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Thiophene-Substituted Phenoxyl-Imidazolyl Radical Complexes with High Photosensitivity

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Phenoxyl-imidazolyl radical complex (PIC) is a novel photochromic compound which generates two nonequivalent radicals upon UV light irradiation. While the color fading speed of PIC can be tuned from tens of nanoseconds to seconds, the low visible sensitivity has limited their potential applications. Here, we developed novel thiophene-substituted PIC derivatives. The visible sensitivity and the increased absorption coefficient were achieved with sustaining the moderate color fading speed by introducing a phenyl group at the 5-position of the thiphene ring.

Photochromism has been extensively studied more than several decades not only from the view points of the fundamental science but also practical applications in industry.[1,2] Among bunch of reported photochromic compounds, fast T-type photoswitch compounds such as bridged imidazole dimers,[3–6] naphthopyrans,[7] oxazines,[8–10] and azobenzene derivatives[11–13] have been paid much attentions because of their potentials for the applications to fluorescent switches,[14–18] dynamic holographies,[19,20] security materials, and photochromic lenses. Recently, pentaarylbiimidazole (PABI)[21] and phenoxyl-imidazolyl radical complex (PIC)[22] were reported as novel fast photoswitch molecules. The color fading speed of these molecules can be tuned from tens of nanoseconds to seconds by changing the radical units or the aryl units in which two radicals are substituted. Thiophene substituted PIC (compound **1** in scheme 1) shows the color fading with a half-life of 1.1 s at 298 K. The time scale from tens of milliseconds to seconds is one of the most important time scale for practical applications involving human daily lives because the time resolution of the human vision is tens of milliseconds. In addition, to develop novel photochromic materials which induce instantaneous dense color changes by photochromic reactions, the slightly slow rate of the thermal back reaction is suitable. It can be easily understood by considering the simple AB system, where the initial A species is

Scheme 1 Photochromic reaction schemes of (a) **1** and **1-Phe**, and (b) **2** and **2-Phe**.
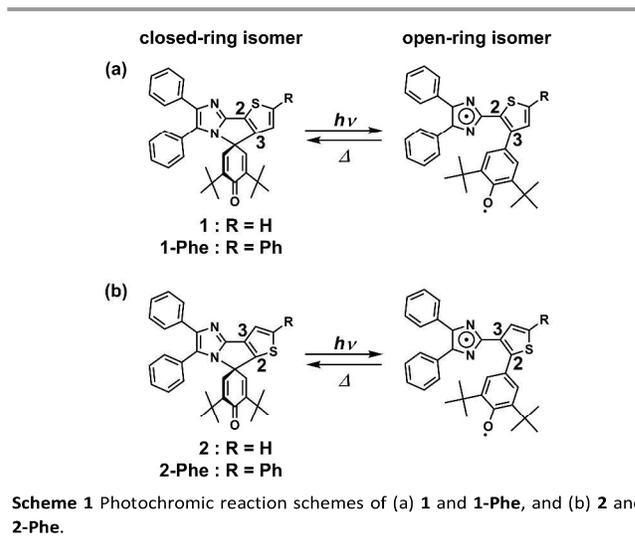
converted to the B species by light irradiation and the back reaction only occurs thermally (the rate constant is written as k_{BA}). The absorbance of B at the photostationary state (Abs_{PS}) can be derived from the rate equation as follows (see electronic supporting information (ESI) for details):[23]

$$Abs_{PS} = \frac{\phi_{AB}\varepsilon_A I_0 F}{k_{BA}+\phi_{AB}\varepsilon_A I_0 F}[A]_0 \varepsilon_B' l \qquad (1)$$

