Electronic Supplementary Information (ESI) – Table of Contents

Photoinduced bending of rod-like millimetre-size crystals of a rhodium dithionite complex with *n*-pentyl moieties

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Experimental details

General	S 2
X-ray crystallography	S 3
Syntheses of 1 ^{Pen} and 2 ^{Pen}	S 4
References	S 6
Tables	
Table S1 Crystallographic data for samples 1, 2, 3, 3 ₋₉₅ , 3 ₋₂₅ and 4	S 7
Table S2 Percentage population of the isomers	S 8
Figures	
Fig. S1 UV-vis spectral changes from 1^{Pen} to 2^{Pen}	S 9
Fig. S2 ¹ H NMR spectra of 1^{Pen} and 2^{Pen}	S 10
Fig. S3 IR spectra of 1 ^{Pen} and 2 ^{Pen}	S11
Fig. S4 Reversible bending of a rod-like crystal of 1^{Pen}	S12
Fig. S5 Bending and unbending of a rod-like crystal of 1^{Pen}	S13
Fig. S6 Photoirradiation of a rod-like crystal of 1^{Pen}	S14
Fig. S7 ORTEP drawings of 2^{Pen} at -165, -95, and -25 °C	S15
Videos	
Video S1 Bending of a rod-like crystal of 1^{Pen}	S 16
Video S2 Reversible bending of a rod-like crystal of 1 ^{Pen}	S 16

Experimental details

General: Solvents were purified by distillation before use. Sodium dithionite, Na₂S₂O₄, was purchased from Aldrich. All other chemicals were obtained from commercial sources and used as received unless otherwise noted. The crystals were irradiated using an LED lamp (Moritex, LLS2: 420-750 nm) and a xenon-lamp (Asahi Spectra, Max-301 and 303: 300 W, 385-740 nm). The crystals were uniformly heated using a Leica 350 microscope heating stage. ¹H and ¹³C NMR spectra were recorded on a Bruker Avance III 600 FT-NMR spectrometer in CDCl₃. Chemical shifts were referenced to *protio* solvent impurities (¹H: δ 7.26, ¹³C: δ 77.0 (CDCl₃)). Infrared spectra were obtained with the KBr method on a Thermo Scientific Nicolet 6700 FT-IR spectrometer. Absorption spectra in a microcrystalline powder film were measured by using a Leica DMLP polarizing microscope connected with a Hamamatsu PMA-11 photodetector. Photographs and videos of the crystals were recorded by using an Olympus SZX7 microscope connected with a digital camera (Nikon digital sight DS-U1). Elemental analyses were performed using a Yanaco CHN-coder MT-5.

X-ray crystallography: All measurements were made on a Rigaku/MSC Saturn CCD diffractometer with confocal monochromated Mo K α radiation ($\lambda = 0.71070$ Å). Data were collected and processed using CrystalClear¹ software (Rigaku). The data were corrected for Lorentz and polarisation effects. Numerical absorption corrections were applied. The structures were solved by a direct method: SIR-92² and expanded using a Fourier technique. All calculations were performed using the CrystalStructure³ crystallographic software package except for refinement, which was performed using SHELXL Version2014/6⁴. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model.

Samples 2, 3, 3₋₉₅, 3₋₂₅: two carbon atoms (C27 and C28) were refined without H.

Samples 3_{-95} and 3_{-25} : the same occupancies as sample 3 were applied to O1, O2, O3, O4, O5 and O6.

Crystallographic data has been deposited with the Cambridge Crystallographic Data Centre (CCDC). CCDC reference number: 1445112 (Sample 1: 1^{Pen}).

Syntheses

The *n*-pentyl derivative ligand precursor, HCp^{Pen} ($\text{Cp}^{\text{Pen}} = \eta^5 - \text{C}_5\text{Me}_4n - \text{C}_5\text{H}_{11}$), was synthesized according to the literature procedures.⁵ The starting material, *trans*-[(RhCp^{Pen})₂(μ -CH₂)₂Cl₂], was synthesized by modifying the procedure for the corresponding Cp^{Me} (η^5 -C₅Me₅) analogue.⁶

[(RhCp^{Pen})₂(μ -CH₂)₂(μ -O₂SSO₂)] (1^{Pen}): A mixture of *trans*-[(RhCp^{Pen})₂(μ -CH₂)₂ Cl₂] (972 mg, 1.31 mmol) and Na₂S₂O₄ (410 mg, 2.36 mmol) in MeOH (100 mL) was stirred for 12 h under N₂ in the dark at room temperature. The solvent was removed under reduced pressure to give a reddish brown solid. The crude product was dissolved in 100 mL of CH₂Cl₂ and the insoluble solid was filtered off. Removal of the solvent afforded 1^{Pen} as a red-orange solid. This solid was washed with Et₂O. Yield 854 mg, 87%. Single crystals suitable for X-ray diffraction analysis were obtained from a saturated solution of 1^{Pen} in *n*-C₆H₁₄/CH₂Cl₂ (6/1) in the dark at room temperature.

