Angewandte Chemie International Edition

DOI: 10.1002/anie.201209497

Polyoxometalates

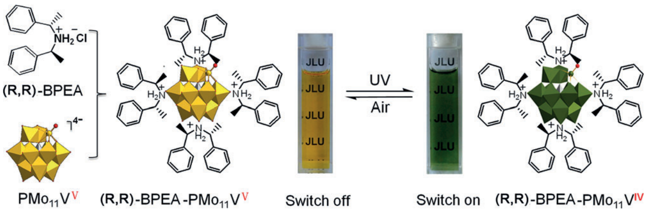
Chiral Heteropoly Blues and Controllable Switching of Achiral Polyoxometalate Clusters**

*Yizhan Wang, Haolong Li, Che Wu, Yang Yang, Lei Shi, and Lixin Wu**

Chirality as a general natural phenomenon always attracts great attention because of the interest in both its mysterious origin and the numerous potential applications, for example, in drugs, catalysts, and, potentially, optical devices.[1] For the creation of functional chiral structures and applicable materials, diverse organic and inorganic artificial compounds have been prepared according to the rule of non-superimposability with their mirror image. However, it is not always an easy task to prepare chiral molecules and assemblies by covalent synthesis owing to the difficulties and limits of detailed chemical procedures. Fortunately, the ability to induce chirality through intermolecular interactions points to a convenient approach for creating chiral materials from achiral molecules or components.[2]

Polyoxometalates (POMs) are nanometer-sized, inorganic functional clusters with abundant compositions and various frame structures that display potential in catalysis, optics, and nanomaterials.[3] Owing to their ability to accept and release electrons without structural changes and to the obvious visible color changes in their reduced state (as heteropoly blues), POMs have been considered as an attractive class of photochromic or electrochromic systems. Significantly, the light-induced reversible color changes make POMs suitable for photoswitching devices.[4] Chiral POMs are of special interest in POM structural chemistry. To date, however, the anticipated chiroptical activities corresponding to the intervalence charge-transfer (IVCT) transition at long-wavelength absorption band (600–800 nm) has not been found, which has hindered the development of chiral POM materials for chiral photochromic applications.[5] All known optical activities of POMs are derived from O→M ligand-to-metal charge-transfer (LMCT) transitions of reduced POMs, at a short-wavelength absorption band (250–400 nm).[5c] Therefore, the current challenge is to create chirality with "blue" electrons in heteropoly blues.

Several detailed synthetic routes have been developed for the construction of chiral POM architectures.[6] However, the instability and rapid racemization in solution make most POMs with chiral structures lose their activity, so that racemic mixtures are usually found both in solution and in the crystalline state.[7] Until now, chiroptical activities with IVCT transitions in heteropoly blues have not been found. Therefore, the development of a general and simple strategy for the introduction of chirality into achiral POMs while retaining their intrinsic features is of great interest. Herein, we describe the use of a chiral organic cation to enwrap POMs with photochromic properties; through an electrostatic interaction, chiral organic-cation–POM complexes were obtained (Scheme 1). As a result of the chiral induction of the organic cations, the achiral POM in the complexes exhibits chiroptical activity not only in the band of LMCT transitions, but also in the region associated with IVCT transitions formed by photoreduction. More interestingly, reversible control of the chiroptical activity was possible through photochromism of the POMs. To the best of our knowledge, the photoswitchable chirality of POM complexes has never been reported previously.



Scheme 1. Schematic illustration of chiroptical switching based on the photochromism of (*R*,*R*)-BPEA–$PMo_{11}V$.

We selected chiral cationic ammonium ions with two stereocenters, bis[(*R*)- and (*S*)-1-phenylethyl]amine hydrochloride ((*R*,*R*)- and (*S*,*S*)-BPEA), to replace the counterions of $H_4[PMo_{11}VO_{40}]\cdot 32.5\,H_2O$ ($PMo_{11}V$) through an electrostatic interaction and provide complexes (*R*,*R*)-BPEA–$PMo_{11}V$ and (*S*,*S*)-BPEA–$PMo_{11}V$.[8a] The characteristic Mo–O vibrational bands of $PMo_{11}V$ are found in the IR spectra of the complexes at 958 ($\nu_{as}(Mo{=}O_d)$), 874 ($\nu_{as}(Mo\text{-}O_b\text{-}Mo)$), and 798 cm^{-1} ($\nu_{as}(Mo\text{-}O_c\text{-}Mo)$);[8b] these bands confirm the well-retained cluster structure. ^1H NMR spectra of the two complexes proved the presence of organic cations. When we compared the ^1H NMR spectrum of (*R*,*R*)-BPEA–$PMo_{11}V$ with that of the free organic cation, we found that the N–H signal shifted from 10.07 ppm in the free cation to 9.24 ppm in (*R*,*R*)-BPEA–$PMo_{11}V$, whereas the signal for the

