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Fast Photochromism of the Imidazole Dimers Bridged by Group 14 Atoms

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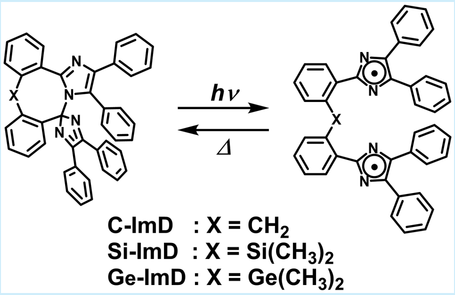
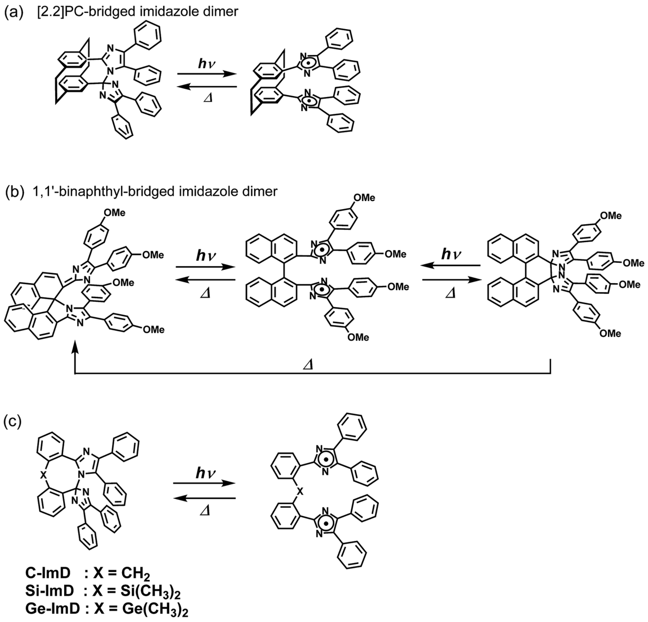
ABSTRACT: We developed fast photochromic imidazole dimers bridged by group 14 atoms. These compounds reversibly break the C−N bond to generate the colored open-ring biradical form. The colored form thermally reproduces the initial colorless form in the microsecond time scales. Furthermore, the color of the biradical can be easily controlled by the introduction of two different types of the imidazolyl radicals. These results give attractive insights for the further development of fast photochromic imidazole dimers.



Photoresponsive molecules are one of the attractive molecules which convert light energy into the changes in photophysical properties. Among the various photoresponsive molecules, organic photochromic molecules which reversibly change the color accompanied by the structural isomerization upon light irradiation have received much attention as molecular switches.[1−6] The artificial photochromic compounds such as diarylethene, azobenzene, and spiropyran have been utilized as photoswitches for light-memory, photomechanical effect, catalysis, fluorescence, and biofunctions.[7−19] These attractive applications of photochromic molecules have been achieved by the efficient utilization of the thermal bistability of the structural isomers generated upon light irradiation. However, because these molecules are not suitable as a switching trigger required for rapid photoresponse, such as real-time control of holographic displays and dynamic process of molecular assemblies,[20,21] the development of fast switchable photochromic molecules showing the rapid thermal back reaction within millisecond time scales has been expected.

We have recently developed fast switchable photochromic compounds, bridged imidazole dimers (Scheme 1).[22−27] The bridged imidazole dimer is synthesized by the radical recombination reaction between two imidazolyl radicals to form the intramolecular C−N bond. Upon UV light irradiation, the C−N bond homolytically cleaves to produce the transient colored biradical species. Because the thermal back reaction rate of the biradical can be controlled from the microsecond to second time scales, these fast photochromic compounds have potential applications to ophthalmic lenses, fluorescence switching,[28,29] and real-time holography.[30−32] We also discovered negative photochromic compounds by using a binaphthyl moiety as a bridging unit for the imidazolyl radicals, binaphthyl-bridged imidazole dimer (BN-ImD), which shows

Scheme 1. Photochromic Reaction Schemes of (a) [2.2]PC-Bridged Imidazole Dimer, (b) Binaphthyl-Bridged Imidazole Dimer, and (c) Group 14 Atom Bridged Imidazole Dimers



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the photoinduced decoloration upon visible light irradiation.[33−35] The most stable colored isomer of BN-ImD has the unconventional C−N bond between the imidazole ring and the 1-position of the binaphthyl unit, leading to the attractive negative photochromic properties. These studies show the potential flexible acceptability of the bridging structure to combine the imidazolyl radicals. Because the relative stabilities of the structural isomers possessing different binding modes between the two imidazole units strongly depend on the bridging unit, the photochromic properties of bridged imidazole dimers are drastically changed depending on the bridging manner. Therefore, the investigation of the effect of unexplored bridging unit on the fast-photochromic properties is important for the development of the study on fast-switchable photoresponsive compounds based on imidazolyl radicals.

