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Photochromic Radical Complexes that Show Heterolytic Bond Dissociation

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ABSTRACT: Photochromic materials have been widely used in various research fields because of their variety of photoswitching properties based on various molecular frameworks and bond breaking processes such as homolysis and heterolysis. However, while a number of photochromic molecular frameworks have been reported so far, there are few reports on photochromic molecular frameworks that show both homolysis and heterolysis depending on the substituents with high durability. The biradicals and zwitterions generated by homolysis and heterolysis have different physical and chemical properties, and different potential applications. Therefore, the rational photochromic molecular design to control the bond dissociation in the excited state on demand expands the versatility for photoswitch materials beyond the framework of a radical dissociation-type photochromic molecule: phenoxyl-imidazolyl radical complex (PIC). While the conventional PIC shows the photoinduced homolysis, the substitution of a strong electron-donating moiety to the phenoxyl moiety enables to switch the bond dissociation process of the excited state of photochromic systems, and the strategy enables to develop further novel radical and zwitterionic photoswitches.

■ INTRODUCTION

Photoinduced bond breaking is one of the most important processes in photochemistry because it strongly influences the direction of the chemical reactions and the reaction photochemical vields. Among various reactions. photochromism, which is defined as a reversible transformation of a chemical species between two forms by light, has been widely applied in biological and materials sciences because of their variety of photoswitching properties based on various molecular frameworks.1-4 Photoinduced bond breaking and making processes of photochromic compounds can be categorized by several processes: pericyclic reactions, E-Z isomerizations, tautomerizations, σ -bond dissociations, and so on.² For examples, photochromic reactions of diarylethene, fulgide, spiropyran, naphthopyran, and naphthooxazine are induced by the 6π electrocyclization reactions. Because the bond breaking and making processes of these reactions are cooperative processes, no intermediate chemical species are detected in ultrafast spectroscopy.⁵ These reactions usually generate closed-shell colored species upon light irradiation.

 σ -bond dissociations are also important bond breaking processes for various photochromic reactions. σ -bond dissociations are classified into two cases: homolysis and heterolysis. Photochromic molecules that show homolysis generate open-shell radical pairs (or biradicals) upon light irradiation. For example, hexaarylbiimidazole (HABI) is a well-known photochromic compound which generates a pair of triphenylimidazolyl radical upon UV light irradiation.6-8 2,3,4,4-Tetrachloro-l-oxo-l,4dihydronaphthalene (β -TKN)⁹ and dimeric nitroso compounds^{10,11} also show the photoinduced homolysis and generate radical pairs upon light irradiation. Because radical species generated by the photoinduced homolysis have relatively high reactivity, these photochromic materials can be applied to the initiator for radical polymerizations and rate-tunable photoswitching materials.12

While the homolytic bond dissociation is the major process for photoinduced σ -bond dissociations, there are several compounds that show the photoinduced heterolysis.¹³⁻²¹ Triarylmethanes and diphenylmethyl halides are well-known examples to show both homolysis and heterolysis depending on the environments and substituents. Systematic investigations by Turro,¹⁴ Hertz,¹³ and Peter groups^{15,17,18} suggest that the photoinduced heterolysis is likely to occur when the potential energy of the S_n (σ , σ^*) state, which has the zwitterionic character, decreases by dissolving in polar solvents or by introducing substituents stabilizing the zwitterion. If the activation barrier for the heterolysis is sufficiently low, the heterolysis from the $S_1(\pi, \pi^*)$ state occurs by the predissociation process. Recently, Winter group gives more detailed explanations of the photoinduced heterolytic bond cleavage

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Scheme 1. (a) Oxidation reactions of phenol and phenothiazine moieties. (b) Photochromic reaction schemes of PIC, 1, and 2.



of carbocation systems using complete active space selfconsistent field (CASSCF) methods.²¹ They suggest that the conical intersection plays a crucial role in the photoinduced heterolysis. Because the zwitterionic species generated by the photoinduced heterolysis have the large dipole moments, these photochromic materials can show photoinduced aggregations and phase separations.²² These properties have been applied to jonic channels and mass transportations.²² Therefore, the switching of the bond dissociation process between homolysis and heterolysis expands the potentials of photochromic molecules.²¹ However, because the photoinduced reactions of triarylmethanes and diphenylmethyl halides have very low reversibility and some of them are irreversible processes, there were almost no photochromic molecular frameworks that show both homolysis and heterolysis upon light irradiation depending on substituents and environments with high durability.

Recently, Abe group has developed a series of radicaldissociation-type photochromic compounds based on and over the HABI framework.^{12,23-30} Among them, phenoxylimidazolyl radical complex (PIC) is one of the recently developed rate-tunable T-type photochromic compounds which reversibly generate an imidazolyl radical and a phenoxyl radical (ring-opening form) in a molecule (Scheme 1b).^{27,29,30} The great advantage of PIC is that the half-life of the generated biradical form can be rationally controlled from tens of nanoseconds to tens of seconds by replacing the central phenylene ring to the thiophene ring. Another important aspect is that PIC is composed of two



Figure 1. (a) ORTEP representations of the molecular structures of 1 and 2 with thermal ellipsoids (50% probability), where nitrogen, oxygen, and sulfur atoms are highlighted in blue, red, and yellow, respectively. (b) Steady-state absorption spectra of 1 and 2 in benzene at room temperature. Vertical lines indicate the theoretical spectra of each molecule (MPW1PW91/6-31+G(d)//M05-2X/6-31G(d) level of the theory).

heterogeneous radical moieties: imidazolyl and phenoxyl radical moieties. It is interesting whether PIC shows homolysis or heterolysis during the photochromic reaction. Moreover, it is expected that the substitution of further electron donating or withdrawing groups to the PIC framework may switch the bond dissociation process from homolysis to heterolysis. The different bond dissociation process results in the products whose photophysical and photochemical properties are different. Therefore, revealing and controlling the photodissociation process is important not only for fundamental photochemistry but also for expanding the versatility of photofunctions over conventional PIC frameworks.^{31,32}