---

[*] Y. Wang, Dr. H. Li, C. Wu, Y. Yang, L. Shi, Prof. Dr. L. Wu
State Key Laboratory of Supramolecular Structure and Materials
College of Chemistry, Jilin University
Changchun 130012 (China)
E-mail: wulx@jlu.edu.cn
Homepage: http://supramol.jlu.edu.cn/people/wulixin/

[**] We acknowledge financial support from the National Basic Research Program (2013CB834503), the National Natural Science Foundation of China (91227110, 21221063), the 111 Project (B06009 for support of the visit of Prof. M. Lee at SNU and fruitful discussions), and the Open Project of the State Key Laboratory of Polymer Physics and Chemistry of the Chinese Academy of Science.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201209497.

hydrogen atoms on the asymmetric carbon atoms moved from 3.90 to 4.12 ppm; these signals for the complexes indicate tight electrostatic interactions.[8c] Elemental analysis demonstrated that all counterions of $PMo_{11}V$ were replaced by organic cations (see Figures S1–S4 in the Supporting Information).

As expected, (*R*,*R*)-BPEA–$PMo_{11}V$ and (*S*,*S*)-BPEA–$PMo_{11}V$ showed distinct mirror-image circular dichroism (CD) signals in methanol and were thus enantiomerically pure (Figure 1). The absorption band at 300–450 nm can be assigned to the O→M (Mo or V) LMCT transition for $PMo_{11}V$. The CD signals in the same range can be assigned to the induced chirality of the POMs in the complexes and ascribed to chirality transfer from (*R*,*R*)- or (*S*,*S*)-BPEA (see Figure S5 in the Supporting Information). The CD and UV/Vis spectra of the two complexes showed no obvious change in several weeks, which indicated that they were enantiomerically stable.

Apparently, the intermolecular interaction acts as the bridge for chirality transfer.[9] To evaluate the influence of the electrostatic interaction on the chirality of the POMs, we examined the CD spectral changes of (*R*,*R*)-BPEA–$PMo_{11}V$ with regard to the temperature and the solvent (Figure 1; see also Figure S6 in the Supporting Information). When the temperature was decreased from 40 to 0 °C, the intensity of the CD signal increased, which indicates that a high temperature is unfavorable for the induced chirality of the POMs. When the solvent polarity was increased by the addition of water to the methanol solution, the intensity of the CD signal decreased. In contrast, a clear increase in induced CD intensity occurred as the volume ratio of dichloromethane to methanol was increased at the same concentration of (*R*,*R*)-BPEA–$PMo_{11}V$. It is known that the electrostatic association can be weakened by increasing the temperature and the solvent polarity;[10] thus, the dependence of the CD intensity on the temperature and solvent polarity confirms this chirality transfer from the organic unit to the POM cluster and the critical role of the electrostatic interaction as a connection.

The complexes exhibited photochromic behavior under irradiation with UV light in methanol. During irradiation, the solution color changed from yellow to green, and a broad absorption band appeared at around 700 nm (Figure 2a). This band can be assigned to the IVCT transition of $PMo_{11}V$ in its reduced state (heteropoly blue).[11] With increasing irradiation time, the color became darker, and the absorption intensity became stronger. In a reverse process, the green color of the solution gradually faded to yellow at room temperature in air. Accompanying the color change, the absorption at 700 nm decreased slowly and almost disappeared in 24 h. This result implies that the POM in the complexes returns to its initial state. This photochromism can be repeated for many cycles without obvious coloration fatigue (Figure 2b; see also Figure S7 in the Supporting Information).

