

# Photoreversible Ultrafast Dynamics of Ring Opening and Increased Conjugation under Spatial Confinement

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## Abstract

Isomerization through stereochemical changes and modulation in bond order conjugation are processes that occur ubiquitously in diverse chemical systems and for photochromic spirocompounds, it imparts them their functionality as phototransformable molecules. However, these transformations have been notoriously challenging to observe in crystals due to steric hindrance but are necessary ingredients for the development of reversible spiro-based crystalline devices. Here we report the detection of spectroscopic signatures of merocyanine due to photoisomerization within thin films of crystalline spiroopyran following 266 nm excitation. Our femtosecond spectroscopy experiments reveal bond breaking, isomerization, and increase in bond order conjugation to form merocyanine on a time scale of  $< 2$  ps. They further unveil a lifetime of several picoseconds of this photoproduct, implying that the system is highly reversible in the solid state. Preliminary femtosecond electron diffraction studies suggest that lattice strain favors the return of photoproduct back to the closed spiroform. Our work thus paves the way for spiroopyran-derived compounds for ultrafast studies and applications.

## Introduction

Controllable chemical reactions hold great promise for creating new dynamical photonic and optoelectronic devices.<sup>1,2</sup> Large structural transformations that accompany chemical metamorphosis concomitant with electronic changes naturally provides an attractive route in this direction. Much focus has recently fallen on photochromic compounds, e.g. diarylethenes,<sup>3</sup> azobenzenes<sup>4</sup> and spiroopyrans,<sup>5</sup> which can switch between one or more isomeric forms via light and thermal activation making them strong candidates for photoswitching applications.<sup>6-8</sup> However, simply triggering the reaction is not enough, and other factors such as switchability and photorigidity must also be considered.<sup>9-11</sup>

An ideal photoswitching device exploiting chemical reactions must be one that can undergo indefinite number of photocycles without degradation, display large changes in chem-

ical and physical properties, and be triggered and ideally reversed in a controllable way. While most of these conditions can be readily met in the liquid phase,<sup>12-15</sup> the progress has been frustrated in the solid state, which is more amenable to device applications.<sup>16</sup> The limitation, especially in crystals, can be related to the lack of free volume that generally prevents large changes from taking place in such sterically confined environments, and greatly limit the scope of this class of photoinduced reactions. Indeed, only a few studies have actually reported the possibility to induce reversible chemical transformation in crystals.<sup>8,17,18</sup> Investigations of photochemical properties of photochromic materials and mechanisms that make them conducive or a hindrance to photoswitching applications remain an active area of research.

Spiroyrans have recently emerged as potential contenders for creating photo-activated devices on account of their remarkable tunable structural and chemical properties.<sup>19,20</sup> Absorption of an ultraviolet (UV) photon triggers bond-breaking and cis-trans isomerization reactions leading to planar merocyanine transformation (MC, see Figure 1a). The process has been readily observed in polymer films,<sup>21</sup> glassy matrices and membranes,<sup>22</sup> and in solution<sup>23-27</sup> but evidence of its occurrence in crystals has been challenging to obtain. The latter will open new avenues for highly directional light control and further enable new studies on fundamental processes responsible for the reaction.

Few studies have hinted at the formation of MC in crystals upon UV irradiation,<sup>19,28-31</sup> however evidence for such claims come chiefly from applying surface-sensitive tools such as diffuse-reflectance spectroscopy<sup>32</sup> which cannot confirm whether the reaction indeed takes place inside the bulk or only on the surface level. Static x-ray diffraction experiments have also been conducted which have remained inconclusive and reveal little about the mechanism of the reaction, including switching timescales and pathways involved.<sup>28,30</sup>

In this article, we address the question whether it is actually possible to induce photochromic reactions in crystals of spiroyrans using 1,3,3-Trimethylindolino- $\beta$ -naphthopyrylospiran (henceforth denoted SP) as a representative example from this class of compounds and also