In this study, we synthesized novel photochromic radical complexes composed of an imidazolyl radical and a phenothiazine or a phenoxazine radical (1 and 2, respectively, Scheme 1b) and investigated the ultrafast bond dissociation processes of these compounds and PIC. Phenothiazine is well-known as a strong electron donor and the highest occupied molecular orbital (HOMO) level of the phenothiazine nonsubstituted (0.32)V vs ferrocene/ferrocenium (Fc/Fc⁺))³³ is higher than those of phenol and triphenylimidazole (0.64 and 0.95 V vs Fc/Fc⁺, respectively).^{34,35} It suggests that the phenothiazine moiety may act as the electron donor to the imidazole moiety during the bond dissociation process. Moreover, phenothiazine shows the similar oxidation reaction to that of phenol as shown in Scheme 1a. This similarity suggests that phenothiazine can be incorporated to the PIC framework as similar to phenol of PIC. The detailed analyses

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Figure 2. Nanosecond to microsecond transient absorption spectra and dynamics of 1 (a and b) and 2 (c and d) in benzene $(7.1 \times 10^{-4} \text{ and } 5.7 \times 10^{-4} \text{ M}, \text{ respectively})$ excited with a 355-nm picosecond laser pulse under argon atmosphere at room temperature. The probe wavelengths are 620 and 600 nm for 1 and 2, respectively. Insets show the semi-logarithmic plots of these time profiles.

with time-resolved visible and infrared (IR) absorption spectroscopies show that the bond dissociation processes of these compounds are different from conventional radical-dissociation-type photochromic compounds and these photochromic reactions are durable.

RESULTS AND DISCUSSION

The syntheses of 1 and 2 are shown in the experimental section. The molecular structures of 1 and 2 were unambiguously determined by X-ray crystallographic analyses. Figure 1a shows the ORTEP representations of these compounds. It shows that the phenothiazine and the phenoxazine units are arranged almost orthogonal to the imidazole skeleton as similar to PICs. The C–N bond lengths of 1 and 2 are 1.502 and 1.488 Å, respectively. These values are longer than those of PABI (1.459 Å)²⁶ and PIC (1.485 Å).²⁷

Figure 1b shows the steady-state absorption spectra of 1, 2 and PIC in benzene at room temperature. While the absorption band of PIC only appears shorter than 360 nm, the absorption spectra of both 1 and 2 have additional absorption bands around 360-500 nm. The time-dependent densitv functional theory (TDDFT) calculations (MPW1PW91/6-31+G(d)//M05-2X/6-31G(d) level of the theory) suggest that the additional absorptions in the visible region of 1 and 2 are ascribed to the $\pi\pi^*$ transitions of the phenothiazine and the phenoxazine moieties (Figures S49 and S51). Absorption spectra are not shifted depending on the solvents (benzene, dichloromethane, acetonitrile, and dimethyl sulfoxide (DMSO), Figure S15). It is important to note that the steady-state emission spectra are not shifted as well depending on the solvents, although the emission spectrum of 2 in benzene could not be measured due to the low emission quantum yield (Figure S16). These

results show that the S_1 states of the closed forms of 1 and 2 do not have the charge transfer (CT) feature.

To investigate the photochromic properties of 1 and 2, the transient absorption measurements from nanosecond to microsecond time scales were conducted using the randomly interleaved pulse train (RIPT) method.³⁶ Figures 2a and 2c show the transient absorption spectra of 1 and 2 in benzene (7.1 \times 10⁻⁴ and 5.7 \times 10⁻⁴ M, respectively) excited at 355 nm of a picosecond laser pulse at room temperature under argon atmosphere. A previous report showed that the photoinduced absorption of PIC due to the ring-opening form, which is the resonance hybrid of the biradical and quinoidal forms, was located at 470 and 660 nm upon excitation with UV light.²⁷ The photogenerated ring-opening form of PIC thermally reverted to the initial closed form with a half-life of 250 ns in benzene at room temperature. On the other hand, both 1 and 2 show the quite broad transient absorption spectra over the visible and the near infrared (NIR) light regions (Figures 2a and 2c). The transient absorption spectra of 1 and 2 are largely shifted to the NIR light region as compared to that of PIC, while the spectral shapes are qualitatively similar to that of PIC. The absorption peaks are located at 460, 610, and 1300 nm for 1 (Figure 2a). 2 shows the similar broad transient absorption spectra to those of 1 and the peaks are located at 450, 600, and 1200 nm (Figure 2c). DFT calculations suggest that the triplet biradical forms are slightly more stable than the singlet biradical forms in 1 and 2 (the energy differences for 1 and 2 are 1.6 kJ/mol). However, while the simulated absorption spectra of the singlet biradical and the quinoidal forms reproduce the characteristic absorption bands at the NIR light regions, the simulated absorption spectrum of the triplet states has the absorption bands only shorter than 600 nm (Figures S50 and S52). It suggests that the ring-opening forms of 1 and 2 exist as the singlet states. TDDFT calculations suggest that the molecular orbitals (MOs) originating to the absorption band at the NIR light region are delocalized over whole imidazole and phenothiazine (phenoxazine) moieties (Figures S50 and S52). The larger delocalizations of MOs of the ring-opening forms of 1 and 2 than that of PIC would be the most plausible reason why the absorption spectra of 1 and 2 are largely redshifted as compared to that of PIC. The transient absorption spectra of 1 and 2 do not change with time and decay monotonically with a time scale of microseconds. These results suggest that the ring-opening form is formed in 1 and 2 by the C-N bond dissociation upon light irradiation as similar to PIC.27

Figures 2b and 2d show the decay profiles of the transient absorbance of 1 and 2 at the same condition to those in Figures 2a and 2c. The probe wavelengths are 620 nm for 1 and 600 nm for 2. The semi-logarithmic plots of the decays (insets of Figures 2b and 2d) clearly show that the decays of the generated transient species follow the first-order kinetics. The half-lives of the transient species are 400 and 310 ns for 1 and 2, respectively. The decay profiles of the transient species of 1 and 2 do not change under air and argon atmospheres, indicating that the triplet excited states are not involved in the transient signals do not degrade even by the irradiation of intense picosecond laser pulses

for more than 1 hour (20 μ J/pulse, 1 kHz), indicating that these photochromic reactions are durable (Figure S18). Moreover, the photochromic reactions can be induced by even 510-nm light for 1 and 480-nm light for 2 (Figures S19-S21). These results show that the $\pi\pi^*$ transitions of the phenothiazine and phenoxazine moieties act as an efficient sensitizer for the photochromic reactions.

