Electronic Supplementary Information (ESI) – Table of Contents

A non-linear phenomenon observed in the photochromic crystals of a rhodium dithionite complex with *n*-propyl moieties

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Experimental details

General: The rhodium dithionite complex $\mathbf{1}^{Pro}$ was synthesized according to the method described in our previous paper.[1] The crystals were irradiated using a xenon-lamp (Asahi Spectra, Max-301: 300 W, 385-740 nm). The crystals were uniformly heated using a Leica 350 microscope heating stage.

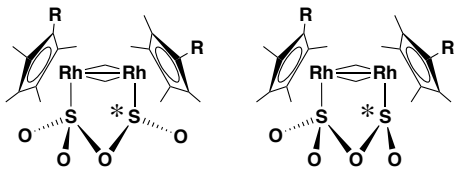
X-ray crystallography: All measurements were made on a Rigaku XtaLAB P200 diffractometer with confocal monochromated Mo Kα radiation (λ = 0.71070 Å). Data were collected and processed using CrysAlisPro[2] software (Rigaku). The data were corrected for Lorentz and polarisation effects. An emperical absorption corrections were applied. The structures were solved by a direct method: SHELXT (Ver. 2014/5)[3] and expanded using a Fourier technique. All calculations were performed using the CrystalStructure[4] crystallographic software package except for refinement, which was performed using SHELXL (Ver. 2014/6)[5]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model.

Samples 2, 13 and 22a–c: two oxygen atoms (O5 and O6) were refined isotropically.

Samples 3, 6, 7 and 10: one oxygen atom (O5 or O6) was refined isotropically.

The occupancy factors of the oxygen atoms of samples 2–10, 13–19 and 22 were fixed by the following treatments (the thermal parameters were refined without any restrictions):

(1) The experimental occupancy factors of O1–O6 were obtained by refinement without any restrictions: the sums of the occupancy factors (O1 + O3 + O5 and O2 + O4 + O6) were 2.0±0.1. Since no *cis*-isomer is present in our photochromic system,[6] ideal sum of the occupancy factors are 2.0000.



$\mathbf{2}^{R}$ (*trans*-isomer) $\mathbf{2}^{R}$ (*cis*-isomer)

(2) In order to fit the experimental values to the ideal value, the experimental occupancy factors were multiplied by factors.

(3) If the calculated occupancy factor was more than 1.0000, the occupancy factor was fixed as 1.0000. The rests of the occupancy factors were treated with the same way.

Crystallographic data has been deposited with the Cambridge Crystallographic Data Centre (CCDC). CCDC reference numbers: 1953611 (Sample 1), 1953612 (Sample 2), 1953613 (Sample 3), 1953614 (Sample 4), 1953615 (Sample 5), 1953616 (Sample 6), 1953854 (Sample 7), 1953855 (Sample 8), 1953856 (Sample 9), 1953857 (Sample 10), 1953858 (Sample 11), 1953859 (Sample 12), 1953860 (Sample 13), 1953861 (Sample 14), 1953862 (Sample 15), 1953863 (Sample 16), 1953864 (Sample 17), 1953865 (Sample 18), 1953866 (Sample 19), 1953867 (Sample 20), 1953868 (Sample 21a), 1953869 (Sample 21b), 1953870 (Sample 21c), 1953871 (Sample 22a), 1953872 (Sample 22b), 1953873 (Sample 22c).

References

1 H. Nakai, M. Hatake, Y. Miyano and K. Isobe, *Chem. Commun.*, 2009, 2685.

2 *CrysAlisPro*: Data collection and Processing Software, Rigaku Corporation (2015). Tokyo 196-8666, Japan.

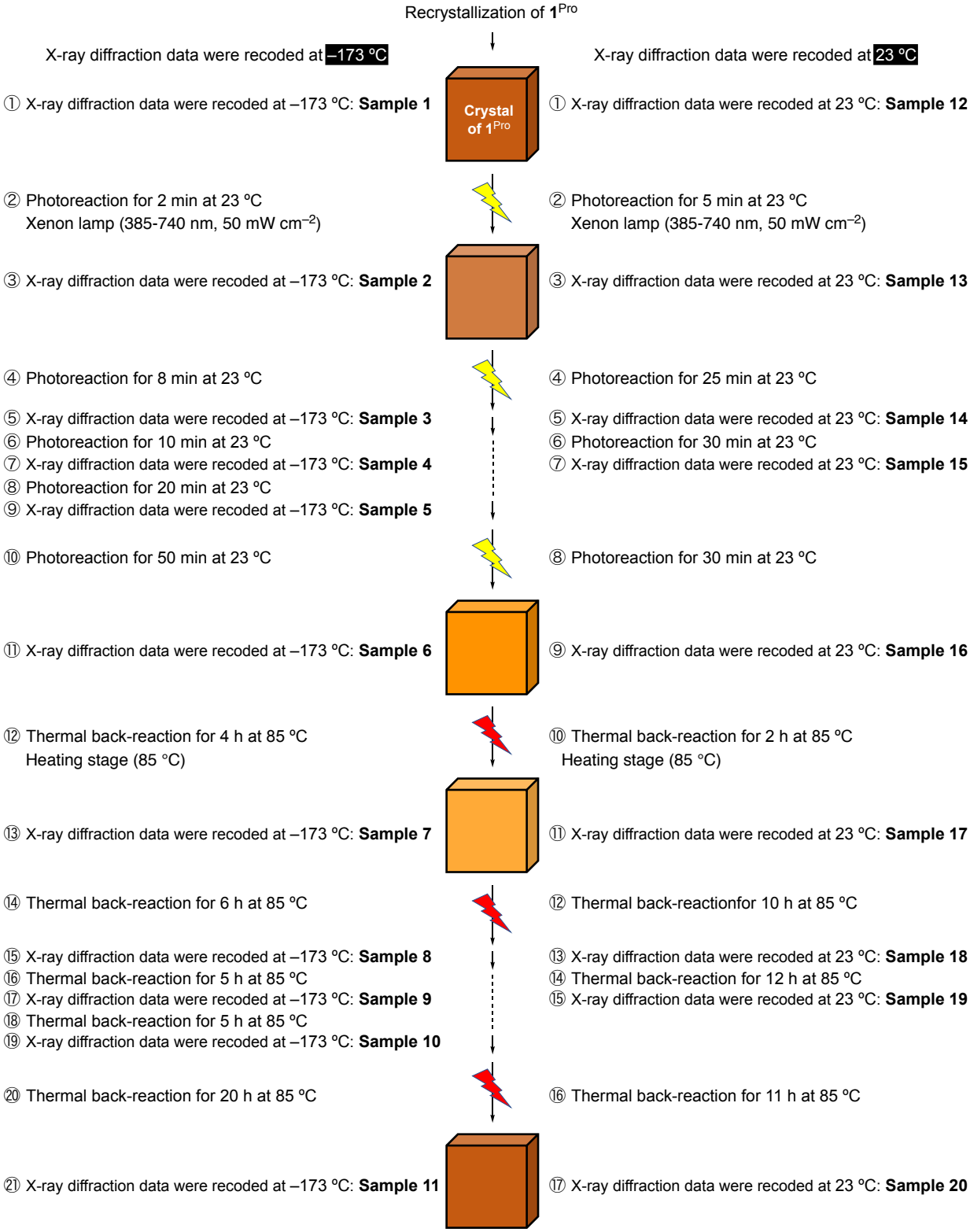
3 G. M. Sheldrick, *Acta Cryst.*, 2014, **A70**, C1437.

