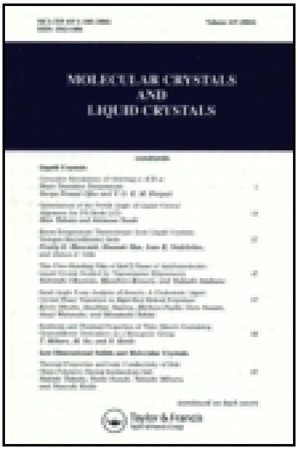

Molecular Crystals and Liquid Crystals

Synthesis of Hybrid Sm-Containing Polyoxotungstates and their Photoluminescent Properties

Dinh Thi Minh Hoa [a], Hee Sang Kim [a], Burm-Jong Lee [a] & Young-Soo Kwon [b]

[a] Department of Chemistry, Institute of Nanotechnology, Inje University, Kimhae, Korea

[b] Department of Electrical Engineering, Dong-A University, Busan, Korea

Version of record first published: 20 Aug 2006

To cite this article: Dinh Thi Minh Hoa, Hee Sang Kim, Burm-Jong Lee & Young-Soo Kwon (2006): Synthesis of Hybrid Sm-Containing Polyoxotungstates and their Photoluminescent Properties, Molecular Crystals and Liquid Crystals, 444:1, 113-120

To link to this article: http://dx.doi.org/10.1080/15421400500365284

Mol. Cryst. Liq. Cryst., Vol. 444, pp. 113–120, 2006
Copyright © Taylor & Francis LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400500365284

Synthesis of Hybrid Sm-Containing Polyoxotungstates and their Photoluminescent Properties

Dinh Thi Minh Hoa
Hee Sang Kim
Burm-Jong Lee
Department of Chemistry and Institute of Nanotechnology,
Inje University, Kimhae, Korea

Young-Soo Kwon
Department of Electrical Engineering, Dong-A University,
Busan, Korea

Two novel hybrid Sm-containing polyoxometalates were synthesized and characterized to show that hydrophilic polyoxometalate cores are encapsulated by hydrophobic shells. Sodium salt of $SmW_{10}O_{36}^{9-}$ *was changed the counter ions by dodecyltrimethylammonium bromide (DDTABr) and dimethyldioctadecylammonium bromide (DODABr) to obtain* $(DDTA)_9SmW_{10}O_{36}$ *and* $(DODA)_9SmW_{10}O_{36}$*. Both of them were synthesized by extraction procedure using chloroform as the solvent and characterized by FT-IR, UV/Vis,* ^{1}*H-NMR, and XPS.* $(DDTA)_9SmW_{10}O_{36}$ *readily dissolves in chloroform and ethanol while* $(DODA)_9SmW_{10}O_{36}$ *dissolves in chloroform, toluene and benzene. The hybrid compounds show photoluminescence activity in the orange region of the visible light*

Keywords: dimethyldioctadecylammonium bromide; dodecyltrimethylammonium bromide; photoluminescence; polyoxometalates; samarium

1. INTRODUCTION

Polyoxometalates (POMs) form a distinct class of inorganic compounds that is of both theoretical and practical interest. The structure of

---

This work was supported by Korea Research Foundation Grant (KRF-2003-002-D00114), Graduate Student Cultivation Program of Korea Industrial Technology Foundation and partly by BPRC of Inje University. We thank Dr. Mi-Sook Won in Korea Basic Science Institute for obtaining XPS spectra.

Address correspondence to Burm-Jong Lee, Department of Chemistry and Institute of Nanotechnology, Inje University, Kimhae 621-749, Korea. E-mail: chemlbj@inje.ac.kr

POMs can be described as molecular fragment of close-packed metal oxides with general formula $X_aM_bO_c$ (M = Mo, W, V... and X = Si, P, B....). Although the mechanism of formation of POMs is not well understood and commonly described as self-assembly process, synthesis of POMs is governed by the reaction conditions, pH, ratio of reactants, and temperature. This class of compounds has received much attention because of their interesting properties and wide applications in diversity fields such as analytical chemistry, catalysis, medicine and materials [1–3].

