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Stealth fast photoswitching of negative photochromic naphthalene-bridged phenoxyl-imidazolyl radical complexes†

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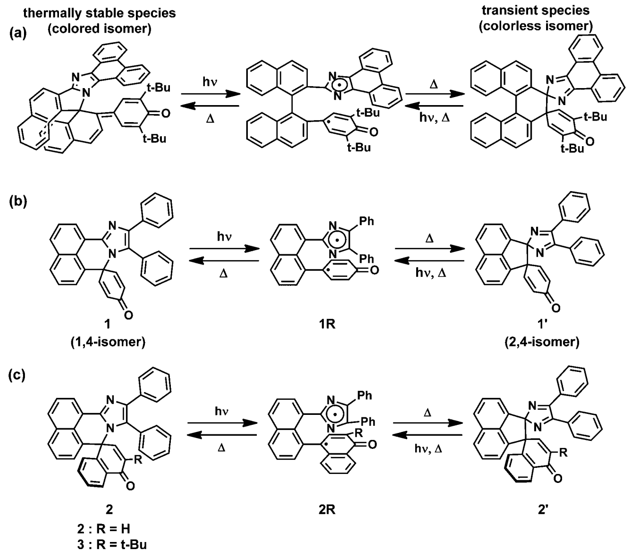
Naphthalene-bridged phenoxyl-imidazolyl radical complex (Np-PIC) is a novel fast switchable negative photochromic compound, which shows the thermal back reaction in the millisecond time scale. Upon UV light irradiation, Np-PIC shows the hypochromic effect in the UVA region due to there being less conjugation in the transient isomer. By replacing the phenoxyl unit with a naphthoxyl unit, the molecular structure has an asymmetric carbon, leading to fast chiroptical switching. This simple molecular design will be a good candidate for the future development of negative photochromic compounds.

Photochromism has been of interest not only in fundamental studies but also for industrial applications.[1] In general T-type photochromic compounds, the stable colorless isomer photoisomerizes into the less stable colored isomer upon UV light irradiation. Fast switchable T-type photochromic compounds have potential applications in ophthalmic lenses,[2] fluorescence switching,[3] real-time holographic materials,[4]as the phototrigger for light induced macroscopic structural changes,[5]and in the control of biological functions[6] due to the instantaneous changes in their electronic and molecular structures. However, the excitation UV light cannot penetrate deeper into the inside of the material because of the reabsorption of the excitation light by the generated colored isomer. This issue limits the application of fast T-type photochromism in bulk materials. The negative photochromic reaction, which causes a decoloration process upon irradiation with light in contrast to conventional photochromic systems, is one of the appropriate approaches to overcome this issue.[7] However, the time scales for the thermal coloration reactions of most reported examples of negative photochromism range from minutes to hours.

Recently, we have developed novel fast switchable negative photochromic compounds[8] based on the photochromism of the bridged imidazole dimer and the phenoxyl-imidazolyl radical complex (PIC).[2a,9] The 1,1′-binaphthyl-bridged PIC (BN-PIC, Scheme 1a) shows a fast thermal back reaction with a half-life of 1.9 s.[8b] Upon irradiation with light, the stable colored isomer generates the short-lived biradical species ($\tau_{1/2}$ = 240 ns at 298 K). The colorless isomer is kinetically generated after the thermal recombination reaction of the biradical species since the activation free energy required to isomerize into the colorless isomer is lower than that into the initial colored isomer. The colorless isomer is thermodynamically less stable as compared to the colored isomer, leading to thermal isomerization into the colored isomer through the thermally accessible biradical species, in the second time scale. While this unprecedented fast switchable



Scheme 1 Photochromic reaction schemes of (a) BN-PIC, (b) **1**, (c) **2** and **3**.

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negative photochromism has the attractive potential to be applied to real-time holographic materials and photoresponsive chiral dopants for liquid crystals,[10] an increase in the rate of the thermal back reaction to the time scale of milliseconds (video frame rate = 30 fps) is required for these applications.

