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Ring Opening Dynamics of a Photochromic Diarylethene Derivative in Solution†

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Photochromic ring opening reaction dynamics of 1,2-bis(2-methylbenzo[*b*]thiophen-3-yl)hexafluorocyclopentene in solution has been studied by femtosecond time-resolved fluorescence and transient absorption measurements. Time profiles of the transient absorption at several different probe wavelengths are identical, showing two time constants, 4 and 22 ps. The spontaneous fluorescence reveals time profiles identical to that in the transient absorption. A simple one step ring opening reaction mechanism is proposed, where the closed form in the excited state reaches the open form in the ground state through nonadiabatic curve crossing. The ring opening reaction rate is determined to be in the range (1.7−4) × 10^{10} s^{-1}. A single 66 cm^{-1} wave packet motion in the excited state is observed, whose role on the ring opening reaction is speculated upon.

I. Introduction

Organic photochromic compounds undergo reversible transformations between two distinct chemical species by different colors of light. The two isomers may show distinct physicochemical properties, which can be exploited to various photonic devices, such as optical memories, switches, and display.[1] Essential requirements in such applications are the thermal stability, fatigue resistance, and prompt reaction rate. Among many molecular systems showing photochromism, diarylethene derivatives with heterocyclic aryl groups have received much attention as one of the most promising photochromic materials due to their remarkable thermal stability and resistance to fatigue.[2−4]

A photochromic reaction of a diarylethene derivative employed in this study is shown in Figure 1. Upon UV irradiation, the open form of 1,2-bis(2-methylbenzo[*b*]-thiophen-3-yl)-hexafluorocyclopentene (o-BTF6) undergoes ring closure reaction, and the closed form (c-BTF6) returns to o-BTF6 by visible light.[5,6] The ring closure/opening reactions of the diarylethene derivatives follow the Woodward−Hoffmann rule based on the π-orbital symmetry. According to the state correlation diagram of the six π-electron electrocyclic reaction in conrotatory pathway,[7] through which the photochromic reactions of BTF6 should occur, there exists a large energy barrier between the closed and the open forms in the electronic ground state, whereas small or no barrier is present in the excited state.[8] Therefore, the ring closure/opening reactions of BTF6 occur by photons, whereas the two forms are thermally stable in the ground state.

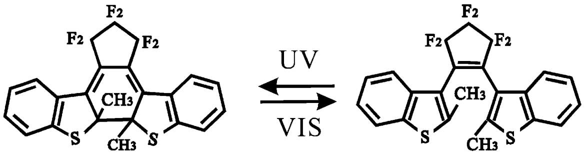

Figure 1. Open and closed forms of 1,2-bis(2-methylbenzo[*b*]thiophen-3-yl)hexafluorocyclopentene (BTF6). UV (visible) light induces ring closure (opening) reaction.

Dynamics of the ring opening and closure reactions for several diarylethene derivatives have been studied by femtosecond time-resolved techniques.[9−13] Both the ring opening and closure reaction rates have been reported to be in the range 1−10 ps from pump/probe transient absorption (TA) measurements.[9−13] Kryschi and co-workers reported that the ring opening of 1,2-bis(5-anthryl-2-methylthien-3-yl)perfluorocyclopentene occurs over a several hundred picosecond time scale through a precursor, which is formed within 1 ps.[10c] The reaction rate, however, is observed to be sensitive to substituents.[10d] The dynamics of the ring closure reaction observed by transient absorption spectra appears to be much more complicated than the ring opening reaction dynamics, partly due to the existence of conformational isomers in the open form.[14]

A TA signal of a molecule consists of several contributions; ground state bleach (GB), excited state stimulated emission (ESE), and excited state absorption (EA). In addition, solvation processes as well as the vibronic and vibrational relaxations make significant contributions to the signal. For a system undergoing photochemical reactions by pump pulses, each chemical species may contribute to the signal through GB, ESE, and EA components. Deconvolution into each component is usually not straightforward. Because the photochromic reactions

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occur in the excited state potential surface, time-resolved spontaneous fluorescence (TRF) would provide unambiguous information on the molecular dynamics of the system. TRF measurements probe excited state population dynamics exclusively, although dark states cannot be interrogated. In addition, an oscillation in a TRF signal must be interpreted to be originated from the wave packet motion in the excited state, whereas it arises from either the ground or the excited state in a TA measurement.[15] Observation of the wave packet motion in the excited state may provide detailed information on the potential surface and the reaction dynamics of the system.

