

Self-Association Study from Electrochemical Behaviours of {Mo₁₅₄} and {Mo₇₂Fe₃₀} in Aqueous Solution

XIANGFENG JIA*, SHUAIQIN YU†, YONGSHAN MA, PEIGANG LI and HUIXUE REN

School of Municipal and Environmental Engineering,
Shandong Jianzhu University, Jinan, Shandong, P.R. China
Fax: (86)(531)86367658; Tel: (86)(531)86361857
E-mail: jiaxf@sdjzu.edu.cn

The electrochemical behaviours of the nanoscale inorganic polyoxomolybdate anions ({Mo₁₅₄} and {Mo₇₂Fe₃₀}) and their aggregations in aqueous solution are examined by cyclic voltammetry. By comparison, it is found that the cyclic voltammograms of the single macro anions ({Mo₁₅₄} and {Mo₇₂Fe₃₀}) and those of their aggregations are similar. From the electrochemical point of view, it is concluded that the self-assembly of this kind of macro anions is driven by physical force.

Key Words: Nanoscale polyoxomolybdate, Cyclic voltammograms, Second organized structure, Vesicle supermolecule, Inorganic polymer.

INTRODUCTION

The giant anions of inorganic polyoxomolybdates, regardless their shapes, masses, number of charges, can dissolve in polar solvent and exist as ions, such as NaCl crystals disappear in water¹⁻⁶. However, these giant ions of polyoxomolybdates can associate into spherical vesicle supramolecular structures (called as "second solute state" in literature¹) continuously, which can be called as "second organized structures" from the view of amphiphilic solutions⁷. The self-association of some giant ions is very slowly, for some giant anions, it even takes several months or years to reach equilibrium at room temperature⁸. The vesicle supramolecular structures are stable and the size of the vesicles does not change over time. Now, more kinds of polyoxometalates (besides polyoxomolybdates and their derivatives)⁹⁻¹³ have been found associating into vesicle structures, but the complex self-association mechanism is still in study. The self-assembly of macro anions is indeed unique, because the macro anions are fully hydrophilic and dissolve in polar solvents, which is disaccord with DLVO theory^{2,14,15} in amphiphilic solutions. Liu *et al.*^{2,3,7} deduced that the driving force for the self-assembly process of macro anions could be very complicated. It is not mainly due to electrostatic interaction, Van der Waals force or chemical interaction (the macro ions separation is about 1-2 nm¹⁶) and also the hydrophobic

†Institute of Ocean Materials and Engineering, Shanghai Maritime University, Shanghai 200135, P.R. China.

interaction and the hydrogen bond cannot be dominant. Therefore, the self-assembly of the hydrophilic macro ions is mainly attributed to the charges on their surfaces. So the "like-charge attraction" effect¹⁵⁻¹⁷, along with Van der Waals' force and possible temporary Fe-O...H-O-Fe does exist in hydrophilic macro ionic solutions. That is to say, the nanoscale polyoxomolybdate anions ("first organized structure") attract each other by sharing the counter ions to form the stable vesicle-like aggregations.

Here, the electrochemistry behaviours of the nanoscale inorganic polyoxomolybdate anions ($\{\text{Mo}_{154}\}$ and $\{\text{Mo}_{72}\text{Fe}_{30}\}$) and their aggregations in aqueous solution are studied. From the electrochemistry point of view, the driving force of the self-assembly of inorganic macro ions is speculated. It is helpful to the research of the complex self-association mechanism.

