

Supporting Information for:

Assigning Optical Absorption Transitions with Light-induced Crystal Structures:

Case Study of a Single-crystal Nanooptomechanical Transducer

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S1 - Materials Synthesis and Characterization Methods for 1

Synthesis of 1. *trans*-[Ru(SO₂)(NH₃)₄(3-methylpyridine)]tosylate₂ (**1**) was synthesized from *trans*-[Ru(SO₂)(NH₃)₄Cl]Cl, which was synthesized according to a literature procedure.[1] 4.4 mg of this precursor was dissolved in 400 μL of 3-methylpyridine with 3.5 mg of *p*-tosyloic acid (> 98% purity, Sigma Aldrich) to form an aqueous solution of **1**. Yellow plate-like crystals precipitated from solution; they were isolated through vacuum filtration and washed with methanol.

Dark and Photo-induced *In-Situ* Single-Crystal X-ray Diffraction of 1. Dark and light-induced crystal structures of **1** were determined using synchrotron-based X-ray photocrystallography, at the ChemMatCARS beamline of the Advanced Photon Source, Argonne National Laboratory, IL, USA. One of two single crystals of **1**, with sizes 0.05 x 0.03 x 0.01 mm³ (crystal I) and 0.17 x 0.09 x 0.01 mm³ (crystal II), were 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. Each crystal was then maintained at 100 K on the diffractometer while 505 nm light was shone onto it for *n* minutes (where *n* = total light exposure time), 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 each light-induced crystal structure. Further experimental details, as well as structure solution and refinement information, are given in the accompanying Crystallographic Information Files. More details of the photocrystallographic aspects of the work are given elsewhere.[2-6]

Single crystal optical absorption spectroscopy and microscopy of 1. A custom-built micro-spectroscopy system was used to record the absorption spectra 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 x 100 channel CCD camera (Princeton Instruments: PIXIS 100BR). A 0.17 x 0.09 x 0.01 mm³ crystal of **1** was mounted on a sapphire disk (9 mm dia., 0.5 mm thick) and fastened with a small amount of viscous perfluoroether oil. The mounted sample was then placed on the cold finger of an optical cryostat (Janis: ST-500-UC) attached to the microscope. The cold finger was drilled through, allowing optical absorption measurements to be made. The crystal was positioned such that only half of the active vertical channels of the CCD camera were used to image a portion of the crystal using a 5 x, 0.13NA objective (Olympus, NeoSPlan); the remaining half of the active detector channels imaged the sapphire substrate. The probe light for optical absorption measurements was provided by the microscope's 100W tungsten-halogen lamp and 0.3 NA condenser optics. A visible bandpass filter (Schott: BG40) and OD 0.9 neutral density filter was placed between the lamp and the condenser to reduce thermal load on the sample and cryostat.

To induce photoisomerization, the crystal was illuminated with 505nm light from a ThorLabs M505F1 fibre 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 143 μW giving an estimated 6.5 μW/mm² 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 20 rows of the detector were illuminated with light that passed through the crystal (I_T); whereas 20 rows of the detector directly above the crystal recorded light that passed through only the sapphire substrate (I_0). Absorption spectra were calculated as $\log_{10}(I_T/I_0)$.

A more detailed description of this custom instrument set up and its operational pipeline, as provisioned to support photocrystallography, is given elsewhere.[7]

S2 – Photochromism of 1 as a function of light exposure time as viewed by single-crystal optical absorption microscopy

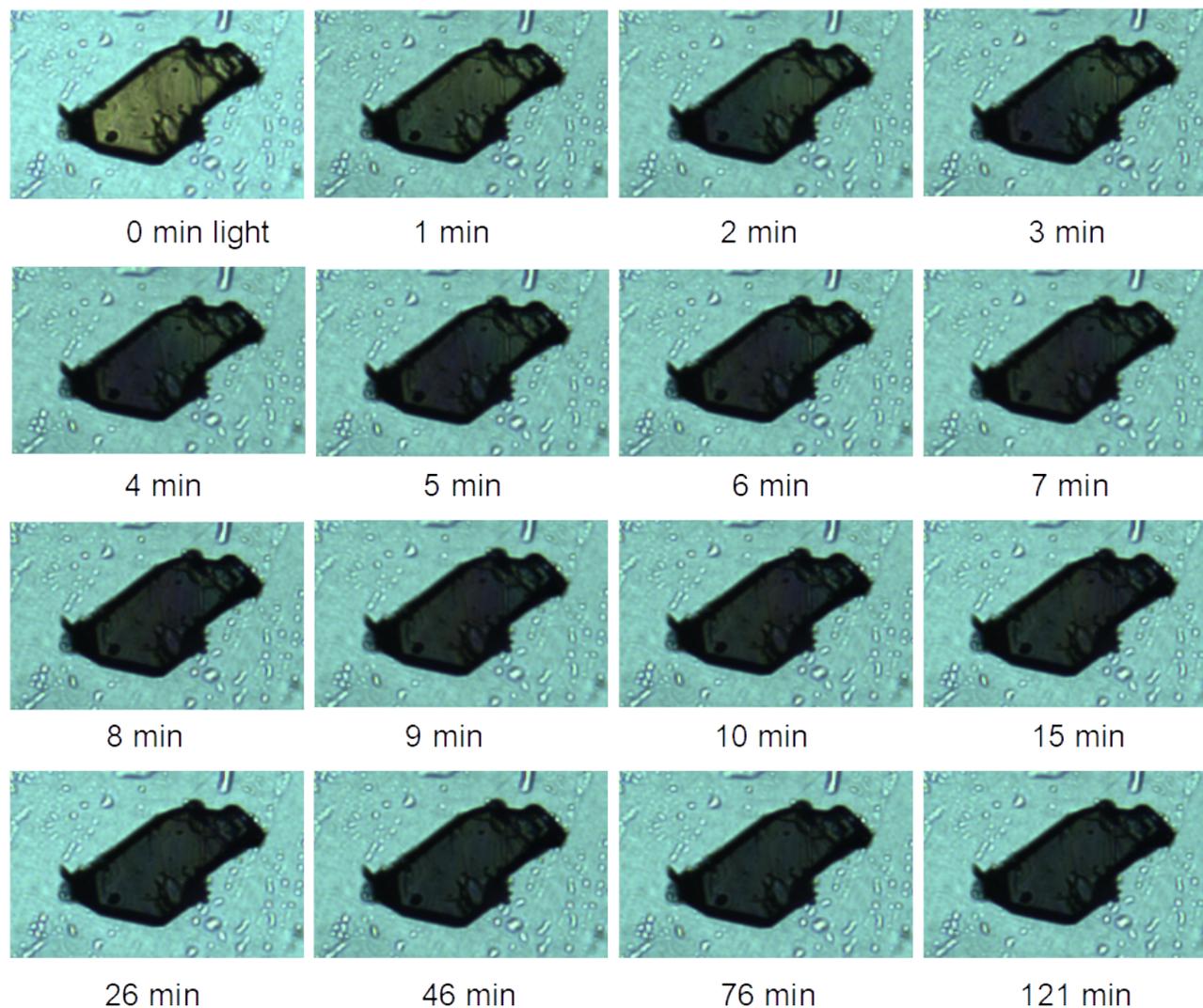


Figure S1 – Photochromism in crystal II of **1** captured as a function of light-exposure time via single-crystal optical microscopy.