Study of the photochromic reaction dynamics of the diarylethene derivatives by TRF, however, has not been reported due to the following reasons. The open isomer has two conformations, where the two benzothiophene rings are oriented in either mirror symmetry (parallel conformation, C_s) or C_2-like symmetry (antiparallel conformation). It is well-known that only the antiparallel conformer undergoes ring closure reaction,[14] whereas the C_s conformation fluoresces significantly. It is also known that the closed isomers do not emit significantly.[2,16] Therefore, TA has been used exclusively in all of the works employing femtosecond techniques.

In this work, we report the ring opening reaction dynamics of the c-BTF6 by employing femtosecond TRF and TA. Because the c-BTF6 prepared by photoreaction of the o-BTF6 exists in one trans conformation, the ring opening reaction would be simpler to study than the ring closure reaction, in which conformational diversity may complicate the analysis. Excitation pulse duration and time resolution of the measurements are kept as short as possible to create and to observe wave packet motions in the excited electronic state, which will give detailed information on the potential surface of the exited electronic state where the reaction occurs.

II. Experimental Section

o-BTF6 was synthesized according to the procedure reported previously.[5,6] c-BTF6 was prepared by UV (~310 nm) irradiation of the o-BTF6 in *n*-hexane solution. A sample reservoir was irradiated by the UV light during data acquisition to keep the solution in photostationary state.

The femtosecond laser system consists of a Ti:sapphire oscillator (Tsunami, Spectra Physics), a home-built multipass Ti:sapphire amplifier, and an optical parametric amplifier (OPA). The oscillator and amplifier were pumped by a 5 W output of a frequency doubled Nd:YVO$_4$ laser (Millennia, Spectra Physics) and 3.5 W output of a frequency doubled Nd:YAG laser (210G, Lightwave), respectively. The pulse energy of the Ti:sapphire amplifier output after pulse compression was 40 μJ at 5 kHz. The OPA was pumped by the second harmonic of the fundamental at 800 nm in a noncollinear geometry[17] to produce 50 fs pulses tunable across the visible wavelength region.

For TA measurements, white light continuum was generated by focusing the remainder of the fundamental at 800 nm into a sapphire window. The TA measurements were performed in two different ways. For a TA spectrum measurement, the continuum probe beam after the sample was dispersed and scanned by a monochromator (SP300i, Acton) while group velocity dispersion (GVD) was corrected by adjusting the pump time delay. For a TA time profile at a single probe wavelength, spectral filtering and GVD compensation of the continuum were achieved prior to the sample by a prism pair and a slit placed at the dispersed region. TRF was measured by the sum frequency generation between the fluorescence and a gate pulse in a 0.5 mm thick type I BBO crystal. Collection and focusing of the fluorescence were achieved by a pair of parabolic mirrors. The remainder of the amplified fundamental output at 800 nm was used as a gate pulse. Time resolutions of the TA and TRF measurements were 70 and 120 fs, respectively, as determined by cross-correlations. TRF on a longer time scale was measured by the time correlated single photon counting (TCSPC) technique. The TCSPC apparatus has instrument time resolution of 40 ps (fwhm) and has been described in detail elsewhere.[18]

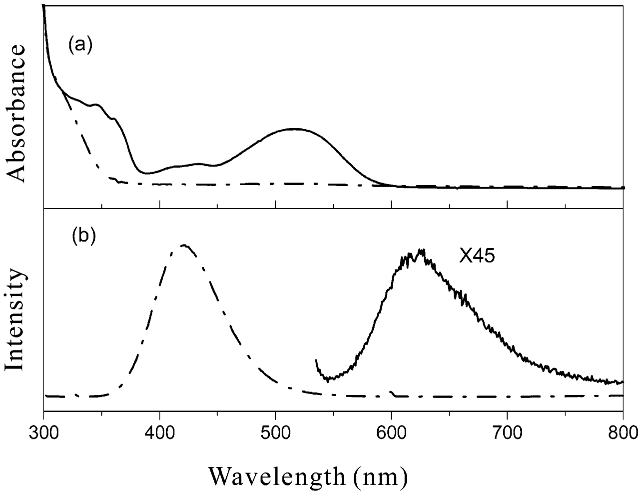

Figure 2. Steady state absorption (a) and emission (b) spectra of the open form (dash dot) and photostationary state (solid line) of BTF6 in *n*-hexane. The 530 nm absorption band (630 nm emission) is assigned to the closed form of BTF6. Fluorescence excitation wavelengths are 310 (open) and 530 nm (closed), respectively.

