Electronic Supplementary Material (ESI) for Dalton Transactions.

Electronic Supplementary Information (ESI) – Table of Contents

Unusual motion of *n*-methoxypropyl moiety observed in the photochromic crystals of an organorhodium dithionite complex with *n*-methoxypropyltetramethylcyclopentadienyl ligands

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Experimental details

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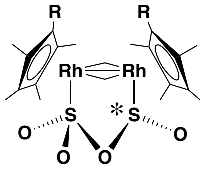
Experimental details

General: All experiments were performed under a dry argon atmosphere using standard Schlenk techniques. All chemicals were obtained from commercial sources and used as received. The crystals were irradiated using a xenon-lump (Asahi Spectra, Max-301: 300 W, 385-740 nm). The crystals were uniformly heated using a EYELA RCH-1000 heating stirrer. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL JNM ECS-400 FT-NMR spectrometer in $CDCl_3$. Chemical shifts were referenced to *protio* solvent impurities (^{1}H: δ 7.26, ^{13}C: δ 77.16 ($CDCl_3$)). Infrared spectra were obtained with the KBr method on a JASCO 4600 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 of the crystals were recorded by using a Leica DMLP polarizing microscope connected with a digital camera (Nikon digital sight DS-U1). Elemental analyses were performed by A Rabbit Science Co., Ltd.

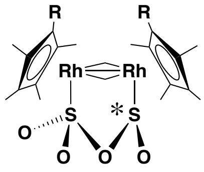
X-ray crystallography: All measurements were made on a Rigaku XtaLAB P200 diffractometer with confocal monochromated Mo Kα radiation (λ = 0.71070 Å). Data were collected and processed using CrysAlisPro[1] software (Rigaku). The data were corrected for Lorentz and polarisation effects. Empirical absorption corrections were applied. The structures were solved by a direct method: SHELXT (Ver. 2014/5)[2] and expanded using a Fourier technique. All calculations were performed using the CrystalStructure[3] crystallographic software package except for refinement, which was performed using SHELXL (Ver. 2014/7)[4]. The absolute structures are confirmed by Flack parameter.[5] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model.

The occupancy factors of the oxygen atoms of samples 2–6 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±0.2. 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: 2113493 (Sample 1), 2113494 (Sample 2), 2113495 (Sample 3), 2113496 (Sample 4), 2113497 (Sample 5), 2113498 (Sample 6), 2113499 (Sample 7).

Syntheses

The *n*-methoxypropyl derivative ligand precursor, $\mathrm{HCp^{MPro}}$ ($\mathrm{Cp^{MPro}} = \eta^5\text{-}\mathrm{C_5Me_4}\textit{n}\text{-}\mathrm{C_3H_6OCH_3}$), was synthesized by modifying the procedure for $\mathrm{HCp^{Pen}}$ ($\mathrm{Cp^{Pen}} = \eta^5\text{-}\mathrm{C_5Me_4}\textit{n}\text{-}\mathrm{C_5H_{11}}$).[6] The starting material, *trans*-$[(\mathrm{RhCp^{MPro}})_2(\mu\text{-}\mathrm{CH_2})_2\mathrm{Cl_2}]$, was synthesized by modifying the procedure for the corresponding $\mathrm{Cp^{Me}}$ ($\eta^5\text{-}\mathrm{C_5Me_5}$) analogue.[7]

$[(\mathrm{RhCp^{MPro}})_2(\mu\text{-}\mathrm{CH_2})_2(\mu\text{-}\mathrm{O_2SSO_2})]$ (**1**$^{\mathrm{MPro}}$): A mixture of *trans*-$[(\mathrm{RhCp^{MPro}})_2(\mu\text{-}\mathrm{CH_2})_2\mathrm{Cl_2}]$ (629 mg, 0.91 mmol) and $\mathrm{Na_2S_2O_4}$ (271 mg, 1.52 mmol) in MeOH (100 mL) was stirred for 12 h under Ar 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 $\mathrm{CH_2Cl_2}$ and the insoluble solid was filtered off. Removal of the solvent afforded **1**$^{\mathrm{Mpro}}$ as a red-orange solid. This solid was washed with $\mathrm{Et_2O}$ (Yield: 459 mg, 67%). Single crystals suitable for X-ray diffraction analysis were obtained from a saturated solution of **1**$^{\mathrm{MPro}}$ in $\mathrm{CH_3COOEt/CH_2Cl_2}$ (6/1) in the dark at room temperature.