In this study, we synthesized the fast switchable negative photochromic compounds, naphthalene-bridged phenoxyl-imidazolyl radial complex (Np-PIC, **1** in Scheme 1b) and naphthalene-bridged naphthoxyl-imidazolyl radical complex (Np-NIC, **2** and **3** in Scheme 1c). Compounds **1–3** show the hypochromic effect in the UVA region after UV light irradiation and a fast thermal back reaction in the millisecond time-scale. There are few reports on invisible photochromism.[11] Invisible photochromism has advantages for use as a light-trigger because the visible light absorption disturbs the performance of opto- or electro-molecular devices used under room light, and disturbs the spectroscopic analysis of combined chromophores in some cases. Moreover, Np-NIC possesses an asymmetric carbon atom by replacing the phenoxyl unit with a naphthoxyl unit. That is, fast chiroptical switching with a negative photochromic reaction is also expected.

The target compounds were synthesized according to Schemes S1–S3 (ESI†). The molecular structures of **1** and **2** were determined using X-ray crystallographic analysis as shown in Fig. 1. Compounds **1** and **2** have an intramolecular C–N bond between the 1-position of the imidazole ring and the 4-position of the cyclohexadienone or naphthalenone ring (1,4-isomer). The C–N bond lengths and the C═O bond lengths of **1** and **2** were estimated to be $d_{\mathrm{C-N(1)}}$ = 1.482 Å, $d_{\mathrm{C-N(2)}}$ = 1.480 Å, $d_{\mathrm{C=O(1)}}$ = 1.228 Å and $d_{\mathrm{C=O(2)}}$ = 1.225 Å, respectively. These bond lengths are almost identical with those of PIC derivatives.[9] The diphenyl imidazole ring is coplanar to the naphthyl moiety, while these two parts are perpendicular to the cyclohexadienone or naphthalenone ring. As discussed later, the Cotton effect is induced in the CD spectrum of **2** by this chiral molecular structure. It is noteworthy that the chiral crystal can be obtained *via* recrystallization from the racemic mixture.

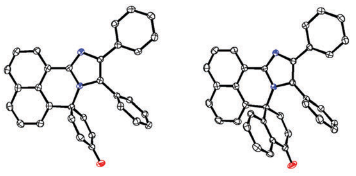

Fig. 1 ORTEP representations of the molecular structures of **1** and **2** with thermal ellipsoids (50% probability), where nitrogen and oxygen atoms are highlighted in blue and red, respectively.

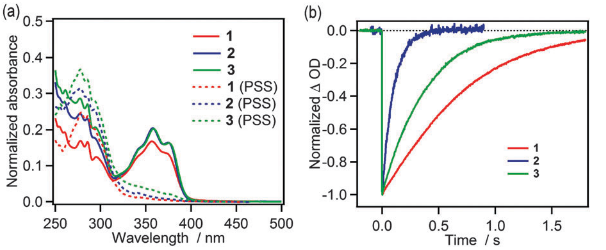

Fig. 2 (a) Steady-state absorption spectra of **1**, **2** and **3** in Me-THF at 153 K (solid), and the absorption spectra at the PSS after 365 nm UV light irradiation (25 mW) in Me-THF at 153 K. Each absorbance was normalized by dividing with the concentration of each solution (**1**: 2.9 × 10^{-5} M, **2**: 3.9 × 10^{-5} M, **3**: 2.5 × 10^{-5} M). (b) Time profiles of the transient absorbance at 380 nm (**1**: 7.4 × 10^{-5} M, **2**: 5.9 × 10^{-5} M, **3**: 4.9 × 10^{-5} M) in Ar-saturated benzene excited by a 355 nm laser pulse (5 ns, 7 mJ) at 298 K.