To measure the quantum yield of the ring opening reaction, o-BTF6 in *n*-hexane was irradiated by 310 nm UV light to reach photostationary state, and the amount converted to the closed form was quantified by NMR spectrum. Typically, less than 10% was converted to the closed form, indicating that the quantum yield of the ring opening reaction at 310 nm is much higher than that of the ring closure reaction. The quantum yield was determined by measuring the transmission of a continuous wave of 532 nm laser light through the sample as a function of time. The quantum yield measurement in this way gives a value close to 0.9, although the uncertainty is large because of the small conversion efficiency to the closed form. Note that the quantum yield of the ring opening reaction for the same compound was reported to be 0.35.[19]

III. Results

Figure 2 shows stationary state absorption and emission spectra of the o-BTF6 and BTF6 in photostationary state. The absorption band peaked at 530 nm can be assigned to the c-BTF6 as in typical diarylethene derivatives.[2] The transition frequencies match very well with the quantum mechanical ab initio calculation.[20] o-BTF6 shows relatively strong fluorescence at 420 nm independent of the excitation wavelength, whereas c-BTF6 shows a rather weak but distinct emission band peaked at 630 nm. TCSPC measurement of o-BTF6 gives a lifetime of 150 ps, which is much longer than the time scale of the ring closure reactions reported previously.[9−13] As stated above, emission of the open isomer may be mostly attributable to the parallel conformation that does not participate in the ring closure reaction. Thus, the 150 ps component can be assigned to the population relaxation of a fluorescent state, where o-BTF6 is in parallel conformation. In contrast, the closed isomer is expected to have only one conformation corresponding to the antiparallel conformation of the open isomer. Therefore, emis-

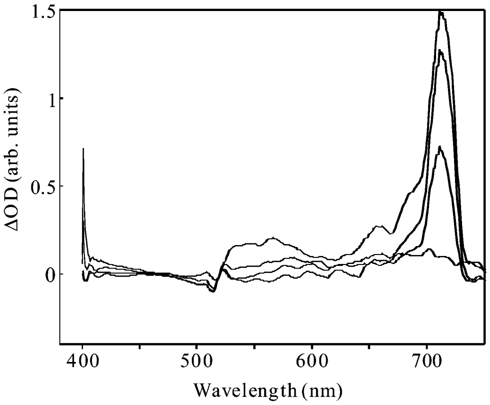

Figure 3. TA spectra measured at time delays of 1, 5, 20, and 120 ps after excitation at 530 nm. Time increases from top to bottom.

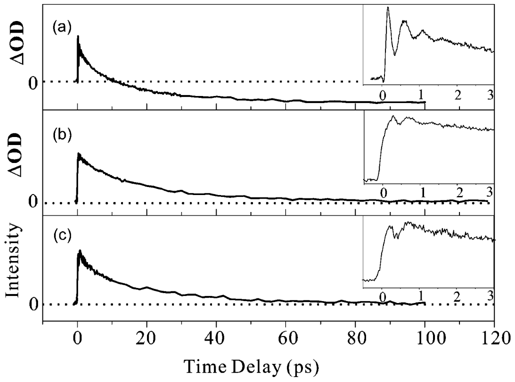

Figure 4. TA signals of c-BTF6 in *n*-hexane probed at 530 nm (a) and 710 nm (b). TheTRF signal of c-BTF6 detected at 635 nm following the excitation at 530 nm is shown in (c). Insets show early time signals to 3 ps.

sion of c-BTF6 may give information related directly to the photochromic reaction.

Figure 3 shows the transient absorption spectra following 530 nm excitation of the closed form for several time delays. The spectra show a strong excited state absorption band at 710 nm and a broad feature over the entire visible region due to GB, ESE, and EA from the S_1 state of c-BTF6 and a precursor, if any.[10b] Figure 4 shows TA time profiles at probe wavelengths 530 and 710 nm. Immediately after the excitation, both transients show instrument-limited rises (increased absorption) and subsequent decays. The 710 nm signal decays to zero by two time constants 4 ps (33%) and 22 ps (67%). The decay profile at 530 nm also shows the same two time constants. In fact, the two transients are superimposable in the picosecond region, when they are normalized and baseline corrected. The two, however, are different in their asymptotic values: the 530 nm transient gives a negative asymptotic value, whereas the 710 nm transient approaches zero. The asymptotic values stay constant over a few nanoseconds time window of our TA apparatus. Because the ESE contribution decays within a few tens of picoseconds, as demonstrated by the TRF measurement (see below, Figure 4c), the 530 nm TA signal at long time delay (>100 ps) must be solely due to the GB contribution. This indicates that a significant portion of the c-BTF6 excited by the pump pulse has undergone ring opening reaction.