EXPERIMENTAL

The giant-wheel shaped and C₆₀ cage-like "Keplerate" spherical polyoxomolybdate molecules ($\{\text{Mo}_{154}\}$ and $\{\text{Mo}_{72}\text{Fe}_{30}\}$) = $\text{Na}_{15}[\text{Mo}_{126}\text{Mo}_{28}^{5+}\text{O}_{426}\text{H}_{14}(\text{H}_2\text{O})_{70}]_{0.5}$ [$\text{Mo}_{124}^{6+}\text{Mo}_{28}^{5+}\text{O}_{457}\text{H}_{14}(\text{H}_2\text{O})_{68}$]_{0.5}. *ca.* 400H₂O and $\{\text{Mo}_{72}\text{Fe}_{30}\} \equiv (\text{Mo}_{72}^{6+}\text{Fe}_{30}^{3+}\text{O}_{252}\text{L}_{102}$. *ca.* 180H₂O L = H₂O/CH₃COO⁻/Mo₂O_{8/9}ⁿ⁻, $\{\text{Mo}_{72}\text{Fe}_{30}\}$), are prepared by following the established procedures¹⁸⁻²⁰. All the reagents are analytical grade without further purification and they were purchased from Shanghai Shiyi Chemicals Teagent. Co. Ltd.

General procedure: The freshly $\{\text{Mo}_{154}\}$ and $\{\text{Mo}_{72}\text{Fe}_{30}\}$ solutions were dialyzed continuously using a dialysis bag of the membrane (Spectra/Por M_{wco} = 14000, Jingkehongda Biotechnology Co., Ltd., Beijing, China). In order to increase the speed of dialysis, the water outside of the membrane was replaced in a short time. When the electric conductivity of the water did not change, in dialysis membrane, there were only the macro anions and the corresponding antiions in two solutions ($\{\text{Mo}_{154}\}$ and $\{\text{Mo}_{72}\text{Fe}_{30}\}$ solutions). The dialyzed $\{\text{Mo}_{154}\}$ and $\{\text{Mo}_{72}\text{Fe}_{30}\}$ solutions were divided into two groups, respectively. One group was examined directly and the other group was placed at certain conditions for some time and in order to make the macro anions self-associate into aggregations. In addition, the $\{\text{Mo}_{154}\}$ solution was placed at 25.0 ± 0.1 °C under N₂ atmosphere in order to preventing oxidation; while the $\{\text{Mo}_{72}\text{Fe}_{30}\}$ solution was placed at 45.0 ± 0.1 °C for the slowly self-assembly speed, in the process of placement.

Detection method: The electrode used in the present experiments was glassy carbon disk of diameter 3 mm insulated in Teflon rod of diameter 7 mm. The electrode was polished with chamois and was cleaned ultrasonically in 95 % ethanol prior to use. Typical procedures for the preparation of modified electrodes are as follows. The glassy carbon electrode was placed in the solutions (the freshly dialyzed $\{\text{Mo}_{154}\}$ and $\{\text{Mo}_{72}\text{Fe}_{30}\}$ solutions), respectively. The single $\{\text{Mo}_{154}\}$ and $\{\text{Mo}_{72}\text{Fe}_{30}\}$ macro anions on glassy carbon electrodes were examined using cyclic voltammetry (equipment, the 600B CHI electrochemistry analytical instrument, USA). A saturated calomel electrode (SCE) and a platinum plate were used as the reference and the

counter electrode, respectively. Three weeks later, in $\{Mo_{154}\}$ solution placed at 25.0 ± 0.1 °C under N_2 atmosphere, the supramolecular structures formed and then it was examined again. While, for the slowly self-assembly speed, the $\{Mo_{72}Fe_{30}\}$ solution was placed for 3 months at least at 45.0 ± 0.1 °C, then most $\{Mo_{72}Fe_{30}\}$ macro anions self-associate into aggregations. After the $\{Mo_{154}\}$ and $\{Mo_{72}Fe_{30}\}$ macro anions completed self-association, so the electrochemistry behaviours of the aggregations could be obtained when they were examined by cyclic voltammetry.

RESULTS AND DISCUSSION

Electrochemistry behaviours of the $\{Mo_{154}\}$ macro anions and aggregations:

The $\{Mo_{154}\}$ macro anions can self-associate into supramolecular structures easily. The laser light scattering (LLS) measurements show that the $\{Mo_{154}\}$ macro anions complete the self-assembly in several weeks at room temperature¹. So, the superstructures were not formed after dialysis rapidly in the freshly $\{Mo_{154}\}$ solution with 0.5 mg mL^{-1} . The glassy carbon electrode was placed in the $\{Mo_{154}\}$ solution and examined using cyclic voltammetry and the cyclic voltammograms of the single $\{Mo_{154}\}$ macro anions were obtained as shown in Fig. 1.