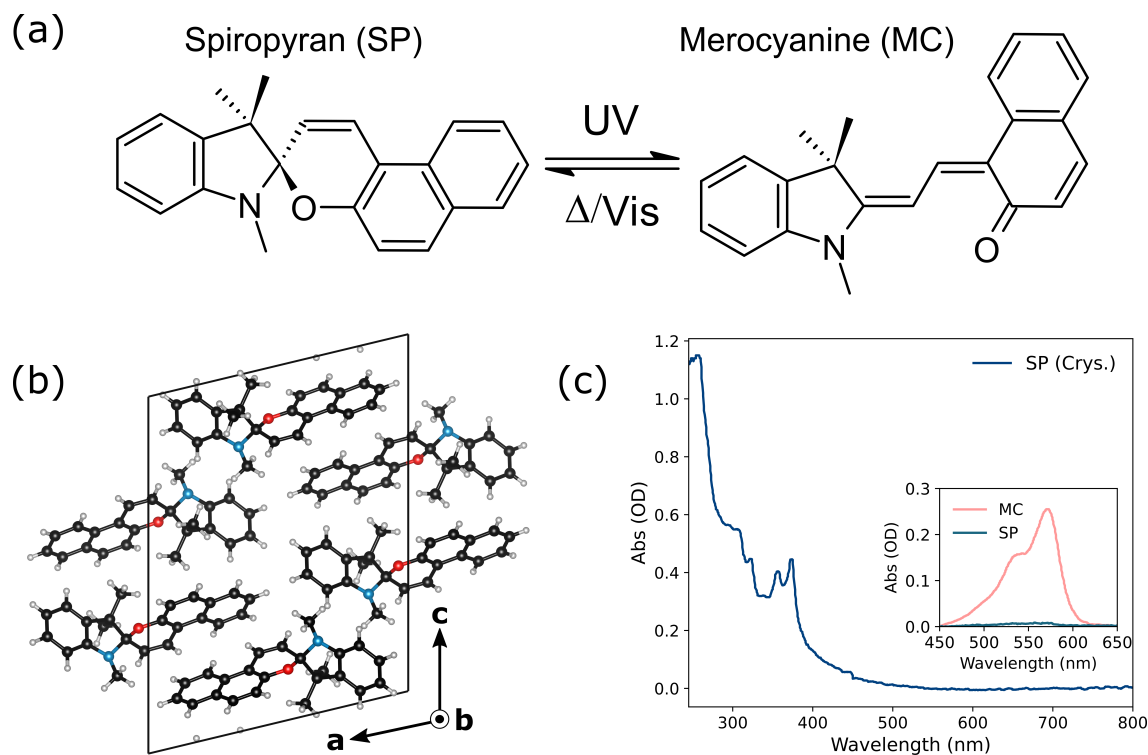


Figure 1: (a) Reaction scheme of SP to MC conversion. The forward reaction requires a UV photon whereas the back reaction occurs either thermally or with visible light activation (b) Crystal structure of SP showing dense packing of non-planar spiropyran molecules. Red: oxygen, Black: carbon, Blue: nitrogen, White: hydrogen (c) Measured steady-state absorption spectrum of SP crystal used in this work. The inset shows the spectra of SP dissolved in acetonitrile solvent measured before and after UV light irradiation. The latter results in the band which is assigned to planar merocyanine products.

investigate the role played by the crystal environment.<sup>33,34</sup> To resolve these, we employ femtosecond transient absorption (fs-TA) spectroscopy which provides sensitive bulk information on structural changes in the form of spectral signatures as a function of pump-probe delay.

## Methods

Optical experiments were performed using a home-built transient absorption setup at room temperature.<sup>35</sup> The fundamental output of a mode-locked, Ti:Sapph oscillator and regenerative amplifier system delivering 35 fs FWHM, 800 nm pulses at 1 kHz was divided using a 90:10 beamsplitter to create pump and probe arms. In the probe arm,  $\approx 2 \mu\text{J}$  of 800

nm light was focused onto a 200  $\mu\text{m}$  window of a cuvette containing water that generated a white light supercontinuum from 380-900 nm. A shortpass cut-off filter centered at 700 nm was placed in the beam path to remove the fundamental beam from the white light. A UV light of 266 nm wavelength and  $\approx 100$  fs FWHM pulse duration was generated in the pump arm using a set of Barium Beta-Borate (BBO) and calcite crystals and focused onto the crystalline sample using a spherical mirror ( $f = 200$  mm). The repetition rate of the probe was set at 1 kHz and the pump was run at 20.83 Hz to ensure ample time for sample relaxation between laser shots.

