

Photocrystallography of $[\text{Ru}(\text{bpy})_2(\text{dmsO})_2]^{2+}$ reveals an O-bonded Metastable State

Electronic Supplementary Information

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Synthesis of $[\text{Ru}(\text{bpy})_2(\text{dmsO})_2][\text{B}(\text{Ph})_4]_2$

The $[\text{Ru}(\text{bpy})_2(\text{dmsO})_2][\text{PF}_6]_2$ salt was synthesized following the procedures in the literature.

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0.2 mmol of $\text{Ru}(\text{bpy})_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$, 2.5 eq of AgPF_6 along with 25 ml of ethanol (previously sparged with Nitrogen) was added to a 50 ml round bottom flask and refluxed for 2 hours under nitrogen. The mixture was then cooled to room temperature and filtered to remove the AgCl and unreacted AgPF_6 . Half the volume of the filtrate was reduced using rotatory evaporator. To this, was added 1ml of DMSO and refluxed for another 2 hours. During this time, the progress of reaction was monitored by UV -Vis spectrophotometer (shoulder at 420nm decreases in intensity as the band at 348nm intensifies). The mixture was cooled to room temperature and put in the freezer for overnight. The yellow precipitate was collected in a frit and washed with ether to give $[\text{Ru}(\text{bpy})_2(\text{dmsO})_2][(\text{PF}_6)_2]$. Yield: 50%.

ESI MS: [M-2PF 6] Calculated m/z: 285.0364 Observed m/z: 285.0357

2g of sodium tetraphenyl borate, $\text{NaB}(\text{Ph})_4$, was dissolved in 50 ml of ethanol. The metal PF_6 salt was dissolved in minimum volume of acetonitrile and was added dropwise to the ethanolic solution of the sodium tetraphenyl borate while stirring. The solution was stirred for half an hour and the precipitate was collected in a frit in stoichiometric amount.

Solid State visible spectroscopy/microscopy of $[\text{Ru}(\text{bpy})_2(\text{dmsO})_2][\text{B}(\text{Ph})_4]_2$

All solid-state visible spectroscopy and imaging was conducted on Olympus IMT-2 inverted microscope. The measurements were collected on a PI-max 3 CCD camera and then processed using Lightfield software. The samples were excited with a 405 nm diode (Thorlabs M405L2) which was coupled to a Thorlabs DC2100 High power LED driver.

Thermal reversibility and X-ray diffraction studies

A crystal, containing $[\text{Ru}(\text{bpy})_2(\text{dmsO})_2][\text{B}(\text{Ph})_4]_2$ and a non stoichiometric amount of acetonitrile, had a complete XRD data set collected to determine the initial ground state structure. After the initial data collection, the same crystal was irradiated *ex-situ* with a 405 nm diode (driver set to 700mA) for 10 minutes and then another XRD data collection was conducted immediately. The sample was then left in the dark (at room temperature) for a week and then the final XRD data collection was performed.

The XRD data was collected on a Bruker SMART APEX2 CCD diffractometer installed with a rotating anode source ($\text{MoK}\alpha=0.71073\text{\AA}$). All the collections were performed in the dark to prevent the room

lights from interfering with photochemical measurements. The sample was cooled to 90K using an Oxford Cryosystems (Cryostream700) nitrogen gas-flow apparatus. Five data sets (360 frames) were collected using the rotation method with a 0.5° frame-width (ω scan) for a complete data collection. The crystal structures were solved in Olex2 with ShelXT via the intrinsic phasing method and refined using ShelXL using the least square minimization. When modelling the mixed S/O-bonded structure, the disorder for each DMSO and the Ru were refined independently. The occupancy of each disordered S-bonded/O-bonded DMSO was also constrained to the sum of 1. The percent conversion to the O-bonded isomer was determined from the resulting occupancies.

***In-situ* irradiation X-ray diffraction study**

For the *in-situ* data collection, a 405 nm diode (driver set to 700mA) was attached via a fiber optic cable (ThorlabsM22L02) to an optical assembly that focuses the light at the sample position inside the diffractometer enclosure. A prolonged X-ray experiment was performed with 6 complete data collections collected back to back while the sample was being irradiated.

