Electronic Supplementary Information (ESI) – Table of Contents

Crystal polymorphism and crystalline-state photochromism of a rhodium dithionite complex with *n*-methoxypropyl moieties

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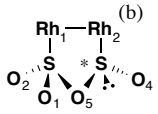
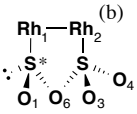
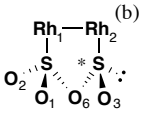
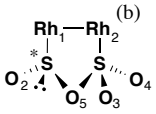
Tables

Table S1 Percentage population of the isomers, $\mathbf{1}^{MPro}$ and $\mathbf{2a}$–$\mathbf{d}^{MPro}$, in the β-crystal[(a)]

	$\mathbf{1}^{MPro}$	 (b) $\mathbf{2a}^{MPro}$ (R)	 (b) $\mathbf{2b}^{MPro}$ (R)	 (b) $\mathbf{2c}^{MPro}$ (S)	 (b) $\mathbf{2d}^{MPro}$ (S)	$\mathbf{2}^{MPro}$ (total)
Sample 1	100	0	0	0	0	0
Sample 2	35	24	41	0	0	65
Sample 3	16	31	53	0	0	84
Sample 4	5	21	74	0	0	95
Sample 5	31	14	55	0	0	69
Sample 6	79	0	21	0	0	21
Sample 7	100	0	0	0	0	0

(a) All the data, except for the data of sample 1 and 7, have ±4% errors based on the errors of the experimental occupancy factors of the oxygen atoms. Although the crystal has mirror images of $\mathbf{2a}$–$\mathbf{d}^{MPro}$, as a set, only one mirror image in the crystal is considered in this treatment (*Angew. Chem., Int. Ed.*, 2006, **45**, 6473; *J. Am. Chem. Soc.*, 2008, **130**, 17836). (b) The four stereoisomers, $\mathbf{2a}$–$\mathbf{d}^{MPro}$, concerned with the μ-O_2SOSO unit. The Cp^{MPro} 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 $\mathbf{2a}$–$\mathbf{d}^{MPro}$ 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 2, the equations were as follows:

$$1.00 \text{ (occupancy of } O_1) = \mathbf{2a}^{MPro} + \mathbf{2b}^{MPro} + \mathbf{2c}^{MPro} + \mathbf{1}^{MPro}$$

$$0.59 \text{ (occupancy of } O_2) = \mathbf{2a}^{MPro} + \mathbf{2c}^{MPro} + \mathbf{2d}^{MPro} + \mathbf{1}^{MPro}$$

$$0.76 \text{ (occupancy of } O_3) = \mathbf{2b}^{MPro} + \mathbf{2c}^{MPro} + \mathbf{2d}^{MPro} + \mathbf{1}^{MPro}$$

$$1.00 \text{ (occupancy of } O_4) = \mathbf{2a}^{MPro} + \mathbf{2b}^{MPro} + \mathbf{2d}^{MPro} + \mathbf{1}^{MPro}$$

$$0.24 \text{ (occupancy of } O_5) = \mathbf{2a}^{MPro} + \mathbf{2d}^{MPro}$$

$$0.41 \text{ (occupancy of } O_6) = \mathbf{2b}^{MPro} + \mathbf{2c}^{MPro}$$

$$\mathbf{2a}^{MPro} = 0.240,\ \mathbf{2b}^{MPro} = 0.410,\ \mathbf{2c}^{MPro} = 0.000,\ \mathbf{2d}^{MPro} = 0.000,\ \mathbf{1}^{MPro} = 0.350.$$

