Electronic Supplementary Information

The absolute asymmetric photoisomerization of a photochromic dithionite complex in chiral crystals

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Experimental Details

General: Solvents were purified by distillation before use. Sodium dithionite, $Na_2S_2O_4$, was purchased from Aldrich. All other chemicals were obtained from commercial sources and used as received unless otherwise noted. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL Lambda 400 FT-NMR spectrometer in $CDCl_3$. Chemical shifts were referenced to *protio* solvent impurities (^{1}H: δ 7.26, ^{13}C: δ 77.0 ($CDCl_3$)). Infrared spectra were obtained with the KBr method on a Horiba FT-720 spectrometer. Absorption spectra in a microcrystalline powder film were measured by using a Leica DMLP polarizing microscope connected with a Hamamatsu PMA-11 photodetector. Circular dichroism (CD) spectra in acetonitrile were measured with a JASCO 820 spectropolarimeter. Elemental analyses were performed by the Advanced Science Research Centre at Kanazawa University on a Yanaco MT-5 CHN autocorder.

Synthesis: The propyl derivative ligand precursor, HCp^{Pro} (Cp^{Pro} = η^5-C_5Me_4*n*-Propyl), was synthesized according to the literature procedures.[1] The starting material, *trans*-$[(RhCp^{Pro})_2(\mu\text{-}CH_2)_2Cl_2]$, was synthesized by modifying the procedure for the corresponding Cp* analogue.[2]

$[(RhCp^{Pro})_2(\mu\text{-}CH_2)_2(\mu\text{-}O_2SSO_2)]$ ($\mathbf{1}^{Pro}$): A mixture of *trans*-$[(RhCp^{Pro})_2(\mu\text{-}CH_2)_2Cl_2]$ (132 mg, 0.209 mmol) and $Na_2S_2O_4$ (55 mg, 0.316 mmol) in MeOH (20 mL) was stirred for 6 h under N_2 in the dark. The solvent was removed under reduced pressure to give a reddish brown solid. The crude product was dissolved in 20 mL of CH_2Cl_2 and the insoluble solid was filtered off. Removal of the solvent afforded $\mathbf{1}^{Pro}$ as a brown solid. This solid was washed with ethyl acetate and Et_2O. Yield 95 mg, 66%. Single crystals suitable for X-ray diffraction analysis were obtained by diffusion of ethyl acetate into a solution of $\mathbf{1}^{Pro}$ in CH_2Cl_2 at room temperature in the dark.

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.46 (2H, s, μ-CH_2), 8.57 (2H, s, μ-CH_2), 2.22 (4H, t, $C_5Me_4CH_2CH_2CH_3$), 1.86 (24H, s, C_5Me_4Pr), 1.52-1.40 (4H, m, $C_5Me_4CH_2CH_2CH_3$), 0.96 (6H, t, $C_5Me_4CH_2CH_2CH_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.7 (μ-CH_2), 107.2 (C_5Me_4Pr), 104.4 (C_5Me_4Pr), 104.0 (C_5Me_4Pr), 26.6 ($C_5Me_4CH_2CH_2CH_3$), 22.8 ($C_5Me_4CH_2CH_2CH_3$), 14.1 ($C_5Me_4CH_2CH_2CH_3$), 9.60 (C_5Me_4Pr), 9.58 (C_5Me_4Pr). Anal. Calc. for $C_{26}H_{42}O_4Rh_2S_2$: C, 45.35; H, 6.15. Found: C, 45.13; H, 6.21%.

[(RhCp^{Pro})$_2$(μ-CH$_2$)$_2$(μ-O$_2$SOSO)] (**2**^{Pro}): The red-brown crystals of **1**^{Pro} were irradiated with xenon light (Asahi Spectra, MAX 301 (385-745 nm) for 3 h at room temperature. The orange-brown crystals of **2**^{Pro} were obtained quantitatively.

