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

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**Experimental details**

**General:** Solvents were purified by distillation before use. Sodium dithionite, Na$_2$S$_2$O$_4$, 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. $^1$H and $^{13}$C NMR spectra were recorded on a Bruker Avance III 600 FT-NMR spectrometer in CDCl$_3$. Chemical shifts were referenced to protio solvent impurities ($^1$H: $\delta$ 7.26, $^{13}$C: $\delta$ 77.0 (CDCl$_3$)). 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 Kα radiation (λ = 0.71070 Å). Data were collected and processed using CrystalClear 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-92 and expanded using a Fourier technique. All calculations were performed using the CrystalStructure crystallographic software package except for refinement, which was performed using SHELXL Version2014/6. 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^pm).
Syntheses

The \( n \)-pentyl derivative ligand precursor, HCp^{Pen} (Cp^{Pen} = \eta^5-C_5Me_4\eta-C_5H_{11})\), was synthesized according to the literature procedures.\(^5\) The starting material, \( \text{trans} -[(\text{RhCp}^{\text{Pen}})_2(\mu-\text{CH}_2)_2\text{Cl}_2] \), was synthesized by modifying the procedure for the corresponding Cp^{Me} (\( \eta^5-C_5\text{Me}_3 \)) analogue.\(^6\)

\[[(\text{RhCp}^{\text{Pen}})_2(\mu-\text{CH}_2)_2(\mu-\text{O}_2\text{SSO}_2)] \tag{1^{\text{Pen}}} \]

A mixture of \( \text{trans} -[(\text{RhCp}^{\text{Pen}})_2(\mu-\text{CH}_2)_2\text{Cl}_2] \) (972 mg, 1.31 mmol) and Na\( _2\)S\( _2\)O\( _4\) (410 mg, 2.36 mmol) in MeOH (100 mL) was stirred for 12 h under N\( _2\) 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 CH\( _2\)Cl\( _2\) and the insoluble solid was filtered off. Removal of the solvent afforded \( 1^{\text{Pen}} \) as a red-orange solid. This solid was washed with Et\(_2\)O. Yield 854 mg, 87\%. Single crystals suitable for X-ray diffraction analysis were obtained from a saturated solution of \( 1^{\text{Pen}} \) in \( n \)-C\(_6\)H\(_{14}\)/CH\(_2\)Cl\(_2\) (6/1) in the dark at room temperature.

\(^1\)H NMR (600 MHz, CDCl\(_3\)): \( \delta 9.45 \) (2H, s, \( \mu-\text{CH}_2\)), \( 8.56 \) (2H, s, \( \mu-\text{CH}_2\)), \( 2.21 \) (4H, t, \( \text{C}_5\text{Me}_4\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3\)), \( 1.86 \) (12H, s, \( \text{C}_5\text{Me}_4\text{en-}C_5\text{H}_{11}\)), \( 1.85 \) (12H, s, \( \text{C}_5\text{Me}_4\text{en-}C_5\text{H}_{11}\)), \( 1.41 \) (4H, quin, \( \text{C}_5\text{Me}_4\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3\)), \( 1.35-1.30 \) (8H, m, \( \text{C}_5\text{Me}_4\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3\)), \( 0.90 \) (6H, t, \( \text{C}_5\text{Me}_4\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3\)). \(^{13}\)C NMR (150 MHz, CDCl\(_3\)): \( \delta 173.6 \) (\( \mu-\text{CH}_2\)), \( 107.4 \) (\( \text{C}_5\text{Me}_4\text{en-}C_5\text{H}_{11}\)), \( 104.5 \) (\( \text{C}_5\text{Me}_4\text{en-}C_5\text{H}_{11}\)), \( 103.9 \) (\( \text{C}_5\text{Me}_4\text{en-}C_5\text{H}_{11}\)), \( 31.7 \) (\( \text{C}_5\text{Me}_4\text{en-}C_5\text{H}_{11}\)), \( 29.2 \) (\( \text{C}_5\text{Me}_4\text{en-}C_5\text{H}_{11}\)), \( 24.7 \) (\( \text{C}_5\text{Me}_4\text{en-}C_5\text{H}_{11}\)), \( 22.4 \) (\( \text{C}_5\text{Me}_4\text{en-}C_5\text{H}_{11}\)), \( 13.9 \) (\( \text{C}_5\text{Me}_4\text{en-}C_5\text{H}_{11}\)), \( 9.61 \) (\( \text{C}_5\text{Me}_4\text{en-}C_5\text{H}_{11}\)), \( 9.55 \) (\( \text{C}_5\text{Me}_4\text{en-}C_5\text{H}_{11}\)). Anal. Calc. for \( \text{C}_{30}\text{H}_{50}\text{O}_4\text{Rh}_2\text{S}_2 \): C, 48.39; H, 6.77. Found: C, 48.11; H, 6.75\%.
[(RhCp\textsuperscript{Pen})\textsubscript{2}(\mu-CH\textsubscript{2})\textsubscript{2}(\mu-O\textsubscript{2}SOSO)] (2\textsuperscript{Pen}): The red-orange crystals of 1\textsuperscript{pen} were irradiated with the LED lamp (420-750 nm, 20 mW/cm\textsuperscript{2}) for 2 h under N\textsubscript{2} at room temperature. The yellow-orange crystals of 2\textsuperscript{Pen} were obtained quantitatively.