4 *CrystalStructure 4.2.2*: Crystal Structure Analysis Package, Rigaku Corporation (2000-2016). Tokyo 196-8666, Japan.

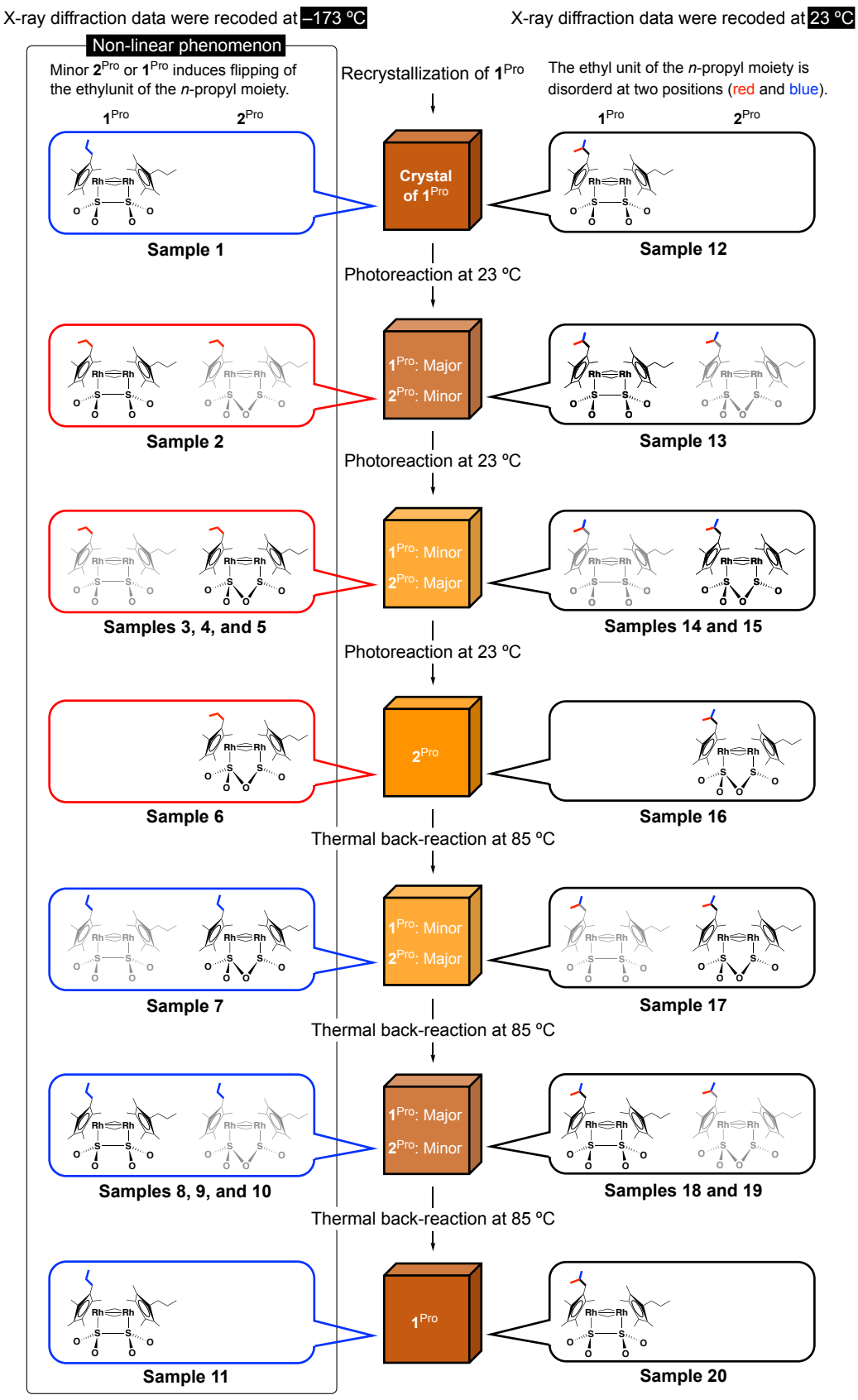
5 G. M. Sheldrick, *Acta Cryst.*, 2008, **A64**, 112.

6 H. Nakai, T. Nonaka, Y. Miyano, M. Mizuno, Y. Ozawa, K. Toriumi, N. Koga, T. Nishioka, M. Irie and K. Isobe, *J. Am. Chem. Soc.*, 2008, **130**, 17836.

Schemes



Scheme S1 Time-dependent X-ray diffraction experiments of the photochromic crystal of **1**^{Pro}.



