Electronic Supplementary Information (ESI)

In-situ Synthesis, Crystallisation, and Thin-film Processing of Single Crystals of *Trans*-[Ru(SO_2)(NH_3)$_4$(H_2O)][*p*-TolSO_3]$_2$ Bearing SO_2 Linkage Photo-isomers: Towards Optical Device Applications†

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1. Multi-temperature solid-state UV-vis absorption spectroscopy

1.1 Experimental setup

The custom-built experimental setup, used to measure the UV-vis absorption spectra at multiple temperatures, is shown in Figure S1. The crystal-containing thin film sample was mounted onto the probe of an Oxford Instruments CF1200 Helium Optical Cryostat. The temperature of the cryostat was controlled and measured by an Oxford Intelligent ITC4 temperature controller *via* the partial integration differentiation (PID) LabView program. The temperature of the sample was fed into a Lakeshore 211 temperature monitor connected to a silicon diode placed close to the sample on the sample holder. A continuous wave Ar$^+$ laser (Coherent Innova 300, 100 mW, λ = 488 nm) was used to photo-induce isomerisation of the SO_2 ligand from the ground state (η^1-SO_2) to the metastable states (η^2-SO_2/η^1-OSO) over a temperature range (T = 20-100 K). These optical wavelength and temperature conditions refer to those found by photo-crystallography to yield maximum photo-conversion levels, without detriment to sample quality owing to crystal lattice strain.[1-3]

In order to acquire solid-state UV-vis absorption spectra capturing these SO_2 photo-isomers, samples were probed using a tungsten white light source (Light Support 150W power supply unit). The transmitted intensity was registered in wavelength increments of 0.545 nm *via* an Instaspec IV spectrometer.

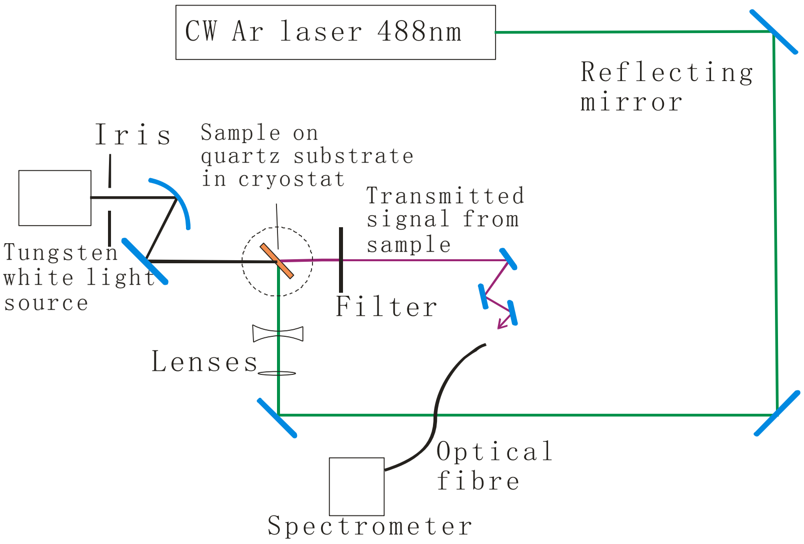

Fig. S1 Custom-built experimental setup for the solid-state, multi-temperature UV-vis absorption spectroscopy measurements. The sample was fixed at an angle of 45° with respect to the beam paths, which were adjusted by Ag mirrors. The transmitted signal passed through an optical density filter, and a suitable intensity was selected and collected by the spectrometer *via* an optical fibre (lower wavelength threshold of the fibre: ~ 320 nm). Photo-isomerisation of SO_2

was induced in perpendicular direction to the white light source, *via* an Ar^+ laser beam, which was focused through a convex lens and expanded by a concave lens to cover the entire sample area. While the laser was on, the white light source was blocked from the sample.