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The generated transient absorption spectra of the ringopening form do not shift depending on the polarity of the solvent (Figures S23 and S26), while the rates of the thermal back reaction increase with the increase in the solvent polarity (Figures S24 and S27). The acceleration of the thermal back reactions of the photogenerated transient species in polar solvents was also observed in conventional radical-dissociation-type photochromic compounds. Insensitivity of the absorption spectra to the solvent polarity and the acceleration of the thermal back reaction in polar solvents of the ring-opening form indicate that the ring-opening form is a neutral species rather than the CT state as discussed later.

It is known that the C-N bond of imidazole-based photochromic compounds (HABI, bridged imidazole dimers, PABI, and PIC) is cleaved by electrochemical reductions. To investigate the bond dissociation processes of 1 and 2 by electrochemical reductions, cyclic voltammogram (CV) measurements were performed. In the case of the CV for PIC,³⁷ the irreversible reduction peak was observed at -2.03 V, which was attributed to the electron transfer-chemical reaction-electron transfer (ECE) mechanism. That is, one electron reduction of PIC produces the closed-ring radical anion, which spontaneously shows the C-N bond dissociation reaction. The subsequent reduction of the radicals generated from the closed-ring radical anion further produces the dianion (an imidazolyl radical anion and a phenoxyl radical anion) at the same reduction potential. The formation of the dianion was evident for the emergence of two oxidation peaks on the return sweep at -0.76 and -0.63 V, which were ascribed to the oxidation of the phenolate anion and the imidazole anion of PIC, respectively.

Figure 3 shows the CVs for 1 (1.1 mM, blue line) and 2 (1.0 mM, red line) in dichloromethane with 0.1 M TBAPF₆ as a supporting electrolyte. The potential scan rate was set to 1 V/s to avoid the gradual decompositions of reacted products. CVs of other potential scan rates are shown in Figure S28. The irreversible reduction peaks of 1 and 2 are observed at -1.92 and -1.99 V, respectively. The differential electrochemical absorption spectra before and after the constant potentials for 40 s are shown in Figure S29. The applied constant potentials are -2.07 and -2.27 V versus Fc/Fc⁺ for 1 and 2, respectively. The differential absorption spectra are well explained by the superposition of the absorption spectra of the dianion species generated by the basic condition of the lophine forms (5 and 8 in Schemes 2 and 3) and the bleach of the absorption spectra of the closed form of 1 and 2. Therefore, the spectroelectrochemistry shows that the imidazole anion is formed under the potential at -2.07 V for 1 and -2.27 V for 2. In the return sweep after the reduction, two oxidation peaks are clearly observed at -1.13 and -0.53 V for 1 and at -1.19 and -0.49 V for 2 as similar to PIC. The second oxidation peaks in the



Figure 3. Cyclic voltammograms of 1 (blue line), and 2 (red line) in dichloromethane containing 0.1 M (TBA)PF₆ as the supporting electrolyte. The concentrations are 1.1 mM and 1.0 mM for 1 and 2, respectively. Potential scan rate was set to 1 V/s.

return sweep are most probably assigned to the oxidation of the imidazole anion to the imidazolyl radical because of the similarity of the results of PIC. The first oxidation peaks can be assigned to the reduction of the phenothiazine and phenoxazine anion. The reduction potentials of the phenothiazine and phenoxazine anions of 1 and 2 are much lower than the phenolate and imidazolyl anions of PIC probably because the phenothiazine and phenoxazine moieties have high electron donating properties. The reduction peaks coupled with the oxidation peaks of the dianion are not observed, most probably due to the fast thermal back reactions of 1 and 2 as compared to the potential scan rate. These results show that the electrochemical reductions of 1 and 2 generate the dianion species and spontaneously cleave the C-N bonds as similar to other imidazole-based photochromic compounds.

To reveal the detail of the bond dissociation processes, the transient absorption measurements from femtosecond to nanosecond time scales were conducted using a UV femtosecond laser pulse as an excitation light. Figure 4 shows the transient absorption spectra of PIC, 1, and 2 in benzene (3.4 \times 10⁻⁴, 6.7 \times 10⁻⁴, and 6.3 \times 10⁻⁴ M, respectively). The excitation wavelength was 330 nm for PIC and 360 nm for 1 and 2. The obtained transient absorption spectra were analyzed by the global analyses with the singular value decomposition (SVD) with the Glotaran program (http://glotaran.org).³⁸ The details of the analyses are shown in SI (Figures S34-S46). In the case of PIC in benzene (Figure 4a), the excited-state absorption instantaneously appeared at ~400 nm just after the excitation at 330 nm (spectrum at 0.15 ps). This signal can be assigned to the excited state absorption from the S₁ state as similar to the previously reported radical-dissociationtype photochromic molecules.³⁹⁻⁴¹ The signal quickly decays with a lifetime of 430 fs and a broad absorption band assigned to the ring-opening form is alternatively generated. It is noted that an isosbestic point was observed at 483 nm until 1 ps (Figure S30a), indicating that the ultrafast process does not have any intermediate species. The possibility that the transient absorption band at ~ 400 nm is the CT state can be excluded because the decay of the band becomes faster with the increase in the solvent polarity (acetonitrile, Figure S46). Therefore, it suggests

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Figure 4. Femtosecond to sub-nanosecond transient absorption spectra of (a) PIC, (b) 1, and (c) 2 in benzene $(3.4 \times 10^{-4}, 6.7 \times 10^{-4}, and 6.3 \times 10^{-4}$ M, respectively) at room temperature. The excitation wavelength was 330 nm for PIC and 360 nm for 1 and 2 at room temperature. The excitation intensity was set to 36 nJ pulse⁻¹ for PIC and 56 nJ pulse⁻¹ for 1 and 2.

that the ring-opening form is instantaneously generated by the photoinduced homolytic bond dissociation as similar to previously reported HABI derivatives and PABI.³⁹⁻⁴¹ The transient absorption signal assigned to the ring-opening form gradually grows with the lifetimes of 1.3 ps and 48 ps most probably ascribable to the gradual increase in the radical-radical interaction by the rotation of the two radicals and vibrational cooling.

On the other hand, in the case of 1 in benzene, while the transient absorption due to the S₁-S_n transition was observed as similar to that of PIC, another transient absorption band alternatively appeared at around 500 nm at 1 ps with the decay of the S_1 - S_n absorption (Figure 4b). The lifetime of the S_1 state of 1 is 380 fs, which is almost identical to that of PIC. The intermediate signal decayed with a time constant of 1.1 ps and the broad transient absorption band assigned to the ring-opening form was alternatively observed at 450-620 nm. The transient absorption band gradually grows with a time constant of 37 ps and the spectrum becomes almost identical to those nanosecond observed at transient absorption measurements. The similar intermediate spectrum was observed in 2 at \sim 1 ps (Figure 4c). These results suggest that the bond dissociation processes of these compounds are different from those of conventional radicaldissociation-type photochromic compounds, which show the photoinduced homolysis.