The SP powder was purchased from TCI Chemicals, Japan and used without further purification. The sample crystals were grown in the dark from a saturated solution of the compound in ethyl acetate. Crystals of SP were then cleaved using an ultramicrotome to the desired thickness for experiments and mounted on a 1 mm thick fused silica disc.

## Results and Discussion

Crystals of SP with a thickness of 250 nm were used for the fs-TA experiments. The dynamics were initiated by the UV pump pulse at an incident fluence of  $2.3 \text{ mJ cm}^{-2}$  and tracked by synchronized time-delayed visible pulses from the white light supercontinuum. Ultrafast pump-probe studies of photochemical changes in photochromic crystals normally necessitate single-shot measurements or photoreversion schemes,<sup>3,35-37</sup> however, remarkably this was not required in our experiments. We will return to this observation later on.

Figure 2a provides an overview of the transient changes in optical absorption,  $\Delta A(\lambda, t)$ , over the entire delay range covered in our study. Spectral traces at selected time delays are provided in Figure 2b alongside kinetic plots at chosen wavelengths shown in Figure 2c. As can be seen from these plots, right at the onset, a broad positive absorption dominates the entire 400-700 nm probe region with a maximum at 515 nm ( $\approx 45$  mOD) featuring a shoulder at around 440 nm ( $\approx 20$  mOD) and a broad tail of similar intensity. In the

