Electronic Supplementary Material (ESI) for RSC Advances.

Supplementary information:

Restriction of the conrotatory motion in photo-induced 6π electrocyclic reaction: formation of the excited state of the closed-ring isomer in the cyclization

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1. Global fitting analysis of the cycloreversion dynamics of DTA(c)

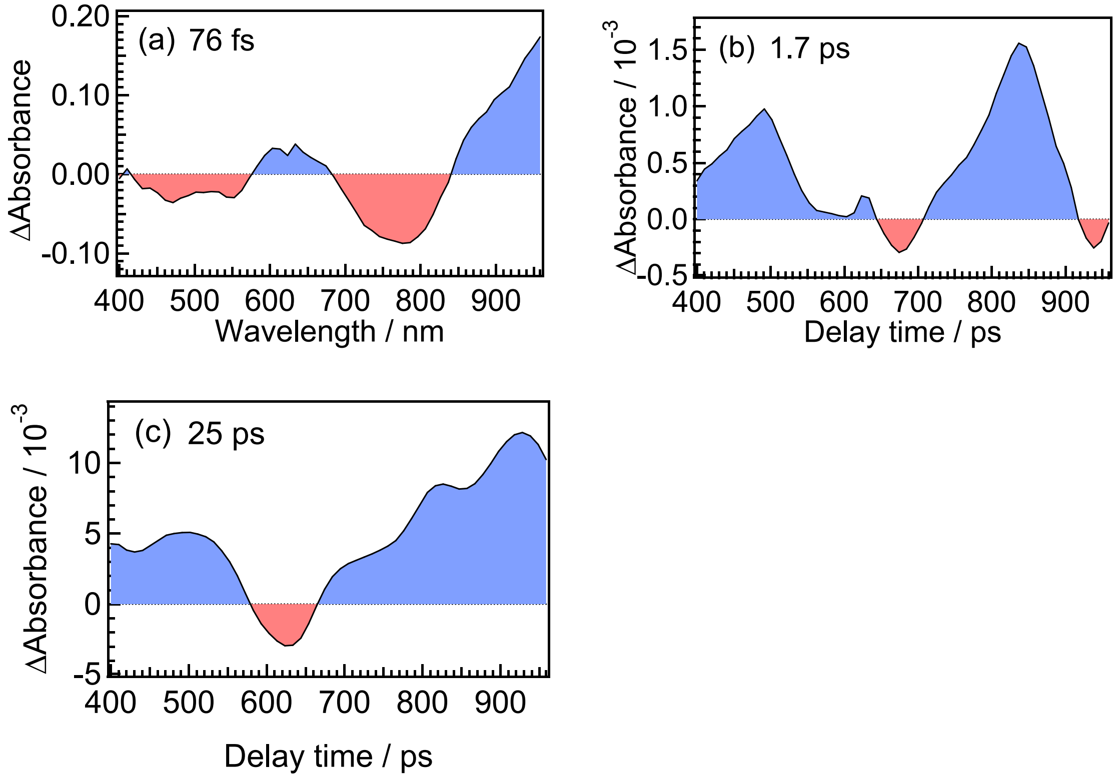

Figure S1. Decay-associated spectra obtained from the global analysis of the transient absorption spectra of **DTA(c).** The extracted time constants for DAS spectra are 76 fs for (a), 1.7 ps for (b) and 25 ps for (c).