^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$): δ 9.46 (2H, s, μ-$\mathrm{CH_2}$), 8.59 (2H, s, μ-$\mathrm{CH_2}$), 3.37 (4H, t, $\mathrm{C_5Me_4CH_2CH_2C}\mathit{H_2}\mathrm{OCH_3}$), 3.33 (6H, s, $\mathrm{C_5Me_4CH_2CH_2CH_2OC}\mathit{H_3}$), 2.31 (4H, t, $\mathrm{C_5Me_4C}\mathit{H_2}\mathrm{CH_2CH_2OCH_3}$), 1.86 (12H, s, $\mathrm{C_5}\mathit{Me}_4\textit{n}\text{-}\mathrm{C_4H_9O}$), 1.86 (12H, s, $\mathrm{C_5}\mathit{Me}_4\textit{n}\text{-}\mathrm{C_4H_9O}$), 1.68 (4H, m, $\mathrm{C_5Me_4CH_2}\mathit{CH_2}\mathrm{CH_2CH_2CH_3}$). ^{13}C NMR (100 MHz, $\mathrm{CDCl_3}$): δ 173.4 (μ-$\mathrm{CH_2}$), 106.4 ($\mathit{C}_5\mathrm{Me_4}\textit{n}\text{-}\mathrm{C_4H_9O}$), 104.4 ($\mathit{C}_5\mathrm{Me_4}\textit{n}\text{-}\mathrm{C_4H_9O}$), 104.3 ($\mathit{C}_5\mathrm{Me_4}\textit{n}\text{-}\mathrm{C_4H_9O}$), 71.3 ($\mathrm{C_5Me_4CH_2CH_2}\mathit{C}\mathrm{H_2OCH_3}$), 58.5 ($\mathrm{C_5Me_4CH_2CH_2CH_2O}\mathit{C}\mathrm{H_3}$), 29.3 ($\mathrm{C_5Me_4}\mathit{C}\mathrm{H_2CH_2CH_2OCH_3}$), 21.1 ($\mathrm{C_5Me_4CH_2}\mathit{C}\mathrm{H_2CH_2OCH_3}$), 9.48($\mathrm{C_5}\mathit{Me}_4\textit{n}\text{-}\mathrm{C_4H_9O}$), 9.29 ($\mathrm{C_5}\mathit{Me}_4\textit{n}\text{-}\mathrm{C_4H_9O}$). Anal. Calc. for $\mathrm{C_{28}H_{46}O_6Rh_2S_2}$: C, 44.92; H, 6.19. Found: C, 44.92; H, 6.28%.

[(RhCp^{MPro})$_2$(μ-CH$_2$)$_2$(μ-O$_2$SOSO)] (**2**^{Mpro}): The red-orange crystals of **1**^{Mpro} were irradiated with the xenon-lump (385-740 nm, 60 mW/cm^2) for 2 h under Air at room temperature. The yellow-orange crystals of **2**^{Mpro} were obtained quantitatively.

