Electronic Supplementary Material (ESI) for CrystEngComm.

Understanding solid-state photoswitching in [Re(OMe$_2$-bpy)(CO)$_3$(η^1-NO$_2$)] crystals *via in-situ* photocrystallography

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Supplementary Information

Contents

1. Supplementary GS structure information for 1 at 150 K

2. Diffuse reflectance spectroscopy

3. Supplementary MS structure information for 1 at 150 K

4. Reaction cavity analysis

5. Steady-state photocrystallographic data for 1 at 170 K

6. Supplementary structure data for pseudo-steady-state studies

7. References

1. Supplementary GS structure information for 1 at 150 K

Figure S1: Void space diagram for the GS X-ray structure of 1 at 150 K.

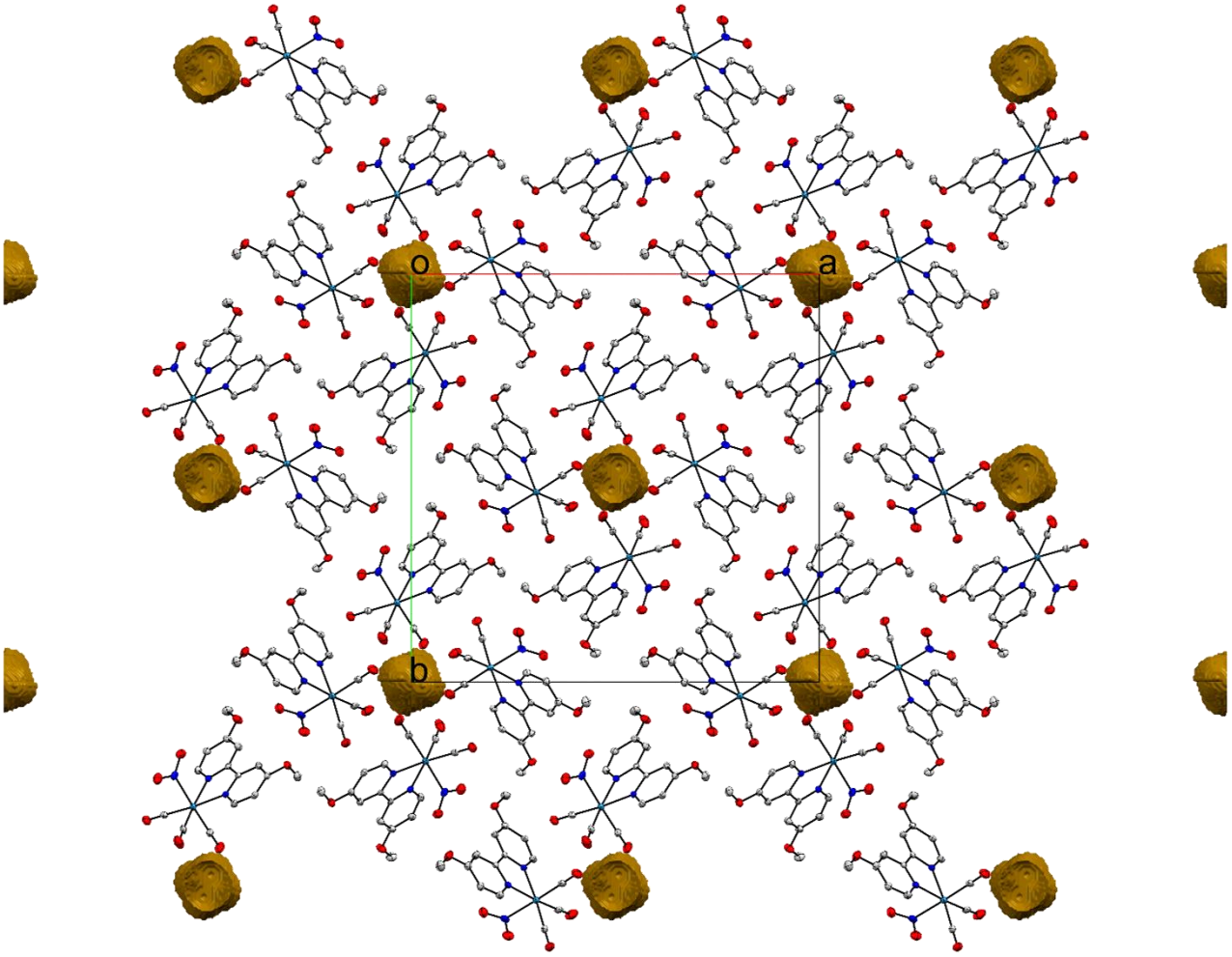


Table S1: Intermolecular C-H…O contacts to the nitro-(η^1-NO_2) isomer in the GS structure of 1 at 150 K.

