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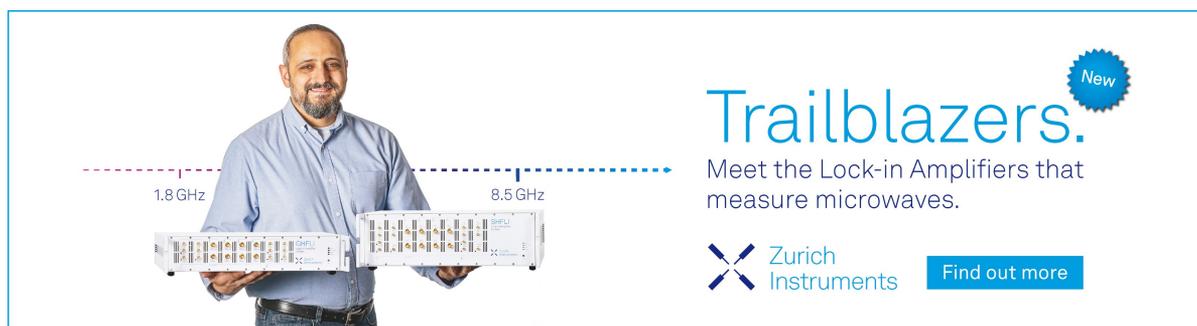
Double crossing conical intersections and anti-Vavilov fluorescence in tetraphenyl ethylene

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ABSTRACT

Conical intersections (CIs) provide effective fast nonradiative decay pathways for electronic excitation, which can significantly influence molecular photoluminescence properties. However, in many cases, crossing a CI does not have direct observables, making studies of CIs experimentally challenging. Herein, the theoretically predicted double CIs by cis–trans twisting and cyclization in tetraphenyl ethylene, a well-known aggregation-induced emission molecule, are investigated with excitation dependent ultrafast UV/IR spectroscopy and fluorescence. Both the fluorescence quantum yield and the efficiency of cyclization are found to be smaller with a shorter excitation wavelength. An abrupt change occurs at about 300–310 nm. The results imply that crossing the twisting CI has a larger barrier than the cyclization CI, and the cis–trans twisting motion is probably involved with large solvation reorganization.

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I. INTRODUCTION

Photoluminescence (PL) is one of the most basic and important properties of optoelectronic molecules. Its efficiency is determined by the rate ratio of radiative decay and nonradiative decays. At an electronic excited state, the intramolecular vibrational relaxation (picosecond time scale) is typically three orders of magnitude faster than fluorescence (FL) (nanosecond time scale).[1] Such a kinetic difference leads to some famous empirical rules describing molecular luminescence, e.g., Kasha's rule stating that the photoemission only takes place considerably at the lowest excited state of a specific multiplicity (singlet for fluorescence or triplet for phosphorescence)[2] and Vavilov's rule stating that the quantum yield of photoluminescence is generally independent of the excitation wavelength.[3] Both rules work well for many molecules, but exceptions are discovered because of various reasons, e.g., intersystem crossing,[4,5] intramolecular charge transfer (ICT),[6–8] excited states intramolecular proton transfer (ESIPT),[9,10] and so on.[11–13]