\textsuperscript{1}H NMR (600 MHz, CDCl\textsubscript{3}): δ 9.50 (1H, s, \mu-CH\textsubscript{2}), 9.04 (1H, s, \mu-CH\textsubscript{2}), 8.61 (1H, s, \mu-CH\textsubscript{2}), 8.13 (1H, s, \mu-CH\textsubscript{2}), 2.28-2.15 (2H, m, C\textsubscript{5}Me\textsubscript{4}CH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{3}), 2.14-2.03 (2H, m, C\textsubscript{5}Me\textsubscript{4}CH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{3}), 1.86-1.83 (12H, m, C\textsubscript{5}Me\textsubscript{4}n-C\textsubscript{5}H\textsubscript{11}), 1.78-1.75 (12H, m, C\textsubscript{5}Me\textsubscript{4}n-C\textsubscript{5}H\textsubscript{11}), 1.43-1.37 (4H, m, C\textsubscript{5}Me\textsubscript{4}CH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{3}), 0.90 (6H, t, C\textsubscript{5}Me\textsubscript{4}CH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{3}). \textsuperscript{13}C NMR (150 MHz, CDCl\textsubscript{3}): δ 178.1 (\mu-CH\textsubscript{2}), δ 168.7 (\mu-CH\textsubscript{2}), 108.2 (C\textsubscript{5}Me\textsubscript{4}n-C\textsubscript{5}H\textsubscript{11}), 108.1 (C\textsubscript{5}Me\textsubscript{4}n-C\textsubscript{5}H\textsubscript{11}), 105.3 (C\textsubscript{5}Me\textsubscript{4}n-C\textsubscript{5}H\textsubscript{11}), 105.1 (C\textsubscript{5}Me\textsubscript{4}n-C\textsubscript{5}H\textsubscript{11}), 104.9 (C\textsubscript{5}Me\textsubscript{4}n-C\textsubscript{5}H\textsubscript{11}), 104.7 (C\textsubscript{5}Me\textsubscript{4}n-C\textsubscript{5}H\textsubscript{11}), 104.6 (C\textsubscript{5}Me\textsubscript{4}n-C\textsubscript{5}H\textsubscript{11}), 104.5 (C\textsubscript{5}Me\textsubscript{4}n-C\textsubscript{5}H\textsubscript{11}), 31.9 (C\textsubscript{5}Me\textsubscript{4}n-C\textsubscript{5}H\textsubscript{11}), 29.2 (C\textsubscript{5}Me\textsubscript{4}n-C\textsubscript{5}H\textsubscript{11}), 29.0 (C\textsubscript{5}Me\textsubscript{4}n-C\textsubscript{5}H\textsubscript{11}), 24.6 (C\textsubscript{5}Me\textsubscript{4}n-C\textsubscript{5}H\textsubscript{11}), 22.5 (C\textsubscript{5}Me\textsubscript{4}n-C\textsubscript{5}H\textsubscript{11}), 13.9 (C\textsubscript{5}Me\textsubscript{4}n-C\textsubscript{5}H\textsubscript{11}), 9.73 (C\textsubscript{5}Me\textsubscript{4}n-C\textsubscript{5}H\textsubscript{11}), 9.67 (C\textsubscript{5}Me\textsubscript{4}n-C\textsubscript{5}H\textsubscript{11}), 9.64 (C\textsubscript{5}Me\textsubscript{4}n-C\textsubscript{5}H\textsubscript{11}), 9.56 (C\textsubscript{5}Me\textsubscript{4}n-C\textsubscript{5}H\textsubscript{11}), 9.47 (C\textsubscript{5}Me\textsubscript{4}n-C\textsubscript{5}H\textsubscript{11}), 9.40 (C\textsubscript{5}Me\textsubscript{4}n-C\textsubscript{5}H\textsubscript{11}), 9.32 (C\textsubscript{5}Me\textsubscript{4}n-C\textsubscript{5}H\textsubscript{11}). Anal. Calc. for C\textsubscript{30}H\textsubscript{50}O\textsubscript{8}Rh\textsubscript{2}S\textsubscript{2}: C, 48.39; H, 6.77. Found: C, 48.17; H, 6.76%.
References

   Tokyo 196-8666, Japan.


