

# Sulfonium Polyoxometalates: A New Class of Solid-State Photochromic Hybrid Organic–Inorganic Materials

Khadija Hakouk,<sup>†</sup> Olivier Oms,<sup>‡</sup> Anne Dolbecq,<sup>‡</sup> Hani El Moll,<sup>‡</sup> Jérôme Marrot,<sup>‡</sup> Michel Evain,<sup>†</sup> Florian Molton,<sup>§</sup> Carole Duboc,<sup>§</sup> Philippe Deniard,<sup>†</sup> Stéphane Jobic,<sup>†</sup> Pierre Mialane,<sup>\*,‡</sup> and Rémi Dessapt<sup>\*,†</sup>

<sup>†</sup>Institut des Matériaux Jean Rouxel, Université de Nantes, CNRS, 2 rue de la Houssinière, BP 32229, 44322 Nantes cedex, France

<sup>‡</sup>Institut Lavoisier de Versailles, UMR 8180, Université de Versailles Saint-Quentin en Yvelines, 45 Avenue des Etats-Unis, 78035 Versailles cedex, France

<sup>§</sup>Université Joseph Fourier Grenoble 1/CNRS, Département de Chimie Moléculaire, UMR 5250, Institut de Chimie Moléculaire de Grenoble, FR-CNRS-2607, BP 53, 38041 Grenoble cedex 9, France

## S Supporting Information

**ABSTRACT:** For the very first time, sulfonium polyoxometalate (POM) assemblies are shown to develop efficient solid-state photochromism in ambient conditions. The optical properties of the already known  $\text{Rb}_{0.75}(\text{NH}_4)_{5.25}[(\text{Mo}_3\text{O}_8)_2\text{O}(\text{O}_3\text{PC}(\text{CH}_2\text{S}(\text{CH}_3)_2)\text{OPO}_3)_2] \cdot 8\text{H}_2\text{O}$  (**1**) and a new material  $(\text{Me}_3\text{S})_4[\text{Mo}_8\text{O}_{26}]$  (**2**) under UV excitation are investigated by diffuse reflectance spectroscopy, revealing that the color change effect is highly tunable playing with the nature of the POM. A mechanism involving the photoreduction of  $\text{Mo}^{6+}$  cations associated with electron transfers from the sulfonium cations toward the POMs is proposed.

In recent years, considerable efforts have been made to elaborate efficient solid-state photochromic materials<sup>1</sup> (organic, inorganic, or hybrid), because their ability to tune their optical properties with light is of great interest in a wide range of technological and marketable applications, such as smart windows, cosmetics, multicolor smart painting, UV sensors, optical switches, and 3D high-density optical data storage. One of the promising systems in this field are hybrid organic–inorganic materials based on polyoxometalates<sup>2</sup> (POMs) and organoammonium cations (OACs).<sup>3</sup> Notably, they offer a wide range of photoinduced coloration, with remarkable coloration contrast and highly tunable coloration and fading rates.<sup>3b,4</sup> The photochromism mechanism of the OAC/POM systems has been investigated in detail<sup>3a,4</sup> and is described in terms of a UV-induced photoreduction of the POM concomitant with an electron transfer assisted by H atom displacement from the OAC toward the POM (see Figure S1 in the Supporting Information, SI, for the detailed mechanism). Unfortunately, as the establishment of direct H-bonds between POMs and OACs is not systematic,<sup>5</sup> certain materials do not develop any photochromic activity. Hence, new strategies have been recently elaborated to better control the OAC/POM interface. For example, the hydrogen-bonding network can be anticipated in materials based on layered  $^{2-}/_{\infty}[\text{Mo}_n\text{O}_{3n+1}]^{2-}$  ( $n = 5, 7, 9$ ) units.<sup>6</sup> Alternatively, a new family of intrinsic photochromic POMs has been elaborated, in which OAC-