To reveal the origin of the intermediate spectra, we investigated the solvent dependence on the transient absorption spectra. The details of the transient absorption spectra in different solvents are shown in SI (Figures S30-S32). Figure 5a shows the transient absorption dynamics at 500 nm of 1 in different solvents: benzene, dichloromethane, acetonitrile, and DMSO. Except the sub-picosecond decay of the S₁ state, the picosecond decay kinetics assigned to the intermediate state were decelerated with the increase in the solvent dielectric constant (Figure S47). The lifetimes of the intermediate state of 1 are 1.1, 4.0, 7.2, and 19 ps for benzene,

dichloromethane, acetonitrile, and DMSO, respectively. Although the decay components assigned to the intermediate were small in 2, the intermediate signal of 2 also follows the similar behavior (Figure S33). The solvent dependence of the intermediate lifetimes also suggests that



Figure 5. (a) Transient absorption dynamics at 500 nm of 1 in different solvents and (b) the assignment of the intermediate spectrum at 1 ps of 1 in benzene with the TDDFT calculation of 1c shown in the inset (MPW1PW91/6-31+G(d)//MPW1PW91/6-31G(d) level of theory). The gray, blue, and yellow atoms in the inset indicate the carbon, nitrogen, and sulfur atoms, respectively.

the viscosity of the solvents is important factor as well as dielectric constants for these lifetimes because the deceleration of the lifetime in DMSO is large as compared to the increase in the dielectric constants. The small difference of the lifetimes in dichloromethane and acetonitrile may be due to the solvent viscosity. It is important to remind that the S₁ state of the closed form does not have the CT feature (Figure S16). Moreover, because we observed one intermediate species during the bond dissociation process in the global analyses (Figure S44a), the stepwise process, namely, electron transfer and then homolysis, is less conceivable. In that case, two intermediate species should be observed because a radical cation and a radical of phenothiazine are formed in the stepwise manner. Therefore, these results strongly suggest that the intermediate state is the CT state generated by the photoinduced heterolysis.

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16 If the CT state is formed, the cation of the phenothiazine unit and the anion of the imidazole unit are formed. It has 18 been reported that the anion of the imidazole unit does not 19 have any absorption in the visible light region.^{37,42} It has been also reported that the absorption spectrum of the 20 cation of the non-substituted phenothiazine shows a similar absorption spectrum, although the absorption peak was 22 shifted to the shorter wavelength (417 nm).⁴³ Moreover, the 23 observed transient absorption spectrum of the 24 intermediate of 1 is well explained by the simulated 25 absorption spectrum of the phenothiazine cation 26 substructure (1c) shown in the inset of Figure 5b by TDDFT 27 calculations. These results suggest that the observed 28 transient absorption spectrum is ascribable to the cation of 29 the phenothiazine moiety. It is noted that the imidazole and 30 phenothiazine moieties are orthogonally aligned before the bond dissociation. The near-orthogonal alignment is 32 expected in the initial formation process of the CT state because the CT state is formed in hundreds of femtoseconds 33 while the rotation of molecules often takes more than 34 picoseconds.44,45 The near-orthogonal alignment of the 35 imidazole and phenothiazine moieties is most probably the 36 reason why the intermediate transient signal is well 37 explained simply by the phenothiazine cation substructure. 38 These results clearly show that the photoinduced 39 heterolysis occurs and the CT state is formed in 1. The decay 40 process of the CT state with a time scale of picoseconds is most probably due to the back electron transfer from the 42 imidazole anion moiety to the phenothiazine cation moiety 43 and the formation of the ring-opening form. 44

After the decay of the CT state, the transient absorption bands at 621 nm for 1 and at 600 nm for 2 in benzene gradually increase with the lifetimes of 37 ps and 51 ps. This behavior was also observed in PABI and the time constant was ~ 10 ps.⁴¹ The gradual growth was attributed to the thermal equilibrium between two transient isomers differing in the contributions of biradical character. It is expected that 1 and 2 show the similar behavior to PABI. This will be discussed in detail in time-resolved IR spectroscopy.

To further investigate the bond dissociation process and the ring-opening form in detail, we measured picosecond time-resolved IR spectra of 1 in CD₂Cl₂. Figure 6a shows the time evolution of the time-resolved IR spectra of 1 in CD₂Cl₂



Figure 6. Picosecond time-resolved IR (a) spectra and (c) dynamics of 1 in CD_2Cl_2 (~1.4 × 10⁻² M) excited at 360 nm of a femtosecond laser pulse at room temperature. (b) The simulated IR spectrum of the singlet biradical, triplet biradical, and quinoidal forms of the ring-opening form of 1 ((U)CAM-B3LYP/6-31G(d) level of theory). The scaling factor (0.955) was multiplied to the calculated IR wavenumbers.

 $(\sim 1.4 \times 10^{-2} \text{ M})$ excited with a 360-nm femtosecond laser pulse at room temperature. A broad absorption band is observed around 1280-1350 cm⁻¹ just after the excitation (0 ps). The transient band is most probably ascribable to the S_1 state of the ring-closing form of 1 as similar to those of PABI.⁴¹ At 2.5 ps after the excitation, an intense absorption peak is observed at 1350 cm⁻¹. This signal is most probably ascribable to the CT state as was observed in the visible transient absorption spectroscopy. Because it is difficult to simulate the CT state by DFT calculations, we tentatively simulated the radical anion of a derivative of 1 (1a), where the nitrogen atom of the phenothiazine moiety is capped with a methyl group (Figure S48). The peaks at 1350 and 1330 cm⁻¹ could be assigned to the C–N stretching modes of the imidazole anion moiety as shown in Figure S48. Therefore, time-resolved IR spectroscopy also supports the photoinduced heterolysis of 1. The peak gradually decays with a time scale of picoseconds and the peaks at 1260, 1290, 1325, and 1365 cm⁻¹ alternatively appeared as shown in Figure 6a. The transient absorption dynamics at 1351 and 1262 cm⁻¹ are well correlated with the decay kinetics of the CT state and the rise kinetics of the ringopening form (Figure 6c). The similarity of the dynamics

