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Photochromic Crystals

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Direct Observation of Photochromic Dynamics in the Crystalline State of an Organorhodium Dithionite Complex**

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One of the essential approaches to developing molecular memory devices and switching materials is to synthesize molecules with highly efficient switching functions based on reversible isomerization reactions that respond to external stimuli.[1–3] Among these, photoinduced crystalline-state reac-

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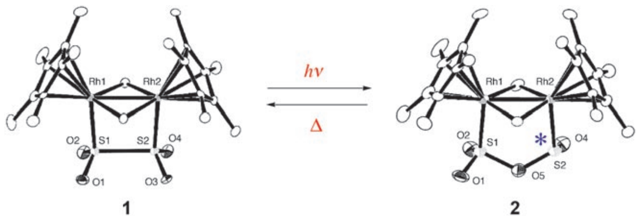
tions proceeding with regio-, stereo-, and even enantiospecificity are the most promising tools for constructing high-density recording media and smart switching materials.[4,5] To date, only a limited number of synthetic methodologies and crystalline-state photochromic compounds have been reported, and their photochromic reaction mechanisms and dynamics are not well analyzed as a result of the low degree of isomerization and instability of the photochromic compounds in the solid phase.[6–10] Our coordination-chemistry approach towards the synthesis of new switching-functional molecular crystals using the $(RhCp^*)_2(\mu\text{-}CH_2)_2$ fragment ($Cp^* = \eta^5\text{-}C_5Me_5$), which can accept two sulfur atoms coordinated parallel to the Rh–Rh bond,[11] and the external-stimulus-responsive $S_2O_4^{2-}$ ion as ligand[12] led successfully to the formation of uniquely photoresponsive and first side-on dithionite complex $[(RhCp^*)_2(\mu\text{-}CH_2)_2(\mu\text{-}O_2SSO_2)]$ (**1**). Herein we disclose the following two processes in single crystals of **1** (Figure 1): 1) fully reversible crystalline-state photochromism between $\mu\text{-}O_2SSO_2$ and $\mu\text{-}O_2SOSO$ complexes (red), and 2) stereoselective oxygen-atom transfer and stereospecific transformation of the photochemically generated $\mu\text{-}O_2SOSO$ isomers into the most stable one (blue).



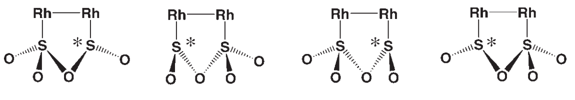
1 **2**

Figure 1. Two processes in a crystal: 1) fully reversible crystalline-state photochromism between $\mu\text{-}O_2SSO_2$ and $\mu\text{-}O_2SOSO$ complexes (red), and 2) stereoselective oxygen-atom transfer and stereospecific transformation of the photochemically generated $\mu\text{-}O_2SOSO$ isomers into the most stable isomer (blue). ORTEP plots of **1** and **2** with 50% probability ellipsoids. Hydrogen atoms are omitted for clarity.

Crystals of **1** suitable for X-ray diffraction analysis were grown from a solution in ethyl acetate/dichloromethane at room temperature. Figure 1 (left) shows the ORTEP plot of **1**. The $\mu\text{-}O_2SSO_2$ ligand in **1** has a weak S–S bond of 2.330(2) Å. On irradiation with the light from two halogen lamps (12 V, 75 W) for 140 h, the red-orange crystals ($\lambda_{max} = 510$ nm, crystal size: $0.08 \times 0.06 \times 0.02$ mm) of **1** change to yellow-orange crystals ($\lambda_{max} = 475$ nm) of a new isomer, $[(RhCp^*)_2(\mu\text{-}CH_2)_2(\mu\text{-}O_2SOSO)]$ (**2**), with almost 100% interconversion ratio (to our knowledge, crystalline-state photochromism usually proceeds with considerably lower interconversion ratios of less than 15%[7–9]) and with about 1% expansion in unit-cell volume from 2319.2(10) to 2334(1) $Å^3$. Complex **2** contains new oxysulfide species O_2SOSO with an oxo bridge between the two S atoms: S1 has two terminal O atoms, while S2 has only one terminal O atom and is asymmetric (Figure 1, right). The O_2SOSO type of oxysulfur and oxysulfide compounds is unknown to date but has been theoretically calculated[13]. The bridging S1–O5 and S2–O5 bonds in **2** differ significantly in length (S1–O5 1.709(5), S2–O5 1.636(6) Å), and the latter has double-bond character. Although **2** has an asymmetric sulfur atom S2, the reaction gives pairs of enantiomers in crystals because of the centrosymmetric space group $P2_1/n$. On leaving crystals of **2** in the dark for three weeks at room temperature, the back reaction takes place and leads to complete regeneration of crystals of **1** (exothermic reaction with liberation of about 4.5 kcal mol^{-1} of heat according to differential scanning calorimetry). The bonding character in **2** indicates that selective cleavage of the weak S1–O5 bond is the lowest-energy path for returning to complex **1**; this may be the only path for isomerization to **1**.

