

CrystEngComm

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.



Journal Name

ARTICLE

In-situ Synthesis, Crystallisation, and Thin-film Processing of Single Crystals of *Trans*-[Ru(SO₂)(NH₃)₄(H₂O)][*p*-TolSO₃]₂ Bearing SO₂ Linkage Photo-isomers: Towards Optical Device Applications†

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

J. M. Cole,^{a,b*} K. Y. M. Yeung,^{a,c} G. Pace,^{a,d} S. O. Sylvester,^a D. Mersch,^a and R. H. Friend^a

Metastable sulfur dioxide linkage photo-isomers can be generated in a family of ruthenium tetraammine-based complexes in their single-crystal form; this imparts them with attractive prospects as holographic data storage media (dark state = 0; photo-isomer state = 1). Embedding these optically encoded single crystals into thin-film technology *via* a polymer host should present one possible option for their ultimate device application. Crystals of *trans*-[Ru(SO₂)(NH₃)₄(H₂O)][*p*-TolSO₃]₂ ([Ru]-SO₂) were incorporated into a polyvinyl alcohol (PVA) matrix, by *in-situ* synthesis of [Ru]-SO₂ from the reaction of *trans*-[Ru(SO₂)(NH₃)₄Cl]Cl and *p*-toluenesulfonic acid (*p*-TA) in the PVA matrix, and an associated *in-situ* precipitating crystallisation. Transmission electron microscopy and diffraction on the resulting drop-cast thin films identified these [Ru]-SO₂ precipitates and their crystallinity; low-temperature solid-state UV-vis absorption spectroscopy confirmed that the desired SO₂ photo-isomerisation in [Ru]-SO₂ was uncompromised by its inclusion in thin films. The size and distribution of the embedded crystals were optimized by spin coating thin films of various *in situ* crystallised precipitates of [Ru]-SO₂ that emanated from chemical reaction mixtures of *trans*-[Ru(SO₂)(NH₃)₄Cl]Cl / *p*-TA / PVA. Results demonstrate the viability of the inclusion of single crystals of [Ru]-SO₂ in thin films for optical device applications.

Introduction

Ruthenium complexes of the general formula [Ru(SO₂)(NH₃)₄X]Y exhibit SO₂ linkage photo-isomerisation in the solid state. As such, they hold promise as prospective candidates for holographic data storage applications.¹ A dark-state of SO₂ (state 0) subjected to light will experience changes in its bonding mode to ruthenium, converting to one or more SO₂ photo-isomers (light-state, state 1). These distinct SO₂ states are spatially encoded within a single-crystal and are coupled to a photo-chromic change. The molecular configuration of the SO₂ linkage photo-isomer, its stability and photo-conversion efficiency can be tuned by varying the sample temperature, the optical wavelength of the light source, the ligand X in *trans*-position to SO₂, and/or the counterion Y.

This solid-state optical switching phenomenon is metastable below a temperature threshold, which is determined by the nature of X and Y. In this family of complexes, *trans*-[Ru(SO₂)(NH₃)₄(H₂O)][*p*-TolSO₃]₂ ([Ru]-SO₂)

holds the current record for the highest known temperature (T = 250 K), at which a metastable photo-isomer has been observed.²⁻¹⁰ A proportion (11%) of its dark-state, characterised by an η¹-SO₂ coordination mode and binding to the ruthenium atom *via* sulphur, was found to photo-isomerise to an η²-SO₂ (side-on) coordination mode when exposed to 488 nm light at T = 90 K, whereupon it remained metastable up to T ≤ 250 K. Photo-inducing [Ru]-SO₂ at T = 13 K with a tungsten lamp and subsequently maintaining the sample at this temperature generates a thermally less stable η¹-OSO configuration (end-on), which coexists in a metastable state with the η²-SO₂ isomer in proportions of 36% and 8%, respectively (56% non-photo-converted isomer).⁹ Above T ~ 100 K, this thermally less stable η¹-OSO photo-isomer thermally transitions into the η²-SO₂ isomer, thus augmenting its overall photoconversion level up to 44% available for optical device applications. This means that optical pumping at T = 13 K instead of T = 96 K ultimately generates a significantly higher proportion of the desirable photo-isomer. These thermally and photo-induced changes of the SO₂ coordination modes are summarised in Figure 1; their solid-state existence has been confirmed using *in situ* X-ray diffraction studies on light-induced single crystals.¹¹⁻¹⁴ The near-ambient temperature, at which the metastable η²-SO₂ photo-isomer of this complex is observable is important from a practical perspective, given that optical devices usually require operating temperatures as close to room temperature as possible. Likewise, the ability of this complex to maintain a

^a Cavendish Laboratory, University of Cambridge, J. J. Thomson Avenue, Cambridge, CB3 0HE, UK. E-mail: jmc61@cam.ac.uk.

