Structural Rearrangement Accompanying the Ultrafast Electrocyclization Reaction of a Photochromic Molecular Switch

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Ⓢ *Supporting Information*

ABSTRACT: Probing the structural rearrangement of a model photochromic molecular switch provides a window on the fundamental dynamics of electrocyclization reactions. Taking advantage of resonance-enhanced femtosecond stimulated Raman scattering (FSRS) with a broadly tunable Raman excitation wavelength, we selectively probe the competing dynamics of both the reactive and nonreactive conformers of a diarylethene (DAE) derivative that are simultaneously present in solution. Measurements that preferentially probe the electrocyclization (ring-closing) reaction of the reactive species reveal an unexpectedly slow nuclear rearrangement, stretching to tens of picoseconds, in striking contrast with the prompt electronic dynamics in the formation of the closed-ring isomer. The different results from transient electronic and vibrational spectroscopies reflect the different aspects of the reaction that are probed by each technique, depending on whether one considers the electronic state of the molecule or the structural rearrangement of the nuclei. Using a different Raman excitation wavelength selectively probes the picosecond-scale intersystem crossing dynamics of the nonreactive conformer, revealing the vibrational spectra of the singlet and triplet excited states for the first time. The present study paves the way to a more complete understanding of the structural mechanisms accompanying the reversible photochromic switching process.
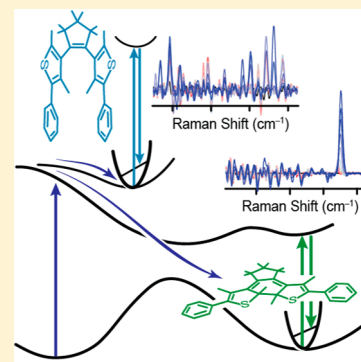
1. INTRODUCTION

Photoisomerization reactions that selectively change the structure of a molecule play a central role in optical data storage, molecular electronics, and many other technological applications. Some of the most popular compounds for these applications are photochromic diarylethene (DAE) derivatives that reversibly transform between open- and closed-ring isomers upon irradiation.[1,2] Typically, UV excitation of the transparent open-ring isomer induces an efficient electrocyclization reaction that rearranges both the electronic and nuclear structure of the molecule, whereas irradiating the closed-ring isomer with visible light regenerates the original compound. In the closed-ring structure, the molecule develops a strong visible absorption band due to extended π-conjugation along the backbone of the nascent isomer. The formation of this electronic absorption band is very rapid, often lasting only a few hundred fs or less, which indicates that the electrocyclization reaction is complete on a similar time scale.[3,4]

Numerous time-resolved studies have probed the fundamental steps of the photoswitching process in DAE derivatives.[3−8] However, most of the earlier studies monitor the dynamics using either transient electronic absorption or fluorescence techniques,[3,4,9−12] both of which lack structural sensitivity. Very few experimental studies have directly reported on the molecular motions associated with ring closure. A stunning exception is the recent work by Miller and co-workers,[6,10] who used time-resolved electron scattering to probe the structural dynamics of the ring-closing reaction of a photochromic molecular switch in a crystalline film on the fs time scale with atomic spatial resolution. Although the nuclear motions associated with the reaction coordinate were revealed in unprecedented detail, scattering techniques are not amenable to solution-phase studies, due to the inherent disorder of such systems.

Further complicating matters in solution, the open-ring isomer of most DAE compounds can adopt more than one conformational state, each with potentially different reaction pathways. For example, the molecule that we study here, 1,2-bis(2,4-dimethyl-5-phenyl-3-thienyl)perfluoro-cyclopentene (DMPT-PFCP), exists in two primary conformations with roughly a 1:1 ratio and an interconversion time of around 90 ms at room temperature.[13] The conformers differ in the relative orientation of the two phenylthienyl side groups. One species is a nonreactive conformer (NRC) with the side groups in a parallel orientation that prohibits the cyclization reaction, and the other is a reactive conformer (RC) with an antiparallel orientation of the side groups that prealigns the frontier orbitals for rapid electrocyclization.[14] Competing signals from the reactive and nonreactive conformers significantly complicate the interpretation of transient absorption measurements. In

fact, the lack of a well-defined initial geometry for the open-ring isomer leads to multiple reaction pathways in solution,[15−17] and therefore requires more selective methods for probing the electrocyclization dynamics than is possible using the broad, overlapping transient electronic absorption bands.