where ϕ_{AB} is the quantum yield of the reaction from A to B, ε_A is the absorption coefficient of A at the excitation wavelength, ε_B' is the absorption coefficient of B at the probe wavelength, I_0 is the total amount of light absorbed by the reaction medium, F is the photokinetic factor depending on the total absorbance at the excitation wavelength, $[A]_0$ is the initial concentration of the A species, and l is the thickness of the sample, respectively. This equation suggests that the color fading speed slower than
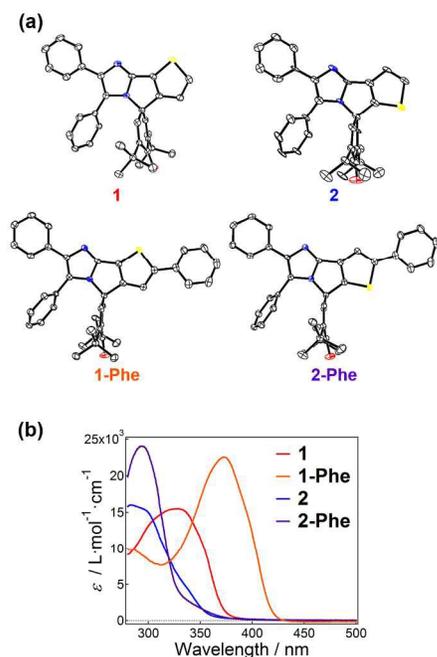
Fig. 1 (a) ORTEP representations of the molecular structures of **1**, **2**, **1-Phe**, and **2-Phe** with thermal ellipsoids (50% probability), where nitrogen, oxygen, and sulfur atoms are highlighted in blue, red, and yellow, respectively. (b) Steady-state absorption spectra of **1**, **2**, **1-Phe**, and **2-Phe** in benzene at 298 K under Ar-saturated condition.

hundreds of milliseconds and the high absorption coefficient (and the high efficiency for the photochromic reaction) are important for high absorptive photochromic films (see ESI for the details). However, while the rate of the thermal back reaction of the thiophene-substituted PIC is sufficiently moderate, the compound is only sensitive to UV light. Therefore, the sensitization of PIC systems to the visible region is necessary for the practical applications such as photochromic lenses.

In this study, we synthesized thiophene-substituted PIC derivatives, **1**, **2**, **1-Phe**, and **2-Phe** (Scheme 1). By substituting a phenyl group at the 5-position of the thiophene ring, the visible sensitization and the increased absorption coefficient were achieved in **1-Phe** with sustaining the moderate fading speed. The tunings of the visible sensitization and the rate of the thermal back reaction are discussed in detail.

As shown in Scheme 1, all PIC derivatives cleave the C–N bond between the imidazole ring and the cyclohexadienone ring upon UV light irradiation and form the open-ring isomers. A phenyl ring is substituted to the 5-position of the thiophene ring to sensitize the PIC derivatives to visible light. We developed PIC derivatives whose imidazole and cyclohexadienone rings are substituted at the 3- and 2-positions of the thiophene ring, respectively (**2** and **2-Phe**). Since it has been known that the 5-position of the thiophene ring is more conjugated with the π-chromophore at the 2-position than at the 3-position of the thiophene ring, the comparison of **1-Phe** and **2-Phe** (as well as **1** and **2**) gives deeper insights of the effect of the substitution on the bathochromic shift and the color fading speed.

The target compounds were synthesized according to the schemes as shown in the ESI. Molecular structures of all compounds were unambiguously determined by X-ray crystallographic analyses as shown in Fig. 1a. In all compounds, the thiophene ring is coplanar to the imidazole ring, while these two parts are perpendicular to the cyclohexadienone ring.

Steady-state absorption spectra of the synthesized compounds are shown in Fig. 1b. The absorption peak of **1** is located at 328 nm, while that of **2** is located at 284 nm, which is largely blue shifted as compared to that of **1**. The DFT calculations suggest that the longest absorption band of **1** is assigned to the π-π* transition around the imidazole ring and the thiophene ring (Figs. S39–42). This result shows that the substituent at the 2-position effectively conjugates with the thiophene ring while that at the 3-position suppresses the π conjugation with the thiophene ring. The effect of the π conjugation on the position of the substituent at the thiophene ring is more pronounced in **1-Phe** and **2-Phe**. The absorption peak of **1-Phe** shifts 45 nm to the longer wavelength as compared to that of **1**. On the other hand, the absorption peak of **2-Phe** is almost identical to that of **2**. This result can be also interpreted that the imidazole ring at the 2-position of the thiophene ring effectively conjugates with the phenyl ring at the 5-position of the thiophene ring, while the imidazole ring at 3-position does not conjugate with the phenyl ring at the 5-position of the thiophene ring. The absorption coefficients of **1-Phe** and **2-Phe** are larger than those of **1** and **2** due to the substitution of the phenyl ring. Since the substitution can be easily achieved by the Suzuki-Miyaura cross-coupling reaction, this synthetic approach would be useful to extend the visible sensitivity and to increase the absorption coefficient.