S3 – Bond-length changes in **1** as a function of light-exposure time from t = 0 – 40 min

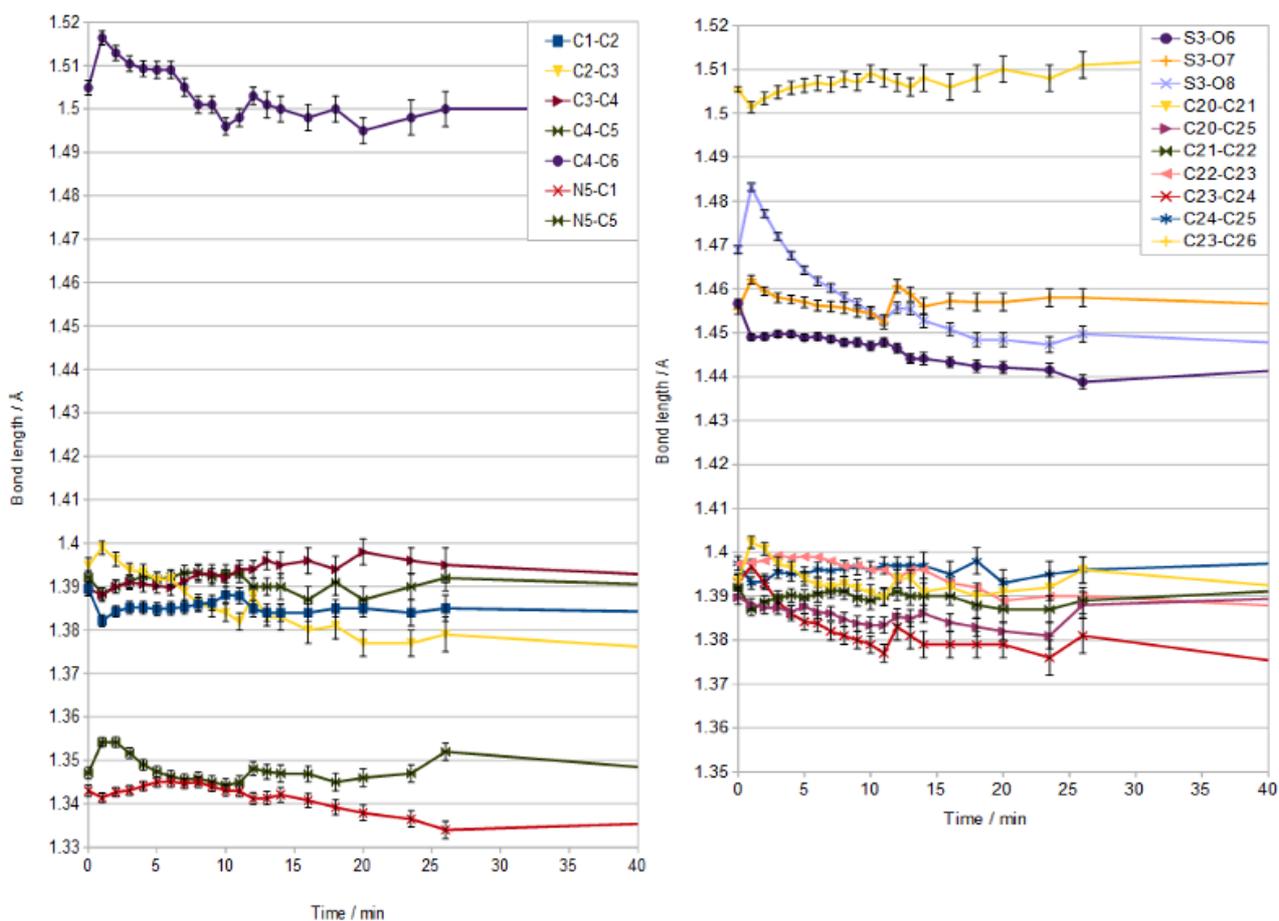


Figure S2 – Bond-length changes in the 3-methylpyridine ligand (top left) and non-disordered tosylate anion (top right) of **1** whose schematic diagram (bottom left) shows the atomic labels.

S4 – Bond-length changes in **1** as a function of light-exposure time from t = 0 – 181 min

