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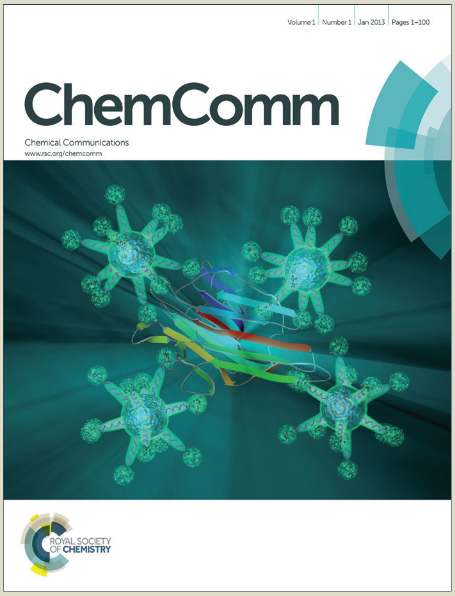

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Rational Molecular Design for Drastic Acceleration of Color-Fading Speed of Photochromic Naphthopyrans

Katsutoshi Arai,[a] Yoichi Kobayashi,[a] and Jiro Abe*[ab]

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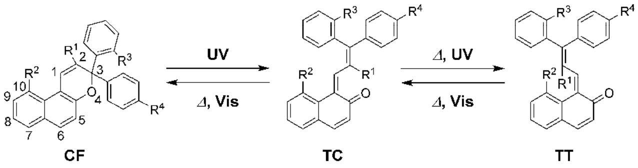
We report rational molecular designs for acceleration of the color-fading speed of photochromic 3*H*-naphthopyrans. By using steric and electrostatic repulsions induced by substituents on the 2– and 10–positions of 3*H*-naphthopyrans, the color-fading speed accelerates from tens of minuites to microsecond time scales. The long-lived residual color, which is an important problem to be solved for industrial applications, can be also suppressed by these strategies.



NP : R^1= H, R^2 = H, R^3= H, R^4 = H
10-Br-NP : R^1= H, R^2 = Br, R^3= H, R^4 = H
2-Br-NP : R^1= Br, R^2 = H, R^3= H, R^4 = H
2,10-Br-NP : R^1= Br, R^2 = Br, R^3= H, R^4 = H
2,10-Ph-NP : R^1= Ph, R^2 = Ph, R^3= $CH(CH_3)_2$, R^4 = OCH_3
2-Py-NP : R^1= Pyrenyl, R^2 = H, R^3= $CH(CH_3)_2$, R^4 = OCH_3

Scheme 1 Photochromic reaction schemes of NP, 10–Br–NP, 2–Br–NP, 2,10–Br–NP, 2,10-Ph-NP and 2-Py-NP.

Since Becker and Michl developed photochromic chromenes in 1966,[1] numerous researches have been conducted and developed various chromene families.[1–10] Among the chromene families, 3*H*–naphtho[2,1-*b*]pyrans (3*H*–naphthopyrans) have been widely studied for fundamental science and applied to commercially available photochromic lenses.[11–24] In the photochromic reaction pathway of naphthopyrans upon UV light irradiation, the cleavage of the C(sp^3)–O bond of the closed form (CF) is initiated from the S_1 state within ps. Then the *transoid–cis* (TC) and *transoid–trans* (TT) isomers are formed through the light-promoted unstable *cisoid–cis* (CC) isomer in ps to tens-of-ps time scales.[25–28] The TC isomer thermally isomerizes to the TT isomer (and vice versa) along the ground state potential surface. The formation ratio of the TC and TT isomers depends on the activation energy barrier between the TC and TT isomers. The TC isomer thermally reverts to the original CF in a few seconds/minutes, whereas the thermal back reaction from the TT isomer to the CF is much slower (several minutes/hours) because the TT isomer is stable and must overcome a relatively large potential energy barrier to isomerize to the TC isomer.[29,30] The residual color by the TT isomer and the slow thermal back reaction of the TC isomer have been considered as one of the important problems to be solved for commercially available photochromic lenses. It has been reported that the formation of the TT isomer of 2*H*–naphtho[1,2-*b*]pyrans (2*H*-naphthopyrans) can be suppressed by bridging between the pyran ring and the naphthalenic core by a fused alkyl chain.[31,32] Though this technique effectively suppressed the formation of the TT isomer, more than 8 synthetic steps were necessary to prepare these compounds. One of the best advantages of naphthopyran-type compounds are easy synthetic schemes with relatively low cost and high durability. Therefore, simpler syntheses are better for applications to the industrial devices. In addition, since naphthopyrans largely change their molecular structures and dipole moments by photochromic reactions, the control of their photochromic reactions will open up novel fast-photoswitch applications such as dynamic holographic materials[33,34] and molecular actuators.[35-37]