The steady-state UV-vis absorption spectra of **1–3** in 2-methyl tetrahydrofuran (Me-THF) at 298 K are shown in Fig. S30 (ESI†). All of the compounds show the characteristic absorption bands at around 360 nm. The molar extinction coefficients of **1–3** at 360 nm were estimated to be 1.3 × 10^4, 1.5 × 10^4 and 1.5 × 10^4 $\mathrm{M^{-1}\,cm^{-1}}$, respectively. The increase in the molar extinction coefficients of **2** and **3**, compared with that of **1**, is due to the extension of the aromatic system from the cyclohexadienone to the naphthalenone ring. The absorption band in **1–3** at around 360 nm is the $S_0 \rightarrow S_2$ transition which can be attributed to the transition from the molecular orbital (MO) delocalized over the diphenyl imidazole ring and the naphthalene ring to the MO localized over the naphthalene ring, using TDDFT calculations (Fig. S33, MPW1PW91/6-31+G(d)//MPW1PW91/6-31G(d), ESI†). Fig. 2a shows the steady-state UV-vis absorption spectra of the Me-THF solutions of **1–3** and those at the photostationary state (PSS) under 365 nm UV light (25 mW) at 153 K. The UV light irradiation leads to the disappearance of the CT absorption bands at 360 nm. The absorption bands of **1–3** were thermally restored with half-lives of 499, 68, and 175 ms at 298 K in benzene, respectively (Fig. 2b). The time profiles of the transient absorbance obey first-order reaction kinetics (Fig. S31, ESI†). That is, the initial 1,4-isomers isomerize into the thermally unstable transient species upon UV light irradiation. The activation energies for the thermal back reactions of the transient species generated from **1**, **2**, and **3** were estimated to be 72.2, 67.3, and 69.6 kJ $\mathrm{mol^{-1}}$ at 298 K, respectively (Fig. S36, ESI†). These compounds show excellent durability against repeated exposure to 355 nm laser pulses (10 Hz, 5 mJ) in spite of the absence of *tert*-butyl groups in **1** and **2** (Fig. S32, ESI†). As shown in Fig. S34 (ESI†), the absorption spectrum at the PSS of **1** can be well explained by the TDDFT calculations (MPW1PW91/6-31+G(d)//MPW1PW91/6-31G(d)) for the optimized structure of the 2,4-isomer, in which the 2-position of the imidazole ring connects with the 4-position of the cyclohexadienone ring (**1′**, Scheme 1b). In contrast to the 1,4-isomer, the permitted transition in the UVA region is not observed due to there being less conjugation between the imidazole and naphthalene rings in the 2,4-isomer. Here, we tentatively assign the molecular structure of the transient species as the 2,4-isomer, and carried out NMR and time-resolved infrared (TRIR) spectroscopy to determine the structure of the transient species.

The ^{1}H and ^{13}C NMR characterizations for the transient species of **1** were carried out using a 400 MHz NMR spectrometer coupled with *in situ* UV light irradiation (Fig. 3). To inhibit the thermal back reaction of the transient species, the solution was cooled to 200 K. After UV light irradiation, the NMR signal assigned to **1** completely disappeared and the new

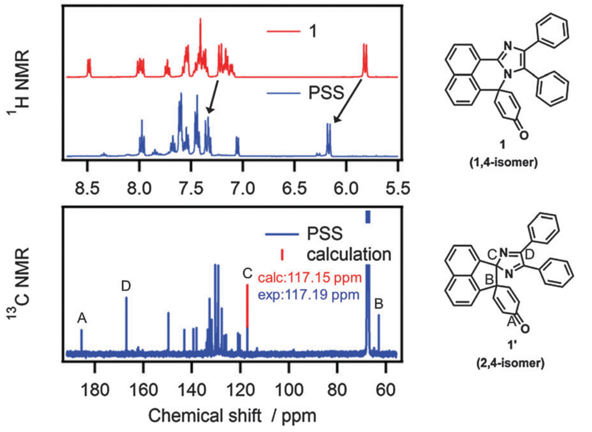

Fig. 3 ^{1}H and ^{13}C NMR spectra of the Me-THF solution of **1** and those at the PSS under UV light irradiation (365 nm, 4 mW) at 200 K. The theoretical ^{13}C peak was calculated for the optimized molecular geometry of the 2,4-isomer.