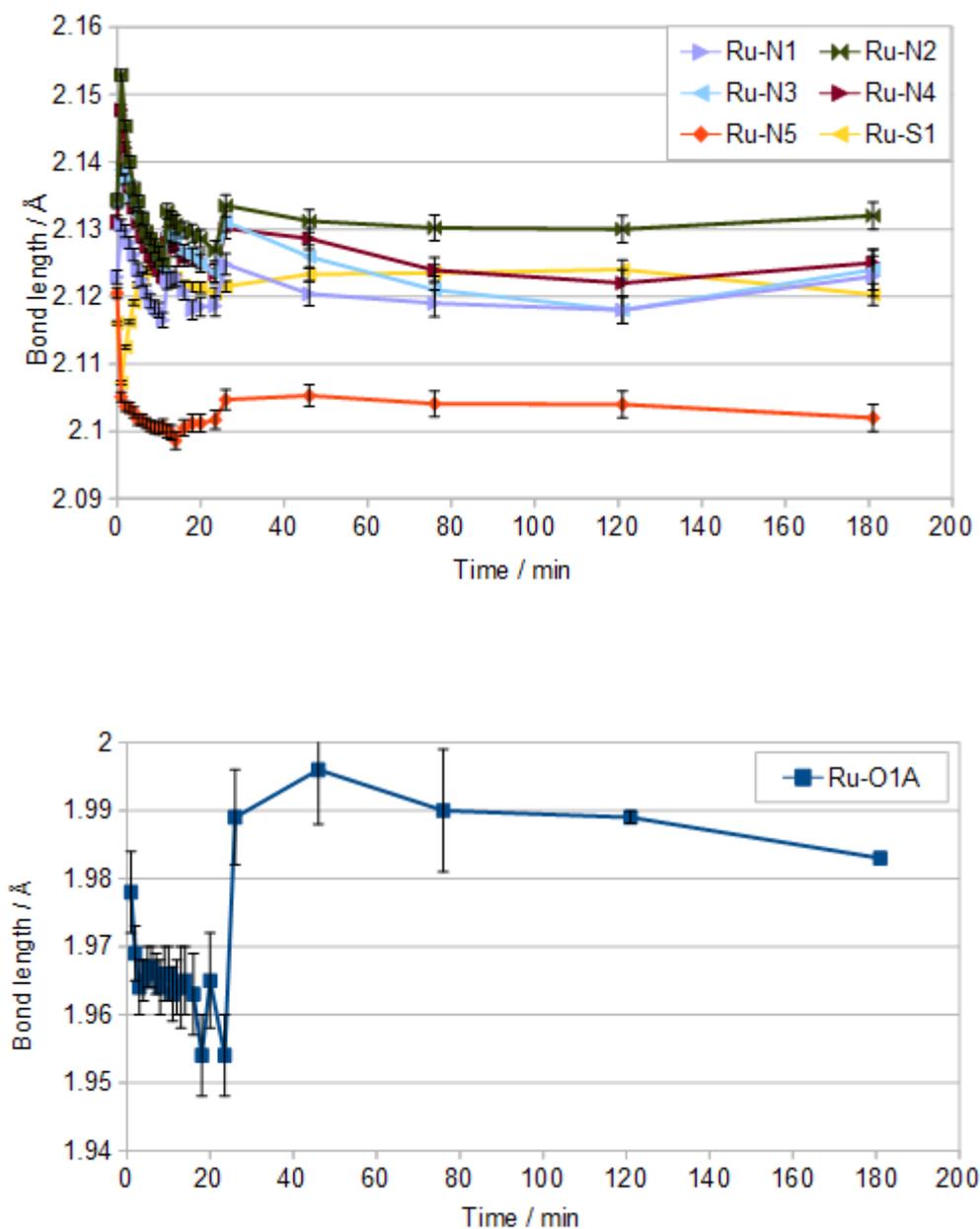


Figure S3 – Bond-length changes in the ruthenium coordination environment of **1** as a function of light-exposure time from t = 0 – 181 min.

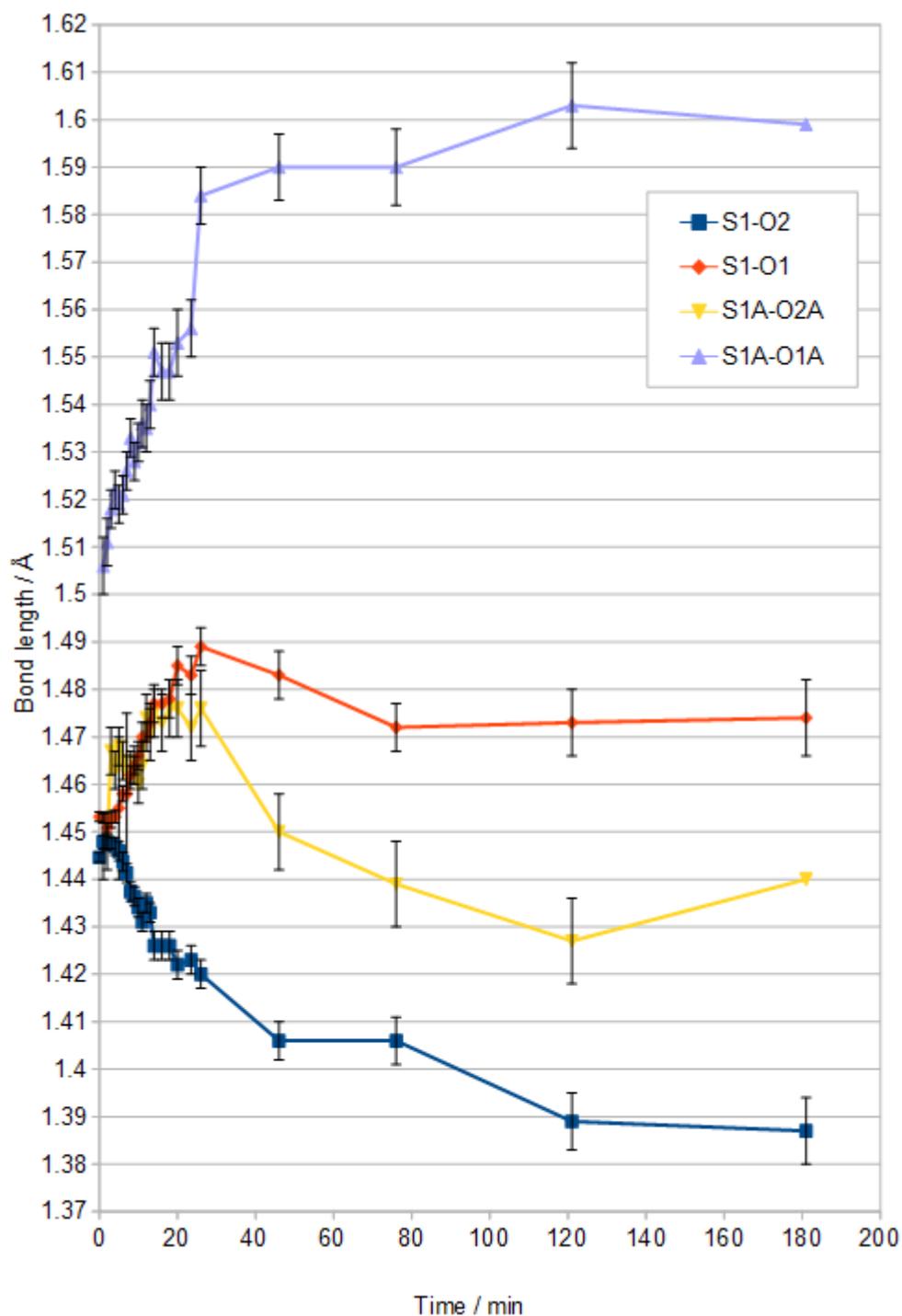


Figure S4 – Bond-length changes in the S-bound η^1 -SO₂ (dark state) and O-bound η^1 -OSO (photoisomer) configurations of **1** as a function of light-exposure time from t = 0 – 181 min.