2. Fluorescence lifetime measurement of DTA(c)

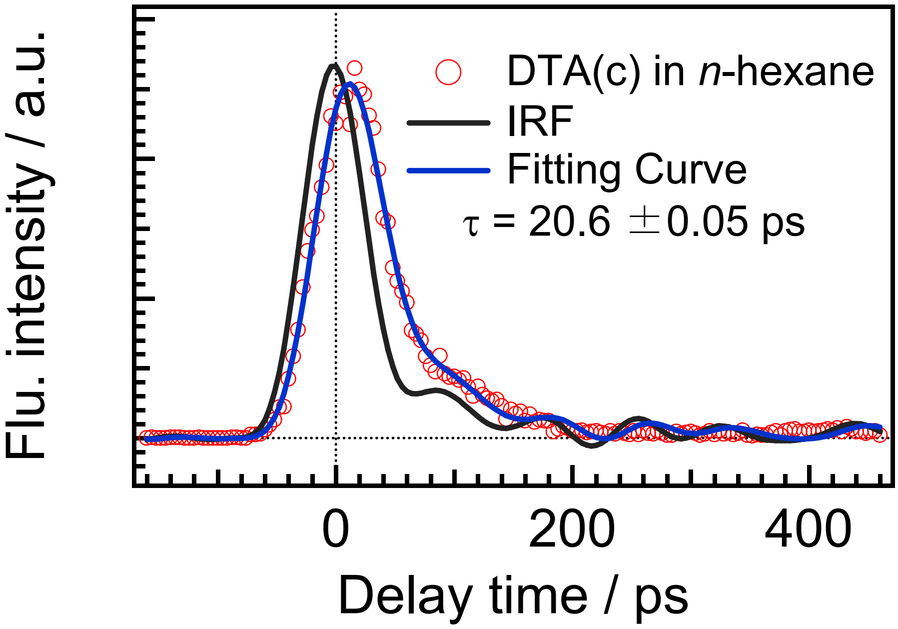

Figure S2. Fluorescence decay curve of **DTA(c)** in *n*-hexane solution, excited with a femtosecond 380-nm laser pulse and monitored at 700 nm.

A fluorescence time profile of **DTA(c)** in Figure S1 was measured by a time-correlated single-photon counting (TCSPC) method. The details of the apparatus were described elsewhere.[1] Briefly, a Ti:Sapphire oscillator (Tsunami, Spectra-Physics, 760 nm, 100 fs, 1.3 W, 80 MHz) was used as the pulsed excitation light source. The repetition rate of its output was reduced to 8 MHz by using an electro-optic modulator (Model 350, Conoptics). A small fraction of the pulse was picked up and detected as a start pulse for the TCSPC measurements. The major portion was converted into the second harmonics at 380 nm and directed into the sample after removing the remaining fundamental pulse at 760 nm with a short-pass filter. The polarization of the excitation pulse was set at the magic angle with respect to that of the fluorescence detection. A monochromator (Acton SP-2150, Princeton Instruments) was placed before a photomultiplier tube (Hamamatsu, R3809U-50) equipped with a pre-amplifier (C5594, Hamamatsu). The sample solution was set in a 1 cm quartz cell and absorbance of the solution at excitation wavelength is around 0.3. The instrumental response function of the system was determined to be approximately 40 ps by measuring the excitation pulse scattered by a colloidal solution.

3. Steady-state fluorescence spectrum of the parallel form of DTA(o)

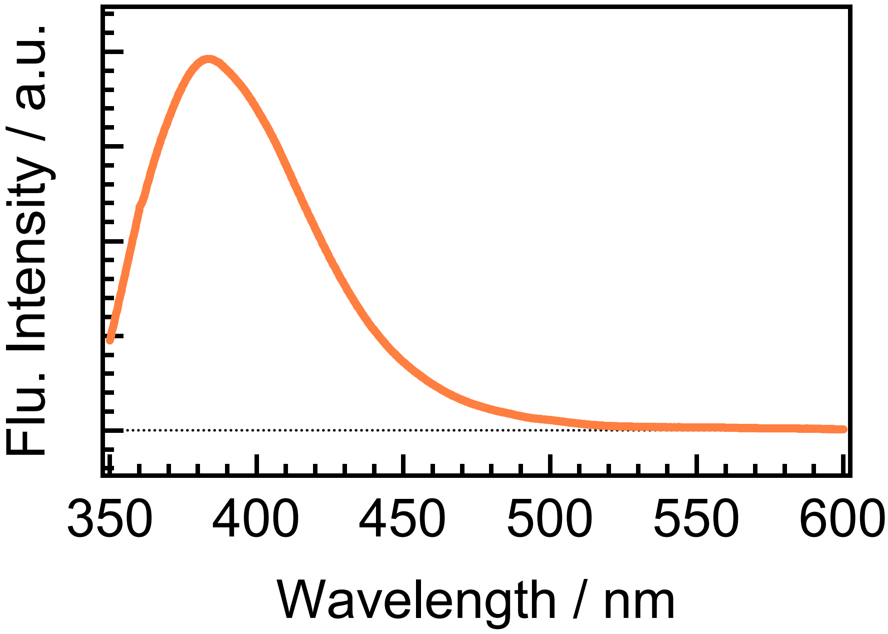

Figure S3. Steady-state fluorescence spectrum of the parallel form of **DTA(o)** excited at 300 nm.