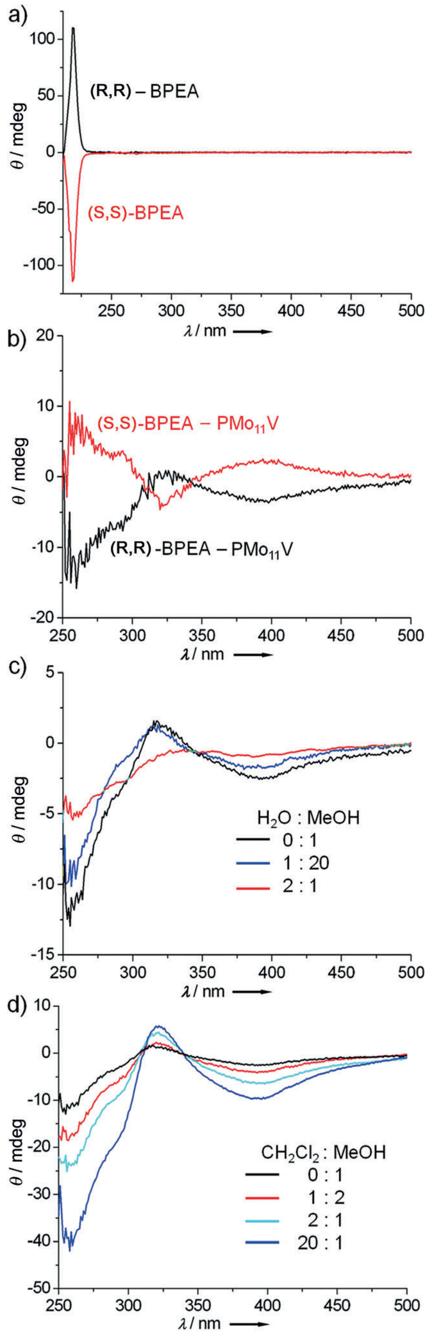


Figure 1. CD spectra at room temperature of a) (*R*,*R*)- and (*S*,*S*)-BPEA in CH_3OH (1.48×10^{-3} mol L^{-1}); b) (*R*,*R*)- and (*S*,*S*)-BPEA–$PMo_{11}V$ in CH_3OH (3.7×10^{-4} mol L^{-1}); c) (*R*,*R*)-BPEA–$PMo_{11}V$ in mixtures of CH_3OH and H_2O at different volume ratios (3.7×10^{-4} mol L^{-1}); d) (*R*,*R*)-BPEA–$PMo_{11}V$ in mixtures of CH_3OH and CH_2Cl_2 at different volume ratios (3.7×10^{-4} mol L^{-1}).

The chiroptical response of the complexes is associated with the photochemical switching, as can be seen clearly from the changes in the CD spectra during the photochromic process (Figure 2c,d). Unexpectedly, after photoreduction, the heteropoly blue solution of (*R*,*R*)-BPEA–$PMo_{11}V$ showed a clear negative Cotton effect at around 700 nm. This effect indicates that the induced chiral activity at long wavelengths is associated with the IVCT transition of the POM. Interestingly, when the solution faded to yellow in air, a disappearance in the absorption in the visible region was accompanied by a return of the solution to a CD-silent state, which further confirmed the chirality of IVCT transition. This