The TRF signal following the excitation of the c-BTF6 at 530 nm is shown in Figure 4c. The TRF decay profile also shows the 4 and 22 ps components observed in TA signals. When normalized, the time profiles of the TRF and the TA at 710 nm are identical. The equivalence indicates that the 710 band in the transient absorption spectra is solely due to the excited state absorption of the state that gives rise to the TRF signal.

In general, a TRF signal is influenced by the solvation process, which causes a dynamic Stokes shift of the emission spectrum. In this case, TRF signals detected at various frequencies show different time profiles; TRF at shorter wavelengths shows a decay following immediate rise, whereas TRF at longer wavelengths shows a rise corresponding to the solvation time scale.[21] Indistinguishable TRF signals were observed when the detection wavelength is varied over the entire emission bandwidth. Absence of the detection wavelength dependence shows that the TRF signal reflects the population of the excited state. In addition, the TRF signal is not sensitive to the wavelength of the pump pulses from 500 to 530 nm.

Apparent in every signal trace is the oscillation that arises from the dynamics of a wave packet created by the impulsive excitation of vibrations. Fourier transform and linear prediction singular value decomposition (LPSVD) analyses reveal only one major oscillation component at 66 cm^{-1}. It is to be emphasized that the 66 cm^{-1} mode is the only vibration observed, although the excitation pulses are short enough to impulsively excite vibrations with much higher frequencies. The oscillation in the TA signals may originate from the wave packet motion in electronic ground and/or excited state, whereas the oscillation in the TRF signal must come from the wave packet motion in S_1 of c-BTF6. The equivalence of the oscillations in the TA signal at 710 nm and the TRF confirms that the 710 nm band in the TA spectra is indeed due to the absorption from the S_1 state of the c-BTF6. Amplitude of the oscillation is much higher in the TA signal at 530 nm, which implies that the oscillation in the 530 nm TA signal is mostly due to the wave packet motion in the ground state of c-BTF6.

IV. Discussion

In almost all diarylethene derivatives, emission of the closed form has not been reported. For the BTF6 molecule employed here, emission of the closed form has been observed in both stationary and time-resolved experiments. The femtosecond TRF measurement together with the TA clarifies several ambiguities encountered in the TA measurement alone. Experimental results may be summarized as follows. (1) No spectral signature of an intermediate has been found in the TA spectra at any time delay.[22] (2) All of the TA and TRF signals show an instrument limited rise and subsequent decay by two time constants 4 and 22 ps with the 22 ps being the major component. (3) The TRF signal does not show detection wavelength dependence. In addition, the TRF signal is not sensitive to the pump wavelengths within the 500−530 nm region. (4) All TA and TRF signals show a 66 cm^{-1} oscillation due to the wave packet motion in the S_1 state of c-BTF6.

The origin of the 4 ps component is not clear. Most of the processes that are known to occur in a few picosecond time scale, such as solvation and vibronic relaxation, predict detection wavelength dependence in TRF. One possibility is the conformational change of the c-BTF6 in the S_1 state to possibly a precursor, which shows a lower transition dipole moment between S_0 and S_1. Another possibility is that the ring opening reaction rate may be energy dependent. That is, prior to the vibronic relaxation in S_1, the reaction rate may be higher, although this is not likely considering the absence of the pump frequency dependence in the TRF. These processes should also show detection wavelength dependence in the TRF. In addition, a multiexponential fit is not robust in general, and only a slight

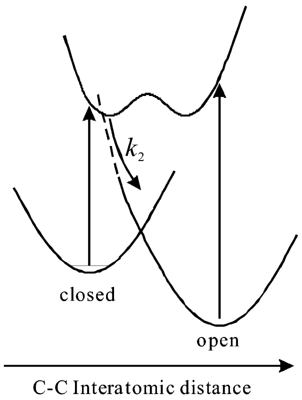

Figure 5. Schematic energy level diagram of BTF6 molecule exhibiting photochromic reaction. The abscissa is the C−C interatomic distance where the bond breakage occurs. The potential energy curve roughly follows the semiempirical calculation reported in ref 23.

deviation from a single-exponential behavior is enough to give a biexponential behavior. Therefore, small spectral relaxation within the noise level would give the biexponential behavior observed in the TA and TRF time profiles. In any case, the major 22 ps component may be regarded as the time scale reflecting the population dynamics of the S_1 state of c-BTF6.