Recently, lanthanide-containing POMs are the focus of much research because they possess the antiviral and anti-HIV activities [4], photoluminescence properties [5], as well as potential application in molecular-based materials and nano-designs [6]. The luminescent properties of Eu-containing POMs have been systematically investigated [5,7,8]. Electroluminescent devices using Ln(III)-POMs as luminescent agents were fabricated through precipitation of Ln(III)-POMs from aqueous solution as Ba salts but the commercial utility of devices is still a challenge because of the small number of internal carriers that produce quite low electroluminescence intensity [8–10].

In the presence of appropriate counterions, POMs can soluble in nearly all media from H_2O to hydrocarbon [2]. There are many literatures reported on changing the inorganic cations of POMs by cationic surfactants. The hybrid POMs not only dissolve in organic solvents such as chloroform, toluene and benzene but also have a synergetic combination of the properties typical of each of the constituent. Those hybrid POMs show the properties suitable for fabrication of Langmuir-Blodgett films. First, E. Coronado and C. Mingotaud reported the fabrication of hybrid Langmuir-Blodgett films by taking advantage of the electrostatic interaction between the heteropolytungstates of the Keggin type and a monolayer of dimethyldioctadecylammonium bromide spread on the water subphase [11,12]. Afterward, D.G. Kurth *et al.* reported for the first time a simple approach to modify the chemical properties of POMs surface with the cationic surfactant, by which the obtained hybrid POMs can form stable Langmuir monolayer and keep their structure when they are spread at an air/water interfaces [13]. Recently, W. Bu *et al.* reported a range of papers related to using that method to obtain hybrid POMs and investigated their activities in Langmuir-Blodgett films. These supramolecular hybrid materials are very promising candidates for the construction of nanodevices [14–16].

Herein, we present two novel surfactant-encapsulated Sm-containing POMs that show the orange photoluminescence. Sodium salt of

$SmW_{10}O_{36}^{9-}$ was changed the counter ions by dodecyltrimethylammonium bromide and dimethyldioctadecylammonium bromide to obtain hybrid POMs.

2. EXPERIMENT

2.1. Materials and Instrument

Sodium tungstate dihydrate ($Na_2WO_4{\cdot}2H_2O$) was used as purchased from Acros Organics Co. Samarium (III) nitrate hexahydrate ($Sm(NO_3)_3{\cdot}6H_2O$), dodecyltrimethylammonium bromide, dimethyldioctadecylammonium bromide, and others chemicals in synthesis were purchased from Aldrich Co. and used without further purification.

IR spectra were recorded on Shimadzu 8201PC. UV-Vis absorption spectra were collected on Shimadzu UV-3100S. PL spectra were recorded on Fluorophotometer Hitachi F-4500. X-ray photoelectron spectroscopy (XPS) was carried out at Korea Basic Science Institute on Busan Branch.

2.2. Synthesis of $Na_9SmW_{10}O_{36}$ $(DDTA)_9SmW_{10}O_{36}$ and $(DODA)_9SmW_{10}O_{36}$

$Na_9SmW_{10}O_{36}$ was freshly prepared from the solution containing samarium nitrate and sodium tungstate of molar ratio 1:10, according to the published procedure [17].

$(DDTA)_9SmW_{10}O_{36}$ and $(DODA)_9SmW_{10}O_{36}$were synthesized using the reported procedure [13,14]. $Na_9SmW_{10}O_{36}$ was dissolved in water and then chloroform solution of DDTABr or DODABr was added with stirring. The initial molar ratio of DDTABr or DODABr to POM was controlled on 9:1. The complete transfer of POM into organic phase was indicated by the colorless aqueous phase. The organic phase was separated and $(DDTA)_9SmW_{10}O_{36}$ and $(DODA)_9SmW_{10}O_{36}$ were collected by evaporating chloroform to dryness. Then the sample was dried in vacuum until the weight remained constant.