Among many factors that can change the rate ratio of radiative and nonradiative decays, crossing conical intersections (CIs) can produce the most dramatic effect where the nonradiative decay time can be accelerated from ns to ps or even hundreds of femtoseconds. It has been applied to explain for the mechanisms of multiple photoluminescence systems such as nanoclusters,[14,15] quantum dots,[16] aggregation-induced emission (AIE) processes,[17,18] and ESIPT processes.[19] However, compared to other pathways such as intersystem crossing, intramolecular charge transfer, or excited states intramolecular proton transfer, crossing CIs does not normally produce apparent phenomena or quantities that can be experimentally directly observed because of its non-radiative nature and the absence of the metastable state during the processes.[20,21] Thus, in most cases, crossing CIs can only be implied via some indirect methods. One classical and useful method is to measure the fluorescence quantum yield as a function of temperature because a nonradiative pathway should be slower at lower temperature. This phenomenon has previously been observed by Ma *et al.* on tetraphenyl ethylene (TPE).[22] The fluorescence intensity increases at lower temperature, which
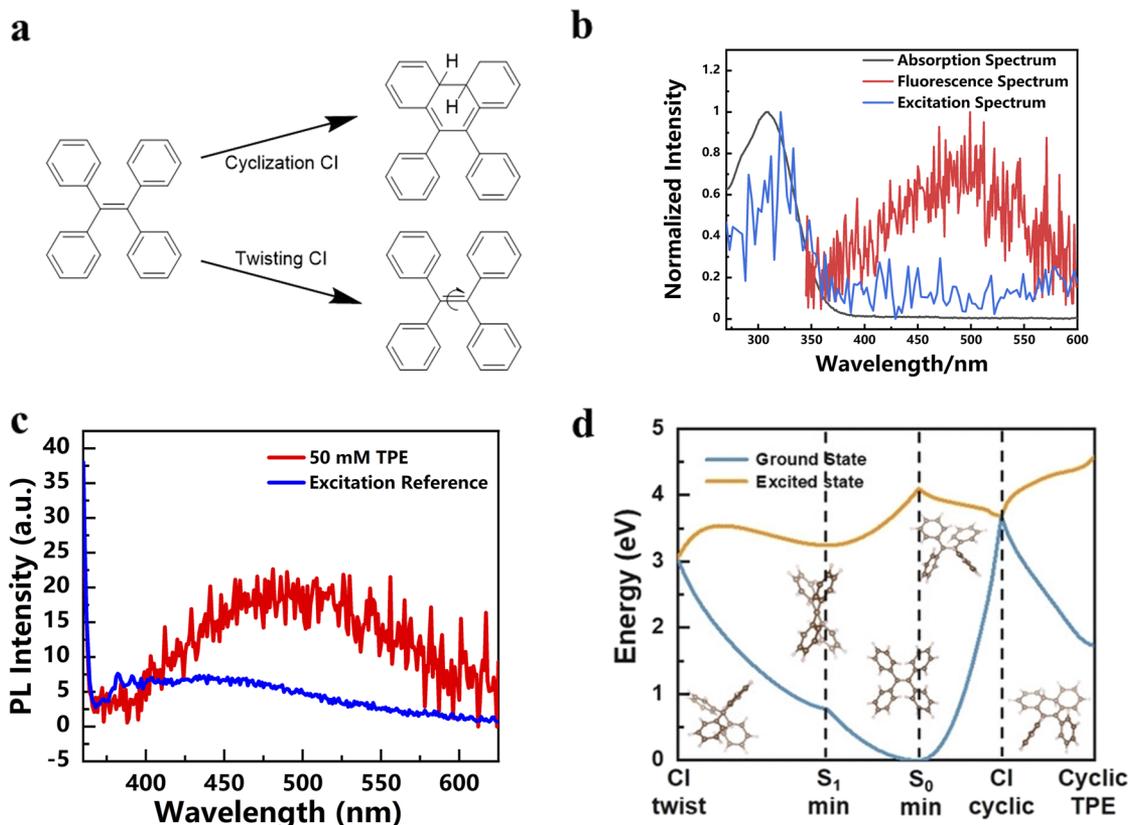
FIG. 1. (a) TPE's two distinct conical intersection pathways and their possible intermediates. (b) The absorption, fluorescence, and excitation spectra of the 50 mM TPE/THF solution. (c) The PL intensity and excitation reference of the 50 mM TPE/THF solution under 350 nm excitation. (d) Computed energy profile of TPE after electronic excitation. Adapted with permission from Guan *et al.*, Angew. Chem., Int. Ed. **59**(35), 14903–14909 (2020). Copyright 2020, Wiley-VCH.

indicates the presence of nonradiative pathways with energy barriers. Recently, with the development of ultrafast spectroscopy, it is possible to observe some CI crossing processes such as TPE's cyclization CI.

In previous studies, the computed energy profile indicates two potential CI pathways for TPE's excited state S_1 to fast dissipate energy: the Woodward–Hoffmann excited state cyclization process and the cis–trans isomerization process via the central carbon–carbon double bond twisting.[18] The cyclization pathway can be monitored by directly detecting the formation of its unique cyclization intermediate, which well explains the AIE mechanism of TPE,[18] whereas the isomerization pathway is difficult to study because of the lack of observable quantities. Nevertheless, the computed energy profile suggests that crossing the cyclization CI is barrierless and crossing the twisting CI has a small barrier [Fig. 1(d)]. If the calculations are correct, we expect that with a shorter wavelength excitation, the excessive energy will be higher so that the effective barrier for the twisting pathway will be smaller, whereas the cyclization pathway is always barrierless. This situation will result in relatively more molecules relaxing through the twisting pathway and fewer molecules going through the cyclization pathway with a shorter excitation wavelength. At the same time, because of the

increase in the nonradiative decay rate with a shorter excitation wavelength, the PL behavior of TPE is expected to be deviated from Vavilov's rule: its luminescence efficiency is expected to be lower rather than constant with a shorter excitation wavelength. Herein, we perform excitation wavelength dependent ultrafast UV/IR and fluorescence experiments to test this prediction.

