Direct Measurement of Photochromic Durability at the Single-molecule Level

Tuyoshi Fukaminato, Tohru Umemoto, Yasuhide Iwata, and Masahiro Irie*
Department of Chemistry and Biochemistry, Graduate School of Engineering, Kyushu University,
6-10-1 Hakozaki, Higashi-ku,Fukuoka 812-8581

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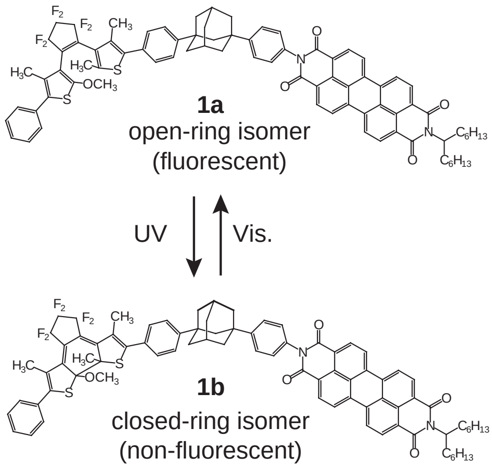
A fluorescent photochromic diarylethene, which has excellent photostability and efficient fluorescence switching character even at the single-molecule level, was synthesized and the fatigue resistant property was quantitatively evaluated.

Photochromic molecules have attracted considerable attention because of their potential application to photonic devices, such as erasable optical memory media and display devices.[1] They can also be used as switching elements to control molecular functions.[2] In these applications, essential properties which the photochromic molecules should posses are thermal irreversibility and fatigue resistance. Among various photochromic molecules,[3] diarylethene derivatives are known to exhibit excellent thermal stability of both isomers and fatigue resistance.[4] Although the thermal stability was quantitatively confirmed by measuring the temperature dependence of the thermal decay of the colored isomers,[5] evaluation of the fatigue resistance was qualitative. In this paper, we report on a quantitative method to evaluate the fatigue resistance.

So far the fatigue resistance was evaluated by measuring the absorption intensity of the colored isomer (or the colorless isomer) after repeated irradiation cycles with UV and visible light.[4a] When the molecule has high fatigue resistance, the absorption intensity remains constant even after many irradiation cycles. The absorption at 530 nm of the hexane solution of bis(2-methylbenzothiophen-3-yl)perfluorocyclpentene upon UV irradiation keeps the intensity as high as 80% of the initial one even after 13000 cycles.[4a] The solution contains a large number of molecules and the number of molecules which undergo photoreaction in each cycle is limited. Not all molecules undergo photoreaction in each cycle. This means the method strongly depends on the concentration of molecules and irradiation conditions, such as power of light and duration of irradiation. If we can measure the photochromic cycles of each molecule, we can say exactly how many times the photochromic cycles can be repeated.

In previous papers,[6,7] it has been shown that photochromic cycles can be directly monitored by measuring the fluorescence switching at the single-molecule level using fluorescent diarylethene derivatives. In these experiments, however, the fluorescent anthracene unit decomposed after a few cycles before the decomposition of the diarylethene switching unit and the durability could not be evaluated. For the durability measurement, it is required to use a robust fluorescent unit. Following fluorescent diarylethene derivative **1a**, which links perylene-3,4,9,10-tetracarboxyl bisimide to 1-(2,4-dimethyl-5-phenylthiophen-3-yl)-2-(2-methoxy-4-methyl-5-phenylyhiophen-3-yl)perfluorocyclo-pentene through an adamantyl unit as a spacer, was synthesized (Scheme 1).



Scheme 1. Photochromism of a fluorescent diarylethene derivative **1**.

The perylenebisimide derivative was chosen as the fluorescent unit because of the photochemical stability, the high fluorescence quantum yield (≈1.0), the low quantum yield of intersystem crossing and the large molar extinction coefficient (88000 $M^{-1}cm^{-1}$ at λ_{max}).[8] The diarylethene unit contains one methoxy group at the reactive carbon. The monomethoxy substituent provides a proper cycloreversion quantum yield for the single-molecule experiment. The structure of **1a** was identified by ^1H NMR, mass spectrum and elemental analysis.[9]

Figure 1 shows the absorption and fluorescence spectral changes upon irradiation with UV light in dichloromethane. The fluorescence intensity decreases when the diarylethene unit converts from the open- to the closed-ring isomers. The quantum yields of photocyclization and photocycloreversion are 0.14 and 1.6×10^{-3}, respectively. The fluorescence quantum yield of the molecule before UV irradiation is 0.98, while it decreases to less than 0.01 in the closed-ring isomer. The decrease of the fluorescence intensity is due to intramolecular energy transfer from the

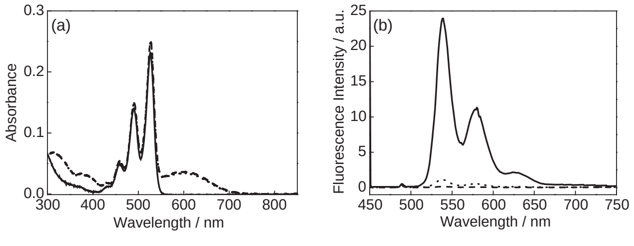


Figure 1. (a) Absorption and (b) fluorescence spectral changes of **1** in CH_2Cl_2 upon irradiation with 313-nm light. The concentration of **1** in CH_2Cl_2 was 2.5×10^{-6} M; (——) open-ring isomer, (- - - - -) closed-ring isomer, (· · · · · ·) photostationary state upon irradiation with 313-nm light.