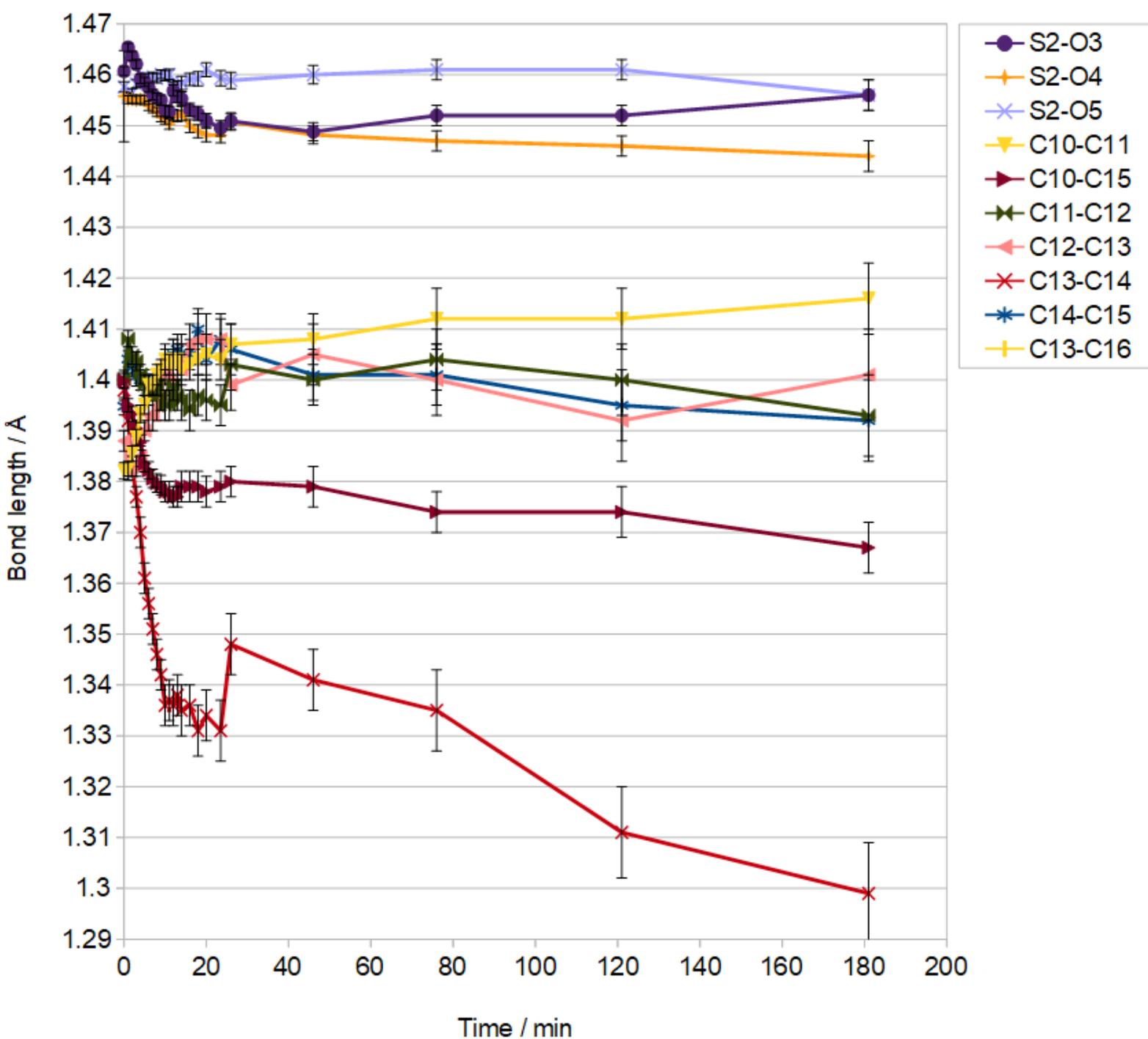


Figure S5 – Bond-length changes in the non-disordered part of the rotor ring in **1** as a function of light-exposure time from $t = 0 - 181$ min.

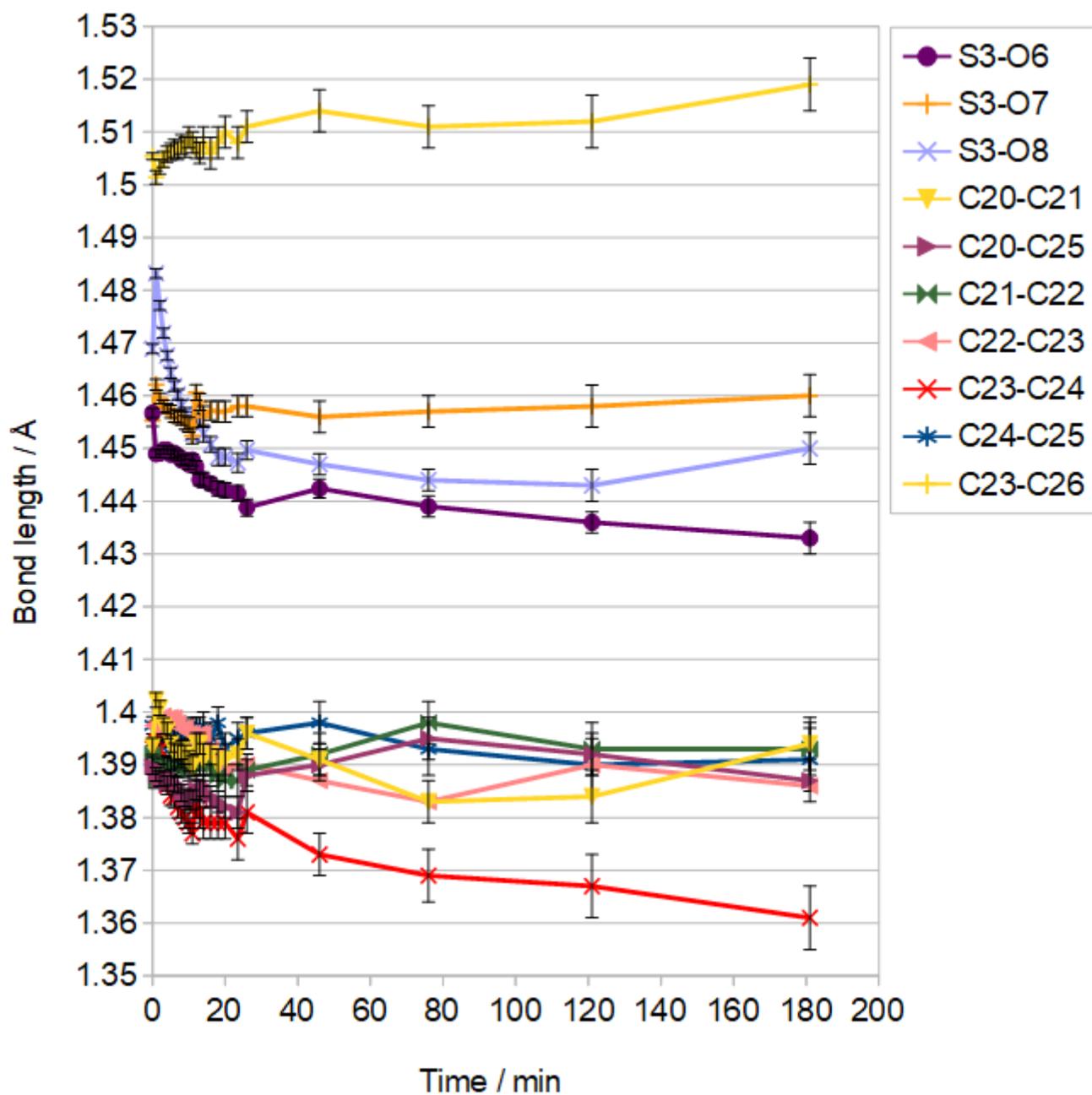


Figure S6 – Bond-length changes in the non-disordered tosylate anion in **1** as a function of light-exposure time from $t = 0$ – 181 min.