Scheme S2 Results of the time-dependent X-ray diffraction experiments of the photochromic crystal of **1**^{Pro}.

Tables

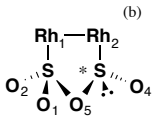
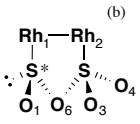
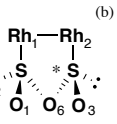
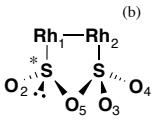
Table S1 Experimental conditions and crystallographic data for samples 1–6

	Sample 1 $\mathbf{1}^{Pro}$	Sample 2 $\mathbf{1}^{Pro}$: $\mathbf{2}^{Pro}$ = 87 : 13	Sample 3 $\mathbf{1}^{Pro}$: $\mathbf{2}^{Pro}$ = 49 : 51	Sample 4 $\mathbf{1}^{Pro}$: $\mathbf{2}^{Pro}$ = 21 : 79	Sample 5 $\mathbf{1}^{Pro}$: $\mathbf{2}^{Pro}$ = 11 : 89	Sample 6 $\mathbf{1}^{Pro}$: $\mathbf{2}^{Pro}$ = 4 : 96
Photoirradiation time (min)	0	2	10	20	40	90
Photoirradiation temperature (ºC)	23	23	23	23	23	23
Data collection temperature (ºC)	–173	–173	–173	–173	–173	–173
Formula	$C_{26}H_{42}S_2O_4Rh_2$	$C_{26}H_{42}S_2O_4Rh_2$	$C_{26}H_{42}S_2O_4Rh_2$	$C_{26}H_{42}S_2O_4Rh_2$	$C_{26}H_{42}S_2O_4Rh_2$	$C_{26}H_{42}S_2O_4Rh_2$
Fw	688.55	688.55	688.55	688.55	688.55	688.55
Crystal system	orthorhombic	orthorhombic	orthorhombic	orthorhombic	orthorhombic	orthorhombic
Space group	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$
a (Å)	8.9949(3)	9.1016(2)	9.1501(2)	9.1902(3)	9.1982(3)	9.2119(3)
b (Å)	13.4322(3)	13.7210(2)	13.7683(3)	13.7947(4)	13.8073(4)	13.8148(4)
c (Å)	22.2195(5)	21.3715(5)	21.2469(6)	21.1368(6)	21.0754(7)	21.0387(7)
α (deg)	90	90	90	90	90	90
β (deg)	90	90	90	90	90	90
γ (deg)	90	90	90	90	90	90
V (Å^3)	2684.59(12)	2668.94(9)	2676.71(11)	2679.64(14)	2676.62(15)	2677.40(15)
Z	4	4	4	4	4	4
μ (cm^{-1})	14.13	14.21	14.17	14.15	14.17	14.16
F(000)	1408	1408	1408	1408	1408	1408
D_{calcd}(g/cm^3)	1.703	1.713	1.708	1.707	1.709	1.708
Reflections	23105	32145	32024	29352	33928	35348
Independent	7775	8059	8174	8103	8176	8140
	(R_{int} = 0.0270)	(R_{int} = 0.0293)	(R_{int} = 0.0332)	(R_{int} = 0.0396)	(R_{int} = 0.0494)	(R_{int} = 0.0503)
Data/parameters	7775/307	8059/315	8174/320	8103/325	8176/325	8139/320
R_1 [$I > 2\sigma(I)$]	0.018	0.0219	0.0311	0.0312	0.0340	0.0392
wR_2 (all data)	0.0415	0.0488	0.0666	0.0669	0.0768	0.0842
Goodness-of-fit	1.061	1.099	1.127	1.085	1.066	1.073
Flack parameter	-0.007(11)	-0.024(10)	-0.015(14)	-0.007(14)	-0.044(16)	-0.04(5)

Table S2 Experimental conditions and crystallographic data for samples 7–11

	Sample 7 $\mathbf{1}^{Pro}$: $\mathbf{2}^{Pro}$ = 26 : 74	Sample 8 $\mathbf{1}^{Pro}$: $\mathbf{2}^{Pro}$ = 64 : 36	Sample 9 $\mathbf{1}^{Pro}$: $\mathbf{2}^{Pro}$ = 78 : 22	Sample 10 $\mathbf{1}^{Pro}$: $\mathbf{2}^{Pro}$ = 87 : 13	Sample 11 $\mathbf{1}^{Pro}$
Heating time (h)	4	10	15	20	40
Heating temperature (ºC)	85	85	85	85	85
Data collection temperature (ºC)	–173	–173	–173	–173	–173
Formula	$C_{26}H_{42}S_2O_4Rh_2$	$C_{26}H_{42}S_2O_4Rh_2$	$C_{26}H_{42}S_2O_4Rh_2$	$C_{26}H_{42}S_2O_4Rh_2$	$C_{26}H_{42}S_2O_4Rh_2$
Fw	688.55	688.55	688.55	688.55	688.55
Crystal system	orthorhombic	orthorhombic	orthorhombic	orthorhombic	orthorhombic
Space group	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$
a (Å)	9.0828(3)	9.0371(2)	9.0217(3)	9.0125(2)	9.0023(3)
b (Å)	13.5665(6)	13.4875(3)	13.4571(4)	13.4564(4)	13.4423(4)
c (Å)	21.9449(7)	22.1334(6)	22.1670(7)	22.2004(6)	22.2172(6)
α (deg)	90	90	90	90	90
β (deg)	90	90	90	90	90
γ (deg)	90	90	90	90	90
V (Å^3)	2704.09(17)	2697.79(11)	2691.21(15)	2692.37(12)	2688.54(14)
Z	4	4	4	4	4
μ (cm^{-1})	14.02	14.06	14.09	14.08	14.10
F(000)	1408	1408	1408	1408	1408
D_{calcd}(g/cm^3)	1.691	1.695	1.699	1.699	1.701
Reflections	35285	33323	35906	34409	33966
Independent	8244	8241	8253	8152	8257
	(R_{int} = 0.0506)	(R_{int} = 0.0331)	(R_{int} = 0.0416)	(R_{int} = 0.0336)	(R_{int} = 0.0438)
Data/parameters	8244/320	8240/316	1	8152/321	8257/307
R_1 [$I > 2\sigma(I)$]	0.0425	0.0293	0.0326	0.0269	0.0317
wR_2 (all data)	0.0944	0.0597	0.0663	0.0591	0.0664
Goodness-of-fit	1.088	1.117	1.083	1.085	1.100
Flack parameter	-0.02(2)	-0.029(12)	-0.014(15)	-0.044(13)	-0.046(16)

