Photochromism in Polymorphic Crystals of a Rhodium Dithionite Complexs

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In polymorph crystal, a certain compound exists in different crystallographic structures. Studies on the polymorphic crystals of photochromic compounds with reversible switching functions are very useful for constructing new switching devices and materials. However, there are limited examples of photochromic compounds that show not only crystalline-state photochromism but also polymorphism.

In this context, we have recently demonstrated that rhodium dinuclear complexes with a photo-responsive dithionite ligand [$(Cp^{R}Rh)_2(\mu\text{-}CH_2)_2(\mu\text{-}O_2SSO_2)$] (**1**^{R}) (Me: CH_3, Pro: *n*-C_3H_7, Pen: *n*-C_5H_{11} etc.) show crystalline-state photochromism with 100% interconversion ratio; **1**^{R} shows type-*T* photochromism in which the $\mu\text{-}O_2SSO_2$ complex (**1**^{R}) isomerizes to the corresponding $\mu\text{-}O_2SOSO$ complex (**2**^{R}) by photoreaction and **2**^{R} returns to **1**^{R} by thermal reaction (Figure 1a).[1] Intriguingly, a newly prepared rhodium dithionite complex with *n*-methoxypropyl moieties (**1**^{MPro}, R = MPro; *n*-$C_3H_6OCH_3$) forms two polymorphic crystals (α- and β-crystals, Figure 1b). The difference between the α- and β-crystals is ascribed to the different arrangement of the Cp^{MPro} ligand in **1**^{MPro} (Figure 1c). Herein, we report photochromism in the α- and β-crystals of **1**^{MPro}.

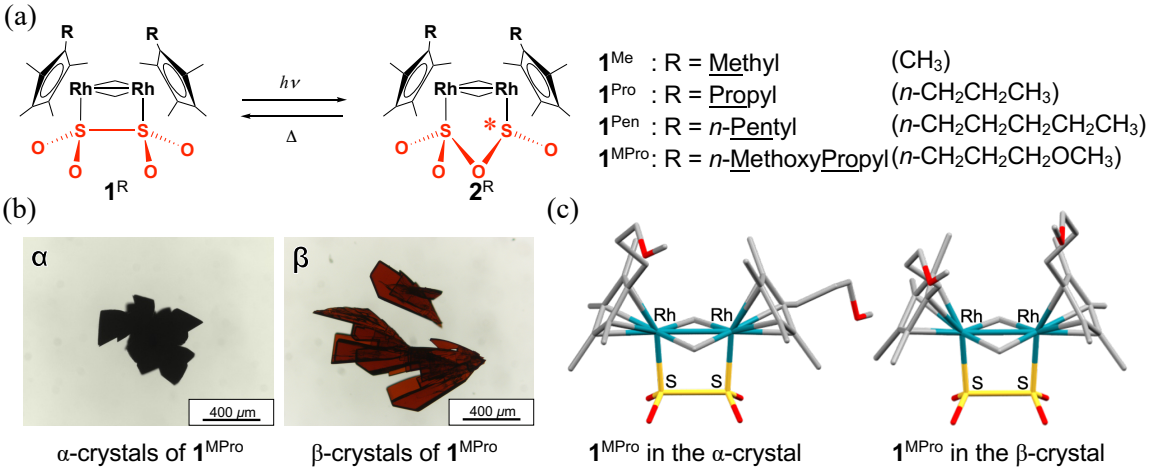

Figure 1. (a) Photochromism of rhodium dithionite complexes, **1**^{R} (R = Me, Pro, Pen, MPro etc.). (b) photographs of the α- (left) and β- (right) crystals of **1**^{MPro}. (c) Capped stick drawings of **1**^{MPro} in the α- (left) and β- (right) crystals.

1) (a) H. Nakai et al., *J. Am. Chem. Soc*. **2008**, *130*, 17836. (b) H. Nakai et al., *Chem. Commun*. **2016**, *52*, 4349. (c) H. Nakai et al., *Dalton Trans*. **2020**, *49*, 1721.