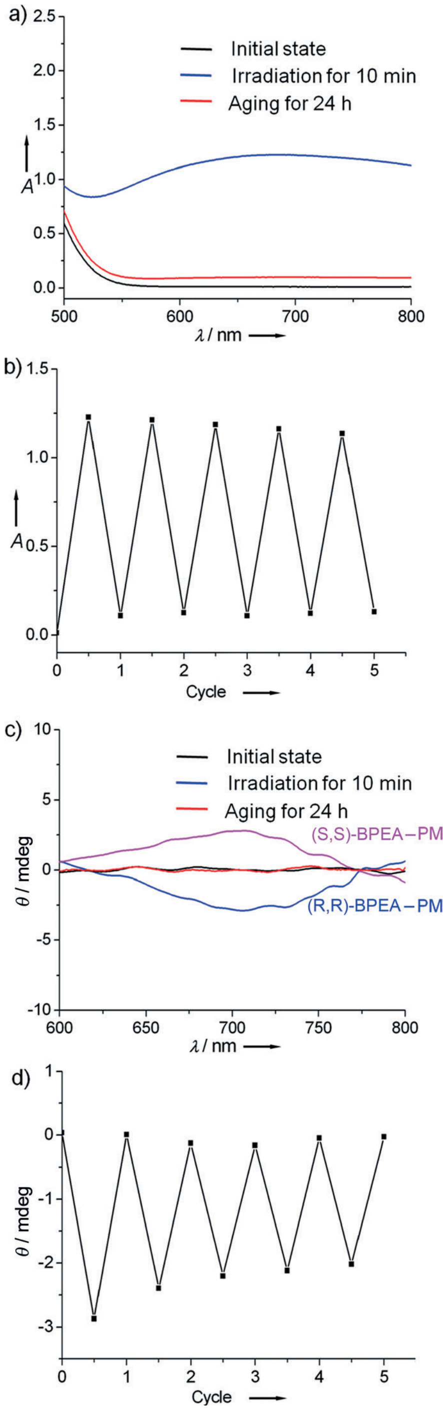


Figure 2. a) UV/Vis spectra of (*R*,*R*)-BPEA–$PMo_{11}V$ (or (*S*,*S*)-BPEA–$PMo_{11}V$) in methanol (2.22×10^{-3} mol L^{-1}) before and after irradiation with UV light for 10 min and then aging in air for 24 h. b) Photochromic cycles, as observed by monitoring the absorption at 700 nm. c) CD spectra of (*R*,*R*)-BPEA–$PMo_{11}V$ and (*S*,*S*)-BPEA–$PMo_{11}V$ in methanol (2.22×10^{-3} mol L^{-1}) before and after irradiation with UV light for 10 min and then aging in air for 24 h. d) CD intensity of (*R*,*R*)-BPEA–$PMo_{11}V$ at 700 nm as a function of the photochromic cycle.

photoswitchable chiroptical response cycle can also be repeated several times. As expected, (*S*,*S*)-BPEA–$PMo_{11}V$ after irradiation with UV light displayed a positive Cotton effect at around 700 nm, and its CD spectrum was nearly the mirror image of that of (*R*,*R*)-BPEA–$PMo_{11}V$; these results further confirmed the origin of the chiroptical activity of POM as the chiral induction of the organic cations.

We investigated the structure of (*R*,*R*)-BPEA–$PMo_{11}V$ in solution before and after light irradiation (see Figures S8–S9 in the Supporting Information). The constant chemical shift at −3.87 ppm for the phosphorus atom of (*R*,*R*)-BPEA–$PMo_{11}V$ in the ^{31}P NMR spectrum with and without irradiation with UV light suggests that the keggin structure of POM in the complex is well-retained.[12] Moreover, the chemical shifts of (*R*,*R*)-BPEA–$PMo_{11}V$ in the ^{1}H NMR spectrum before and after irradiation are almost the same, which confirms that the reduction of $PMo_{11}V$ is not caused by the oxidation of the organic part, because methanol can act as a sacrificial reagent.[4a] The cyclic voltammetric (CV) curves of (*R*,*R*)-BPEA–$PMo_{11}V$, which are similar to the previously reported data, indicate that the reduction potential of the V atom is higher than that of the Mo atoms in the $PMo_{11}V$ cluster (see Figure S10 in the Supporting Information).[13] Thus, in the case of one-electron-reduced mixed-addenda $PMo_{11}V$, the electron is first captured by the more reducible vanadium atom.[14]

We analyzed the reduction efficiency of the complexes during the photochromic process through XPS measurement (see Figure S11 in the Supporting Information).[11] After irradiation with UV light, the binding energies of the Mo^{6+} 3d level became higher than in the initial state, which indicates an increase in electronegativity around the corresponding metal ions after the phototriggered reduction.[10] To confirm this hypothesis, we also used (*R*,*R*)- and (*S*,*S*)-BPEA to enwrap a reduced POM, $(NH_4)_5[PMo_{11}V^{IV}O_{40}]\cdot20\,H_2O$ ($PMo_{11}V^{IV}$), which contains a V^{4+} atom, and construct (*R*,*R*)- and (*S*,*S*)-BPEA–$PMo_{11}V^{IV}$ (see Figures S12–S15 in the Supporting Information). For (*R*,*R*)-BPEA–$PMo_{11}V^{IV}$, the binding energies of the Mo^{6+} 3d level are very close to those of (*R*,*R*)-BPEA–$PMo_{11}V$ after photoreduction. This similarity confirms that the Mo atoms of (*R*,*R*)-BPEA–$PMo_{11}V$ are hardly reduced in this state. Meanwhile, the binding energy (BE) of V^{5+} $2p_{3/2}$ in (*R*,*R*)-BPEA–$PMo_{11}V$ before irradiation is 517.5 eV, whereas the binding energy of V^{4+} $2p_{3/2}$ in (*R*,*R*)-BPEA–$PMo_{11}V^{IV}$ is 516.7 eV (Figure 3). In the case of (*R*,*R*)-BPEA–$PMo_{11}V$ after irradiation, the peak of V $2p_{3/2}$ was found shifted to a lower value and could be deconvoluted into two peaks with binding energies of 517.7 and 516.8 eV, which just match the values of V^{5+} $2p_{3/2}$ and V^{4+} $2p_{3/2}$. The latter peak clearly indicates that V was partially reduced during irradiation, and not only the Mo atoms. From the calculation for the deconvoluted spectra, the concentration of V^{4+} was approximately 63 %. These results clearly indicate that the electrons yielded by the reduction are mainly trapped on V atoms in the mixed-addenda POM complexes.

