDPI[2.2]PC (4) and pseudogem-TMDPI-DPI[2.2]PC (5) were synthesized according to Scheme 2, using pseudogem-[4-formyl-13-(4,5-diphenyl-1H-imidazol-2-yl)][2.2]paracyclophane as a starting material. *Pseudogem*-[4-formyl-13-(4,5-diphenyl-1H-imidazol-2-yl)][2.2]paracyclophane<sup>3b</sup> (1) and 3,3',4,4'-Tetramethoxybenzil<sup>4</sup> (2) were prepared according to a literature procedure.

pseudogem-(4,5-Diphenyl-1H-imidazol-2-yl-4,5-(3,4,-dimethoxyphenyl)-1H-imidazol-2-yl)[2.2]paracyclophane (3). *pseudogem*-[4-Formyl-13-(4,5-diphenyl-1*H*-imidazol-2-yl)][2.2]paracyclophane (176 mg, 0.387 mmol), 3,3',4,4'-tetramethoxybenzil (153 mg, 0.463 mmol) and ammonium acetate (1.846 g, 23.95 mmol) were refluxed in acetic acid (9 mL) for 1 day. The reaction mixture was cooled with an ice bath, and neutralized with aqueous NH<sub>3</sub>, to form a yellow precipitate. The aqueous layer was extracted with dichloromethane. The combined organic layer was washed with water and brine, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and evaporated. The product was purified with silica gel column chromatography twice, using hexane/THF = 1/1 and then  $CH_2Cl_2$ /ethyl acetate = 2/1, as eluents respectively, to give a brown amorphous solid (3), 165 mg (0.216 mmol, 55.7%). <sup>1</sup>H NMR (500 MHz, DMSO- $d_6$ )  $\delta$ : 11.61 (s, 1H), 11.52 (s, 1H), 7.22 (d, J = 7.1 Hz, 2H), 7.18–7.13 (m, 3H), 7.08–6.98 (m, 8H), 6.87 (s, 1H), 6.79-6.77 (m, 3H), 6.71-6.69 (m, 2H), 6.64-6.61 (m, 3H), 4.58-4.52 (m, 2H), 3.74 (s, 3H), 3.67 (s, 3H), 3.44 (s, 3H), 3.14–3.04 (m, 6H); FAB–MS: m/z 765  $[M + H]^+$ .

*pseudogem*-DPI-TMDPI[2.2]PC (4) and *pseudogem*-TMDPI-DPI[2.2]PC (5). All manipulations were carried out with the exclusion of light. Under nitrogen, to a solution of 3 (99 mg, 0.129 mmol) in benzene (10 mL) was added the solution of potassium ferricyanide (2.270 g, 6.895 mmol) and KOH (0.78 g, 13.90 mmol) in water (20 mL), and the reaction mixture was vigorously stirred for 30 min at room temperature. The organic layer was separated, exhaustively washed with water, and concentrated in vacuo. Then the crude mixture of 4 and 5 was separated with silica gel column chromatography using hexane/AcOEt = 2/3as eluent. The separated 4 was recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/hexane to give colorless crystals, 72 mg (0.0944 mmol, 72%). An 8 mg (0.01 mmol, 8%) yield of yellow crystals of the separated 5 was obtained from the recrystallization from CHCl<sub>3</sub>/hexane. As can be found from molecular structures, both of the [2.2] paracyclophanebridged imidazole dimers 4 and 5 could have diastereomers due to hindered rotation about the C-C bond between the imidazole ring and the dimethoxy-substituted phenyl ring. Though the existence of diastereomers of 5 was confirmed by the NMR spectrum at room temperature, 4 was found to have only one diastereomeric conformer or the rate of interconversion between the diastereomeric conformers of 4 is fast. Colorless crystals (4). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.51–7.48 (m, 1H), 7.30-7.28 (m, 3H), 7.22 (d, J = 7.5 Hz, 1H), 7.13-7.03 (m, 6H), 6.93 (d, J = 1.3 Hz, 1H), 6.87–6.84 (m, 2H), 6.80–6.62 (m, 6H), 6.50 (d, J = 7.7 Hz, 1H), 6.45 (dd, J = 7.7 Hz, 1H), 4.58–4.53 (m, 1H), 3.91 (s, 3H), 3.88 (s, 3H), 3.78 (s, 3H), 3.72 (s, 3H), 3.06–2.93 (m, 7H). FAB–MS: m/z 763[M + H]<sup>+</sup>. Yellow crystals (5). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) mixture of diastereomers  $\delta$ : 7.71–7.69 (m, 1H one diastereomer), 7.53–7.43 (m, 3H, two diastereomers), 7.41-7.29 (m, 11H, two diastereomers), 7.25–7.20 (m, 3H, two diastereomers), 7.13 (dd, J = 8.3, 1.9 Hz, 1H, one diastereomer), 7.09 (dd, J = 8.3, 1.3 Hz, 2H, one diastereomer), 7.00-6.87 (m, 7H, two diastereomers), 6.81 (d, J = 1.9 Hz, 1H, one diastereomer), 6.66–6.59 (m, 11H, two diastereomers), 6.52–6.44 (m, 4H, two diastereomers), 4.60–4.50 (m, 1H, one diastereomers), 4.25–4.18 (m, 1H, one diastereomer), 3.78 (s, 6H, two diastereomers), 3.70 (s, 3H, one diastereomer), 3.65 (s, 3H, one diastereomer), 3.56 (d, J = 6.4 Hz, 6H, two diastereomers), 3.37-2.92 (m, 20H, two diastereomers). FAB-MS: m/z 763[M+H]<sup>+</sup>.