Identifier	D…A Distance / Å	D…H distance† / Å	DHA angle† / °
C(15)-H(15B)…O(2)	3.62(1)	2.65	168.6
C(10)-H(10)…O(2)	3.51(1)	2.63	155.1
C(10)-H(10)…O(1)	3.39(1)	2.51	153.2
C(7)-H(7)…O(2)	3.81(1)	2.92	155.7
C(7)-H(7)…O(1)	3.63(1)	2.73	159.2
C(5)-H(5)…(O1)	3.15(1)	2.28	153.2
Average value	3.52(2)	2.62	157.5

†D…H distances and DHA angles have no esd as all hydrogens were refined to fixed distances using a riding model (AFIX instruction)

2. Diffuse reflectance spectroscopy

Solid state diffuse reflectance spectra were collected using an Ocean Optics Maya 200 PRO High Sensitivity Spectrometer equipped with an Ocean Optics DH-2000-BCA UV-Vis-NIR light source.
Spectra were collected on evenly-ground powder samples, prepared from pure single-crystals. Figure S2 shows the experimental diffuse reflectance spectra of **1**. Figure S3 shows the normalised absorption profiles for **1**, converted from the diffuse reflectance data using the Kubelka Munk function:

$$A = \frac{(1 - R_\infty)}{2R_\infty}$$

where *A* = calculated absorbance and *R* = diffuse reflectance.[1]

Figure S2: Solid state diffuse reflectance spectrum for 1 at room temperature.

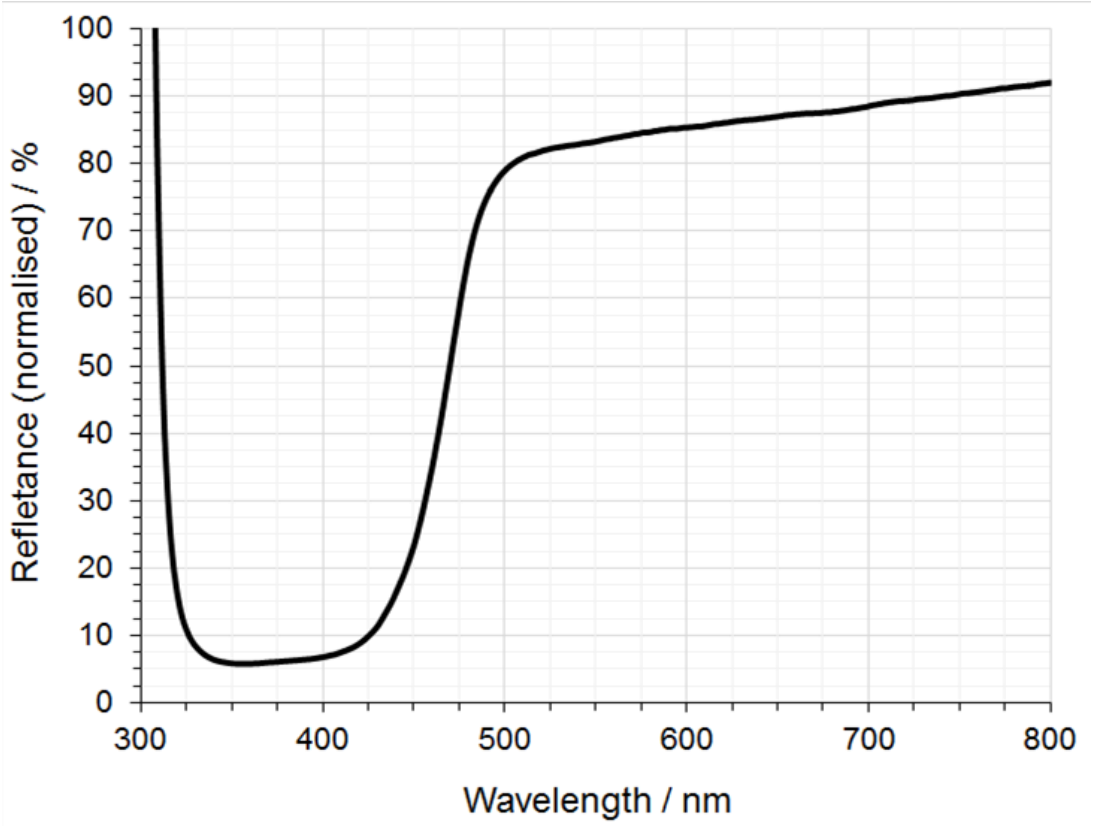
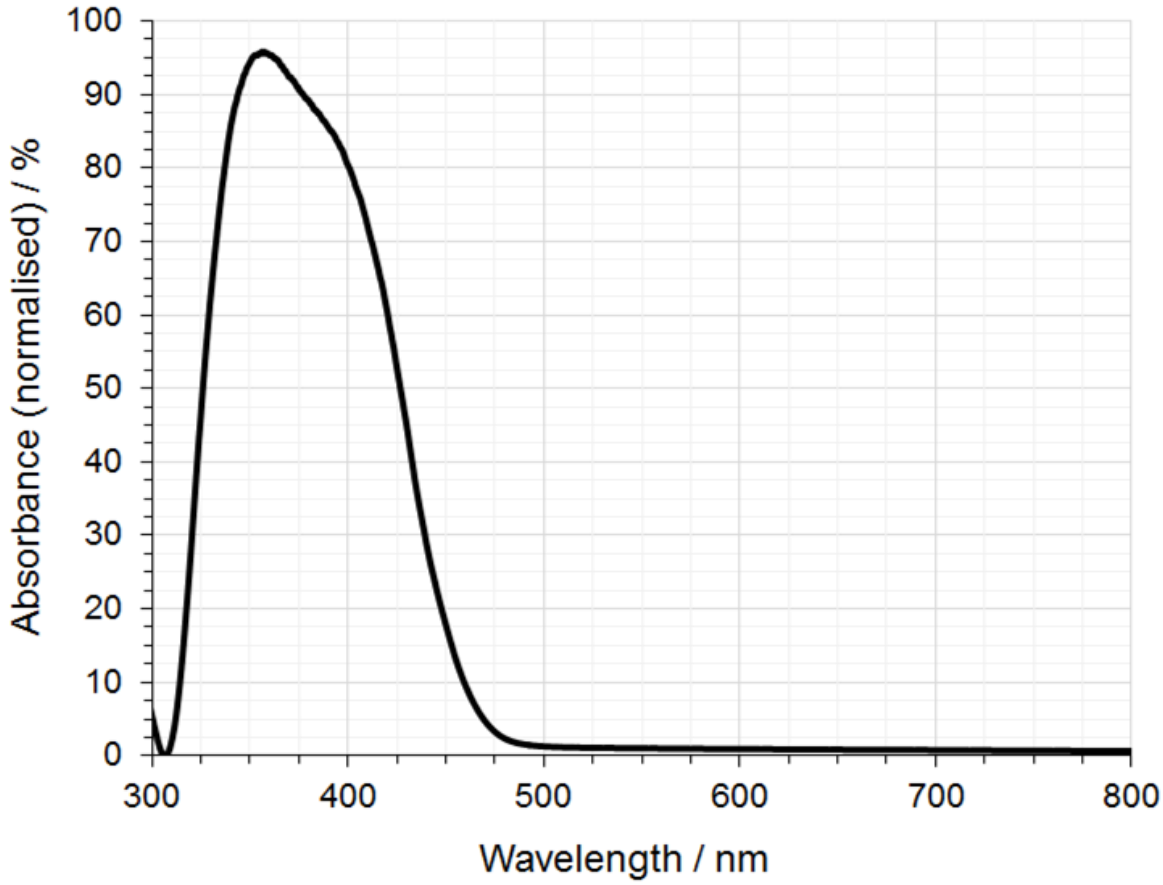