Table S3 Percentage populations of the isomers, $\mathbf{1}^{Pro}$, $\mathbf{2a}^{Pro}$, $\mathbf{2b}^{Pro}$, $\mathbf{2c}^{Pro}$ and $\mathbf{2d}^{Pro}$ in the crystals of samples 1–11 (samples 1–6 for the photoisomerization, samples 7–11 for the thermal back-reaction).[(a)] X-ray diffraction data were recorded at –173 ºC

	$\mathbf{1}^{Pro}$	$\mathbf{2}^{Pro}$ (total)	 (b) $\mathbf{2a}^{Pro}$ (R)	 (b) $\mathbf{2b}^{Pro}$ (R)	 (b) $\mathbf{2c}^{Pro}$ (S)	 (b) $\mathbf{2d}^{Pro}$ (S)
Sample 1	100	0	0	0	0	0
Sample 2	87	13	5	8	0	0
Sample 3	49	51	15	35	0	1
Sample 4	21	79	23	54	0	2
Sample 5	11	89	24	63	0	2
Sample 6	4	96	23	67	2	4
Sample 7	26	74	12	61	0	1
Sample 8	64	36	0	36	0	0
Sample 9	78	22	0	22	0	0
Sample 10	87	13	0	13	0	0
Sample 11	100	0	0	0	0	0

(a) All the data have ±2% errors based on the errors of the experimental occupancy factors of the oxygen atoms.

(b) The four stereoisomers, $\mathbf{2a}^{Pro}$–$\mathbf{2d}^{Pro}$, concerned with the μ-O_2SOSO unit. The Cp^{Pro} and μ-CH_2 ligands are omitted for clarity. The absolute configurations of the sulfur atoms are shown in parentheses.

The values of % for stereoisomers $\mathbf{2a}^{Pro}$–$\mathbf{2d}^{Pro}$ were calculated from the simultaneous equations based on the occupancy of the oxygen atoms determined by X-ray diffraction analysis. In the case of sample 6, the equations were as follows:

$$0.9606 \text{ (occupancy of } O_1) = \mathbf{2a}^{Pro} + \mathbf{2b}^{Pro} + \mathbf{2c}^{Pro} + \mathbf{1}^{Pro}$$

$$0.3325 \text{ (occupancy of } O_2) = \mathbf{2a}^{Pro} + \mathbf{2c}^{Pro} + \mathbf{2d}^{Pro} + \mathbf{1}^{Pro}$$

$$0.7677 \text{ (occupancy of } O_3) = \mathbf{2b}^{Pro} + \mathbf{2c}^{Pro} + \mathbf{2d}^{Pro} + \mathbf{1}^{Pro}$$

$$0.9832 \text{ (occupancy of } O_4) = \mathbf{2a}^{Pro} + \mathbf{2b}^{Pro} + \mathbf{2d}^{Pro} + \mathbf{1}^{Pro}$$

$$0.2717 \text{ (occupancy of } O_5) = \mathbf{2a}^{Pro} + \mathbf{2d}^{Pro}$$

$$0.6430 \text{ (occupancy of } O_6) = \mathbf{2b}^{Pro} + \mathbf{2c}^{Pro}$$

$$\mathbf{2a}^{Pro} = 0.2323,\ \mathbf{2b}^{Pro} = 0.6675,\ \mathbf{2c}^{Pro} = 0.0168,\ \mathbf{2d}^{Pro} = 0.0394,\ \mathbf{1}^{Pro} = 0.0440.$$

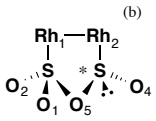
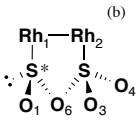
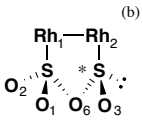
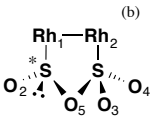
Table S4 Experimental conditions and crystallographic data for samples 12–16

	Sample 12 $\mathbf{1}^{Pro}$	Sample 13 $\mathbf{1}^{Pro}$: $\mathbf{2}^{Pro}$ = 74 : 26	Sample 14 $\mathbf{1}^{Pro}$: $\mathbf{2}^{Pro}$ = 10 : 90	Sample 15 $\mathbf{1}^{Pro}$: $\mathbf{2}^{Pro}$ = 5 : 95	Sample 16 $\mathbf{1}^{Pro}$: $\mathbf{2}^{Pro}$ = 4 : 96
Photoirradiation time (min)	0	5	30	60	90
Photoirradiation temperature (ºC)	23	23	23	23	23
Data collection temperature (ºC)	23	23	23	23	23
Formula	$C_{26}H_{42}S_2O_4Rh_2$	$C_{26}H_{42}S_2O_4Rh_2$	$C_{26}H_{42}S_2O_4Rh_2$	$C_{26}H_{42}S_2O_4Rh_2$	$C_{26}H_{42}S_2O_4Rh_2$
Fw	688.55	688.55	688.55	688.55	688.55
Crystal system	orthorhombic	orthorhombic	orthorhombic	orthorhombic	orthorhombic
Space group	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$
a (Å)	9.1085(2)	9.1411(2)	9.1896(2)	9.1909(2)	9.1889(2)
b (Å)	13.6961(4)	13.7205(4)	13.7710(5)	13.7781(5)	13.7799(5)
c (Å)	22.0657(6)	22.0086(7)	21.9398(7)	21.9247(8)	21.9332(8)
α (deg)	90	90	90	90	90
β (deg)	90	90	90	90	90
γ (deg)	90	90	90	90	90
V (Å^3)	2752.72(13)	2760.33(13)	2776.48(15)	2776.39(16)	2777.23(16)
Z	4	4	4	4	4
μ (cm^{-1})	13.78	13.74	13.66	13.66	13.65
F(000)	1408	1408	1408	1408	1408
D_{calcd}(g/cm^3)	1.661	1.657	1.647	1.647	1.647
Reflections	35955	35137	33831	33844	33423
Independent	8264	8254	8204	8234	8220
	(R_{int} = 0.0360)	(R_{int} = 0.0384)	(R_{int} = 0.0414)	(R_{int} = 0.0407)	(R_{int} = 0.0409)
Data/parameters	8263/337	8252/345	8204/355	8234/355	8220/355
R_1 [$I > 2\sigma(I)$]	0.0214	0.0333	0.0291	0.0290	0.0295
wR_2 (all data)	0.0485	0.0745	0.0635	0.0659	0.0658
Goodness-of-fit	1.075	1.176	1.065	1.049	1.063
Flack parameter	-0.004(13)	0.012(16)	-0.041(17)	-0.041(17)	-0.052(17)