II. EXPERIMENTAL SECTION

Tetraphenyl ethylene (TPE) was purchased from MACKLIN and was used to prepare 50 mM Tetrahydrofuran (THF) solutions for measurements. UV–vis absorption was measured with a Shimadzu UV3600Plus spectrophotometer. The excitation spectrum was measured with an Edinburgh FLSP 920. The PL intensity and quantum yield were measured using an Edinburgh FLS 980 spectrometer with a supercontinuum excitation light source and integrating sphere accessory. In quantum yield experiments, we measured the spectrum of TPE/THF solution under different excitation wavelengths in a sealed 100-μm CaF2 cell. The spectrum of THF was also measured in the same setup as a comparison to eliminate the influence of the instrumental background. The ultrafast UV–infrared data were collected from a home-built system. In

this system, laser pulses (1 kHz, ~50 fs FWHM, and 800 nm) are generated from an amplified Ti–sapphire laser system (Uptek Phidia) and split into two parts. One is guided into an optical parametric amplifier (Light Conversion TOPAS-Prime) to generate tunable excitation lights from 267 to 800 nm with ~60 fs FWHM in 1 kHz, which served as the pump light. The other part is guided into another optical parametric amplifier (Quantronix Palitra) to generate a tunable mid-IR pulse from 1300 to 3500 cm^{-1} with bandwidth of ~200 cm^{-1} in 1 kHz repetition rate, which served as the probe light. In experiments, the ~100 μW pump pulse is focused via a BK7 planoconvex lens on the sample in a 100-μm CaF$_2$ cell, the probe pulse is focused via a gold-coated parabolic mirror on the same spot of the pump pulse and then guided into a spectrometer with a liquid nitrogen cooled 2 × 64 pixel mercury cadmium telluride detector to obtain the frequency-domain intensity data in a ~3 cm^{-1} resolution. Two polarizers are inserted into the probe light pathway immediately before and after the sample. The polarizer before the sample is used to rotate the polarization of the probe light, and the polarizer after the sample is used to select the desired parallel or perpendicular polarization of the probe light related to the pump pulse, which is horizontally polarized. By setting the polarization of the probe light at the magic angle (54.7°) toward the pump light, we can obtain the rotation-free signal from the parallel signal and perpendicular signal as indicated in the following equation:

$$P_{magic\ angle}(t) = \frac{P_{\text{parallel}}(t) + 2P_{\text{perpendicular}}(t)}{3}. \qquad (1)$$

III. RESULTS AND DISCUSSION

Unlike the CI pathway caused by cyclization, the cis–trans twisting CI does not have an observable intermediate [Fig. 1(a)], so an indirect method of study is needed. As displayed in Fig. 1(b), although both the excitation and fluorescence spectra are noisy due to an ultrathin sample cell (to avoid saturated absorption) and the low FL quantum yield, the excitation spectrum (the fluorescence intensity at 500 nm normalized with the power of each excitation wavelength), nevertheless, looks different from the absorption spectrum, and the difference seems to be more salient in the shorter wavelength range. The PL intensity and excitation reference under 350 nm excitation are displayed in Fig. 1(c). The PL intensity is very low, and the quantum yield is only 0.035%. There is one likely reason contributing to the difference in the excitation spectrum from the absorption spectrum in Fig. 1(b): the fluorescence intensity decreases with a shorter wavelength excitation—anti-Vavilov's phenomenon to be discussed in the following. Figure 1(d) displays the calculated energy profile of TPE. The cyclization CI pathway has nearly no energy barrier to overcome, and the molecular coordinate change is relatively mild. The twisting CI pathway has a potential barrier, and the change in the nuclear coordinates is much larger, which makes the barrier even higher in a practical system where solvent molecules are solvating the excited TPE molecules. These calculations suggest that crossing the twisting CI can be accelerated by extra excitation energy to overcome the potential barrier, whereas crossing the cyclization CI is leveled off because its barrierless or the barrier is significantly lower. To test this assumption, the PL intensity and quantum yield of the 50 mM TPE/THF solution under excitation from 260 to 350 nm in a 100 μm cell are

measured to evaluate the dependency on the excitation wavelength. The absorption percentages and quantum yields are listed in Table I. The original data are provided in the supplementary material.

