Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information:

Cyclization Reaction Dynamics of an Inverse Type Diarylethene Derivative as Revealed by Time-Resolved Absorption and Fluorescence Spectroscopies

Hikaru Sotome,[†] *Daichi Kitagawa,*[§] *Tatsumoto Nakahama,*[§] *Syoji Ito,*[†] *Seiya Kobatake,*[§] *Masahiro Irie,**[‡] *Hiroshi Miyasaka**[†]

†Division of Frontier Materials Science and Center for Advanced Interdisciplinary Research, Graduate School of Engineering Science, Osaka University, Toyonaka, Osaka 560-8531, Japan,

§Department of Applied Chemistry, Graduate School of Engineering, Osaka City University, Sumiyoshi, Osaka 558-8585, Japan,

‡Department of Chemistry and Research Center for Smart Molecules, Rikkyo University, 3-34-1 Nishi-Ikebukuro, Toshima-ku, Tokyo 171-8501, Japan.

Content

1. Transient absorption spectra in the nanosecond-microsecond time region.

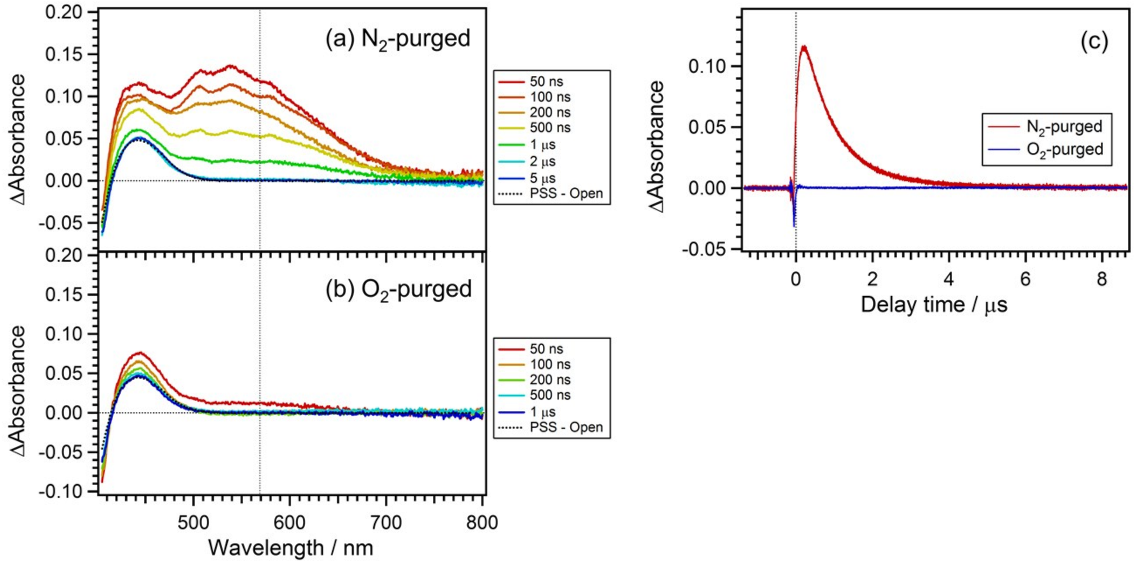

Figure S1. Transient absorption spectra of **iDAE(o)** in *n*-hexane solution excited with a nanosecond laser pulse at 355 nm. (a) N_2-purged solution and (b) O_2-purged one. (c) Time profiles of transient absorbance of **iDAE(o)** in N_2- and O_2-purged *n*-hexane solutions monitored at 570 nm.