^{1}H NMR (400 MHz, CDCl$_3$): δ 9.51 (1H, s, μ-CH$_2$), 9.04 (1H, s, μ-CH$_2$), 8.62 (1H, s, μ-CH$_2$), 8.14 (1H, s, μ-CH$_2$), 2.32-2.18 (2H, m, $C_5Me_4C\mathit{H}_2CH_2CH_3$), 2.15-2.04 (2H, m, $C_5Me_4C\mathit{H}_2CH_2CH_3$), 1.85 (3H, s, $C_5\mathit{Me}_4CH_2CH_2CH_3$), 1.84 (9H, s, $C_5\mathit{Me}_4CH_2CH_2CH_3$), 1.76 (9H, s, $C_5\mathit{Me}_4CH_2CH_2CH_3$), 1.75 (3H, s, $C_5\mathit{Me}_4CH_2CH_2CH_3$), 1.51-1.40 (4H, m, $C_5Me_4CH_2C\mathit{H}_2CH_3$), 0.97 (3H, t, $C_5Me_4CH_2CH_2C\mathit{H}_3$), 0.96 (3H, t, $C_5Me_4CH_2CH_2C\mathit{H}_3$). ^{13}C NMR (100 MHz, CDCl$_3$): δ 178.2 (μ-CH$_2$), 168.7 (μ-CH$_2$), 108.1 (C_5Me_4Pr), 107.8 (C_5Me_4Pr), 105.2 (C_5Me_4Pr), 105.1 (C_5Me_4Pr), 104.9 (C_5Me_4Pr), 104.8 (C_5Me_4Pr), 104.6 (C_5Me_4Pr), 26.6 ($C_5Me_4\mathit{C}H_2CH_2CH_3$), 22.8 ($C_5Me_4CH_2\mathit{C}H_2CH_3$), 22.6 ($C_5Me_4CH_2\mathit{C}H_2CH_3$), 14.2 ($C_5Me_4CH_2CH_2\mathit{C}H_3$), 9.69 ($C_5\mathit{Me}_4Pr$), 9.44 ($C_5\mathit{Me}_4Pr$), 9.37 ($C_5\mathit{Me}_4Pr$), 9.31 ($C_5\mathit{Me}_4Pr$). Anal. Calc. for $C_{26}H_{42}O_4Rh_2S_2$: C, 45.35; H, 6.15. Found: C, 45.06; H, 6.14%.

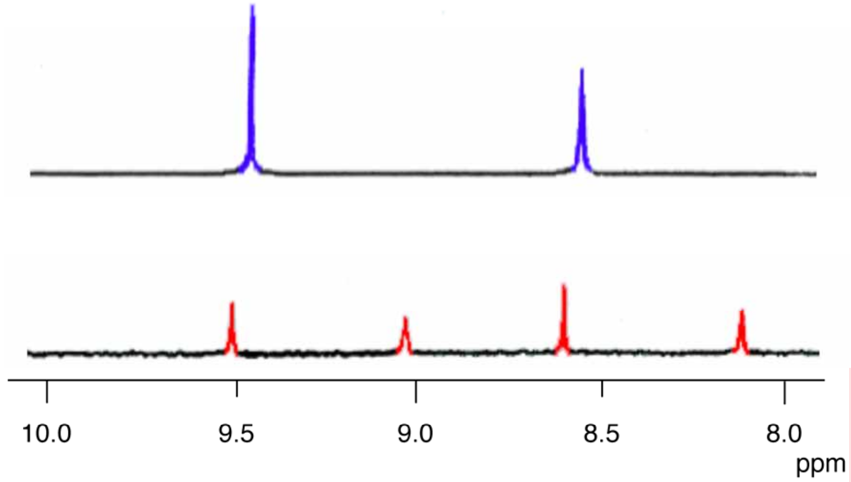

Fig. S1 The μ-CH$_2$ signals in ^{1}H NMR spectra of **1**^{Pro} (blue) and **2** ^{Pro} (red).