According to the above results, we propose the following chiral photochromism process. The reduction of the POM in (*R*,*R*)-BPEA–$PMo_{11}V$ takes place at the V atom in methanol under irradiation with UV light, which gives rise to photochromism due to the IVCT transition from V^{4+} to Mo^{6+}. Simultaneously, owing to the chiral induction of the organic cations covering the POM surface through an electrostatic

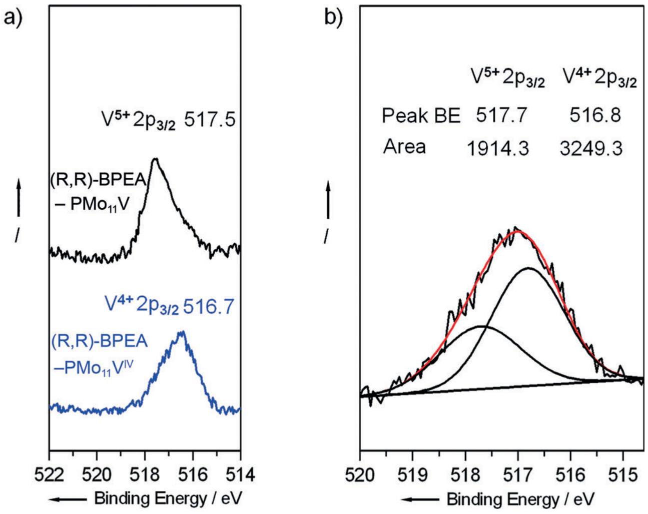


Figure 3. XPS spectra of the V 2p level for a) (*R*,*R*)-BPEA–$PMo_{11}V$ and (*R*,*R*)-BPEA–$PMo_{11}V^{IV}$; b) (*R*,*R*)-BPEA–$PMo_{11}V$ after irradiation with UV light for 10 min.

interaction, the chirality transfers to the achiral reduced POM cluster, which results in the appearance of the Cotton effect associated with the IVCT transition at 700 nm. For the reverse process, the reduced POM complexes are oxidized gradually by the air, and V^{4+} returns to the V^{5+} state, which causes the disappearance of the chiral IVCT transition until the complex is next irradiated with light.

To identify the role of V^{4+} in the induced chirality in the photochromic process, we detected the chiroptical activity of (*R*,*R*)- and (*S*,*S*)-BPEA–$PMo_{11}V^{IV}$ with a definite V^{4+} atom. As expected, the mirror-image Cotton effects found at long wavelengths (620–780 nm) indicated that the chirality of the IVCT transition was associated with the V^{4+} atom (see Figures S16 and S17 in the Supporting Information). Moreover, we also used (*R*,*R*)- and (*S*,*S*)-BPEA to enwrap the reduced POMs $K_5[PW_{11}V^{IV}O_{40}]\cdot 8H_2O$ ($PW_{11}V^{IV}$) and $K_6[SiW_{11}V^{IV}O_{40}]\cdot 2H_2O$ ($SiW_{11}V^{IV}$) and construct the complexes (*R*,*R*)- and (*S*,*S*)-BPEA–$PW_{11}V^{IV}$ and (*R*,*R*)- and (*S*,*S*)-BPEA–$SiW_{11}V^{IV}$ (see Figures S18–S27 in the Supporting Information). All complexes showed Cotton effects in the region associated with the IVCT transitions of the reduced POMs. Therefore, for mixed-addenda POMs containing V atoms, it is clear that the chirality transfer from the organic cation to the heteropoly blue state of the POMs is derived from the IVCT transition of V^{4+} atoms.

