JACS
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Communication

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Photochromic Phenoxyl-Imidazolyl Radical Complexes with Decoloration Rates from Tens of Nanoseconds to Seconds

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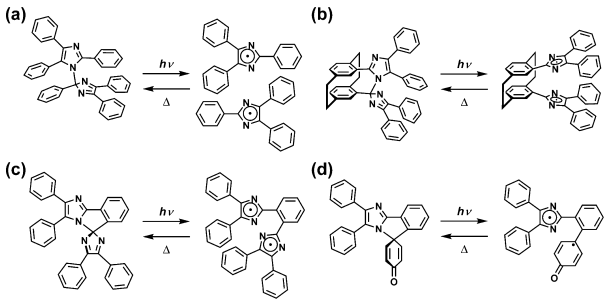
Supporting Information

ABSTRACT: We report a novel photochromic molecular system, phenoxyl-imidazolyl radical complex (PIC), in which both a phenoxyl radical site and an imidazolyl radical site are reversibly and simultaneously generated upon UV light irradiation. PIC consists of the three parts: an aromatic linker, a diarylimidazole moiety, and a 4*H*-cyclohexadienone ring. Upon UV light irradiation, the C−N bond between the 4*H*-cyclohexadienone ring and the imidazole ring in the colorless closed-ring isomer of PIC undergoes a homolytic cleavage, leading to the formation of the transient colored open-ring isomer. Based on the substituents on the imidazoyl/4*H*-cyclohexadienone rings and the nature of the aromatic linker, the half-life of the colored open-ring isomer can be varied between tens of nanoseconds and seconds. PIC derivatives containing a 1,2-phenylene linker exhibit high fatigue resistance toward repeated photochromic reactions. Analysis using laser flash photolysis reveals that the absorption spectra of the open-ring isomers are not readily rationalized by a straightforward superposition of the spectra of the two component radical fragments and the photogenerated radicals are electronically coupled through the aromatic linker. Furthermore, the open-ring isomer can be treated as a hybrid of the pure open-shell biradical and closed-shell quinoid resonance structures.

Photochromism is simply defined as a light-induced, reversible transformation of a chemical species between two forms that have different absorption spectra. Photochromic materials are a well-known class of molecules that change their color upon irradiation with light. Fast photochromic molecules whose coloration−decoloration cycle completes in microsecond to millisecond time scales can be used as a trigger pulse to induce unfolding of proteins,[1,2] motions of protein motors,[3] and isomerization of DNAs[4,5] in addition to switchable fluorophores for super-resolution imaging[6−8] and industrial applications such as holographic displays[9,10] and security-recognition devices.[11] Organic radicals are usually encountered in the study of organic photochromism because homolytic bond cleavage is a common reaction pathway preferred by the excited state molecules. Upon UV light irradiation, hexaarylbiimidazole (HABI) generates a pair of 2,4,5-triphenylimidazolyl radicals (TPIRs) via the homolytic cleavage of the C−N bond between the two imidazole rings (Scheme 1a).[12] In the dark, TPIRs slowly dimerize to regenerate

Scheme 1. Photochromism of (a) HABI, (b) [2.2]PC-Bridged Imidazole Dimer, (c) PABI, and (d) PIC



the colorless HABI. Since the discovery of HABI and its photoinduced chemical transformation, other photochromic bridged imidazole dimers have been developed. Subsequent generations of photochromic imidazole dimers have contained a linker between the two imidazole rings capable of restricting the diffusion of imidazolyl radicals and ensuring control over the rate of decoloration, which varied between a few microseconds and hundreds of milliseconds.[13−18] Previously, we developed a unique series of photochromic [2.2]PC-bridged imidazole dimers, wherein the [2.2]paracyclophane ([2.2]PC) moiety linked two diphenylimidazole groups (Scheme 1b).[14,17] Solutions of these dimers exhibit instantaneous coloration upon exposure to UV light and the colors fade rapidly in the dark. The rapid response exhibited by these photochromic imidazole dimers make them suitable for use as excellent probes and triggers to reveal and control phenomena that occur in similar time scales (tens of milliseconds). However, previously reported radical-generating photochromic molecules are dimers of two structurally identical radicals such as substituted imidazoles or tetraphenylpyrryls.[19] Except for the [2.2]PC-bridged imidazole dimers (where the substitution patterns on the imidazole rings are different), photochromic materials generating two structurally and electronically different radicals have not been previously reported. Here we report the photochromic behavior of a novel photochromic compound, phenoxyl-imidazolyl radical complex (PIC), which generates two different radical species when irradiated with light (Scheme 1d). Though the radical dimers connected between the carbon atoms at the 4-position of 2,6-di-*tert*-butylphenoxyl radicals are reported,[20,21] the radical complex

Received: March 5, 2015

DOI: 10.1021/jacs.5b02353
J. Am. Chem. Soc. XXXX, XXX, XXX−XXX

consisting of a phenoxyl radical and another radical has not been demonstrated. The basic concept of the molecular design of PIC is inspired by the similarities in the reactivity of the oxidation products between phenol and imidazole. This report presents the first instance of the simultaneous generation of phenoxyl and imidazolyl radicals upon light irradiation.