The results in Table I suggest a trend that the quantum yield is smaller with a shorter excitation wavelength, a deviation from Vavilov's rule. Very interestingly, there seems to be a jump between 300 and 310 nm despite the relatively large uncertainty caused by the extremely low quantum yields (Only around 0.0001–0.0003). The results suggest that either the cyclization CI pathway indeed has a barrier, which is dependent on the excitation wavelength, or there is additional CI pathway, which has a barrier larger than the cyclization CI pathway, other than other factors such as intersystem crossing.

The origins of lower fluorescence with a shorter excitation wavelength can be distinguished by ultrafast UV–infrared measurements with different excitation wavelengths. If there is no additional CI and the cyclization CI pathway has a barrier, there will be more formation of cyclization intermediate with a shorter excitation wavelength. If the twisting CI pathway does exist and has a higher barrier than the cyclization CI as predicted by calculations, there will be less formation of the cyclization intermediate with a shorter excitation wavelength. As displayed in Fig. 2, following our previous work,[18] the peaks at 1440 and 1510 cm^{-1} at time zero can be labeled the signal of excited TPE molecules, and the peak at 1474 cm^{-1} is used as the representative of the cyclization CI process, which reaches its maximum at ~10 ps.

In order to evaluate the excitation efficiency for cyclization, we need to eliminate the influence of the absorbance difference at different excitation wavelengths. Assuming that any TPE molecule can only be excited by a single photon, the amount of excited TPE molecules is directly proportional to the amount of absorbed photons,

$$N_{excited} \propto N_{photon}. \qquad (2)$$

The intensity of signal (ΔO.D.) is proportional to the corresponding excited molecules. Thus, we have

$$\Delta O.D._{\text{state i}} \propto N_{state\ i}. \qquad (3)$$

TABLE I. Absorption percentages and quantum yields of TPE/THF 50 mM solution under different excitation wavelength.

