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

Zhang, Li-Zhi; Gu, Wen; Liu, Xin; Dong, Zhili; Li, Bing

2008

Zhang, L. Z., Gu, W., Liu, X., Dong, Z., & Li, B. (2008). Solid-state photopolymerization of a photochromic hybrid based on Keggin tungstophosphates. *CrystEngComm*, 10(6), 652-654.

<https://hdl.handle.net/10356/95787>

<https://doi.org/10.1039/b718523e>

© 2008 The Royal Society of Chemistry. This is the author created version of a work that has been peer reviewed and accepted for publication by CrystEngComm, The Royal Society of Chemistry. It incorporates referee's comments but changes resulting from the publishing process, such as copyediting, structural formatting, may not be reflected in this document. The published version is available at: [<http://dx.doi.org/10.1039/b718523e>].

Downloaded on 26 Apr 2023 20:04:04 SGT

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

Li-Zhi Zhang,^{ab} Wen Gu,^a Xin Liu,^{*a} Zhili Dong^{*b} and Bing Li^{ab}

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

DOI: 10.1039/b000000x

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-stimulated⁶ or guest desorption/absorption-induced⁷ 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)] [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]^{3–} anion and the [Gd₂(NMP)₁₂(PW₁₂O₄₀)]³⁺ cation in which either of Gd^{III} ions is coordinated with 6 NMP molecules and connected by [PW₁₂O₄₀]^{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), WO₆ (red), PO₄ (purple); (b) ball and stick and polyhedral representations of **2**. The color code is as follows: Gd (yellow), O (red), N (blue), C (gray), WO₆ (deep-blue), PO₄ (purple).

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

^aDepartment of Chemistry, Nankai University, Tianjin, 300071, People's Republic of China. E-mail: liuxin64@nankai.edu.cn; Tel: +86 2350 5020

^bSchool of Materials Science and Engineering, Nanyang Technological University, Singapore, 639798, Singapore. E-mail: zldong@ntu.edu.sg; Tel: +65 6790 6727

† 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

Fig. 3 The solid-state UV-vis spectra before (black curve) and after (blue curve) irradiation with sunlight.

(mean value 2.316 Å). The torsion angle between the top plane and the bottom plane is 27.89°.

When exposed to sunlight, colorless crystals of **1** turn deep blue gradually. This observation should be attributed to the electron transfer between electron donors of organic molecules and electron acceptors of polyoxometalate anions. The final result is that W^{VI} atoms of the polyanions are reduced and mixed-valence compounds are formed, leading to the observed photochromism.² UV-vis spectra (Fig. 3) indicated that, after irradiation with sunlight, the absorption band at 700 nm in the visible region appeared due to metal-to-metal extra intervalence charge transfer (IVCT) ($W^{5+} \rightarrow W^{6+}$).⁸ Compared with those well-reported discrete charger-transfer alkylammonium-polyoxometalates,² the speculated photochromic mechanism of **1** is slightly different. A reasonable mechanism should involve the absorption of photons by the Keggin structure, resulting in the generation of an electron-hole pair which directly oxidizes NMP into NMP^+ through O–Gd–O not the hydrogen bond.

When we performed the X-ray analyses on the resulted deep blue crystals, unexpectedly, structural transformation occurred in the photochromic hybrid and a new compound belonging to a monoclinic system, $[Gd(NMP)_6(PW_{12}O_{40})]_n$ (**2**), was obtained.† Compound **2** consists of a 1-D infinite zigzag chain built from alternate polyanions and $[Gd(NMP)_6]^{3+}$ subunits and displays an $\{(anion)M\text{-donor}\}_n$ ($M = Gd$; anion = $PW_{12}O_{40}^{3-}$; donor = NMP) type of structure (Fig. 1b). The coordination polyhedron of Gd^{III} may be represented as a distorted, bicapped trigonal prism (Fig. 2b). The Gd–O bond lengths are within the range of 2.255–2.526 Å (mean value 2.359 Å). The torsion angle between the top plane and the bottom plane is 7.29°, which is smaller than that of compound **1** ($\Delta = 20.60^\circ$).

To further contrast **1** with **2**, in the packing framework of **1**, we can find a discontinuous zigzag chain (Fig. 4). The distance of adjacent polyanions is 137.77 Å (defined by the P⋯P separation), which is equal to that in the continuous zigzag chain of **2**. The turning angle of $P\cdots Gd\cdots P$ (104.73°) in **1** is slightly smaller than that (125.81°) in **2** ($\Delta = 21.08^\circ$; the difference is almost equal to that in the torsion angle of Gd^{III} coordination polyhedrons). In addition, the NMP ligands in both **1** and **2** are highly disordered. These structural values and factors provide a potential environment for

Fig. 4 A discontinuous zigzag chain existing in the packing structures of **1**.