Figure S3: Solid state Kubelka Munk absorption spectrum for 1 at room temperature.



3. Supplementary MS structure information for 1 at 150 K

Table S2: Nitro:nitrito isomer occupancy ratios refined from single-crystal X-ray data during all steady-state photocrystallographic studies with **1** at 150 K, as a function of temperature and irradiation time

Temp / K	Irradiation time / min	Nitrite occupancy level	
		Nitro-NO_2	Nitrito-ONO
150	0	1.00	0.00
150	1	0.71	0.29
150	5	0.58	0.42
150	15	0.52	0.48
150	60	0.46	0.54
150	180	0.42	0.58
175	180	0.42	0.58
200	180	0.49	0.51
210	180	0.69	0.31
220	180	1.00	0.00
230	180	1.00	0.00
250	180	1.00	0.00

Figure S4: Crystal packing diagram for the MS structure of 1 at 150 K.

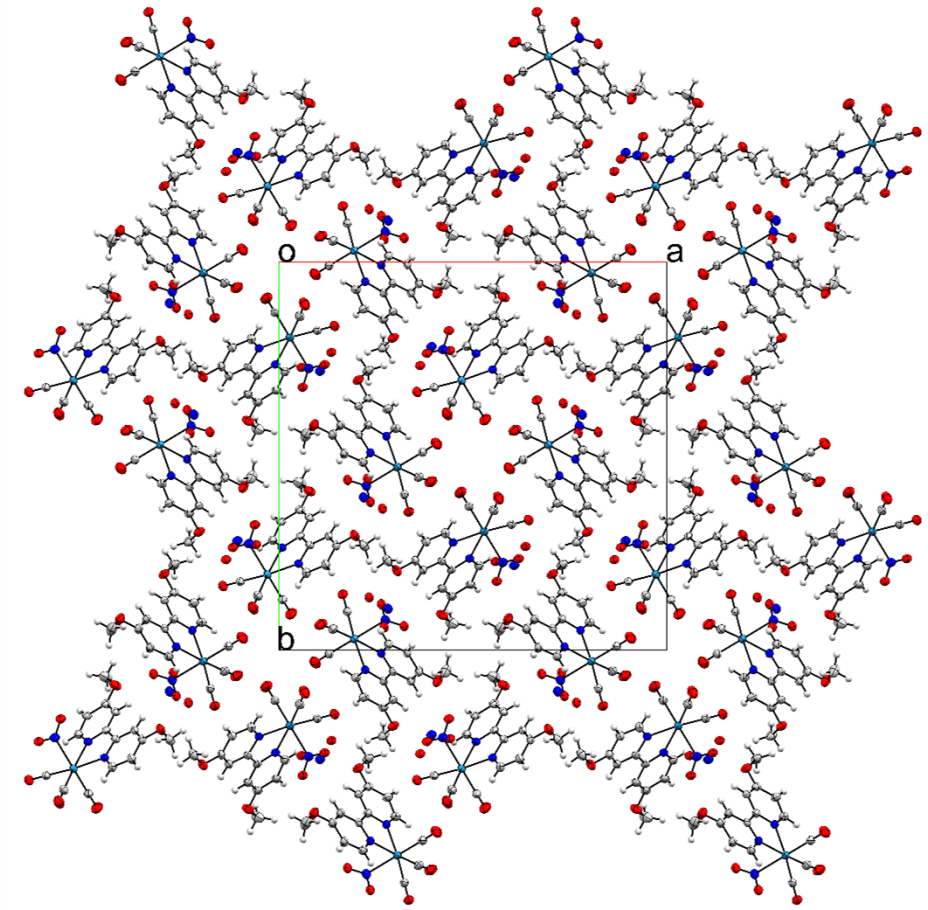


Table S3: Single crystal X-ray data for steady state photocrystallographic studies with 1 at 150 K. Selected crystal data for **1** under illumination with 405nm, collected under steady state photocrystallographic conditions between 1 and 60 min total irradiation time

	1 min 405 nm	5 min 405 nm
Photoconversion	29 %	42 %
Temperature	150(2) K	150(2) K
Wavelength	0.71073 Å	0.71073 Å
Empirical formula	C15 H12 N3 O7 Re1	C15 H12 N3 O7 Re1
Formula Weight	532.48 g mol^{-1}	532.48 g mol^{-1}
Crystal system	Tetragonal	Tetragonal
Space group	I-4	I-4
Unit cell parameters (constrained)	a = 22.4161(5) Å	a = 22.5083(8) Å
	c = 6.6101(3) Å	c = 6.5855(4) Å
Volume	3321.4(2) $Å^3$	3336.4(3) $Å^3$
Z	8	8
Density (calculated)	2.130 g cm^{-1}	2.120 g cm^{-1}
Absorption coefficient μ	7.362 mm^{-1}	7.329 mm^{-1}
F(000)	2032	2032
R(int)	0.0567	0.0760
Completeness (to ϑ = 25.00°)	0.998	0.998
$R1$ (observed data $I > 2\sigma(I)$)	0.0456	0.0532
$wR2$ (all data)	0.0881	0.0982
Reflections (independent)	6060 (2918)	6083 (2918)
Flack parameter	-0.027(17)	-0.03(2)

	15 min 405 nm	60 min 405 nm
Photoconversion	48 %	54 %
Temperature	150(2) K	150(2) K
Wavelength	0.71073 Å	0.71073 Å
Empirical formula	C15 H12 N3 O7 Re1	C15 H12 N3 O7 Re1
Formula Weight	532.48 g mol^{-1}	532.48 g mol^{-1}
Crystal system	Tetragonal	Tetragonal
Space group	I-4	I-4
Unit cell parameters (constrained)	a = 22.5635(5) Å	a = 22.6151(5) Å
	c = 6.5794(2) Å	c = 6.5646(3) Å
Volume	3349.65(19) $Å^3$	3357.4(2) $Å^3$
Z	8	8
Density (calculated)	2.112 g cm^{-1}	2.107 g cm^{-1}
Absorption coefficient μ	7.300 mm^{-1}	7.283 mm^{-1}
F(000)	2032	2032
R(int)	0.0569	0.0625
Completeness (to ϑ = 25.00°)	0.998	0.9968
$R1$ (observed data $I > 2\sigma(I)$)	0.0428	0.0449
$wR2$ (all data)	0.0824	0.0858
Reflections (independent)	6080 (2928)	6059 (2928)
Flack parameter	-0.038(16)	-0.04(2)

Figure S5: Mercury[2] void space diagram for the MS structure of 1 at 150 K.