Excitation wavelength (nm)	Absorption percentage (%)	Quantum yield (‰)	Integration uncertainty (‰)
260	86.4	1.6	0.7
270	79.3	1.8	0.6
280	65.4	2.0	0.8
290	90.9	1.9	0.9
300	95.4	1.7	0.9
310	95.8	3.3	0.8
320	95.9	3.3	0.7
330	96.2	3.2	0.7
340	96.6	3.3	0.9
350	96.5	3.5	0.8
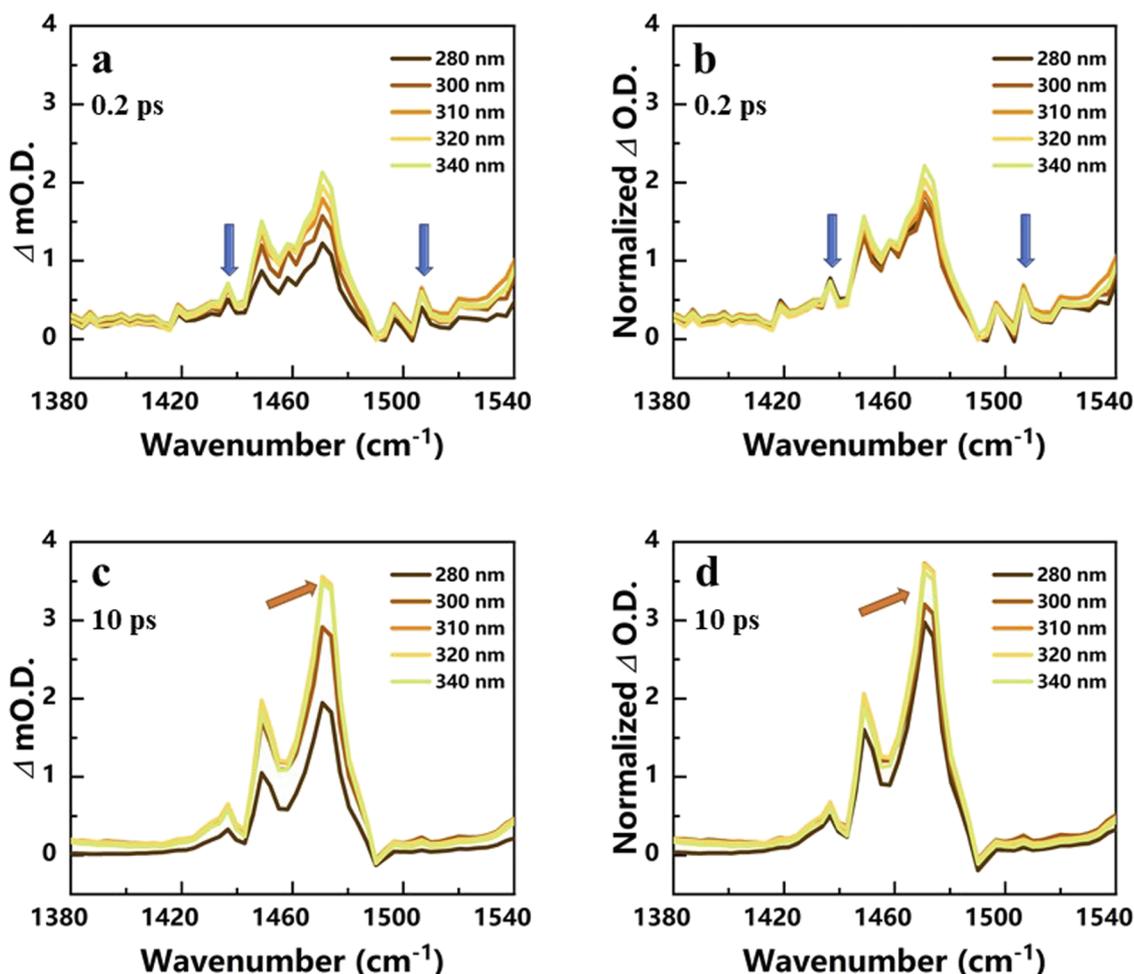
FIG. 2. Original (a) and (c) and normalized by absorbance (b) and (d) UV–infrared pump–probe spectrum of 50 mM TPE/THF solution at 0.2 ps (a) and (b) and 10 ps (c) and (d). The peaks representing the direct excited TPE molecules are indicated by blue arrows, and the peak representing the cyclization CI pathway is indicated by orange arrows.

For any cross section in a light path, the total power of light can be calculated from the number of photons passing the section per unit time and the energy of the single photon. For a monochromatic light, we have

$$P_{light} = \frac{N_{photon}h\nu_{photon}}{t}. \tag{4}$$

Thus, when the total power of different excitation wavelengths is the same, we can estimate the amount of photons absorbed from the absorption percentage and the wavelength of excitation light. In this work, the absorption percentage is measured by comparing the intensity of excitation light in a photometric integrating sphere with or without the TPE sample in the same setup of the ultrafast experiments. The calculated absorption percentage is listed in Table I, and the original data are listed in the supplementary material.

For peaks at 1440 and 1510 cm^{-1}, when normalized by the absorption percentage, different pump wavelengths generate similar signal intensities. However, for the peak at 1474 cm^{-1}, which is from the vibrational transition of the cyclization intermediate, the normalized signal intensity drops when the pump wavelength is shorter, indicating that the formation of cyclization intermediate is less. Similar to the fluorescence quantum yield measurements, there also seems to be a jump at around 310 nm. The results indicate that an additional crossing CI pathway, which has a higher barrier, does exist, and it is probably the predicted twisting CI pathway.