Time-resolved vibrational spectroscopy provides in principle the sensitivity to resolve the dynamics of multiple conformational states, as well as the desired structural information related to the electrocyclization reaction.[18] Surprisingly, very few transient vibrational measurements have been reported for the ring-closing reaction of photochromic DAE molecular switches,[19] leaving many unresolved questions about the fundamental dynamics of these popular molecules. In this paper, we use resonance-enhanced femtosecond stimulated Raman scattering (FSRS)[20−24] to preferentially probe the ultrafast dynamics of the ring-closing reaction, even in the presence of competing reactions, and then contrast the electronic and nuclear dynamics of the electrocyclization reaction. Specifically, we probe the evolution of the vibrational spectrum following photoexcitation, while taking advantage of the wavelength tunability of our narrowband Raman probe[24] to selectively monitor the response of the different molecular conformers that contribute to the transient signal. Electronic resonances provide a convenient means of selectively probing the different species via resonance enhancement of the transient Raman response. Our results provide important benchmarks for theoretical studies of DAE photoswitching reactions, as well as new insight on the nonadiabatic dynamics of electrocyclization.

2. EXPERIMENTAL METHODS

The experiment was performed in the Femtoscopy Laboratory at "Sapienza" University (Rome). Details of the femtosecond stimulated resonance Raman setup have been described elsewhere.[24] Briefly, the setup is driven by an amplified Ti:sapphire laser (Coherent Legend Elite HE) producing 3.6 mJ, 35 fs pulses at 800 nm (450 cm^{-1} bandwidth) and 1 kHz repetition rate. A portion of the laser fundamental is frequency tripled via successive stages of second harmonic generation and sum frequency generation to give <100 fs duration, 265 nm actinic pulses that are resonant with the UV absorption band of the closed-ring isomer of DMPT-PFCP. The evolution of the molecule is then probed via either transient electronic absorption or transient stimulated Raman scattering.

Widely tunable Raman pump pulses are an essential component of the resonance-enhanced femtosecond stimulated Raman scattering (FSRS) setup used here. The narrow bandwidth Raman pump pulses in the range 350−600 nm are generated from a commercial two-stage OPA (Light Conversion TOPAS-C) that produces tunable IR-visible pulses, followed by frequency doubling in a 25 mm BBO crystal. The final stage of second harmonic generation in the long BBO crystal is the key to generating narrow-band pulses via spectral compression. This technique takes advantage of the group velocity mismatch between the fundamental and second harmonic in the long BBO crystal to create few-ps duration pulses with typical bandwidths of ∼15 cm^{-1}.[24−26] Sharp edges in the temporal pulse profile that are characteristic of the spectral compression method can cause spectral ringing for vibrational bands associated with relatively long (>1−2 ps) dephasing times. We recently discussed these effects, and showed that a simple spectral filter significantly improves the line shape of Raman pump pulses obtained via spectral

compression,[27] although such pulse shaping was not necessary for the present experiment due to the short dephasing times (i.e., broad natural line widths) of the transitions observed here.

The femtosecond Raman probe is a white-light continuum generated by focusing the laser fundamental into a CaF$_2$ crystal that is continuously translated perpendicular to the beam to prevent damage. The transmitted WLC is collected through a spectrometer (Acton Spectra Pro 2500i) and dispersed on a CCD device (Princeton Instruments Pixis 100), which allows single shot acquisition. A synchronized chopper blocks alternating Raman pump pulses in order to obtain the Raman gain using successive probe pulses, and a second chopper blocks the actinic pump at 250 Hz in order to obtain Raman gain spectra with and without actinic excitation. We typical average 10^5 laser shots to obtain the transient Raman spectrum at each delay time. Details of the baseline subtraction method are provided as Supporting Information.

The molecular switch (DMPT-PFCP) was purchased from TCI America, and dissolved in cyclohexane (Sigma-Aldrich, ≥ 99.9%) to a concentration that gives 10% transmission of the 265 nm actinic pulses through a 500 μm path length. The sample circulates through a flow-cell during the measurement in order to refresh the sample volume in the laser focus (∼70 μm fwhm) before every laser pulse. The Raman pump energy is typically set at 800 nJ per pulse, and the actinic pump at 2 μJ per pulse.