Thus, unusual unimolecular type T inverse photochromism [i.e., the back reaction occurs thermally, $\lambda_{max}(\mathbf{1}) > \lambda_{max}(\mathbf{2})$][14] in the crystal has been observed for an organorhodium compound. The photochromic system is stable and repeatable in the crystalline state. In contrast, in solution the photoreaction gives a mixture of **2** and further oxidation products such as $[(RhCp^*)_2(\mu\text{-}CH_2)_2(\mu\text{-}SO_3)]$.[15] It is noteworthy that the absorption coefficient of λ_{max} in **2** is smaller than that in **1** by about one-third (see the Supporting Information): as the photoreaction proceeds, light is able to pass more easily through the crystal.[16] These physical properties result in the unique full reversibility, which is advantageous for clarifying the reaction dynamics by spectroscopic methods (see the Supporting Information) and other techniques.

The crystalline-state photochromic process can be directly followed by conventional single-crystal X-ray diffraction. During the photoreaction positional disorder of the oxygen atoms (see the Supporting Information) and occupancy changes with irradiation time are observed in X-ray diffraction analyses. In contrast, the thermal back reaction does not show any disorder phenomena except for that due to the formation of **1**. This observation is consistent with the bonding character in **2**. A careful analysis of time dependence of the positional disorder[17–19] and the S···S distance during photoreaction at 20°C indicates that at the initial stage of the reaction (unconverted starting complex exists to 72%) four species **2a–d** that cause the positional disorder of the oxygen atoms are generated in respective yields of 10, 8, 5, and 5% (Figure 2 and Table 1). In the present treatment only one asymmetric unit in the crystal was considered.



2a (*R* form) **2b** (*R* form) **2c** (*S* form) **2d** (*S* form)

Figure 2. Stereoisomers of **2**. The Cp* and $\mu\text{-}CH_2$ ligands are omitted for clarity.

Isomers **2a** and **2c** are a pair of enantiomers, **2a** and **2b** are identical species but differ orientationally in the cavity, and **2c** and **2d** are also identical but differ in orientation. Isomers of **2a–d** exist in the *trans* form. We found no evidence for the existence of the *cis* isomer in the disorder analysis, and DFT calculations also suggest that the *cis* isomer is energetically less stable than the *trans* isomer by 2.0 kcal mol^{-1} (see the Supporting Information). The population of **2a** increases

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Table 1: Percentage population of photochemically generated isomers[a] in one asymmetric unit in the crystal.

Entry[b]	*t* [h][c]	*T* [°C][c]	**1**	**2a**	**2b**	**2c**	**2d**
1	0	20	100	0	0	0	0
2	2	20	72	10	8	5	5
3	6	20	32	35	23	4	6
4	18	20	7	62	25	2	4
5	40	20	2	77	15	3	3
6	98	20	1	86	7	4	2
7	140	20	0	100	0	0	0
8	12	−158	72	5	12	8	3
9	149	−158	6	43	25	20	6

[a] All the parameters, except for entries 1 and 7, have errors of ±1% according to the estimated standard deviations of the occupancy parameters of the oxygen atoms. [b] X-ray crystallographic data were recorded at −173 °C. Crystal sizes: 0.08×0.06×0.02 mm^3 (entries 1 and 7), 0.10×0.08×0.06 mm^3 (entries 2, 3, 4, 5, and 6), and 0.08×0.06×0.02 mm^3 (entries 8 and 9). [c] Irradiation conditions.

with increasing irradiation time, and in the final stage of the reaction only **2a** is formed and the positional disorder disappears. This disappearance means that the thermodynamically unstable μ-O_2SOSO isomers generated in the crystal are converted under irradiation to the most stable species **2a**. In contrast, the photoreaction at −158 °C clearly shows a different reaction rate and population from those at 20 °C (Table 1, entries 8 and 9). The dependence of the population of the photochemically generated isomers at −158 °C on irradiation time shows that the most stable product **2a** is not necessarily generated in the highest population in the initial stage of the reaction (Table 1 and Figure 3). In the dark, the temperature dependence of the population of the isomers generated at −158 °C after 149 h of irradiation shows that isomer **2c** is directly transformed into **2a** without irradiation (see the Supporting Information). These results strongly indicate that at −158 °C mainly the kinetically controlled reaction takes place. What is responsible for the selectivity of the photoreaction at the initial stage at −158 °C and the specific formation of only **2a** in the final stage at 20 °C?