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between visible and IR spectroscopies suggests that the decay and the rise kinetics of the IR signals indicate the transformation from the CT state to the ring-opening form. The peaks at 1262 and 1325 cm⁻¹ gradually increase with the time scale of tens-to-hundreds of picoseconds (Figure 6a). These peaks can be attributable to the closed-shell quinoidal form of the ring-opening form of 1 as shown in Figure 6b. The simulated IR spectrum of the triplet biradical form is almost identical to that of the singlet biradical form in these regions. However, we tentatively excluded the contribution of the triplet biradical form based on the 10 results for the nanosecond visible transient absorption 11 measurements as shown in Figure S49. The transient IR 12 spectrum at 1 ns can be assigned to the superposition of the 13 simulated IR spectra of the singlet biradical and quinoidal 14 forms. Therefore, time-resolved IR spectroscopy also 15 suggests the dynamic evolution of the biradical character of the ring-opening form as similar to PABI.⁴¹ However, more 16 sophisticated quantum chemical calculations such as the 17 extended multistate complete active space second-order 18 perturbation theory (XMS-CASPT2) are necessary to 19 discuss the details of the open-shell characteristics of the 20 ring-opening form of 1. 21

A possible reason why 1 and 2 show the photoinduced heterolysis is probably the decrease in the energy level of the CT state generated by the photoinduced heterolysis in these compounds. The stabilization of the CT state results in the decrease in the activation barrier of the photoinduced heterolysis. When the activation barrier of the photoinduced heterolysis becomes lower than that of the photoinduced homolysis, the photoinduced heterolysis preferentially occurs. To verify the hypothesis, we estimate the relative energy level of the CT state to the S₁ state (ΔG_{CT}) of PABI, PIC, 1, and 2 by assuming that the imidazole moiety acts as the acceptor while the other moiety (imidazole, phenol, phenothiazine, and phenoxazine for PABI, PIC, 1, and 2, respectively) acts as the donor with the Rehm-Weller equation as below.44,46

$$\Delta G_{\rm CT} = F(E_{\rm ox} - E_{\rm red}) - \Delta G_{\rm D^*} - \frac{N_{\rm A}e^2}{4\pi\varepsilon_0\varepsilon r_{\rm CT}}$$
(1)

F, E_{ox} , E_{red} , ΔG_{D^*} , N_A , ε , ε_0 , r_{CT} , and e indicate the Faraday constant, the oxidation potential of the electron donor, the reduction potential of the electron acceptor, the energy of the S_0 - S_1 transition of the donor, the Avogadro constant, the relative dielectric constant of the medium, the vacuum dielectric constant, the distance between the donor and the acceptor, and the elementary charge, respectively. We used the reduction potentials of PABI, PIC, 1, and 2 for E_{red} , which is the reduction potential of these imidazole moieties (acceptors), because all reduction reactions produced the imidazole anion. On the other hand, because it was difficult to measure E_{ox} of the donor moieties of these compounds, we tentatively used the oxidation potentials of nonsubstituted triphenylimidazole, phenol, phenothiazine, and phenoxazine for E_{0x} .^{33–35} The reduction and oxidation potentials measured in different solvents ($\Delta_{solv}E$, acetonitrile and dichloromethane) were corrected for the benzene solution by using the Born equation as below. NT 2

$$\Delta_{\rm solv}E = -\frac{N_{\rm A}e^2}{8\pi\varepsilon_0} \left(\frac{1}{r^+} + \frac{1}{r^-}\right) \left(\frac{1}{\varepsilon_{\rm r}} - \frac{1}{\varepsilon}\right) \tag{2}$$

 r^+ and r^- are the radii of the anion and cation, respectively. In the actual estimation, the r^+ and r^- values were tentatively set to be 0.5 and 0.6 nm based on the optimized molecular structures of the DFT calculations, respectively. ε_r is the relative dielectric constant of the solvent employed for the electrochemical measurements and ε is the relative dielectric constant of benzene, 2.28. The details of the calculations are shown in the supporting information. The estimated ΔG_{CT} values of PABI, PIC, 1, and 2 in benzene are 0.20, 0.07, -0.18, and -0.19 eV, respectively. The simple calculation suggests that the formations of the CT states of 1 and 2 are energetically possible, while those of PABI and PIC are not. The stabilization of the CT state in 1 and 2 will lower the activation barrier for the photoinduced heterolysis. Thus, the pathway of the photoinduced heterolysis could be the dominant process for the bond dissociation over the pathway of the photoinduced homolysis. Although it is difficult to directly compare the activation barriers for the photoinduced homolysis and heterolysis by this calculation, the stabilization of the CT state by introducing the phenothiazine and the phenoxazine moieties is the most plausible reason why 1 and 2 show the photoinduced heterolysis while PABI and PIC show the photoinduced homolysis.

The fact that the photoinduced heterolysis preferentially occurs than the photoinduced homolysis in 1 and 2 suggests that the activation barrier for the photoinduced heterolysis is lower than that of the photoinduced homolysis in the closed form, and may suggest that the pathway of the heterolytic bond dissociation is an adiabatic process. It suggests that the CT state generated by the heterolysis is more stable than the biradical generated by the homolysis around the closed form geometry. However, after the formation of the CT states of 1 and 2 generated by the photoinduced heterolysis, the back electron transfer occurs and the neutral ring-opening form is generated. This result indicates that the neutral ring-opening form becomes more stable than the CT state in the ring-opening form geometry. In the PIC and PABI frameworks, the spin-spin interaction between two radical sites gradually increases after the bond dissociation by the rotation of these moieties from the initial orthogonal geometry.⁴¹ The increased spin-spin interaction dynamically stabilizes the biradical and the quinoidal forms during the formation of the ring-opening forms. The gradual increase in the spin-spin interaction would be the most plausible reason why the CT state formed by the photoinduced heterolysis is subsequently converted to the neutral ring-opening form in 1 and 2.