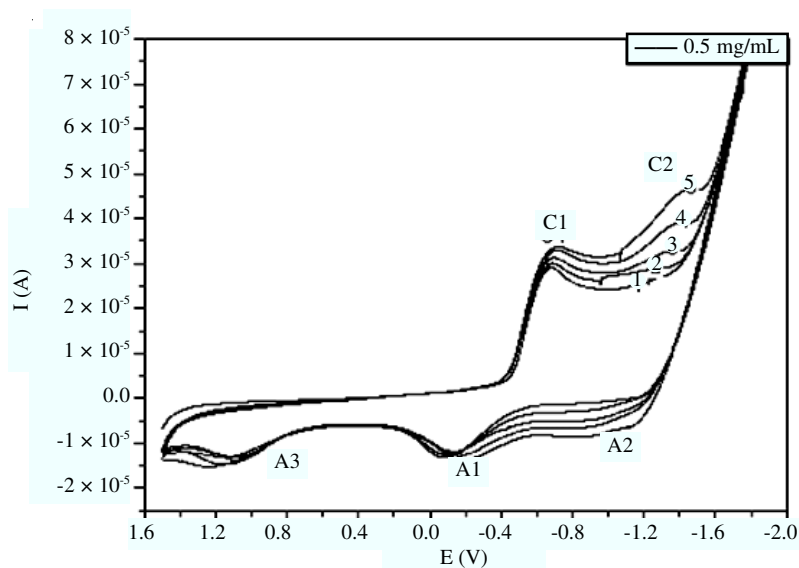


Fig. 1. Cyclic voltammograms of the $\{Mo_{154}\}$ macro anions with 0.5 mg mL^{-1} solution in potential range between 1.5 to -1.8 V. Scan rate: 0.1 V/s

Fig. 1 shows cyclic voltammograms (CVs) of the macro anions in the freshly dialyzed $\{Mo_{154}\}$ solution with 0.5 mg mL^{-1} at room temperature ($T = \sim 23$ °C). A scan of the $\{Mo_{154}\}$ macro anions solution in the potential range is between 1.5 to -1.8 V, during potential cycling at a scan rate of 0.1 V/s. In Fig. 1, there are two redox couples (C1 and A1, C2 and A2) and one evident oxidation wave (A3) at 1.1

V. For two redox couples, the large shift in potential (> 58 mV) between anodic and cathodic peaks can be found, which shows it is irreversible electrochemical processes and the electrons transfer continuously in the processes. The anodic wave is associated with the cathodic wave. Here, the cathodic waves are caused by the reduction of the higher valence of Mo. The cathode wave C1 is caused by the Mo(VI) reduction and the other cathode wave C2 is corresponding with the Mo(V) reduction. With the potential cycling, peak current of the cathode wave C2 is increase, because the Mo(V) from Mo(VI) reduction is increase with the potential cycling on the glassy carbon electrode.

When the dialyzed $\{Mo_{154}\}$ solution was placed for 3 weeks under N_2 atmosphere the macro anions could complete the self-association, then, it was examined by cyclic voltammetry again. The cyclic voltammograms of the $\{Mo_{154}\}$ supermolecule aggregations could be obtained as shown in Fig. 2. By comparing Fig. 1 and Fig. 2, it is clearly seen that the cyclic voltammograms (CVs) are similar at the same potential range, which indicates that the electrochemical behaviours is unchanged when $\{Mo_{154}\}$ aggregations formed. As the assistant examination, the $\{Mo_{154}\}$ aggregations in solution placed for 3 weeks were examined on a computer-manipulated spectrometer (UV-vis 4100). The UV-vis spectroscopy (Fig. 3) shows absorption bands at 741 and 1073 nm, respectively, which corresponding with that of $\{Mo_{154}\}$ macro anions (two absorption bands: 745 and 1073 nm) in the literature¹⁸. That is to say, the function groups of the $\{Mo_{154}\}$ macro anions do not change when they self-associate into aggregations.