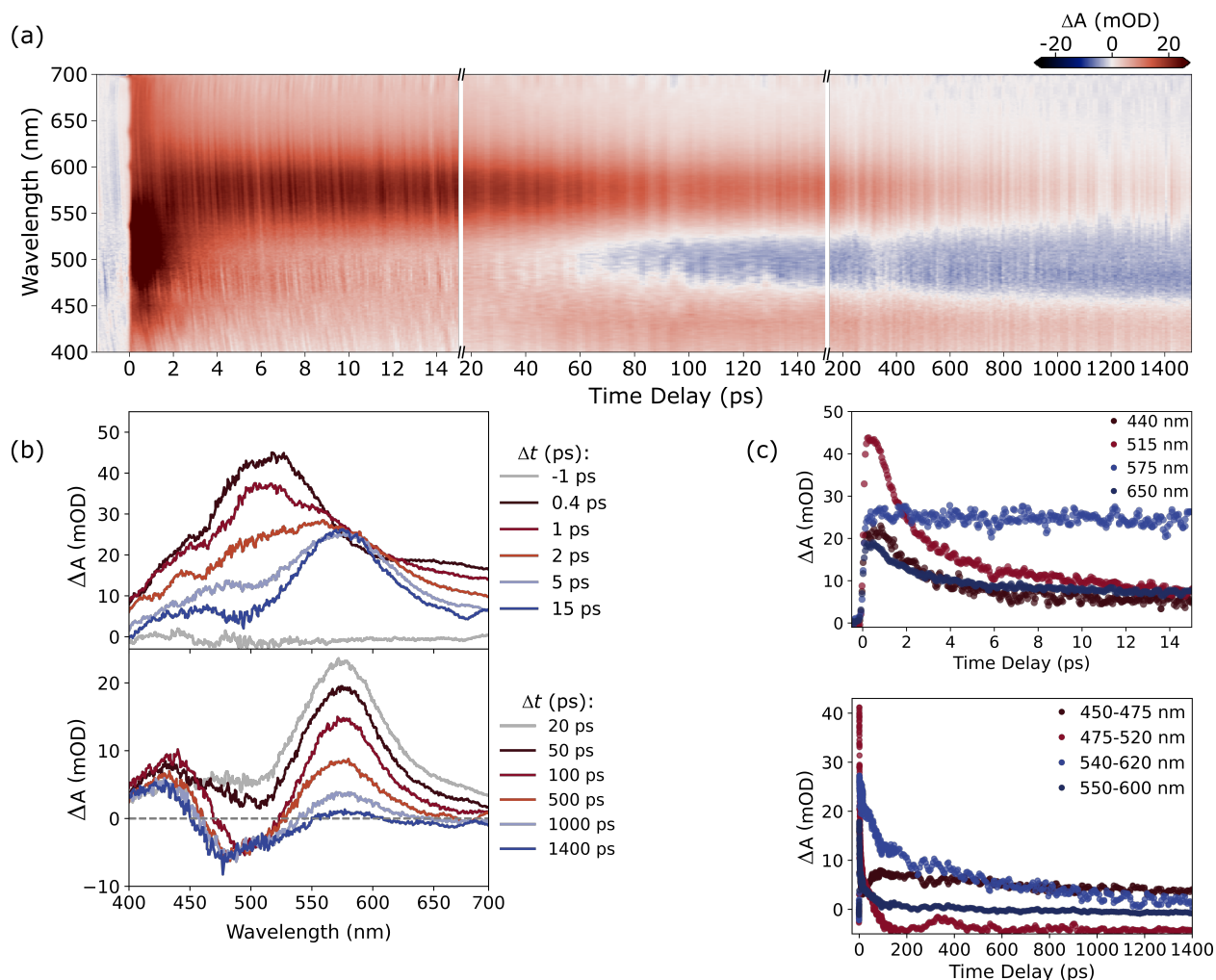


Figure 2: (a) Two-dimensional transient absorption map of SP up to 1.5 ns measured using white-light supercontinuum following 266 nm excitation (b) Transient spectra at selected time delays showing complex dynamics of spiropyran to merocyanine conversion (c) Kinetic profiles at selected wavelengths for the first 15 ps (top panel) and time-evolution of the transient absorption spectra integrated over chosen wavelength range (bottom panel). Slow apparent oscillations can be seen from the integrated plots.

next few picoseconds, these features undergo decay as spectral evolution involving red-shift and bandwidth narrowing takes place until 10 ps, at which point the 515 nm peak has decayed by more than 70% of its initial value and a new maximum at around 570 nm emerges. The subsequent transient data between 10 ps and 40 ps display very minor dynamics as can be seen in Figure 2a. Thereafter, around 45 ps, the onset of slow decay of the visible band is witnessed leading to a rise in optical density in the 400-450 nm region and

appearance of a negative differential signal between 450 nm and 550 nm over long time delays. The latter can be an indication of photobleaching of trapped products which can lead to rapid photofatigue and eventual crystal damage<sup>38</sup> or it can point to one of the emissive photochemical deactivation processes, e.g. stimulated emission and fluorescence.<sup>39</sup>

To rule out the origin of the negative band in our data being sample damage and/or product accumulation,<sup>35</sup> measurements were repeated on a fresh spot on the crystal and the order of the time delay sequence was reversed, i.e. the acquisition was started at the maximum delay and the stage was stepped backward towards negative delays. The results obtained this way were found to be identical to those measured with the previous sequence on several repeats, thus assigning the negative band to a bonafide photochemical process and not sample damage or an unknown experimental artifact.

Following their emergence, the new absorption features persist for the remainder of the permissible delay range covered in our work spanning 1.5 ns. The signal around selected bands was also binned along the wavelength axis and plotted as a function of pump-probe delay as shown in the lower panel of Figure 2c, which revealed apparent oscillations with a period on the order of tens of picoseconds.

To disentangle the complex evolution, we divided the TA data into two separate time windows and reduced each data set by employing global target analysis.<sup>40</sup> Results obtained this way can be presented in the form of species-associated difference spectra (SADS), which represent the spectra of transient species defined within a coupled rate model.<sup>41,42</sup> The data up to 15 ps were modelled according to a step-wise evolution of species, i.e.  $A \xrightarrow{\tau_{AB}} B \xrightarrow{\tau_{BC}} C \xrightarrow{\tau_{CD}} D$  (where  $\tau$  is the time constant). The SADS and corresponding concentration profiles in this range are provided in Figure 3a. The first SADS is associated with species A created immediately following excitation. The spectral features contained here match with that of the absorption from SP in the singlet excited state, i.e.  $S_1 \rightarrow S_n$  in solution.<sup>27</sup> As the excited state species A decays, it transforms into species B (second SADS) with  $\tau_{AB} = 0.28$  ps. It is known from the literature that following UV excitation, propagation of the created wave

