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Electronic Supplementary Information (ESI) for

Synchronized Photoreversion of Spirooxazine Ring Opening in Thin Crystals to Uncover Ultrafast Dynamics

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1 Sample preparation

1,3-Dihydro-1,3,3-trimethylspiro[2H-indole-2,3'-[3H]naphth[2,1-b][1,4]oxazine] (Spirooxazine, SNO) was purchased from Sigma-Aldrich (#322547) and used without further purification. Single crystals of SNO were grown by dissolving an approximate quantity of 10 mg of powdered SNO in ethanol (5 ml) under mild heating ($\sim 40^\circ\text{C}$) and slowly evaporating the saturated solution in dark. Crystals formed having an area of 1 to 4 mm² and thickness of roughly 1 mm were sliced to thickness of 100 nm and 500 nm using ultramicrotomy. Crystallinity of the samples was confirmed by measuring a static electron diffraction pattern (Fig. S1a). For transient absorption experiments, crystals of 500 nm thickness were placed on a fused silica disc of 1 mm thickness. Crystals were stored under nitrogen saturated environment to avoid sample oxidation.

2 Steady-state absorption spectroscopy measurements

Steady state absorption measurements in solution and solid-state were performed using a home-built spectrometer based on the design by Kirchner et al.¹ It is an all-reflective setup that focus the probe light to a 100 μm spot on the sample allowing the measurement of the absorption spectrum from a very small area. A deuterium-halogen balanced lamp covering the range from 215 to 2500 nm coupled to a 100 μm optical fiber was used as the probe source. The transmitted light intensities were recorded by a fiber optic spectrometer. Solutions of SNO with a 0.5 mM concentration were prepared by dissolving SNO powder in high purity ethanol and used for absorption measurements. A quartz cuvette with a 2 mm path length was used and the reference spectrum was measured using a cuvette containing ethanol. Static absorption spectra were recorded before and after irradiating the sample using 266 nm light (0.6 μJ). The absorption spectrum of the 500 nm SNO crystals supported on a fused silica disc of 1 mm thickness was measured using the disc without the sample as a reference (Fig. S1b).

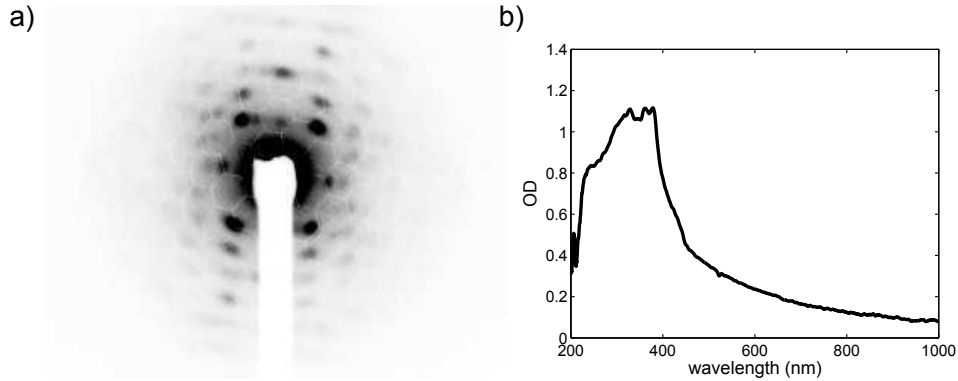


Figure S1: **a)** Static electron diffraction pattern of a SNO crystal with a thickness of 100 nm. The diffraction image was acquired using a home-built femtosecond electron diffraction setup described in Ref. 2. **b)** Steady-state absorption spectrum of 500 nm SNO crystal.