2. Nuclear motion of coherent molecular vibration.

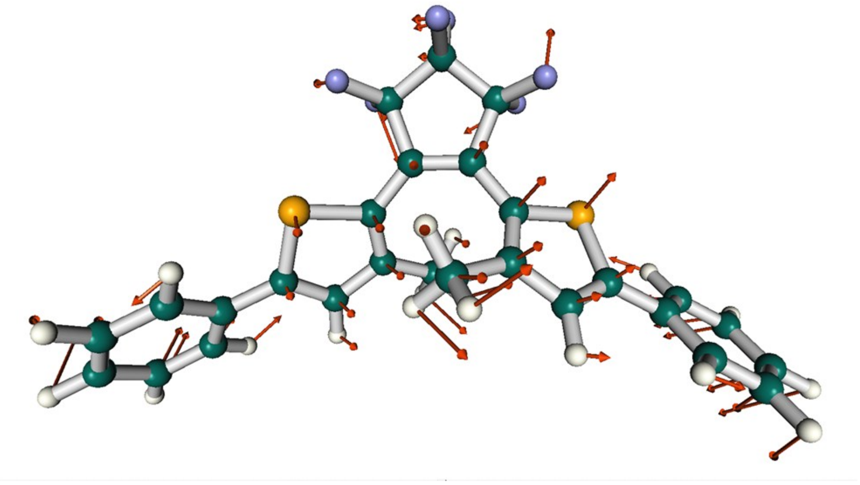

Figure S2. Vibrational mode of **iDAE(o)** in the AP1 conformer at 30.4 cm^{-1} calculated using the 6-31G(d) basis set at the B3LYP level. The molecular structure was optimized in the S_0 state and vibrational calculation was performed in the S_1 state. The red arrows indicate nuclear displacement.

3. Optimized molecular geometry in the S_1 state.

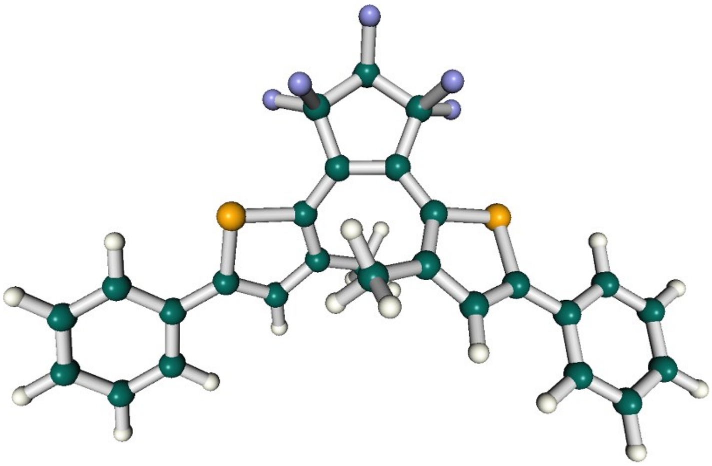

Figure S3. Molecular geometry of **iDAE(o)** (AP1) in the S_1 state. The optimization was performed using the 6-31G(d) basis set at the B3LYP level. The distance between two reacting carbon atoms is 3.44 Å.

4. Global fitting analysis in the picosecond time region.

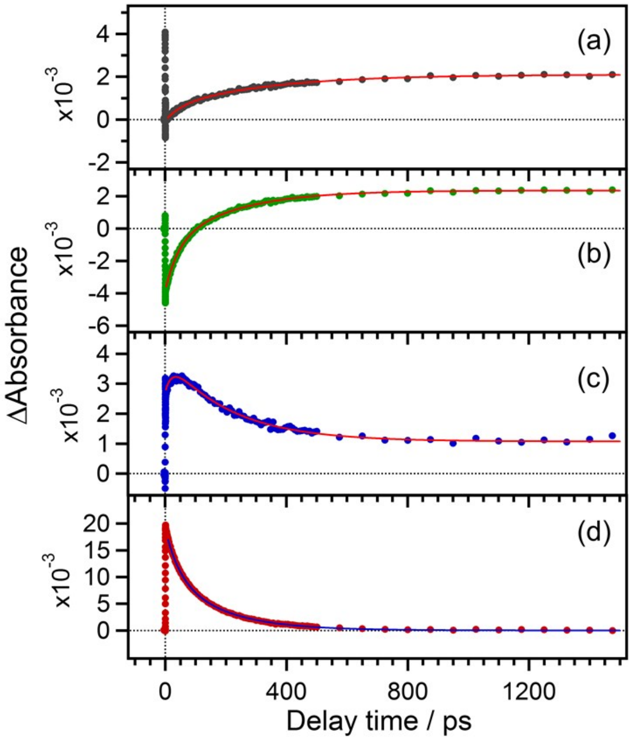

Figure S4. Time profiles of transient absorbance of **iDAE(o)** in *n*-hexane solution excited with a femtosecond laser pulse at 401 nm, monitored at 570 nm, (a), 520 nm, (b) 430 nm, (c), and 710 nm, (d). The fitting curves obtained from global analysis are also shown.

