Solid-state photopolymerization of a photochromic hybrid based on Keggin tungstophosphates†

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Reversible photochromism occurring with reversible photopolymerization between 0-D and 1-D under irradiation with sunlight was clarified by X-ray analyses.

Photochromic compounds are a subject of growing interest because of their potential technological applications in the areas of information display devices, solar energy conversion, high-density memory devices, and photoelectric sensors.[1] It is well-known that one of the most important properties of polyoxometalates is the capability to accept various numbers of electrons giving rise to mixed-valency colored species (heteropolyblues or heteropolybrowns),[2] which make them suitable for photochromic and electrochromic materials.[2–4] Since the investigation of inorganic–organic hybrid materials became an expanding field, the preparation, microstructure, and photochromic process of polyoxometalates-based hybrid composites have been extensively investigated.[5]

On the other hand, despite the inherent strong barriers of simultaneous bond breaking and formation in more than one direction, single-crystal-to-single-crystal (SCSC) transformations in the solid state have been studied widely in recent years.[6,7] However, much of the work has focused on thermal-stimulated[6] or guest desorption/absorption-induced[7] types, while the photo-induced type received less attention.

Herein, we report an interesting discovery of a photo-polymerized SCSC transformation in a photochromic polyoxometalates-based hybrid, $[Gd_2(NMP)_{12}(PW_{12}O_{40})][PW_{12}O_{40}]$ (NMP = *N*-methyl-2-pyrrolidone) (**1**), in which reversible photochromism occurred with reversible structural transformation under irradiation with sunlight.

Reaction of $GdCl_3$, $H_3PW_{12}O_{40}$ and NMP in CH_3CN/H_2O (2 : 1, v/v) followed by slow evaporation at room temperature in the black position resulted in colorless single crystals.‡ X-Ray analyses‡ reveal that compound **1**, having a triclinic crystal system, exhibits an ionic, asymmetric structure consisting of the $[PW_{12}O_{40}]^{3-}$ anion and the $[Gd_2(NMP)_{12}(PW_{12}O_{40})]^{3+}$ cation in which either of Gd^{III} ions is coordinated with 6 NMP molecules and connected by $[PW_{12}O_{40}]^{3-}$ (Fig. 1a). The coordination polyhedron of Gd^{III} may be represented as a highly distorted, single-capped trigonal prism (Fig. 2a). The Gd–O bond lengths are within the range from 2.212 to 2.514 Å

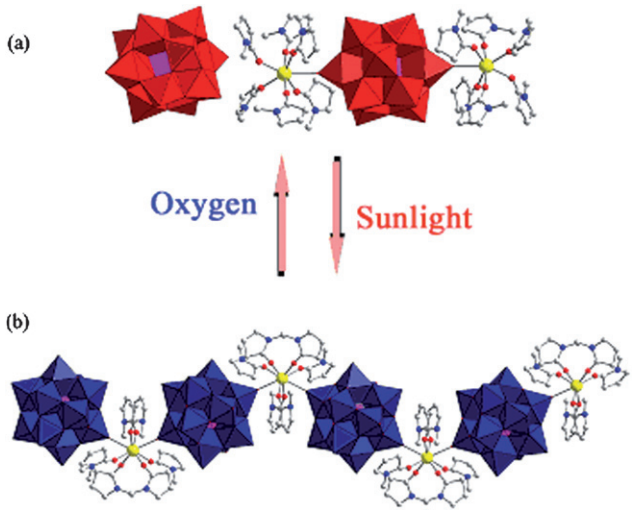

Fig. 1 Process of photochromism and SCSC transformation. (a) Ball and stick and polyhedral representations of **1**. The color code is as follows: Gd (yellow), O (red), N (blue), C (gray), WO_6 (red), PO_4 (purple); (b) ball and stick and polyhedral representations of **2**. The color code is as follows: Gd (yellow), O (red), N (blue), C (gray), WO_6 (deep-blue), PO_4 (purple).

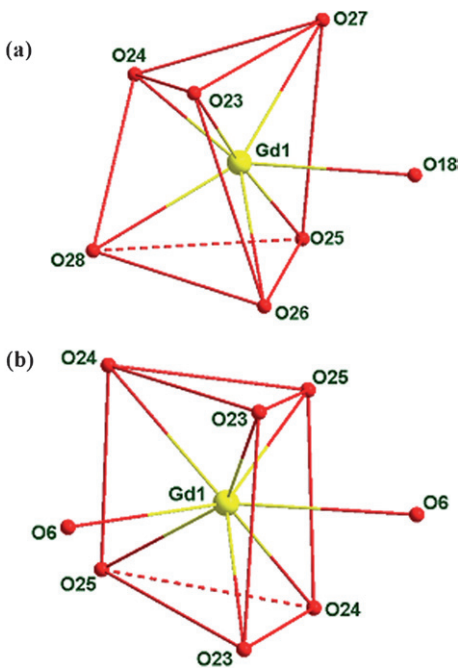

Fig. 2 (a) Coordination polyhedron around Gd^{III} in **1**; (b) coordination polyhedron around Gd^{III} in **2**.

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† Electronic supplementary information (ESI) available : Photographs of samples, and tables of selected bond lengths and angles. See DOI: 10.1039/b718523e.CCDC reference numbers 611433 and 633062. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b718523e