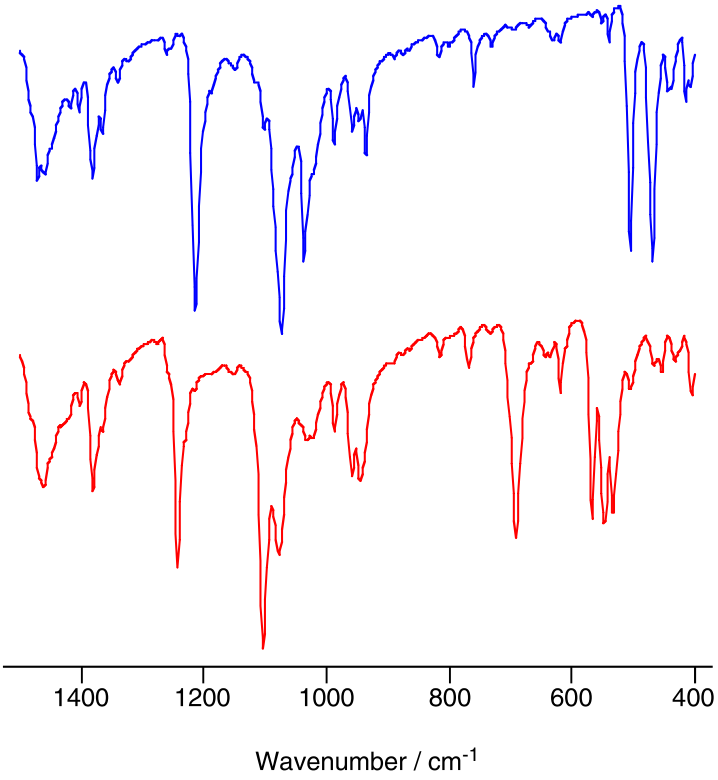

Fig. S2 IR spectra (KBr) of **1**$^{\mathrm{Pro}}$ (blue) and **2**$^{\mathrm{Pro}}$ (red).

X-ray crystallography: All measurements were made on a Rigaku/MSC Mercury CCD diffractometer with graphite monochromated Mo Kα radiation (λ = 0.71070 Å). Data were collected and processed using CrystalClear[3] software (Rigaku). The data were corrected for Lorentz and polarization effects. Empirical absorption corrections were applied. The structures were solved by a direct method: SIR-92[4] and expanded using a Fourier technique. All calculations were performed using the CrystalStructure[5,6] crystallographic software package except for refinement, which was performed using SHELXL-97. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated idealized positions. Crystallographic data have been deposited with the Cambridge Crystallographic Data Center (CCDC). CCDC reference numbers: 718200 ((P)- **1**$^{\mathrm{Pro}}$), 718201 ((M)- **1**$^{\mathrm{Pro}}$), 718202 ((P)- **2**$^{\mathrm{Pro}}$) and 718203 ((M)- **2**$^{\mathrm{Pro}}$).

