

Supporting information

S-1. Principles and theory

(a) Transient grating (TG) method

The TG signal is generated from the photoinduced refractive index change (δn).¹⁻¹⁰ The signal consists of δn due to the temperature change [$\delta n_{\text{th}}(t)$; thermal grating] and that of the created (or depleted) chemical species (the species grating). The species grating signal intensity is given by the difference of the refractive index changes due to the reactant (δn_R) and the product (δn_P). The total TG signal [$I_{\text{TG}}(t)$] is expressed as:

$$I_{\text{TG}}(t) = \alpha \{ \delta n_{\text{th}}(t) + \delta n_P(t) - \delta n_R(t) \}^2$$

where α is a constant.

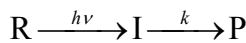
When the molecular diffusion coefficient (D) is independent of time, the temporal profile of the species grating signal can be calculated by the molecular diffusion equation. The q -Fourier component of the concentration profile decays with a rate constant of Dq^2 for the reactant and the product. Hence, the time development of the TG signal for describing molecular diffusion can be expressed by:

$$I_{\text{TG}}(t) = \alpha \{ \delta n_P \exp(-D_P q^2 t) - \delta n_R \exp(-D_R q^2 t) \} \quad (\text{S-1})$$

where D_R and D_P are diffusion coefficients of the reactant and the product, respectively. Furthermore, $\delta n_R(>0)$ and $\delta n_P(>0)$ are the initial refractive index changes due to the changes in the reactant and the product concentrations, respectively.

(b) Time-dependent diffusion coefficient

The apparent D could be time-dependent by the following reaction



R, I, P, and k represent the reactant, an initial product (intermediate), the final product and the rate constant of the change, respectively. In this case, the time dependencies of the refractive indices due to these species are given by⁶⁻¹⁰

$$\begin{aligned} \delta n_R(t) &= \delta n_R \exp(-D_R q^2 t) \\ \delta n_I(t) &= \delta n_I \exp\{-(D_I q^2 + k)t\} \\ &\quad + \delta n_P \frac{k}{(D_P - D_I)q^2 - k} [\exp\{-(D_I q^2 + k)t\} - \exp(-D_P q^2 t)] \end{aligned} \quad (\text{S-2})$$

where δn_I and D_I are the refractive index change due to the creation of the I species and the diffusion coefficient of the intermediate, respectively.

S-2. Equilibrium between monomer and dimer

The equilibrium was investigated quantitatively using the TG method at various temperatures. The TG signal should be expressed by a superposition of Reactions A and B by the

following biexponential functions:

$$I_{TG}(\text{Reaction A}) = \alpha \{ \delta n_1(t) \}^2 = \alpha \{ \delta n_{DI} * \exp(-D_{DI} * q^2 t) - \delta n_M \exp(-D_M q^2 t) \}^2 \quad (\text{S-3})$$

$$I_{TG}(\text{Reaction B}) = \alpha \{ \delta n_2(t) \}^2 = \alpha \{ -\delta n_{DI} \exp(-D_{DI} q^2 t) + \delta n_{DI} * \exp(-D_{DI} * q^2 t) \}^2$$

where δn_M and δn_{DI} are the refractive index changes of the monomer and dimer as reactants, respectively. δn_{DI*} is the refractive index change of the photoproduct dimer. Since the initial intensity of the diffusion signal is almost zero at any temperature, one can find a relation of

$$\delta n_M = \delta n_{DI} = \delta n_{DI*}$$

at any temperature. The observed TG signals should be expressed by the sum of these contributions,

$$I_{TG} = \alpha \{ f_M \delta n_1(t) + \delta n_2(t) \}^2 \quad (\text{S-4})$$

where f_M is the fraction of the photoreaction due to the monomer. If the quantum yield of these reactions are equal, one may find $f_M = [M]/[DI]$ ($[M]$ and $[DI]$ are the concentrations of the monomer and dimer, respectively). Therefore, one may obtain $[M]$ and $[DI]$ from the following equation;

$$[M] = C_0 f_M / (2 + f_M) \quad (\text{S-5})$$

$$[DI] = C_0 / (2 + f_M)$$

where C_0 is the total concentration of the monomer unit, $[M] + 2[DI] = C_0$,

From the determined f_M , we calculated the equilibrium constant K between monomer and dimer for each temperature.

$$K = [DI]/[M]^2 \quad (\text{S-6})$$

S-3. Volume change

The refractive index change due to volume change (δn_v) is given by ^{3,5,9,10}

$$\delta n_v = V(dn/dV)\Delta V \Delta N \quad (\text{S-7})$$

where $V(dn/dV)$ is the refractive index change divided by the molecular volume change. By taking the ratio of δn_v to δn_{th} of a calorimetric reference sample with a known solvent property ($V(dn/dV)$), ΔV was determined from the signal intensity.

The change in the thermal expansion coefficient ($\Delta \alpha_{th}$) was measured from the temperature dependence of the volume change.^{3,9}

$$(1/V)(\partial \Delta V / \partial T) = \Delta \alpha_{th} \quad (\text{S-8})$$

The thermal expansion volume $V \Delta \alpha_{th}$ was determined from the slope of a plot of ΔV vs. T .

S-4. Temperature dependent volume change

Figure S-1(a) shows the observed TG signals representing the initial volume change over a temperature range of 283–303 K at relatively large q^2 ($q^2 = 3.5 \times 10^{12} \text{ m}^{-2}$) at a concentration of 700 μM . These signals were normalized by δn_{th} at 293 K. The values of this volume change were calculated using eq.(S-7) of the above section from the amplitudes of the refractive index changes and were plotted against the temperature (Fig. S-2(b)).