In this study, we present the novel molecular design for the photochromic imidazole dimers, diphenyl-methane, diphenyl-dimethyl-silane, and diphenyl-dimethyl-germane bridged imidazole dimers (**C-ImD**, **Si-ImD**, and **Ge-ImD**, respectively). These imidazole dimers show the fast-thermal recombination in the microsecond time scale and the straightforward tunability of the absorption spectra for the colored biradicals over the visible and near-infrared (NIR) light region.

Compounds **C-ImD**, **Si-ImD**, and **Ge-ImD** were synthesized according to Schemes S1−S3 (Supporting Information). The molecular structures of **C-ImD**, **Si-ImD**, and **Ge-ImD** were revealed by X-ray crystallographic analysis (Figure 1).

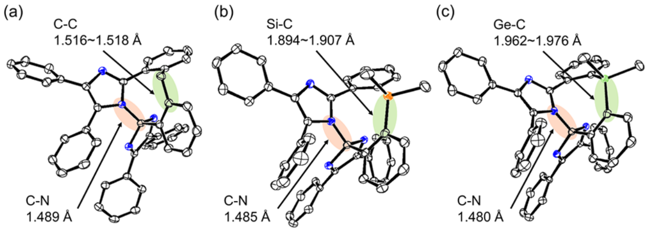

Figure 1. ORTEP representations of the molecular structures of C-ImD, Si-ImD and Ge-ImD (thermal ellipsoids at 50% probability; N, Si and Ge atoms are shown in blue, orange and green, respectively). H atoms and solvent molecules are omitted for clarity.

These imidazole dimers have the C−N bond between the two imidazole rings to form the 1,2′-isomers. The other structural isomers such as the 1,4′-isomer and the 2,2′-isomer[36−38] could not be obtained by the oxidation reaction of the precursor lophine with potassium ferricyanide at room temperature. The lengths of the C−N bonds of **C-ImD**, **Si-ImD** and **Ge-ImD** were determined to be 1.489, 1.485, and 1.480 Å, respectively, as long as those of typical imidazole dimers.[22−24] Compounds **C-ImD**, **Si-ImD**, and **Ge-ImD** form the eight-membered ring structure between the imidazole dimer and the bridging unit in the closed-ring forms.

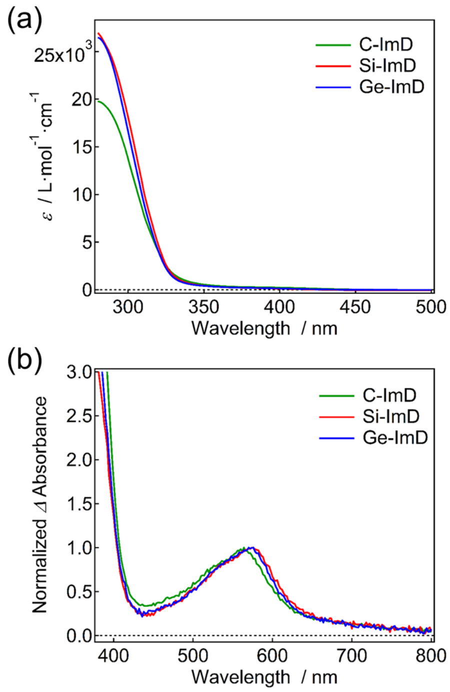

Figure 2. (a) UV−vis absorption spectra of **C-ImD**, **Si-ImD**, and **Ge-ImD** in benzene at 298 K. (b) Transient absorption spectra of **C-ImD**, **Si-ImD**, and **Ge-ImD** (1.0×10^{-3}, 1.3×10^{-3}, and 1.4×10^{-3} M, respectively) in benzene upon 355 nm laser pulse irradiation (pulse width = 5 ns, power = 3.0 mJ/pulse).