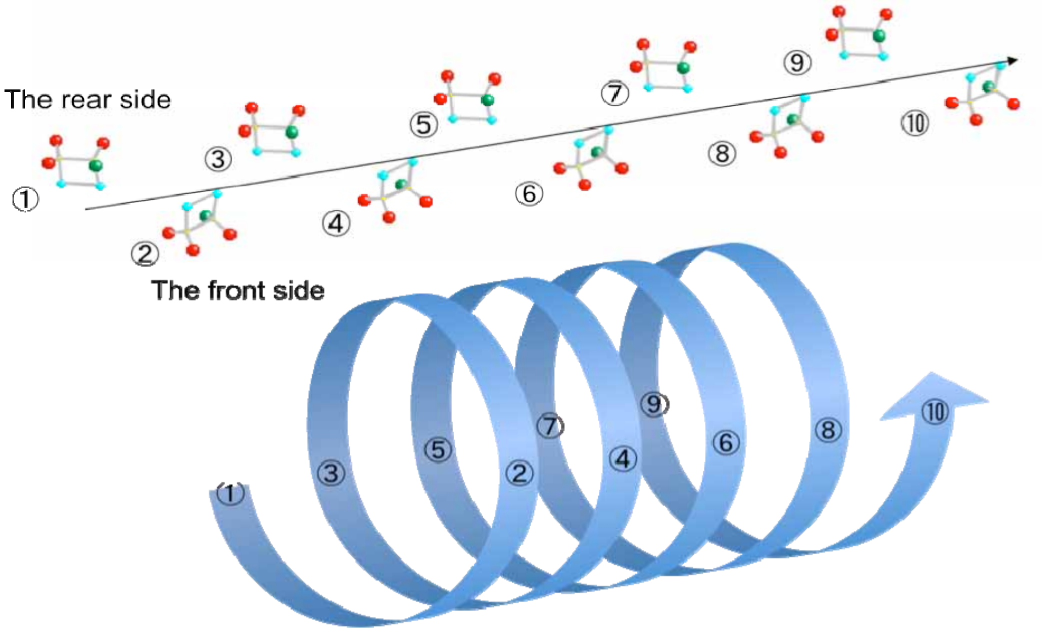

Fig. S3 2-fold helical arrangements formed in a clockwise direction between the molecules along the b axis in the crystal of (P)-**1**$^{\mathrm{Pro}}$. Blue: Rhodium, Red: Oxygen, Green: O2.

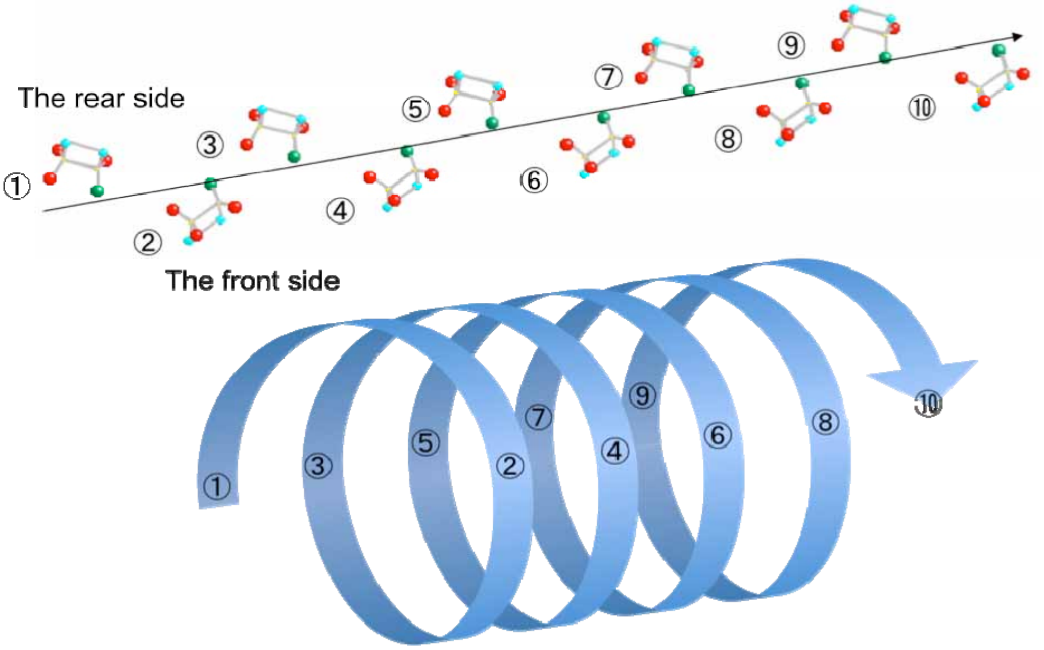

Fig. S4 2-fold helical arrangements formed in an unticlockwise direction between the molecules along the b axis in the crystal of (M)-**1**$^{\mathrm{Pro}}$. Blue: Rhodium, Red: Oxygen, Green: O4.