CONCLUSION

In summary, we developed novel photochromic compounds composed of an imidazolyl radical and a phenothiazine or a phenoxazine radical. These compounds show the photoinduced heterolysis in spite that the molecular framework is based on the radical-dissociationtype photochromic molecule. These compounds show visible-sensitized and durable photochromic reactions which induce the absorption change up to the NIR light region. The lifetime of the current CT state is at most tens of picoseconds in the polar solvent. However, further improvements of the molecular structures such as the combination of donor and acceptor type moieties would



extend the lifetimes of the CT state and zwitterion-type fast photoswitches could be developed based on the PIC framework. The fast photoswitching property will increase the photostability of zwitterion-type photochromic molecules.³⁰ Moreover, the fast and large modulation of the dipole moment may be also advantageous for the temporal controls of photoinduced aggregations and phase separations. The different bond dissociation process results in the different photoproducts, and will expand the versatility for the photochromic materials.

EXPERIMENTAL SECTION

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). All reagents and solvents were obtained from commercial suppliers (Sigma-Aldrich, Wako Chemicals, TCI) and the reagents were used without further purification.

3-bromo-10H-phenothiazine (3): 10H-phenothiazine (2.1 g, 1.0 equiv.) was dissolved in dry THF (20 mL). The solution was deaerated by a constant stream of nitrogen through a syringe for 30 min and cooled to 0 °C (ice bath/water). N-Bromosuccinimide (NBS, 1.9 g, 1.0 equiv.) was dissolved in dry and degassed THF (20 mL) and the NBS solution was slowly dropped to the cooled solution over 1 h. Then the solution was stirred for 12 h at 0 °C (ice bath/water) and allowed to room temperature. A saturated aqueous solution of sodium sulfite was added to the solution and the solution was extracted several times with dichloromethane. The organic layer was dried with anhydrous Na₂SO₄ and filtered. The solvent was removed in vacuo and the residue was purified by chromatography on silica gel (hexane/ethyl acetate = 4/1) to give compound 3 (1.0 g, 31%) as a colorless solid. ¹H NMR (DMSO- d_{6} , 400 MHz) δ: 8.73 (s, 1H), 7.16-7.11 (m, 2H), 7.00 (ddd, J = 8.0, 2.0 Hz, 3H), 6.91 (dd, J = 8.0 Hz, 2.4 Hz, 1H), 6.77 (ddd, J = 7.8 Hz, 2.0 Hz, 1H), 6.66 (dd, J = 8.4, 2.0 Hz, 1H), 6.60 (d, J = 8.8 Hz, 1H).

2-(10H-phenothiazin-3-yl)benzaldehyde (4) : Compound 3 (386 mg, 1.0 equiv.), 2-formylphenylboronic acid (230 mg, 1.1 equiv.), Pd(PPh₃)₄ (83.6 mg, 0.03 equiv.) and K_2CO_3 (364 mg, 1.9 equiv.) were added to degassed DME (30 mL) and water (10 mL). The light brown suspension was heated to reflux under nitrogen for 80 hours. After cooling to room temperature, dichloromethane was added to the reaction mixture and the solution was extracted with water. The organic layers were dried with anhydrous Na₂SO₄, the solvent was removed in vacuo and the residue was purified by column chromatography on silica gel (dichloromethane/hexane = 5:1) to give compound 4 (255 mg, 62 %) as yellow solid. ¹H NMR (DMSO-*d*₆, 400 MHz) δ : 9.91 (s, 1H), 7.86 (dd, *J* = 8.0 Hz, 1.6 Hz, 1H), 7.70 (ddd, *J* = 7.8 Hz, 1.6 Hz, 1H), 7.52 (t, *J* = 7.6 Hz, 1H), 7.47 (d, *J* = 8.0 Hz, 1H), 7.05-6.99 (m, 3H), 6.94 (d, *J* = 8.0 Hz, 1H), MARDI-TOFMS: *m/z* 303 [M + H]⁺.

3-[2-(4,5-diphenyl-1H-imidazol-2-yl)phenyl]-10H-

phenothiazine (5): Compound 4 (196 mg, 1.0 equiv.), benzil (218 mg, 1.6 equiv.), and ammonium acetate (900 mg, 18 equiv.) were stirred at 110 °C in acetic acid (2 mL) in a sealed tube for 15 h. The reaction mixture was cooled to room temperature and neutralized by aqueous NH_3 . The

Scheme 3. Synthetic procedure for 2.



precipitate was filtered and washed with water. The crude product was purified by silica gel column chromatography (AcOEt/hexane = 1:1), to give compound 5 as a pale-yellow powder, (248 mg 78%). ¹H NMR (DMSO- d_6 , 400 MHz) δ : 11.96 (s, 1H), 8.67 (s, 1H), 7.70 (d, J = 8.0 Hz, 1H), 7.52-7.42 (m, 5H), 7.33 (s, 5H), 7.26-7.15 (m, 3H), 7.06 (t, J = 7.8 Hz, 1H), 6.92 (d, J = 8.0 Hz, 1H), 6.86 (dd, J = 10.4 Hz, 2.4 Hz, 1H), 6.82 (d, J = 2.4 Hz, 1H), 6.76 (t, J = 7.8 Hz, 1H), 6.70 (d, J = 8.0 Hz, 1H), 6.65 (d, J = 8.4 Hz, 1H), MARDI-TOFMS: m/z 494 [M + H]⁺.

2,3-diphenylspiro[imidazo[2,1-a]isoindole-5,3'-

phenothiazine] (1): A solution of potassium ferricyanide (3.0 g, 36 equiv.), KOH (1.6 g, 112 equiv.) in water (40 mL) was added to a suspension of compound 5 (125 mg, 1.0 equiv.) in benzene (100 mL). After stirring for 6 h at room temperature, the resultant mixture was then extracted with benzene. The organic extract was washed with water and dried in vacuo. After removal of the solvents, the crude product was purified by gel permeation chromatography (GPC). The yellow powder was obtained, 103.8 mg (84%). ¹H NMR (DMSO-*d*₆, 400 MHz) δ:, 7.87 (d, *J* = 7.6 Hz, 1H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.49 (d, *J* = 8.0 Hz, 2H), 7.42 (t, *J* = 7.6 Hz, 1H), 7.39-7.26 (m, 7H), 7.25-7.20 (m, 5H), 7.15 (t, *J* = 7.4 Hz, 1H), 6.15 (d, *J* = 9.6 Hz, 1H), 6.32 (dd, *J* = 5 Hz, 2.8 Hz, 1H), 6.15 (d, *J* = 2.4 Hz, 1H), HRMS (ESI-TOF) calculated for C₃₃H₂₁N₃S [M+H]⁺: 492.1529, found: 492.1524.