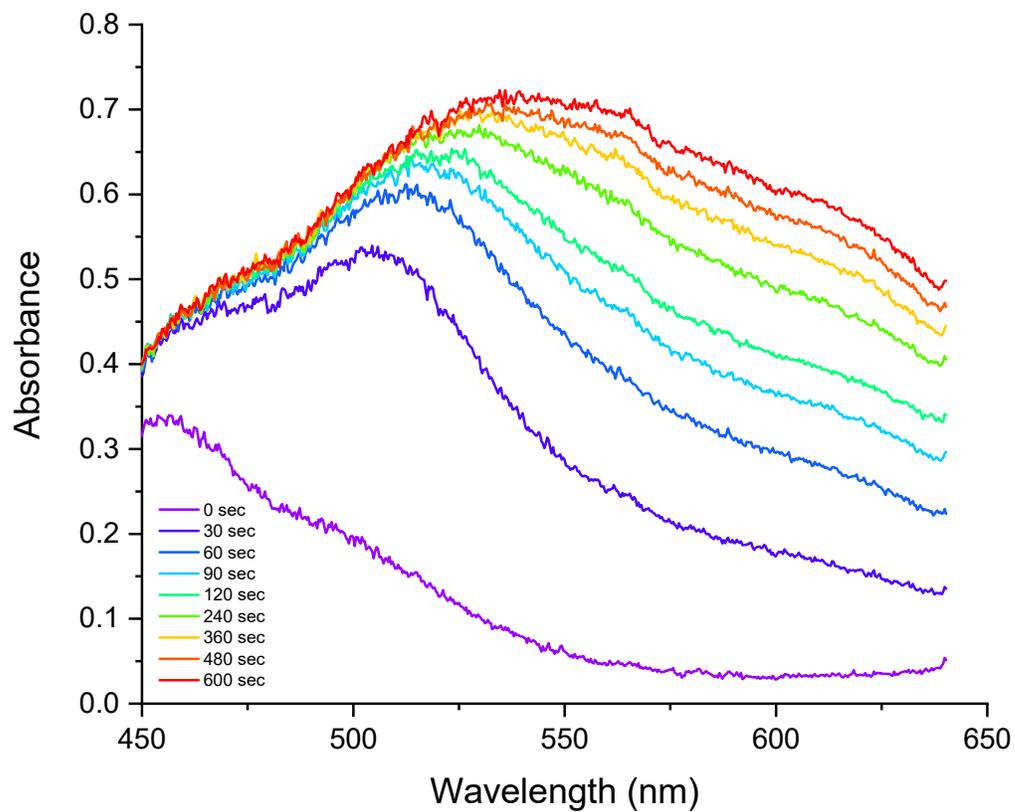


Figure S1. Solid-state visible absorption spectra of the crystal while being irradiated *in situ* with 405 nm light.

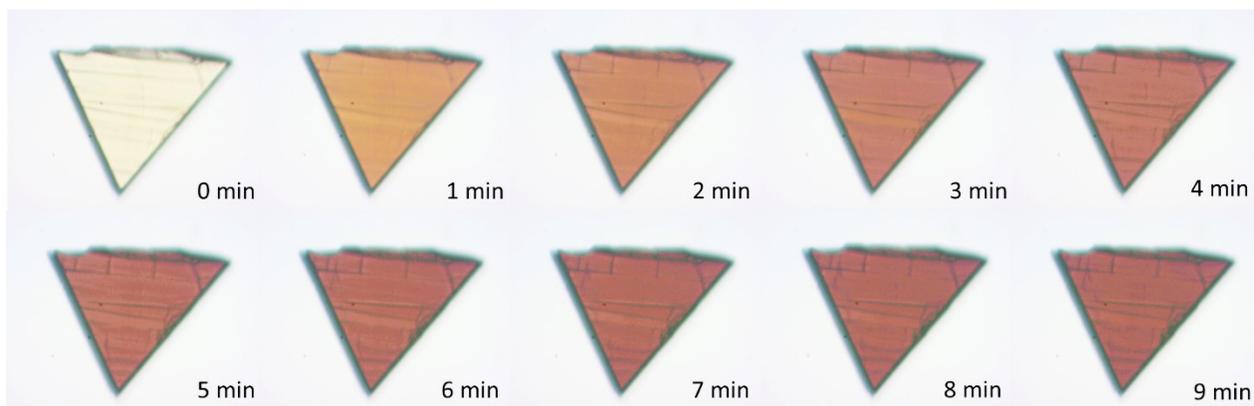


Figure S2. Image of a crystal irradiated with 405 nm light for a total on 9 min with pictures taken at every 1 min interval.