4. Steady-state excitation spectra of DTA

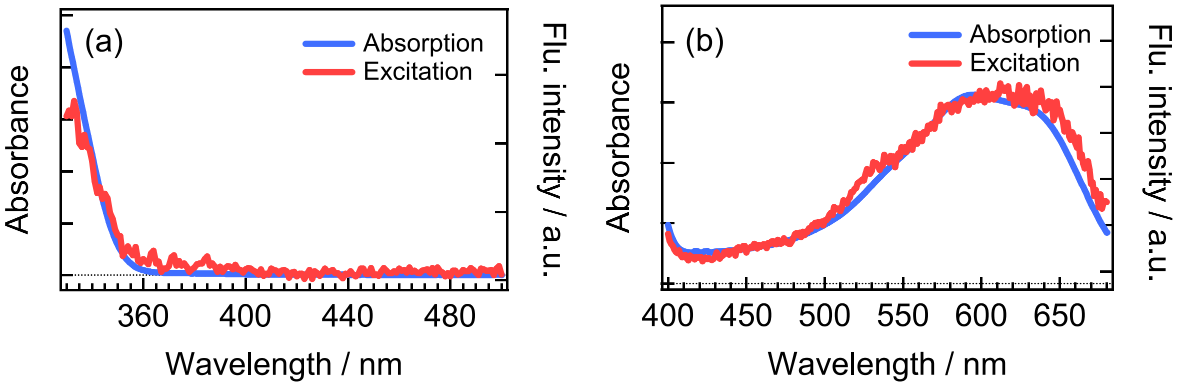

Figure S4. Excitation spectra of (a) the open form and (b) closed form of **DTA** in *n*-hexane solution. The fluorescence was detected at 740 nm in both the measurements. The excitation spectra were plotted by the solid red line and the corresponding absorption spectra (solid blue line) were also shown for comparison.

5. Determination of the branching ratio of two distinct reaction pathways

As described in the main text, the photoexcited open form of **DTA** reacts into the closed form through two distinct reaction pathways: conventional route via the 2A/1A conical intersection and newly found route directly leading to the excited state of **DTA(c)**. We quantitatively determined the branching ratio of the above reaction pathways in the following three steps.

1. Determination of the absorption coefficient of the reference sample
2. Determination of the absorption coefficient of **DTA(c)** in the excited state
3. Determination of the branching ratio of the two reaction pathways

1. Determination of the absorption coefficient of the reference sample

As the reference sample, we used zinc tetraphenylporphyrin (ZnTPP) in *N*,*N*-dimethylformamide (DMF) solution, which is a typical standard dye for transient absorption spectroscopy. We determined the molar absorption coefficient of the excited state of ZnTPP by using a picosecond laser photolysis system with a repetitive mode locked Nd^{3+}:YAG laser.[2] This laser system provides rather strong visible output (532 nm, 0.5-1.0 mJ, 15 ps fwhm), and it can pump all the ZnTPP molecules in the ground state to the excited state.

2. Determination of the absorption coefficient of **DTA(c)** in the excited state

We measured transient absorption spectra of ZnTPP and **DTA(c)** under the same excitation condition to determine the molar absorption coefficient of **DTA(c)** in the excited state. Table S1 shows transient absorbance of the samples at 2 ps thus obtained. At 2 ps, almost all **DTA(c)** still remains in the excited state. Other parameters such as absorbance of the samples and absorption coefficients of the reference sample are also shown.

Table S1. Parameters required for the determination of the molar absorption coefficient of the excited state of **DTA**.

Transient absorbance of **DTA(c)** @933 nm at 2 ps (ΔA_{DTA})	9.00×10^{-2}
Transient absorbance of ZnTPP @454 nm at 2 ps (ΔA_{ZnTPP})	0.183
Molar abs. coefficient of ZnTPP in the excited state @454 nm (ε_{ex}^{ZnTPP})	41500 M^{-1}cm^{-1}
Molar abs. coefficient of ZnTPP in the ground state @454 nm (ε_{gr}^{ZnTPP})	2090 M^{-1}cm^{-1}
Molar abs. coefficient of **DTA(c)** in the ground state @933 nm (ε_{gr}^{DTA})	0 M^{-1}cm^{-1}
Abs. of **DTA(c)** @excitation wavelength, 600 nm (Abs_{DTA})	1.07
Abs. of ZnTPP in DMF @excitation wavelength, 600 nm (Abs_{ZnTPP})	0.925

Transient absorbance after the excitation of closed form, ΔA_{DTA} is represented by eq. (1)

$$\Delta A_{DTA} = \left(\varepsilon_{ex}^{DTA} - \varepsilon_{gr}^{DTA}\right) \cdot n_{ex} \cdot C_0 \cdot l \qquad (1)$$

Here, ε^{DTA}_{ex} and ε^{DTA}_{gr} are molar absorption coefficients of the excited state and the ground state of **DTA(c)**, respectively. C_0 is the concentration of **DTA(c)**. l is the length of cell. The excitation fraction, n_{ex} is given by eq. (2)

$$n_{ex} = \frac{C_{ex}}{C_0} = \frac{N_{photon} \cdot \left(1 - 10^{-Abs_{DTA}}\right)}{S \cdot N_A \cdot C_0 \cdot l} \tag{2}$$