All the experimental observations point to the fact that the only transient chemical species created by the pump pulse is the S_1 state of c-BTF6. The wave packet motion observed in the excited state suggests that the potential energy surface along the reaction coordinate is bound, although, in principle, it could still be repulsive, and the 66 cm^{-1} is the vibration orthogonal to it. Insensitivity of the TRF signal to the pump wavelength and absence of the emission from the excited state of the open form also suggest that the closed S_1 is a bound state with a relatively high barrier to the open form. The large GB contribution in the 530 nm TA signal at long time confirms that the reaction quantum yield is significant. Therefore, it is suggested that the initially prepared state undergoes ring opening reaction by nonadiabatic curve crossing. The resulting simple model of the ring opening reaction is summarized schematically in Figure 5.

In this model, populations of the S_0^c, S_1^c, and S_0^o states have the same time dependence, where the superscripts c and o stand for the closed and open form, respectively. This will lead to the same time profiles for the TA and TRF signals as observed in the experiment. Populations immediately after the pump can be set to $P(S_1^c) = 1$ and $P(S_0^c) = P(S_0^o) = 0$, because only the molecules excited by the pump pulses contribute to the TA and TRF signal. The populations (normalized to 1) of each chemical species at time t are

$$P(S_1^c) = \exp\{-(k_1 + k_2)t\}$$

$$P(S_0^c) = \frac{k_1}{k_1 + k_2}[1 - \exp\{-(k_1 + k_2)t\}]$$

$$P(S_0^o) = \frac{k_2}{k_1 + k_2}[1 - \exp\{-(k_1 + k_2)t\}]$$

where k_1 is the rate of the population relaxation back to the ground state and k_2 is the ring opening reaction rate. The TRF and the EA and ESE components of TA are proportional to $P(S_1^c)$, and the GB component of TA signal is proportional to $P(S_0^c) - 1$ weighted with extinction coefficients. Thus, time profiles of the TA should be the same at any probe wavelengths, although the sign and the asymptotic value of the signal depend on the probe wavelength. For example, the TA signal at 530 nm is dominated by the GB of S_0^c and EA of S_1^c. Because the extinction coefficient of the S_1^c at 530 nm should be larger than that of S_0^c, ΔOD is positive initially due to the EA and becomes negative at long times due to the GB contribution. The signal at 710 nm is entirely due to the EA of S_1^c, so that ΔOD should be positive initially and approaches zero at long times. These are exactly what have been observed.

Because the decay rate of the S_1^c has been measured unambiguously by TRF to be 1/(22 ps), k_1 and k_2 can be determined from the quantum yield of the reaction, $k_2/(k_1 + k_2)$. For the quantum yield of 0.9, the reaction rate, k_2, is 1/(24 ps). If the quantum yield of 0.35 is used as reported by Uchida et al.,[19] the reaction rate is calculated to be 1/(62 ps).

Oscillation in the spontaneous fluorescence may provide detailed information on the S_1 potential surface of the Franck−Condon region of the c-BTF6. Because the 66 cm^{-1} mode is the only vibration active in the electronic transition, that is, the ground and excited state potential surfaces are displaced significantly along this mode only, it may play a role in the ring opening reaction. This mode also dephases rapidly, especially in the excited state. More theoretical work is clearly needed to pursue this implication further.

V. Conclusions

We report femtosecond time-resolved spontaneous fluorescence of the closed form in the photochromic reaction of a diarylethene for the first time. High time resolution transient absorption spectra have also been measured to facilitate the analysis. Wave packet motion in the electronic excited state of the closed form was observed through TRF. From the TRF and TA, the ring opening reaction time constant can be determined to be 20−60 ps. Absence of any spectral signature of an intermediate or a precursor suggests that the ring opening reaction may proceed directly from the initially prepared S_1 state. Together with the insensitivity of the TRF decay to the pump wavelengths within 500−530 nm region, wave packet motion in the electronic excited state observed through TRF suggests that the barrier of the ring opening reaction in the excited electronic state is reasonably high.

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