^b Argonne National Laboratory, 9700 S. Cass Avenue, Argonne, IL 60439, USA.

^c Current address: School of Engineering and Applied Sciences, Harvard University, 33 Oxford St, Cambridge, MA 02138, USA.

^d Current address: Center for Nano Science and Technology @PoliMi, Istituto Italiano di Tecnologia, Via Pascoli, 70/3, 20133 Milano, Italy.

† Electronic supplementary information (ESI) available; for details regarding the solid-state UV-vis absorption spectroscopy, see DOI: 10.1039/x0xx00000x

clean separation between the “0” and “1” states under near-ambient conditions is fortuitous.

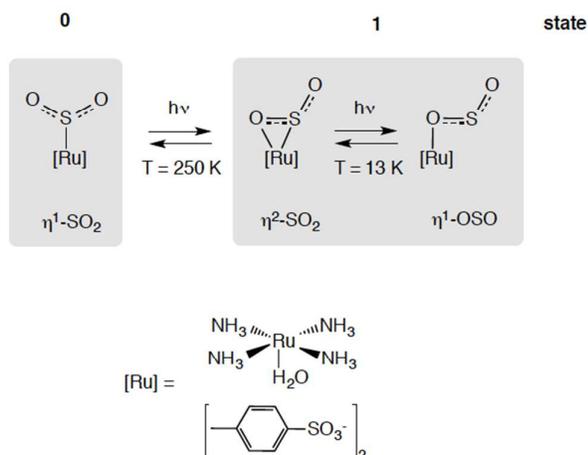


Fig. 1 Chemical structures of the $[\text{Ru}]\text{-SO}_2$ photo-isomers and their conversion between the $\eta^1\text{-SO}_2$ isomer (0 state; GS) and the $\eta^2\text{-SO}_2/\eta^1\text{-OSO}$ isomers (1 state; MS).

Given previous successful reports on the incorporation of photo-responsive organic or organometallic materials in thin films,^{15,16} and the increasing use of thin film technology for optical device media, it seemed pertinent to establish a means by which single crystals of $[\text{Ru}]\text{-SO}_2$ could be embedded in a matrix and processed as thin films, while retaining their characteristic solid-state photo-isomeric features.

This paper begins by describing the *in situ* chemical synthesis and crystallisation of $[\text{Ru}]\text{-SO}_2$ within a polymer medium. This is accomplished by a ligand exchange reaction between *trans*- $[\text{Ru}(\text{SO}_2)(\text{NH}_3)_4\text{Cl}]\text{Cl}$ and H_2O , followed by counter-ion exchange with *p*-toluenesulfonic acid (*p*-TA), where all reactions take place within a polyvinyl alcohol (PVA) matrix. It will be shown that thin films containing single crystals of $[\text{Ru}]\text{-SO}_2$ can be generated from this mixture *via* drop casting or spin coating. The presence of embedded single crystals of $[\text{Ru}]\text{-SO}_2$ in the drop-cast thin films was confirmed by transmission electron microscopy (TEM); while their size and distribution was optimized *via* spin coating, using optical microscopy as a qualifier. In order to verify that the previously reported photo-isomerization of individual (mm-sized) single crystals of $[\text{Ru}]\text{-SO}_2$ is reproducible when embedded as microcrystals in thin films, low-temperature solid-state UV-vis absorption spectroscopy measurements conducted, the results of which corroborate such reproducibility. With this proof-of-principle in hand, we are able to offer a viable method to produce thin films that host photo-isomerisable $[\text{Ru}]\text{-SO}_2$ in the form of good quality crystals, whose habit bears high levels of homogeneity in both size and shape. Such single-crystal attributes are important qualifiers for their ultimate application in optical device media.

