

Electronic Supplementary Information for:

**Rapid build up of nanooptomechanical transduction in single crystals of a
ruthenium-based SO₂ linkage photoisomer**

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Video of optical microscopy image time sequence of applying 505 nm light to a crystal of 1 (see associated file).	

Dark- and light-induced *in-situ* single-crystal X-ray diffraction

The light-induced crystal structure of **1** was determined using synchrotron-based X-ray photocrystallography, at the ChemMatCARS beamline of the Advanced Photon Source, Argonne National Laboratory, IL, USA. A 50 x 25 x 25 μm^3 single crystal of **1** was mounted onto a Huber three-circle diffractometer equipped with a Pilatus 3 x CdTe 1M shutterless pixel array detector and a 100 K nitrogen open-flow cryostream delivered by an Oxford cryojet. Crystallography data were acquired using a 100 x 100 μm X-ray beam of wavelength 0.41328 Å. For control purposes, the ambient lighting in the experimental hutch of the beamline was extinguished while data were being collected. A reference dataset for the dark-state crystal structure was first obtained. The crystal was then maintained at 100 K on the diffractometer and rotated continuously while 505 nm light was shone onto it for 2.5 h, using a Thorlabs M505L3 light emitting diode (LED) whose head power output was 1000 mA constant current and 3.3 V forward voltage. This light was switched off before acquiring data for the light-induced crystal structure. Further experimental details, as well as structure solution and refinement information, are given in the accompanying Crystallographic Information Files (CIFs).

Single-crystal optical characterisation

A custom-built microspectroscopy system was used to record the absorption spectrum of single crystals under a variety of environmental conditions. The system was built around an inverted microscope (Olympus: IX71) coupled to a 300 mm focal length spectrograph (Princeton Instruments: Acton Series 2300i) and 1320 × 100 channel CCD camera (Princeton Instruments: PIXIS 100BR). A 50 × 25 × 25 μm³ crystal of **1** was mounted on a sapphire disk (9 mm diam, 0.5 mm thick) and fastened with a small amount of viscous perfluoroether oil. The mounted sample was then placed on the coldfinger of an optical cryostat (Janis: ST-500-UC) attached to the microscope. The coldfinger was drilled through, allowing optical absorption measurements to be made. The crystal was positioned such that only one-half of the active vertical channels of the CCD camera were used to image a portion of the crystal using a 20×, 0.3 NA objective (Olympus UMPlanFL); the remaining one-half of the active detector channels imaged the sapphire substrate. The probe light for optical absorption measurements was provided by the microscope's 100 W tungsten–halogen lamp and 0.3 NA condenser optics. A visible bandpass filter (Schott: BG40) and OD 9 neutral density filter was placed between the lamp and the condenser to reduce the thermal load on the sample and cryostat.

To induce photoisomerization, the crystal was illuminated with 505 nm light from a ThorLabs M505F1 fiber optically coupled light-emitting diode (LED). The light from the LED was collimated and then coupled into the microscope through a side port, focusing it onto the back aperture of the objective, thus filling the field of view and evenly illuminating the entire

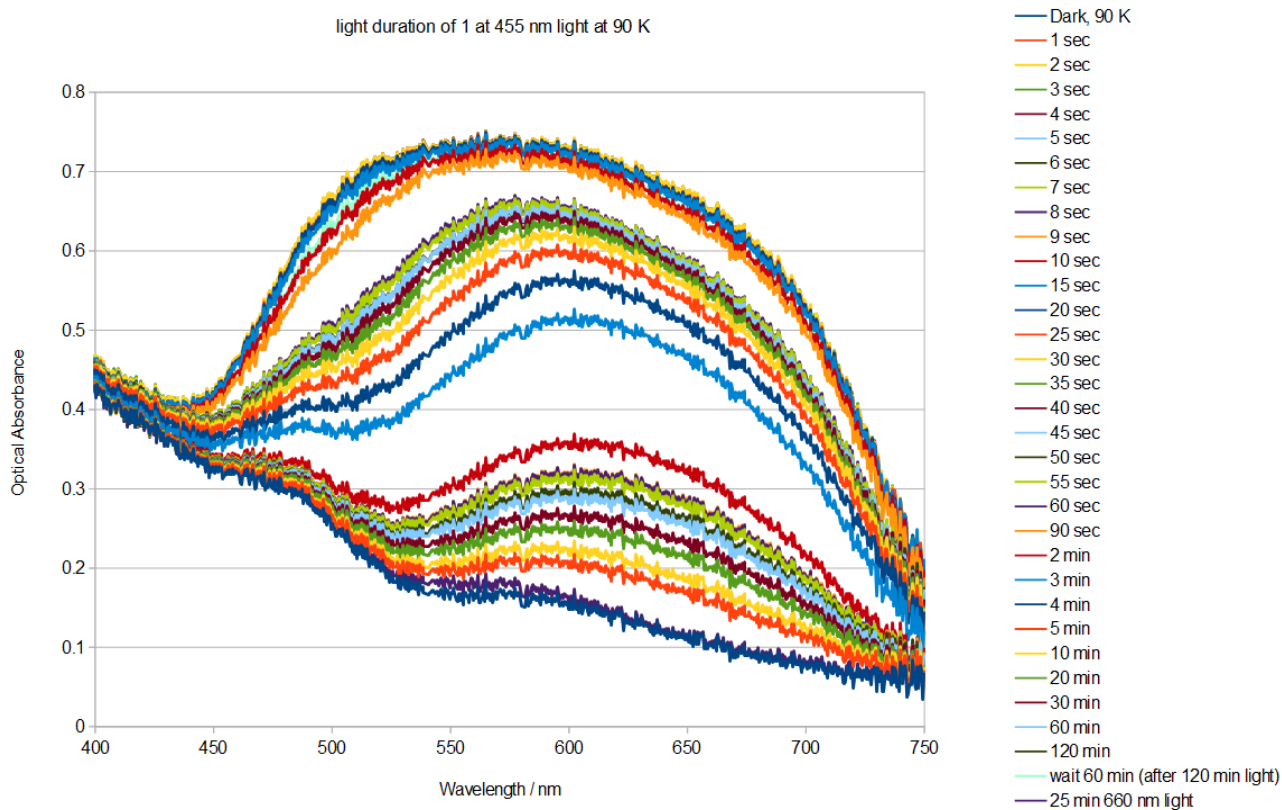
crystal. The excitation power measured at the objective was typically 360 μW giving an estimated 261 μW illuminating the field of view.