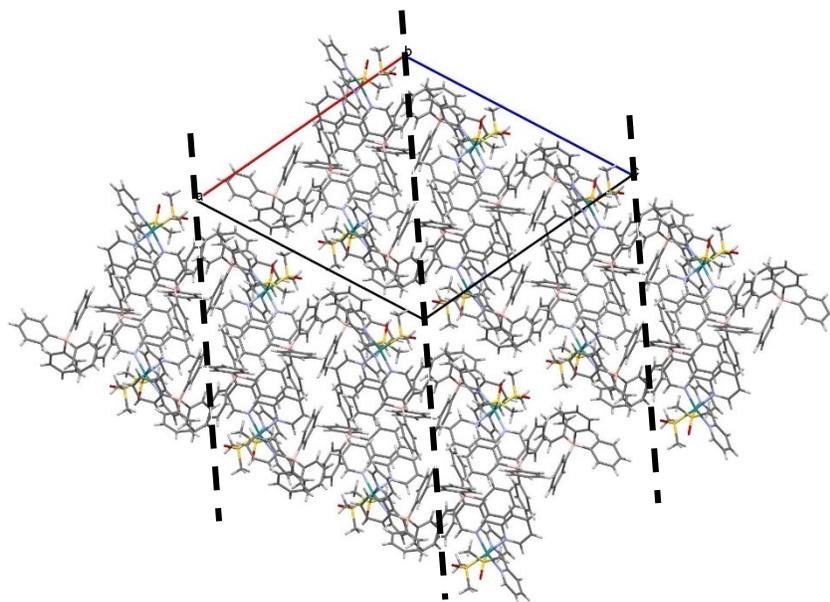


Figure S3. Crystal packing diagram viewed down $[010]$. The dashed lines represent cleavage planes along $(\bar{1}01)$.

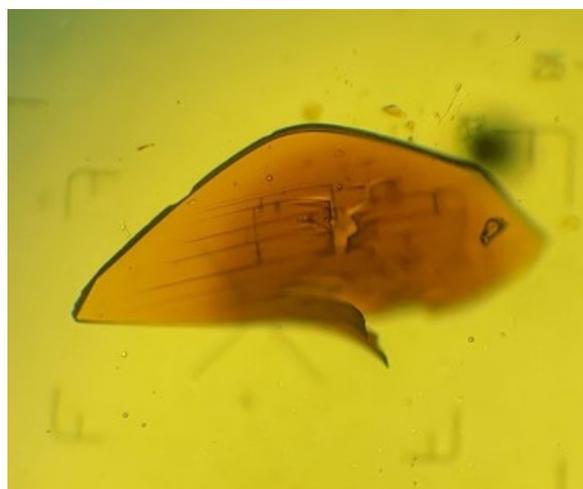


Figure S4. Delamination of the crystal parallel to (100) after prolonged exposure ($>30\text{min}$) to 405 nm light.

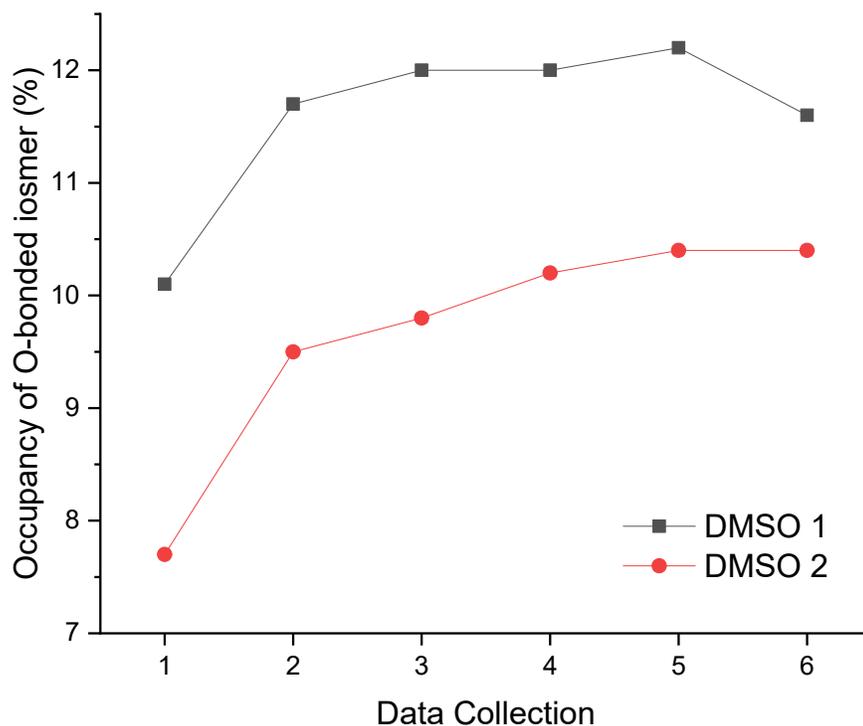


Figure S5. Plot demonstrating the increase in the percent occupancy determined through X-ray diffraction of the O-bonded isomer for the individually refined DMSO molecules. DMSO 1 contains O1 while DMSO 2 contains O2.