3. RESULTS AND DISCUSSION

Figure 1 shows the electronic absorption spectra of the open- and closed-ring isomers of DMPT-PFCP in cyclohexane.
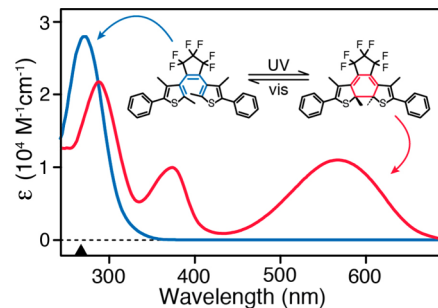
Figure 1. Static electronic absorption spectra of the open- and closed-ring isomers of DMPT-PFCP in cyclohexane. The arrowhead indicates the actinic pump wavelength of 265 nm.

Irradiating a solution of the transparent open-ring isomer with a 265 nm actinic laser pulse produces the transient electronic absorption spectra in Figure 2. The transient signal is initially dominated by two broad absorption bands centered near 400 and 580 nm, respectively, and then partially decays over several tens of picoseconds before reaching a stable state that lasts for more than a nanosecond. The steady-state spectrum beyond ∼100 ps contains contributions from both the relaxed ground state of the closed-ring product and a long-lived excited state of the NRC, as illustrated by the dashed lines in the top panel of Figure 2.

The bottom panel of Figure 2 shows the time evolution of the transient absorption signal at two probe wavelengths. Importantly, the rapid rise of the electronic absorption at 560 nm, the maximum of the product absorption band, indicates that the electrocyclization reaction is complete within a few hundred fs of the initial excitation.[3,4,9] The ps-scale decay of the

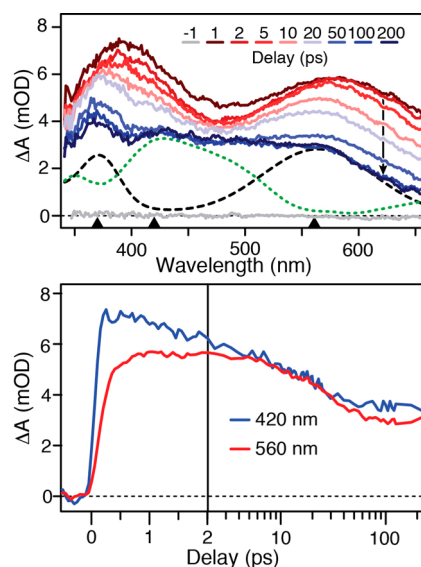**Figure 2.** Evolution of the transient electronic absorption spectrum following 265 nm excitation. The transient spectrum reaches a steady state by ~100 ps, with contributions from the closed-ring product (dashed black line) and the triplet excited state of the nonreactive conformer (dotted green line). Arrowheads in the top panel indicate the Raman pump wavelengths of 370, 420, and 560 nm. Note that the evolution of the transient absorption at 420 and 560 nm in the bottom panel is shown on a linear time scale below 2 ps and a logarithmic time scale above 2 ps.

Figure 3. Experimental and theoretical Raman spectra for the open-ring (red) and closed-ring (blue) isomers of DMPT-PFCP in cyclohexane. The experimental stimulated Raman spectra are measured with a 370 nm Raman pump, and the asterisk indicates an artifact from solvent subtraction. The calculated spectra (B3LYP/6-31G*) include 15 cm^{-1} line broadening.

transient absorption spectrum is therefore assigned as a contribution from the NRC. Although the geometry of the "non-reactive" conformer is not favorable for cyclization, this species experiences interesting excited-state dynamics on a time scale of 23 ps. By analogy with the closely related DAE compound 1,2-bis(2-methyl-3-benzothienyl)perfluoro-cyclopentene, we assign the 23 ps decay as intersystem crossing (ISC) in the nonreactive conformer. The rapid, ps-scale ISC is also strikingly similar to the behavior of the isolated side group (2,4-dimethyl-5-phenylthiophene, DMPT), which undergoes a singlet–triplet transition on a time scale of 22 ps in cyclohexane.[28] The NRC relaxes from the triplet state back to the ground state of the open-ring isomer on a ns–μs time scale.[4,29]