In this study, we report a simple strategy to suppress the formation of the TT isomer and to accelerate the thermal back reaction from the TC isomer to the CF. The 3*H*-naphthopyran derivatives and the photochromic reaction investigated in this study are depicted in Scheme 1. The R^1 and R^2 substituted on the 2– and 10– positions are important for the isomerization processes of the TC and TT isomers because the steric and electrostatic repulsions induced by these substituents are expected to strongly affect these isomerization processes. The

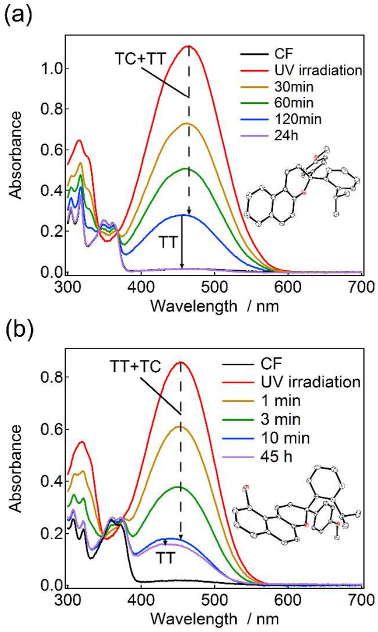


Fig. 1 Absorption spectra of (a) NP (4.9×10^{-5} M) and (b) 10–Br–NP in benzene (4.7×10^{-5} M) at room temperature before and after CW UV light irradiation (365 nm). Insets show ORTEP representations of the molecular structures of each compound with thermal ellipsoids (50% probability). Oxygen atoms are highlighted in red the hydrogen atoms and the solvent molecules are omitted for clarity.

effects of substitutions on the photochromic reactions of naphthopyrans have been extensively investigated especially in industries.[14,38-40] However, almost all those reports deal with the substitutions on 5– to 10– positions and on the phenyl groups at the 3–position to change the color and the fading speed of the generated isomers. Although a recent paper reported the syntheses of naphthopyran derivatives substituted on the 2–position (such as carboxyl and cyano groups), their photochromic properties were not studied.[41] The idea for this study is to destabilize the TT and TC isomers by steric repulsion of the bulky substitutions at R^1 and R^2 positions, which leads to the suppression of the formation of the long-lived TT isomer and the acceleration of the thermal back reaction from the TC isomer to the CF. We apply the bromo, phenyl, and pyrenyl groups as bulky substituents to achieve the fast photochromic 3*H*-naphthopyrans.

Fig. 1a shows absorption spectra of NP before and after continuous wave (CW) UV light irradiation (365 nm). Insets show the ORTEP representations of the molecular structures revealed by X-ray crystallographic analysis. The absorption spectrum before UV light irradiation is assigned to the CF. Upon UV light irradiation, the TC and TT isomers are formed and a strong absorption band appears at around 463 nm. The transient absorption spectra gradually decays with a half–life ($\tau_{1/2}$) of 34 min and an additional long–decay component remains. The slow component decays with $\tau_{1/2}$ = 98 min and disappears within several hours in the dark. The initial fast-decay component is assigned to the thermal back reaction from the TC isomer to the CF. The slow-decay component is assigned to the thermal back reaction from the TT isomer to the CF via the TC isomer. In the case of non-substituted 3*H*–naphthopyran, 3,3–diphenyl–3*H*–naphtho[2,1-*b*]pyran, the half–life of the thermal back reaction from the TC isomer to the CF is 4 sec, which is much faster than that of NP. This result suggests that the isopropyl and methoxy moieties at the phenyl groups at the 3–position decelerate the thermal back reaction from the TC isomer to the CF.