Experimental section

Materials and methods

Starting materials. PVA (average $M_w = 85,000\text{--}146,000$) and *p*-TA (> 98% purity) were purchased from Sigma Aldrich and used without further purification. The precursor *trans*- $[\text{Ru}(\text{SO}_2)(\text{NH}_3)_4\text{Cl}]\text{Cl}$ was synthesized according to literature procedures.¹⁷

Sample preparation of $[\text{Ru}]\text{-SO}_2$ crystals embedded in PVA and drop-cast into thin films for materials characterization.

An aqueous solution of $[\text{Ru}]\text{-SO}_2$ was prepared by dissolving *trans*- $[\text{Ru}(\text{SO}_2)(\text{NH}_3)_4\text{Cl}]\text{Cl}$ (4.4 mg) and *p*-TA (3.2 mg) in distilled water (300 μL). The resulting pink solution was mixed thoroughly with a transparent PVA gel (v:v = 3:2) at room temperature, obtained from dissolving PVA (40 mg) in water (200 μL) at $T = 90^\circ\text{C}$, which is tantamount to a 0.0187 M concentration of $[\text{Ru}]\text{-SO}_2$ in this gel. For further characterisation of this material, the gel was drop cast into thin films. For the optical spectroscopy measurements, uniformly coloured thin films were manufactured by drop casting the gel on quartz substrates, followed by drying the films under nitrogen gas. The sample thickness across the sample substrate was 750–1600 nm. For the TEM measurements, thin films were drop cast onto a fine copper grid (400 mesh).

Materials characterization of the drop-cast $[\text{Ru}]\text{-SO}_2$ crystal-embedded PVA thin films

TEM and electron diffraction. TEM images of $[\text{Ru}]\text{-SO}_2$ crystals within the PVA matrix were obtained from a Philips Tecnai 20 TEM, using an accelerating voltage of 80 kV. For the associated electron diffraction experiments, a camera length of 890 mm was employed, and the lattice spacings were calibrated by reference images of TICl.

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

A custom-built experimental setup was used to measure multi-temperature UV-vis absorption spectra of the crystal-containing thin films. The overarching setup design is shown in the ESI. Regarding the specifics, thin film samples were 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, $\lambda = 488 \text{ nm}$) was used to photo-induce isomerisation of the SO_2 ligand from the ground state ($\eta^1\text{-SO}_2$) to the metastable states ($\eta^2\text{-SO}_2/\eta^1\text{-OSO}$) over a temperature range ($T = 20\text{--}100 \text{ K}$). 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.^{2,3,12} In order to acquire solid-state UV-vis absorption spectra that capture the optical signatures of these SO₂ 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.

Spin coating of [Ru]-SO₂ crystals embedded into PVA for optimizing crystal quality within thin films

In order to achieve homogeneous and high-quality crystals within the polymer host, thin films were spin coated from PVA gels containing [Ru]-SO₂, which were prepared under a different temperature regime relative to the drop-cast thin films. In addition, the molar ratio between *trans*-[Ru(SO₂)(NH₃)₄Cl]Cl and *p*-TA was increased from the previously used 1:4 (drop-cast samples) to 1:8; this stoichiometric alteration circumvented the formation of high concentrations of unreacted *trans*-[Ru(SO₂)(NH₃)₄Cl]Cl, which had been observed at 1:4 ratios.

PVA (50 mg) was initially dissolved in water (450 μL) at T ≈ 80 °C. Much care was taken to dissolve the PVA entirely, before *trans*-[Ru(SO₂)(NH₃)₄Cl]Cl was added, as the former was found to dissolve only very reluctantly in the presence of the latter. After the PVA was completely dissolved, the temperature was decreased to T = 55 °C and *trans*-[Ru(SO₂)(NH₃)₄Cl]Cl (5 mg, 0.021 mmol) was added. At this temperature, the complex dissolved readily in the PVA gel, and no visible deterioration was observed on the timescale of the experiment. After stirring the solution for 2 min, a solution of *p*-TA (30 mg, 0.174 mmol) in water (50 μL) was added. In order to prevent spontaneous crystallization and to ensure an equal distribution of all components, the solution was kept at this temperature and stirred for another 2 min. As it is feasible to assume that the temperature gradient of the solution has a profound effect on the size and distribution of the obtained crystals, one reaction mixture was spin-coated immediately after the addition of *p*-TA, whereas a second was maintained at T = 55 °C for 2 min following the addition of *p*-TA, before being allowed to slowly cool to room temperature (3 min) by removing the heat source, prior to spin coating the film. From each solution, a small aliquot (50 μL) was spin coated (2500 rpm, 1 min) onto a glass substrate. As reference samples, aliquots of pure PVA, as well as of PVA gels containing similar concentrations of *trans*-[Ru(SO₂)(NH₃)₄Cl]Cl or *p*-TA were spin coated on glass substrates. The quality of the resulting thin films was investigated using an Olympus BX51 optical microscope (5 x magnification).