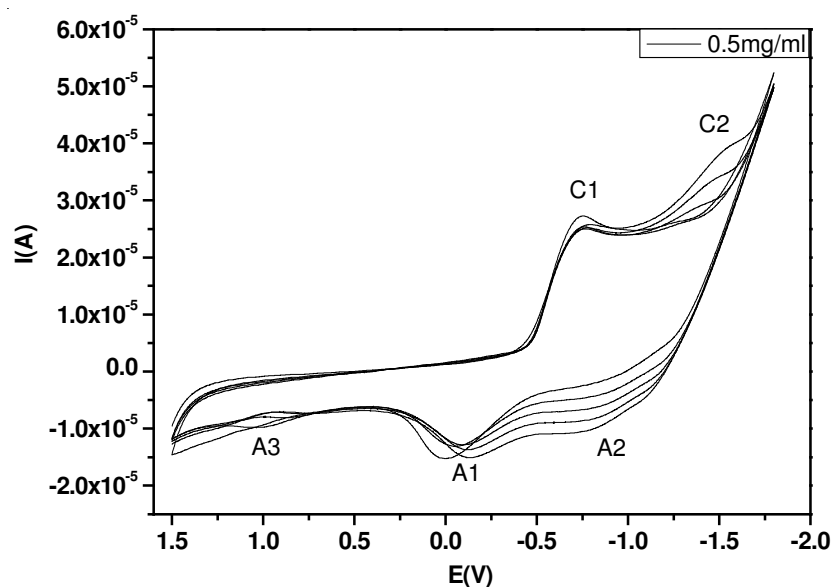


Fig. 2. Cyclic voltammograms of $\{Mo_{154}\}$ solution (0.5 mg mL^{-1}) placed for 2 weeks at 25.0 ± 0.1 °C in potential range between 1.5 to -1.8 V. Scan rate: 0.1 V/s

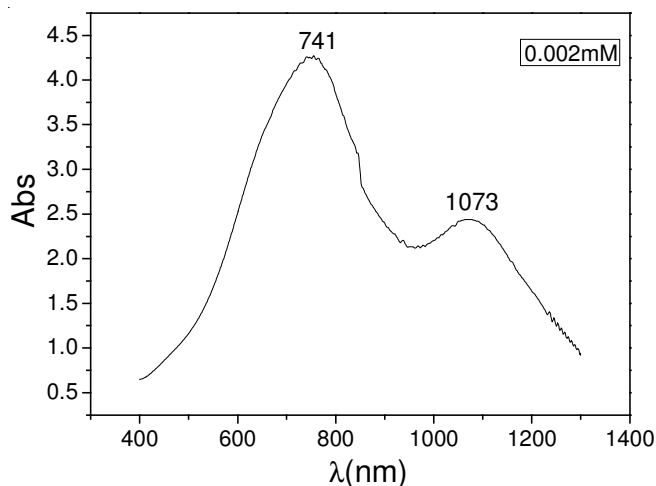


Fig. 3. UV/Vis spectra of typical well-shaped $\{Mo_{154}\}$ solution placed for 3 weeks

Electrochemical behaviours of the $\{Mo_{72}Fe_{30}\}$ macro anions and aggregations:

In the freshly dialyzed $\{Mo_{72}Fe_{30}\}$ solution with 0.5 mg mL^{-1} , the $\{Mo_{72}Fe_{30}\}$ exist as single macro anions. It was examined using cyclic voltammetry and the cyclic voltammograms of the single $\{Mo_{72}Fe_{30}\}$ macro anions were obtained (Fig. 4).