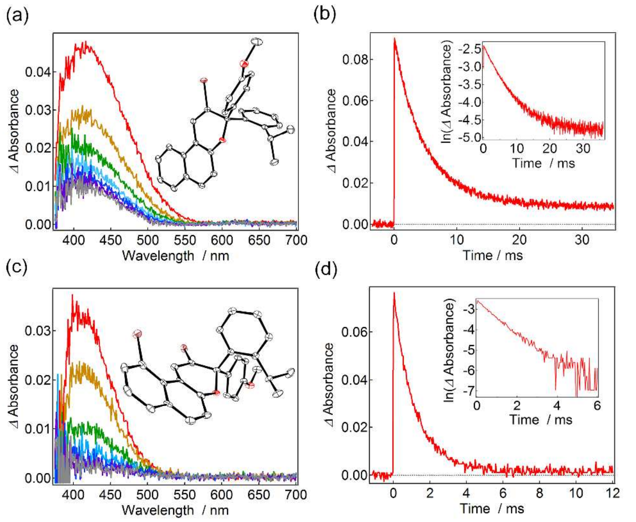


Fig. 2 Transient absorption spectra and dynamics of (a, b) 2–Br–NP (8.5×10^{-5} M) and (c, d) 2,10–Br–NP (2.1×10^{-4} M) in degassed benzene (excitation wavelength, 355 nm; pulse duration, 5 ns; power 7 mJ/pulse). Each of the spectra was recorded at 3 ms and 1 ms intervals after excitation with a nanosecond laser pulse, respectively. Insets of Fig. 2a and 2c show ORTEP representations of the molecular structures of each compound with thermal ellipsoids (50% probability). Oxygen atoms are highlighted in red the hydrogen atoms and the solvent molecules are omitted for clarity. Insets of Fig. 2b and 2d show the logarithmic plots of Fig. 2b and 2d, respectively.

Fig. 1b shows the absorption spectra of 10–bromo substituted NP (10–Br–NP) before and after CW UV light irradiation (365 nm). While the absorption spectra of 10–Br–NP are very similar to those of NP, there are two notable differences between 10–Br–NP and NP. Firstly, the thermal back reaction from the TC isomer to the CF of 10–Br–NP is more than 20 times faster ($\tau_{1/2}$ = 1.3 min) than that of NP. Secondly, the decay of the TT isomer of 10–Br–NP is extremely decelerated and most of the TT isomer remains even after 45 h. The slow thermal isomerization reaction from the TT isomer to the TC isomer of 10-Br-NP compared with that of NP indicates that the activation energy barrier toward the formation of the TC isomer from the TT isomer of 10-Br-NP is larger than that of NP. This idea is supported by the DFT calculations at the CAM-B3LYP/6-31G(d) level of theory (Table S7). The energy levels of the TT isomers are 12.0 and 1.6 kJ mol^{-1} above those of the TC isomers of NP, and 10-Br-NP, respectively. Thus, increasing in the free energy of activation for the TT to TC isomerization is expected for 10-Br-NP from the linear free energy relationship.

Fig. 2a–2d show transient absorption spectra and their dynamics of 2–bromo substituted NP (2–Br–NP) and 2,10–

Table 1 The molar absorption coefficients of the CF at 355 nm (ε_{355}), peak wavelengths of the transient absorption spectra (λ_{max}), half–lives of the fast decays ($\tau_{1/2}$) of the NP derivatives.