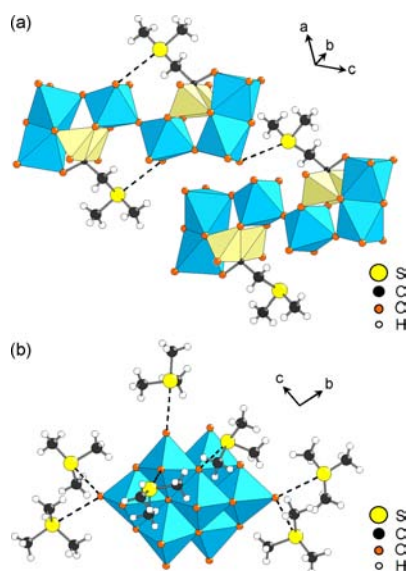
functionalized bisphosphonate (BP) ligands are directly grafted on dodeca- ( $\text{Mo}_{12}(\text{BP})_4$ )<sup>7</sup> and hexamolybdate ( $\text{Mo}_6(\text{BP})_2$ )<sup>8</sup> cores.

A new approach in rupture with those developed above could consist in developing hybrid POMs for which the photochromism mechanism involves an electron transfer from the organic cation toward the POM by freeing itself the dependence of the hydrogen-bonding network. With this aim, sulfonium cations  $\text{R}_1\text{R}_2\text{R}_3\text{S}^+$  ( $\text{R}_i$  are alkyl chains) clearly appear as promising candidates to generate such assemblies, because the S atom possesses both the positive charge susceptible to directly interact with the nucleophilic oxo ligands of the POM, and a nonbonding electron pair, which could be transferred toward the POM. Nevertheless, to the best of our knowledge, only one sulfonium/POM system,  $\text{Rb}_{0.75}(\text{NH}_4)_{5.25}[(\text{Mo}_3\text{O}_8)_2\text{O}(\text{O}_3\text{PC}(\text{CH}_2\text{S}(\text{CH}_3)_2)\text{OPO}_3)_2] \cdot 8\text{H}_2\text{O}$  (**1**), has been successfully synthesized, and its potential photochromic properties have not been explored. We thus present here the investigation of its optical properties. In addition, we report a new supramolecular assembly  $(\text{Me}_3\text{S})_4[\text{Mo}_8\text{O}_{26}]$  (**2**) as a good model material to point out the active role of the sulfonium cations in the photoactivity of sulfonium POMs. The photochromic properties of **2** have been studied and compared with those of  $(\text{HDEA})_2(\text{NH}_4)_2[\text{Mo}_8\text{O}_{26}]$  (**3**) ( $\text{HDEA}^+$  is the diethylammonium cation  $(\text{CH}_3\text{CH}_2)_2\text{NH}_2^+$ ), which is a new OAC/POM material and contains the same octamolybdate unit. Finally, a mechanism is proposed to describe the UV-induced color change effects in **1** and **2**.

**1** contains the  $[(\text{Mo}_3\text{O}_8)_2\text{O}(\text{O}_3\text{PC}(\text{CH}_2\text{S}(\text{CH}_3)_2)(\text{O})\text{PO}_3)_2]^{6-}$  polyanion<sup>9</sup> ( $\text{Mo}_6(\text{Sul})_2$ ), which is built upon two sulfonium bisphosphonate ligands covalently grafted on a hexanuclear  $\{\text{Mo}_6\}$  core (Figure 1a). The  $\{\text{Mo}_6\}$  core is composed of two trimeric units which are corner-shared connected via a common O atom. Single crystals of **2** and **3** have been obtained at room temperature (SI). Single X-ray diffraction (Table S1 in the SI) and FT-IR spectroscopy (Figure S2 in the SI) analyses reveal that both materials contain the discrete  $\beta$ - $[\text{Mo}_8\text{O}_{26}]^{4-}$  block ( $\text{Mo}_8$ ) (Figure 1b), which is