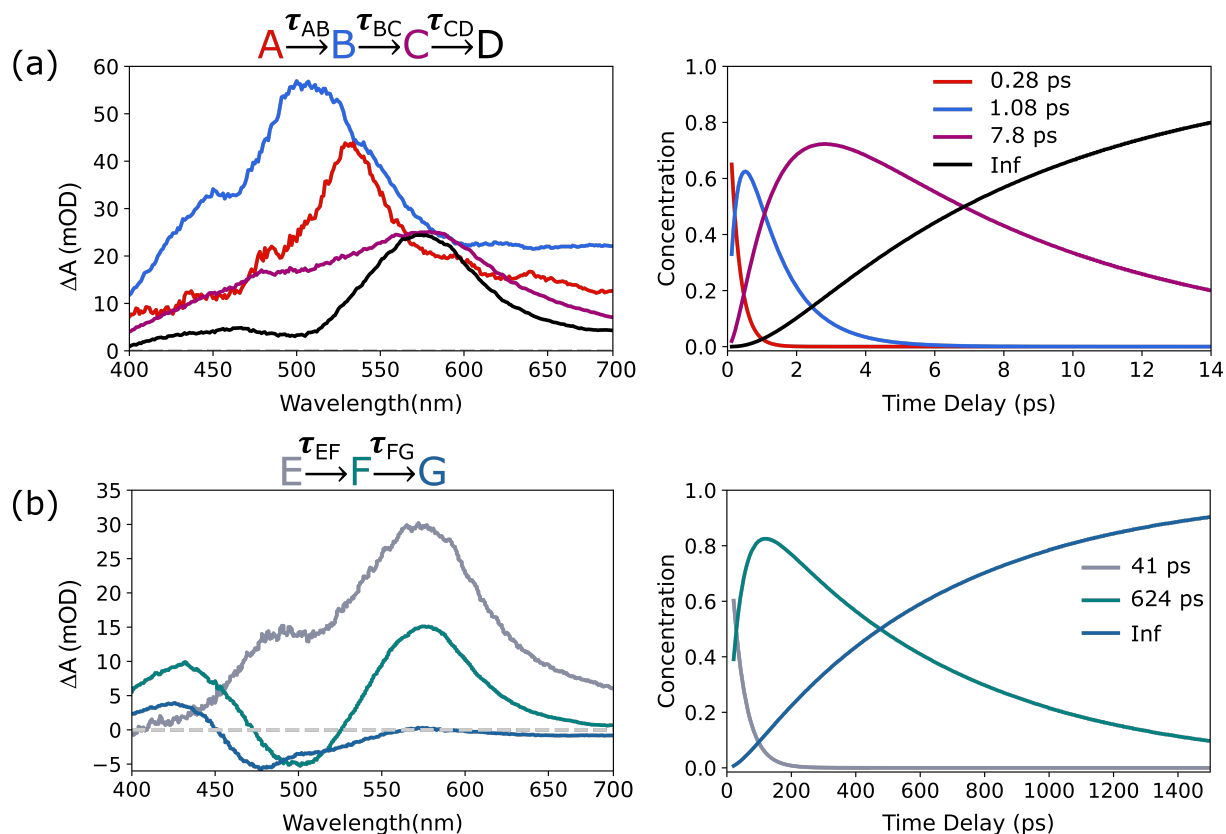


Figure 3: (a) Species-associated difference spectra obtained from a step-wise model of the short-range (0-15 ps) data with corresponding concentration profiles (b) Results from target analysis of long term data.

packet on the  $S_1$  surface leads to C-O bond dissociation and formation of a non-planar, ring-opened intermediate, Z-merocyanine.<sup>27,35</sup> The process takes place on sub-300 fs timescales which is in good agreement with the time constant recovered for the  $A \rightarrow B$  rate step.

The third SADS represents species C formed with  $\tau_{BC} = 1.08$  ps. Upon inspection, the spectrum has a shape which bears notable similarities (in appearance of a peak and shoulder) with the merocyanine absorption band<sup>26,27</sup> in solution of acetonitrile shown in Figure 1c, albeit it is broader and more diffuse hinting that it is likely from vibrationally hot species. In the solution phase, photoisomerization from ring-opened intermediate to planar MC occurs via a conical interaction (CI) and is possible due to void spaces allowing fluid motions. In solids, on the other hand, such conditions are not always available due to the steric hindrance in a crystalline environment as previously alluded. However, the strong



resemblance to the MC band—which evolves slowly to species D following some narrowing due presumably to thermal energy transfer to the phonon bath—strongly suggests the formation of incipient planar MC species in crystalline SP. Remarkably, the time scale on which planarization takes place is only 1.1 ps. This implies that not only is MC formation possible in the bulk crystal of SP, but that it occurs on ultrafast time scales. Therefore, based on these findings, the underlying mechanism of the MC formation in SP crystal can be considered to be very similar to that in solution (see later and the ESI).