Results and Discussion

Characterization of [Ru]-SO₂ crystal-embedded PVA thin films

To prove unambiguously that single crystals of [Ru]-SO₂ were embedded in the PVA-based thin films, drop-cast film samples were examined by TEM, and a corresponding electron

micrograph is shown in Figure 2. The associated electron diffraction pattern (Figure 2, inset) confirms its crystallinity, and the nature of this pattern, derived from a crystal oriented approximately along the crystallographic *b,c* plane, shows that its lattice spacings are consistent with the unit cell of [Ru]-SO₂.²

Testing the retention of SO₂ photo-isomerisation from bulk crystals to [Ru]-SO₂ microcrystals embedded in PVA thin films

Previous photo-crystallography studies have demonstrated solid-state photo-isomerisation in bulk (mm-sized) single crystals of [Ru]-SO₂.^{2,3,9} An implementation of this desirable optical attribute in thin-film device technology is, however, only feasible if the photo-isomerisation of [Ru]-SO₂ is retained within the polymer matrix. It was therefore necessary to test if the PVA-embedded microcrystals of [Ru]-SO₂ were susceptible to light-induced photo-isomerisation in the same fashion as seen in the bulk crystals. A detailed account of the photo-isomerisation of bulk crystals of [Ru]-SO₂ has been described previously,²⁻¹⁰ and therefore, the following section will be concerned with the specifics of the incorporation of crystalline [Ru]-SO₂ in the PVA matrix.

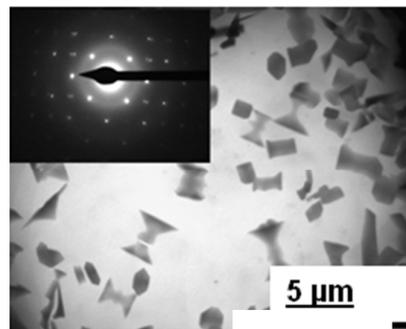


Fig. 2 Transmission electron micrograph and corresponding electron diffraction pattern (inset) of PVA-embedded [Ru]-SO₂ microcrystals.

Thin-film samples were subjected to pump-probe UV-vis measurements at temperatures, whose range ensured the presence of each metastable SO₂ photo-isomer (for the detailed experimental set-up, see ESI). UV-vis absorption spectroscopy measurements were focused on the η¹-OSO isomer, as it exhibits, in contrast to η²-SO₂ isomer, an observable optical absorption signature. As a diagnostic tool, the η¹-OSO isomer still is suited for confirming the presence of the η²-SO₂ isomer, since the η²-SO₂ isomer coexists with the η¹-OSO isomer where present, and the thermally induced decay of the latter at T ≈ 100 K increases the proportion of the former.

Initially, solid-state UV-vis absorption signatures were obtained for [Ru]-SO₂ in PVA in its original non-light exposed η¹-SO₂ (S-bound) GS, as well as under light-irradiation conditions (λ = 488 nm) at T = 15 K and 96 K. The reference GS

signatures at room temperature ($T = 296$ K), $T = 92$ K, and $T = 17$ K were almost identical, except for a monotonic change in the overall signal-to-noise ratio with decreasing temperature. This 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.

Subsequently, a series of light-irradiated ($\lambda = 488$ nm) UV-vis absorption spectra, collected as a function of increasing temperature, established that the η^1 -OSO photo-isomer, which exhibits a broad optical absorption peak around $\lambda = 650$ nm, was no longer metastable at $T > 30$ K. As the η^1 -OSO photo-isomer converts into the η^2 -SO₂ photo-isomer over the temperature range $T = 13$ -100 K,^{2,3,9} the immediate solid-state environment of the η^1 -OSO photo-isomer should contain more cationic neighbours that feature the η^2 -SO₂ photo-isomer as the temperature rises.