   Tokyo 196-8666, Japan.


# Tables

## Table S1 Crystallographic data for samples 1, 2, 3, 3.95, 3.25 and 4

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<th>Sample 1</th>
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<td>(Rint = 0.0389)</td>
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<td>(Rint = 0.0345)</td>
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<td>0.05(2)</td>
<td>0.05(3)</td>
<td>-0.03(3)</td>
<td>0.013(19)</td>
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Table S2 Percentage population of the isomers, 1\(^{\text{Pen}}\), 2a\(^{\text{Pen}}\), 2b\(^{\text{Pen}}\), 2c\(^{\text{Pen}}\) and 2d\(^{\text{Pen}}\) in the crystal\(^{(a)}\)

<table>
<thead>
<tr>
<th></th>
<th>1(^{\text{Pen}})</th>
<th>2a(^{\text{Pen}}) (R)</th>
<th>2b(^{\text{Pen}}) (R)</th>
<th>2c(^{\text{Pen}}) (S)</th>
<th>2d(^{\text{Pen}}) (S)</th>
<th>2(^{\text{Pen}}) (total)</th>
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</table>

(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 \(\mu\)-O\(_2\)SOSO unit. The Cp\(^{\text{Pen}}\) and \(\mu\)-CH\(_2\) 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:

\[
\begin{align*}
0.7628 \text{ (occupancy of O}_1) & = 2a^{\text{Pen}} + 2b^{\text{Pen}} + 2c^{\text{Pen}} + 1^{\text{Pen}} \\
0.8450 \text{ (occupancy of O}_2) & = 2a^{\text{Pen}} + 2c^{\text{Pen}} + 2d^{\text{Pen}} + 1^{\text{Pen}} \\
0.9475 \text{ (occupancy of O}_3) & = 2b^{\text{Pen}} + 2c^{\text{Pen}} + 2d^{\text{Pen}} + 1^{\text{Pen}} \\
0.9083 \text{ (occupancy of O}_4) & = 2a^{\text{Pen}} + 2b^{\text{Pen}} + 2d^{\text{Pen}} + 1^{\text{Pen}} \\
0.2897 \text{ (occupancy of O}_5) & = 2a^{\text{Pen}} + 2d^{\text{Pen}} \\
0.2467 \text{ (occupancy of O}_6) & = 2b^{\text{Pen}} + 2c^{\text{Pen}} \\
\end{align*}
\]

\[2a^{\text{Pen}} = 0.0525, \quad 2b^{\text{Pen}} = 0.1550, \quad 2c^{\text{Pen}} = 0.0917, \quad 2d^{\text{Pen}} = 0.2372, \quad 1^{\text{Pen}} = 0.4636.\]
Figures

Fig. S1 The UV-vis spectral changes from $1^{\text{Pen}}$ (blue) to $2^{\text{Pen}}$ (red) in a microcrystalline powder film.
Fig. S2 $^1$H NMR spectra of (a) $\text{1}^{\text{Pen}}$ (blue) and (b) $\text{2}^{\text{Pen}}$ (red) in CDCl$_3$ in the range of $\mu$-CH$_2$ signals.
Fig. S3 IR spectra of (a) $1^{\text{Pen}}$ (blue) and (b) $2^{\text{Pen}}$ (red) in KBr.
Fig. S4 Reversible bending of a rod-like crystal \{1.5 mm (length) \times 15 \mu m (width) \times 8 \mu m (depth)\} of $^{\text{Pen}}$ by alternate irradiation (385–740 nm, 60 mW/cm$^2$, 2 s) and heating (105–110 °C, 30 min).
Fig. S5 Bending and unbending of a rod-like crystal \{2.1 \text{ mm} (length) \times 20 \text{ µm} (width) \times 8 \text{ µm} (depth)\} of $1^\text{Pen}$ by prolonged photoirradiation from the right side (385–740 nm, 20 mW/cm$^2$).
**Fig. S6** Photoirradiation of a rod-like crystal of $1^{\text{Pen}}$ for X-ray diffraction analysis: the crystal was rotated around its long axis ($c$-axis) and irradiated uniformly.
Fig. S7 ORTEP drawings of $2^{\text{hpa}}$ with 50% probability ellipsoids at (a) $-165\degree$, (b) $-95\degree$ and (c) $-25\degree$ 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 μm (width) x 8 μm (depth)} of 1\textsuperscript{Pen}. The crystal was irradiated from right side (385–740 nm, 60 mW/cm\textsuperscript{2}, 5 s).

**Video S2.** Reversible bending of a rod-like crystal {4.8 mm (length) x 44 μm (width) x 20 μm (depth)} of 1\textsuperscript{Pen}. First, the crystal was irradiated from right side, and then from left side (385–740 nm, 20 mW/cm\textsuperscript{2}, 10 s).