3-bromo-10H-phenoxazine (6): 10H-phenoxazine (2.52 g, 1.0 equiv.) was dissolved in dry THF (20 mL). The solution was deaerated by a constant stream of nitrogen through a

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syringe for 30 min and cooled to 0 °C (ice bath/water). NBS 1 (2.20 g. 1.0 equiv.) was dissolved dry and degassed THF (20 2 mL) and the solution was slowly dropped to the cooled 3 phenoxazine solution over 1 h, then stirred for 2 h at 0 °C 4 (ice bath/water) and allowed to come to room temperature. A saturated aqueous solution of sodium sulfite and the 5 aqueous layer was added to the solution and the solution 6 was extracted several times with dichloromethane. The 7 combined organic layers were dried with anhydrous Na₂SO₄ 8 and filtered. The solvents were removed in vacuo and the 9 residue was purified by chromatography on silica gel 10 (hexane/ethyl acetate 4:1) to give compound 6 (38%) as a 11 colorless solid. ¹H NMR (CDCl₃-d₆, 400 MHz) δ: 6.88-6.68 (m, 12 7H).

13 2-(10H-phenoxazin-3-yl)benzaldehyde (7) : Compound 14 6 (573 mg, 1.0 equiv.), 2-formylphenylboronic acid (387 mg, 15 1.2 equiv.), Pd(PPh₃)₄ (82.1 mg, 0.03 equiv.) and Na₂CO₃ 16 (433mg, 1.8 equiv.) were added degassed toluene (30 mL) and ethanol (10 mL). The light brown suspension was 17 heated to reflux under nitrogen for 18h. After cooling to 18 room temperature, the reaction mixture was extracted with 19 dichloromethane and the organic layer was washed with 20 water. The organic layers were dried with anhydrous 21 Na₂SO₄, the solvents were removed in vacuo, and the 22 residue was purified by column chromatography on silica 23 gel (dichloromethane/hexane =5:1) to give compound 7 (42) 24 %) as orange solid. ¹H NMR (DMSO- d_{6} , 400 MHz) δ : 9.94 (s, 25 1H), 8.47 (s, 1H), 7.85 (d, J = 8.0 Hz, 1H), 7.69 (t, J = 7.6 Hz, 26 1H), 7.52 (t, J = 7.6 Hz, 1H), 7.5 (dd, J = 13.6 Hz, 8.0 Hz, 2H), 27 6.78-6.72 (m, 3H), 6.65-6.54 (m, 2H), 6.49 (d, J = 8.0 Hz, 1H), MARDI-TOFMS: m/z 287 [M + H]* 28

29 3-[2-(4,5-diphenyl-1H-imidazol-2-yl)phenyl]-10Hphenoxazine (8): Compound 7 (111.7 mg, 1 equiv.), benzil 30 (147 mg, 1.8 equiv.), and ammonium acetate (830 mg, 28 31 equiv.) were stirred at 110 °C in acetic acid (2 mL) in a 32 sealed tube for 18 h. The reaction mixture was cooled to 33 room temperature and neutralized by aqueous NH₃. The 34 precipitate was filtered and washed with water. The crude 35 product was purified by silica gel column chromatography 36 (AcOEt/hexane = 1:1), to give compound 8 as a pale-peach 37 powder, (78%). ¹H NMR (DMSO-d₆, 400 MHz) δ: 11.99 (s, 38 1H), 8.27 (s, 1H), 7.68 (d, I = 8.0 Hz, 1H), 7.52-7.46 (m, 3H), 39 7.46-7.40 (m, 3H), 7.33 (s, 5H), 7.25 (t, / = 8.0 Hz, 2H), 7.18 40 (t, J = 8.0 Hz, 1H), 6.73 (t, J = 8.0 Hz, 1H), 7.46-7.40 (m, 4H),41 6.46 (d, J = 8.0 Hz, 1H), 6.40 (d, J = 8.0 Hz, 1H), MARDI-

42 TOFMS: *m*/*z* 478 [M + H]⁺ 43 **2,3-diphenylspiro[imidazo[2,1-a]isoindole-5,3'-**

phenoxazine] (2) : A solution of potassium ferricyanide 44 (623 mg, 34 equiv.), KOH (350 g, 123 equiv.) in water (30 45 mL) was added to a suspension of compound 8 (35.6 mg, 1.0 46 equiv.) in benzene (50 mL). After stirring for 90 min at room 47 temperature, the resultant mixture was then extracted with 48 benzene. The organic extract was washed with water and 49 dried in vacuo. After removal of the solvents, the crude 50 product was purified by GPC. The ocher powder was 51 obtained, 21.6 mg (61%). ¹H NMR (400 MHz, DMSO-d6) δ: 52 7.87 (d, / = 8.0 Hz, 1H), 7.55 (t, / = 7.6 Hz, 1H), 7.48 (d, / = 7.6 53 Hz, 1H), 7.45-7.34 (m, 4H), 7.31- 7.19 (m, 5H), 7.17- 7.08 54 (m, 2H), 7.01 (d, J = 8.0 Hz, 1H), 6.44 (d, J = 9.6 Hz, 1H), 6.33 (d, J = 4.8 Hz, 2.0 Hz, 1H), 5.54 (d, J = 9.6 Hz, 1H), HRMS (ESI-55 TOF) calculated for C₃₃H₂₁N₃O [M+H]+: 476.1757, found: 56 476.1756. 57

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Setups for Material Characterization and Steady-State Absorption Measurements. Proton nuclear magnetic resonance (¹H NMR) spectra were recorded at 400 MHz by JNM-ECS 400 MHz (JEOL). Matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF-MS) were recorded on Axima-CFRplus (Shimadzu). High resolution (HR) ESI-TOF-MS spectra were recorded on a Bruker micrOTOF II-AGA1 (Bruker). High performance liquid chromatography (HPLC) was conducted with Chromaster (Hitachi High-Technologies) equipped with a reverse phase analytical column (Mightysil RP-18GP II, 25 cm × 4.6 mm, 5 µm particle) from Kanto Chemical Industries, a linear photodiode array (PDA) detector. GPC was conducted with a recycling preparative HPLC (Japan Analytical Industry Co., Ltd.) series equipped with two GPC columns (JAIGEL-1H-A and JAIGEL-2H-A) and UV detector. CHCl₃ was used as an eluent with the flow rate of 3.5 mL/min. The diffraction data of the single crystal were collected on Rigaku XtaLAB mini II with Mo Ka radiation (λ = 0.71073 Å) at 100 K. Data integration and reduction were undertaken with Rigaku CrysAlis^{Pro}. The data refinement was carried out by Olex² software package with SHELXL program.⁴⁷⁻⁴⁹ All non-hydrogen atoms were anisotropically refined. Steady-state absorption spectra were measured with UV-3600 (Shimadzu).