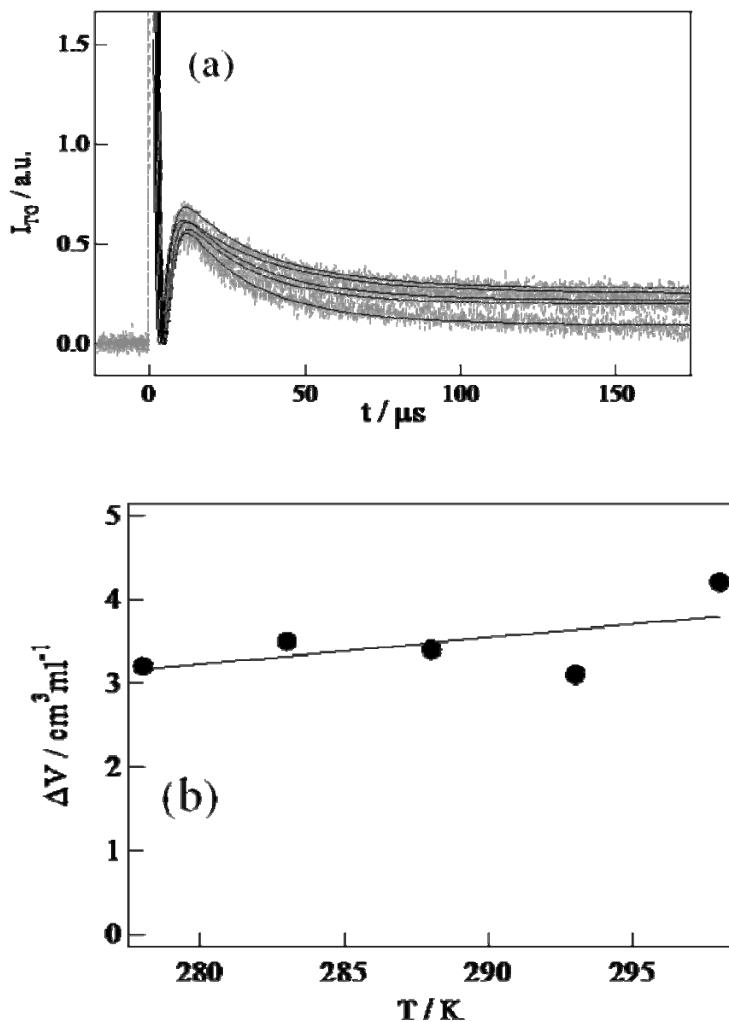


Fig.S-1

(a) The TG signals that represent the initial volume change at various temperatures. (b) The temperature dependence of the volume change (ΔV_1).

Figure S-2(a) shows the observed TG signals representing the volume change associated with the dimerization process in a temperature range of 283–303 K at a concentration of 700 μM ($q^2=1.6\times10^{11} \text{ m}^{-2}$). These signals were normalized by δn_{th} at 293 K. The calculated values for the volume change were plotted against temperature (Fig. S-2(b))).

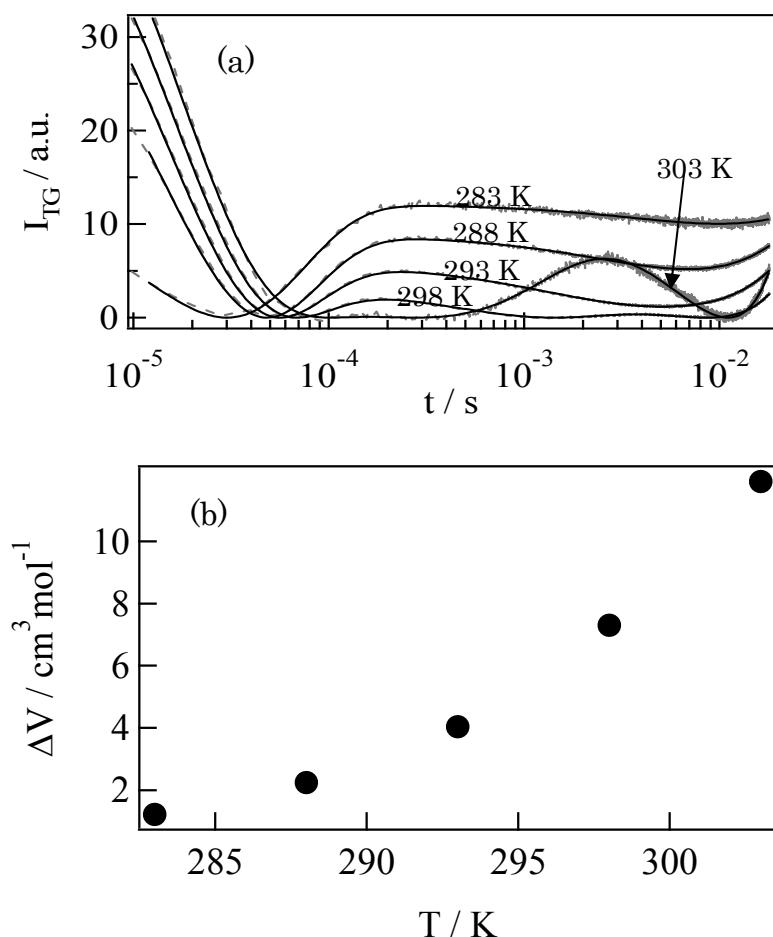


Fig.S-2

- (a) Temperature dependence of the TG signals after the initial conformational change. The signals include the volume change associated with dimerization. The amplitude of the refractive index change associated with the volume change was determined using eq.(S-7).
 (b) Temperature dependence of the volume change (ΔV_2).

Reference

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