Here, C_{ex} is the concentration of the excited state of **DTA(c)**. N_{photon} is the number of irradiated photons per excitation pulse. S is the area of the excitation spot. N_A is the Avogadro constant. Eq. (3) is obtained from eqs. (1) and (2).

$$\Delta A_{DTA} = \frac{N_{photon} \cdot \left(\varepsilon^{DTA}_{ex} - \varepsilon^{DTA}_{gr}\right)\left(1 - 10^{-Abs_{DTA}}\right)}{S \cdot N_A} \tag{3}$$

In the same manner, transient absorbance of ZnTPP, ΔA_{DTA} is represented by eq. (4).

$$\Delta A_{ZnTPP} = \frac{N_{photon} \cdot \left(\varepsilon^{ZnTPP}_{ex} - \varepsilon^{ZnTPP}_{gr}\right)\left(1 - 10^{-Abs_{ZnTPP}}\right)}{S \cdot N_A} \tag{4}$$

N_{photon} and S are common in eqs. (3) and (4) due to the same excitation condition. By dividing eq. (3) by eq. (4), we obtained ΔA_{DTA} as shown eq. (5).

$$\frac{\Delta A_{DTA}}{\Delta A_{ZnTPP}} = \frac{\left(\varepsilon^{DTA}_{ex} - \varepsilon^{DTA}_{gr}\right)\left(1 - 10^{-Abs_{DTA}}\right)}{\left(\varepsilon^{ZnTPP}_{ex} - \varepsilon^{ZnTPP}_{gr}\right)\left(1 - 10^{-Abs_{ZnTPP}}\right)} \tag{5}$$

By substituting the experimental parameters in Table S1, we finally determined the molar absorption coefficient of the excited state of **DTA(c)** (ε^{DTA}_{ex}) to be 19700 $M^{-1}cm^{-1}$ at 933 nm (absorption maximum wavelength).

3. Determination of the branching ratio of the two reaction pathways

Finally, we determined the branching ratio of the two reaction pathways in the cyclization reaction. The branching ratio of newly found pathway, R is defined as eq. (6).

$$R = \frac{C_{closed\_ex}}{C_{open\_FC}} \qquad (6)$$

Here, C_{open_FC} is the concentration of the open form which is initially populated in the Franck-Condon region by photoexcitation. C_{closed_ex} is the concentration of the closed form produced via the newly found pathway. Table S2 shows a set of experimental parameters required for the calculation of C_{open_FC} and C_{closed_ex}.

Table S2. Parameters required for the determination of the branching ratio.

Molar abs. coefficient of **DTA(c)** in the ground state @597 nm[3]	9500 $M^{-1}cm^{-1}$
Transient absorbance of **DTA(o)** @933 nm at 2 ps	8.78×10^{-3}
Transient absorbance of **DTA(c)** @597 nm at 150 ps	7.10×10^{-3}

Absorbance of the finally formed **DTA(c)** in the ground state was 7.10×10^{-3} at the absorption maximum wavelength, which corresponds to 3.74×10^{-6} M. This concentration equals to that of the initially formed excited state of **DTA(o)** because the cyclization reaction quantum yield is almost 1 in the present case. Thus, $C_{open\_FC} = 3.74 \times 10^{-6}\ M$.

On the other hand, C_{closed_ex} can be obtained from transient absorbance (8.78×10^{-3}) 2 ps after the photoexcitation of the open form. At this delay time, the formation of the excited state of **DTA(c)** is already completed. By using the molar absorption coefficient of the excited state of **DTA(c)** (19700 $M^{-1}cm^{-1}$), we calculated C_{closed_ex} to be 2.23×10^{-6} M. Thus, the branching ratio of the reaction pathway found in the present study is obtained as 60%, as shown in eq. (7).

$$R = \frac{2.23 \times 10^{-6}\ M}{3.74 \times 10^{-6}\ M} = 60\% \tag{7}$$

Reference

1. Y. Nagasawa, T. Itoh, M. Yasuda, Y. Ishibashi, S. Ito, H. Miyasaka, *J. Phys. Chem. B*, 2008, **112**, 15758−15765.
2. H. Miyasaka, H. Masuhara and N. Mataga, *Laser Chem.*, 1983, **1**, 357–386.
3. S. Fukumoto, T. Nakashima and T. Kawai, *Angew. Chem. Int. Ed.*, 2011, **50**, 1565–1568.