Figures

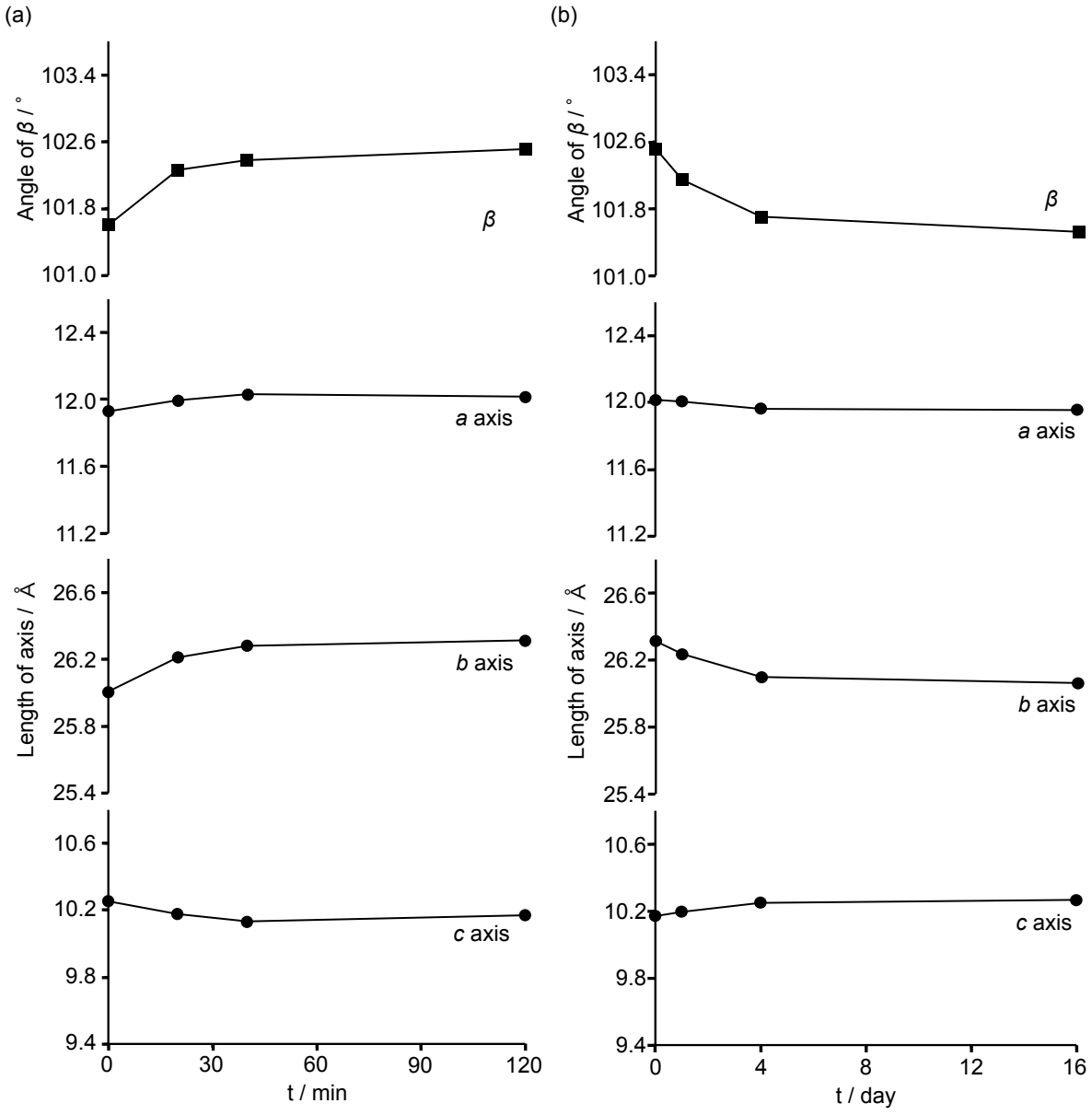


Fig. S1 (a) Changes in the unit cell parameters (β angle and a, b, and c axes) with (a) irradiation (samples 1–4, 0 min data: sample 1) and (b) heating time (samples 4–7, 0 day data: sample 4). X-ray diffraction data were recorded at 23 ºC. Crystal size: 0.25 x 0.10 x 0.05 mm^3.