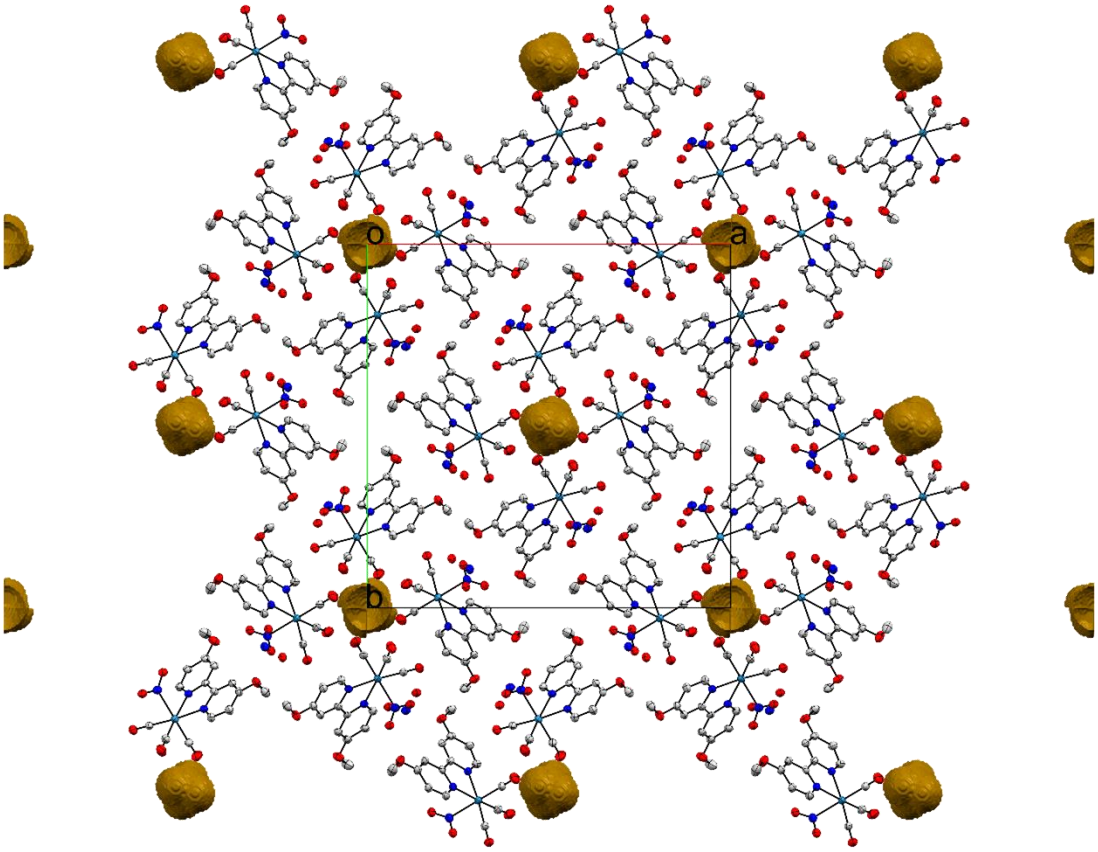


Table S4: Single crystal X-ray data for variable temperature studies with 1 after irradiation. Selected crystal data for **1** with increasing temperature, following irradiation for 180 min with 405 nm LED light

	VT 175 K	VT 200 K
ONO conversion level	58 %	51 %
Temperature	175(2) K	200(2) K
Wavelength	0.71073 Å	0.71073 Å
Empirical formula	C15 H12 N3 O7 Re1	C15 H12 N3 O7 Re1
Formula Weight	532.48 g mol^{-1}	532.48 g mol^{-1}
Crystal system	Tetragonal	Tetragonal
Space group	I-4	I-4
Unit cell parameters (constrained)	a = 22.7219(11) Å	a = 22.6358(9) Å
	c = 6.5890(6) Å	c = 6.5964(4) Å
Volume	3401.8(5) $Å^3$	3379.9(3) $Å^3$
Z	8	8
Density (calculated)	2.079 g cm^{-1}	2.093 g cm^{-1}
Absorption coefficient μ	7.188 mm^{-1}	7.235 mm^{-1}
F(000)	2032	2032
R(int)	0.0761	0.0499
Completeness (to ϑ = 25.00°)	0.996	0.997
$R1$ (observed data $I > 2\sigma(I)$)	0.0635	0.0411
$wR2$ (all data)	0.1109	0.0608
Reflections (independent)	5838 (3036)	6019 (3044)
Flack parameter	0.01(2)	-0.006(14)