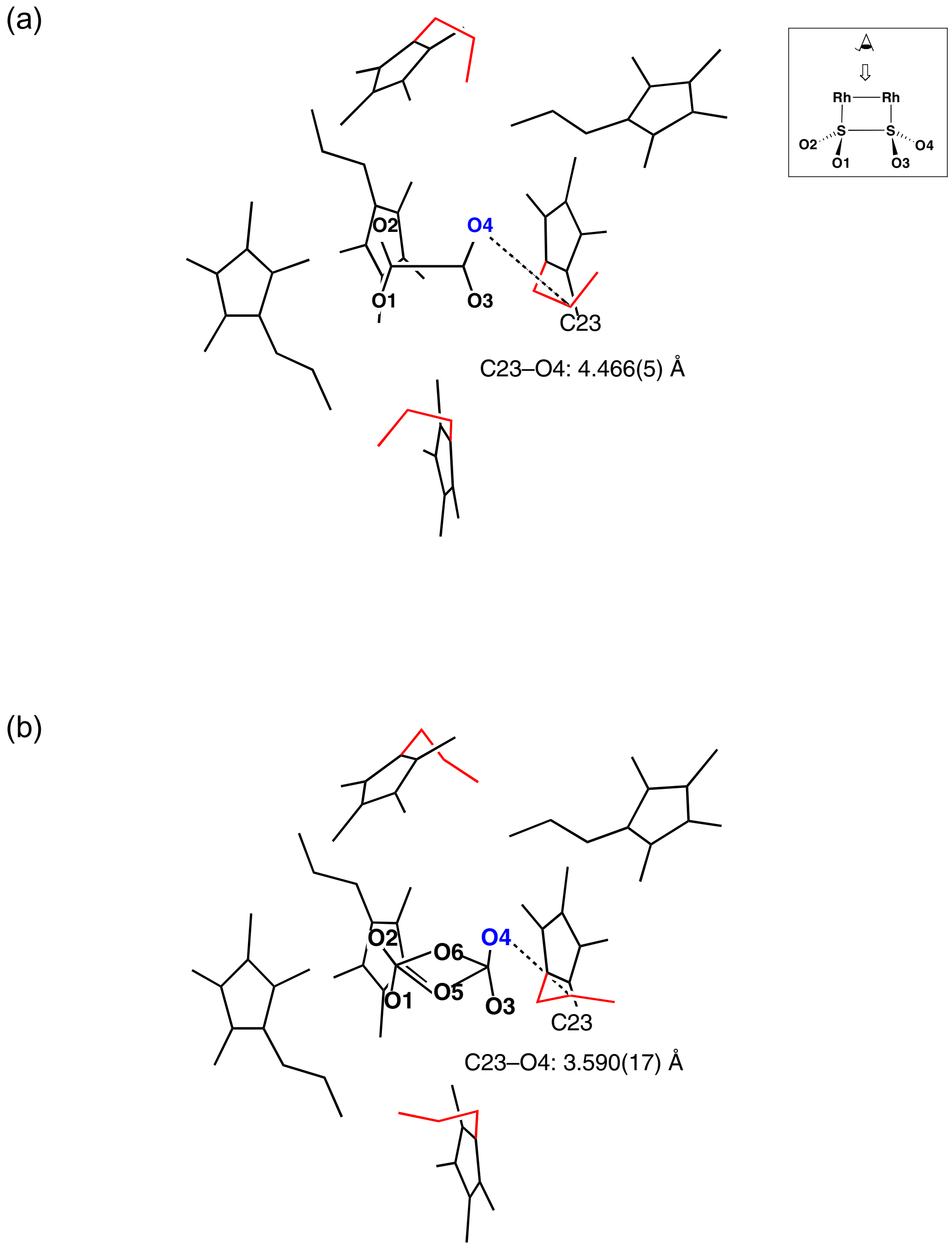

Fig. S5 Reaction cavities of the dithionite ligand of (a) (M)-$\mathbf{1}^{\mathrm{Pro}}$ and (b) (M)-$\mathbf{2}^{\mathrm{Pro}}$. The *n*-propyl moiety, which shows a flipping motion, is indicated in red.