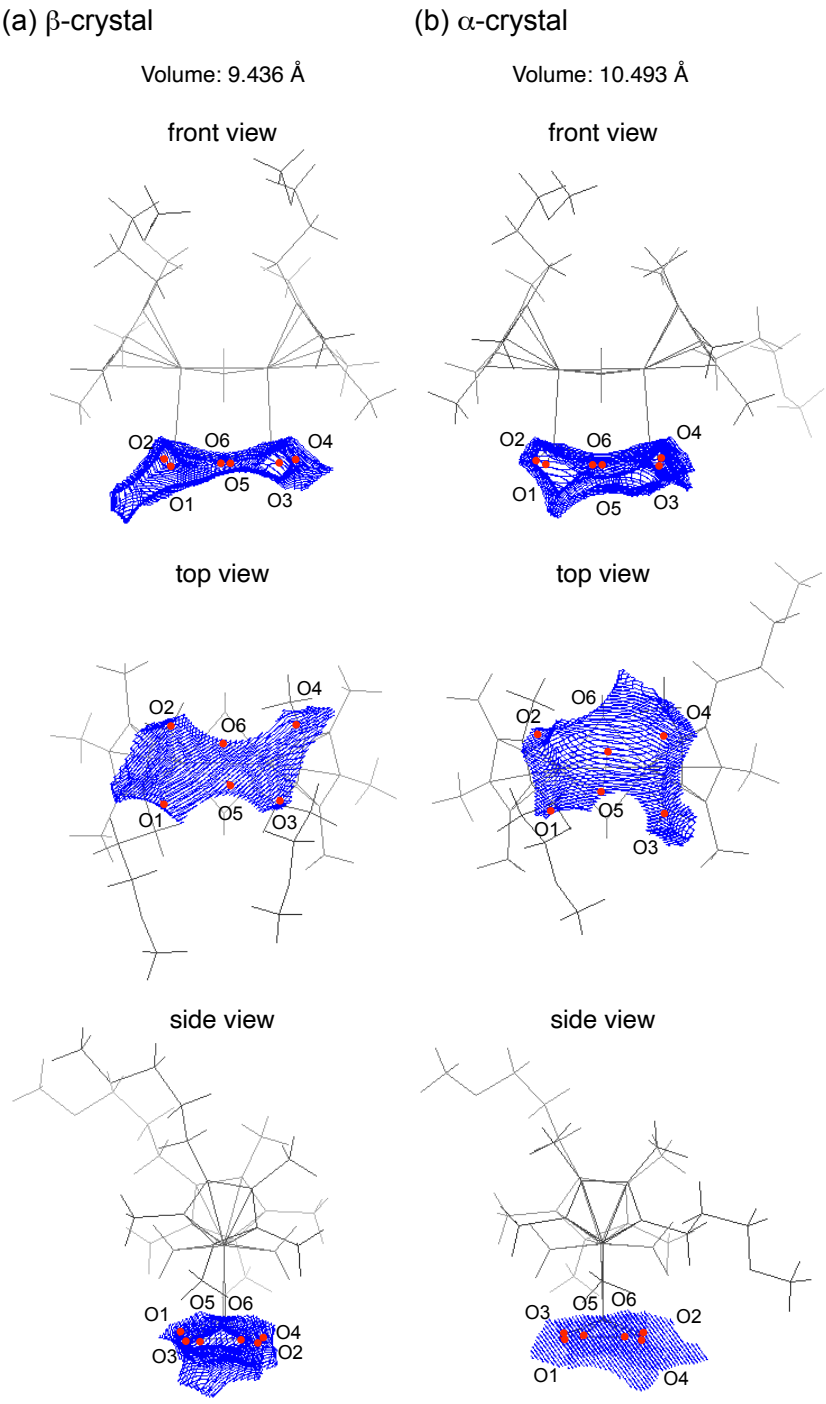


Fig. S2 Cavities (front, top and side views) in sample 4 (**2**^{MPro}) of the (a) β- and (b) α-crystals. The contours are drawn in sections separated by 0.10 Å.