Transient vibrational spectroscopy provides a more selective probe of the *structural* evolution of the system following UV excitation. For reference, Figure 3 shows the experimental and theoretical Raman spectra of both the open- and closed-ring isomers of DMPT-PFCP. The stimulated Raman spectra were obtained experimentally with a 370 nm Raman pump wavelength, which is resonant with the second absorption band of the closed-ring isomer (see Figure 1). The experimental spectra are in good agreement with the calculated Raman spectra obtained from B3LPY/6-31G* with a frequency scaling factor[30] of 0.960 and 15 cm^{-1} line broadening to simulate our experimental resolution. The spectrum of the closed-ring isomer is dominated by a strong vibrational band at 1503 cm^{-1}, which has been assigned as a delocalized C=C stretching mode of the extended π-conjugated polyenic backbone of the molecule.[31] The time evolution of the 1503 cm^{-1} mode following ring closure is described in detail below. In excellent agreement with the calculated spectrum in the figure, the ethylenic band is relatively intense due to the large polarizability of the conjugated backbone of the closed-ring
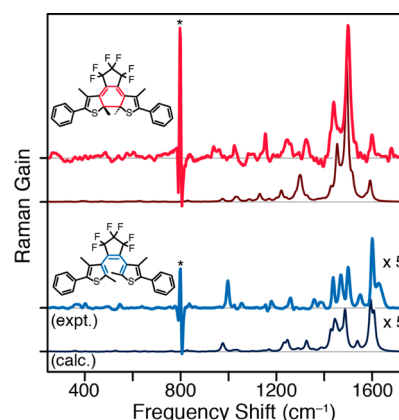
isomer. Additionally, the intensity of the ethylenic band may be further enhanced due to the Raman pump being resonant with the second absorption band of the molecule,[31,32] although this effect is not included in the calculated spectrum.

Time-resolved resonance-enhanced stimulated Raman scattering allows us to distinguish the different dynamics of the reactive and nonreactive conformers of DMPT-PFCP following excitation with a ~100 fs actinic laser pulse at 265 nm. First, we exploit the minimum in the absorption spectrum of the closed-ring isomer near 420 nm in order to selectively probe the dynamics of the NRC. The NRC singlet and triplet excited states are entirely responsible for the residual transient absorption in this wavelength range once the electrocyclization reaction is complete (~300 fs).

The evolution of the 420 nm stimulated Raman spectrum is shown in Figure 4. As expected, the transient vibrational spectrum evolves on an ~23 ps time scale (bottom panel) that matches the ISC time obtained from the transient electronic absorption measurement. Specifically, some of the observed vibrational modes rise and others decay on the same time scale as the population dynamics between S$_1$ and T$_1$ of the NRC conformer. Remarkably, no significant variations of the transition frequencies are observed, implying negligible heating effects upon photoexcitation.[33,34] The only vibrational band that does not evolve with the ISC time appears on a slightly longer time scale at ~1525 cm^{-1}. This outlier may be associated with a large-amplitude structural relaxation of the triplet excited state, similar to the behavior of the closed-ring product described below. Notably, we do not observe the characteristic Raman band of the closed-ring isomer at 1503 cm^{-1}, despite the fact that this molecule is electronically preresonant with the 420 nm Raman pump. The lack of Raman signal at 1503 cm^{-1}, even at the longest delay times, indicates that the resonance enhancement of the singlet and triplet states of the NRC dominates the transient vibrational spectrum at this pump wavelength. The open-ring isomer does not contribute to the 420 nm stimulated Raman spectrum because that molecule is a weak Raman scatterer that absorbs only below ~330 nm (see Figure 1).

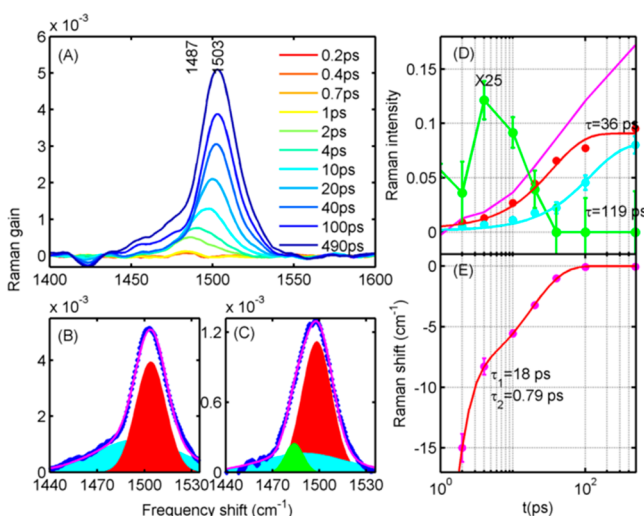We now explore other electronic resonances in order to resolve the dynamics associated with the reactive conformer of

Figure 4. Transient stimulated Raman spectra obtained with a 420 nm Raman pump (top panel) and corresponding evolution of the Raman gain (bottom panel) for several features.