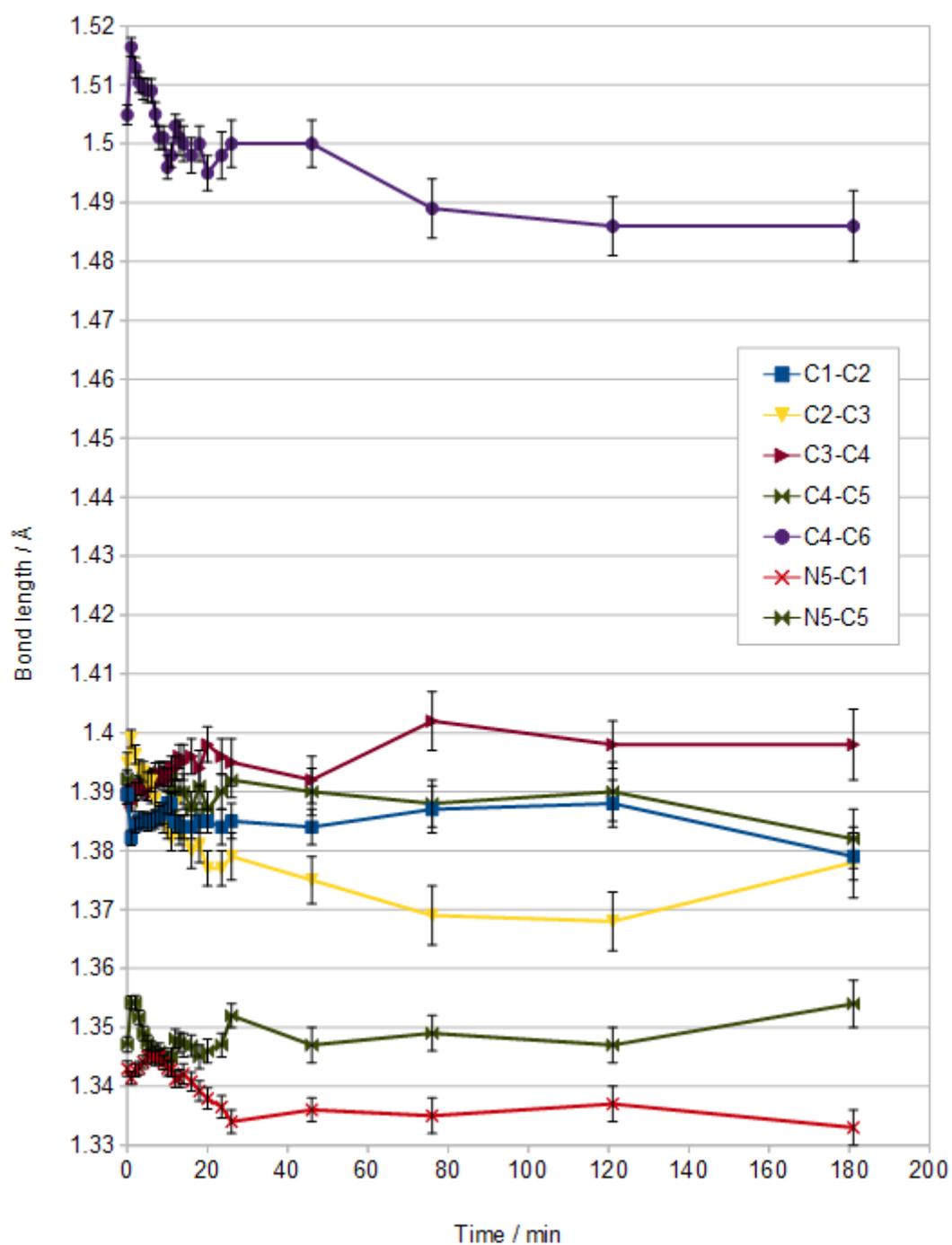
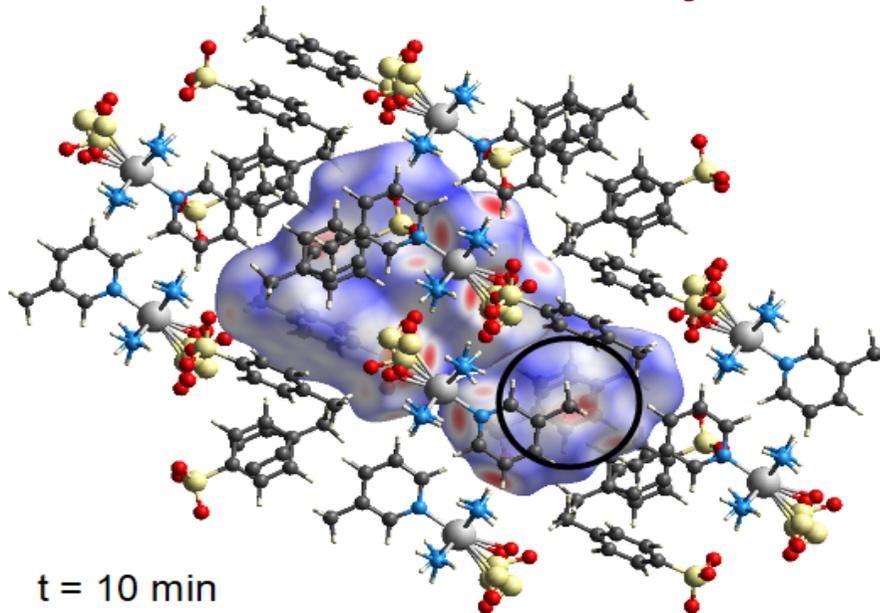
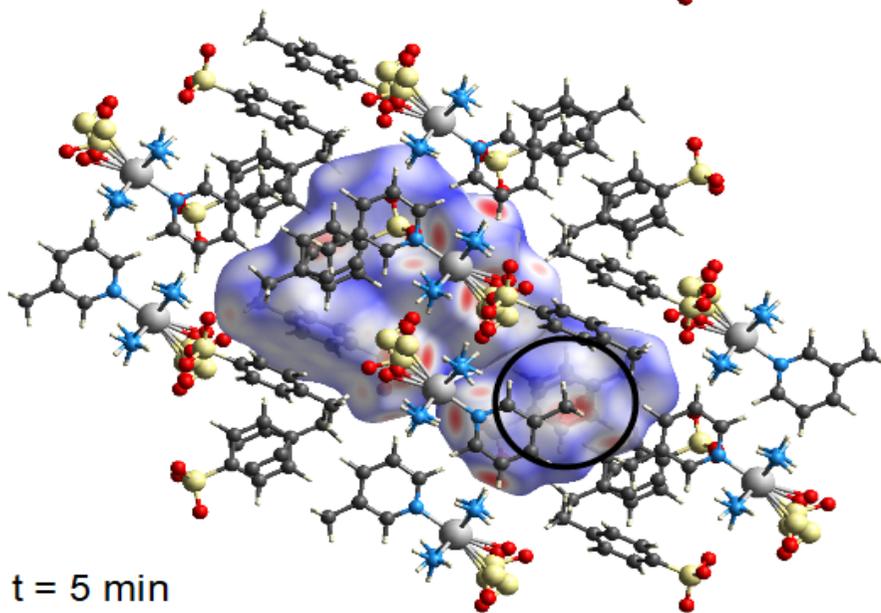
