Two-Photon-Induced Stepwise Photochromism of Bisnaphthopyran Derivatives

Yuki Inagaki, Katsuya Mutoh, Jiro Abe

Department of Chemistry, Aoyama Gakuin University,
5-10-1 Fuchinobe, Chuo-ku, Sagamihara, Kanagawa 252-5258, Japan
E-mail: jiro_abe@chem.aoyama.ac.jp

There has been increasing interest in the design of molecules including more than two photochromophores in a molecule because of their potential for the advanced optical systems beyond a one-photon chemical reaction of the corresponding monomer. In this study, we have newly designed bispyran derivatives, bis-NP and bis-PQ which have a couple of 3*H*-naphthopyran units and 8*H*-pyranoquinazoline units in a molecule, respectively. Both bispyrans show the drastic bathochromic shift between the one-photon generated isomers (open-closed forms) and the two-photon generated isomers (open-open forms) under UV light irradiation because of the strong synergistic coupling between the two photochromophores. Moreover, bis-PQ shows the rapid sequential color fading with the negligible effect of the long-lived colored *transoid-trans* form (TT form) owing to the intramolecular hydrogen bond in the TC form.[1] To confirm the two-photon absorption process of bis-PQ, the excitation intensity dependence on the amount of the open-open form was investigated by nanosecond laser flash photolysis measurement. The *Δ*absorbance at 610 nm corresponding to the open-open form shows a quadratic dependence on the excitation intensity of the UV laser pulse, indicating that bis-PQ absorbs two photons in a stepwise manner. Furthermore, it is expected that the two-photon absorption also triggers the drastic change in the planarity of these bispyran derivatives. Such characteristic features have a potential for the applications not only to smart windows, sensors and lenses but to molecular actuators.

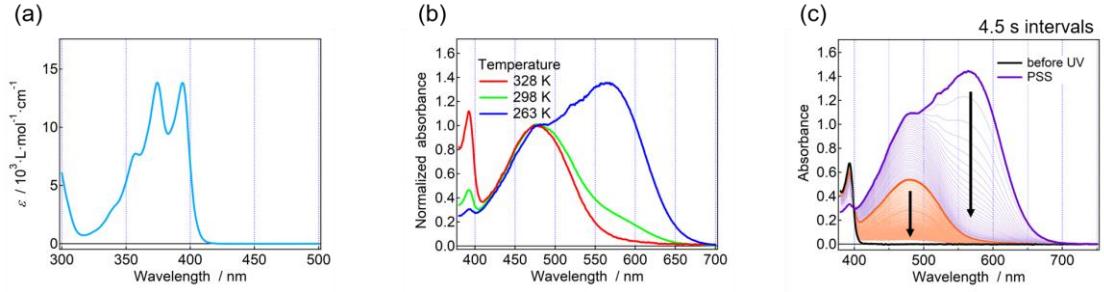

Figure 1. (a) UV-Vis absorption spectrum of bis-PQ in toluene at 298 K. (b) UV-Vis absorption spectra of bis-PQ in toluene (5.0×10^{-5} M) at the PSS under CW UV light irradiation (120 mW) at 263, 298 and 328 K. (c) Time-dependent absorption spectra of bis-PQ in toluene (5.0×10^{-5} M) at 263 K after ceasing the UV light irradiation (365 nm, 120 mW, for 20 s), recored at 4.5 s intervals.

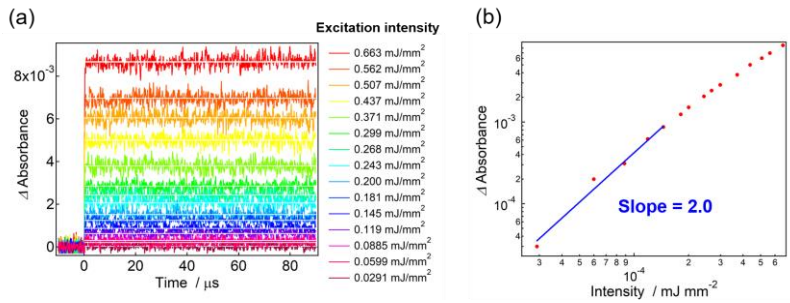

Figure 2. (a) Time profiles of *Δ*absorbance at 610 nm of bis-PQ in toluene (5.0×10^{-5} M) upon single pulse laser excitation with 355 nm (pulse width = 5 ns, pulse energy = 0.092–2.1 mJ) at 298 K. (b) Double logarithmic plots of the average of the *Δ*absorbance at 610 nm of bis-PQ in toluene (5.0×10^{-5} M) monitored for 100 μs just after excitation with 355 nm laser pulse.

[1] Y. Inagaki, Y. Kobayashi, K. Mutoh, J. Abe, *J. Am. Chem. Soc.*, **2017**, *139*. 13429.