3 Experimental setups and data acquisition scheme

3.1 Non-collinear optical parametric amplifier (NOPA)

The non-collinear optical parametric amplifier (NOPA) was built in-house and was based on the design from Riedle³. A fraction of the output from the regenerative amplifier (800 nm, 200 μ J, 40 fs pulse duration) was split into two arms using a 90:10 (transmission:reflection) ratio beam splitter (BS). The transmitted beam was sent to a second harmonic generation (SHG) stage and the reflected 10% was used for supercontinuum generation. The SHG stage consisted of a 1 mm thick, type I Barium Beta Borate (BaB_2O_4 , BBO) crystal cut with an angle $\theta = 29.3^\circ$. 400 nm light generated with an efficiency of 30% was used as the pump. White light supercontinuum was generated by focusing 800 nm (1.6 μ J) light into a 2 mm thick sapphire (Al_2O_3) disc using a fused silica convex lens (focal length = 75 mm, L_1). A variable neutral density (VND) filter and an iris were placed before the lens to adjust the pulse energy and change the beam diameter, respectively. The supercontinuum covering 450-950 nm was collimated using a fused silica lens (focal length = 30 mm, L_2). The two beams were mixed inside another BBO crystal also having the 29.3° cut angle. The crossing angle was set to 6° . The delay of the white light seed was adjusted until temporal overlap with the 400 nm pump was established. This led to amplification of the seed in the range from 500-700 nm. The wavelength was tuned to 600 nm for the experiments. The scheme of the setup is presented in Fig. S2, where the spectrum of the NOPA light used in the experiments is also displayed. The bandwidth of the NOPA output was roughly 25 nm (full width at half maximum).

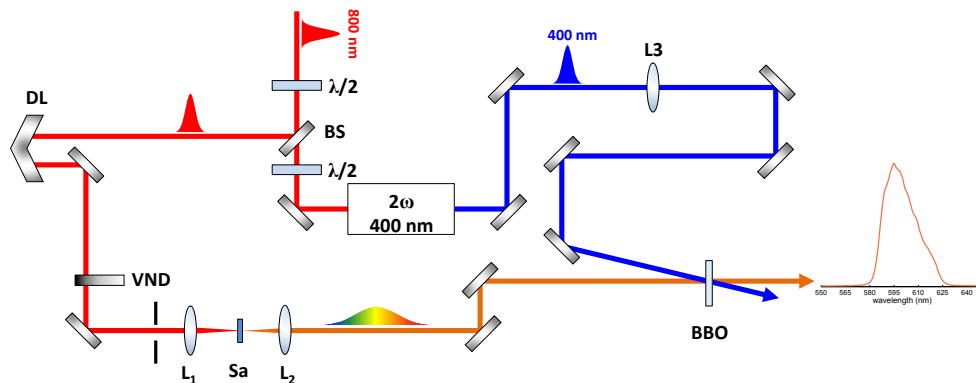


Figure S2: The schematic of the non-collinear optical parametric amplifier. **BS:** Beam Splitter, **L_1 :** 75 mm FS lens, **L_2 :** 30 mm FS lens, **L_3 :** 750 mm FS lens, **Sa:** Sapphire, **DL:** Delay line, **VND:** Variable neutral density filter

3.2 Transient absorption spectroscopy

Transient absorption spectroscopy was performed using a home-built spectrometer. A simplified scheme of the setup is shown in Fig. S3. Briefly, a portion of the output from the regenerative amplifier was split into two beams of which one was used to pump the NOPA and the other beam was sent to the transient absorption spectrometer. The repetition rate of the latter was modulated to 250 Hz by employing two choppers operating in series and phased-locked with the laser frequency. The beam was split to create the pump and the probe beams. In the pump arm, the fundamental was frequency-tripled generating a 266 nm beam and a 1:8 chopper blade was used to reduce the frequency of the beam down to 31.25 Hz. The residual 400 nm and 800 nm beams were removed by a combination of a 350 nm short-pass filter and high reflection mirrors optimized for 266 nm. The beam was focused onto the sample by a lens with a 300 mm focal length down to diameter of $140\ \mu\text{m}$ (full width at half maximum). Beam sizes were determined by placing a set of pin holes with known diameters at the sample position and measuring the transmitted intensity. A slow photodiode (PD2) connected to a data acquisition (DAQ) card was placed after the chopper and received a small fraction of the pump beam to monitor the power of the pulses going through the chopper blade. When the beam was allowed to pass by the chopper, the photodiode recorded the intensity which corresponded to the pump ON sequence and conversely when it was blocked it corresponded to the pump OFF.