Figure 2a shows the absorption spectra of **C-ImD**, **Si-ImD**, and **Ge-ImD** in benzene. The absorption spectra have the large absorption band in the UV region. Upon UV light irradiation, the transient absorption band at 570 nm was observed in addition to the sharp absorption band below 400 nm (Figure 2b). The transient absorption spectral shapes of **C-ImD**, **Si-ImD**, and **Ge-ImD** are similar with that of typical triphenyl imidazolyl radical (TPIR), indicating the generation of the transient radical species by the C−N bond cleavage.[39] Generally, the photogenerated biradical species of the bridged imidazole dimers show the broad absorption bands in the whole visible light region because the absorption band at around 800 nm appears by the through-space interaction between the generated imidazolyl radicals in addition to the absorption bands of TPIRs.[38] Therefore, the similar absorption spectra of the biradicals of **C-ImD**, **Si-ImD**, and **Ge-ImD** with that of TPIR indicate no interaction between the two imidazolyl radicals despite that the radicals are closely connected by the bridging unit. It was previously demonstrated that the through-space interaction between the imidazolyl radicals can be controlled by changing the relative configuration of the two imidazolyl radicals.[38] That is, the small overlap between the wave functions of the imidazolyl radicals decreases the absorption band at 800 nm. The TDDFT calculation for the biradicals of **C-ImD**, **Si-ImD**, and **Ge-ImD** were performed to predict the transient absorption spectra upon UV light irradiation. The two optimized structures were predicted for the biradical species by the DFT calculations (Figure 3). These calculated absorption spectra for **C-ImD**, **Si-ImD**, and **Ge-ImD** were consistent with the experimental results. The DFT results suggest that the two imidazolyl radicals are spatially separated, resulting in the small overlap integral between the wave functions of the two imidazole radicals. Therefore, the absorption spectra of the biradicals of **C-ImD**, **Si-ImD**, and **Ge-ImD** show the similar spectral shapes with that of the individual TPIR.

The time profiles of the transient absorbance at 570 nm for **C-ImD**, **Si-ImD**, and **Ge-ImD** are shown in Figure 4. The transient absorption spectra monotonically decay in the whole spectral region (see the Supporting Information) because the differences in the thermodynamical stabilities between the two conformations of the biradicals are negligibly small (approximately <5 kJ/mol, Table S10), indicating that the two

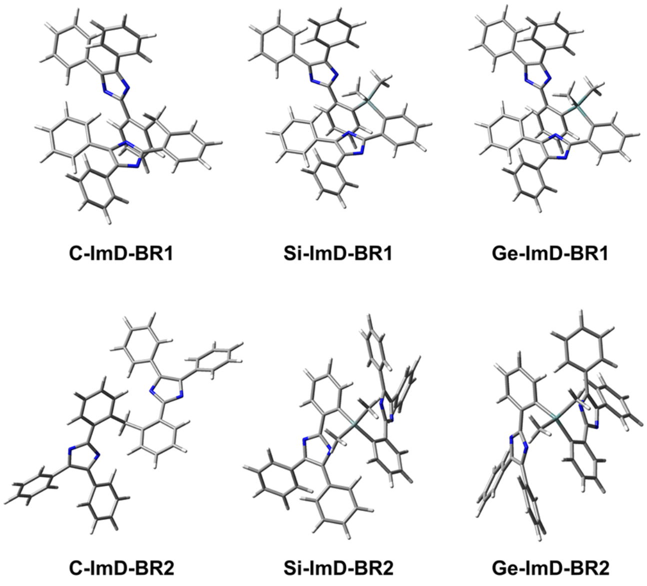

Figure 3. Optimized structures of the two conformations of the biradicals for **C-ImD**, **Si-ImD**, and **Ge-ImD** by DFT (UCAM-B3LYP/6-31+G(d,p)).