^{1}H NMR (400 MHz, CDCl$_3$): δ 9.51 (1H, s, μ-CH$_2$), 9.06 (1H, s, μ-CH$_2$), 8.62 (1H, s, μ-CH$_2$), 8.16 (1H, s, μ-CH$_2$), 3.37 (2H, t, $\mathrm{C_5Me_4CH_2CH_2C}\mathit{H_2}\mathrm{OCH_3}$), 3.36 (2H, t, $\mathrm{C_5Me_4CH_2CH_2C}\mathit{H_2}\mathrm{OCH_3}$), 3.33 (3H, s, $\mathrm{C_5Me_4CH_2CH_2CH_2OC}\mathit{H_3}$), 3.33 (3H, s, $\mathrm{C_5Me_4CH_2CH_2CH_2OC}\mathit{H_3}$), 2.36-2.17 (4H, m, $\mathrm{C_5Me_4C}\mathit{H_2}\mathrm{CH_2CH_2OCH_3}$), 1.86-1.84 (12H, m, $\mathrm{C_5}\mathit{Me_4n}\text{-}\mathrm{C_4H_9O}$), 1.77-1.75 (12H, m, $\mathrm{C_5}\mathit{Me_4n}\text{-}\mathrm{C_4H_9O}$), 1.71-1.63 (4H, m, $\mathrm{C_5Me_4CH_2C}\mathit{H_2}\mathrm{CH_2OCH_3}$). ^{13}C NMR (100 MHz, CDCl$_3$): δ 178.0 (μ-CH$_2$), 168.7 (μ-CH$_2$), 107.1 ($\mathit{C_5}\mathrm{Me_4}\mathit{n}\text{-}\mathrm{C_4H_9O}$), 107.0 ($\mathit{C_5}\mathrm{Me_4}\mathit{n}\text{-}\mathrm{C_4H_9O}$), 105.3 ($\mathit{C_5}\mathrm{Me_4}\mathit{n}\text{-}\mathrm{C_4H_9O}$), 105.1 ($\mathit{C_5}\mathrm{Me_4}\mathit{n}\text{-}\mathrm{C_4H_9O}$), 105.1 ($\mathit{C_5}\mathrm{Me_4}\mathit{n}\text{-}\mathrm{C_4H_9O}$), 104.9 ($\mathit{C_5}\mathrm{Me_4}\mathit{n}\text{-}\mathrm{C_4H_9O}$), 104.9 ($\mathit{C_5}\mathrm{Me_4}\mathit{n}\text{-}\mathrm{C_4H_9O}$), 104.3 ($\mathit{C_5}\mathrm{Me_4}\mathit{n}\text{-}\mathrm{C_4H_9O}$), 71.6 ($\mathrm{C_5Me_4CH_2CH_2}\mathit{C}\mathrm{H_2OCH_3}$), 58.6 ($\mathrm{C_5Me_4CH_2CH_2CH_2O}\mathit{C}\mathrm{H_3}$) 29.4 ($\mathrm{C_5Me_4CH_2}\mathit{C}\mathrm{H_2CH_2OCH_3}$), 29.2 ($\mathrm{C_5Me_4CH_2}\mathit{C}\mathrm{H_2CH_2OCH_3}$), 21.2 ($\mathrm{C_5Me_4}\mathit{C}\mathrm{H_2CH_2CH_2OCH_3}$), 21.2 ($\mathrm{C_5Me_4}\mathit{C}\mathrm{H_2CH_2CH_2OCH_3}$), 9.69 ($\mathrm{C_5}\mathit{Me_4n}\text{-}\mathrm{C_4H_9O}$), 9.65 ($\mathrm{C_5}\mathit{Me_4n}\text{-}\mathrm{C_4H_9O}$), 9.54 ($\mathrm{C_5}\mathit{Me_4n}\text{-}\mathrm{C_4H_9O}$), 9.52 ($\mathrm{C_5}\mathit{Me_4n}\text{-}\mathrm{C_4H_9O}$), 9.42 ($\mathrm{C_5}\mathit{Me_4n}\text{-}\mathrm{C_4H_9O}$), 9.32 ($\mathrm{C_5}\mathit{Me_4n}\text{-}\mathrm{C_4H_9O}$), 9.13 ($\mathrm{C_5}\mathit{Me_4n}\text{-}\mathrm{C_4H_9O}$), 9.10 ($\mathrm{C_5}\mathit{Me_4n}\text{-}\mathrm{C_4H_9O}$).

References

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

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

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

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6 H. Nakai, K. Matsuba, M. Akimoto, T. Nozaki, T. Matsumoto, K. Isobe, M. Irie and S. Ogo, *Chem. Commun.*, 2016, **52**, 4349.

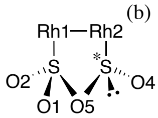
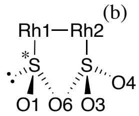
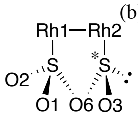
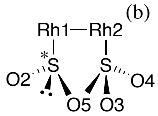
7 H. Nakai, T. Nonaka, Y. Miyano, M. Mizuno, Y. Ozawa, K. Toriumi, N. Koga, T. Nishioka, M. Irie and K. Isobe, *J. Am. Chem. Soc.*, 2008, **130**, 17836.