¹H NMR (600 MHz, CDCl₃): δ 9.45 (2H, s, μ -CH₂), 8.56 (2H, s, μ -CH₂), 2.21 (4H, t, C₅Me₄*CH*₂CH₂CH₂CH₂CH₂CH₃), 1.86 (12H, s, C₅*Me*₄*n*-C₅H₁₁), 1.85 (12H, s, C₅*Me*₄*n*-C₅H₁₁), 1.41 (4H, quin, C₅Me₄CH₂CH₂CH₂CH₂CH₂CH₃), 1.35-1.30 (8H, m, C₅Me₄CH₂CH₂CH₂CH₂CH₃), 0.90 (6H, t, C₅Me₄CH₂CH₂CH₂CH₂CH₂CH₃). ¹³C NMR (150 MHz, CDCl₃): δ 173.6 (μ -CH₂), 107.4 (C_5 Me₄*n*-C₅H₁₁), 104.5 (C_5 Me₄*n*-C₅H₁₁), 103.9 (C_5 Me₄*n*-C₅H₁₁), 31.7 (C_5 Me₄*n*-C₅H₁₁), 29.2 (C_5 Me₄*n*-C₅H₁₁), 24.7 (C_5 Me₄*n*-C₅H₁₁), 22.4 (C_5 Me₄*n*-C₅H₁₁), 13.9 (C_5 Me₄*n*-C₅H₁₁), 9.61 (C_5 Me₄*n*-C₅H₁₁), 9.55 (C_5 Me₄*n*-C₅H₁₁). Anal. Calc. for C₃₀H₅₀O₄Rh₂S₂: C, 48.39; H, 6.77. Found: C, 48.11; H, 6.75%.

[(RhCp^{Pen})₂(μ -CH₂)₂(μ -O₂SOSO)] (2^{Pen}): The red-orange crystals of 1^{Pen} were irradiated with the LED lamp (420-750 nm, 20 mW/cm²) for 2 h under N₂ at room temperature. The yellow-orange crystals of 2^{Pen} were obtained quantitatively.

¹H NMR (600 MHz, CDCl₃): δ 9.50 (1H, s, μ -CH₂), 9.04 (1H, s, μ -CH₂), 8.61 (1H, s, μ -CH₂), 8.13 (1H, s, μ -CH₂), 2.28-2.15 (2H, m, C₅Me₄*CH*₂CH₂CH₂CH₂CH₃), 2.14-2.03 (2H, m, C₅Me₄*CH*₂CH₂CH₂CH₂CH₃), 1.86-1.83 (12H, m, C₅*Me*₄*n*-C₅H₁₁), 1.78-1.75 (12H, m, C₅*Me*₄*n*-C₅H₁₁), 1.43-1.37 (4H, m, C₅Me₄CH₂CH₂CH₂CH₂CH₂CH₃), 1.36-1.29 (8H, m, C₅Me₄*C*H₂CH₂*CH*₂*CH*₂CH₃), 0.90 (6H, t, C₅Me₄*C*H₂CH₂CH₂CH₂*CH*₃). ¹³C NMR (150 MHz, CDCl₃): δ 178.1 (μ -CH₂), δ 168.7 (μ -CH₂), 108.2 (*C*₅Me₄*n*-C₅H₁₁), 108.1 (*C*₅Me₄*n*-C₅H₁₁), 105.3 (*C*₅Me₄*n*-C₅H₁₁), 105.1 (*C*₅Me₄*n*-C₅H₁₁), 104.9 (*C*₅Me₄*n*-C₅H₁₁), 104.7 (*C*₅Me₄*n*-C₅H₁₁), 104.6 (*C*₅Me₄*n*-C₅H₁₁), 104.5 (*C*₅Me₄*n*-C₅H₁₁), 31.9 (*C*₅Me₄*n*-C₅H₁₁), 29.2 (*C*₅Me₄*n*-C₅H₁₁), 29.0 (*C*₅Me₄*n*-C₅H₁₁), 24.6 (*C*₅Me₄*n*-C₅H₁₁), 22.5 (*C*₅Me₄*n*-C₅H₁₁), 13.9 (*C*₅Me₄*n*-C₅H₁₁), 9.73 (*C*₅Me₄*n*-C₅H₁₁), 9.40 (*C*₅Me₄*n*-C₅H₁₁), 9.32 (*C*₅Me₄*n*-C₅H₁₁). Anal. Calc. for C₃₀H₅₀O₄Rh₂S₂: C, 48.39; H, 6.77. Found: C, 48.17; H, 6.76%.