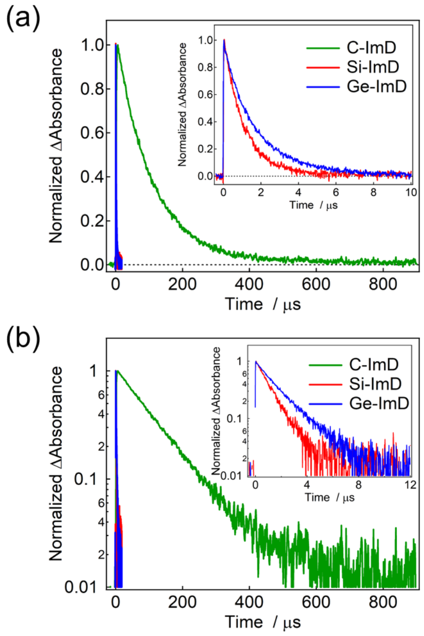

Figure 4. (a) Decay profiles of the transient biradicals of **C-ImD**, **Si-ImD**, and **Ge-ImD** (2.0×10^{-4}, 2.0×10^{-4}, and 4.7×10^{-4} M, respectively) in benzene at 298 K monitored at 570 nm upon 355 nm laser pulse irradiation (pulse width = 5 ns, power = 3.0 mJ/pulse). (b) The first-order plots for the decay profiles.

conformations are thermally equilibrated at 298 K. The half-lives of the transient biradicals of **C-ImD**, **Si-ImD**, and **Ge-ImD** were measured to be 79, 0.77, and 1.2 μs at 298 K, respectively. The fatigue resistances of **C-ImD**, **Si-ImD**, and **Ge-ImD** against the repetitive laser irradiation are shown in Figure S68. The thermal back reactions of **C-ImD**, **Si-ImD**, and **Ge-ImD** are drastically accelerated into the time scales of micro- or submicroseconds, compared with that of the [2.2]PC-bridged imidazole dimer,[22] only by bridging the TPIRs with group 14 atoms. We investigated the temperature dependence of the thermal back reaction rates in the temperature range from 278 to 313 K to estimate the activation parameters (the enthalpy and entropy of activation, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, and the free energy barrier $\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger}$) as shown in Table 1. The Eyring plots produced excellent straight lines, and the activation parameters were estimated from standard least-squares analysis (Supporting Information). The $\Delta S^{\ddagger}$ values are same between the thermal back reactions of **C-ImD**, **Si-ImD**, and **Ge-ImD**, indicating little difference in the conformational change accompanied with the thermal recombination reactions. In contrast, the $\Delta H^{\ddagger}$ value of **C-ImD** is much larger than those of **Si-ImD** and **Ge-ImD**. The DFT calculations were performed to obtain the structures of the transition states and to calculate the activation energy barriers (Supporting Information). Because the two states for the optimized structures (BR1 and BR2) of the biradicals (Figure 3) are almost degenerate, the sum of the activation barriers from BR1 and BR2 are compared. Although the calculated values of the activation barriers are not quantitatively consistent with the experimental data, the results suggest that the sum of the activation barriers for **C-ImD** is the largest in those of **C-ImD**, **Si-ImD**, and **Ge-ImD**. The structures of the transition states are shown in Figure S69. The large difference between the transition states of **C-ImD**, **Si-ImD**, and **Ge-ImD** is the bond distances of the 14 atoms-bridged unit as similar with the 1,2′-isomers. This difference causes the change in the orientation of two imidazole rings which make the C−N bond to produce the 1,2′-isomer. While these differences may be related to the difference in the thermal back reaction rates, the detailed explanation of the remarkable acceleration of the thermal back reactions of **Si-ImD** and **Ge-ImD** have still been under investigation.

Table 1. Activation Parameters for the Thermal Back Reactions of C-ImD, Si-ImD, and Ge-ImD

	$\Delta H^{\ddagger}$ (kJ/mol)	$\Delta S^{\ddagger}$ (J/K mol)	$\Delta G^{\ddagger}$ (kJ/mol)	$\tau_{1/2}$ (μs)
C-ImD	35.0	−52.1	50.5	79
Si-ImD	23.8	−51.4	39.1	0.77
Ge-ImD	24.6	−52.1	40.2	1.2