Figure 5. Transient Raman spectra obtained with 370 nm (top panel) and 560 nm (bottom panel) Raman pump wavelengths.

DMPT-PFCP. Figure 5 shows the evolution of the transient stimulated Raman spectrum for excitation wavelengths of 560 and 370 nm, which are resonant with the first and second absorption bands of the closed-ring isomer, respectively (see Figure 1). As expected, both spectra develop a strong band near 1503 cm^{-1} that closely resembles the dominant ethylenic mode of the closed-ring isomer in Figure 3. The 370 nm Raman pump is also resonant with the singlet and triplet excited states of the NRC, which explains the additional features (e.g., at 985

and 1405 cm^{-1}) that follow the same behavior as the 420 nm transient Raman spectrum.

The ethylenic stretch near 1503 cm^{-1} is a clear signature of the formation of the closed-ring isomer, and therefore reveals the structural dynamics of the electrocyclization reaction. However, considering the rapid, sub-ps appearance of the associated electronic absorption bands, the formation of this characteristic vibrational mode occurs on a surprisingly slow time scale. Critically, no evidence for the ethylenic mode shows up in the spectra within the first few ps, and even then the band does not fully develop for several tens of picoseconds. The 560 nm transient Raman signal probes the surprising behavior of the product vibration most directly, because this excitation wavelength is primarily resonant with the first absorption band of the closed-ring isomer.

The frequency of the delocalized ethylenic stretching mode is sensitive to the structure of the closed-ring isomer, and therefore is an excellent probe of the evolution along the electrocyclization reaction coordinate. Perhaps more importantly, the amplitude of the 1503 cm^{-1} mode is sensitive to the degree of conjugation along the backbone of the molecule, because delocalization of the π-electrons increases the polarizability, and therefore also the Raman cross section. In other words, although the high-frequency 1503 cm^{-1} vibration is not directly involved in ring closure, this mode provides a sensitive probe of the structural dynamics of the electrocyclization reaction. The delayed appearance of the intense 1503 cm^{-1} mode suggests that the molecule does not reach the equilibrium ground state of the closed-ring product for several tens of ps.

Figure 6A displays the 560 nm transient Raman spectrum in the 1400−1600 cm^{-1} region in finer detail. Remarkably, for time delays <5 ps, the largest contribution to the transient Raman spectrum in this range is located around 1485 cm^{-1}. The frequency of this mode is similar to the 1487 cm^{-1} mode that we assigned to the S_1 state of the NRC in the 420 nm transient Raman spectrum (Figure 4). However, we do not observe a comparable band near 1571 cm^{-1}, which suggests that the 1485 cm^{-1} vibration in the 560 nm transient Raman spectrum is not due to the NRC. An alternative explanation is that the weak 1485 cm^{-1} mode is a signature of the hot ground state of the closed-ring product, such as an ethylenic stretch that is shifted to lower energy and has reduced intensity compared with the relaxed molecule. The relatively weak contribution disappears at longer delay times, when this region of the spectrum is dominated instead by the strong ethylenic band of the closed-ring product at 1503 cm^{-1}.

Interestingly, even at long delay times, the Raman band at ∼1503 cm^{-1} cannot be modeled by a single mode, because of an additional, broad contribution at slightly lower energy than the dominant narrow feature. Figure 6B shows the decomposition of the Raman peak at 490 ps into a sum of two Gaussian bands, one centered at 1503 cm^{-1} and the other at slightly lower frequency. The lower-frequency 1485 cm^{-1} mode does not contribute at this long delay time.

Given the different bands observed, we model the evolution of the vibrational spectrum in this region as a sum of three Gaussian modes, one to account for the peak related to the hot photoproduct at 1485 cm^{-1} and the other two to reproduce the two contributions that appear at longer delay times. The only free parameters used to fit the Raman spectrum at each time delay are the peak intensities of each band and the frequency shift of the two contributions from the closed-ring isomer relative to the long-time limit. The best fit of the transient

Figure 6. (A) Transient Raman spectra for the 560 nm Raman pump in the region of the conjugated C=C ethylenic mode of the closed-ring isomer. (B) Best fit to the Raman spectrum at 490 ps delay, where the only contributions are from two vibrational bands of the relaxed closed-ring isomer. (C) Best fit to the Raman spectrum at 10 ps delay, which includes contributions from both the hot photoproduct at 1485 cm^{-1} (green) and two bands that are frequency-shifted relative to the relaxed closed-ring isomer. (D) Evolution of the transient Raman gain associated with each of the vibrational bands. Green markers are the band at 1485 cm^{-1}, and red and cyan markers are the narrow and broad frequency-shifted bands of the closed-ring isomer, respectively. The lines are exponential fits, except the magenta line, which is the sum of the two contributions from the relaxed closed-ring isomer bands. (E) Time-dependent frequency shift of the closed-ring isomer bands. The solid line is a biexponential fit.