However, as noted earlier, the visible band—assigned now to the planar MC product—vanishes at long time delays. Therefore, in order to gain insight into the fate of the MC photoproduct, the second part of the global target analysis was carried out from 15 ps onward until the end of delay range. This required a two-step model involving three species. The generated SADS and temporal concentration profiles are presented in Figure 3b. The first SADS corresponds to species E, i.e. the thermalized MC photoproduct, before it evolves into species F, whose spectrum is represented in the second SADS and features rise in the 400-450 nm region coincident with the suppression of the MC band as well the formation of the negative band between 450-500 nm. Since a single time constant of  $\tau_{EF} = 41$  ps describes these spectral changes, it can be concluded that they do not occur independently. This however, complicates the interpretation as it is not obvious whether the two bands emerge from the same species or have different origins. While this is not the main focus of the present work, this aspect could be investigated more closely in future studies.

The time constant,  $\tau_{FG}$  of 624 ps for the  $F \rightarrow G$  rate step establishes the slow decay of merocyanine products. It is difficult to provide a plausible explanation for this observation at the present stage based on the available information, as any MC formed is generally expected to remain trapped under spatial confinement.<sup>28,43,44</sup> However, a conjecture could be made in which MC product formation leads to transient distortion of the crystal lattice resulting in strain which leaves the system in an energetically unfavorable state. As the surrounding lattice molecules are not as free to move as they would be in solution to stabilize the MC

photoproduct state, this steric constraint on lattice relaxation reduces the barrier for the back reaction in single crystals in comparison to the solution phase. Thus, the built-up stress is released by reverting MC products back to spiro-form via restoring forces causing strain wave propagation manifesting as the apparent oscillations on several tens of picoseconds timescales.

We have further examined the plausibility of this hypothesis with preliminary femtosecond electron diffraction (FED) experiments which can provide direct information about the crystalline lattice.<sup>45–47</sup> Pump-probe diffraction patterns were measured on a 150 nm thick SP crystal film for up to 10 ps time delay using electron bunches generated from a home-built setup based on a DC electron gun with radio frequency compression.<sup>48,49</sup> Each bunch was accelerated to 95 keV and contained approximately  $10^5$  electrons. The results of these measurements are presented in Figure 4 and show changes in the diffraction pattern averaged over all measured time delays following photoexcitation with 266 nm at  $1.3 \text{ mJ cm}^{-2}$ . A butterfly pattern—in which the central part shows suppression of Bragg peak intensity whereas the wings display rise—is observed for the labelled diffraction orders in Figure 4a, of which one is selected for closer examination in Figure 4c. These changes reflect (non-uniform) lattice strain causing peak broadening.<sup>50</sup> A simplified model involving area integrated Gaussian profiles can be used to illustrate the effect of broadening (Figure 4d): the  $\text{Pump}_{\text{ON}}$  peak is 40% broader than the initial width ( $\text{Pump}_{\text{OFF}}$ ), and the difference between  $\text{Pump}_{\text{ON}}$  and ( $\text{Pump}_{\text{OFF}}$ ) yields a peak profile which match that which is observed in the experiment giving credence to our prediction that lattice strain is at play.