Received: November 13, 2012

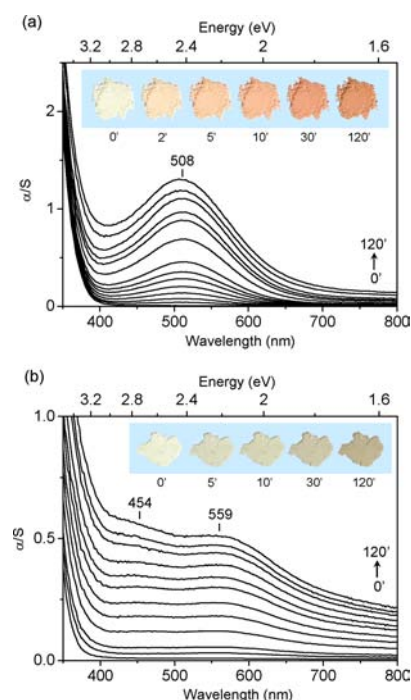
Published: January 8, 2013



**Figure 1.** Mixed ball and stick and polyhedral representations of (a) the  $\text{Mo}_6(\text{Sul})_2$  anions in **1** (yellow tetrahedra =  $\text{PO}_3\text{C}$ , blue octahedra =  $\text{MoO}_6$ ), (b) the  $\text{Mo}_8$  anion surrounded by the  $\text{Me}_3\text{S}^+$  cations in **2** (blue octahedra =  $\text{MoO}_6$ ). In **1** and **2**, the sulfonium groups develop electrostatic and van der Waals interactions with the POM units (the  $\text{S}\cdots\text{O}$  interactions are represented as dotted lines).

built upon eight distorted edge-sharing  $\{\text{MoO}_6\}$  octahedra.<sup>10</sup> In **1** and **2**, both the sulfonium cations and the POM units strongly interact via electrostatic and van der Waals interactions. The sulfonium group adopts a trigonal pyramidal geometry with all  $\text{C}-\text{S}-\text{C}$  angles far smaller than  $109^\circ$ , due to the space at the S atom lone electron pair. Notably, the  $\text{S}\cdots\text{O}$  distances are 3.22 and 3.33 Å in **1** (within inter and intramolecular interactions respectively), and in the range 2.77–3.30 Å in **2**, most of them being shorter than 3.32 Å that is the sum of the O and S atom van der Waals radii.<sup>11</sup> Such interactions between the positively charged sulfonium S and electron rich O atoms are commonly observed in protein structures.<sup>12</sup> The supramolecular 3D-network of **3** is built upon  $\text{Mo}_8$  blocks,  $\text{NH}_4^+$  and  $\text{HDEA}^+$  cations which connect the POMs via strong  $\text{N}-\text{H}\cdots\text{O}$  interactions (Figure S3 in the SI).

The solid-state photochromic properties of the aforementioned compounds have been investigated in ambient conditions by diffuse reflectance spectroscopy. White microcrystalline powders of **1**, **2**, and **3** exhibit optical gaps of 356 nm (3.48 eV), 333 nm (3.72 eV) and 344 nm (3.60 eV), respectively (Figure S4 in the SI). Under UV excitation at 365 nm (3.4 eV), the color of **1** gradually shifts to purplish-red with a high coloration contrast (Figure 2a), in agreement with the growth of a broad absorption band in the visible ( $\lambda_{\text{max}} = 508$  nm). This latter is quite comparable with those of other photochromic  $\text{Mo}_6(\text{BP})_2$  once irradiated,<sup>8b</sup> confirming that the nature of the POM core dictates the photogenerated hue.<sup>3b</sup> Under similar UV exposure, **2** develops a light grayish-brown color (Figure 2b) (two broad absorption bands at  $\lambda_{\text{max}} = 454$  and 559 nm). The color change of **2** is clearly noticeable even if it is less pronounced than in **1**. By comparison, **3** develops a very poor photoresponse. Its color shifts to pale gray ( $\lambda_{\text{max}} = 454$  nm) (Figure S5 in the SI) with a low coloration contrast (the color change is weakly detectable with naked eyes only after 90 min).