Tables

Table S1 Experimental conditions and crystallographic data for samples 1–7

	Sample 1 $\mathbf{1}^{\mathrm{MPro}}$	Sample 2 $\mathbf{1}^{\mathrm{MPro}} : \mathbf{2}^{\mathrm{MPro}} = 48 : 52$	Sample 3 $\mathbf{1}^{\mathrm{MPro}} : \mathbf{2}^{\mathrm{MPro}} = 23 : 77$	Sample 4 $\mathbf{1}^{\mathrm{MPro}} : \mathbf{2}^{\mathrm{MPro}} = 6 : 94$	Sample 5 $\mathbf{1}^{\mathrm{MPro}} : \mathbf{2}^{\mathrm{MPro}} = 51 : 49$	Sample 6 $\mathbf{1}^{\mathrm{MPro}} : \mathbf{2}^{\mathrm{MPro}} = 75 : 25$	Sample 7 $\mathbf{1}^{\mathrm{MPro}} : \mathbf{2}^{\mathrm{MPro}} = 100 : 0$
Photoirradiation time/temperature (min / ºC)	0 / 23	20 / 23	40 / 23	120 / 23	–	–	–
Heating time/temperature (h / ºC)	–	–	–	–	6 / 70	12 / 70	48 / 70
Data collection temperature (ºC)	23						
Formula	$C_{28}H_{46}S_2O_6Rh_2$						
Fw	748.60						
Crystal system	monoclinic						
Space group	Cc						
a (Å)	15.0178(5)	15.0709(6)	15.1193(5)	15.1520(6)	15.0590(6)	15.0793(6)	15.0360(6)
b (Å)	19.5152(7)	19.4318(9)	19.3382(9)	19.2929(11)	19.1869(8)	19.4818(10)	19.5219(8)
c (Å)	10.5665(3)	10.6012(3)	10.6585(5)	10.7055(5)	10.7664(4)	10.5855(4)	10.5714(4)
α (deg)	90.0000	90.0000	90.0000	90.0000	90.0000	90.0000	90.0000
β (deg)	93.806(3)	93.251(3)	92.909(4)	92.884(4)	95.169(3)	93.612(3)	93.949(3)
γ (deg)	90.0000	90.0000	90.0000	90.0000	90.0000	90.0000	90.0000
V (Å^3)	3089.95(18)	3099.6(2)	3112.3(2)	3125.5(3)	3098.1(2)	3103.5(2)	3095.7(2)
Z	4						
μ (cm^{-1})	12.39	12.35	12.30	12.25	12.36	12.34	12.37
F(000)	1536.00	1536.00	1536.00	1536.00	1536.00	1536.00	1536.00
D_{calcd}(g/cm^3)	1.609	1.604	1.598	1.591	1.605	1.602	1.606
Reflections collected	16536	18268	16997	18758	17280	16265	16413
Independent reflection	7972 (R_{int} = 0.0297)	8023 (R_{int} = 0.0296)	7191 (R_{int} = 0.0302)	8106 (R_{int} = 0.0363)	7672 (R_{int} = 0.0295)	7491 (R_{int} = 0.0270)	7740 (R_{int} = 0.0271)
Data/parameters	7972/353	8023/371	7191/371	8106/370	7672/371	7491/362	7740/353
R_1 [$I > 2\sigma(I)$]	0.0280	0.0356	0.0374	0.0422	0.0333	0.0343	0.0331
wR_2 (all data)	0.0737	0.0963	0.0985	0.1088	0.0817	0.0862	0.0825
Goodness-of-fit	1.043	1.030	1.054	1.055	1.042	1.042	1.052
Flack parameter	-0.01(2)	-0.01(3)	-0.05(4)	-0.06(3)	-0.04(2)	-0.02(2)	-0.05(2)

Table S2 Percentage population of the isomers, $\mathbf{1}^{\mathrm{MPro}}$ and $\mathbf{2a}$–$\mathbf{d}^{\mathrm{MPro}}$, in the crystal(a)