Such a solid-state environmental effect, which is somewhat analogous to the solvatochromism commonly seen in solution-based UV-vis absorption spectra, is consistent with the data obtained. The variably distributed fractions of the light-induced [Ru]-SO₂ isomers throughout the crystal should moreover represent a range of solid-state environments, which is reflected in the broad optical absorption signature of the subject data. While the temperature was gradually raised, the kinetic decay of the η^1 -OSO isomer into the η^2 -SO species was monitored by collecting a time-evolution sequence of the UV-vis absorption spectra (Fig. 3).

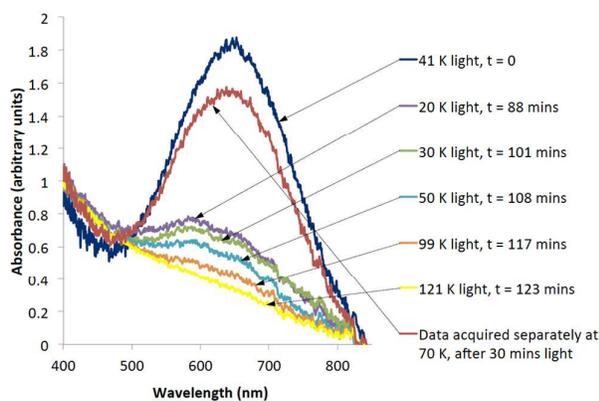


Fig. 3. Photo-isomerisation-induced change of the UV-vis absorption spectrum of PVA-embedded [Ru]-SO₂, shown as a time-dependent sequence under a concomitant monotonic increase of temperature ($T = 20$ -121 K; $t = 88$ -123 min after irradiation at $\lambda = 488$ nm).[‡]

Following these temperature scans, a final reference UV-vis absorption spectrum was acquired, immediately after having exposed the sample to light irradiation ($\lambda = 488$ nm) for $t = 30$ min at $T = 70$ K. This spectrum reproduced the strong optical

absorption signature of the η^1 -OSO isomer, capturing it at a temperature between the penultimate and ultimate temperature-scan points, where the signature of the η^1 -OSO photoisomer persisted. This result supports the aforementioned spectral interpretation of the decaying η^1 -OSO photoisomer and the possible origins of the hypsochromic shift: any UV/vis absorption spectrum acquired prior to a substantial decay of the η^1 -OSO photoisomer 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.

Overall, the consistency of these findings, with respect to previous photo-crystallography results on the bulk crystals, confirm the notion that the SO₂ photo-isomer attributes of [Ru]-SO₂ crystals are retained when embedded into PVA-based thin films. Accordingly, these materials may be manufactured in thin films for optical data storage applications, without compromise in optical function.

Nevertheless, in order to meet practical device requirements for thin-film technology, such as material reproducibility, another issue concerning the processing of these thin films needs attention: the homogeneity of the embedded crystals. Indeed, as Figure 2 portrays, the size and shape uniformity and overall quality of crystals afforded by drop-casting thin-film processing methods is highly variable. A significant improvement in thin-film processing was therefore sought. To this end, spin-coating options were explored as an alternative to drop-casting.

Improving the homogeneity of [Ru]-SO₂ crystals embedded in a PVA matrix via spin coating

A broad range of spin-coating conditions for the crystallization and distribution of crystalline [Ru]-SO₂ in the PVA matrix was examined: spin-coating duration, speed; relative reagent concentrations, reagent mixing methods. In general, molar ratios of 1:8 between *trans*-[Ru(SO₂)(NH₃)₄Cl]Cl and *p*-TA yielded uniformly shaped crystals of [Ru]-SO₂. At lower concentrations of *p*-TA, crystallization was hampered. The most homogeneous distributions of [Ru]-SO₂ in the PVA matrix was observed when *trans*-[Ru(SO₂)(NH₃)₄Cl]Cl and PVA were thoroughly mixed, before *p*-TA was added.

The most suitable crystallization strategy is best illustrated via a comparison of several distinct crystallization conditions presented in Figure 4. An optical micrograph (5 x magnification) of the starting material, *trans*-[Ru(SO₂)(NH₃)₄Cl]Cl embedded in PVA, is provided for reference (Figure 4, left). These needle-shaped crystals vary substantially from those of [Ru]-SO₂ illustrated via the optical micrographs shown alongside (Figure 4, middle and right), thus corroborating the success of the concerted *in situ* reaction and crystallization of the desired product.