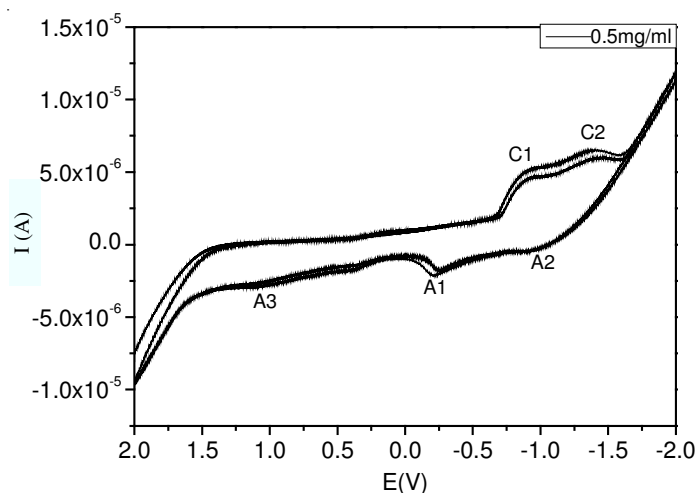


Fig. 4. Cyclic voltammograms of the $\{Mo_{72}Fe_{30}\}$ macro anions with 0.5 mg mL^{-1} solution in potential range between 2.0 to -2.0 V. Scan rate: 0.1 V/s

In Fig. 4, a scan of $\{Mo_{72}Fe_{30}\}$ macro anions in the potential range is between 2.0 and -2.0 V. Two cathode peaks at 0.92 V (C1) and -1.40V (C2) appear and their corresponding anode wave appears at -0.25 V (A1) and -0.92 V (A2), at 1.1V, there is an un conspicuous anode wave (A3). It is clear that a large shift ($> 58 \text{ mV}$) in

potential between anodic and cathodic peaks for two redox couples (C1 and A1, C2 and A2), similar with Figs. 1 and 2, which indicates it is irreversible electrochemical processes and the electrons transfer continuously in the processes. The cathode wave C1 is caused by the Mo(VI) reduction. No Mo(V) in $\{\text{Mo}_{72}\text{Fe}_{30}\}$ anions, here, Mo(VI) is reduced to Mo(V) firstly and then appear the second cathode wave C2 with the Mo(V) reduction. In addition, the peak current of the $\{\text{Mo}_{72}\text{Fe}_{30}\}$ macro anions is less than that of $\{\text{Mo}_{154}\}$ macro anions with the same concentration, though the content of Mo(VI) in $\{\text{Mo}_{72}\text{Fe}_{30}\}$ is higher than that of in $\{\text{Mo}_{154}\}$. The main reason is probably because the Fe(III) binding with Mo(VI) causes the Mo(VI) more stable in $\{\text{Mo}_{72}\text{Fe}_{30}\}$.

The dialyzed $\{\text{Mo}_{72}\text{Fe}_{30}\}$ solution with 0.5 mg mL^{-1} placed at $45.0 \pm 0.1 \text{ }^\circ\text{C}$ for 3 months, the $\{\text{Mo}_{72}\text{Fe}_{30}\}$ macro anions self-associate into aggregations. Then, it was examined again using cyclic voltammetry as the former. The cyclic voltammograms of the single $\{\text{Mo}_{72}\text{Fe}_{30}\}$ aggregations were obtained shown in Fig. 5. Comparing Figs. 4 and 5, it is easily to be seen that the peaks shapes of the $\{\text{Mo}_{72}\text{Fe}_{30}\}$ macro anions and aggregations are similar and the peak current of $\{\text{Mo}_{72}\text{Fe}_{30}\}$ aggregations is higher than that of the macro anions. The diameter of the supramolecular structure (aggregations) reaches to 40-60 nm, which is larger than the size of $\{\text{Mo}_{72}\text{Fe}_{30}\}$ macro anions (2.5 nm diameter). So, the local concentration near the glassy carbon electrode in the $\{\text{Mo}_{72}\text{Fe}_{30}\}$ aggregations solution is higher than that in the single macro anions solution, which makes the peak currents increase when aggregations formed. Just as the $\{\text{Mo}_{154}\}$ electrochemical behaviours, the similarity of Figs. 4 and 5 shows that the electrochemistry behaviours of the $\{\text{Mo}_{72}\text{Fe}_{30}\}$ macro anions is the same as that of their aggregations.