Fig. 5 XRPD patterns of (a) **1** and (b) **2**. The figures showed the Miller indices of each reflection ($2\theta < 14^\circ$).

the SCSC transformation. To further examine the phase purity of this system, X-ray powder diffraction was carried out on **1** and **2**, respectively (Fig. 5). A comparison between the experimental pattern and the calculated pattern (based on single-crystal data) shows that both **1** and **2** are pure.

When the crystals of **2** are placed in the air and sheltered from the light, they gradually turn back to their original colorlessness. X-Ray analyses reveal that with the color changes compound **2** simultaneously converts 1-D zigzag chains into original 0-D ionic structures. If color-changed samples are put in nitrogen atmosphere and sheltered from the light, their color does not fade, indicating that the fading process is a chemical one and that it is the oxygen in the air that has reoxidized W^V into W^{VI} , not the self-redox occurring in the system. The whole process might concisely proceed in Fig. 1. Also deserving attention, by heating at 90 °C in air under sunlight, the color and structural reversal also occur in compound **2**, which indicates that the reverse SCSC transformation of **2** to **1** can be also considered as a thermal-stimulated type; however, nothing occurs when heating is carried out in nitrogen atmosphere, which further indicates that reverse transformation of **2** to **1** is significantly affected by oxygen.

In summary, a photochromic 12-tungstophosphate-based hybrid has been synthesized, in which a reversible photopolymerization interestingly occurred. To the best of our knowledge, this communication provides the first polyoxometalates-based example of SCSC transformations. Furthermore, it is highly interesting to study the photomagnetism, electrochemistry, and photoelectricity in the system, because there is not only SCSC transformation but also deoxidized W^V atoms under irradiation with sunlight. All this work is currently in progress.

We are thankful for financial support from the National Natural Science Foundation of China (Grants 20371027 and 20071020), the Tianjin Science Foundation (Grant 033609211) and the NTU Research Scholarship.

Notes and references

‡ Synthesis of compound **1**: An aqueous solution (10 mL) containing $\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot n\text{H}_2\text{O}$ (1.3 g) and $\text{GdCl}_3 \cdot 6\text{H}_2\text{O}$ (0.1487 g, 0.4 mmol) was heated to dryness at 90 °C in a water bath. *N*-Methyl-2-pyrrolidone (0.5 mL) was then added into the resultant dry solid with stirring until the mixture became a paste. Finally, the paste was dissolved in an acetonitrile/water (2 : 1, v/v) mixed solution (10 mL), filtered and left standing to concentrate at room temperature in the dark. After a few days, colorless crystals suitable for X-ray analyses were obtained (1.16 g, yield 80 %). Anal. Calcd (%) for **1**: C 9.9, H 1.5, N 2.3; Found: C 10.1, H 1.7, N 2.2. IR (KBr, ν): 3405 (s), 2937 (w), 1641(vs), 1513 (m), 1407 (w), 1308 (w), 1260 (w), 1259 (m), 1082 (vs), 984 (vs), 895 (vs), 814 (vs), 523(m) cm^{-1} . UV-vis (solid-state, λ_{max}): 250 nm. Crystal data of **1**: $\text{C}_{60}\text{H}_{108}\text{N}_{12}\text{O}_{92}\text{P}_2\text{Gd}_2\text{W}_{24}$, $M_r = 7258.42$, triclinic, $P\bar{1}$, $a = 12.119(2)$ Å, $b = 13.598(3)$ Å, $c = 22.210(4)$ Å, $\alpha = 80.328(3)^\circ$, $\beta = 85.395(3)^\circ$, $\gamma = 67.725(3)^\circ$, $V = 3338.3(11)$ Å³, $Z = 1$, $\rho_{\text{calcd}} = 3.610$ g cm^{-3} , $2\theta_{\text{max}} = 50.04^\circ$ ($-14 \leq h \leq 14$, $-16 \leq k \leq 11$, $-26 \leq l \leq 26$), $T = 294(2)$ K, $F(000) = 3222$, GOF = 1.054, $R_1 = 0.0536$, $wR_2 = 0.1135$. CCDC 611433. Synthesis of compound **2**: When exposed to sunlight for 5 h, crystals of **1** completely turned deep blue and produced compound **2**. Anal. Calcd (%) for **2**: C 9.9, H 1.5, N 2.3; Found: C 10.2, H 1.6, N 2.3. IR (KBr, ν): 3403 (s), 2932 (w), 1639 (vs), 1514 (m), 1408 (w), 1309 (w), 1260 (w), 1259 (m), 1081 (vs), 985 (vs), 899 (vs), 809 (vs), 522 (m) cm^{-1} . UV-vis (solid-state, λ_{max}): 250, 700 nm. Crystal data of **2**: $\text{C}_{30}\text{H}_{54}\text{N}_6\text{O}_{46}\text{PGdW}_{12}$, $M_r = 3629.21$, monoclinic, $C2/c$, $a = 22.058(7)$ Å, $b = 12.811(7)$ Å, $c = 24.390(9)$ Å, $\alpha = 90^\circ$, $\beta = 107.460(6)^\circ$, $\gamma = 90^\circ$, $V = 6574(5)$ Å³, $Z = 4$, $\rho_{\text{calcd}} = 3.667$ g cm^{-3} , $2\theta_{\text{max}} = 50.02^\circ$ ($-26 \leq h \leq 23$, $-11 \leq k \leq 15$, $-26 \leq l \leq 29$), $T = 294(2)$ K, $F(000) = 6444$, GOF = 1.142, $R_1 = 0.0523$, $wR_2 = 0.1245$. CCDC 633062.