The transient absorption spectra of **C-ImD**, **Si-ImD**, and **Ge-ImD** can be easily modulated because of the small interaction between the two imidazolyl radicals. We demonstrated that the introduction of the two different imidazolyl radicals gives a superposed absorption spectrum in the visible light region. Figure 5 shows the transient absorption spectra of the diphenyl-dimethyl-silane bridged imidazole dimer composed of the diphenyl imidazole and the phenanthro-imidazole rings (**Si-ImPhen**) and that composed of the diphenyl imidazole and pyrenyl-imidazole rings (**Si-ImPy**) upon UV light irradiation. The molecular structures of these imidazole dimers were revealed by X-ray crystallography (Figures S53 and S54). The heteroimidazolyl radical pair was generated by the photoinduced C−N bond breaking reaction. The photogenerated radical pairs of **Si-ImPhen** and **Si-ImPy** also show the rapid thermal back reactions in the microsecond time scale (Figures S65 and S67). The radical pair absorbs the whole range of visible light. The transient absorption spectra of **Si-ImPhen** and **Si-ImPy** show good overlap with the superposition of the absorption spectra of the corresponding individual imidazolyl radicals (**Phen$^{\bullet}$** and **Si-ImD** in Figure 5a or **Py$^{\bullet}$** and **Si-ImD** in Figure 5b), indicating that the independency of the imidazolyl radicals is maintained even by

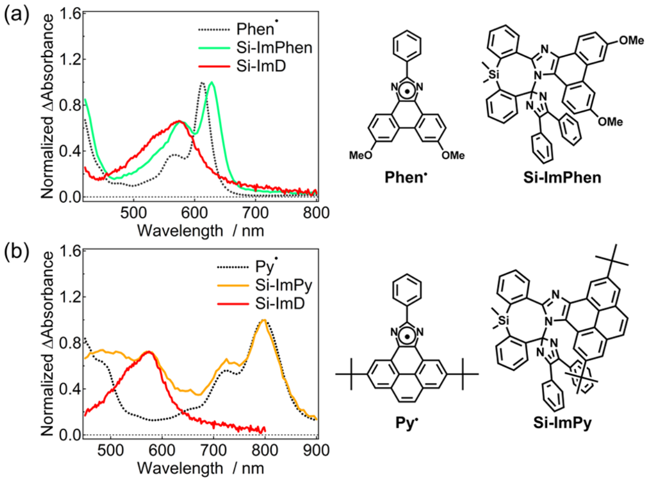

Figure 5. (a) Transient absorption spectra of **Si-ImPhen** and **Si-ImD** and the absorption spectrum of Phen• in benzene. (b) Transient absorption spectra of **Si-ImPy** and **Si-ImD** and the absorption spectrum of Py• in benzene.

the introduction of the π-extended imidazolyl radicals. Therefore, the various types of the combination of the radical species will be expected for the further enhancement of the photochromic properties.

In conclusion, we developed the novel series of the fast-photochromic bridged imidazole dimer, group 14 atoms-bridged imidazole dimers, **C-ImD**, **Si-ImD**, and **Ge-ImD**. Compounds **C-ImD**, **Si-ImD**, and **Ge-ImD** can reversibly form the colored biradical by the photoinduced C−N bond breaking. The thermal back reaction of the biradical accelerates to the microsecond time scale only by bridging the TPIRs with group 14 atoms. In addition, the different types of the imidazolyl radicals can be easily introduced to the bridged imidazole dimer. Because of the small interaction between the two imidazolyl radicals, the absorption spectrum of the biradical reflects the superposition of each absorption spectrum of the introduced imidazolyl radical, resulting in the on-demand control of the absorption spectra. These novel molecular designs bridged by group 14 atoms will open up the further development of the fast-photochromic imidazole dimers.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.0c02072.

> Synthesis, NMR and ESI-TOF-MS spectra, DFT calculation, and the other experimental results (PDF)