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

$$0.9809\ (\text{occupancy of } O_1) = \mathbf{2a}^{\mathrm{Pro}} + \mathbf{2b}^{\mathrm{Pro}} + \mathbf{2c}^{\mathrm{Pro}} + \mathbf{1}^{\mathrm{Pro}}$$

$$0.2875\ (\text{occupancy of } O_2) = \mathbf{2a}^{\mathrm{Pro}} + \mathbf{2c}^{\mathrm{Pro}} + \mathbf{2d}^{\mathrm{Pro}} + \mathbf{1}^{\mathrm{Pro}}$$

$$0.7674\ (\text{occupancy of } O_3) = \mathbf{2a}^{\mathrm{Pro}} + \mathbf{2b}^{\mathrm{Pro}} + \mathbf{2c}^{\mathrm{Pro}} + \mathbf{1}^{\mathrm{Pro}}$$

$$0.9914\ (\text{occupancy of } O_4) = \mathbf{2a}^{\mathrm{Pro}} + \mathbf{2b}^{\mathrm{Pro}} + \mathbf{2c}^{\mathrm{Pro}} + \mathbf{1}^{\mathrm{Pro}}$$

$$0.2577\ (\text{occupancy of } O_5) = \mathbf{2a}^{\mathrm{Pro}} + \mathbf{2d}^{\mathrm{Pro}}$$

$$0.7151\ (\text{occupancy of } O_6) = \mathbf{2b}^{\mathrm{Pro}} + \mathbf{2c}^{\mathrm{Pro}}$$

$\mathbf{2a}^{\mathrm{Pro}} = 0.2326$, $\mathbf{2b}^{\mathrm{Pro}} = 0.7125$, $\mathbf{2c}^{\mathrm{Pro}} = 0.0086$, $\mathbf{2d}^{\mathrm{Pro}} = 0.0191$, $\mathbf{1}^{\mathrm{Pro}} = 0.0272$.

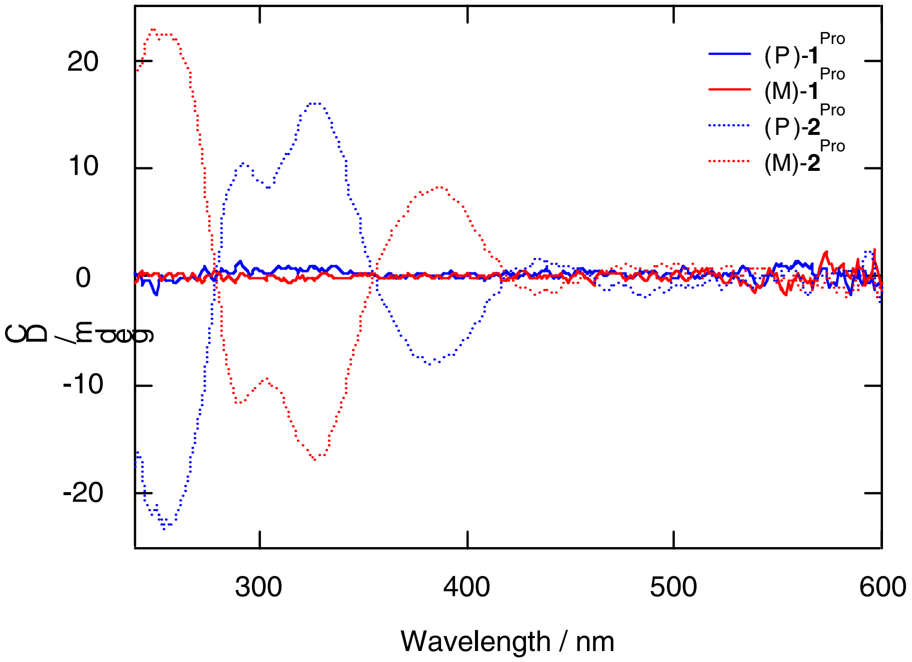

Fig. S6 Circular dichroism (CD) spectra of (P)-$\mathbf{1}^{\mathrm{Pro}}$, (M)-$\mathbf{1}^{\mathrm{Pro}}$, (P)-$\mathbf{2}^{\mathrm{Pro}}$ and (M)-$\mathbf{2}^{\mathrm{Pro}}$ in acetonitrile.

References

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