Electron spin resonance (ESR) measurements were performed to confirm the radical characters of the open-ring isomers. Figs. S26-29 show the ESR spectra of **1**, **2**, **1-Phe**, and **2-Phe**. All compounds show clear ESR signals, which show that all compounds generate radical species upon UV light irradiation. The ESR signals are split into several peaks due to the hyperfine coupling and exchange interaction between the two radical sites. It indicates that the imidazolyl and phenoxyl radicals are coupled in the open-ring isomers. However, it was difficult to reveal the exchange interactions of the two radical sites because it has been reported that the imidazolyl radical itself has the complicated ESR spectrum due to the delocalization of the radical over the phenyl rings and because the hyperfine coupling constant of the monoradical is difficult to be determined.[24]

Fig. 2 shows the time evolutions of the transient absorption spectra of **1**, **2**, **1-Phe**, and **2-Phe** in benzene (6.7×10^{-5}, 9.2×10^{-5}, 4.9×10^{-5}, and 6.0×10^{-5} M, respectively) excited with the 365-nm continuous wave (CW) UV light (ca. 100 mW). The absorption spectrum of the open-ring isomer of **1** shows three peaks at 345, 432, and 695 nm. The transient absorption spectrum of **2** is very similar to that of **1** irrespective of their different steady-state absorption spectra. This result indicates that the flipping the substituted position of the imidazolyl and phenoxyl radicals between the 2- and 3-positions of the thiophene ring does not affect the absorption spectra of the
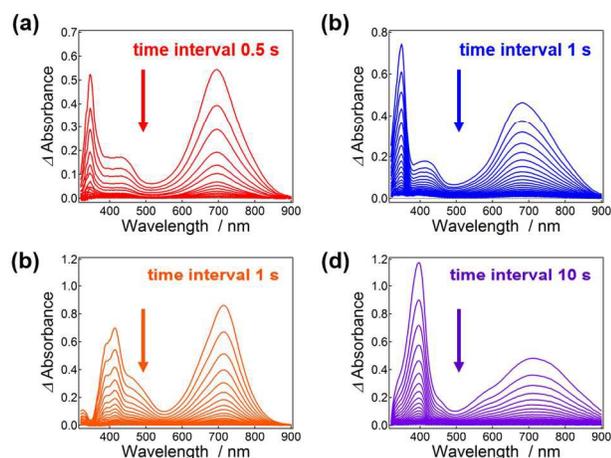
Fig. 2 Transient absorption spectra of **1**, **2**, **1-Phe**, and **2-Phe** in benzene (6.7×10^{-5}, 9.2×10^{-5}, 4.9×10^{-5}, and 6.0×10^{-5} M, respectively) after irradiating the 365-nm CW light (100 mW) at 298 K under Ar-saturated condition.

Fig. 3 Time profiles of the transient absorbance of **1**, **2**, **1-Phe**, and **2-Phe** (6.7×10^{-5}, 9.2×10^{-5}, 4.9×10^{-5}, and 6.0×10^{-5} M, respectively) in benzene excited by CW 365-nm light (100 mW) and probed at 700 nm at 298 K under Ar-saturated condition. The UV light was irradiated for 30 s in all solutions.

radical species. That is, the imidazolyl and phenoxyl radicals are strongly coupled in the radical species of **1** and **2**. The absorbance change at 695 nm of **1** as compared to that at 345 nm looks larger than that of **2** due to the superposition of the ground state bleach signal at around 345 nm (see Figure S34). The absorption spectrum of the open-ring isomer of **1-Phe** contains similar bleach effect at the shorter wavelength. The absorption spectra of the open-ring isomers of **1-Phe** and **2-Phe** shift to the longer wavelength as compared to those of **1** and **2** due to the extended π-conjugation by the phenyl ring at the 5-position of the thiophene ring. While the spectral shape of **1-Phe** at 714 nm is similar to that of **1**, the absorption band of **2-Phe** is slightly broadened as compared to that of **2**. The photochromism of **1-Phe** can be also initiated with 400-nm CW light (full width half maximum is 10 nm and power is 3 mW) as shown in Figures S30 and S31. This shows that the visible sensitivity of the PIC system can be efficiently enhanced by the introduction of the phenyl ring to the 5-position of the thiophene ring.