Our experience with the synthesis and study of the photochromic pentaarylbiimidazole (PABI) (Scheme 1c) guided the design of PIC (Scheme 1c). PABI is easy to synthesize, exhibits rapid photochromic response (on the order of few microseconds), and also exhibits high fatigue resistance toward repeated photochromic reactions.[22] Furthermore, even when incorporated in a polymer matrix, PABI retains its rapid response and exhibits no residual color when the light source is removed. PIC can be considered as a PABI analogue, wherein the 2*H*-imidazole motif is replaced with the 4*H*-cyclohexadienone motif. PIC derivatives are readily prepared using readily accessible reagents (Figure 1a). In the final step toward the synthesis of

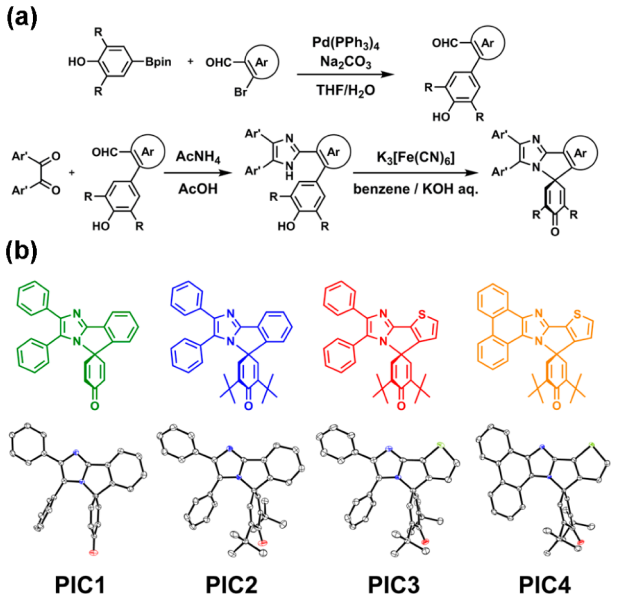


Figure 1. (a) General synthetic scheme of PIC derivatives, where Bpin = 4,4,5,5-tetramethyl-1,3,2-dioxaborolanyl, and (b) ORTEP representations of the molecular structures of **PIC1**−**4** with thermal ellipsoids (50% probability), where nitrogen, oxygen, and sulfur atoms are highlighted in blue, red, and green, respectively.

PABI, oxidation of the precursor affords a colored bisimidazolylradical[23−27] (open-ring isomer), which readily undergoes an intramolecular cyclization, resulting in the formation of the C−N bond between the adjacent imidazole rings and affording the colorless closed-ring isomer. Along similar lines, the colorless closed-ring isomers of PIC derivatives are obtained as a result of intramolecular recombination of the phenoxyl and imidazolyl radicals. All PIC compounds consist of the three critical structural motifs: an aromatic linker, the diarylimidazole moiety, and the 4*H*-cyclohexadienone ring. We synthesized four PIC derivatives, **PIC1**−**4** (Figure 1b). X-ray diffraction analyses of the crystals of the PIC derivatives have confirmed the molecular structures of the closed-ring isomers. The imidazole ring and the ring of the aromatic linker occupy a single plane, while the plane of the 4*H*-cyclohexadienone ring is oriented perpendicular to this plane.