Accession Codes

CCDC 1892467−1892471 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Crano, J. C.; Guglielmetti, R. J. *Organic Photochromic and Thermochromic Compounds*; Plenum Press: New York, 1999.
(2) Feringa, B. L. *Molecular Switches*; Wiley-VCH: Weinheim, Germany, 2001.
(3) *Photochromism: Molecules and Systems*; Dürr, H., Bouas-Laurent, H., Eds.; Elsevier: Amsterdam, The Netherlands, 2003.
(4) *New Frontiers in Photochromism*; Irie, M., Yokoyama, Y., Seki, T., Eds.; Springer: Japan, 2013.
(5) Irie, M.; Fukaminato, T.; Matsuda, K.; Kobatake, S. Photochromism of Diarylethene Molecules and Crystals: Memories, Switches, and Actuators. *Chem. Rev.* **2014**, *114*, 12174.
(6) *Photochromic Materials*; Tian, H., Zhang, J., Eds.; Wiley-VCH: Weinheim, Germany, 2016.
(7) Berkovic, G.; Krongauz, V.; Weiss, V. Spiropyrans and Spirooxazines for Memories and Switches. *Chem. Rev.* **2000**, *100*, 1741.
(8) Irie, M.; Fukaminato, T.; Sasaki, T.; Tamai, N.; Kawai, T. A Digital Fluorescent Molecular Photoswitch. *Nature* **2002**, *420*, 759.
(9) Fukaminato, T.; Sasaki, T.; Kawai, T.; Tamai, N.; Irie, M. Digital Photoswitching of Fluorescence Based on the Photochromism of Diarylethene Derivatives at a Single-Molecule Level. *J. Am. Chem. Soc.* **2004**, *126*, 14843.
(10) Kobatake, S.; Takami, S.; Muto, H.; Ishikawa, T.; Irie, M. Rapid and Reversible Shape Changes of Molecular Crystals on Photoirradiation. *Nature* **2007**, *446*, 778.
(11) Ikeda, T.; Nakano, M.; Yu, Y.; Tsutsumi, O.; Kanazawa, A. Anisotropic Bending and Unbending Behavior of Azobenzene Liquid-Crystalline Gels by Light Exposure. *Adv. Mater.* **2003**, *15*, 201.
(12) Nath, N. K.; Pejov, L.; Nichols, S. M.; Hu, C.; Saleh, N.; Kahr, B.; Naumov, P. Model for Photoinduced Bending of Slender Molecular Crystals. *J. Am. Chem. Soc.* **2014**, *136*, 2757.
(13) Yam, V. W.-W.; Lee, J. K.-W.; Ko, C.-C.; Zhu, N. Photochromic Diarylethene-Containing Ionic Liquids and N-Heterocyclic Carbenes. *J. Am. Chem. Soc.* **2009**, *131*, 912.
(14) Göstl, R.; Senf, A.; Hecht, S. Remote-Controlling Chemical Reactions by Light: Towards Chemistry with High Spatio-Temporal Resolution. *Chem. Soc. Rev.* **2014**, *43*, 1982.

(15) Bartels, E.; Wassermann, N. H.; Erlanger, B. F. Photochromic Activators of the Acetylcholine Receptor. *Proc. Natl. Acad. Sci. U. S. A.* **1971**, *68*, 1820.

(16) Kumita, J. R.; Smart, O. S.; Woolley, G. A. Photo-Control of Helix Content in a Short Peptide. *Proc. Natl. Acad. Sci. U. S. A.* **2000**, *97*, 3803.

(17) Koçer, A.; Walko, M.; Meijberg, W.; Feringa, B. L. A Light-Actuated Nanovalve Derived from a Channel Protein. *Science* **2005**, *309*, 755.

(18) Fujita, D.; Murai, M.; Nishioka, T.; Miyoshi, H. Light Control of Mitochondrial Complex I Activity by a Photoresponsive Inhibitor. *Biochemistry* **2006**, *45*, 6581.

(19) Kamei, T.; Fukaminato, T.; Tamaoki, N. A Photochromic ATP Analogue Driving a Motor Protein with Reversible Light-Controlled Motility: Controlling Velocity and Binding Manner of a Kinesin—Microtubule System in an in Vitro Motility Assay. *Chem. Commun.* **2012**, *48*, 7625.

(20) Pham, V. P.; Manivannan, G.; Lessard, R. A.; Bornengo, G.; Pó, R. New Azo-Dye-Doped Polymer Systems as Dynamic Holographic Recording Media. *Appl. Phys. A: Mater. Sci. Process.* **1995**, *60*, 239.

(21) Rasmussen, P. H.; Ramanujam, P. S.; Hvilsted, S.; Berg, R. H. A Remarkably Efficient Azobenzene Peptide for Holographic Information Storage. *J. Am. Chem. Soc.* **1999**, *121*, 4738.

(22) Kishimoto, Y.; Abe, J. A Fast Photochromic Molecule That Colors Only under UV Light. *J. Am. Chem. Soc.* **2009**, *131*, 4227.

(23) Harada, Y.; Hatano, S.; Kimoto, A.; Abe, J. Remarkable Acceleration for Back-Reaction of a Fast Photochromic Molecule. *J. Phys. Chem. Lett.* **2010**, *1*, 1112.