5. Oscillatory feature in various solvents with different viscosities.

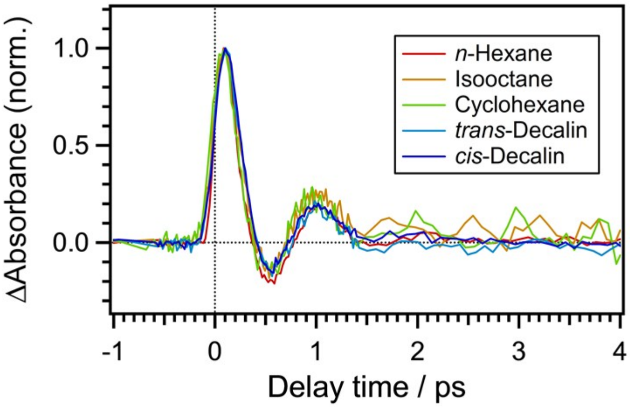

Figure S5. Time profiles of transient absorbance of **iDAE(o)** in five solvents with different viscosities. The monitoring wavelength was 570 nm.

6. Time profiles of transient absorbance in different solvents.

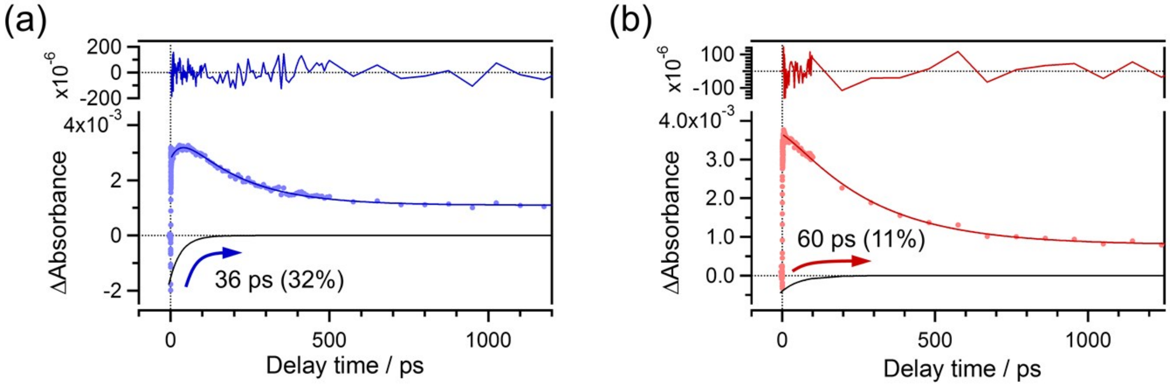

Figure S6. Time profiles of transient absorbance of **iDAE(o)** in (a) *n*-hexane and (b) *cis*-decalin solution monitored at 430 nm. The samples were excited with a femtosecond laser pulse at 401 nm. The time profiles were analyzed by fitting analysis using a double-exponential function, and the rise component is shown as a black curve. Their time constant and amplitude are also shown.

In the framework of the Debye-Stokes-Einstein model, the rate constant of isomerization reactions is formulated by the equation (1).

$$k_{iso} \propto \frac{1}{\eta} \quad (1)$$

Here, k_{iso} and η are the rate constant of the isomerization and solvent viscosity. In the present case, we assume following three pathways in the excited state of the AP1 conformer: (1) cyclization, (2) intersystem crossing, and (3) nonradiative deactivation. Thus, the excited state lifetime and the cyclization reaction yield are formulated by the equations (2), (3).

$$\tau = \frac{1}{k_{iso} + k_{isc} + k_{nr}} \qquad (2)$$

$$\Phi_{iso} = \frac{k_{iso}}{k_{iso} + k_{isc} + k_{nr}} \qquad (3)$$

Here, k_{isc} and k_{nr} are respectively the rate constants of the intersystem crossing and nonradiative deactivation. τ and Φ_{iso} are respectively the excited state lifetime and cyclization reaction yield. From the equations (1), (2) and (3), we can expect that the excited state lifetime becomes longer and the cyclization reaction yield decreases with an increase of solvent viscosity. To extract the excited state lifetime of the AP1 conformer, we analyzed the rise component at 430 nm (Figure S6), which corresponds to the formation of the photoproduct, using a double-exponential function as shown below.

$$\Delta A = A_1 exp\left(-\frac{t}{\tau_1}\right) + A_2 exp\left(-\frac{t}{\tau_2}\right) + Offset \qquad (4)$$