3. RESULTS AND DISCUSSION

3.1. Synthesis and Structure Characterization of $(DDTA)_9SmW_{10}O_{36}$ and $(DODA)_9SmW_{10}O_{36}$

The decatungstosamarate (-9) anion was first synthesized by R. D. Peacock and T. J. R. Weakly [17] with the original formula as $SmW_{10}O_{35}^{7-}$. It is now known to have composition as $SmW_{10}O_{36}^{9-}$ in

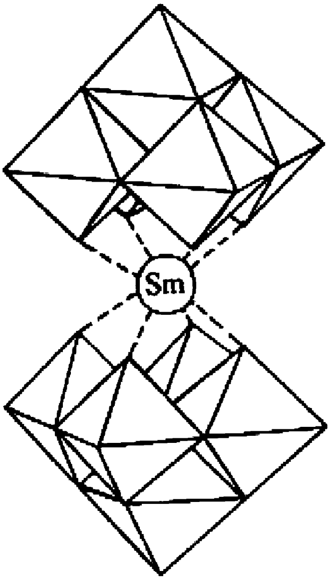

FIGURE 1 Polyhedral representation of $SmW_{10}O_{36}^{9-}$.

which Sm^{3+} is sandwiched between two $W_5O_{18}^{6-}$ fragments (each containing of five WO_6 octahedral sharing edges) and has eight coordination bonds (Fig. 1).

The POM itself is only soluble in water whereas $(DDTA)_9SmW_{10}O_{36}$ and $(DODA)_9SmW_{10}O_{36}$ are immiscible in water but readily dissolve in organic solvents. $(DDTA)_9SmW_{10}O_{36}$ is dissolves in chloroform and ethanol and $(DODA)_9SmW_{10}O_{36}$ dissolves in chloroform, benzene and toluene. This proved that POM has been successfully encapsulated with organic cations.

IR spectra (Fig. 2) show the absorption peaks at 2918 cm^{-1} and 2850 cm^{-1} represent to CH_2-antisymmetric and symmetric stretching modes of alkyl chains. This indicates that the DDTA and DODA alkyl chain are well-ordered in the solid state of $(DDTA)_9SmW_{10}O_{36}$ and $(DODA)_9SmW_{10}O_{36}$. The peaks at 3458 cm^{-1} and 1653 cm^{-1} assigned to water crystalline. The peaks observed below 1000 cm^{-1} represent characteristic POM vibrations and the intensity of these peaks reduces with the increase in the length of alkyl chains.

^{1}H-NMR spectra (not shown here) of the hybrid POMs provide more evident for the attachment of DDTA and DODA to the surface of POM. The peaks representing methyl groups were not changed in chemical shift but more broad compared with that in the ^{1}H-NMR spectra

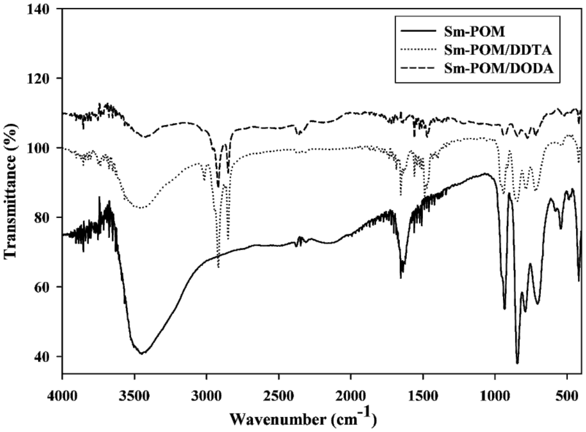

FIGURE 2 IR spectra of POM and hybrid POMs.

of DDTABr and DODABr. This is attributed to the electrostatic interaction between DDTA or DODA and POM. The positive head of cationic surfactants attached to the negative surface of POM so that reduce the mobility of the long alkyl chain.

All dilute solutions of POM and hybrid POMs show no absorption band in the visible region (Fig. 3). Only the shoulder bands are observed in UV region, particularly $(DDTA)_9SmW_{10}O_{36}$ in ethanol and $(DODA)_9SmW_{10}O_{36}$ in ethanol-hexane show a shoulder at around 260 nm. This band may be assigned to O → W charge transition, which

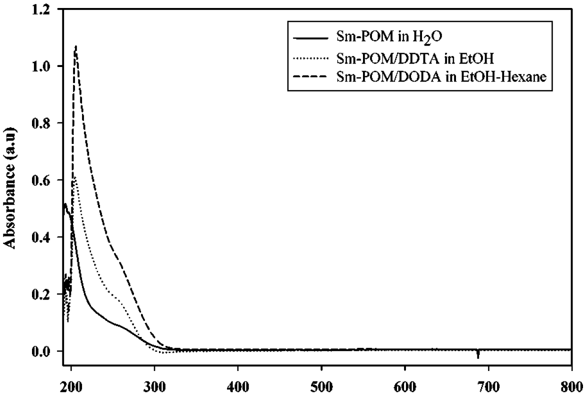

FIGURE 3 Absorption spectra of POM and hybrid POMs.