	VT 210 K	VT 220 K
ONO conversion level	31 %	0 %
Temperature	210(2) K	220(2) K
Wavelength	0.71073 Å	0.71073 Å
Empirical formula	C15 H12 N3 O7 Re1	C15 H12 N3 O7 Re1
Formula Weight	532.48 g mol^{-1}	532.48 g mol^{-1}
Crystal system	Tetragonal	Tetragonal
Space group	I-4	I-4
Unit cell parameters (constrained)	a = 22.5343(9) Å	a = 22.4172(8) Å
	c = 6.6415(5) Å	c = 6.6766(5) Å
Volume	3372.5(4) $Å^3$	3355.2(3) $Å^3$
Z	8	8
Density (calculated)	2.097 g cm^{-1}	2.108 g cm^{-1}
Absorption coefficient μ	7.251 mm^{-1}	7.288 mm^{-1}
F(000)	2032	2032
R(int)	0.0485	0.0473
Completeness (to ϑ = 25.00°)	0.998	0.998
$R1$ (observed data $I > 2\sigma(I)$)	0.0416	0.0394
$wR2$ (all data)	0.0643	0.0611
Reflections (independent)	6021 (3049)	6018 (3044)
Flack parameter	-0.021(14)	-0.019(13)

	VT 230 K	VT 250 K
ONO conversion level	0 %	0 %
Temperature	230(2) K	250(2) K
Wavelength	0.71073 Å	0.71073 Å
Empirical formula	C15 H12 N3 O7 Re1	C15 H12 N3 O7 Re1
Formula Weight	532.48 g mol^{-1}	532.48 g mol^{-1}
Crystal system	Tetragonal	Tetragonal
Space group	I-4	I-4
Unit cell parameters (constrained)	a = 22.3673(5) Å	a = 22.3700(6) Å
	c = 6.6855(2) Å	c = 6.6942(3) Å
Volume	3344.73(18) $Å^3$	3349.9(2) $Å^3$
Z	8	8
Density (calculated)	2.115 g cm^{-1}	2.112 g cm^{-1}
Absorption coefficient μ	7.311 mm^{-1}	7.300 mm^{-1}
F(000)	2032	2032
R(int)	0.0383	0.0388
Completeness (to ϑ = 25.00°)	0.994	0.994
$R1$ (observed data $I > 2\sigma(I)$)	0.0376	0.0388
$wR2$ (all data)	0.0808	0.0776
Reflections (independent)	6911 (2995)	6895 (2998)
Flack parameter	-0.034(11)	-0.035(11)

Table S5: C-H…O distances for the MS structure of 1 at 150 K.

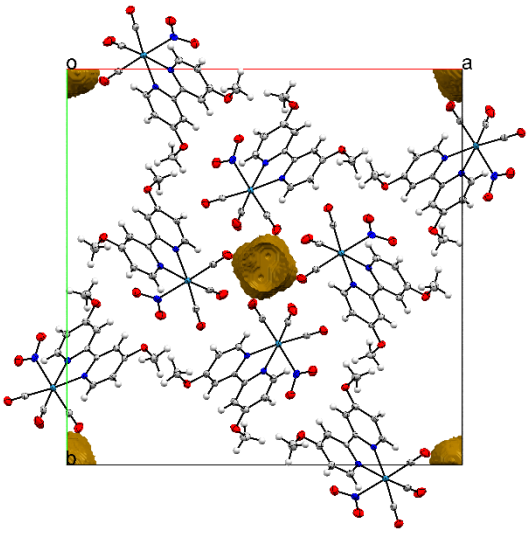
Identifier	D…A Distance / Å	D…H distance† / Å	DHA angle† / °
C(4)-H(4)…O(2A)	3.87(2)	3.00	158.0
C(15)-H(15C)…O(2A)	3.26(3)	2.33	153.0
Average value	3.57(4)	2.67	155.5

†D…H distances and DHA angles have no esd as all hydrogens were refined to fixed distances using a riding model (AFIX instruction)

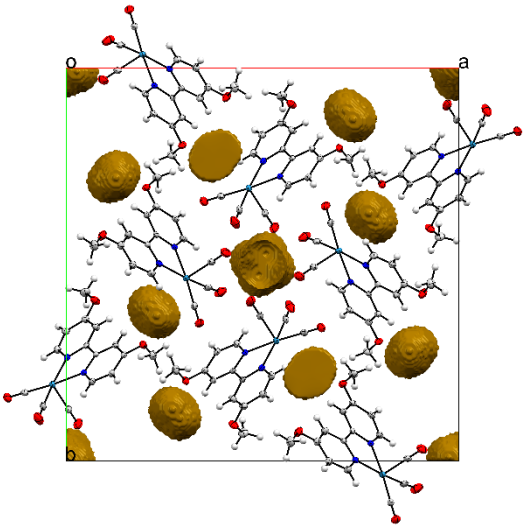
4. Reaction cavity analysis

Figure S6: Mercury[2] void space diagrams showing the shape of the reactions cavity for the GS and MS of 1 at 150 K. (a) Initial void space diagram for the GS unit cell (no reaction cavity), (b) void space diagram including the reaction cavities around the photoactive nitrite ligand, (c) initial void space diagram for the MS unit cell (no reaction cavity), (d) void space diagram including the reaction cavities around the photoactive nitrite ligand.