From the above results, it can be predicted that the localization of the reduced atom is favorable for the generation of chiral heteropoly blues. As an example, (*R*,*R*)- and (*S*,*S*)-BPEA–PMo_{12}, prepared by enwrapping $H_3PMo_{12}O_{40}$ (PMo_{12}) with (*R*,*R*)- and (*S*,*S*)-BPEA, showed typical mirror-image Cotton effects at short wavelengths (see Figures S28–S33 in the Supporting Information). However, no detectable chiral signals associated with an IVCT transition were found after photoreduction. We infer that when the PMo_{12} cluster is reduced, the obtained "blue" electron delocalizes among the 12 identical Mo atoms,[15] which increases the symmetry of the whole POM cluster and thus leads to a weakened induced chirality of the heteropoly blue. Therefore, the localization of "blue" electrons is a critical factor for the induced chirality of the heteropoly blue. To further confirm the role of localized "blue" electrons for the induced chirality of heteropoly blues, we enwrapped a POM with two V atoms, $H_5[PMo_{10}V_2O_{40}]\cdot 32H_2O$. Although the distribution of the two V atoms is multiform, the localization on the V atoms of the electron derived by reduction also enables (*R*,*R*)- and (*S*,*S*)-BPEA–$PMo_{10}V_2$ to exhibit opposite Cotton effects in the region associated with the IVCT transition after irradiation with light (see Figures S34–S39 in the Supporting Information). Because the induced chirality is associated tightly with the "blue" electron, the reversible photochromism of POM complexes is intrinsically a smart chiral switching.

In conclusion, the chirality of organic cations can be transferred to an achiral POM cluster in supramolecular complexes through an electrostatic interaction. This induced chirality is influenced by modulation of the intermolecular interaction through changes in temperature and the polarity of the solvent. In contrast to all known POM systems, the unique induced chirality in the visible-light region is in close association with the photochromism of selected POMs. The localization of the reduced atom in the POM is responsible for the generation of a chiral heteropoly blue. The present findings have general significance for the functionalization of the POM family because the photoswitchable chirality of the complexes is meaningful for the synthesis of chiral POM materials. The present study offers a useful protocol for the construction of chiroptical switches based on inorganic clusters. We believe that the principle of this study can also be applied to electrochromic chiral switchable systems, which are more attractive for devices.

Received: November 27, 2012

Keywords: chirality · chiroptical switching · circular dichroism · photochromism · polyoxometalates

---

[1] a) B. L. Feringa, R. A. van Delden, N. Koumura, E. M. Geertsema, *Chem. Rev.* **2000**, *100*, 1789; b) Y. Qiu, P. Chen, P. Guo, Y. Li, M. Liu, *Adv. Mater.* **2008**, *20*, 2908; c) J. W. Canary, *Chem. Soc. Rev.* **2009**, *38*, 747.
[2] a) M. Suárez, N. Branda, J.-M. Lehn, A. Decian, J. Fischer, *Helv. Chim. Acta* **1998**, *81*, 1; b) D. B. Amabilino, J. Veciana, *Top. Curr. Chem.* **2006**, *265*, 253; c) Y. Hase, K. Nagai, H. Iida, K. Maeda, N. Ochi, K. Sawabe, K. Sakajiri, K. Okoshi, E. Yashima, *J. Am. Chem. Soc.* **2009**, *131*, 10719.
[3] a) M. T. Pope, A. Müller, *Angew. Chem.* **1991**, *103*, 56; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 34; b) A. Proust, B. Matt, R. Villanneau, G. Guillemot, P. Gouzerha, G. Izzet, *Chem. Soc. Rev.* **2012**, *41*, 7605; c) D.-L. Long, R. Tsunashima, L. Cronin, *Angew. Chem.* **2010**, *122*, 1780; *Angew. Chem. Int. Ed.* **2010**, *49*, 1736.
[4] a) T. Yamase, *Chem. Rev.* **1998**, *98*, 307; b) Z. Wang, Y. Ma, R. Zhang, A. Peng, Q. Liao, Z. Cao, H. Fu, J. Yao, *Adv. Mater.* **2009**, *21*, 1; c) W. Qi, H. Li, L. Wu, *J. Phys. Chem. B* **2008**, *112*, 8257.
[5] a) J. Garvey, M. T. Pope, *Inorg. Chem.* **1978**, *17*, 1115; b) L. Yan, X. López, J. J. Carbó, R. Sniatynsky, D. C. Duncan, J. M. Poblet, *J. Am. Chem. Soc.* **2008**, *130*, 8223; c) M. Carraro, G. Modugno,