**Figure 2.** (a) Evolution of the photogenerated absorption in **1** after 0, 1, 2, 4, 6, 8, 10, 12.5, 20, 30, 40, 50, 90, and 120 min of UV irradiation (365 nm). Inset: Photographs of powder of **1** at different UV irradiation time (in min). (b) Evolution of the photogenerated absorption in **2** after 0, 5, 10, 20, 30, 40, 50, 60, 70, 90, 100, and 120 min of UV irradiation (365 nm). Inset: Photographs of powder of **2** at different 365 nm UV irradiation time (in min).

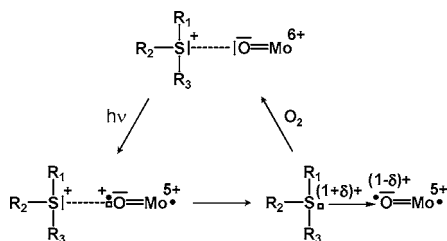
The color changes in **1** and **2** are due to the photoreduction of the POMs. The formation of reduced metallic centers can be well evidenced by EPR spectroscopy. The spectra of **1** and **2** recorded after UV irradiation are characteristic of the signatures of materials incorporating  $4d^1\ ^{96}\text{Mo}^{5+}$  ions ( $S = 1/2$ ;  $I = 0$ ),<sup>13</sup> with  $g$ -values of  $g_1 = 1.924$ ,  $g_2 = 1.916$ , and  $g_3 = 1.887$  for **1** and  $g_1 = 1.937$ ,  $g_2 = 1.922$ , and  $g_3 = 1.880$  for **2** (Figure S6 in the SI). The coloration kinetics of **1**, **2** and **3** have been quantified by analyzing their reflectance values versus the irradiation time ( $R(t)$ ). Details of the coloration kinetic parameters are given in Table S2 in the SI. In OAC/POM systems, the decrease of  $R^{\lambda_{\text{max}}}(t)$  (i.e., the reflectance at the wavelength of the maximum absorption in the visible) with the irradiation time is correlated to the decrease of the concentration of reducible  $\text{Mo}^{6+}$  cations, according to a pseudo second order kinetic law.<sup>4a</sup> It is worth noting the similar kinetic law for **1** and **2** (see SI for the detailed coloration kinetic model). The  $R^{508}(t)$  vs  $t$  curve relative to **1** is perfectly fitted as  $[R^{508}(t) - R^{508}(\infty)]^{-1} = At + B$  (Figure S7 in the SI), and the coloration rate constant is directly proportional to the slope of this linear curve. **1** shows a fast photoresponse ( $t_{1/2} = 4.84$  min), and it competes with the faster photochromic  $\text{Mo}_6(\text{BP})_2$  materials<sup>8b</sup> (the coloration rate constant ratio  $k_1/k_i$  is in the range 6.3–0.6) (Table S3 in the SI). **2** shows a coloration rates slower than **1** ( $t_{1/2} = 30$  min), however, its coloration change is much faster than that of **3** ( $t_{1/2} = 125$  min; and  $k_2/k_3 = 4$ ) (Figure S8 in the SI), proving that the photoreduction of the  $\text{Mo}_8$  unit is more efficient in **2** than in **3**. The slow photochromic effects in **2** and **3** can be attributed to the high difficulty to reduce the  $\text{Mo}_8$  anion.<sup>2a</sup>