It should be mentioned that the early onset of strain generation within 10 ps post-excitation convolved with the formation of the intermediate and MC product hinders unambiguous determination of their structures from FED. Conversely, strain relaxation facilitates the eventual return of MC to the spiro form over long time scales meaning that the system is exceptionally reversible, surviving several million photocycles as found in this study. To put these numbers in context, a crystal of spirooxazine with very similar chemical makeup

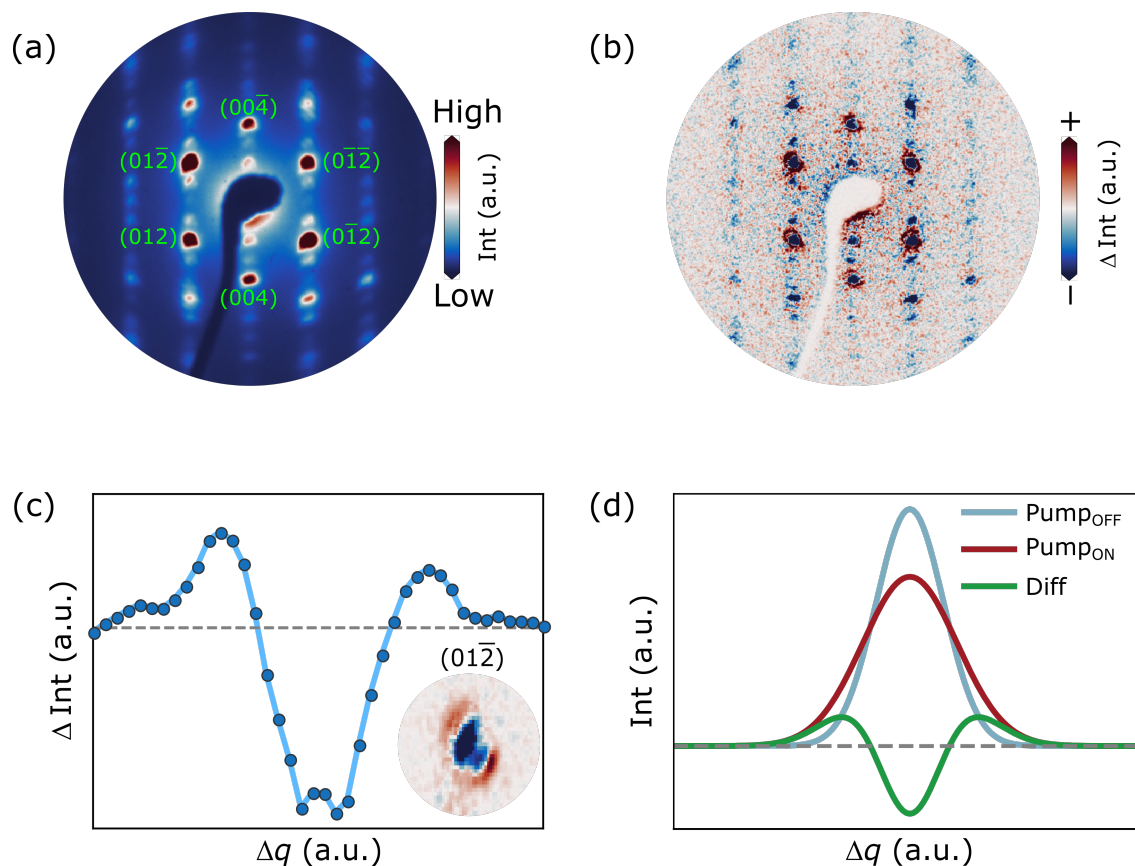


Figure 4: Femtosecond electron diffraction of crystalline SP (a) Static diffraction pattern of 150 nm crystal film of SP looking down [100] axis (b) Averaged difference pattern obtained following 266 nm excitation (c) Difference intensity plot of  $(01\bar{2})$  peak (d) Illustration of the effect of broadening on diffraction peaks due to lattice strain.

was investigated previously using fs-TA spectroscopy and FED,<sup>51</sup> and was found to rapidly lose long-range order due to permanent product accumulation from fewer than a hundred UV laser shots and required novel photoreversion schemes to prevent sample damage. In the latter scenario under fully reversible conditions, UV excitation was found to only create the ring-opened, non-planar intermediate that remained trapped in crystal for several hundred of picoseconds without any evidence of planar MC formation. In contrast, in the present work not only bond breaking followed by isomerization and increased double bond conjugation occurred, but assisted by strain, these large amplitude motions were reversed on relatively fast time scales. As a consequence, at least six orders of magnitude more photochemical cycles could be attained bereft of any noticeable sample degradation and without the need