Table S5 Experimental conditions and crystallographic data for samples 17–20

	Sample 17 $\mathbf{1}^{Pro}$: $\mathbf{2}^{Pro}$ = 10 : 90	Sample 18 $\mathbf{1}^{Pro}$: $\mathbf{2}^{Pro}$ = 64 : 36	Sample 19 $\mathbf{1}^{Pro}$: $\mathbf{2}^{Pro}$ = 87 : 13	Sample 20 $\mathbf{1}^{Pro}$
Heating time (h)	2	12	24	35
Heating temperature (ºC)	85	85	85	85
Data collection temperature (ºC)	23	23	23	23
Formula	$C_{26}H_{42}S_2O_4Rh_2$	$C_{26}H_{42}S_2O_4Rh_2$	$C_{26}H_{42}S_2O_4Rh_2$	$C_{26}H_{42}S_2O_4Rh_2$
Fw	688.55	688.55	688.55	688.55
Crystal system	orthorhombic	orthorhombic	orthorhombic	orthorhombic
Space group	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$
a (Å)	9.1739(3)	9.1362(3)	9.1186(2)	9.1109(3)
b (Å)	13.7586(5)	13.7345(5)	13.7072(4)	13.6934(4)
c (Å)	21.9560(8)	22.0425(6)	22.0615(7)	22.0688(8)
α (deg)	90	90	90	90
β (deg)	90	90	90	90
γ (deg)	90	90	90	90
V (Å^3)	2771.29(17)	2765.92(16)	2757.48(13)	2753.29(16)
Z	4	4	4	4
μ (cm^{-1})	13.68	13.71	13.75	13.77
F(000)	1408	1408	1408	1408
D_{calcd}(g/cm^3)	1.650	1.653	1.658	1.661
Reflections	31251	36115	30283	32774
Independent	8223	8327	8175	8218
	(R_{int} = 0.0406)	(R_{int} = 0.0424)	(R_{int} = 0.0411)	(R_{int} = 0.0509)
Data/parameters	8223/355	8326/346	8175/346	8218/337
R_1 [$I > 2\sigma(I)$]	0.0317	0.0292	0.0319	0.0282
wR_2 (all data)	0.0758	0.0797	0.0804	0.0700
Goodness-of-fit	1.047	1.052	1.069	1.078
Flack parameter	-0.07(2)	-0.025(18)	-0.016(16)	-0.029(19)

Table S6 Percentage populations of the isomers, **1**^{Pro}, **2a**^{Pro}, **2b**^{Pro}, **2c**^{Pro} and **2d**^{Pro} in the crystals of samples 12–20 (samples 12–16 for the photoisomerization, samples 17–20 for thermal back-reaction).[(a)] X-ray diffraction data were recorded at 23 ºC

	1^{Pro}	**2**^{Pro} (total)	 (b) **2a**^{Pro} (R)	 (b) **2b**^{Pro} (R)	 (b) **2c**^{Pro} (S)	 (b) **2d**^{Pro} (S)
Sample 12	100	0	0	0	0	0
Sample 13	74	26	4	19	0	3
Sample 14	10	90	24	63	2	1
Sample 15	5	95	25	69	1	0
Sample 16	4	96	25	70	1	0
Sample 17	10	90	19	68	0	3
Sample 18	64	36	0	36	0	0
Sample 19	87	13	0	13	0	0
Sample 20	100	0	0	0	0	0

(a) All the data have ±2% errors based on the errors of the experimental occupancy factors of the oxygen atoms.

(b) The four stereoisomers, **2a**^{Pro}**–2d**^{Pro}, concerned with the μ-O_2SOSO unit. The Cp^{Pro} and μ-CH_2 ligands are omitted for clarity. The absolute configurations of the sulfur atoms are shown in parentheses.