**2.2.** X-ray Crystallographic Analysis. The diffraction data of the single crystal of 4 and 5 were collected on the Bruker APEX II CCD area detector (Mo K $\alpha$ ,  $\lambda = 0.71073$  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>5</sup> All non-hydrogen atoms were anisotropically refined.

**2.3. Laser Flash Photolysis.** The laser flash photolysis experiments were carried out with a Unisoku TSP-1000 time-resolved spectrophotometer. A Continuum Minilite II Nd:YAG (Q-switched) laser with the third harmonic at 355 nm (ca. 8 mJ per 5 ns pulse) was employed for the excitation light. The probe beam from an OSRAM HLX64623 halogen lamp 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 Hamamatsu R2949 photomultiplier tube through a spectrometer (Unisoku MD200). Sample solutions were deaerated by argon bubbling prior to the laser flash photolysis experiments.

**2.4. DFT Calculations.** All calculations were carried out using the Gaussian 03 program (Revision E.01).<sup>6</sup> The molecular structures 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. The TDDFT calculations were performed at the MPW1PW91/6-31+G(d) level of the theory for the optimized geometries.



Figure 1. ORTEP representation of the molecular structures of (a) 4 and (b) 5 with thermal ellipsoids (50% probability), where nitrogen and oxygen atoms are highlighted in blue and red, respectively. The hydrogen atoms and the solvent molecules are omitted for clarity.

#### 3. RESULTS AND DISCUSSION

3.1. X-ray Crystallographic Analysis. The molecular structures of 4 and 5 revealed by X-ray crystallographic analysis are shown in Figure 1. As described before, while 4 has only one diastereomeric conformer at room temperature, 5 has diastereomeric conformers due to hindered rotation about the C-C bond between the imidazole ring and the dimethoxy-substituted phenyl ring. Recrystallization from the dilute solution (CHCl<sub>3</sub>/ hexane) of 5 gave the single crystal composed of only one of the diastereomeric conformers. Each C-N bond lengths connecting two imidazole rings (4, 1.4851(18) Å; 5, 1.480(3) Å) are approximately equal to that of *pseudogem*-bisDPI[2.2]PC (1.4876(15) Å). It can be found that the imidazole ring of 4 attached with the dimethoxy-substituted phenyl rings is an electron-withdrawing Im2, whereas the imidazole ring of 5 attached with the dimethoxy-substituted phenyl rings is an electron-donating Im1. Though we could not observe the significant difference in the bond lengths of 5 compared with those of pseudogem-bisDPI-[2.2]PC, the bond lengths of the C-C bond between the imidazole ring and the dimethoxy-substituted phenyl rings of 4 are considerably different from those in *pseudogem*-bisDPI[2.2]PC. These differences in the molecular geometries can be plausibly explained by the contribution from the intramolecular CT resonance between the electron-donating dimethoxy-substituted phenyl rings and the electron-withdrawing imidazole ring (Figures S6 and S7 and Tables S3 and S4, Supporting Information).