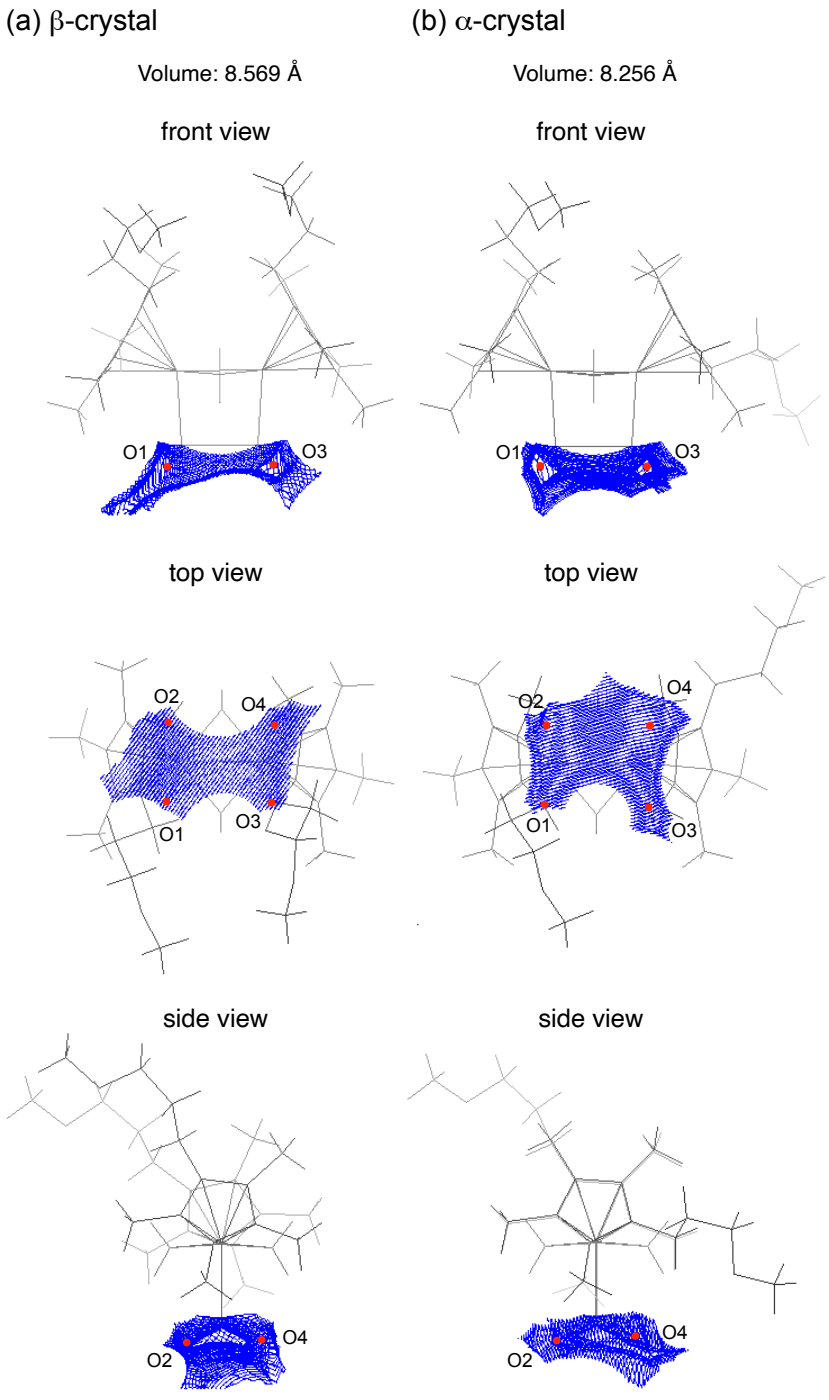


Fig. S3 Cavities (front, top and side views) in sample 1 (**1**^{MPro}) of the (a) β- and (b) α-crystals. The contours are drawn in sections separated by 0.10 Å.