Table S7 Crystallographic data for samples 21 and 22

	Sample 21a **1**^{Pro}	Sample 21b **1**^{Pro}	Sample 21c **1**^{Pro}	Sample 22a **1**^{Pro} : **2**^{Pro} = 78 : 22	Sample 22b **1**^{Pro} : **2**^{Pro} = 77 : 23	Sample 22c **1**^{Pro} : **2**^{Pro} = 77 : 23
Data collection temperature (ºC)	23	–173	23	23	–173	23
Formula	$C_{26}H_{42}S_2O_4Rh_2$	$C_{26}H_{42}S_2O_4Rh_2$	$C_{26}H_{42}S_2O_4Rh_2$	$C_{26}H_{42}S_2O_4Rh_2$	$C_{26}H_{42}S_2O_4Rh_2$	$C_{26}H_{42}S_2O_4Rh_2$
Fw	688.55	688.55	688.55	688.55	688.55	688.55
Crystal system	orthorhombic	orthorhombic	orthorhombic	orthorhombic	orthorhombic	orthorhombic
Space group	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$
a (Å)	9.1040(3)	8.9898(3)	9.1076(4)	9.1279(4)	9.1070(3)	9.1319(4)
b (Å)	13.6965(5)	13.4342(4)	13.7017(5)	13.7226(6)	13.7339(4)	13.7198(7)
c (Å)	22.0624(8)	22.2250(7)	22.0801(8)	22.0317(10)	21.3545(6)	22.0525(14)
α (deg)	90	90	90	90	90	90
β (deg)	90	90	90	90	90	90
γ (deg)	90	90	90	90	90	90
V (Å^3)	2751.03(17)	2684.13(15)	2755.37(19)	2759.7(2)	2670.91(14)	2762.9(3)
Z	4	4	4	4	4	4
μ (cm^{-1})	13.78	14.13	13.76	13.74	14.20	13.73
F(000)	1408	1408	1408	1408	1408	1408
D_{calcd}(g/cm^3)	1.662	1.704	1.660	1.657	1.712	1.655
Reflections	23014	27738	22097	24480	24229	19706
Independent	7949	7892	8009	8099	7911	7951
	(R_{int} = 0.0341)	(R_{int} = 0.0373)	(R_{int} = 0.0328)	(R_{int} = 0.0464)	(R_{int} = 0.0442)	(R_{int} = 0.0422)
Data/parameters	7949/337	7879/317	8008/337	8099/345	7911/325	7950/345
R_1 [$I > 2\sigma(I)$]	0.0233	0.0359	0.0247	0.0383	0.0309	0.0372
wR_2 (all data)	0.0529	0.0876	0.0579	0.1024	0.0727	0.0835
Goodness-of-fit	1.033	1.163	1.040	1.039	1.049	1.072
Flack parameter	-0.003(18)	-0.005(17)	-0.026(18)	0.04(2)	-0.01(2)	0.03(3)

Figures

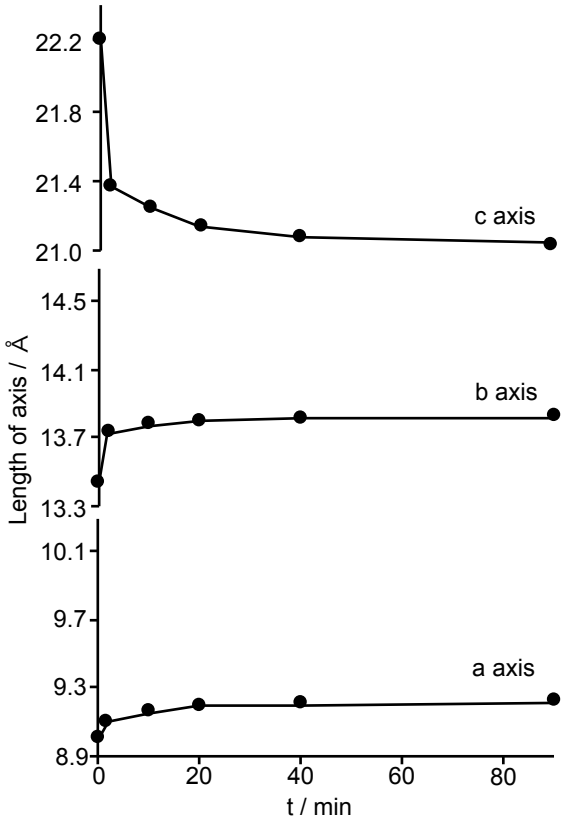


Fig. S1 Changes in the unit cell parameters (a, b, and c axes) for samples 1–6 with irradiation time (0 min data: sample 1). X-ray diffraction data were recorded at –173 ºC. Crystal size: 0.30 x 0.28 x 0.25 mm^3.

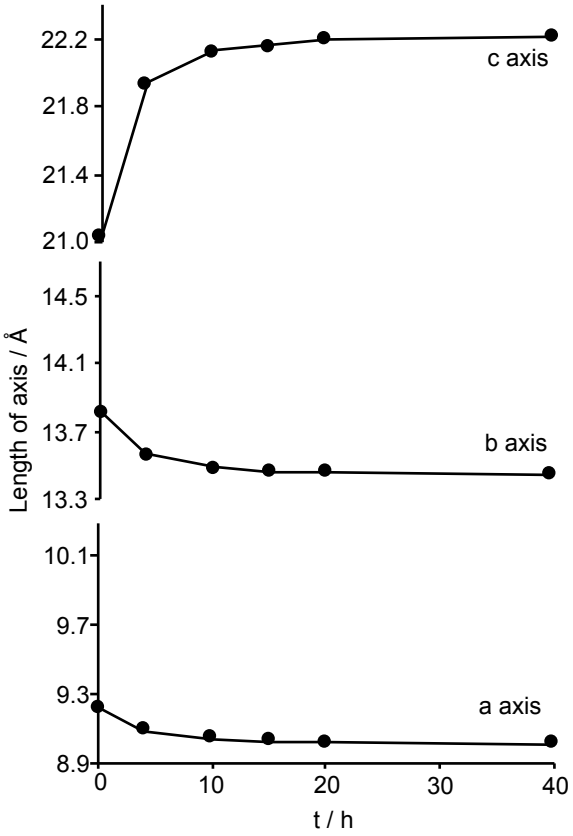


Fig. S2 Changes in the unit cell parameters (a, b, and c axes) for samples 6–11 with heating time (0 h data: sample 6). X-ray diffraction data were recorded at –173 ºC. Crystal size: 0.30 x 0.28 x 0.25 mm^3.