**3.2. UV–Vis Absorption Spectra.** Figure 2 shows the UV–vis absorption spectra of 4 and 5 in the acetonitrile solution, along with those calculated by the TDDFT method (MPW1PW91/ 6-31+G(d)//MPW1PW91/6-31G(d)) for the optimized molecular geometries. The blue curves are the experimental spectra and the calculated oscillator strengths are shown by the red perpendicular lines. It should be noted that a clearly distinct absorption band is found in the UVA radiation region for the UV-vis absorption spectra of 4, whereas 5 does not show the similar absorption band in the same region. The  $S_0 \rightarrow S_2$  transition at 372 nm (f = 0.159) of 4 demonstrated by the TDDFT calculation is described by HOMO-1  $\rightarrow$  LUMO transition. This transition can be attributed to the intramolecular CT transition from the dimethoxy-substituted phenyl rings to the electron-withdrawing Im2 (Figure 3). Moreover, both of the  $S_0 \rightarrow S_4$  transition at 351 nm (f = 0.075) and  $S_0 \rightarrow S_5$  transition at 348 nm (f = 0.066) are associated with HOMO-3  $\rightarrow$  LUMO and HOMO-4  $\rightarrow$  LUMO transitions. These excited states are also characterized by the same type of the



Figure 2. UV-vis absorption spectra and TDDFT calculations for (a) 4 and (b) 5. The calculated spectra (MPW1PW91/6-31+G(d)// MPW1PW91/6-31G(d)) are shown by the red perpendicular lines.

intramolecular CT transition. On the other hand, the dimethoxysubstituted phenyl rings are connected to the electron-donating Im1 for 5 as shown in Figure 1. Thus, the intramolecular CT transition from the electron-donating dimethoxy-substituted phenyl rings to the electron-withdrawing Im2 would have small oscillator strength because of the small orbital overlap between the molecular orbitals (MOs) delocalized over the dimethoxysubstituted phenyl rings and the MOs delocalized over Im2. Indeed, as shown in Figure 2b, significant absorption bands are not found both in the experimental and theoretical absorption spectra of 5 in the UVA radiation region. The solvent effects on the absorption spectrum of 4 are also investigated. The maximum wavelength of the absorption in the UVA radiation region is slightly red-shifted depending on the increase in the permittivity of the solvent (Figure 4). This result also supports the CT nature of the absorption in the UVA radiation region. These structure-spectra relationships are the definitive evidence for the presence of the intramolecular CT band from the electron-donating substituents to the electron-withdrawing Im2.

Thus, the photosensitivity of [2.2]PC-bridged imidazole dimers can be readily controlled through appropriate design of the phenyl rings attached to the imidazole rings. The introduction of electron-donating substituents into the phenyl rings attached to the electron-withdrawing Im2 would enhance the photosensitivity with the aid of the intramolecular CT transitions.

**3.3. Laser Flash Photolysis Measurement.** Both of the solutions of **4** and **5** undergo photochromic reaction involving a color change from colorless to blue upon UV light irradiation, and



Figure 3. Relevant molecular orbitals of (a) 4 and (b) 5 obtained at the MPW1PW91/6-31+G(d) level.



Figure 4. UV-vis absorption spectra of 4 in benzene, acetonitrile, and a mixture of acetonitrile and water.

generate the identical colored species **R** as shown in Scheme 3. The solutions reach the photostationary equilibrium very rapidly under continuous irradiation, and after irradiation ceases, the absorption decreases very quickly according to monoexponential thermalbleaching kinetics. As described in the Experimental Section, the oxidation of the precursor **3** gives the crude mixture of **4** and **5**, and

Scheme 3. Photochromic Reactions of 4 and 5



**Figure 5.** Transient vis–NIR absorption spectra of 4 in degassed benzene at 25 °C ( $2.1 \times 10^{-4}$  M, light path length: 10 mm). Each of the spectra was recorded at 20 ms intervals after excitation with a nanosecond laser pulse (excitation wavelength, 355 nm; pulse width, 5 ns; power 8 mJ/pulse).

consequently the photochromic reaction of 4 leads to the formation of the mixture of 4 and 5 via the colored species **R**. The formation of 4 by the photochromic reaction of 5 is also true. Thus the repeated irradiation of UV light to the solution of 4 would gradually change to the mixture of thermal equilibrium of 4 and 5.