The photochromic behavior of PIC is considered to be the result of a homolytic cleavage of the C−N bond, i.e., the bond between the C-4 of the 4*H*-cyclohexadienone ring and the N-1 of the imidazole ring. Frontier molecular orbitals of the closed-ring isomer of PIC are similar to those of PABI, suggesting that the lowest excited states of PABI and PIC derivatives are similar (Figure S64). DFT calculations of PIC derivatives provide further support in favor of the homolytic cleavage on irradiation by light since LUMOs of the molecules containing the relevant C−N bond exhibit antibonding characteristics. Next, we measured the electron spin resonance (ESR) spectra of the light-irradiated benzene solutions of PIC derivatives to confirm the formation of radical species. Though ESR signals were not detected for solutions of **PIC1**, **PIC2**, and **PIC4**, which is attributed to the low levels of open-ring isomers under continuous UV light irradiation (see below), an ESR signal representing a paramagnetic species with unpaired electrons was observed for the solution of **PIC3** at room temperature (Figure S63). When the irradiation was stopped, the ESR signal instantaneously disappeared. This observation is an evidence for the homolytic cleavage of the C−N bond. While the ring-opening reaction of the five-membered ring of PIC derivatives is reminiscent of the dihydroindolizines-based photochromic molecules, it must be noted here that the former generates radicals and that the latter affords a zwitterionic species.[28,29]

Flash photolysis experiments were performed using a nanosecond laser pulse as an excitation light source to investigate the photochromic behaviors of PIC derivatives. While the pulse repetition rate for the measurements for **PIC1**, **PIC2**, and **PIC3** were 10, 10, and 0.1 Hz, respectively, the data for **PIC4** was obtained by a single shot irradiation of the laser pulse. Transient absorption spectra and decay profiles of the open-ring isomers of PIC derivatives are shown in Figure 2a−e. Contribution to the absorption spectra from any triplet−triplet absorption can be excluded since these spectra were little affected by the presence of molecular oxygen (Figures S58−S61). Through rational design of the molecules, half-lives of radical species can be varied over a wide time range, from tens of nanoseconds to seconds. Moreover, it is worth noting that **PIC1** readily undergoes several coloration−decoloration cycles despite the absence of the bulky *tert*-butyl groups on the carbons ortho to the phenolic carbon. No significant differences are observed when the decay profile of a freshly prepared solution of open-ring isomer of **PIC1** is compared to that measured for the sample after 13,000 exposures to laser pulses (335 nm; 5 ns duration; and 4 mJ power). This indicates that **PIC1** can undergo fatigue resistant photochromic reactions (Figure S54). Intriguingly, phenoxyl radicals unencumbered by bulky groups are highly reactive.[30] However, in the case of **PIC1**, it is very likely that the reaction of the phenoxyl radicals with intramolecularly accessible diphenylimidazolyl radical takes precedence over other potential intermolecular reactions; the diphenylimidazolyl radical moiety sterically stabilizes the phenoxyl radical. In addition, the spin delocalization through the 1,2-phenylene linker contributes to the thermodynamic stabilization of phenoxyl radical. It is likely that the two factors, proximity to the diphenylimidazolyl radical and spin delocalization, contribute to the observed stability of the open-ring isomer of **PIC1** in spite of the absence of bulky substituents that are typically installed to prevent access to the highly reactive phenoxyl radical.

Our studies reveal that the half-life of the open-ring isomer, i.e., the rate of decoloration, is predominantly dependent on the molecular structure of the open-ring isomer. A possible structural change in a coloration−decoloration cycle begins when the C−N bond starts breaking on the excited state potential energy surface.