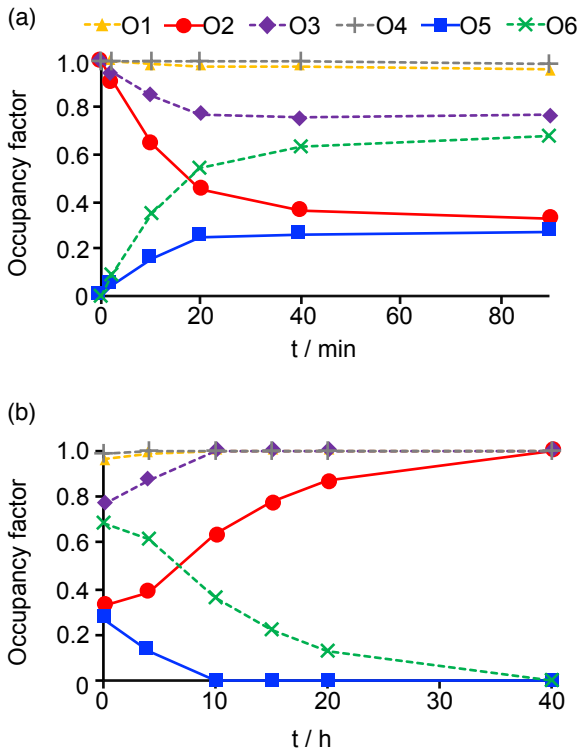


Fig. S3 Changes in the occupancy factors of the oxygen atoms O1–O6 for (a) samples 1–6 with irradiation time (0 min data: sample 1) and (b) samples 6–11 with heating time (0 h data: sample 6). X-ray diffraction data were recorded at –173 ºC. Crystal size: 0.30 x 0.28 x 0.25 mm^3.

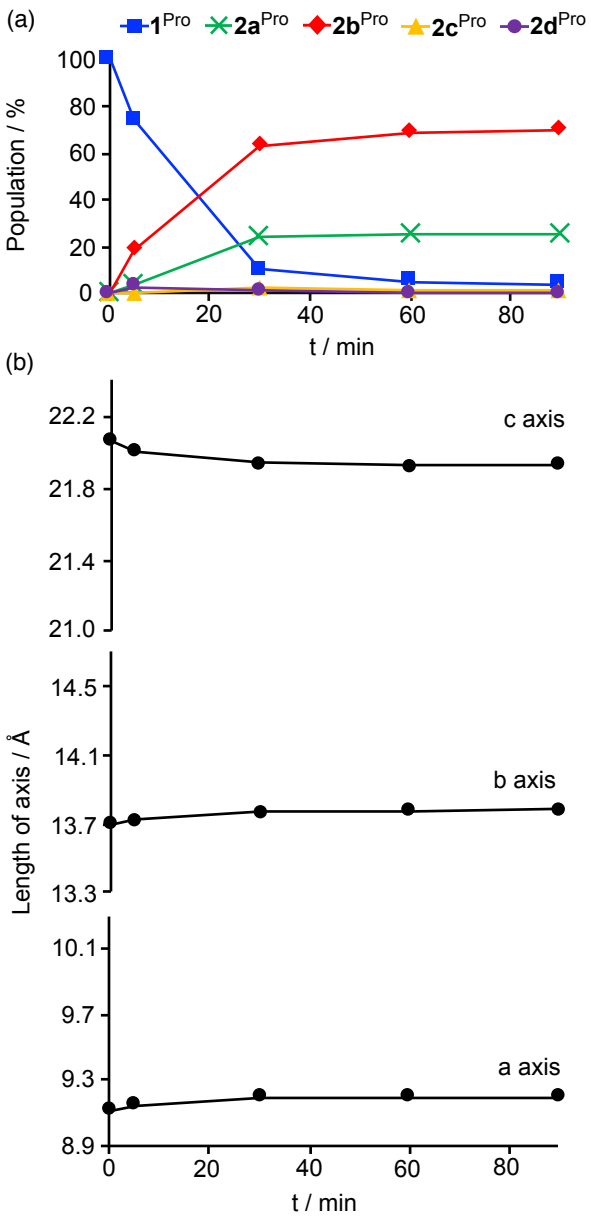


Fig. S4 (a) Changes in the populations of the photochemically generated isomers for samples 12–16 with irradiation time (0 min data: sample 12); all the plots except for 0 min data have ±2% errors based on the errors of the experimental occupancy factors of the oxygen atoms. (b) Changes in the unit cell parameters (a, b, and c axes) for samples 12–16 with irradiation time (0 min data: sample 12). X-ray diffraction data were recorded at 23 ºC. Crystal size: 0.32 x 0.28 x 0.28 mm^3.

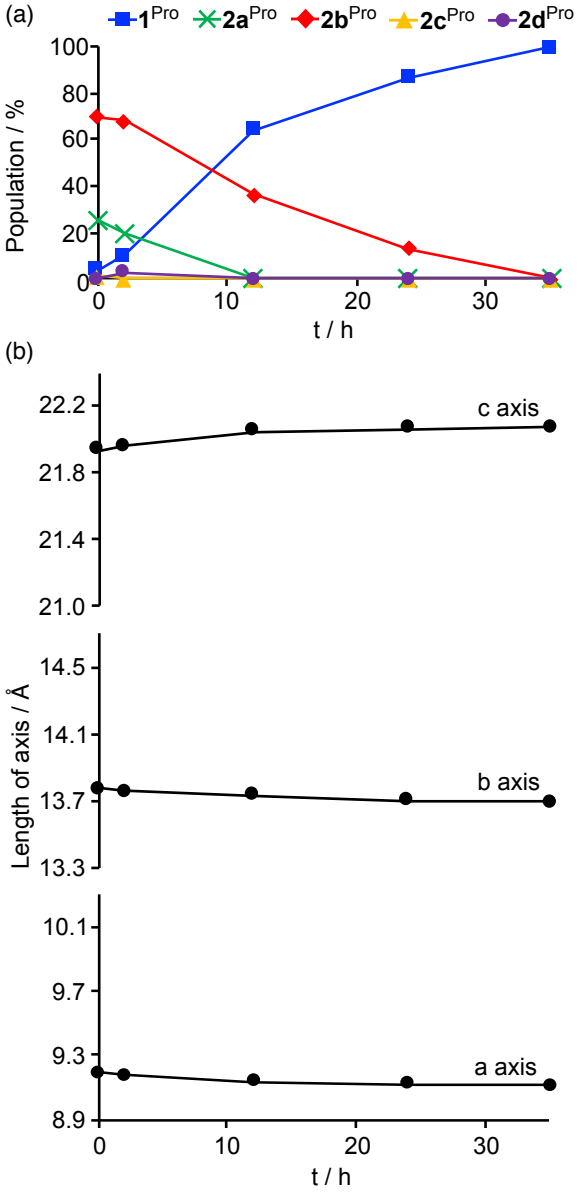


Fig. S5 (a) Changes in the populations of the thermochemically generated isomers for samples 16–20 with heating time (0 h data: sample 16); all the plots have ±2% errors based on the errors of the experimental occupancy factors of the oxygen atoms. (b) Changes in the unit cell parameters (a, b, and c axes) for samples 16–20 with heating time (0 h data: sample 16). X-ray diffraction data were recorded at 23 ºC. Crystal size: 0.32 x 0.28 x 0.28 mm^3.