Figure 5 shows the transient vis-NIR absorption spectra of 4 in benzene at 25 °C measured by a nanosecond laser flash photolysis experiment. A sharp absorption band at 400 nm and a broad absorption band ranging from 500 to 1000 nm can be ascribed to the colored species R. All of the absorption bands decay with the same time constant, indicating the presence of a single conformation of the colored species R. The thermal bleaching process obeys first-order kinetics, and the half-life of the colored species is 55 ms at 25 °C. Figure 6 shows the decay profiles of the transient absorbance at 400 nm of the colored species **R**, measured over the temperature range from 5 to 40  $^{\circ}$ C. As described above, we can consider two kinds of reaction paths for the radical dimerization reaction to form the imidazole dimer. The reaction path 1 forms 4 with the reaction rate constant  $k_1$ , and 5 is formed with the reaction rate constant  $k_2$  along the reaction path 2 (Scheme 3). Therefore, the rate constant obtained from the first order plots of the time profile of the transient absorbance for the colored species R shown in Figure 6 should be a sum of  $k_1$  and  $k_2$  (Table S5, Supporting Information). Because the ratio of  $k_1$  and  $k_2$  can be estimated from the concentration ratio of 4 and 5 after the thermal back reaction, we measured the concentration ratio of 4 and 5 from HPLC

Table 1. Variation of the Ratio of 4 and 5 for the Solution Standing in the Dark after the Oxidation Reaction of the Precursor 3 in the Temperature Range from 10 to 40  $^{\circ}$ C

degassed benzene (4,  $2.1 \times 10^{-4}$  M; light path length, 10 mm). The

measurements were performed in the temperature range from 5 to 40 °C.

	iso	mer ratio
T/°C	4	5
10	1	0.103
20	1	0.119
30	1	0.134
40	1	0.153

chromatograms after the oxidation reaction of the precursor **3** over the temperature range from 10 to 40 °C in the dark (Table 1). The activation parameters for the thermal backreactions via the path 1 and path 2 were estimated from the Eyring plots (Figure S9, Supporting Information). The Eyring plots produce an excellent straight line, and the  $\Delta H^{\ddagger}$  and  $\Delta S^{\ddagger}$  values are estimated from the standard least-squares analysis of the Eyring plots. The free energy barriers ( $\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger}$ ) at 25 °C of the path 1 and path 2 are 67.0 kJ mol<sup>-1</sup> and 72.1 kJ mol<sup>-1</sup>, respectively.

The difference in the radical recombination reaction rate for the path 1 and path 2 can be explained by the Marcus theory<sup>7</sup> as described in our previous paper.<sup>3b</sup> Following standard Marcus theory, an increase in the change in Gibbs energy,  $\Delta G^0$ , between the reactant and the product would lead to a decrease in the free

Table 2. Kinetic Parameters Associated with the ThermalBack Reaction at 298 K

	$\Delta H^{*}/\mathrm{kJ}$ mol <sup>-1</sup>	$\Delta S^{\dagger}/J$ mol <sup>-1</sup> K <sup>-1</sup>	$\Delta G^{*}/\mathrm{kJ}$ mol <sup>-1</sup>	$ au_{1/2}/\mathrm{ms}$
reaction path 1	57.5	-31.9	67.0	60
reaction path 2	65.1	-23.5	72.1	485

energy of activation,  $\Delta G^{\dagger}$ , and consequently, the rate constant for the reaction would be accelerated. We have considered that the  $\Delta G^0$  of the thermal-back reaction could be enlarged by destabilizing the colored species, and designed *pseudogem*-DPI-PI[2.2]PC,<sup>3b</sup> with a [2.2]PC moiety that couples diphenylimidazole and phenanthroimidazole groups. The steric repulsion between the rigid phenanthroimidazole group and the phenyl rings facing each other should destabilize the biradical state, whereas the rotational motion along the C-C single bond between the imidazole group and the phenyl ring in *pseudogem*-bisDPIR[2.2]PC should relax the steric hindrance between the phenyl rings facing each other. The thermal back-reaction of the colored species of pseudogem-DPI-PI[2.2]PC is actually accelerated about 1000 times compared with that of *pseudogem*-bisDPIR[2.2]PC. As can be found from Table 2, the free energy of activation for the path 1,  $\Delta G^{\dagger}_{1}$ , is smaller than that for the path 2,  $\Delta G_{2}^{\dagger}$ . Therefore, it is suggested that the Gibbs energy of 4,  $\Delta G^{0}_{1}$ , is presumed to be larger than that of 5,  $\Delta G^{0}_{2}$ . In other words, 4 is more stable than 5 because 4 has a resonance stabilization energy attributable to the intramolecular CT between the electron-donating dimethoxy-substituted phenyl rings and the electron-withdrawing Im2. The sum of the electronic and zeropoint energies of 4 calculated by the DFT method (MPW1PW91/ 6-31G(d) is 6.2 kJ mol<sup>-1</sup> smaller than that of 5. Thus, the X-ray crystallographic analysis and the DFT calculations support the resonance stabilization of 4.