	$\mathbf{1}^{\mathrm{MPro}}$	(b)  $\mathbf{2a}^{\mathrm{MPro}}$ (*R*)	(b)  $\mathbf{2b}^{\mathrm{MPro}}$ (*R*)	(b)  $\mathbf{2c}^{\mathrm{MPro}}$ (*S*)	(b)  $\mathbf{2d}^{\mathrm{MPro}}$ (*S*)	$\mathbf{2}^{\mathrm{MPro}}$ (total)
Sample 1	100	0	0	0	0	0
Sample 2	48	0	15	23	14	52
Sample 3	23	2	18	34	23	77
Sample 4	6	5	14	49	26	94
Sample 5	51	0	2	26	21	49
Sample 6	75	0	13	12	0	25
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 sulfur-bound oxygen atoms. Although the crystal has mirror images of $\mathbf{2a}$–$\mathbf{d}^{\mathrm{MPro}}$, 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, $\mathbf{2a}$–$\mathbf{d}^{\mathrm{MPro}}$, 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 isomers $\mathbf{2a}$–$\mathbf{d}^{\mathrm{MPro}}$ were calculated from the simultaneous equations based on the occupancy of the sulfur-bound oxygen atoms determined by X-ray diffraction analysis. In the case of sample 2, the equations were as follows:

$$0.86\ (\text{occupancy of } O_1) = \mathbf{2a}^{\mathrm{MPro}} + \mathbf{2b}^{\mathrm{MPro}} + \mathbf{2c}^{\mathrm{MPro}} + \mathbf{1}^{\mathrm{MPro}}$$

$$0.85\ (\text{occupancy of } O_2) = \mathbf{2a}^{\mathrm{MPro}} + \mathbf{2c}^{\mathrm{MPro}} + \mathbf{2d}^{\mathrm{MPro}} + \mathbf{1}^{\mathrm{MPro}}$$

$$1.00\ (\text{occupancy of } O_3) = \mathbf{2b}^{\mathrm{MPro}} + \mathbf{2c}^{\mathrm{MPro}} + \mathbf{2d}^{\mathrm{MPro}} + \mathbf{1}^{\mathrm{MPro}}$$

$$0.77\ (\text{occupancy of } O_4) = \mathbf{2a}^{\mathrm{MPro}} + \mathbf{2b}^{\mathrm{MPro}} + \mathbf{2d}^{\mathrm{MPro}} + \mathbf{1}^{\mathrm{MPro}}$$

$$0.14\ (\text{occupancy of } O_5) = \mathbf{2a}^{\mathrm{MPro}} + \mathbf{2d}^{\mathrm{MPro}}$$

$$0.38\ (\text{occupancy of } O_6) = \mathbf{2b}^{\mathrm{MPro}} + \mathbf{2c}^{\mathrm{MPro}}$$

$$\mathbf{2a}^{\mathrm{MPro}} = 0.000,\ \mathbf{2b}^{\mathrm{MPro}} = 0.150,\ \mathbf{2c}^{\mathrm{MPro}} = 0.230,\ \mathbf{2d}^{\mathrm{MPro}} = 0.140,\ \mathbf{1}^{\mathrm{MPro}} = 0.480.$$