1.2 Background

The intensity was registered according to the Beer-Lambert law (Equation 1):

$$I = I_0 \cdot e^{-\mu dc} \quad , \tag{1}$$

where I_o is the transmitted intensity for a pure PVA film on the quartz substrate. The absorbance A is then defined by Equation 2:

$$A = \mu dc, \tag{2}$$

where μ is the extinction coefficient, d the thickness of the sample film, and c the concentration of the **[Ru]-SO$_2$** complex in the PVA gel. Assuming that the transmission through the PVA gel is the same for the reference and for the **[Ru]-SO$_2$** samples, the absorbance for each sample is calculated by Equation 3:

$$A = \ln(\frac{I_0}{I}) \tag{3}$$

In order to observe the light-induced changes in the optical properties, the difference in absorbance between the original ground state (GS) and the photo-induced metastable states (MS) was calculated, whereby the errors from the difference in PVA transmissions from the reference and the samples conveniently cancel each other out:

$$A_{MS} - A_{GS} = (\mu_{MS} - \mu_{GS})(dc) = \ln(\frac{I_{GS}}{I_{MS}}) \tag{4}$$

The photo-isomerisation yield was assumed to be sufficiently low that the final concentration of the original GS could be assumed to remain constant during the photo-isomerisation process.[4]

The transmission signal for each sample was recorded, and the absorbance at the indicated temperatures was calculated from Equation 3 (see Figure 3 and 4) before and after each laser irradiation.

*1.3 Testing the retention of SO_2 photo-isomerisation from bulk crystals to **[Ru]-SO_2** microcrystals embedded in PVA thin films*

In order to test the retention of the SO_2 photo-isomerism in PVA-embedded microcrystals of **[Ru]-SO_2**, pump-probe UV-vis spectroscopy measurements were carried out on the thin-film samples, at temperatures whose range ensures the presence of each metastable SO_2 photo-isomer. Indeed, while it is the high thermal stability of the η^2-SO_2 configuration in **[Ru]-SO_2** that makes it an attractive material for optical device applications, UV-vis measurements were focused on the η^1-OSO isomer, as it exhibits a much stronger (*i.e.* observable) optical absorption signature relative to the η^2-SO_2 isomer. The η^1-OSO isomer is a highly suitable diagnostic tool to confirm the presence of the η^2-SO_2 isomer, as the η^2-SO_2 isomer will coexist with the η^1-OSO isomer where present, and the thermally induced decay of the latter at T ~ 100 K increases the proportion of the former.

The test comprised two salient experiments. First, solid-state UV-vis absorption spectral signatures of **[Ru]-SO_2** in PVA were obtained in its original η^1-SO_2 (S-bound) GS, and under light-irradiation conditions (λ = 488 nm) at T = 15 K and

96 K. These temperatures were selected as they allow a discrimination of the metastable forms of each photo-isomer, as shown previously *via* photo-crystallography: at the lower temperature, the η^1-OSO and η^2-SO_2 photo-isomers coexist with the GS species in a metastable form,[5] while only the η^2-SO_2 photoisomer has been observed at T = 96 K in a metastable state together with the GS configuration.[1,2] Figure 2 displays three reference GS signatures at room temperature (T = 296 K), T = 92 K, and T = 17 K. These spectra are naturally almost identical, except for a monotonic change in the overall signal-to-noise ratio with decreasing temperature, which reflects increasingly inhibited transitions between molecular conformations and probably a slight modulation in sample scattering characteristics, caused by temperature-dependent morphological changes of the PVA matrix. The spectra at T = 92 K and T = 17 K serve as reference signatures for the light-irradiated (λ = 488 nm) UV-vis absorption spectra obtained at the same temperatures, even though they are subject to a small error (2-4 K), owing to the practical limitations of the temperature controller.