Optical absorption spectra were recorded by imaging the crystal on the entrance slit (75 μm) of the spectrometer and dispersing the light, using a 150 line/mm grating, onto the detector. The image was positioned such that 30 rows of the detector were illuminated with light that passed through the crystal (I_T), whereas 30 rows of the detector directly above the crystal recorded light that passed through only the sapphire substrate (I_0). Absorption spectra were then calculated as $-\log_{10}(I_T/I_0)$.

Rate constant calculations

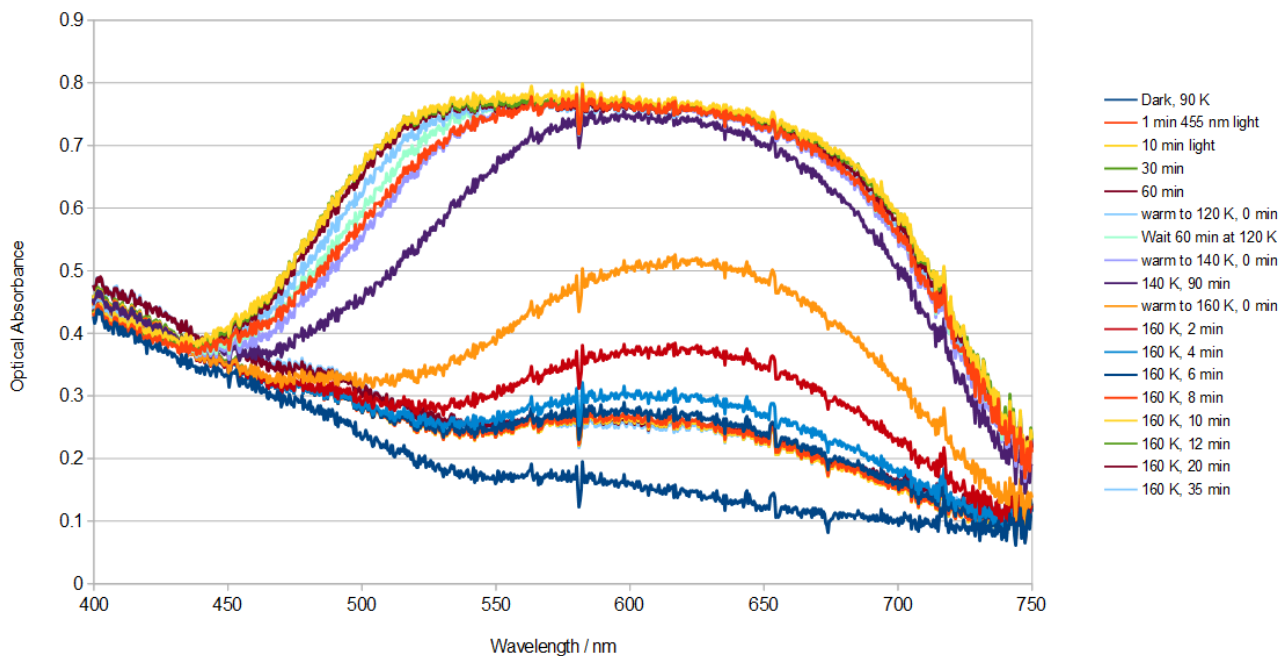
The rate constant associated with the photoisomerisation process of **1** was calculated using the light-induced area under each curve of each single-crystal optical absorption spectrum, as a proxy metric for the concentration of photoisomer species. The calculation proceeded in four steps: (i) the active area under each spectrum (400-715 nm) was numerically integrated using the composite Simpson's rule, which is well suited to this task given that there are a large number of finely-spaced data points; (ii) the area of the dark-state spectrum was subsequently subtracted from that of each light-induced spectrum, yielding the metric, $\text{area}(\text{light-dark})$; (iii) the order of the photoisomerisation process was then determined by exploring the relationship between temperature and the light-driven change in area. This revealed that the photoisomerisation is first order, judging from the straight line of a temperature versus $\ln(\text{area}(\text{light-dark}))$ plot. The first-order classification of this photoisomerisation process is consistent with previous findings from photocrystallography, infrared spectroscopy and optical absorption spectroscopy on other members of this family of complexes. (iv) The negative gradient of this plot was thus determined, yielding the rate constant, k .

Single-crystal optical absorption spectra of 1 when exposed to 455 nm external light



Single-crystal optical absorption spectra of 1 when exposed to 455 nm external light and warmed to 160 K and monitored at t minutes after reaching this temperature

thermal bathochromic shift and decay of 1 upon warming after 60 min 455 nm light



Single-crystal optical absorption spectra of 1 when exposed to 405 nm external light and warmed to 160 K and monitored at t minutes after reaching this temperature

Thermal hypsochromic shift and decay of 1 upon warming to 160 K after exposure to 405 nm light