**1** and **2** show reversible color change effects. The bleaching of both materials once irradiated occurs in air and at room

temperature (Figure S9 in the SI), and the fading process is slower than the coloration one (typically, for UV irradiation duration of 2 h which corresponds to a photoreduction degree  $Y(t)$  of about 96 and 80% in **1** and **2**, respectively (Figure S10 in the SI), the color of the samples totally disappears after 3 h). Similarly as observed for OAC/POM systems,<sup>3a,4b</sup> the bleaching of **1** and **2** is correlated to the back oxidation of the  $\text{Mo}^{5+}$  cations by  $\text{O}_2$  in ambient conditions (no color change occurs when **1** and **2** are kept in  $\text{O}_2$  free atmosphere). The fading process is strongly accelerated by keeping the samples under moderate heating at  $50^\circ\text{C}$  (the purple coloration of **1** disappears after a few minutes). To date, for **1** and **2**, about 15 coloration/fading cycles at room temperature as well as at  $50^\circ\text{C}$  can be performed without detecting any fatigue resistance with naked eyes.

Considering all these results, the photochromic effect in **1** and **2** could arise according to the mechanism proposed in Scheme 1. The UV excitation induces an electron transfer into

**Scheme 1. Proposed Mechanism of Photocoloration in 1 and 2 Involving an Electron Transfer from the Sulfonium Cation Towards the Adjacent POM<sup>a</sup>**



<sup>a</sup>The mechanism depicted here implies a  $\text{Mo}=\text{O}$  terminal O atom, but it can be quite transposable to the bridging O atoms.

the POM from an oxo ligand to an adjacent  $\text{Mo}^{6+}$  site. Then, the excited electron should be trapped onto the Mo atom, while concomitantly, the S atom lone electron pair of a sulfonium group should be strongly polarized toward the POM to stabilize the electron-deficient O atom. Consequently, the coloration should be due to the photoreduction of  $\text{Mo}^{6+}$  cations into  $\text{Mo}^{5+}$  ones and the photogenerated hole should partially move onto the S atom. The spatially segregated charge carrier allows maintaining the coloration after switching off the UV irradiation.

In conclusion, we have successfully highlighted that sulfonium polyoxometalates develop efficient solid-state photochromism in ambient conditions. Their UV-induced coloration can be modulated by playing with the nature of the POM unit. The photoreduction of the POM has been evidenced and the sulfonium cations (covalently grafted on the POM or not) act as electron donors, which stabilize the reduced  $\text{Mo}^{5+}$  centers. Importantly, compared to their OAC counterparts, the sulfonium/POM systems are more promising photoactive materials, because the electron transfers at the organic–inorganic interface do not require direct H-bonding interactions between the POM and the organic moiety, and the  $\text{S}\cdots\text{O}$  contacts seem more easily predictable. We are now embarked on a prospective research of new sulfonium/POM assemblies to consolidate the proposed coloration mechanism and to investigate the fading one. Notably, the influence of the nature of the sulfonium cations (size, alkyl side-chain length) on the coloration and fading kinetics is under study.

## ■ ASSOCIATED CONTENT

### 📄 Supporting Information

X-ray crystallographic data of **2** and **3** in CIF format, experimental procedures, single-crystal X-ray diffraction data of **2** and **3**, FT-IR, EPR, and UV–vis spectra, and complementary detailed coloration kinetic models. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## ■ AUTHOR INFORMATION

### Corresponding Author

\*Fax: (+33)240-373-995 (R.D.); (+33)139-254-381 (P.M.). E-mail: [remi.dessapt@cnrs-immn.fr](mailto:remi.dessapt@cnrs-immn.fr) (R.D.); [mialane@chimie.uvsq.fr](mailto:mialane@chimie.uvsq.fr) (P.M.).

### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

This work was supported by the CNRS, the Ministère de l'Enseignement Supérieur et de la Recherche, the "TGE Réseau National de RPE Interdisciplinaire", Grant FR-CNRS 3443, and the ANR-11-BS07-011-01 BIOPOPOM.