DOI: 10.1021/jacs.5b02353
J. Am. Chem. Soc. XXXX, XXX, XXX−XXX

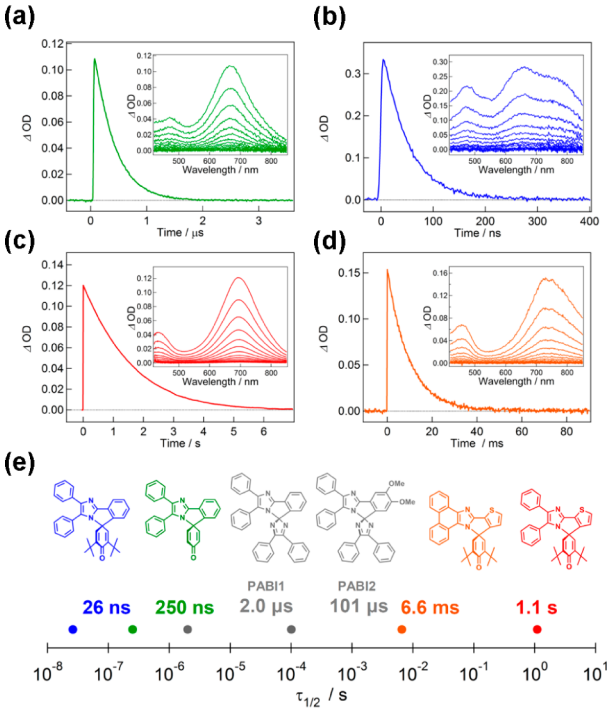


Figure 2. Decay profiles of the open-ring isomers of (a) **PIC1**, (b) **PIC2**, (c) **PIC3**, and (d) **PIC4** in degassed benzene at 25 °C (excitation wavelength, 355 nm; pulse width, 5 ns; power, 4 mJ/pulse; the concentrations of **PIC1**, **PIC2**, **PIC3**, and **PIC4** are 1.0×10^{-3}, 1.0×10^{-3}, 6.1×10^{-5}, and 2.4×10^{-5} M, respectively). Insets of panels a–d show transient absorption spectra of the open-ring isomers of **PIC1–4**. (e) Plots of the half-lives of the open-ring isomers of PIC and PABI derivatives on a logarithmic time scale.

The planes containing the aromatic rings of the phenoxyl and imidazolyl radicals, which are oriented perpendicular to each other as the C–N bond is broken, are reoriented as the phenoxyl radical rotates in an attempt to form the π-bond. However, the steric repulsion between the phenoxyl and imidazolyl radicals precludes the open-ring isomer from adopting the planar quinoidal conformation. The conformation adopted by the open-ring isomer is a key factor that regulates the $\Delta G^{\ddagger}$ of the ring-closing reaction (C–N bond formation) that leads to the regeneration of the colorless closed-ring isomer. Open-ring isomers of **PIC1** and **PIC2** have half-lives of 250 and 26 ns in benzene at 298 K, respectively. The difference in the half-lives of these molecules can be rationalized based on the effect of the substituted *tert*-butyl groups. The presence of the bulky *tert*-butyl groups on the carbons ortho to the phenolic carbon forces the open-ring isomer to adopt a nonplanar twisted conformation. As the energy of the open-ring conformer of the **PIC2** is closer to that of the transition state in the ring-closing reaction, **PIC2** has shorter half-life than **PIC1**.

The open-ring isomer of **PIC3** displays a half-life of 1.1 s in benzene at room temperature. Replacement of the phenylene ring linker by a thienyl ring effectively prolongs the half-life of the PIC. It is likely that both geometric and electronic characteristics of the thienyl ring significantly contribute to the elongation of the half-life. The conformation of the open-ring isomer is likely to become relatively more planar when the six-membered ring linker is replaced by a five-membered ring, as the steric clash between the phenoxyl and imidazolyl radicals is partially relieved. Furthermore, distance between the bond forming carbon and nitrogen atoms increases, leading to an increase in the $\Delta G^{\ddagger}$ of the ring-closing reaction. The nature of thiophene, which is less aromatic when compared with benzene, also influences the electronic structure of the open-ring isomer (see below).[31] Meanwhile, replacement of the diphenylimidazole with a rigid phenanthroimidazole can create higher barriers for the adoption of a planar conformation and further decrease the stability of the open-ring isomer. Not surprisingly, the half-life of the open-ring isomer of **PIC4** (6.6 ms) is nearly 3 orders of magnitude shorter than that of **PIC3**, indicating the decrease in the $\Delta G^{\ddagger}$ of the ring-closing reaction in the case of **PIC4**. Rate constants and activation parameters for the ring-closing reactions, half-lives for the open-ring isomers of PABI, and PIC derivatives are summarized in Table 1.

Table 1. Rate Constants and Activation Parameters for the Ring-Closing Reaction, Half-Lives for the Open-Ring Isomers of PABI1, PIC1–4 in Degassed Benzene at 25 °C; Molecular Structure of PABI1 Is Shown in Figure 2e

	k [s^{-1}]	$\tau_{1/2}$ [s]	$\Delta H^{\ddagger}$ [kJ/mol]	$\Delta S^{\ddagger}$ [J/mol·K]	$\Delta G^{\ddagger}$ [kJ/mol]
PABI1	3.5×10^{5}	2.0×10^{-5}	35.4	−20.0	41.4
PIC1	2.8×10^{6}	2.5×10^{-7}	31.7	−14.9	36.2
PIC2	2.6×10^{7}	2.6×10^{-8}	26.3	−15.1	30.7
PIC3	6.4×10^{-1}	1.1×10^{0}	66.7	−26.1	74.5
PIC4	2.2×10^{2}	6.6×10^{-3}	55.5	−19.5	61.3

