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. 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), which make them suitable for photochromic and electrochromic materials. 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.

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. However, much of the work has focused on thermal-stimulated or guest desorption/absorption-induced 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, [Gd₂(NMP)₁₂(PW₁₂O₄₀)]²⁺[PW₁₂O₄₀](NMP = N-methyl-2-pyrrolidone) (1), in which reversible photochromism occurred with reversible structural transformation under irradiation with sunlight.

Reaction of GdCl₃, H₃PW₁₂O₄₀ and NMP in CH₃CN/H₂O (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 [PW₁₂O₄₀]⁻⁻ anion and the [Gd₂(NMP)₁₂(PW₁₂O₄₀)]²⁺ cation in which either of Gd³⁺ ions is coordinated with 6 NMP molecules and connected by [PW₁₂O₄₀]⁻⁻ (Fig. 1a). The coordination polyhedron of Gd³⁺ 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.

‡ 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