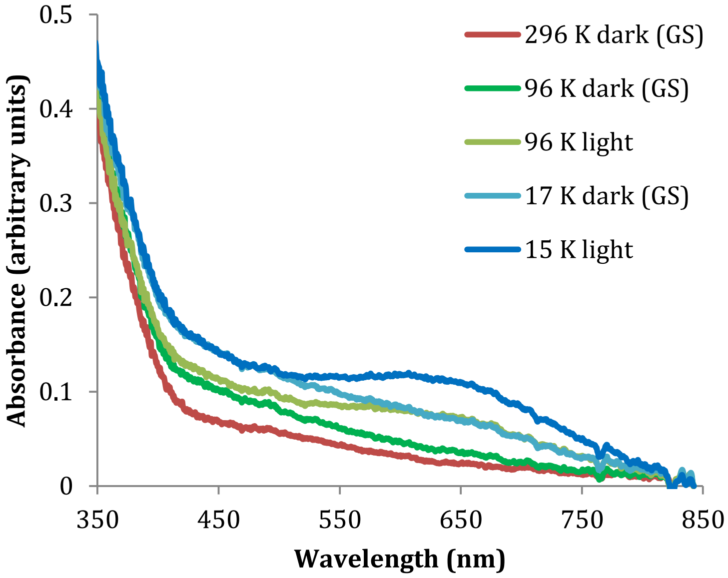

Fig. 2 Solid-state UV-vis absorption spectra of PVA-embedded **[Ru]-SO$_2$** before ("dark") and after ("light") photoirradiation (Ar$^+$ laser; λ = 488 nm) at low temperatures (T = 15-17 K and T = 92-96 K). A room temperature UV-vis absorption spectrum of "dark" PVA-embedded **[Ru]-SO$_2$** provides a consistent reference for the original GS of the sample.

Light excitation for 20 min at T = 15 K produced a persistent, broad optical absorption peak around λ = 650 nm. Light excitation for 20 min at T = 96 K initially produced the same optical feature, but this decayed after 1 h. The broad feature was attributed to the η^1-OSO photo-isomer, as it is known to be metastable at T = 13 K[5] but not at T = 100 K,[1,2] and since its absorption characteristics will dominate.

Having established the primary optical absorption characteristics of **[Ru]-SO$_2$** in PVA at these key reference temperatures, the stability of this η^1-OSO photo-isomer was studied. A series of UV-vis absorption spectra collected as a function of increasing temperature established that the η^1-OSO photo-isomer was no longer metastable at T > 30 K. The kinetic decay of this photo-isomer was subsequently monitored by collecting a time-evolution sequence of the UV-vis absorption spectra, while the temperature was gradually raised. Having irradiated (λ = 488 nm) the sample for 25 min at T = 30±11 K, a UV-vis spectrum was acquired at T = 41±1 K, immediately after extinguishing the laser light (t = 0 min). Even though this afforded a strong optical absorption feature centered on λ = 650 nm, representative of the η^1-OSO photo-isomer (Figure 3), signal intensity decayed quickly at this temperature. So the sample was cooled to T = 20 K, *i.e.* the temperature region where the η^1-OSO photo-isomer is metastable, and its optical spectra studied as a function of increasing temperature. Accordingly, the first UV-vis absorption spectrum was recorded at T = 20 K and t = 88 min, followed by T = 30, 50, 99, and 121 K in 6-13 min intervals, whereby intervals reflect the time necessary to warm the sample to the desired target temperature and record UV-vis absorption data. Figure 3 reveals a monotonic decay of the broad peak observed at T = 20 K, becoming untraceable at T = 121 K. The optical absorption signature of the dark-state (GS) was subtracted from these spectra according to Equation 4. Given that the η^1-OSO photo-isomer is no longer metastable at T > 100 K, the spectrum at T = 121 K should therefore only manifest optical absorption from the η^2-SO_2 photo-isomer, as this is metastable at T ≤ 250 K. This spectrum is essentially featureless, which is consistent with the findings that relate to Figure 2. The decaying broad peak as a result of rising temperatures should thus be exclusively due to the η^1-OSO photo-isomer.

While the $\lambda_{\max}^{peak}$ value of this spectrum seems to shift slightly with temperature, it is, owing to its very broad nature, difficult to locate exactly and therefore remains consistent with a peak at λ = 650 nm, subject to a possible blue-shift. While any hypsochromic shift can only be suggestive with these data, such a phenomenon would not be entirely surprising, since the immediate solid-state environment of the η^1-OSO photo-isomer will be gradually changing as its photo-converted fraction decreases with increasing temperature. It is known that the η^1-OSO photo-isomer converts into the η^2-SO_2 photo-isomer over the temperature range T = 13-100 K,[1,2,5] and the immediate solid-state environment of the η^1-OSO photo-isomer will hence feature progressively more cationic neighbours that feature the η^2-SO_2 photo-isomer as the temperature rises. In other words, a solid-state environmental effect that is somewhat analogous to solvatochromism, commonly seen in solution-based UV-vis absorption spectra, could readily manifest. The variably distributed fractions of the light-induced **[Ru]-SO$_2$** isomers throughout the crystal would reflect a range of solid-state environments, *i.e.* the broad optical absorption signature that is observed in the subject data.