Compound	ε_{355} / L mol^{-1} cm^{-1}	λ_{max} / nm	$\tau_{1/2}$
NP	4.6×10^3	465	34 min
10–Br–NP	5.1×10^3	455	1.4 min
2–Br–NP	6.8×10^3	415	2.5 ms
2,10–Br–NP	6.6×10^3	415	0.80 ms
2,10–Ph–NP	8.3×10^3	430	5.1 µs
2–Py–NP	2.1×10^4	452	46 µs

dibromo substituted NP (2,10–Br–NP) observed at 400 nm. The transient absorption spectra of 2–Br–NP and 2,10–Br–NP are very similar to those of NP and 10–Br–NP although the spectrum of 2,10–Br–NP slightly shifts to the red region and becomes broad. On the other hand, the thermal back reactions of 2–Br–NP and 2,10–Br–NP are greatly accelerated ($\tau_{1/2}$ = 2.5 and 0.8 ms, respectively). As can be speculated from Scheme 1, the TC isomers of 2–Br–NP and 2,10–Br–NP have a large steric and electrostatic repulsions between the R^1 group at 2–position and the C=O group. Actually the calculated energy differences between the TC isomer and the CF of 2-Br-NP (66 kJ mol^{-1}) and 2,10-Br-NP (63 kJ mol^{-1}) are about twice larger than those of NP (32 kJ mol^{-1}) and 10-Br-NP (31 kJ mol^{-1}) (Table S7). This is the most probable reason for the acceleration of the thermal back reaction from the TC isomer to the CF in 2–Br–NP and 2,10–Br–NP. Since the half–lives of the thermal back reactions from the TC isomer to the CF of 2–Br–NP and 2,10–Br–NP are similar, the substitution at the 2–position is found to be important to accelerates the thermal back reaction from the TC isomer to the CF. After the fast decay due to the TC isomer, there is a small amount of the relatively slow decay due to the TT isomer in 2–Br–NP. The TT isomer of 2–Br–NP exists at longer time scale, suggesting that the TT isomer is stabilized in a similar manner as 10–Br–NP (Fig. S47, Table S7). On the other hand, the transient absorption dynamics of 2,10–Br–NP does not have a residual component due to the TT isomer and only the single exponential decay due to the TC isomer is observed. These results show that the substitutions of the bromo groups both at the 2– and 10–positions completely suppress the formation of the TT isomer.

Although 2,10–Br–NP effectively suppresses the formation of the TT isomer and accelerates the thermal back reaction from the TC isomer to the CF, the photostability of the halogen substituted compounds are usually not so high. In fact, the transient absorption dynamics of 2,10–Br–NP completely changed after 3000 shots of ns laser pulses (355 nm, power: 5 mJ, Fig. S48). To increase the photostability with simple synthetic procedures, aryl groups are used for the substituents (2,10-Ph-NP) instead of bromo groups because the bromo groups can be easily substituted by aryl groups by the Suzuki–Miyaura cross-coupling reaction. In addition, if the formation of the TT isomer can be suppressed only by the substitution at the 2–position, the synthesis of the fast photochromic naphthopyrans would be much easier than the naphthopyrans substituted on both the 2– and 10–positions. For this reason, 2–pyrenyl substituted derivative (2–Py–NP) was synthesized because the pyrenyl group is larger than the bromo and phenyl groups, and therefore the pyrenyl group is expected to effectively suppress the formation of the TT isomer. It is noteworthy that the synthesis of 2–Py–NP is just 3 steps with high efficiency from commercially available 3*H*–naphthopyran.