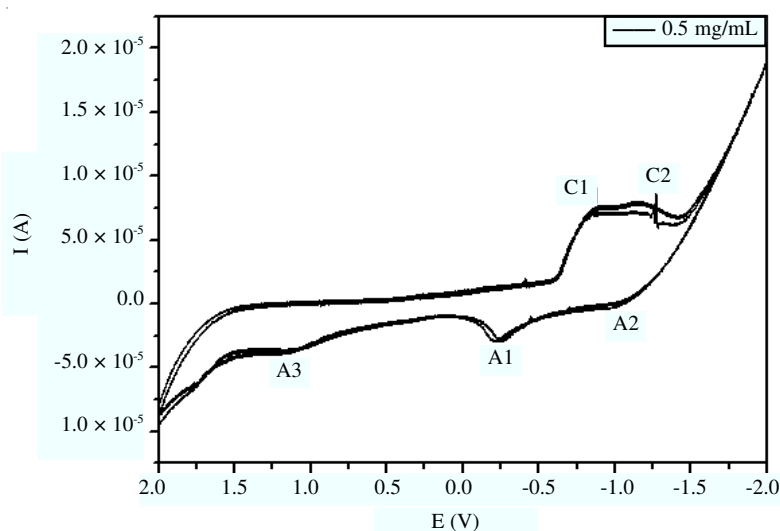


Fig. 5. Cyclic voltammograms of $\{\text{Mo}_{72}\text{Fe}_{30}\}$ solution (0.5 mg mL^{-1}) placed for 3 months at $45.0 \pm 0.1 \text{ }^\circ\text{C}$ in potential range between 2.0 to -2.0 V. Scan rate: 0.1 V/s

From the electrochemical behaviours of $\{\text{Mo}_{154}\}$ and $\{\text{Mo}_{72}\text{Fe}_{30}\}$ solutions and their aggregations, one can see that the chemical behaviours do not change when the macro anions self-assemble aggregations. At the same time, the UV-vis spectroscopy of the $\{\text{Mo}_{72}\text{Fe}_{30}\}$ aggregations (Fig. 6) in the solution placed for 3 months was measured. There is one absorption band at 340 nm, which according with that of the $\{\text{Mo}_{72}\text{Fe}_{30}\}$ macro anions in fresh solution¹⁹.

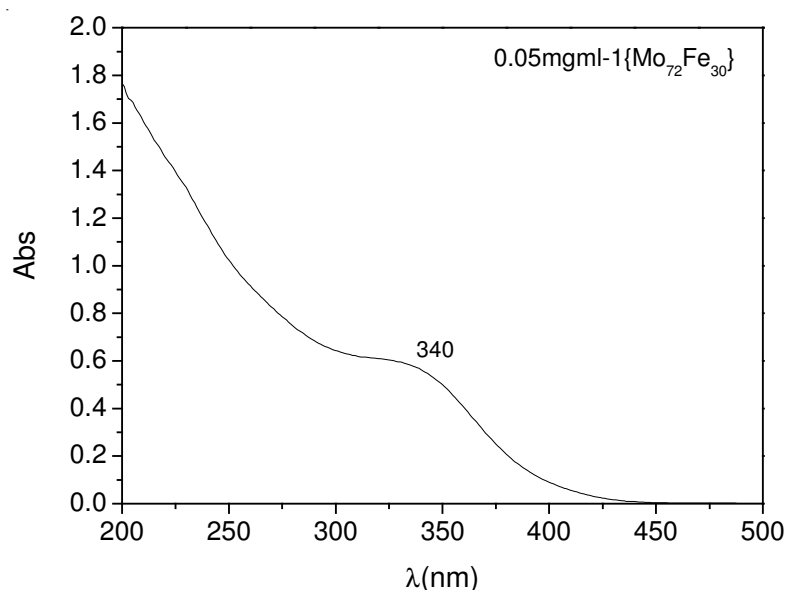


Fig. 6. UV/Vis spectra of 0.5 mg mL^{-1} $\{\text{Mo}_{72}\text{Fe}_{30}\}$ solution placed for three months

From the above results, it can be seen when the macro anions self-associate into vesicle supramolecular structures, the chemical behaviours do not change. So, the driving force of the self-association about $\{\text{Mo}_{154}\}$ macro anions is not due to chemical bond, it should be physical driving force such as Van der Waals force, for their big size and weight. Which are important for the study of the complex driving forces of the inorganic macro anions self-assembly.