A. Sartorel, G. Scorrano, M. Bonchio, *Eur. J. Inorg. Chem.* **2009**, 5164.

[6] a) B. Hasenknopf, K. Micoine, E. Lacôte, S. Thorimbert, M. Malacria, R. Thouvenot, *Eur. J. Inorg. Chem.* **2008**, 5001; b) J. Zhang, J. Hao, Y. Wei, F. Xiao, P. Yin, L. Wang, *J. Am. Chem. Soc.* **2010**, *132*, 14; c) H. An, E. Wang, D. Xiao, Y. Li, Z. Su, L. Xu, *Angew. Chem.* **2006**, *118*, 918; *Angew. Chem. Int. Ed.* **2006**, *45*, 904; d) H. Naruke, J. Iijima, T. Sanji, *Inorg. Chem.* **2011**, *50*, 7535; e) U. Kortz, M. G. Savelieff, F. Y. A. Ghali, L. M. Khalil, S. A. Maalouf, D. I. Sinno, *Angew. Chem.* **2002**, *114*, 4246; *Angew. Chem. Int. Ed.* **2002**, *41*, 4070; f) M. Carraro, A. Sartorel, G. Scorrano, C. Maccato, M. H. Dickman, U. Kortz, M. Bonchio, *Angew. Chem.* **2008**, *120*, 7385; *Angew. Chem. Int. Ed.* **2008**, *47*, 7275; g) C. Jahier, M. Cantuel, N. D. McClenaghan, T. Buffeteau, D. Cavagnat, F. Agbossou, M. Carraro, M. Bonchio, S. Nlate, *Chem. Eur. J.* **2009**, *15*, 8703; h) Z. Zhang, Y. Li, S. Yao, E. Wang, Y. Wang, R. Clérac, *Angew. Chem.* **2009**, *121*, 1609; *Angew. Chem. Int. Ed.* **2009**, *48*, 1581.

[7] a) X. Fang, T. M. Anderson, C. L. Hill, *Angew. Chem.* **2005**, *117*, 3606; *Angew. Chem. Int. Ed.* **2005**, *44*, 3540; b) D. Liu, H. Tan, W. Chen, Y. Li, E. Wang, *CrystEngComm* **2010**, *12*, 2044.

[8] a) Y. Wang, H. Li, W. Qi, Y. Yang, Y. Yan, B. Li, L. Wu, *J. Mater. Chem.* **2012**, *22*, 9181; b) M. Nakayama, H. Komatsu, S. Ozuka, K. Ogura, *Electrochim. Acta* **2005**, *51*, 274; c) H. Li, Y. Yang, Y. Wang, W. Li, L. Bi, L. Wu, *Chem. Commun.* **2010**, *46*, 3750.

[9] K. Miyoshi, Y. Kuroda, J. Takeda, H. Yoneda, I. Takagi, *Inorg. Chem.* **1979**, *18*, 1425.

[10] Z. He, Y. Yan, B. Li, H. Ai, H. Wang, H. Li, L. Wu, *Dalton Trans.* **2012**, *41*, 10043.

[11] Z. Wang, Y. Ma, R. Zhang, D. Xua, H. Fu, J. Yao, *J. Solid State Chem.* **2009**, *182*, 983.

[12] A. Rudnitskaya, J. A. F. Gamelas, D. V. Evtuguinc, A. Legind, *New J. Chem.* **2012**, *36*, 1036.

[13] X. Hao, M. Luo, X. Wang, X. Feng, Y. Li, Y. Wang, E. Wang, *Inorg. Chem. Commun.* **2011**, *14*, 1698.

[14] a) J. J. Altenau, M. T. Pope, R. A. Prados, H. So, *Inorg. Chem.* **1975**, *14*, 417; b) J. M. Maestre, X. Lopez, C. Bo, J. M. Poblet, N. C. Pastor, *J. Am. Chem. Soc.* **2001**, *123*, 3749.

[15] R. A. Prados, M. T. Pope, *Inorg. Chem.* **1976**, *15*, 2547.