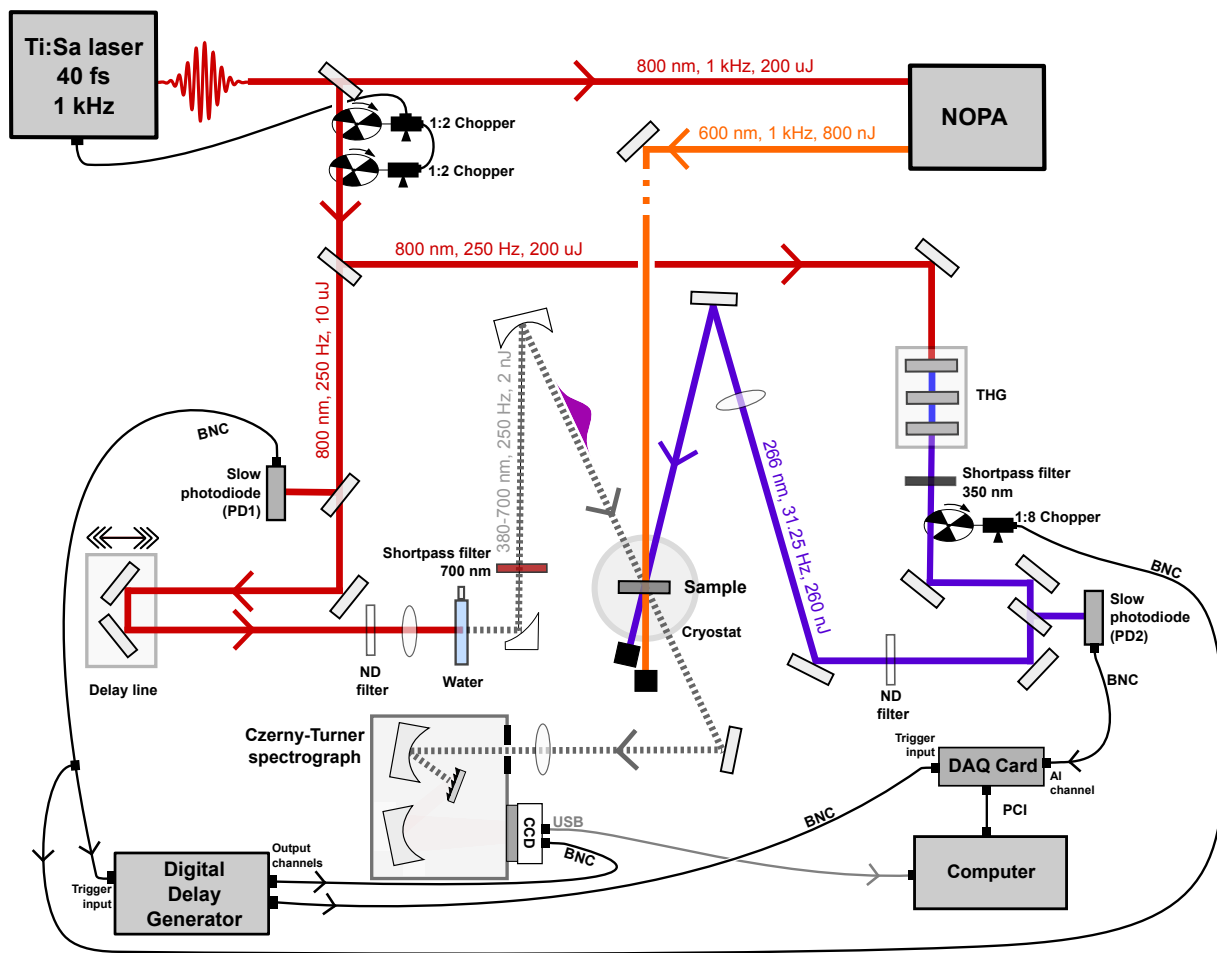


Figure S3: Scheme of the experimental setup for transient absorption spectroscopy. **THG:** third harmonic generator, **ND:** neutral density filter.

The optical path length of the probe arm was changed by a delay line in order to tune the time delay of the probe pulse with respect to the pump, with a maximum achievable delay of 1.5 ns. Approximately $2\ \mu\text{J}$ of this beam was focused with a lens of 50 mm focal length into a 2 mm-path-length cuvette filled with ultrapure water to generate a white light supercontinuum beam with a spectrum covering the region between 380 nm and 900 nm. A short-pass filter was used to remove the region above 700 nm. An off-axis parabolic mirror (focal length = 50 mm) collimated

the beam and a concave mirror (focal length = 150 mm) focused it to a 70 μm spot at the sample position. The beam was overlapped with the pump.