excited perylene bisimide unit to the closed-ring diarylethene unit.[7]

The fluorescence switching was monitored at the single-molecule level by using a confocal or a total-internal-reflection microscope, equipped with a high NA objective (×100). The sample was excited with circularly polarized 488-nm light from an argon ion laser (Spectra Physics), and the fluorescence was collected, guided suitable filters to remove the excitation light and detected with an avalanche photodiode (APD) detector (Perkin Elmer/EG & G) for intensity trajectory and an electric-cooled CCD camera (Hamamatsu) for imaging, respectively. UV light (325 nm) from a He–Cd laser (KINMON) was used for the photocyclization reaction. The very dilute dichloromethane solution of the closed-ring isomer (10^{-11} M) was spin-coated on a Zeonex polymer film (≈200 nm) and the film was used for the measurement.

Figure 2a shows the fluorescence image of **1a** single molecules under excitation with only 488-nm laser light. In contrast to our previous molecules,[6,7] **1a** exhibited excellent photostability. The average number of the detected photons before photobleaching was around 4×10^5 (Figure 2b). Taking into account the detection efficiency of the measurement system (≈3%), the molecule can be excited around 10^7 times before decomposition.

Figure 3a shows the time trace of the fluorescence intensity of a single molecule irradiated with intense 488-nm light (100 W/cm^2) and weak 325-nm light (0.25 mW/cm^2). The frequent fluorescence decrease is not due to photophysical blinking,[10] such as triplet formation, because the frequency decreased by decreasing the intensity of 325-nm light. From the number of decrease of fluorescence or fluorescence switching, it is possible to estimate how many photochromic cycles can be repeated before decomposition of the diarylethene unit. After the decomposition of the diarylethene unit, the perylenebisimide unit still keeps the emission for some time and then decomposes. The photostability of the diarylethene unit is comparable to that of the perylenebisimide unit. Figure 3b shows the distribution of the observed cycles for 110 molecules. The derivative can repeat the photochromic cycles about 100 times. Although the number seems too small, the small number is due to the low cycloreversion quantum yield. The photoswitching response shown in Figure 3 suggests that one photochromic cycle requires around 10^4 absorbed photons. Therefore, the cycle number indicates that the diarylethene unit keeps the photochromic performance even after being excited around 10^6 times. In other words, the quantum yield of the decomposition reaction is less than 10^{-6}. It is safe to say that the diarylethene unit is extremely robust.

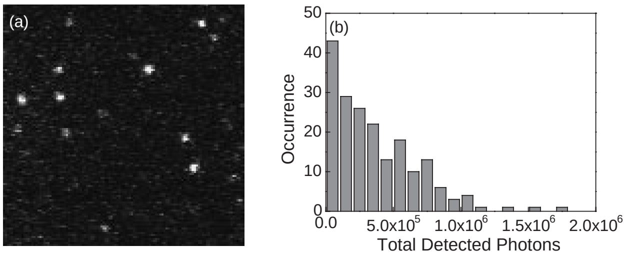


Figure 2. (a) Fluorescence image of **1a** single molecules in embeded a Zeonex film under 488-nm excitation. Image size: 20 × 20 µm. (b) Histogram of total detected photons before photobleaching derived from 191 molecules excited with 488-nm light (100 W/cm^2).

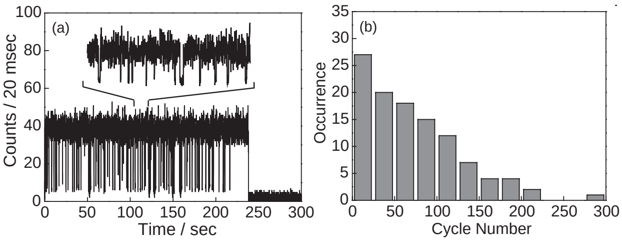


Figure 3. (a) Time trajectory of fluorescence intensity of **1** embedded in a Zeonex film upon irradiation with both intense 488-nm light (100 W/cm^2) and weak 325-nm light (0.25 mW/cm^2). (b) Histogram of cycle numbers of photocyclization/cycloreversion reaction derived from 110 molecules.

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9 Analytical Data for **1a**: ^{1}H NMR (400 MHz, CDCl$_3$): δ 0.829 (t, $J = 6.6$ Hz, 6H), 1.14–1.36 (m, 16H), 1.76–1.92 (brs, 2H), 1.84 (brs, 2H), 2.00 (s, 3H), 2.05 (s, 3H), 1.94–2.08 (brs, 2H), 2.11 (s, 10H), 2.18–2.22 (brs, 2H), 2.31 (s, 3H), 2.34–2.42 (brs, 2H), 3.77 (s, 3H), 5.20 (brs, 1H), 7.27–7.48 (m, 11H), 7.62 (d, $J = 8.8$ Hz, 2H), 8.62–8.80 (m, 8H); MS-FAB m/z 1345 (M + H$^+$); Anal. Calcd for $C_{82}H_{74}F_6N_2O_5S_2$: C, 73.19; H, 5.54; N, 2.08%. Found: C, 72.89; H, 5.53; N, 2.09%.

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