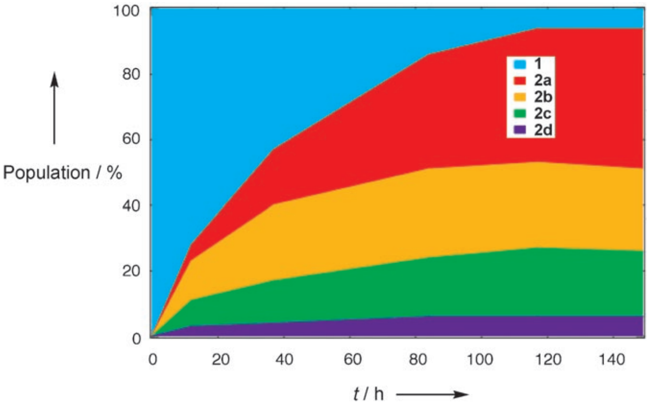

Figure 3. Change in population of the photochemically generated isomers with irradiation time at −158 °C.

We investigated possible causes for this. Since the crystals of **1** and **2** have the same space group and molecular arrangement, by comparison of a certain molecule in the unit cell of **1** with that in **2**, it can be readily seen which terminal oxygen atom in the μ-O_2SSO_2 ligand of **1** is transformed into the bridging oxygen atom in **2** (see the Supporting Information). It is the O3 atom (Figure 1). In the μ-O_2SSO_2 ligand, the four oxygen atoms are stereochemically nonequivalent in the cavity formed by six Cp* ligands: they do not have an equal chance to undergo transfer. The O3 atom is the most congested by methyl groups of the Cp* ligands (see the Supporting Information). Thus, migration of the O3 atom is more difficult compared with the other O atoms. This is the origin of the kinetically controlled reaction at −158 °C (Figure 3): the population reflects the selectivity based on the shape of the cavity in the crystal, that is, **2a** is the kinetically unfavorable product. Since **2a** accumulates through the repetitive photochromic process (**2b** (or **2d**)→**1**→**2a**, Table 1) and direct thermal conversion from **2c** to **2a** (see the Supporting Information), specificity of oxygen transfer is observed at 20 °C: **2a** is the thermodynamically favorable product. Further low-temperature X-ray analysis is in progress to elucidate whether direct thermal conversion process of **2b** (or **2d**) to **2a** is present or not.

In conclusion, we have demonstrated that a new class of photochromic compounds, a rhodium dinuclear complex **1** with the photoreactive dithionite ligand, undergoes a fully reversible crystalline-state photochromic reaction with stereoselective oxygen-atom transfer and thermodynamically controlled isomerization. This photochromic process is a repetitive crystalline-state reaction accompanied by, in addition to the color change, 1) alternating expansion–shrinkage of the crystal lattice with about 1% change in volume, 2) alternating gain–loss of the asymmetric center but with retention of the space group $P2_1/n$. Our findings offer attractive new prospects for the construction of functional molecular crystals.

Experimental Section

Detailed synthetic procedures for **1** and **2** are described in the Supporting Information.

X-ray crystallographic analysis was carried out on a Rigaku RAXIS-RAPID Imaging Plate diffractometer with $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). Crystal data for **1**: $C_{22}H_{34}O_4Rh_2S_2$, $M = 632.44$, monoclinic, space group $P2_1/n$, $Z = 4$, $T = 100$ K, $a = 8.394(2)$, $b = 36.532(8)$, $c = 8.430(2)$ Å, $\beta = 116.213(10)°$, $V = 2319.2(10)$ Å^3, GOF = 1.024, $R1 = 0.0567$ ($I > 2\sigma(I)$), $wR2 = 0.1039$ (all data). Crystal data for **2**: $C_{22}H_{34}O_4Rh_2S_2$, $M = 632.44$, monoclinic, space group $P2_1/n$, $Z = 4$, $T = 100$ K, $a = 8.339(2)$, $b = 36.750(9)$, $c = 8.447(2)$ Å, $\beta = 115.594(10)°$, $V = 2334(1)$ Å^3, GOF = 1.039, $R1 = 0.0650$ ($I > 2\sigma(I)$), $wR2 = 0.1365$ (all data). CCDC-603301 (**1**), -603302 (**2**), -612865 (entry 3 in Table 1), and -612866 (entry 9 in Table 1) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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