Raman spectrum at 10 ps, which includes contributions from all three vibrational bands, is shown in Figure 6C. Parts D and E of Figure 6 show the evolution of the Raman intensities and frequency shifts that we extract from the transient Raman spectrum.

The center frequency of the most intense band, assigned as the extended polyenic vibrational mode of the relaxed closed-ring isomer, shifts exponentially on a time scale of ∼18 ps, while the band intensity increases on a time scale that is slower by at least a factor of 2 (Figure 6D,E). Similarly, the broad band continues to evolve even beyond ∼100 ps. In principle, the Raman gain can be affected by transient absorption dynamics that alter the resonance condition. This seems not to be the case here because the TA at 560 nm initially rises in ∼300 fs, and then reaches the equilibrium condition with the 23 ps time scale of intersystem crossing in the NRC, even though the ethylenic mode of the RC continues to increase on a longer time scale. Consequently, the longer time scale observed in the Raman gain is a direct indication of structural changes specific to the closed-ring isomer, and is probably associated with conformational dynamics and vibrational cooling that has been previously observed on a time scale of ∼80−90 ps.[12] The shorter time scale observed for the frequency shift (18 ps) indicates a more substantial structural change, such as the motion of the molecule as it becomes more planar following ring closure, which shifts the vibrational frequency of the ethylenic mode due to anharmonic coupling with other vibrational modes.[33]

It is remarkable that the ps-scale nuclear dynamics that dominate the transient Raman spectrum are not evident in the transient electronic absorption spectrum. Although the analysis of the latter is complicated by broad, overlapping contributions from the NRC, the transient Raman measurement clearly indicates that the nuclear dynamics of the ring-closing reaction occur on a much longer time scale than the electronic spectroscopy suggests. This result is not entirely unexpected, given the significant structural rearrangement involved in the electrocyclization of DAE derivatives. However, it is interesting to highlight the different results obtained from electronic and vibrational spectroscopy, based on the different aspects of the molecular structure that are probed in each case. The "time scale" of the ring-closing reaction depends on whether one considers the *electronic* state of the molecule or the *structural* rearrangement of the nuclei.

Finally, we reiterate the value of the high-frequency ethylenic stretching vibration as an indirect probe of the structural dynamics of the electrocyclization reaction. This mode reports on both the degree of conjugation (via the amplitude) and the molecular structure (via the vibrational frequency), even though the high-frequency C=C stretching motion is not directly involved in the large-amplitude (i.e., low frequency) motion along the reaction coordinate. This contrasts with the more direct structural information obtained from electron scattering experiments by Miller and co-workers[6,10] but leads to a more versatile measurement that can be applied when scattering techniques are not possible due to conformational disorder.

4. CONCLUSION

We have used a broadly tunable resonance Raman probe to selectively monitor the dynamics of the reactive and non-reactive conformers of a diarylethene-type molecular switch. The nonreactive conformer undergoes intersystem crossing from a singlet to a triplet state in 23 ps that is clearly observed in the evolution of both the electronic and vibrational spectra. The vibrational spectra of the singlet and triplet excited states of the nonreactive conformer of DMPT-PFCP are reported here for the first time. The main result of this paper, however, is the ability to track the structural dynamics accompanying the electrocyclization reaction of the molecule. Specifically, the sub-ps electronic dynamics are accompanied by a much slower structural rearrangement, extending up to 100 ps. Through more detailed analysis and comparison with theory,[35] the structural sensitivity of the resonance-enhanced stimulated Raman technique promises to reveal new information about the nuclear dynamics that are responsible for the ultrafast switching reaction (and ps-scale structural relaxation) of prototypical photochromic molecular switches such as DMPT-PFCP.

■ ASSOCIATED CONTENT

ⓈSupporting Information

A description of the baseline subtraction method for obtaining transient stimulated Raman spectra with resonant Raman pump wavelengths is provided. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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