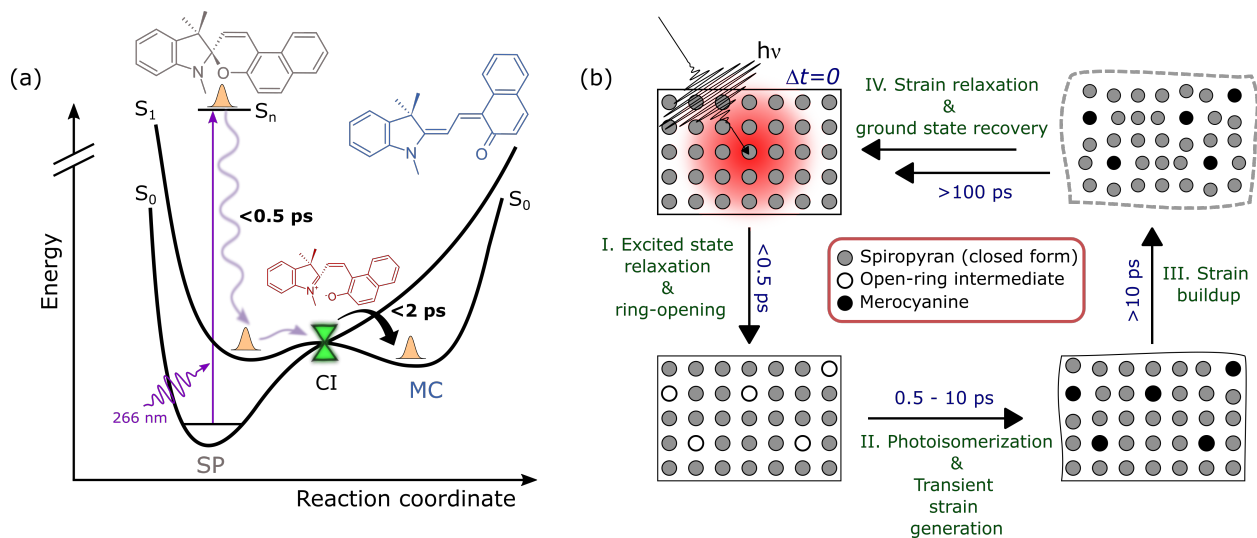


Figure 5: Summary of proposed events following 266 nm excitation of crystalline SP (a) Ultraviolet laser excitation creates a propagating wave packet along the C-O bond stretching coordinate leading to C-O bond breaking and ring-opening followed by hybridization and isomerization to planar merocyanine. CI: conical intersection (b) Sketch depicting the buildup of lattice strain due to SP to MC switching and eventual relaxation to SP.

for inducing any photoreversion between pump laser shots.

## Conclusions

In conclusion, we have observed ultrafast spectral signatures of planar MC photoproduct formation in bulk crystalline SP. The proposed events are summarized in Figure 5. The timescale of SP-MC conversion is  $\sim 1\text{-}2$  ps, very similar to that in solution suggesting that a sterically hindered crystalline environment is not creating a significant barrier relative to the forces directing the chemistry leading to bond breaking coupled to isomerization and changes in double bond conjugation. The formed merocyanine product is long-lived, but not permanent over a nanosecond timescale resulting in very high number of photocycles ( $> 10^6$ ) that were achieved in SP crystals, which bodes very well for their prospects towards ultrafast photoswitching applications.

Furthermore, our fs-TA and FED measurements indicate that inherent steric constraints within the solid state leads to strain that in turn create forces opposing the formation of

the fully relaxed product states. This insight provides a means to engineer lattice strain as a tool for controlling the overall reaction pathways with spiro-based devices forming a model system to explore this concept.<sup>52</sup> Finally, further studies are warranted to fully capture the mechanism behind SP-MC interconversion using both theoretical and experimental approaches, especially in the time-domain to clarify the identity of the photo-generated isomer and the select reaction modes that lead to the specific stereochemistry driven by the increased double bond conjugation. This selective mode coupling and possible photodark intermediates will fully resolve the driving forces for this eminent class of chemical reactions. To this end, the stability of SP crystals under photoexcitation enable unlimited sampling of the reaction dynamics to provide an ideal model system to explore these details at the highest possible spatiotemporal resolution.

## Conflicts of interest

Authors declare no conflicts of interest.

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