Figures

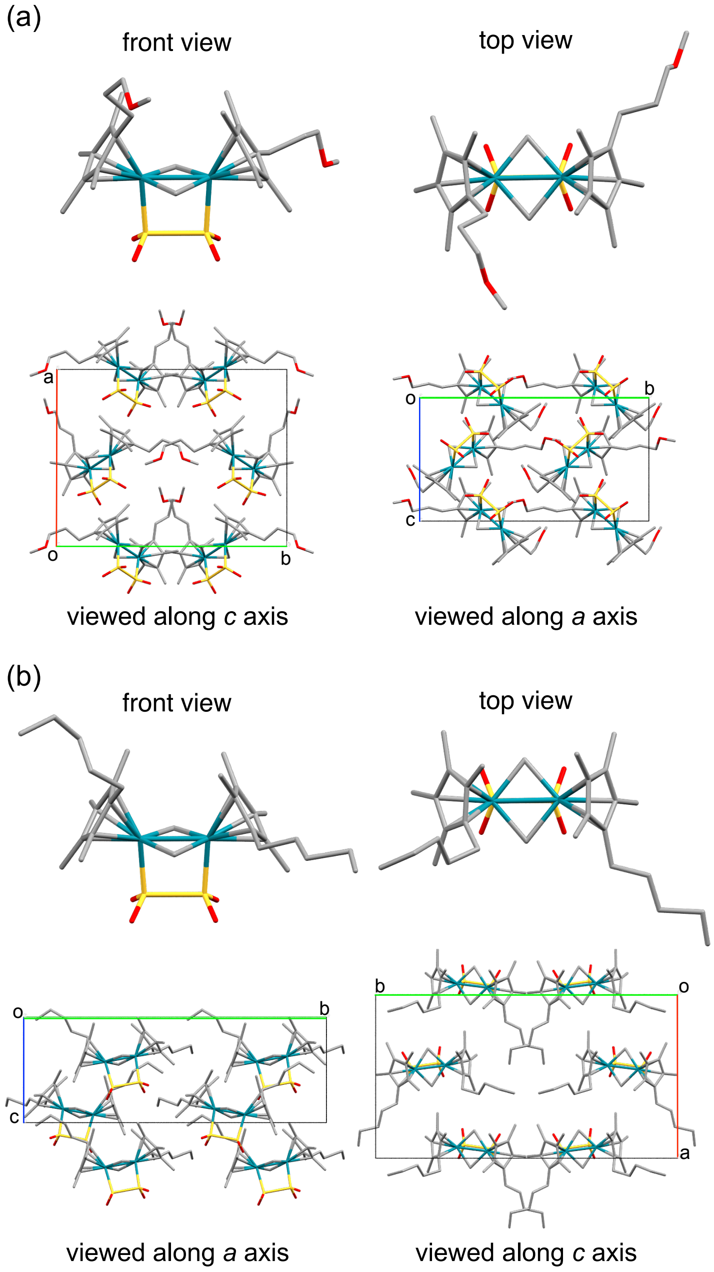


Fig. S1 Capped stick drawings (front and top views) and molecular packing diagrams of (a) $\mathbf{1}^{\mathrm{MPro}}$ and (b) $\mathbf{1}^{\mathrm{Pen}}$ with *n*-pentyl moieties (*Chem*. *Commun*., 2016, **52**, 4349).

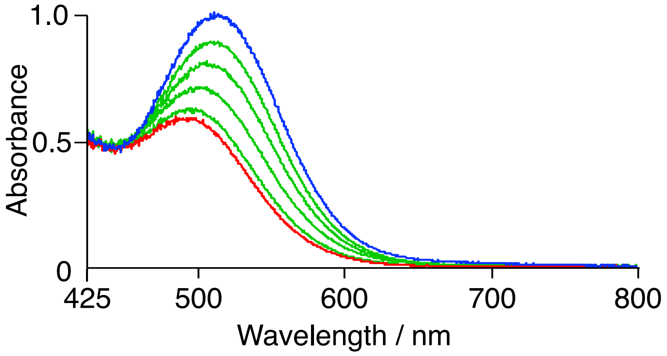


Fig. S2 UV-vis spectral changes from $\mathbf{1}^{\mathrm{MPro}}$ (blue) to $\mathbf{2}^{\mathrm{MPro}}$ (red) in a microcrystalline powder film.