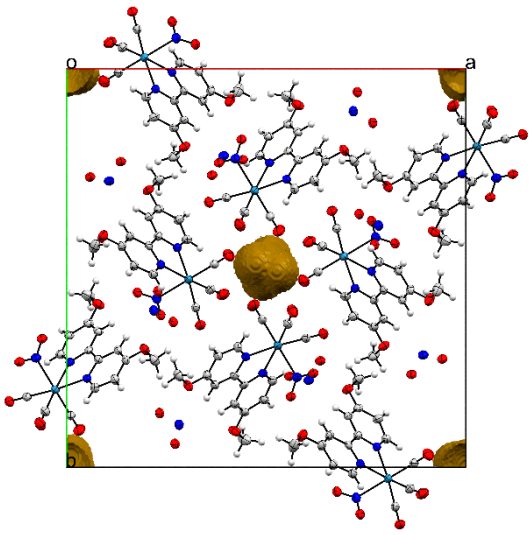
(a)



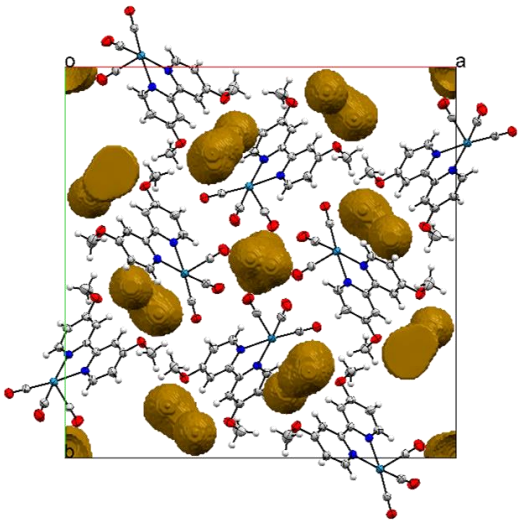
(b)



(c)



(d)



5. Steady-state photocrystallographic data for 1 at 170 K

Table S6: Single crystal X-ray data for 1 at 170 K. Selected crystal data for the ground state (GS) and the metastable state (MS) at 170 K

	Ground State (GS)	Metastable State (MS)
Photoconversion	0 %	66 %
Irradiation time (total)	0 min	180 min
Temperature	170(2) K	170(2) K
Wavelength	0.71073 Å	0.71073 Å
Empirical formula	C15 H12 N3 O7 Re1	C15 H12 N3 O7 Re1
Formula Weight	532.48 g mol-1	532.48 g mol-1
Crystal system	Tetragonal	Tetragonal
Space group	I-4	I-4
Unit cell parameters (constrained)	a = 22.3068(3) Å	a = 22.6722(6) Å
	c = 6.6532(2) Å	c = 6.5648(3) Å
Volume	3310.6(2) $Å^3$	3374.5(2) $Å^3$
Z	8	8
Density (calculated)	2.137 g cm^{-1}	2.096 g cm^{-1}
Absorption coefficient μ	7.386 mm^{-1}	7.246 mm^{-1}
F(000)	2032	2032
R(int)	0.0456	0. 0536
Completeness (to θ = 25.00°)	0.998	0.998
R1 (observed data I > 2σ(I))	0.0283	0.0453
wR2 (all data)	0.0448	0.1121
Reflections (independent)	10308 (3365)	8014 (3440)
Flack parameter	-0.028(9)	-0.010(11)

6. Supplementary structure data for pseudo-steady-state studies

Table S7: Nitro:nitrito isomer occupancy ratios refined from single-crystal X-ray data during all pseudo-steady-state photocrystallographic studies with **1** at 150 K, as a function of temperature

Temp / K	Nitrite occupancy level	
	Nitro-NO_2	Nitrito-ONO
150	0.41	0.59
175	0.34	0.66
200	0.36	0.64
210	0.40	0.60
220	0.62	0.38
230	0.74	0.26
240	1.00	0.00
250	1.00	0.00