Here, τ_1 and τ_2 are respectively time constants of the cyclization process and subsequent dynamics of the unreactive conformers. A_1 and A_2 are corresponding amplitudes of transient absorbance. The offset component shows the absorbance of the finally remaining T_1 state and closed-ring isomer. The excited state lifetimes (τ_1) in *n*-hexane (0.313 cP) and *cis*-decalin (3.381 cP) solutions were detected as 36 ps and 60 ps, respectively. This result is consistent with the expected solvent viscosity dependence. In addition, the relative amplitudes were calculated as 32% and 11%, respectively, which is also in line with the lower reaction yield in the viscous solvent. In a similar manner, we applied the curve fitting analysis using a double or triple exponential function to the transient absorption data in other solvents (isooctane, cyclohexane and *trans*-decalin), and obtained the corresponding time constants. However, the resultant time constants were arbitrary to experimental data and less reliable, which is due to very tiny amplitude of the rise signal at 430 nm as seen in *cis*-decalin. But the solvent viscosity dependence of the cyclization reaction yield definitely supports that the cyclization process of **iDAE(o)** proceeds in a few tens picoseconds unlike normal type derivatives. By considering these results comprehensively, we may deduce that the viscous solvent decreases the rate constant of the cyclization reaction.

7. Concentration dependence of steady-state absorption spectra.

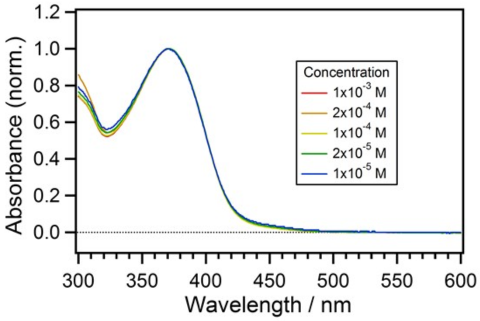

Figure S7. Steady-state absorption spectra of **iDAE(o)** in *n*-hexane solution with different concentrations.

8. Concentration dependence of fluorescence decay curves.

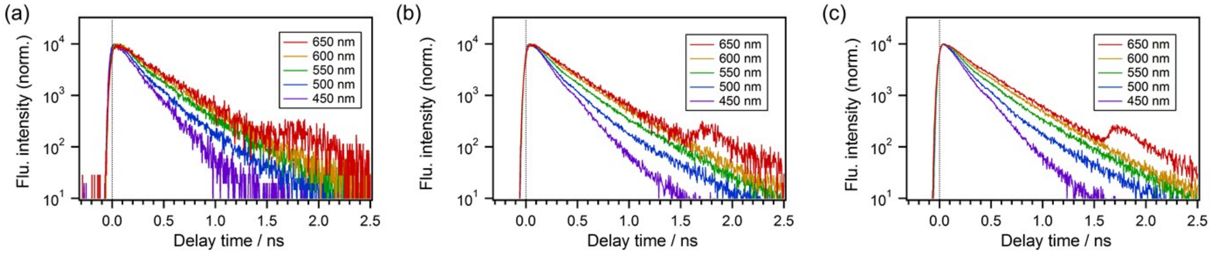

Figure S8. Fluorescence decay curves of iDAE(o) in *n*-hexane solution with different concentrations. (a) 8.5x10^{-5} M (b) 1.1x10^{-5} M (c) 2.5x10^{-6} M. The observation wavelengths were 450, 500, 550, 600 and 650 nm.

9. Calculated absorption spectra of three conformers in the ground state

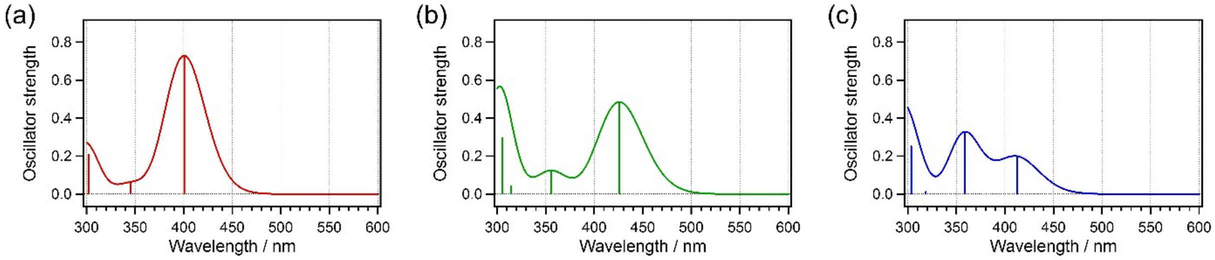

Figure S9. Absorption spectra of **iDAE(o)** in the ground state calculated using the 6-31G(d) basis set at the B3LYP level. (a) AP1 (b) P1 (c) AP2. The geometries of the conformers were optimized in the ground state (S_0 state). The spectral width was set to 3000 cm^{-1}.