(24) Iwasaki, T.; Kato, T.; Kobayashi, Y.; Abe, J. A Chiral BINOL-Bridged Imidazole Dimer Possessing Sub-Millisecond Fast Photochromism. *Chem. Commun.* **2014**, *50*, 7481.

(25) Yamashita, H.; Abe, J. Pentaarylbiimidazole, PABI: An Easily Synthesized Fast Photochromic Molecule with Superior Durability. *Chem. Commun.* **2014**, *50*, 8468.

(26) Yamashita, H.; Ikezawa, T.; Kobayashi, Y.; Abe, J. Photochromic Phenoxyl-Imidazolyl Radical Complexes with Decoloration Rates from Tens of Nanoseconds to Seconds. *J. Am. Chem. Soc.* **2015**, *137*, 4952.

(27) Mutoh, K.; Nakagawa, Y.; Sakamoto, A.; Kobayashi, Y.; Abe, J. Stepwise Two-Photon-Gated Photochemical Reaction in Photochromic [2.2]Paracyclophane-Bridged Bis(imidazole dimer). *J. Am. Chem. Soc.* **2015**, *137*, 5674.

(28) Mutoh, K.; Sliwa, M.; Abe, J. Rapid Fluorescence Switching by Using a Fast Photochromic [2.2]Paracyclophane-Bridged Imidazole Dimer. *J. Phys. Chem. C* **2013**, *117*, 4808.

(29) Mutoh, K.; Sliwa, M.; Fron, E.; Hofkens, J.; Abe, J. Fluorescence Modulation by Fast Photochromism of a [2.2]-Paracyclophane-Bridged Imidazole Dimer Possessing a Perylene Bisimide Moiety. *J. Mater. Chem. C* **2018**, *6*, 9523.

(30) Ishii, N.; Kato, T.; Abe, J. A Real-Time Dynamic Holographic Material Using a Fast Photochromic Molecule. *Sci. Rep.* **2012**, *2*, 819.

(31) Ishii, N.; Abe, J. Fast Photochromism in Polymer Matrix with Plasticizer and Real-Time Dynamic Holographic Properties. *Appl. Phys. Lett.* **2013**, *102*, 163301.

(32) Kobayashi, Y.; Abe, J. Real-Time Dynamic Hologram of a 3D Object with Fast Photochromic Molecules. *Adv. Opt. Mater.* **2016**, *4*, 1354.

(33) Hatano, S.; Horino, T.; Tokita, A.; Oshima, T.; Abe, J. Unusual Negative Photochromism via a Short-Lived Imidazolyl Radical of 1,1'-Binaphthyl-Bridged Imidazole Dimer. *J. Am. Chem. Soc.* **2013**, *135*, 3164.

(34) Yamaguchi, T.; Hatano, S.; Abe, J. Multistate Photochromism of 1-Phenylnaphthalene-Bridged Imidazole Dimer That Has Three Colorless Isomers and Two Colored Isomers. *J. Phys. Chem. A* **2014**, *118*, 134.

(35) Yamaguchi, T.; Kobayashi, Y.; Abe, J. Fast Negative Photochromism of 1,1'-Binaphthyl-Bridged Phenoxyl-Imidazolyl Radical Complex. *J. Am. Chem. Soc.* **2016**, *138*, 906.

(36) Tanino, H.; Kondo, T.; Okada, K.; Goto, T. Structures of Three Isomeric Dimers of 2,4,5-Triphenylimidazolyl. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 1474.

(37) Goto, T.; Tanino, H.; Kondo, T. Photochemical and Thermal Interconversions of Three Dimers of 2,4,5-Triphenylimidazolyl (Lophyl). *Chem. Lett.* **1980**, *9*, 431.

(38) Shima, K.; Mutoh, K.; Kobayashi, Y.; Abe, J. Enhancing the Versatility and Functionality of Fast Photochromic Bridged Imidazole Dimers by Flipping Imidazole Rings. *J. Am. Chem. Soc.* **2014**, *136*, 3796.

(39) Maeda, K.; Hayashi, T. Photochromic Color Change of the Dimer of Triphenylimidazolyl at Low Temperatures. *Bull. Chem. Soc. Jpn.* **1969**, *42*, 3509.