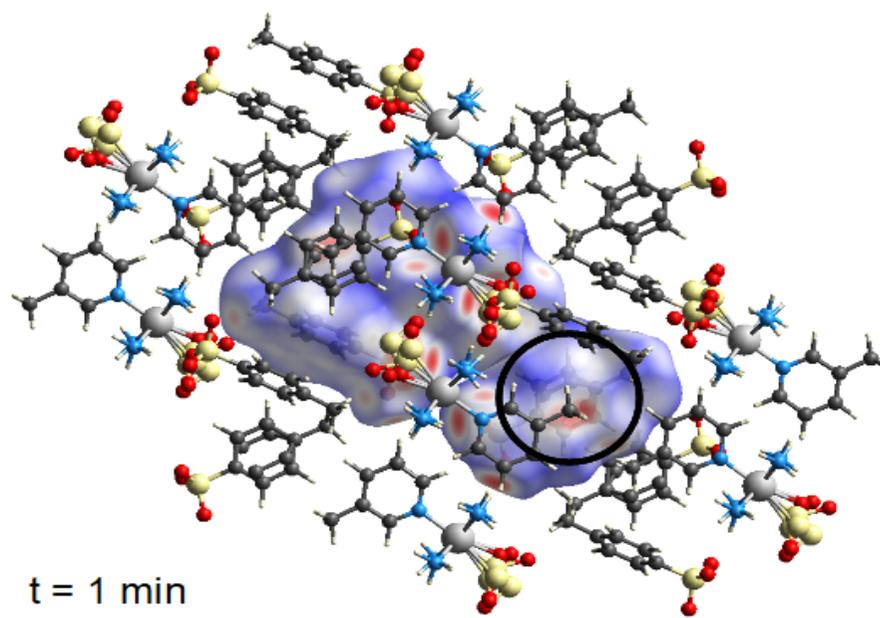
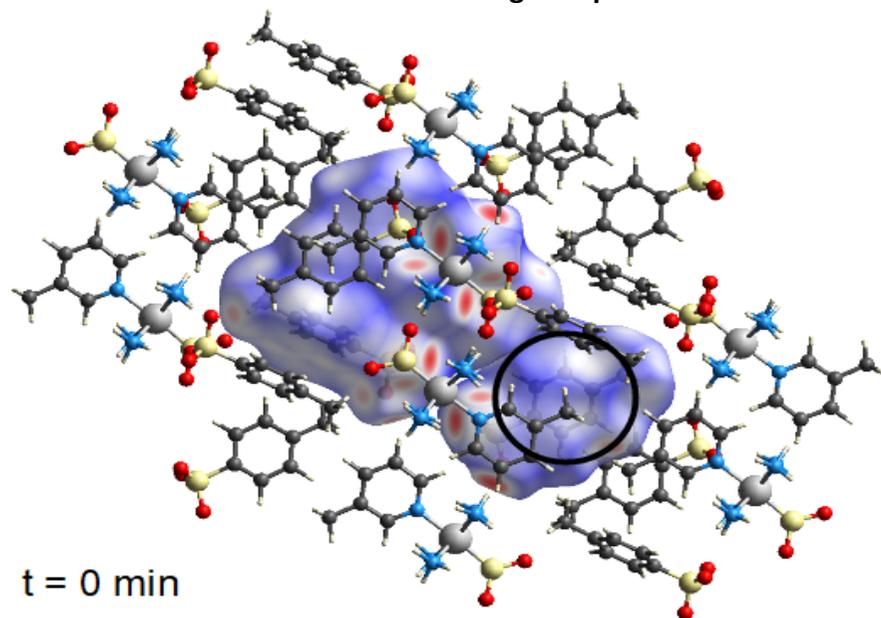
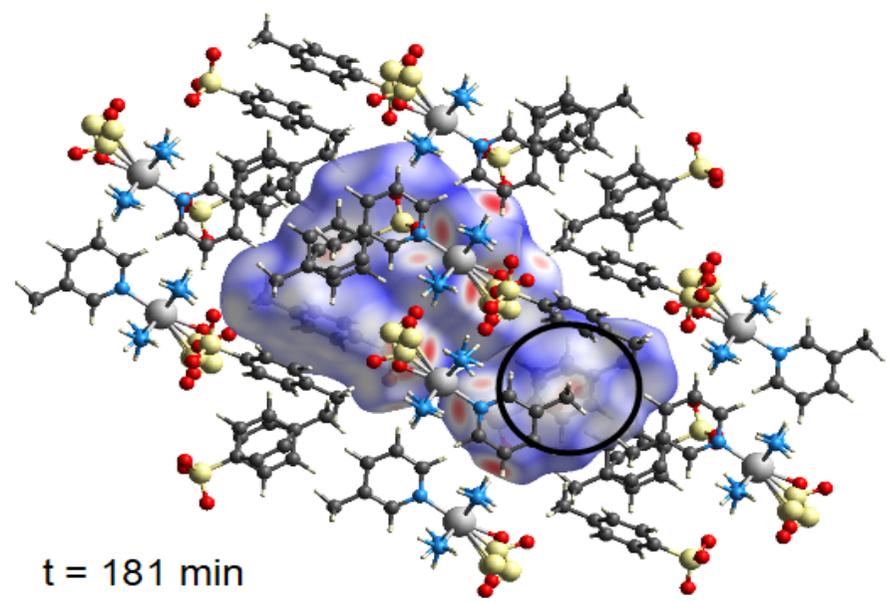
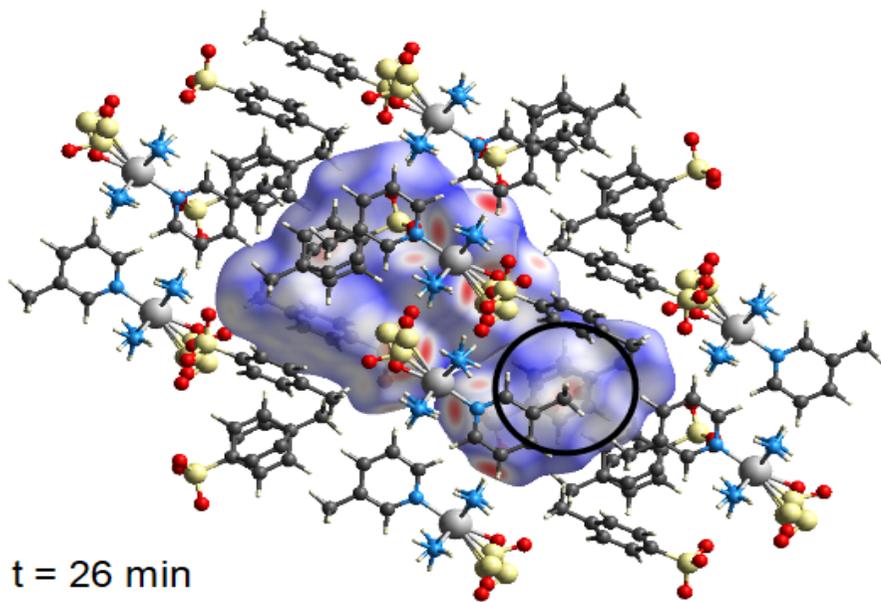