As discussed above, the intensity of the peak at 1474 cm^{-1} drops when excited with a shorter wavelength, indicating the existence of at least a fast competing energy dissipation pathway with a higher energy barrier. This pathway is assigned to the twisting isomerization pathway based on calculations. However, other factors, such as intersystem crossing, cannot be completely ruled out yet.
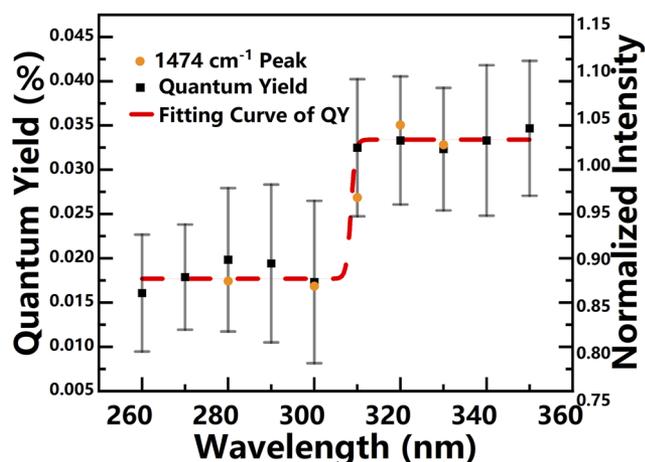
FIG. 3. The PL quantum yields with the error bar and the normalized intensity of 1474 cm^{-1} peak of the TPE/THF 50 mM solution.

Nevertheless, intersystem crossing, in general, is very slow (ns or even slower, three order of magnitude slower than ps discussed in this work) in organic systems without a heavy atom. In addition, experimentally, no sign of phosphorescence or new transient IR peaks of the triplet state under shorter excitation wavelengths is observed. Therefore, summarizing all experimental and theoretical evidence available, we conclude that the twisting CI pathway probably exists and it has a higher effective barrier than the cyclization pathway.

The PL quantum yields and normalized 1474 cm^{-1} peak intensities are plotted together in Fig. 3 to illustrate their decreasing trends with shorter wavelength. From Fig. 3, we can find that the decreasing trend of quantum yield and the normalized intensity of 1474 cm^{-1} peak follow a very similar trend.

We further analyzed the dynamic behaviors of 1474 and 1440 cm^{-1} peaks in Fig. 4. From the data, we can find that the dynamic of the cyclization process (1474 cm^{-1} peak) shows no dependency toward different excitation wavelengths, which rules out the potential possibility of the acceleration of the cyclization CI process under shorter excitation wavelengths. However, for
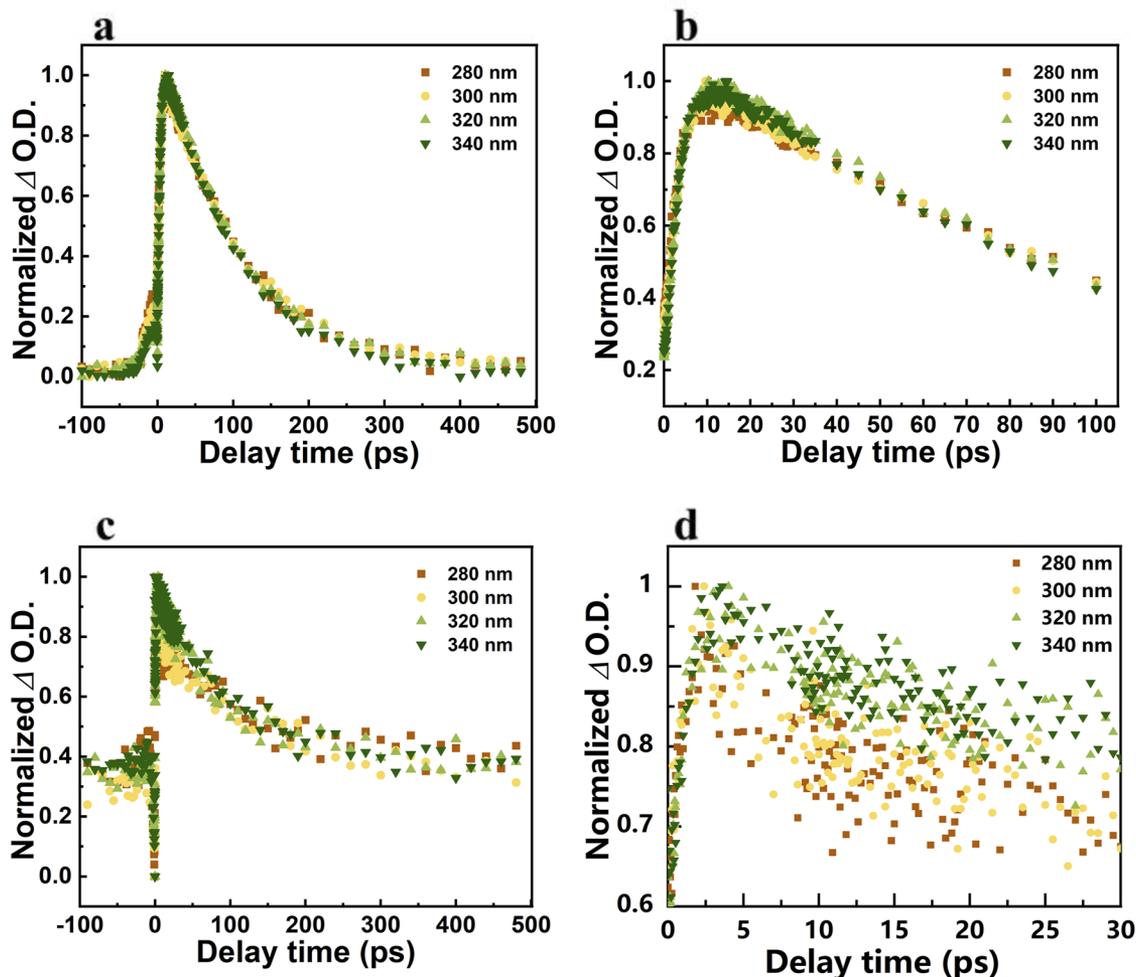
FIG. 4. The UV–infrared pump–probe dynamics of the 1474 cm^{-1} peak (a) and (b) and 1440 cm^{-1} peak (c) and (d) for 50 mM TPE/THF solution under different excitation wavelengths. To make the difference clear, the part of major variation is shown separately (b) and (d).