10. Time-resolved fluorescence spectra reconstructed from fluorescence decay curves.

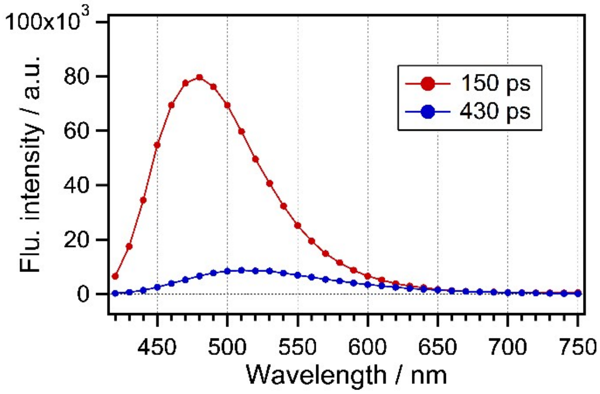

Figure S10. Fluorescence spectra of two component with time constants of 150 and 430 ps reconstructed from fluorescence decay curves of **iDAE(o)** in *n*-hexane solution.

11. Effect of purge gas on temporal evolution of absorbance upon photoirradiation.

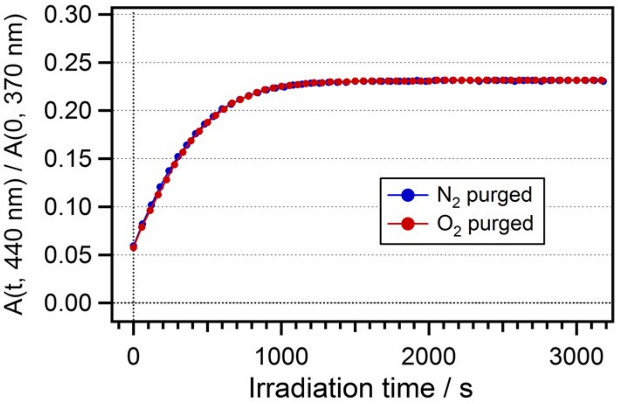

Figure S11. Temporal evolution of absorbance of **iDAE(o)** in *n*-hexane solution upon continuous irradiation at 370 nm.

12. Energy diagram of three conformers in the singlet and triplet states

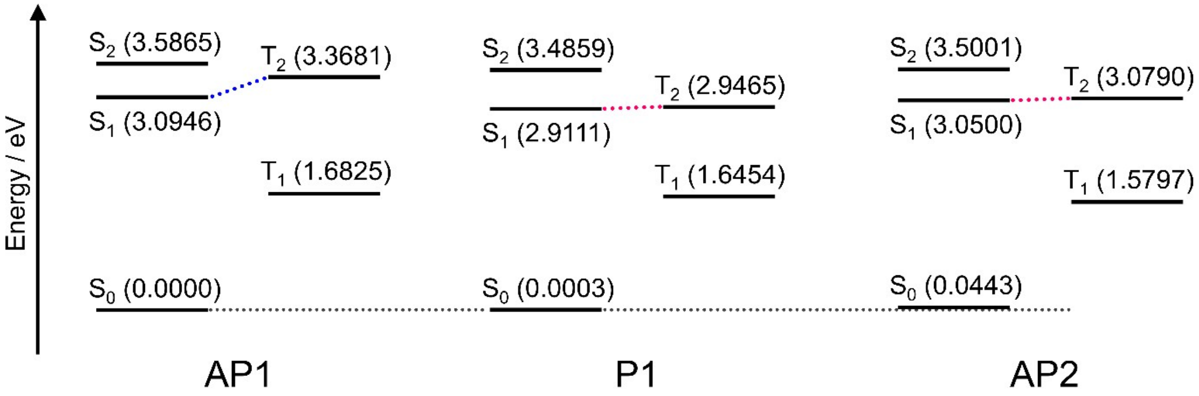

Figure S12. Relative energies of three conformers of **iDAE(o)** in the singlet and triplet states. The molecular geometries were optimized in the S_1 and T_1 states, respectively.