Table S8: Reaction cavity (V_c) analysis for the pseudo-steady-state structures of 1 at 150 and 175 K. V_c determined by removing the nitrite group and performing a contact surface void space calculation in Mercury[2] (probe radius 1.2 Å, grid spacing 0.1 Å) and subtracting the initial void volume

	V_c per unit cell / Å^3	V_c per molecule / Å^3	ΔV_c (MS-GS) / Å^3	ΔV_c (MS-GS) / %
PSS 150 K	192.38	24.05	-1.02	-0.5
PSS 170 K	191.36	23.92		

Table S9: Single crystal X-ray data for pseudo-steady-state studies with 1 at 200 – 250 K

	PSS 200 K	PSS 210K
Photoconversion	64 %	60 %
Temperature	200(2) K	210(2) K
Wavelength	0.71073 Å	0.71073 Å
Empirical formula	C15 H12 N3 O7 Re1	C15 H12 N3 O7 Re1
Formula Weight	532.48 g mol^{-1}	532.48 g mol^{-1}
Crystal system	Tetragonal	Tetragonal
Space group	I-4	I-4
Unit cell parameters (constrained)	a = 22.738(2) Å	a = 22.7012(19) Å
	c = 6.5434(9) Å	c = 6.5603(9) Å
Volume	3383.0(8) $Å^3$	3380.8(7) $Å^3$
Z	8	8
Density (calculated)	2.091 g cm^{-1}	2.092 g cm^{-1}
Absorption coefficient μ	7.228 mm^{-1}	7.233 mm^{-1}
F(000)	2032	2032
R(int)	0.0804	0.0995
Completeness (to ϑ = 25.00°)	0.997	0.996
R1 (observed data $I > 2\sigma$(I))	0.0774	0.0957
wR2 (all data)	0.1663	0.2319
Reflections (independent)	5957 (2899)	5229 (2958)
Flack parameter	-0.04(4)	-0.048(11)

	PSS 220 K	PSS 230K
Photoconversion	38 %	26 %
Temperature	220(2) K	230(2) K
Wavelength	0.71073 Å	0.71073 Å
Empirical formula	C15 H12 N3 O7 Re1	C15 H12 N3 O7 Re1
Formula Weight	532.48 g mol^{-1}	532.48 g mol^{-1}
Crystal system	Tetragonal	Tetragonal
Space group	I-4	I-4
Unit cell parameters (constrained)	a = 22.543(2) Å	a = 22.581(2) Å
	c = 6.625(1) Å	c = 6.665(1) Å
Volume	3366.7(9) $Å^3$	3398.3(10) $Å^3$
Z	8	8
Density (calculated)	2.101 g cm^{-1}	2.081 g cm^{-1}
Absorption coefficient μ	7.263 mm^{-1}	7.196 mm^{-1}
F(000)	2032	2032
R(int)	0.1366	0.1444
Completeness (to ϑ = 23.21°)	0.998	0.998
R1 (observed data $I > 2\sigma(I)$)	0.1062	0.0934
wR2 (all data)	0.2401	0.2233
Reflections (independent)	6256 (2412)	6266 (2430)
Flack parameter	0.00(6)	-0.04(5)

	PSS 240 K	PSS 250K
Photoconversion	0 %	0 %
Temperature	240(2) K	240(2) K
Wavelength	0.71073 Å	0.71073 Å
Empirical formula	C15 H12 N3 O7 Re1	C15 H12 N3 O7 Re1
Formula Weight	532.48 g mol^{-1}	532.48 g mol^{-1}
Crystal system	Tetragonal	Tetragonal
Space group	I-4	I-4
Unit cell parameters (constrained)	a = 22.393(2) Å	a = 22.358(2) Å
	c = 6.657(1) Å	c = 6.674(1) Å
Volume	3338.0(8) $Å^3$	3336.1(9) $Å^3$
Z	8	8
Density (calculated)	2.119 g cm^{-1}	2.120 g cm^{-1}
Absorption coefficient μ	7.326 mm^{-1}	7.330 mm^{-1}
F(000)	2032	2032
R(int)	0.1261	0.1043
Completeness (to ϑ = 23.21°)	0.997	0.996
*R*1 (observed data $I > 2\sigma(I)$)	0.0883	0.0786
*wR*2 (all data)	0.1896	0.1811
Reflections (independent)	6200 (2377)	6308 (2386)
Flack parameter	-0.05(4)	0.02(3)

7. References

1. M. P. Fuller and P. R. Griffiths, *Analytical Chemistry*, 1978, **50**, 1906-1910.
2. C. F. Macrae, I. J. Bruno, J. A. Chisholm, P. R. Edgington, P. McCabe, E. Pidcock, L. Rodriguez-Monge, R. Taylor, J. v. d. Streek and P. A. Wood, *Journal of Applied Crystallography*, 2008, **41**, 466-470.