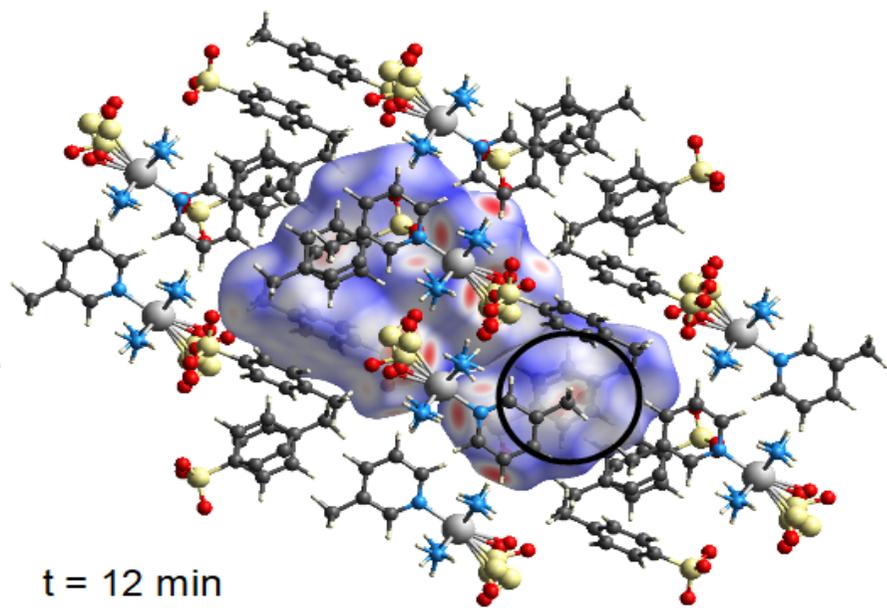
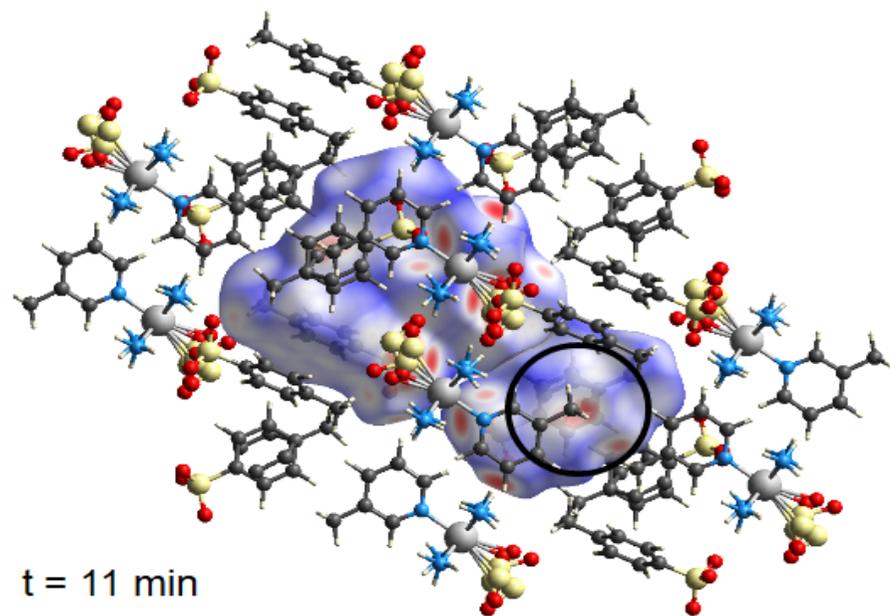
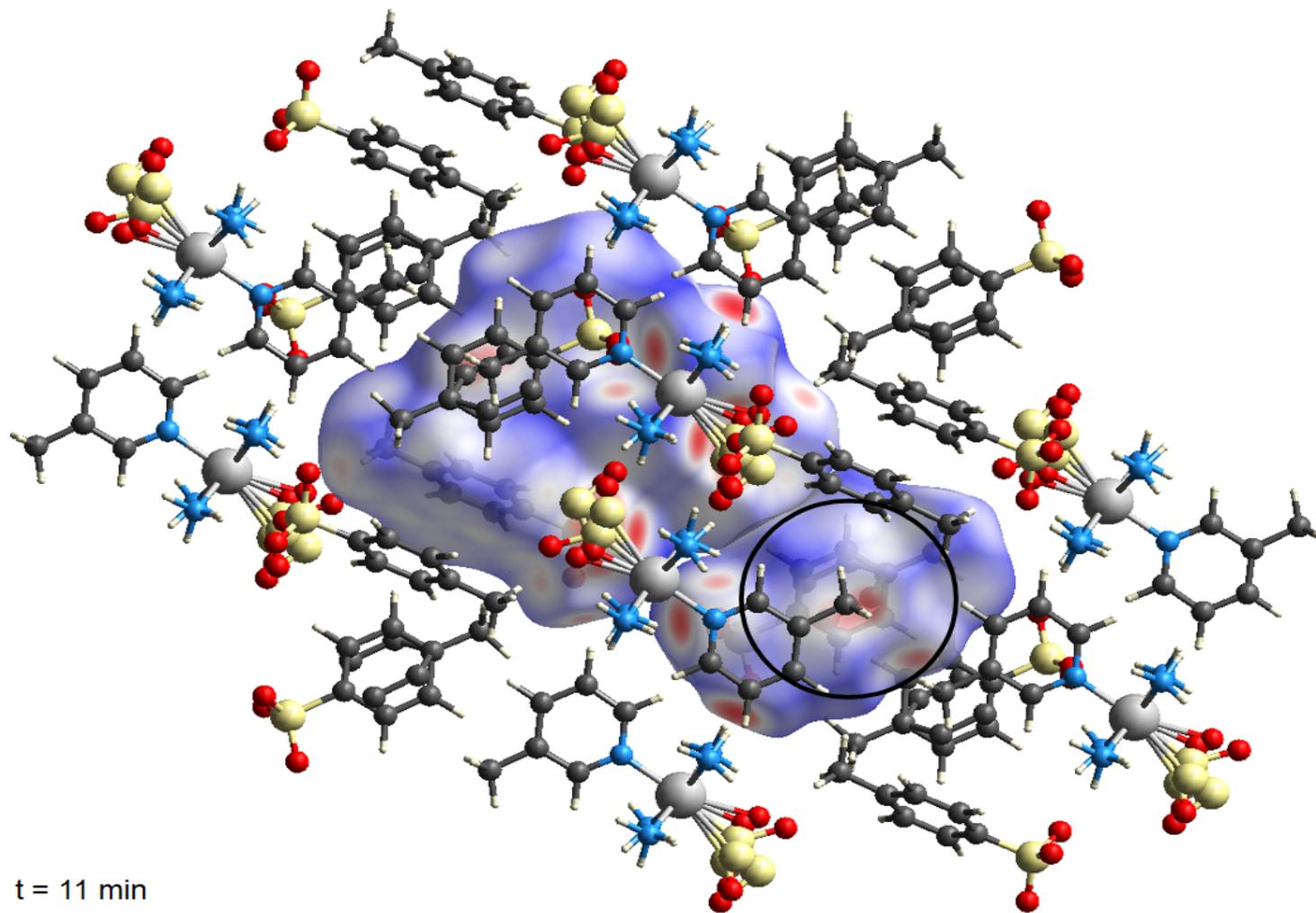