## ■ REFERENCES

- (1) (a) Irie, M. *Chem. Rev.* **2000**, *100*, 1685–1716. (b) Ohkoshi, S.-I.; Tsunobuchi, Y.; Matsuda, T.; Hashimoto, K.; Namai, A.; Hakoe, K.; Tokoro, H. *Nature Chem.* **2010**, *2*, 539–545. (c) Pardo, R.; Zayat, M.; Levy, D. *Chem. Soc. Rev.* **2011**, *40*, 672–687. (d) Wang, M.-S.; Xu, G.; Zhang, Z.-J.; Guo, G.-C. *Chem. Commun.* **2010**, *46*, 361–376.
- (2) (a) Pope, M. T. *Heteropoly and Isopoly Oxometalates*; Springer-Verlag: New York, 1983. (b) Long, D.-L.; Burkholder, E.; Cronin, L. *Chem. Soc. Rev.* **2007**, *36*, 105–121. (c) Dolbecq, A.; Dumas, E.; Mayer, C. R.; Mialane, P. *Chem. Rev.* **2010**, *110*, 6009–6048. (d) Kortz, U.; Müller, A.; Salgeren, J. V.; Schnack, J.; Dalal, N. S.; Dressel, M. *Coord. Chem. Rev.* **2009**, *253*, 2315–2327. (e) Gouzerh, P.; Proust, A. *Chem. Rev.* **1998**, *98*, 77–111.
- (3) (a) Yamase, T. *Chem. Rev.* **1998**, *98*, 307–325. (b) Coué, V.; Dessapt, R.; Bujoli-Doeuff, M.; Evain, M.; Jobic, S. *Inorg. Chem.* **2007**, *46*, 2824–2835. (c) He, T.; Yao, J. *Prog. Mater. Sci.* **2006**, *51*, 810–879.
- (4) (a) Dessapt, R.; Collet, M.; Coué, V.; Bujoli-Doeuff, M.; Jobic, S.; Lee, C.; Whangbo, M.-H. *Inorg. Chem.* **2009**, *48*, 574–580. (b) Dessapt, R.; Gabard, M.; Bujoli-Doeuff, M.; Deniard, P.; Jobic, S. *Inorg. Chem.* **2011**, *50*, 8790–8796.
- (5) Fang, R.-Q.; Zhang, X.-M.; Wu, H.-S.; Ng, S. W. *Acta Crystallogr.* **2004**, *E60*, m359–m361.
- (6) Bujoli-Doeuff, M.; Dessapt, R.; Deniard, P.; Jobic, S. *Inorg. Chem.* **2012**, *51*, 142–149.
- (7) Compain, J.-D.; Deniard, P.; Dessapt, R.; Dolbecq, A.; Oms, O.; Sécheresse, F.; Marrot, J.; Mialane, P. *Chem. Commun.* **2010**, *46*, 7733–7735.
- (8) (a) Sergienko, V. S. *Russ. J. Coord. Chem.* **2001**, *27*, 723–753. (b) El Moll, H.; Dolbecq, A.; Mbomekalle, I. M.; Marrot, J.; Deniard, P.; Dessapt, R.; Mialane, P. *Inorg. Chem.* **2012**, *51*, 2291–2302.
- (9) El Moll, H.; Zhu, W.; Oldfield, E.; Marleny Rodriguez Albelo, L.; Mialane, P.; Marrot, J.; Vila, N.; Mbomekallé, I. M.; Rivière, E.; Duboc, C.; Dolbecq, A. *Inorg. Chem.* **2012**, *51*, 7921–7931.
- (10) Hubbard, D. J.; Johnston, A. R.; Sanchez Casalongue, H.; Narducci Sarjeant, A. N.; Norquist, A. J. *Inorg. Chem.* **2008**, *47*, 8518–8525.
- (11) Bondi, A. J. *Phys. Chem.* **1964**, *68*, 441–451.
- (12) Markham, G. D.; Norrby, P.-O.; Bock, C. W. *Biochemistry* **2002**, *41*, 7636–7646.
- (13) Baffert, C.; Boas, J. F.; Bond, A. M.; Kögerler, P.; Long, D.-L.; Pilbrow, J. R.; Cronin, L. *Chem.—Eur. J.* **2006**, *12*, 8472–8483.