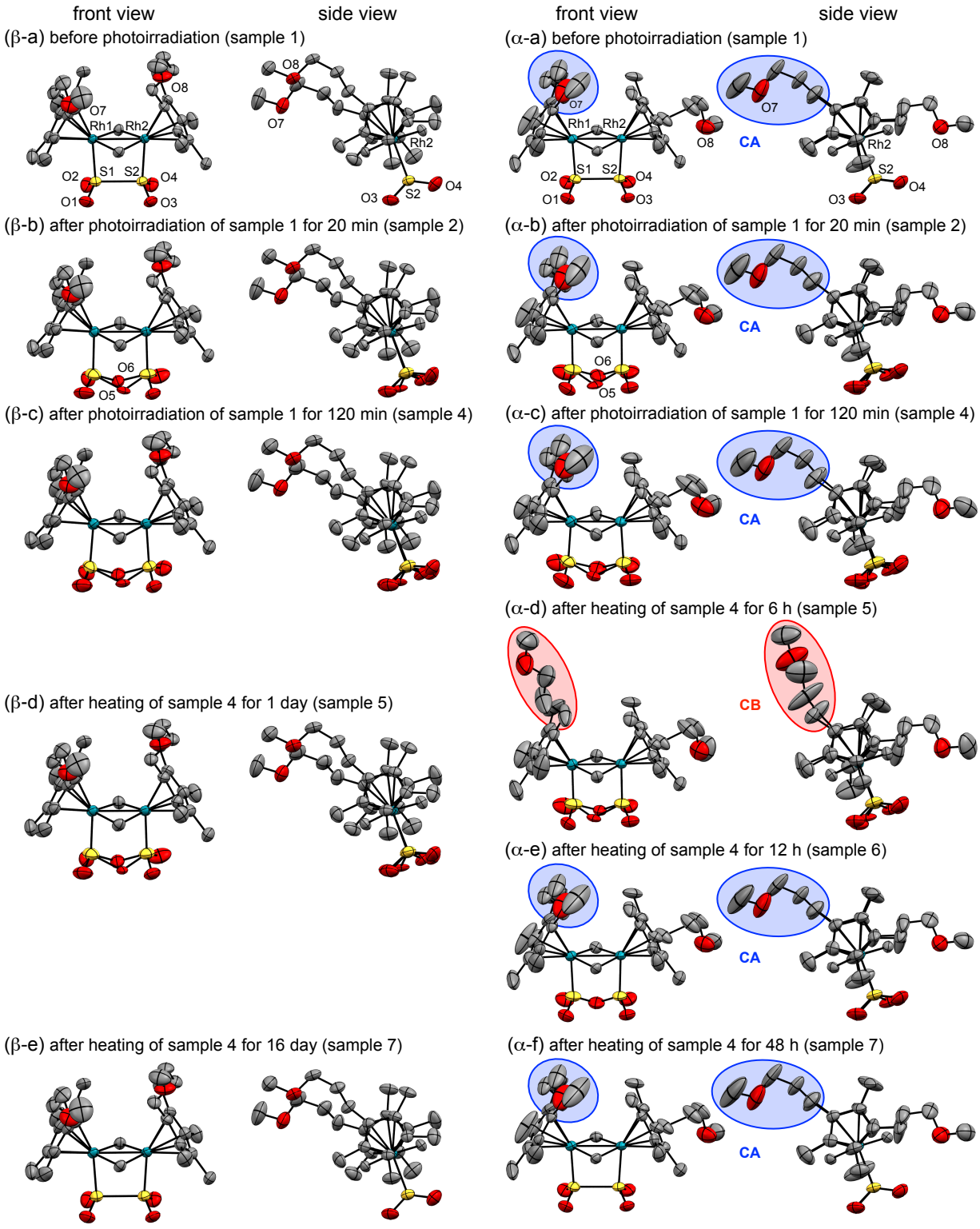


Fig. S4 ORTEP drawings of **1**^{MPro} (50% probability ellipsoids, front and side views) in samples of (β-a–e) the β-crystal and (α-a–f) α-crystal. The hydrogen atoms are omitted for clarity. Data of α-crystal: *Dalton Trans.*, 2022, **51**, 48.