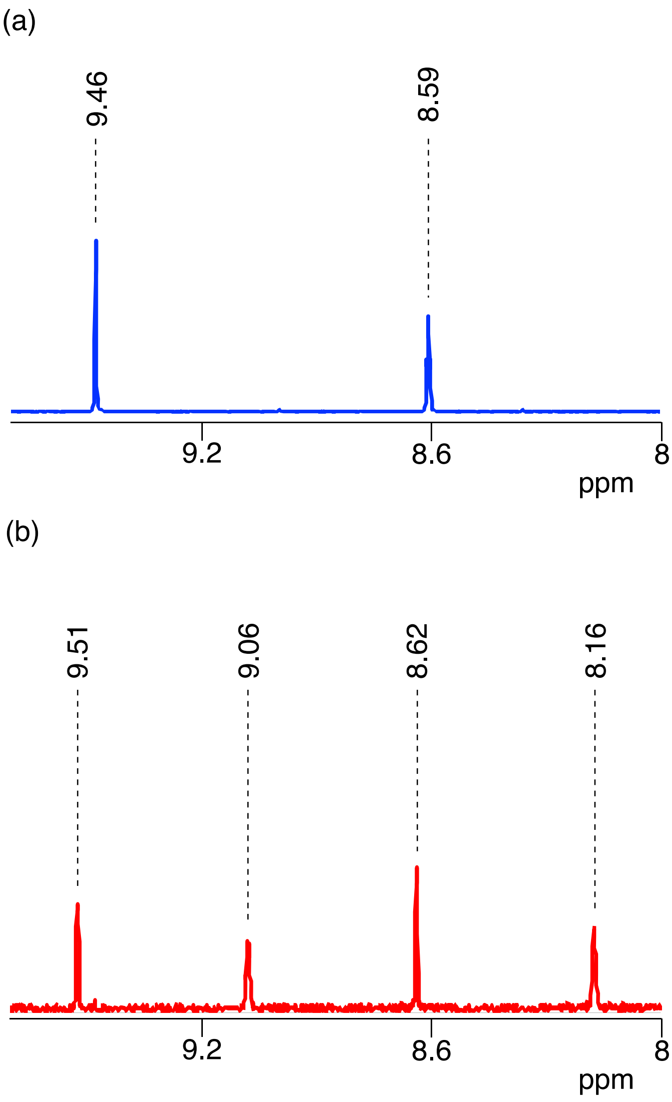
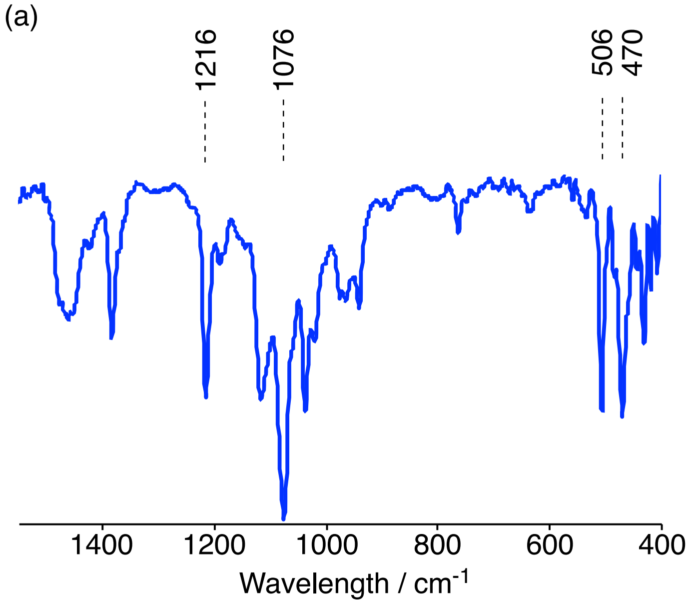


Fig. S3 ^{1}H NMR spectra of **1**$^{\mathrm{MPro}}$ (blue) and (b) **2**$^{\mathrm{MPro}}$ (red) in $CDCl_3$ in the range of μ-CH_2 signals.



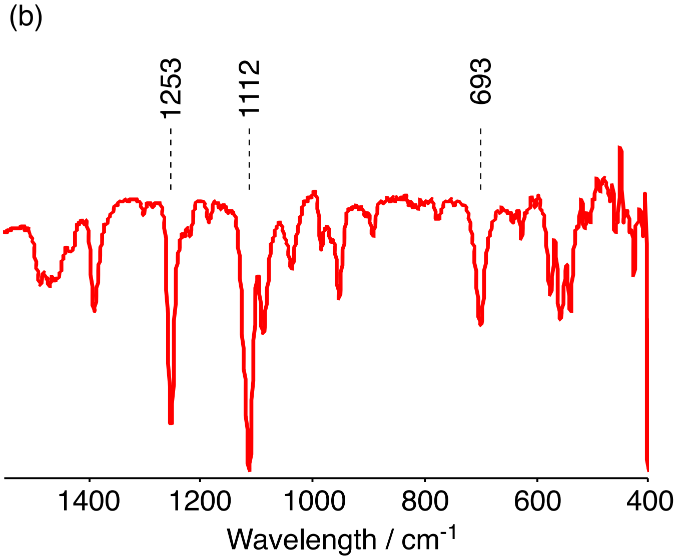


Fig. S4 IR spectra of (a) **1**$^{\mathrm{MPro}}$ (blue) and (b) **2**$^{\mathrm{MPro}}$ (red) in KBr.