Following these temperature scans, a final reference UV-vis absorption spectrum was acquired, immediately after having exposed the sample to light irradiation (λ = 488 nm) for t = 30 min at T = 70 K. This spectrum enabled a strong optical absorption signature of the η^1-OSO photo-isomer to be captured at a temperature between the penultimate and ultimate points of the temperature scan, where the signature of the η^1-OSO photo-isomer persisted. This result supports the aforementioned spectral interpretation of the decaying η^1-OSO photo-isomer and the possible origins of the hypsochromic shift, since any UV-vis absorption spectrum acquired prior to a substantial decay of the η^1-OSO photo-isomer will not be subject to any blue-shifting; indeed, it is not and its profile is in fact very similar to that of the initial spectrum collected at T = 41 K.

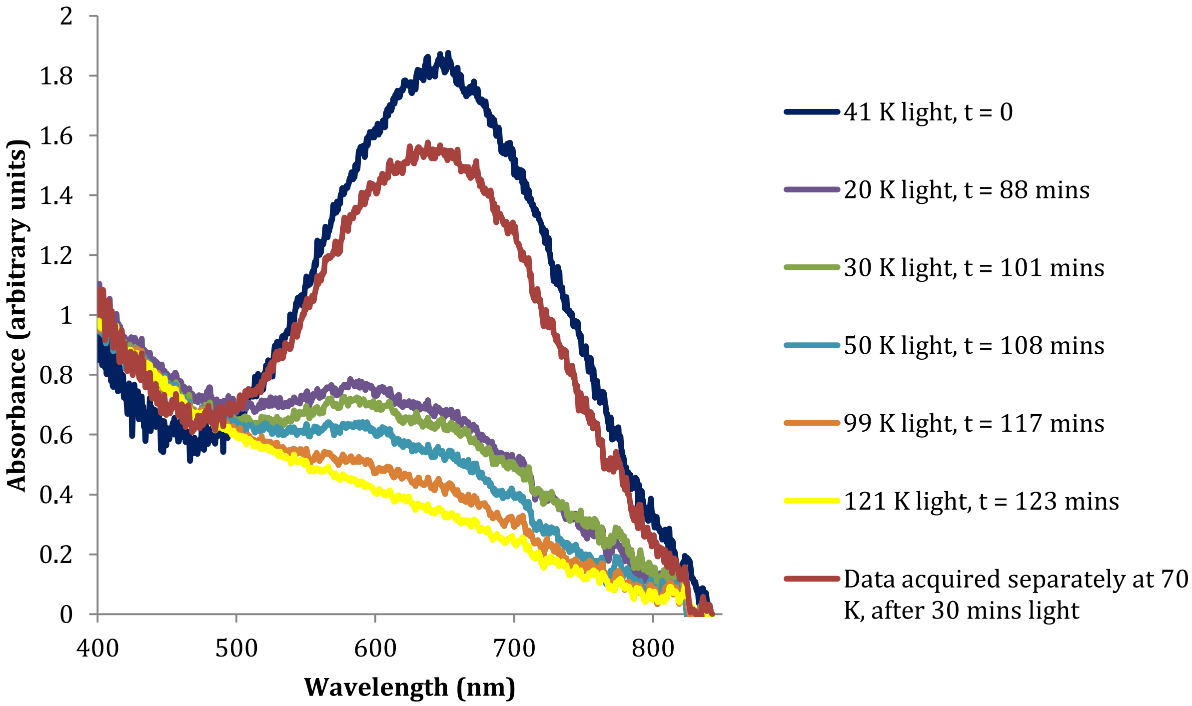

Fig. 3 Photo-isomerisation-induced change of the UV-vis absorption spectrum of PVA-embedded **[Ru]-SO₂**, shown as a time-dependent sequence under concomitantly monotonically increasing temperature (T = 20-121 K; t = 88-123 min after irradiation at □ = 488 nm). A spectrum of the original GS of the sample, acquired at T = 24 K prior to irradiation, was subtracted from all spectra according to Equation (4); in order to correct background variations, all spectra were normalized at λ = 400 nm.

Overall, the consistency of these findings, with respect to previous photo-crystallography results on the bulk crystals, confirm the notion that the SO_2 photo-isomer attributes of **[Ru]-SO₂** crystals are retained when embedded into PVA-based thin films.

2. References

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