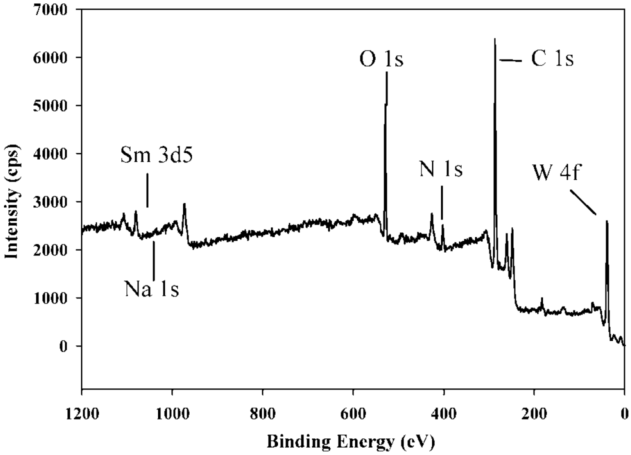

FIGURE 4 XPS spectrum of $(DDTA)_9SmW_{10}O_{36}$.

are the characteristic band for some heteropolytungstate complexes [18]. Absorption peak around 204 nm is assigned to the absorption of solvents.

XPS spectra of hybrid POMs are shown in Figures 4 and 5. The carbon peaks appear intensively while the sodium peaks disappear. Combine with the quantitative analysis of the component elements; we could confirm that all sodium cations were exchanged by DDTA and DODA.

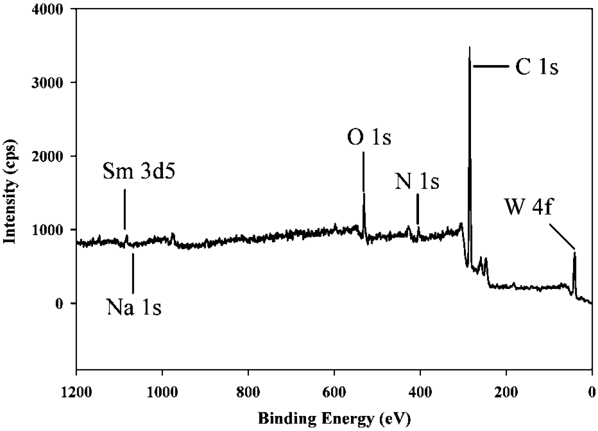

FIGURE 5 XPS spectrum of $(DODA)_9SmW_{10}O_{36}$.

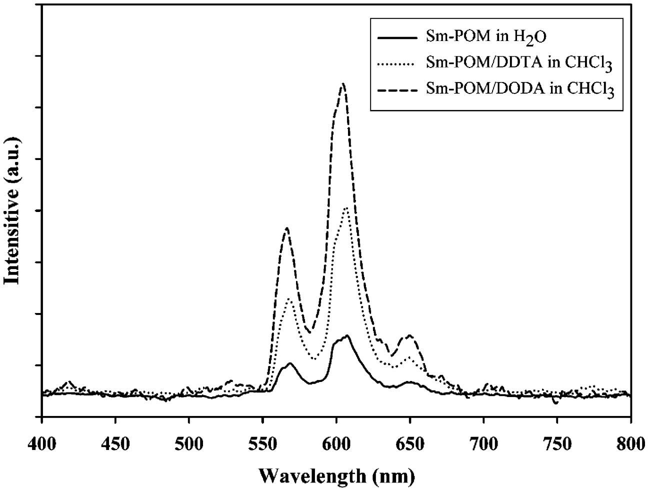

FIGURE 6 Photoluminescence spectra of POM and hybrid POMs.