- (a) G. H. Brown, *Photochromism*, Wiley, New York, 1971; (b) J. N. Yao, K. Kashimoto and A. Fujishima, *Nature*, 1992, **355**, 624; (c) J. N. Yao, P. Chen and A. Fujishima, *J. Electroanal. Chem.*, 1996, **406**, 223; (d) S. Nagashima, M. Murata and H. Nishihara, *Angew. Chem., Int. Ed.*, 2006, **45**, 4298; (e) M. Bossi, V. Belov, S. Polyakova and S. W. Hell, *Angew. Chem., Int. Ed.*, 2006, **45**, 7462.
- T. Yamase, *Chem. Rev.*, 1998, **98**, 307.
- I. Moriguchi and J. H. Fendler, *Chem. Mater.*, 1998, **10**, 2205.
- S. Q. Liu, D. G. Kurth, H. Möhwald and D. Volkmer, *Adv. Mater.*, 2002, **14**, 225.
- (a) C. L. Hill, D. A. Bouchard, M. Kadkhodayan, M. Williamson, J. A. Schmidt and E. F. Hilinski, *J. Am. Chem. Soc.*, 1988, **110**, 5471; (b) G. R. Pedro and L. C. Morica, *Adv. Mater.*, 1997, **9**, 144; (c) P. Maguerès, S. M. Hubig, S. V. Lindeman, P. Veya and J. K. Kochi, *J. Am. Chem. Soc.*, 2000, **122**, 10073; (d) G. Zhang, W. Yang and J. Yao, *Adv. Funct. Mater.*, 2005, **15**, 1255; (e) S. Liu, H. Möhwald, D. Volkmer and D. G. Kurth, *Langmuir*, 2006, **22**, 1949.
- (a) C. Hu and U. Englert, *Angew. Chem., Int. Ed.*, 2005, **44**, 2281; (b) J.-P. Ma, Y.-B. Dong, R.-Q. Huang, M. D. Smith and C.-Y. Su, *Inorg. Chem.*, 2005, **44**, 6143; (c) J.-P. Zhang, Y.-Y. Lin, W.-X. Zhang and X. M. Chen, *J. Am. Chem. Soc.*, 2005, **127**, 14162; (d) J. D. Ranford, J. J. Vittal and D. Wu, *Angew. Chem., Int. Ed.*, 1998, **37**, 1114; (e) J. D. Ranford, J. J. Vittal, D. Wu and X. Yang, *Angew. Chem., Int. Ed.*, 1999, **38**, 3498.
- (a) C.-L. Chen, A. M. Goforth, M. D. Smith, C.-Y. Su and H.-C. zur Loye, *Angew. Chem., Int. Ed.*, 2005, **44**, 6673; (b) G. J. Halder and C. J. Kepert, *J. Am. Chem. Soc.*, 2005, **127**, 7891; (c) K. Takaoka, M. Kawano, M. Tominaga and M. Fujita, *Angew. Chem., Int. Ed.*, 2005, **44**, 2151; (d) O. Ohmori, M. Kawano and M. Fujita, *J. Am. Chem. Soc.*, 2004, **126**, 16292; (e) S. Kitagawa and K. Uemura, *Chem. Soc. Rev.*, 2005, **34**, 109; (f) C.-D. Wu and W. Lin, *Angew. Chem., Int. Ed.*, 2005, **44**, 1958; (g) M. Nihei, L. Han and H. Oshio, *J. Am. Chem. Soc.*, 2007, **129**, 5312.
- M. T. Pope, *Heteropoly and Isopoly Oxometalates*, Springer-Verlag, Berlin, 1983.