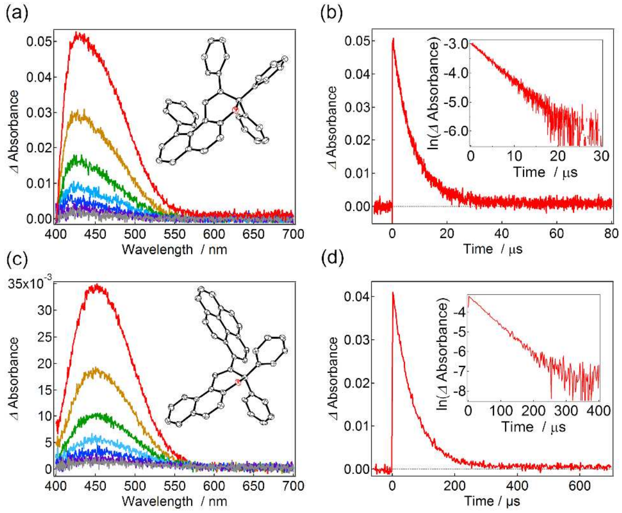


Fig. 3 Transient absorption spectra and dynamics of (a, b) 2,10–Ph–NP (2.6 × 10^{-5} M) and (c, d) 2–Py–NP (7.0 × 10^{-5} M) in degassed benzene (excitation wavelength, 355 nm; pulse duration, 5 ns; power 7 mJ/pulse). Each of the spectra was recorded at 4 µs and 40 µs intervals after excitation with a nanosecond laser pulse, respectively. Insets of Fig. 3a and 3c show ORTEP representations of the molecular structures of each compound with thermal ellipsoids (50% probability). Oxygen atoms are highlighted in red the hydrogen atoms and the solvent molecules are omitted for clarity. Insets of Fig. 3b and 3d show the logarithmic plots of Fig. 3b and 3d, respectively.

Fig. 3a–3d show transient absorption spectra and dynamics of 2,10–Ph–NP and 2–Py–NP in degassed benzene. While these transient absorption spectra are similar to those of 2,10–Br–NP, these dynamics (observed at the 450 nm) are greatly accelerated as compared to those of 2,10–Br–NP. The half–lives of 2,10–Ph–NP and 2–Py–NP are 5.1 and 46 µs, respectively. The acceleration of the thermal back reaction from the TC isomer to the CF is ascribed to the larger steric and electrostatic repulsions by the phenyl and pyrenyl groups. The residual components due to the TT isomer are not observed in both 2,10–Ph–NP and 2–Py–NP, which shows that even the substitution only at the 2–position can effectively suppress the formation of the TT isomer. The molar absorption coefficients of the CF at 355 nm, the peak wavelengths of the transient absorption spectra, half–lives of the fast decays ($\tau_{1/2}$) are summarized in Table 1. The half–lives of the fast decays are accelerated from tens of minutes to microsecond orders with the increase of the size of the substituents (Br, Ph, and Py). The transient absorption signals of 2,10–Ph–NP and 2–Py–NP do not change even after 5000 shots of ns laser pulses (355 nm, power: 5 mJ, Fig. S49 and 50). Furthermore, the color fading of the polymer films containing these compounds completes within several ms and the no residual color remains in the polymer matrices (Fig. S51-S54). These results show that 2,10–Ph–NP and 2–Py–NP are robust and they are promising for fast photoswitch materials in sub ms time regions.

In summary, we demonstrated that the substitutions on the 2– and 10–positions of the 3*H*-naphthopyrans drastically accelerate their color-fading speeds from tens of minutes to μs time regions. These substitutions effectively suppress the formation of the TT isomer and their color fading are still fast in polymer matrices. These simple strategies are important for all naphthopyran derivatives and would have impacts directly on industry as well as the fundamental photochemistry fields. In addition, since photochromism of naphthopyrans induces the large structural and dipole changes, fast photochromic naphthopyrans have potentials for fast-response holographic materials, molecular actuators.

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Notes and references

[a] *Department of Chemistry, School of Science and Engineering, Aoyama Gakuin University, 5-10-1 Fuchinobe, Chuo-ku, Sagamihara, Kanagawa 252-5258, Japan*
E-mail: jiro_abe@chem.aoyama.ac.jp; Fax: +81-42-759-6225; Tel: +81-42-759-6225
[b] *CREST, Japan Science and Technology Agency, K's Gobancho, 7 Gobancho, Chiyoda-ku, Tokyo 102-0076, Japan*

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