Voltammetry Measurements. All CV measurements were performed in a conventional three-electrode cell. A glassy carbon electrode (0.6 cm in diameter) was employed as a working electrode after polishing with 1 µm diamond on a diamond polishing pad and then with 0.05 μm alumina on an alumina polishing pad attached to a glass plate (ALS Co., Ltd.). The electrode was rinsed with pure acetone and dried in air before use. A platinum wire was used as a counter electrode, and an Ag/Ag⁺ reference electrode (Ag wire, 1 mM AgNO₃, 0.1 M tetrabutylammonium hexafluorophosphate in acetonitrile) was employed. All CV measurements were achieved from 0.05 to 1 V/s in solutions of 0.1 M (TBA)PF₆ in dichloromethane at room temperature. Prior to each experiment, the solutions were deoxygenated by bubbling with nitrogen, and the nitrogen atmosphere was maintained throughout the course of the experiments. All potentials are referenced to the reversible formal potential for the Fc/Fc⁺ couple. µAutolab III potentiostat/ galvanostat (MetrohmAutolab B. V.) under computer control (General Purpose Electrochemical System software) was used for the CV measurement.

Spectroelectrochemical Measurements. Quartz glass cells with a 0.5 mm path length and a 1.0 cm path length were used for the spectroelectrochemistry for all the compounds. A standard three-electrode arrangement with a Pt mesh as a working electrode, a platinum wire as a counter electrode, and Ag/Ag⁺ as a reference electrode was employed. A spectrophotometer (Ocean-FX, Ocean Optics, Inc.) was used to record the absorption spectra in the range from 350 to 900 nm. All measurements were performed using N₂ bubbled solutions.

Nanosecond to Microsecond Transient Absorption Measurements. Nanosecond to microsecond transient absorption measurements were conducted by the randomly-interleaved-pulse-train (RIPT) method.³⁶ A picosecond laser, PL2210A (EKSPLA, 1 kHz, 25 ps, 3.4 mJ/pulse for 355 nm), and a supercontinuum (SC) radiation source (SC-450, Fianium, 20 MHz, pulse width: 50–100 ps depending on the wavelength, 450–2000 nm), were employed as the pump–pulse and probe sources, respectively. The wavelength of the excitation pulse was altered from 355 nm to 510 nm depending on the experiments. The measurements were performed in a benzene solution placed in a 2-mm quartz cell under argon condition with stirring at room temperature.

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Femtosecond to Nanosecond Transient Absorption Measurements. Transient absorption measurements on the femtosecond to nanosecond time scale were conducted by a homemade pump-probe system. An amplified femtosecond laser, Spirit One 1040-8 (Spectra-Physics, 1040 nm, the pulse width: \sim 270 fs), was split into two beams with a ratio of 1:9. The stronger beam was directed to a noncollinear optical parametric amplifier (NOPA), Spirit-NOPA-3H (Spectra-Physics) to generate the 330- or 360-nm femtosecond laser pulse for the pump beam. The pump beam was chopped prior to the sample at 500 Hz for signal differencing. The other weaker beam was focused to a deuterated water placed in a 10-mm quartz cuvette to generate the white light continuum for the probe beam. Both pump and probe beams were focused to the sample solution placed in the 2-mm quartz cuvette. The excitation beam was focused to a spot with the full width at the half maximum (FWHM) of \sim 70 μ m. The spot size was measured by knife-edge method assuming a Gaussian laser beam. The polarization between the pump and probe pulses was set at magic angle. The intensity of the pump pulse was set to 36 nJ pulse⁻¹ for PIC and 56 nJ pulse⁻¹ for 1 and 2. The transmitted probe beam was detected with multichannel detection system, PK120-C-RK (UNISOKU), composed of a CMOS linear image sensor and a polychromator. The obtained spectra were calibrated for group velocity dispersion using the data obtained by the optical Kerr signal of CH₂Cl₂ between the pump pulse and the white-light continuum. The instrumental response function was shorter than approximately 100 fs. The sample solution was stirred with a stirrer during the experiments and the measurements were performed at room temperature.

39 Picosecond **Time-Resolved** IR Absorption 40 Measurements. The detail of the experimental setup was 41 described in the previous study of the excitation dynamics 42 of PABI.⁴¹ The fundamental output from a Ti:sapphire 43 regenerative amplifier (Solstice Ace, Spectra Physics, 44 wavelength; 800 nm, repetition rate; 1 kHz, pulse duration; 45 190 fs) was used to excite two optical parametric amplifiers 46 (TOPAS-C and TOPAS-prime, Light Conversion) and 47 generate pump UV pulse (wavelength; 360 nm, energy at 48 the sample point; 1 µJ/pulse) and probe IR pulse (spectral coverage; $1250 \sim 1520$ cm⁻¹, < 0.4 μ J/pulse). The pump UV 49 pulse was modulated at half the repetition rate by a 50 mechanical chopper and focused onto the sample non-51 collinearly against the probe pulse. The probe IR pulse was 52 passed through the photo-excited sample and detected with 53 a 19-cm spectrograph (TRIAX190, HORIBA JOBIN YVON), a 54 multichannel liquid-nitrogen-cooled HgCdTe detector array 55 and box-car integrators (IR-12-128, InfraRed Associates). 56 The cross-correlation between the pump and probe pulses 57

was estimated to be ~0.5 ps. To remove the artificial signal that appears in transient IR spectra for all time delay, the spectrum at -400 ps, when the probe pulse comes before the pump pulse, was subtracted from the all transient IR spectra.

1 in CD_2Cl_2 solution filled in a BaF_2 cell (optical path length; 200 µm) was measured. The accumulation time was 1 hour for each time delay and totally 18 hours for all time delays. Since the sample stage was moved right and left (velocity; 1 mm/s) during the measurement, transient and steady-state IR spectra of the sample was not changed even after the 18-hours experiment.

Supporting Information

Details of characterizations, spectroscopic analyses, and DFT calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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40 41 42	(20)
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