From the valence bond approach, the electronic structure of the open-ring isomer has significant contributions from both open-shell biradical and closed-shell quinoid resonance structures. The quinoid resonance structure, with its ability to form the π-bond, is more stable than the biradical structure; however, the quinoid resonance structure loses the resonance energy. When the resonance energy is large enough to compete with the stabilization energy associated with the formation of the π-bond, the contribution from the biradical resonance structure to the electronic structure of the open-ring isomer is negligible. We estimated the energies of the two resonance structures of *o*-quinodimethane and its thiophene analogue by the Hückel approximation. The difference in the energies of the biradical and quinoid resonance structures (ΔE_{BR-Q}) for *o*-quinoidmethane and the thiophene analogue are $1.95|\beta|$ and $2.21|\beta|$, respectively. The larger ΔE_{BR-Q} value in the case of the thiophene analogue indicates that replacement of the phenylene ring with the thienyl ring further minimizes the contribution of the biradical resonance to the open-ring isomer. The quinoid resonance structure prefers the planar conformation, thereby increasing the $\Delta G^{\ddagger}$ of the ring-closing reaction.

The transient absorption spectra of the open-ring isomers are shown in Figure 2 (see inset). The intense absorption bands in the visible region (600–800 nm) can be ascribed to the radical–radical interaction between the imidazolyl and phenoxy radicals. For example, a solution of the open-ring isomer of **PIC2** can be considered as a mixture of two independent radical species, 2,4,5-triphenylimidazolyl radical and 2,6-di-*tert*-butyl-4-phenylphenoxyl radical. The 2,4,5-triphenylimidazolyl radical absorbs light between 500 and 600 nm in addition to a sharp band at ~460 nm, whereas 2,6-di-*tert*-butyl-4-phenylphenoxyl radical has weak absorption peaks at ~348, ~418, ~498, and ~534 nm.[32] It is evident from the absorption spectrum of the open-ring isomer of **PIC2** that it is not simply a superposition of spectra of the imidazolyl and phenoxyl radicals. While the open-shell biradical and the closed-shell quinoid resonance structures contribute to

DOI: 10.1021/jacs.5b02353
J. Am. Chem. Soc. XXXX, XXX, XXX–XXX

the electronic structure of the open-ring isomer, the transient absorption spectra of the open-ring isomer of PIC derivatives indicate the existence of a strong through-bond electron spin exchange coupling. Thus, the wave function of the open-ring isomer of PIC can be described neither by an open-shell biradical state nor a closed-shell quinoidal state; these factors indicate the challenges associated with obtaining the correct wave function by using a simple DFT calculation based on a single Slater determinant. Generally, the theoretical calculation for a biradicaloid species[33] requires the multireference SCF approaches[34] such as CASSCF (complete active space SCF) and CASPT2 (CASSCF with second order MP perturbation theory), which are too expensive for straightforward application to large conjugated systems as PIC derivatives.

In conclusion, we report a novel photochromic molecular system based on phenoxyl and imidazolyl structural motifs. The molecules disclosed here represent the first example of a family of photochromic compounds that generate two structurally and electronically different stable radicals upon UV light irradiation. It should be emphasized here that the colored open-ring isomer of **PIC1** is stable despite the absence of *tert*-butyl groups on the carbons ortho to the phenolic carbon. Moreover, we have developed a strategy for controlling the $\Delta G^{\ddagger}$ of the ring-closing reaction, allowing for an ability to tune and predict the half-lives of the open-ring isomers. The half-lives of the colored open-ring isomers of PIC derivatives span a wide range of half-lives, i.e., from tens of nanoseconds to seconds. A rigorous analysis of the absorption spectra of the open-ring isomer of a PIC derivative is a nontrivial task and is considerably more complex than the straightforward superposition of the spectra of its structural fragments. The design of PIC, two structurally and electronically distinct moieties connected through a linker, the modifications of which can regulate the rate of photochromic reactions, provides a unique platform to develop and study various radical complexes leading to a new direction in radical chemistry.

■ ASSOCIATED CONTENT

Supporting Information

Synthesis, ^{1}H NMR, HR-ESI−TOF−MS spectra, HPLC chromatogram, X-ray crystallographic analysis, UV−vis absorption spectra, ESR spectrum, experimental detail for laser flash photolysis measurements, kinetics for the ring-closing reaction in benzene, DFT calculations, and the movie for the photochromic behavior of **PIC3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported partly by the Core Research for Evolutionary Science and Technology (CREST) program of the Japan Science and Technology Agency (JST) and a Grant-in-Aid for Scientific Research on Innovative Areas “Photosynergetics” (No. 26107010) from MEXT, Japan. Financial assistance for this research was also provided by the MEXT-Supported Program for the Strategic Research Foundation at Private Universities, 2013−2017.

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DOI: 10.1021/jacs.5b02353
J. Am. Chem. Soc. XXXX, XXX, XXX−XXX