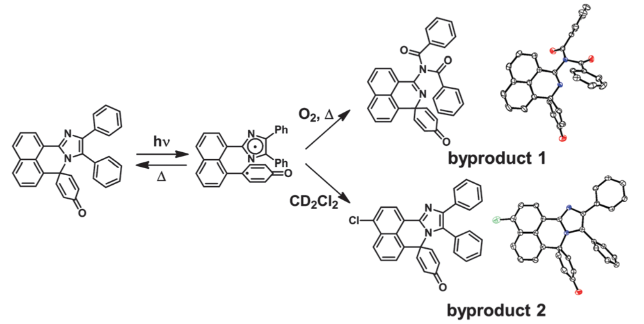

Fig. 4 Reaction scheme to generate the byproducts and the ORTEP representations of the molecular structures of the byproducts generated from **1** with thermal ellipsoids (50% probability), where nitrogen, oxygen and chlorine atoms are highlighted in blue, red, and green, respectively.

signals appeared. The two doublet peaks assigned to the protons of the cyclohexadienone ring were shifted after the photo-isomerization reaction, indicating that there was a change in the binding mode between the imidazole ring and the hexacyclodienone ring. The ^{13}C NMR spectrum after UV light irradiation shows a single characteristic peak at 117.19 ppm. The calculated chemical shift, subtracted from the shielding value obtained for TMS by the GIAO-DFT (MPW1PW91/6-31+G(d,p)//MPW1PW91/6-31G(d) level of the theory), indicates that the ^{13}C NMR peak at 117 ppm can be attributed to the sp^3 carbon on the imidazole ring of the 2,4-isomer. The colorless isomer of BN-PIC which has a similar sp^3 carbon on the imidazole ring also shows a single ^{13}C NMR peak at around 110 ppm.[8b] We also carried out time-resolved FT-IR spectroscopy (see ESI†). We observed a shift of the C=O stretching vibration of the cyclohexadienone ring upon UV light excitation, indicating a change in the binding mode between the imidazole ring and the cyclohexadienone ring as well as the result of the NMR spectroscopy. Moreover, the characteristic band at 1557 cm^{-1} in the transient IR spectrum can be ascribed to the C–N stretching vibration on the imidazole ring of the 2,4-isomer. Therefore, we concluded that the 2,4-isomer is generated by UV light irradiation of the 1,4-isomer.

The nanosecond laser flash photolysis measurements of **1–3** did not show any absorption bands assigned to the biradical species. However, the biradical species should be generated just after the C–N bond cleavage reaction of **1–3** as we have definitely demonstrated the generation of the biradical species in the photochromic reactions of the PIC derivatives.[9] Efficient demonstration of the generation of the radical species is necessary to reveal the specific reaction of the radical species.[12] As previously reported, the triphenylimidazolyl radical reacts with molecular oxygen, resulting in the generation of O_2 adducted products.[13,14] The typical reaction between the imidazolyl radical and molecular oxygen produces a byproduct which has a dioxetane structure, which demonstrates the thermal degradation of the imidazole ring.[14] Therefore, we isolated **byproduct 1** generated after 365 nm light irradiation of **1** in CD_2Cl_2 at 200 K, using SiO_2 column chromatography (CH_2Cl_2/AcOEt = 20/1). The X-ray crystallographic analysis of **byproduct 1** revealed that the imidazole ring was decomposed by the reaction of the photogenerated imidazolyl radical with molecular oxygen (Fig. 4) because the lifetime of the photogenerated biradical species of **1** would increase enough to react with molecular oxygen at 200 K. To inhibit the reaction of the biradical species with the molecular oxygen, the CD_2Cl_2 solution was degassed using freeze–pump–thaw cycles. However, **1** quickly reacts with CD_2Cl_2 upon UV light irradiation at 193 K. The X-ray crystallographic analysis for another **byproduct 2** indicates that a hydrogen atom at the 4-position of the naphthalene moiety is substituted with a chlorine atom (Fig. 4), which is also supported by HR-ESI-TOF-MS (Fig. S25, ESI†). These results show the generation of the biradical species as short lived intermediates upon UV light irradiation as shown in Scheme 1.