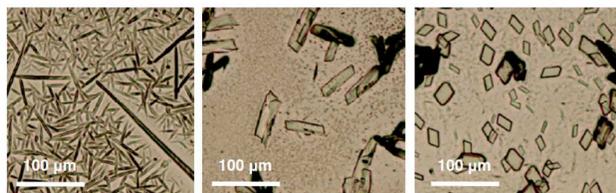


Fig. 4 Optical micrographs of spin coated films in PVA at 5 x magnification. Left: starting material, *trans*-[Ru(SO₂)(NH₃)₄Cl]Cl embedded in PVA; Middle: [Ru]-SO₂ obtained from reacting PVA / *trans*-[Ru(SO₂)(NH₃)₄Cl]Cl / *p*-TA, where the Ru complex and *p*-TA were mixed prior to addition of the PVA and spin coated directly after addition of the acid; Right: [Ru]-SO₂ produced *via* reaction of PVA / *trans*-[Ru(SO₂)(NH₃)₄Cl]Cl / *p*-TA, where the Ru complex and PVA were mixed prior to adding the *p*-TA, annealing (1. T = 55 °C, 2 min; 2. cooling, 3 min), and spin coating.[§]

The two different sets of PVA-embedded [Ru]-SO₂ crystals shown in Figure 4 (middle, right) were both obtained using a mixture of PVA / *trans*-[Ru(SO₂)(NH₃)₄Cl]Cl / *p*-TA reagents, one of which was spin coated immediately following addition of *p*-TA (Figure 4, middle), while the other was spin coated from a sample that was heated to and maintained at T = 55 °C for 2 min after the addition of *p*-TA, followed by a cooling period of 3 min (Figure 4, right). The second crystallization method is clearly superior to that obtained without a cooling cycle (Figure 4, middle), affording regularly shaped, high-quality crystals of a parallelepiped habit, whereby sizes range from 5–50 µm in length and 1–10 µm in width. This technique should therefore represent an appropriate approach to produce thin-film crystals with high levels of homogeneity in size and shape, suitable for their ultimate use in optical device media.

Conclusions

A fabrication method that produces thin films of ruthenium-sulfur dioxide linkage photo-isomers for optical data storage applications has been demonstrated. Single crystals of *trans*-[Ru(SO₂)(NH₃)₄(H₂O)] [p-TolSO₃]₂ ([Ru]-SO₂) were embedded into a PVA matrix *via in-situ* synthesis and crystallisation within a polymer gel and subsequent thin-film processing. The resulting thin films were characterized by TEM and associated diffraction. Low-temperature solid-state UV-vis absorption spectroscopy confirmed that the optically addressable property attributes of the dark-state SO₂ isomer (state 0) and its SO₂ photo-isomers (state 1), previously observed in their bulk form (single crystals), are retained in these thin films. While the thermally more stable photoisomer (η^2 -SO₂) is of primary interest for device applications, the UV-vis spectroscopy measurements pinpoint the η^2 -SO₂ photoisomer indirectly using optical spectroscopy signatures for the thermally less stable species (η^1 -OSO) in the thin films: evidence for η^1 -OSO directly implies that η^2 -SO₂ has been generated, as η^1 -OSO converts into η^2 -SO₂ at T ~ 100 K. Two

processing methods for thin films, namely drop casting and spin coating, were explored. High-quality single crystals, displaying high levels of homogeneity in crystal size and habit, were obtained by spin coating reaction mixtures of PVA, *trans*-[Ru(SO₂)(NH₃)₄Cl]Cl, and *p*-TA, where the precipitation of the crystallizing product [Ru]-SO₂ was judiciously controlled. The results provide an option for this family of ruthenium-sulfur dioxide linkage photo-isomers to find applications in thin-film technology, with their ultimate goal to serve in optical data storage devices.

Acknowledgements

J. M. C. thanks the Fulbright Commission for a UK-US Fulbright Scholar Award hosted by Argonne National Laboratory (Argonne, IL, USA), where work done was supported by DOE Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357. S. O. S. acknowledges the Cambridge Commonwealth Trust for a PhD scholarship. This work was also supported by the EPSRC Cambridge NanoDTC, EP/G037221/1 (for D.M.). The authors are grateful to Dr. Anthony E. Phillips, formerly of the Cavendish Laboratory, for providing a starting material for one of the experiments; and to John J. Rickard from the electron microscopy facility at the same laboratory, for technical assistance.

Notes and references

‡ Prior to irradiation, a spectrum of the original GS of the sample, was acquired at T = 24 K and subtracted from all spectra. In order to correct for background variations, all spectra were normalised at $\lambda = 400$ nm.