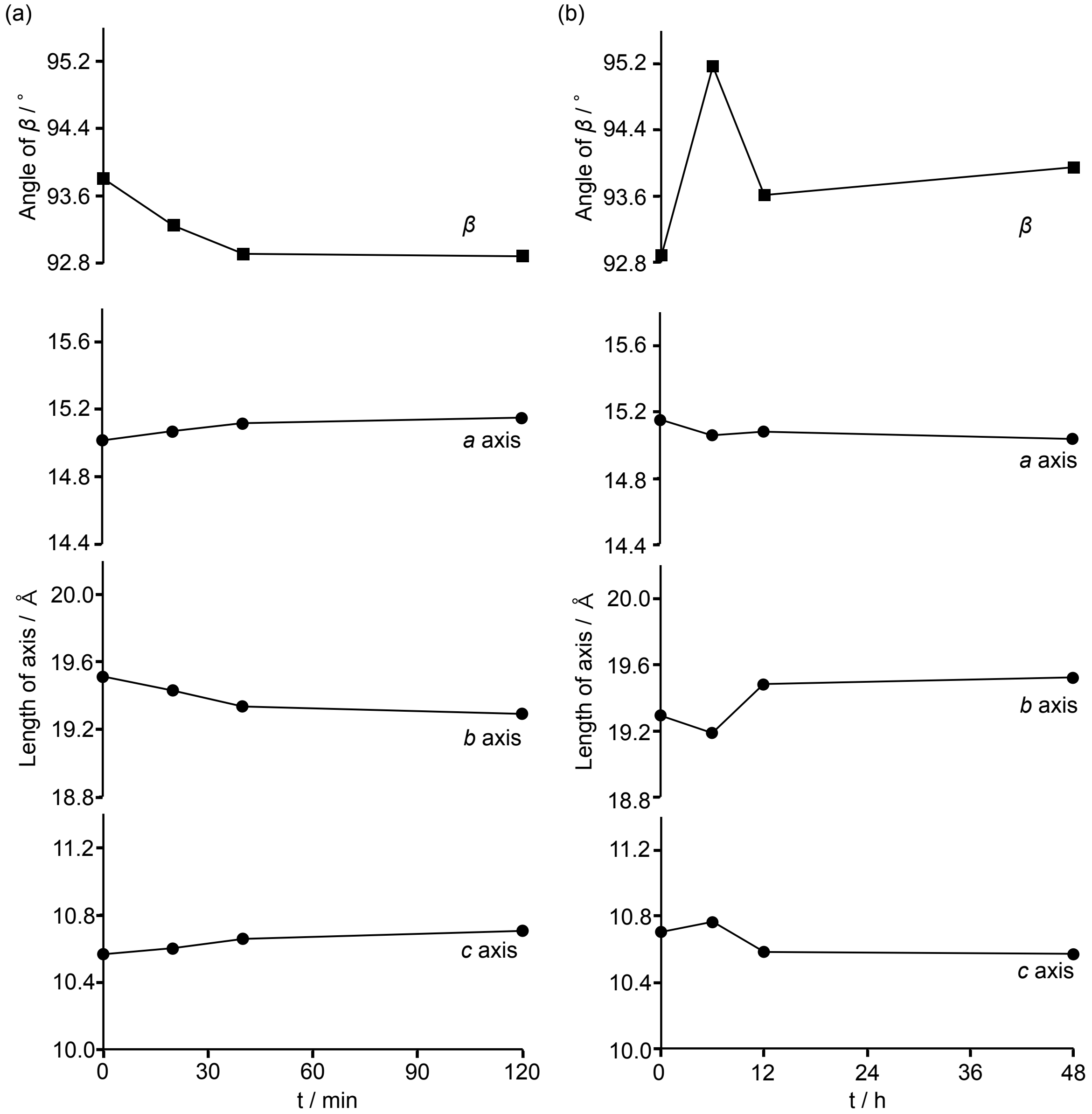


Fig. S5 (a) Changes in the unit cell parameters (β angle and a, b, and c axes) with (a) irradiation (samples 1–4, 0 min data: sample 1) and (b) heating time (samples 4–7, 0 h data: sample 4). X-ray diffraction data were recorded at 23 ºC. Crystal size: 0.20 x 0.15 x 0.10 mm^3.