In the three beams experiments the output of the NOPA operating at 1 kHz and centered at 600 nm was used as the photoreversion pulse and was focused and overlapped with the pump and probe beams. The focal spot was on the order of 170 μm at the sample position. The beam was delayed by about 10 ns from the pump and probe pulses.

The white light transmitted through the sample was directed to a home-build Czerny-Turner spectrograph coupled to a low-noise linear array charge-coupled device (CCD) containing 2048 pixels which was used to measure the wavelength-resolved intensity of each separate probe pulse. An important feature of this spectrometer is that it allows shot-to-shot acquisition at a frequency of up to 2 kHz.

As already stated here and also described in the main text, the repetition rates used in the experiments were 250 Hz (probe), 31.25 Hz (pump) and 1 kHz in case of the NOPA. Therefore the probe:pump ratio was 8:1, i.e. for each pump pulse there were 8 probe pulses separated by 4 ms to each other.

For DAQ, a small portion of the beam used to generate the probe was detected by a slow photodiode (PD1). The PD1 signal was used to phase-lock the 1:8 chopper of the pump beam and trigger a digital delay generator (DDG). Two separate outputs of DDG were used to trigger the CCD exposure and the DAQ card. The DAQ was performed using a home-made software which controlled the hardware involved in the experiment (delay line, DDG, CCD, DAQ card), sorted and displayed the data, and stored it for further analysis. For each time delay, 10 bunches comprising 80 probe shots each were measured. This returned 800 probe spectra and 800 values of the pump beam power. By using the information provided by the pump power, the spectra were labeled from 0 to 7 according to their distance to the immediately preceding pump pulse. Consequently, spectra labeled “0” corresponded to the ones obtained with the probe beam hitting the sample at a time delay defined by the position of the delay line, spectra labeled “1”, to the ones obtained with the probe hitting the sample (4 ms + time delay) after the pump, etc. The transient absorption spectrum was calculated by comparing the spectra labeled “0” (corresponding to pump ON) and “7” (corresponding to pump OFF). A time step of 100 fs was used in all the experiments.

Transient absorption experiments on thin crystals were performed at room temperature and the mounted samples were placed inside a cryostat filled with nitrogen gas. The data acquired for thin crystals were averaged over three different sample positions and smoothed using a Savitzky–Golay filter along the time delays (for $t > 0.5$ ps) and a 3×3 median filter to allow better visualization of the 2D plots. The latter was also applied to the solution phase data. The transient spectra shown in Fig. 4c and 4d of the main text were also smoothed along the wavelength using a Savitzky–Golay filter.

The solution-phase experiments were performed by flowing the sample in a 0.5 mm-path-length quartz flow cell by means of a high performance miniature pump to ensure the use of a fresh sample after each pump-probe cycle. In this case, the repetition rate of the probe was 500 Hz and that of the pump, 250 Hz. 250 pump-probe cycles were run at each time delay and a transient absorption spectra were calculated for each pump-probe pair of pulses and then averaged over the 250 cycles to get the spectra of the corresponding time delays.

4 Transient absorption spectroscopy without photoreversion scheme

The results of the transient absorption experiment without the use of the NOPA photoreversion pulse are shown in Fig. S4. The conditions used were the following: 266 nm pump (1.4 mJ cm^{-2}) operating at 31.25 Hz hit the sample 100 times and white light continuum covering the visible region and having a repetition rate of 250 Hz, probed the changes in the absorption. Initially, a strong broad absorption from 400 nm to 500 nm was observed. After about 3 ps, the bleach signal corresponding to the excitation of the trapped photoproduct (merocyanine) was clearly distinguished.

Fig. S5 shows a photograph of the microtomed crystals used in the experiment. Spectra corresponding to the labelled regions are shown on the right panel of the figure. Region marked (a) corresponded to an undamaged area of the crystal. Region (b) was used in the experiment and showed strong colouration due to production of the merocyanine form.