To reveal the absorption coefficients of the open-ring isomers, we measured the absorption spectra at the photostationary state upon 365-nm CW light irradiation (100 mW) at 263 K (Figure S34). Under the low temperature condition, the half-lives of the thermal back reactions of these compounds become several minutes. In such condition, the initial closed-ring isomers are almost completely converted to the open-ring isomers at the photostationary state because the thermal back reaction can be neglected as compared to the forward reactions to generate the open-ring isomers. The absorption coefficients of the open-ring isomers of **1** and **1-Phe** at the peak located at around 700 nm are revealed to be 2.3×10^{4} and 2.6×10^{4} M^{-1} cm^{-1}, respectively. The absorption coefficient of **1-Phe** is slightly larger than that of **1** due to the substitution of the phenyl ring. On the other hand, the absorption coefficients of the open-ring isomers of **2** and **2-Phe** (1.6×10^{4} and 1.1×10^{4} M^{-1} cm^{-1} at the peak located at around 700 nm, respectively) are small as compared to those of **1** and **1-Phe**.
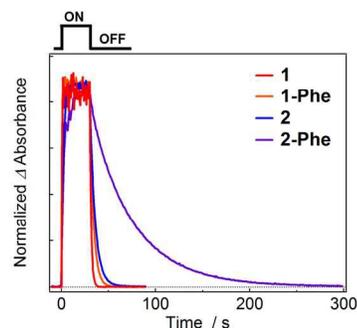
However, since **2** and **2-Phe** are somehow unstable in toluene solution under UV irradiation, these absorption coefficient values may contain the effect of the degradation of the samples. Fig. 3 shows time profiles of the transient absorbance observed at 700 nm after irradiation of the 365-nm UV light for 30 s. Time profiles of the transient absorbance of each compounds are shown in Figs. S35–38. In all compounds, the absorbance increases upon UV irradiation and decays once UV light stops. These decays follow the single exponential decay kinetics and the half-lives at 298 K are 1.1, 3.6, 3.0, and 33 s for **1**, **2**, **1-Phe**, and **2-Phe**, respectively. The thermal back reaction of **1-Phe** was decelerated about three times than that of **1** by substituting the phenyl ring at the 5-position of the thiophene ring. On the other hand, the half-life of the thermal back reaction of **2-Phe** is more than 10 times longer than that of **2**. In the previous report of PABI, the substitution of the donor group to the *para*-position of the radical decelerated the thermal back reaction more than 50 times due to the stabilization of the imidazolyl radical.[21] This result indicates that the effect of the substitution of the phenyl ring at the 5-position on the color fading speed is small in **1-Phe,** while it greatly increases the photosensitivity. In the case of previously reported PABI and PIC systems, while PABI generates two imidazolyl radicals, PIC generates an imidazolyl radical and a phenoxyl radical. The difference between these structures is whether one of the radical is an imidazolyl radical or a phenoxyl radical. On the other hand, the thermal back reaction of PIC (half-life is tens to hundreds of nanoseconds) is largely accelerated as compared to that of PABI (2 μs).[21,22] It indicates that the difference of these structures causes the variation in the speed of the thermal back reactions. That is, it suggests that the phenoxyl radical is less stable than the imidazolyl radical. This discussion can be used to explain the reason why the rate of the thermal back reaction of **2-Phe** is greatly decelerated as compared to that of **1-Phe**. Since the phenoxyl radical is less stable than the imidazolyl radical, the stabilization of the phenoxyl radical by a phenyl ring would be larger than that of the imidazolyl radical. The stabilization of the radical species leads to the increase in the activation energy of the thermal back reaction

by the linear free energy relationship. Since the substituent at the 5-position effectively interacts with the substituent at the 2-position more than that at the 3-position, the phenoxyl radical at the 2-position of the thiophene ring (**2-Phe**) is more stabilized by the phenyl ring at the 5-position of the thiophene ring than the imidazolyl radical at the 2-position of the thiophene ring (**1-Phe**). This clearly explains the reason why the thermal back reaction of **2-Phe** is largely decelerated than that of **1-Phe**.

In conclusion, we developed novel thiophene-substituted PIC derivatives and revealed that the substitution of the phenyl ring at the 5-position of the thiophene ring of **1** is an effective method to increase the visible sensitivity. Since the phenyl ring can be easily substituted by the Suzuki-Miyaura cross-coupling reaction, this method can be a powerful tool for PIC systems to apply various fields of science and technology.

Notes and references

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