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<u>Tables</u>

	Sample 1 1 ^{Pen}	Sample 2 $1^{Pen}: 2^{Pen} = 46: 54$	Sample 3 2 ^{Pen}	Sample 3_{-95} 2^{Pen}	Sample 3_{-25} 2^{Pen}	Sample 4 $1^{\text{Pen}}_{\text{heating}}$
Temperature (K)	108	108	108	178	248	108
Formula	$C_{30}H_{50}S_2O_4Rh_2$	$C_{30}H_{45}S_2O_4Rh_2$	$C_{30}H_{45}S_2O_4Rh_2$	$C_{30}H_{45}S_2O_4Rh_2$	$C_{30}H_{45}S_2O_4Rh_2$	$C_{30}H_{50}S_2O_4Rh_2$
Fw	744.65	739.61	739.61	739.61	739.61	744.65
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	Cc	Cc	Cc	Cc	Cc	Cc
<i>a</i> (Å)	13.970(6)	13.980(6)	13.978(7)	14.055(8)	14.064(6)	13.945(7)
<i>b</i> (Å)	25.545(10)	25.674(11)	25.578(14)	25.770(14)	25.810(12)	25.590(13)
<i>c</i> (Å)	8.975(4)	9.040(4)	9.041(5)	9.091(5)	9.094(4)	8.978(5)
α (deg)	90.0000	90.0000	90.0000	90.0000	90.0000	90.0000
β (deg)	97.362(5)	97.005(6)	96.859(7)	96.816(7)	96.631(6)	97.283(9)
γ(deg)	90.0000	90.0000	90.0000	90.0000	90.0000	90.0000
$V(\text{\AA}^3)$	3177(2)	3221(2)	3209(3)	3270(3)	3279(3)	3178(3)
Ζ	4	4	4	4	4	4
μ (cm ⁻¹)	12.00	11.83	11.88	11.66	11.62	12.00
<i>F</i> (000)	1536.00	1516.00	1516.00	1516.00	1516.00	1536.00
$D_{\rm calcd}({\rm g/cm^3})$	1.557	1.525	1.531	1.502	1.498	1.556
Reflections	12666	12815	12814	12928	12978	12755
Independent	6531	6619	6626	6708	6747	6926
	$(R_{\rm int} = 0.0282)$	$(R_{\rm int} = 0.0312)$	$(R_{\rm int} = 0.0351)$	$(R_{\rm int} = 0.0389)$	$(R_{\rm int} = 0.0462)$	$(R_{\rm int} = 0.0345)$
Data/parameters	6531/353	6619/370	6626/370	6708/370	6747/370	6926/353
$R_1 \left[I > 2\sigma(I) \right]$	0.0311	0.0389	0.0439	0.0425	0.0388	0.0448
wR_2 (all data)	0.0664	0.0815	0.1071	0.1047	0.0765	0.1027
Goodness-of-fit	1.061	1.045	1.046	1.034	1.020	1.090
Flack parameter	0.039(15)	0.04(2)	0.05(2)	0.05(3)	-0.03(3)	0.013(19)

Table S1 Crystallographic data for samples $1, 2, 3, 3_{-95}, 3_{-25}$ and 4

						-
	1 ^{Pen}	$\begin{array}{c} {}^{\text{Rh}_{1} - {}^{\text{Rh}_{2}}(b)} \\ {}^{\text{O}_{2}, \vee S} & * {}^{\text{S}, \vee } \\ {}^{\text{O}_{1}, \vee S} & * {}^{\text{S}, \vee } \\ {}^{\text{O}_{1}, \vee S} & * {}^{\text{S}, \vee } \\ {}^{\text{O}_{1}, \vee S} \\ {}^{\text{Pen}} (R) \end{array}$	$ \begin{array}{c} \mathbf{Rh}_{1} - \mathbf{Rh}_{2}^{(b)} \\ \cdot & \mathbf{S} \\ \cdot & \mathbf{S} \\ \mathbf{O}_{1} & \mathbf{O}_{6} & \mathbf{O}_{3} \end{array} \\ \cdot & \mathbf{D}_{1} & \mathbf{O}_{6} & \mathbf{O}_{3} \end{array} $ $ \begin{array}{c} \mathbf{2b}^{\text{Pen}} (\mathbf{R}) \end{array} $	$\begin{array}{c} {}^{Rh_{1}-Rh_{2}} (b) \\ {}^{I} \\ {}^{J} \\ {}^{S} $	$\begin{array}{c} {}^{{{\text{Rh}}_{1}} - {{\text{Rh}}_{2}}^{(b)}} \\ {}^{*}{}^{ }{}^{} \\ {}^{\circ}{}$	2 ^{Pen} (total)
Sample 1	100	0	0	0	0	0
Sample 2	46	5	16	9	24	54
Sample 3	1	12	39	12	36	99
Sample 4	100	0	0	0	0	0