Because it is difficult to estimate the extinction coefficient of the short-lived biradical species, the quantum yield for the photogeneration of the biradical species could not be definitely determined. In contrast, the conversion efficiencies of **1**, **2**, and **3** from the 1,4-isomer to the 2,4-isomer can be experimentally estimated using laser actinometry.[15] The conversion efficiencies of **1**, **2**, and **3** were estimated to be 0.18, 0.06, and 0.04, respectively, by using benzophenone as a standard (see experimental details in ESI†). DFT calculations suggest that the activation free energy barrier for the thermal recombination reaction from the biradical species into the 2,4-isomer is smaller than that into the 1,4-isomer (Fig. S51, ESI†). This result supports the idea that the 2,4-isomer is kinetically generated through the thermal recombination reaction of the photogenerated biradical species upon UV light irradiation. The thermodynamics and reaction kinetics of the negative photochromism are discussed in ESI.†

Finally, we demonstrated chiroptical switching with the negative photochromism of **2** which has chirality originating from the asymmetric carbon. Both enantiomers of **2** were optically resolved using chiral HPLC and recrystallization. The optical purities of the *R*- and *S*-enantiomers were up to 99% ee (Fig. S29, ESI†). Fig. 5 shows the circular dichroism (CD) spectra of the Me-THF solution of **2** and those at the PSS upon UV light irradiation at 153 K. The absolute configuration of

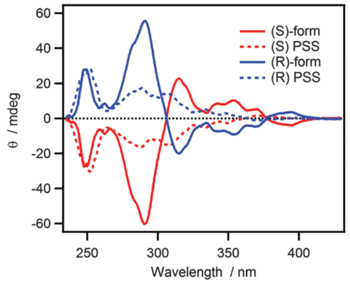

Fig. 5 CD spectra of the Me-THF solution of **2** (solid line) and those at the PSS (dashed line) under 365 nm light irradiation (10 mW) at 153 K.

each enantiomer is determined by the comparison of the Cotton effect with the configuration estimated from the TDDFT calculation (Fig. S48, ESI†). The large Cotton effect mainly originates from the electronic transition between the diphenylimidazolyl naphthalene and the naphthalenone moieties which are perpendicularly arranged around the asymmetric carbon. On the other hand, this Cotton effect could not be observed in the CD spectra at the PSS. The CD spectra at the PSS are simulated by the TDDFT calculation for the 2,4-isomer (Fig. S50, ESI†). Moreover, no racemization was observed after repetitive UV light irradiation. These results indicate that rapid switching of the chiroptical properties will be expected especially by using Np-NIC derivatives as the chiral dopants for chiral nematic liquid crystals.

In conclusion, we developed novel Np-PIC derivatives and investigated the fast negative photochromic reaction in detail. We succeeded in accelerating the thermal back reaction to the time scale of milliseconds which is suitable for the real-time switching of the fluorescence and for holographic materials. The hypochromic effect in the UVA region was clearly observed with the negative photochromic reaction due to there being less conjugation in the transient 2,4-isomer as compared to the stable 1,4-isomer. The very short life-time of the photogenerated biradical species within nanosecond time scales gives excellent fatigue resistance against repetitive laser excitation at room temperature. Although it was difficult to design the fast negative photochromic compounds, the simple molecular designs and the ease of the functionalization to Np-PIC will open up possibilities for the attractive development of photochromic compounds. Moreover, fast negative photochromism will become a powerful tool as a light-trigger to induce instantaneous stimuli and to control phenomena in the condensed condition.

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