Conclusion

In this work, the electrochemical behaviours of the $\{\text{Mo}_{154}\}$ and $\{\text{Mo}_{72}\text{Fe}_{30}\}$ were analyzed using cyclic voltammetry. By comparing the cyclic voltammograms of the $\{\text{Mo}_{154}\}$ and $\{\text{Mo}_{72}\text{Fe}_{30}\}$ macro anions as well as their aggregations, it was found that the electrochemical behaviours do not change when the macro anions formed into vesicles. It indicates that the oxidation-reduction behaviours of the inorganic macro anions do not change when their aggregations formed. From the electrochemistry point of view, it is also concluded that the major driving forces of the self-assembly is the physical force *i.e.*, Van der Waals force. It is helpful for the research of the macro anions self-association mechanism.

ACKNOWLEDGEMENTS

This work was supported by the Community of Shan Dong Nature Science Foundation (No. ZR2009BQ005), Shandong Provincial Natural Science Foundation, China (Y2007B42) and the Scientific Research Foundation of Shandong Jianzhu University (No. 824016).

REFERENCES

1. T. Liu, E. Diemann and H. Li, *Nature*, **426**, 59 (2003).
2. G. Liu and T. Liu, *J. Am. Chem. Soc.*, **127**, 6942 (2005).
3. G. Liu, Y. Cai and T. Liu, *J. Am. Chem. Soc.*, **126**, 16690 (2004).
4. G. Liu, M. Cons and T. Liu, *J. Mol. Liq.*, **118**, 27 (2005).
5. G. Liu and T. Liu, *Lagmuir*, **21**, 2713 (2005).
6. T. Liu, *J. Am. Chem. Soc.*, **124**, 10942 (2002).
7. T. Liu, *J. Am. Chem. Soc.*, **125**, 312 (2003).
8. X. Jia, D. Fan, P. Tang, J. Hao and L. Ma, *Acta Phys. Chim. Sin.*, **22**, 1300 (2006).
9. G. Liu, T. Liu, S.S. Mal and U. Kortz, *J. Am. Chem. Soc.*, **128**, 10103 (2006).
10. D. Li, J. Zhang, K. Landskron and T. Liu, *J. Am. Chem. Soc.*, **130**, 4226 (2008).
11. J. Zhang, Y. Song, L. Cronin and T. Liu, *J. Am. Chem. Soc.*, **130**, 14408 (2008).
12. B.V. Derjaguin and L. Landau, *Acta Physicochim. USSR*, **14**, 633 (1941).
13. E.J. Verwey and J.T.G. Overbeek, Elsevier, Amsterdam (1948).
14. A. Müller and S. Roy, *Coord. Chem. Rev.*, **245**, 153 (2003).
15. N. Ise, *Proc. Jpn. Acad. Ser. B*, **78**, 192 (2007).
16. G.M. Kepler and S. Fraden, *Phys. Rev. Lett.*, **73**, 356 (1944).
17. J.C. Crocker and D.G. Grier, *Phys. Rev. Lett.*, **77**, 1897 (1996).
18. A. Müller, S.K. Das, V.P. Fedin, E. Krickemeyer, C. Beugholt, H. Bogge, M. Schmidtman and B.Z. Hauptfleisch, *Anorg. Allg. Chem.*, **625**, 1187 (1999).
19. A. Müller, S. Sarkar, S.Q. Nazir Shah, H. Bogge, M. Schmidtman, S.H. Sarkar, P. Kogerler, B. Hauptfleisch, A.X. Trautwein and V. Schunemann, *Angew. Chem. Int. Ed. Engl.*, **38**, 3238 (1999).
20. A. Müller, E. Krickemeyer, H. Bögge, M. Schmnidtmann and F. Peters, *Angew. Chem. Int. Ed.*, **37**, 3359 (1998).

(Received: 22 March 2010;

Accepted: 31 July 2010)

AJC-8934