1440 cm^{-1} peak, which represents the direct excited TPE molecules, its dynamic is influenced by different excitation wavelengths. Under 280 nm and 300 nm excitation, the 1440 cm^{-1} peak decays faster than under 320 or 340 nm, which indicates the presence of a new way for TPE to relax through. Suggested by the computational result shown in Fig. 1(d), it is reasonable to assume that the new pathway is probably crossing the twisting CI. Regarding the plausible jump around 300–310 nm, our tentative explanation is that probably the major contribution to the actual barrier of the twisting CI pathway is the reorganization of the solvation shell, which needs a threshold to trigger. In solution, the TPE molecules are surrounded by the solvent molecules, which adds an additional barrier for the conformational change. The recent study by Kayal et al. has proved that the vibrational state of the S1 state might play a crucial role in TPE's excited state's behaviors.[23] Under the different excitation wavelengths, it is conceivable that the TPE molecules could be excited to other electronic excited states other than S1. However, according to our calculations, the S2 transition wavelength is about 250 nm, which is much higher than 280 nm. Therefore, under excitation with wavelength longer than 280 nm, the major contribution is probably from S1. Within S1, TPE is excited to different vibrational and rotational excited states under different excitation wavelengths. A shorter excitation wavelength means that the excited TPE molecule has more excessive energy and is more likely to change its conformation. Compared to the cyclization process, twisting of the central carbon–carbon double bond leads to more significant alteration of its conformation, which means that it needs more excessive energy to reach the twisting CI point. Thus, only for excitation wavelength shorter than a certain value, e.g., 310 nm, the excessive energy can be sufficiently large to overcome the additional barrier and reach the twisting CI point, which causes the jump around 300–310 nm.

IV. CONCLUSION

In this work, a 50 mM TPE/THF solution is investigated with excitation wavelength dependent ultrafast UV/IR and fluorescence experiments. It is found that the fluorescence quantum yield is smaller with a shorter excitation wavelength, an anti-Vavilov phenomenon. The cyclization intermediate by crossing the cyclization CI is also less with a shorter excitation wavelength. Combining experimental results and calculations, the most probable mechanism responsible for the observations is that there is another pathway by crossing the twisting CI where the energy barrier is larger than the cyclization CI pathway. The explanation is further supported by dynamic measurements, which show that the excitation of TPE molecules decays faster with a shorter wavelength, whereas the growth rate constant of the cyclization intermediate remains constant with different excitation wavelengths. A plausible jump with excitation between 300 and 310 nm is observed, which is possibly caused by the large solvent reorganization associated with the cis–trans twisting isomerization motions.

SUPPLEMENTARY MATERIAL

See the supplementary material for the absorption spectrum of dilute TPE/THF solution, the original measurement data of absorption percentage, and the measurement data of PL intensity of 50 mM TPE/THF solution.

AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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