3.4. Photoisomerization between 4 and 5. As described above, both of the photochromic reaction of 4 and the oxidation of the precursor 3 lead to the formation of the mixture of 4 and 5 via the colored species R. The photoisomerization between 4 and 5 was investigated by UV-vis absorption spectroscopy and HPLC analysis. We confirmed that while the isomerization would not proceed in the dark over the temperature range from 10 to 50 °C (Figure S11, Supporting Information), the UV-vis absorption spectra of the acetonitrile solution of 4 changed with isosbestic points after the irradiation with UV laser pulses at 20 °C (Figure 7a). The absorption band around 350 nm of 4 can be assigned to the intramolecular CT transition from the dimethoxy-substituted phenyl rings to the electron-withdrawing Im2. On the other hand, 5 does not have significant absorption bands in the UVA radiation region as shown in Figure 2. Thus, the spectral changes induced by the UV light irradiation can be tentatively attributable to the photoisomerization of 4 yielding 5. Actually, as shown in Figure 7b, the HPLC analysis for the UV laser pulse-irradiated solution of 4 revealed the increase in the concentration of 5 with increasing the number of irradiation cycles. Figure 8 shows the ratio of isomers against the number of irradiation cycles of the laser pulse, determined by the HPLC analysis. The system reached the photostationary state after irradiating the laser pulses more than 500 times. As can be found from Figure 2, the absorption coefficient of 5 at 355 nm is apparently smaller than that of 4 due to the absence of the intramolecular CT transition. Therefore, the excitation efficiency of 5 should be poor under this experimental condition.



**Figure 7.** (a) UV–vis absorption spectra for the degassed acetonitrile solution (20 °C,  $1.2 \times 10^{-5}$  M) of 4 measured after the irradiation with UV laser pulses. (b) HPLC chromatograms for the UV laser pulse-irradiated acetonitrile solution of 4 measured at 20 °C. The mobile phase was water:CH<sub>3</sub>CN = 1:9 with a flow rate of 1.0 mL/min, detection wavelength = 267 nm (isosbestic point).



**Figure 8.** Variation of the ratio of **4** and **5** with the number of irradiation cycles of laser pulse determined by the HPLC analysis.

Therefore, as shown in Figure 9, the  $\Delta$ OD values immediately after laser excitation for the UV laser pulse-irradiated solutions, which are the mixture of 4 and 5, were smaller than that of the solution of 4. The fatigue resistance of the photochromic cycle was evaluated in benzene at 25 °C. The time profiles for the transient absorbance at 400 nm for the solution of the photostationary state after irradiating the laser pulses about 500 times and the solution after irradiation with 20000 laser pulses are



Time / ms

Figure 9. Decay profiles of the colored species R generated in the UV laser pulse-irradiated acetonitrile solution of 4 monitored at 400 nm (20  $^{\circ}$ C).

almost indistinguishable, indicating excellent durability for applications in ophthalmic lenses.

# 4. CONCLUSIONS

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The present study demonstrated the structure-property relationships of newly designed [2.2]PC-bridged imidazole dimers, and an efficient strategy for designing high-performance fast-photochromic molecules with increased photosensitivity to solar UVA radiation. The [2.2]PC-bridged imidazole dimer consists of two types of imidazole rings, Im1 and Im2. Im1 is characterized by a  $6\pi$  electron system with an electron-donating characteristic, whereas Im2 is distinguished by a  $4\pi$  electron system with an electron-withdrawing characteristic. The difference in the electronic environment between these two imidazole rings is extremely important to control the photosensitivity of [2.2]PC-bridged imidazole dimers. An appropriate design of the phenyl rings attached to the imidazole rings makes it possible to enhance the photosensitivity in the UVA radiation region. Indeed, we can demonstrate that the introduction of electrondonating substituents into the phenyl rings attached to the electron-withdrawing Im2 would enhance the photosensitivity with the aid of the intramolecular CT transitions. The diversity of the molecular design and the ease of synthesis make this class of photochromic molecules highly attractive for revolutionary optical switching devices.

# ASSOCIATED CONTENT

**Supporting Information.** <sup>1</sup>H NMR spectra of *pseudogem*-(4,5-diphenyl-1*H*-imidazol-2-yl-4,5-(3,4,-dimethoxyphenyl)-1*H*-imidazol-2-yl)[2.2]paracyclophane, 4 and 5. HPLC chromatograms, X-ray crystallographic analysis data (including separate cif format files), kinetics for the thermal back-reaction, thermal stability, and details of the DFT calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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