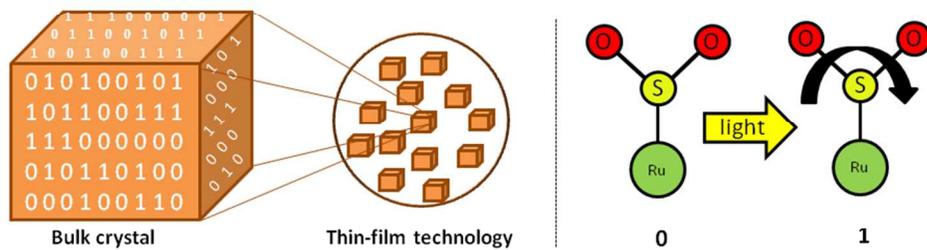
§ The two-dimensional nature of these images provide an optical illusion in crystal size variation, as some crystals lie on their sides; in these cases, their comparative lengths, relative to the face-up crystals, indicate their regularity in crystal size.

- 1 a) T. Woike, W. Kirchner, G. Schetter, T. Barthel, K. Hyung-sang and S. Haussühl, *Opt. Commun.*, 1994, **106**, 6. b) S. Haussühl, G. Schetter and T. Woike, *Opt. Commun.*, 1995, **114**, 219. c) M. Imlau, R. Schieder, R. A. Rupp and T. Woike, *Appl. Phys. Lett.*, 1999, **75**, 16. d) M. Imlau, T. Woike, R. Schieder and R. A. Rupp, *Europhys. Lett.*, 2001, **53**, 471. e) M. Imlau, M. Fally, T. Weisemoeller, D. Schaniel, P. Herth and T. Woike, *Phys. Rev.*, 2006, **B73**, 205113. f) J. M. Cole, *Z. Kristallogr.*, 2008, **223**, 363.
- 2 A. Y. Kovalevsky, K. A. Bagley, J. M. Cole and P. Coppens, *Inorg. Chem.*, 2003, **42**, 140.
- 3 A. Y. Kovalevsky, K. A. Bagley, and P. Coppens, *J. Am. Chem. Soc.*, 2002, **124**, 9241.
- 4 A. E. Phillips, J. M. Cole and T. d'Almeida, *Inorg. Chem.*, 2012, **51**, 1204.
- 5 A. E. Phillips, J. M. Cole and T. d'Almeida, *Phys. Rev. B*, 2010, **82**, 155118.
- 6 S. O. Sylvester and J. M. Cole, *J. Phys. Chem. Lett.*, 2013, **4**, 3221.
- 7 S. O. Sylvester and J. M. Cole, *Adv. Mater.*, 2013, **25**, 3324.
- 8 S. O. Sylvester, J. M. Cole and P. G. Waddell, *J. Am. Chem. Soc.*, 2012, **134**, 11860.
- 9 K. F. Bowes, J. M. Cole, S. L. G. Husheer, P. R. Raithby, T. L. Savarese, H. A. Sparkes, S. J. Teat and J. E. Warren, *Chem. Commun.*, 2006, 2448.

COMMUNICATION

Journal Name

- 10 S. O. Sylvester, J. M. Cole, P. G. Waddell, H. Nowell and C. Wilson, *J. Phys. Chem. C*, 2014, **118**, 16003.
- 11 P. Coppens, D. V. Fomitchev, M. D. Carducci and K. Culp, *J. Chem. Soc., Dalton Trans.*, 1998, **6**, 865.
- 12 J. M. Cole, *Chem. Soc. Rev.*, 2004, **33**, 501.
- 13 J. M. Cole, *Acta Crystallogr. A*, 2008, **64**, 259.
- 14 J. M. Cole, *Analyst*, 2011, **136**, 448.
- 15 S. Ghorai, J. C. Sumrak, K. M. Hutchins, D.-K. Bučar, A. V. Tivanski and L. R. MacGillivray, *Chem. Sci.*, 2013, **4**, 4304.
- 16 D. S. Tyson, C. A. Bignozzi and F. N. Castellano, *J. Am. Chem. Soc.*, 2002, **124**, 4563.
- 17 L. H. Vogt Jr., J. L. Katz and S. E. Wiberley, *Inorg. Chem.*, 1965, **4**, 1157.



254x190mm (96 x 96 DPI)