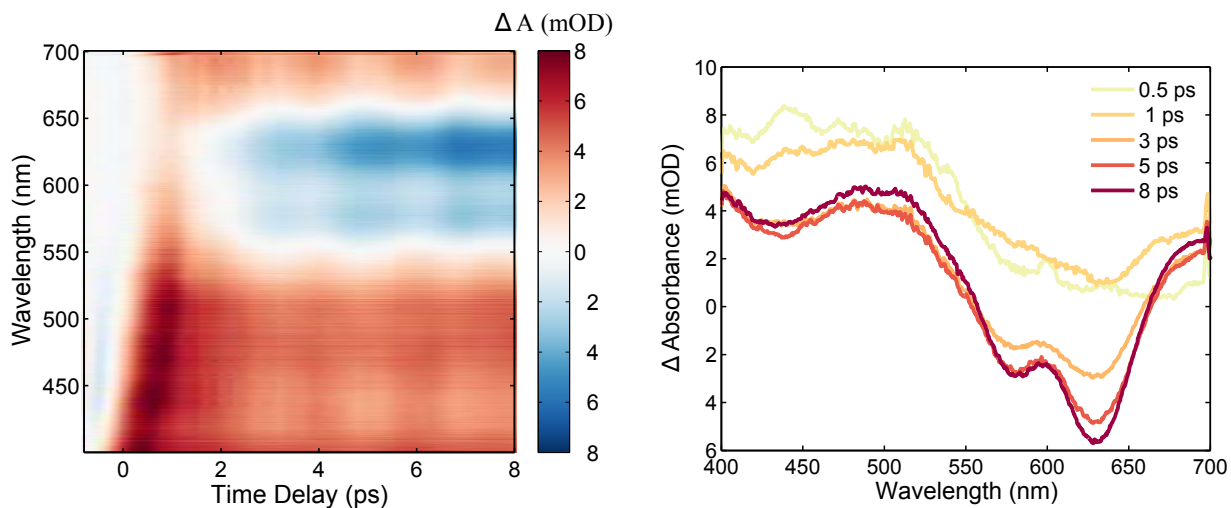


Figure S4: 2D transient absorption map and spectral traces of a thin SNO crystal pumped with 1.4 mJ cm^{-2} 266 nm in absence of NOPA. The bleach band due to photoproduct build-up in the crystal is clearly seen.

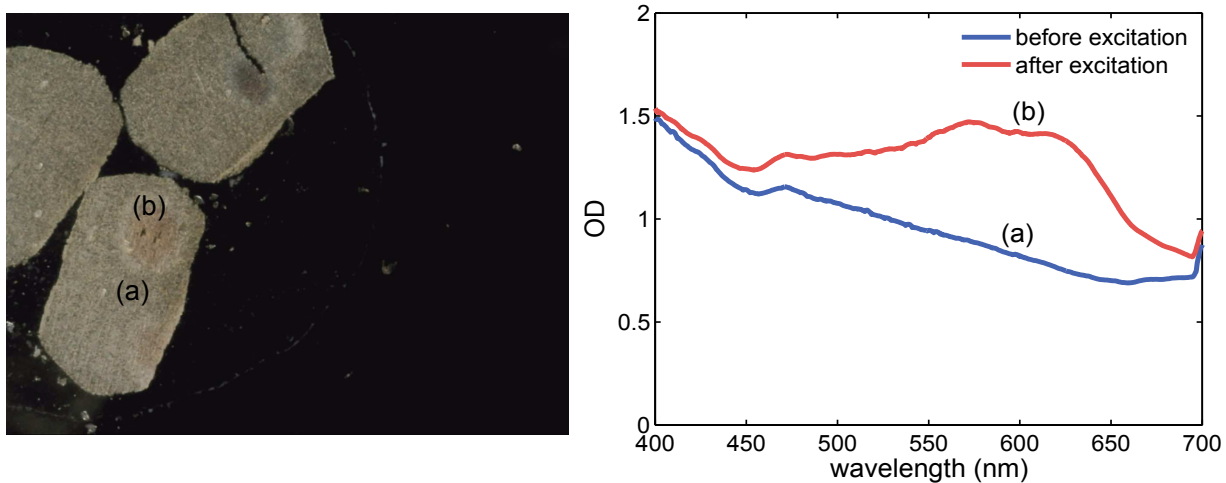


Figure S5: **Left:** A magnified photograph of the thin crystal slices showing the regions where the absorption spectra were measured. **Right:** Absorption spectra corresponding to regions marked in photograph.

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