 $\textbf{Table S2} \text{ Percentage population of the isomers, } \mathbf{1}^{\text{Pen}}, \mathbf{2a}^{\text{Pen}}, \mathbf{2b}^{\text{Pen}}, \mathbf{2c}^{\text{Pen}} \text{ and } \mathbf{2d}^{\text{Pen}} \text{ in the crystal}^{(a)}$

(a) Although the crystal has mirror images of $2a^{\text{Pen}}-2d^{\text{Pen}}$ as a set, only one asymmetric unit 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, $2a^{\text{Pen}}-2d^{\text{Pen}}$, concerned with the μ -O₂SOSO unit. The Cp^{Pen} and μ -CH₂ ligands are omitted for clarity. The absolute configurations of the sulfur atoms are shown in parentheses.

The values of % for stereoisomers $2a^{\text{Pen}}-2d^{\text{Pen}}$ 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:

0.7628 (occupancy of
$$O_1$$
) = $2a^{Pen} + 2b^{Pen} + 2c^{Pen} + 1^{Pen}$
0.8450 (occupancy of O_2) = $2a^{Pen} + 2c^{Pen} + 2d^{Pen} + 1^{Pen}$
0.9475 (occupancy of O_3) = $2b^{Pen} + 2c^{Pen} + 2d^{Pen} + 1^{Pen}$
0.9083 (occupancy of O_4) = $2a^{Pen} + 2b^{Pen} + 2d^{Pen} + 1^{Pen}$
0.2897 (occupancy of O_5) = $2a^{Pen} + 2d^{Pen}$
0.2467 (occupancy of O_6) = $2b^{Pen} + 2c^{Pen}$

$$2\mathbf{a}^{\text{Pen}} = 0.0525, \mathbf{2b}^{\text{Pen}} = 0.1550, \mathbf{2c}^{\text{Pen}} = 0.0917, \mathbf{2d}^{\text{Pen}} = 0.2372, \mathbf{1}^{\text{Pen}} = 0.4636.$$

<u>Figures</u>



Fig. S1 The UV-vis spectral changes from 1^{Pen} (blue) to 2^{Pen} (red) in a microcrystalline powder film.



Fig. S2 ¹H NMR spectra of (a) $\mathbf{1}^{Pen}$ (blue) and (b) $\mathbf{2}^{Pen}$ (red) in CDCl₃ in the range of μ -CH₂ signals.



Fig. S3 IR spectra of (a) $\mathbf{1}^{Pen}$ (blue) and (b) $\mathbf{2}^{Pen}$ (red) in KBr.



Fig. S4 Reversible bending of a rod-like crystal {1.5 mm (length) x 15 μ m (width) x 8 μ m (depth)} of **1**^{Pen} by alternate irradiation (385–740 nm, 60 mW/cm², 2 s) and heating (105–110 °C, 30 min).



Fig. S5 Bending and unbending of a rod-like crystal {2.1 mm (length) x 20 μ m (width) x 8 μ m (depth)} of **1**^{Pen} by prolonged photoirradiation from the right side (385–740 nm, 20 mW/cm²).



Fig. S6 Photoirradiation of a rod-like crystal of 1^{Pen} for X-ray diffraction analysis: the crystal was rotated around its long axis (*c*-axis) and irradiated uniformly.



Fig. S7 ORTEP drawings of 2^{Pen} with 50% probability ellipsoids at (a) -165, (b) -95 and (c) -25 °C (Table S1, Sample 3, 3₋₉₅ and 3₋₂₅, respectively). The hydrogen atoms are omitted for clarity.

Legends of Supporting Videos

Video S1. Bending of a rod-like crystal {1.3 mm (length) x 14 μ m (width) x 8 μ m (depth)} of 1^{Pen}. The crystal was irradiated form right side (385–740 nm, 60 mW/cm², 5 s).

Video S2. Reversible bending of a rod-like crystal {4.8 mm (length) x 44 μ m (width) x 20 μ m (depth)} of 1^{Pen}. First, the crystal was irradiated from right side, and then from left side (385–740 nm, 20 mW/cm², 10 s).