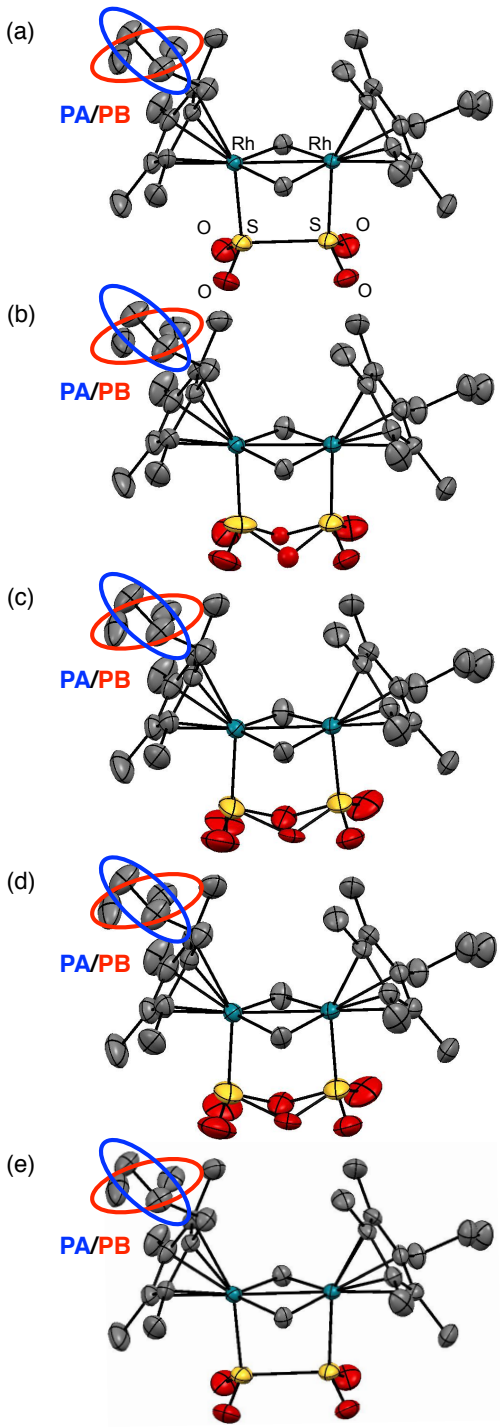


Fig. S6 ORTEP drawings of **1**^{Pro} with 50% probability ellipsoids (a) before photoirradiation (sample 12) and after (b) 5 min and (c) 90 min photoirradiation (samples 13 and 16, respectively) and after (d) 2 h and (e) 35 h heating of sample 16 (samples 17 and 20, respectively). The hydrogen atoms are omitted for clarity. All the ethyl units of the left side *n*-propyl moiety are disordered at two positions corresponding to **PA** and **PB**. X-ray diffraction data were recorded at 23 ºC. Crystal size: 0.32 x 0.28 x 0.28 mm^3.

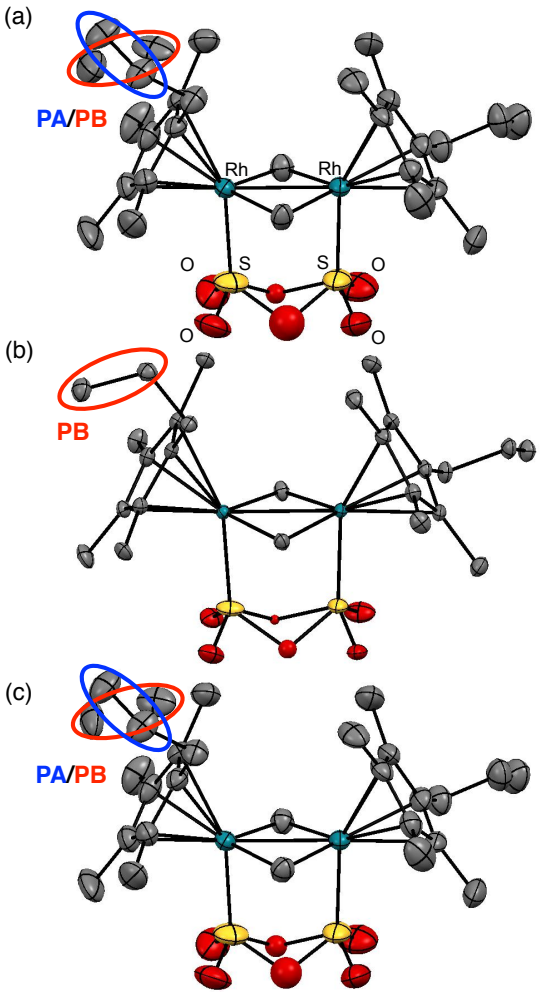


Fig. S7 ORTEP drawings of **1**^{Pro} with 50% probability ellipsoids after 4 min photoirradiation. The hydrogen atoms are omitted for clarity. X-ray diffraction data were recorded in order at (a) 23, (b) –173 and (c) 23 ºC (samples 22a, 22b and 22c, respectively). Crystal size: 0.20 x 0.20 x 0.15 mm^3. The ethyl units of the left side *n*-propyl moiety of samples 22a, 22b and 22c are disordered (**PA**/**PB**), ordered (**PB**) and disordered (**PA**/**PB**), respectively.