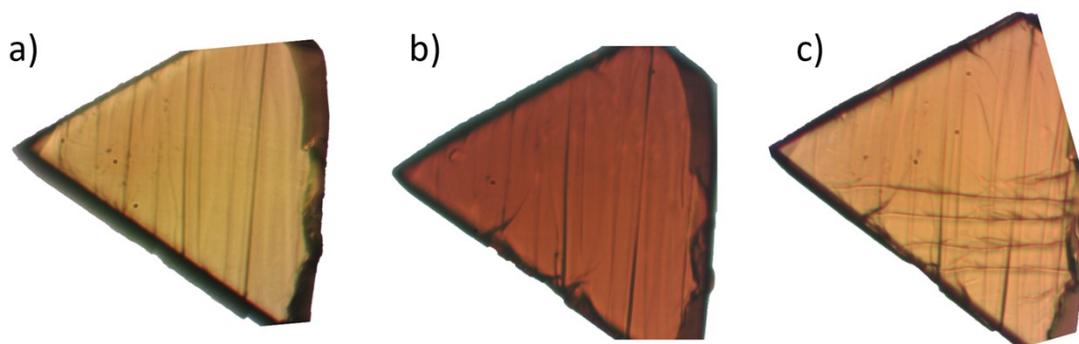


Figure S6. Image of the crystal used for the thermal reversibility study prior to irradiation (A). Image of the same crystal after *ex situ* irradiation with 405 nm light for 10 min (B). Image of the same crystal after sitting a week in the dark at room temperature (C).

Table S1. Crystallographic Parameters

	[Ru(bpy) ₂ (dmsO) ₂][B(Ph) ₄] ₂	[Ru(bpy) ₂ (dmsO) ₂][B(Ph) ₄] ₂ after irradiation	[Ru(bpy) ₂ (dmsO) ₂][B(Ph) ₄] ₂ after 1 week in dark
Formula	C _{73.5} H _{70.26} B ₂ N _{4.75} O ₂ RuS ₂	C _{73.52} H _{70.28} B ₂ N _{4.76} O ₂ RuS ₂	C _{73.5} H _{70.1} B ₂ N _{4.75} O ₂ RuS ₂
MW (g/mol)	1239.00	1239.21	1238.78
T (K)	90	90	90
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	P2 ₁ /c	P2 ₁ /c	P2 ₁ /c
a (Å)	22.0253(7)	22.0479(8)	22.0415(9)
b (Å)	14.2617(5)	14.2689(6)	14.2574(6)
c (Å)	22.4081(8)	22.3824(9)	22.4105(9)
α (°)	90	90	90
β (°)	119.2740(10)	119.1730(10)	119.2530(10)
γ (°)	90	90	90
V (Å ³)	6139.9(4)	6148.3(4)	6144.5(4)
Z	4	4	4
ρ _{calc} (g/cm ³)	1.340	1.339	1.339
μ (mm ⁻¹)	0.376	0.375	0.375
Crystal size (mm ³)	0.14 mm×0.14 mm×0.02 mm	0.14 mm×0.14 mm×0.02 mm	0.14 mm×0.14 mm×0.02 mm
Radiation	MoKα (λ=0.71073)	MoKα (λ=0.71073)	MoKα (λ=0.71073)
2θ range for data collection (°)	3.536 to 56.752	3.534 to 53.53	2.118 to 56.204
Reflections collected	122,962	108,163	120,670
Independent reflections	15,300	13,089	14,979
R _{int} , R _{sigma}	0.0673, 0.0421	0.0602, 0.0386	0.0571, 0.0345
Data completeness	100%	100%	100%
Data/restraints/parameters	15,300/0/781	13,089/163/868	14,979/103/800
Goodness of fit on F ²	1.037	1.027	1.047
Final R indexes [I>2σ(I)]	R ₁ =0.0436, wR ₂ =0.1025	R ₁ =0.0410, wR ₂ =0.1018	R ₁ = 0.0413, wR ₂ = 0.0974