3.2. Photoluminescent Property of POM and Hybrid POMs

We investigated the photoluminescence property of POM and two hybrid POMs in dilute solutions (10^{-3} mol.L^{-1}). Figure 6 shows the photoluminescence spectra of $Na_9SmW_{10}O_{36}$ in water, $(DDTA)_9SmW_{10}O_{36}$ and $(DODA)_9SmW_{10}O_{36}$ in chloroform. The measurements were carried out at room temperature and at the same excitation wavelength of $\lambda = 270$ nm. All spectra show three emission peaks at 570 nm, 608 nm and 653 nm in which the peak at 608 nm has the highest intensity. This peak belongs to the orange region of the visible light. And the photoluminescence intensity of both hybrid POMs in chloroform is higher than that of POM in water.

4. CONCLUSION

$(DDTA)_9SmW_{10}O_{36}$ and $(DODA)_9SmW_{10}O_{36}$ were synthesized and characterized. These hybrid substances contain the POM core encapsulated by surfactants. $(DDTA)_9SmW_{10}O_{36}$ readily dissolves in chloroform and ethanol while $(DODA)_9SmW_{10}O_{36}$ dissolves in chloroform, benzene and toluene. Both of them show the orange luminescence at 608 nm. The fabrication EL device using $(DDTA)_9SmW_{10}O_{36}$ and $(DODA)_9SmW_{10}O_{36}$ as the emitting layers is in progress.

REFERENCES

[1] Pope, M. T. (1983). *Heteropoly and Isopoly Oxometalates*, Springer: Heidelberg.

[2] Hill, C. L. (Ed.) (1998). The entire issue devoted to polyoxometalates. *Chem. Rev*, *98*(1).

[3] Pope, M. T. & Müller, A. (1991). *Angew. Chem. Int. Ed. Engl.*, *30*, 34–48.

[4] Rhule, J. T., Hill, C. L., Judd, D. A., & Schinazi, R. F. (1998). *Chem. Rev.*, *98*(1), 327–357.

[5] Zheng, Y. X., Lin, J., Liang, Y. J., Lin, Q., & Zhang, H. J. (2001). *J. Mater. Chem.*, *11*, 2615.

[6] Muller, A., Peters, F., Pope, M. T., & Gatteschi, D. (1998). *Chem. Rev*, *98*(1), 239–271.

[7] Lis, S. (2000). *J. Alloys Comp.*, *300–301*, 88–94.

[8] Yamase, T. & Naruke, H. (1991). *Coordination Chemistry Review*, *111*, 83–90.

[9] Yamase, T. (1998). *Chem. Rev.*, *98*(1), 307–325.

[10] Katsoulis, D. E. (1998). *Chem. Rev.*, *98*(1), 359–387.

[11] Chemente-Leon, M., Agricole, B., Mingotaud, C., Gomez-Garcia, C. J., Coronado, E., & Delhaes, P. (1997). *Langmuir*, *13*, 2340–2347.

[12] Chemente-Leon, M., Agricole, B., Mingotaud, C., Gomez-Garcia, C. J., Coronado, E., & Delhaes, P. (1997). *Angew. Chem. Int. Ed. Engl.*, *36*, 1114–1116.

[13] Kurth, D. G., Lehmann, P., Volkmer, D., Cölfen, H., Koop, M. J., Müller, A., & Chesne, A. D. (2000). *Chem. Eur. J.*, *6*(2), 385–393.

[14] Bu, W., Fan, H., Wu, L., Hou, W., Hu, C., Zhang, G., & Zhang, X. (2002). *Langmuir*, *18*, 6398–6403.

[15] Bu, W., Wu, L., Zhang, X., & Tang, A. (2003). *J. Phys. Chem.*, *B 107*, 13425–13431.

[16] Bu, W., Li, W., Li, H., Wu, L., & Tang, A. (2004). *J. Colloid and Interface Sci.*, *274*(1), 200–203.

[17] Ballardini, R., Mulazzani, Q. G., Venturi, M., Bolletta, F., & Balzani, V. (1984). *Inorg. Chem.*, *23*, 300.

[18] Wang, J., Wang, H., Liu, F., Fu, L., & Zhang, H. (2003). *Material Letters*, *57*, 1210.