Figure S7 – Bond-length changes in the 3-methylpyridine ligand of **1** as a function of light-exposure time from $t = 0 - 181$ min.

S5 – Hirshfeld surfaces of 1 as a function of light-exposure time







$t = 11$ min

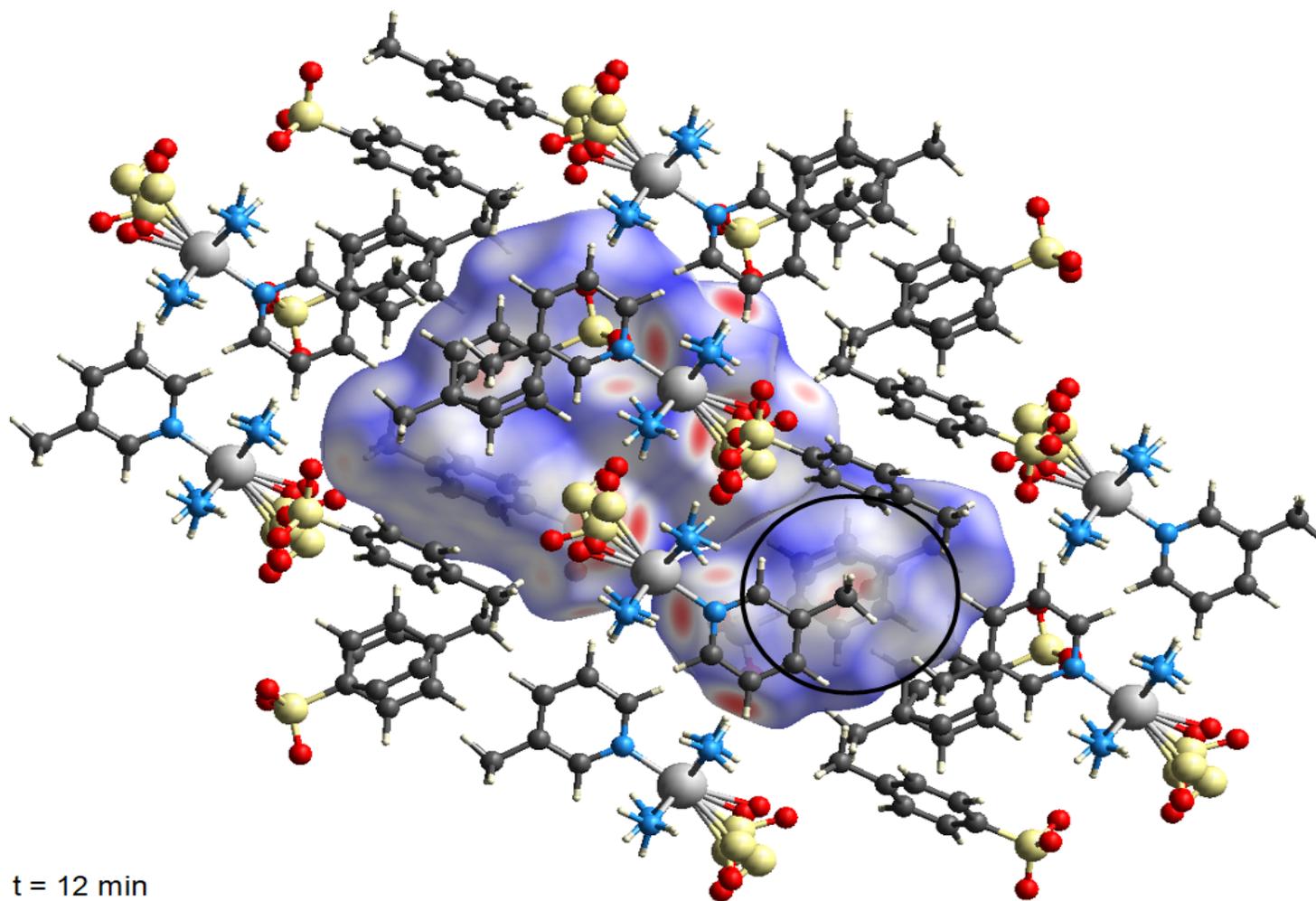


Figure S8 - Hirshfeld surfaces of **1** after 0, 1, 5, 10, 11, 12, 26 and 181 min of light exposure, as viewed looking down the crystallographic a axis. Larger images are also shown for t = 11 and 12 min to highlight the point at which there is a step change in non-bonded interactions. The red, white and blue regions show positive, neutral and negative isoenergies. The encircled regions highlight a close non-bonded contact (in red) between the methyl group of the 3-methylpyridine ligand in **1** and its tosylate anion that exhibits rotational disorder in order to alleviate the crystal lattice strain that is caused by this close interaction. This methyl group rotates between t = 11 and 12 min of light exposure to lessen the strain; *cf.* the red area in the encircled region shifts to the center of the ring. All images were generated via CrystalExplorer.[8]

S6 – References

- [1] Vogt, L. H.; Katz, J. L.; Wiberley, S. E. The Crystal and Molecular Structure of Ruthenium-Sulfur Dioxide Coordination Compounds. I. Chlorotetraammine(sulfur dioxide)ruthenium(II) Chloride. *Inorg. Chem.* **1965**, *4*, 1157-1163.
- [2] Coppens, P.; Fomitchev, D. V.; Carducci, M. D.; Culp, K. Crystallography of molecular excited states. Transition-metal nitrosyl complexes and the study of transient species. *J. Chem. Soc., Dalton Trans.* **1998**, *6*, 865-872.
- [3] Cole, J. M. Single-crystal X-ray diffraction studies of photo-induced molecular species. *Chem. Soc. Rev.* **2004**, *33*, 501-513.
- [4] Cole, J. M. Photocrystallography. *Acta Crystallogr., Sect. A: Found. Crystallogr.* **2008**, *64*, 259-271.
- [5] Cole, J. M. A new form of analytical chemistry: distinguishing the molecular structure of photo-induced states from ground-states. *Analyst* **2011**, *136*, 448-455.
- [6] Cole, J. M., Applications of photocrystallography: a future perspective. *Z. Kristallogr.* **2008**, *223*, 363-369.
- [7] Cole, J. M.; Gosztola, D. J.; Velazquez-Garcia, J. J.; Chen, Y-S. Systems Approach of Photoisomerization Metrology for Single-Crystal Optical Actuators: A Case Study of Ru(SO₂)(NH₃)₄Cl]Cl. *J. Phys. Chem. C* **2020**, *124*, 51, 28230–28243.
- [8] Turner, M. J.; McKinnon, J. J.; Wolff, S. K.; Grimwood, D. J.; Spackman, P. R.; Jayatilaka, D.; Spackman, M. A. CrystalExplorer17 (2017). University of Western Australia. <https://hirshfeldsurface.net>.