LA-UR- 08-7743

Title: Ionic Liquid Polyoxometalates as Light Emitting Materials

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Intended for: publication in Electrochemical Society Transaction

Ionic Liquid Polyoxometalates As Light Emitting Materials

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The low melting point, negligible vapor pressure, good solubility, and thermal and chemical stability make ionic liquids useful materials for a wide variety of applications. Polyoxometalates are early transition metal oxygen clusters that can be synthesized in many different sizes and with a variety of heterometals. The most attractive feature of POMs is that their physical properties, in particular electrical, magnetic, and optical properties, can be easily modified following known procedures. It has been shown that POMs can exhibit cooperative properties, as superconductivity and energy transfer. POM ionic liquids can be obtained by selecting the appropriate cation. Different alkyl ammonium and alkyl phosphonium salts are being used to produce new POM ionic liquids together with organic or inorganic luminescent centers to design light emitting materials. Ammonium and phosphonium cations with activated, polymerizable groups are being used to further polymerize the ionic liquid into transparent, solid materials with high metal density.

Introduction

Ionic liquids (ILs) are commonly used as solvents in many applications, such as in synthesis and catalysis. ILs have also been used extensively in biology, electron conductivity and transfer, and spectroscopy because of their low melting point, negligible vapor pressure, good solubility, and thermal and chemical stability. Additionally, they have been exploited as new materials in many applications, including batteries, thermal fluids, and optics.

Polyoxometalates (POMs) are well-defined, early transition metal-oxide anionic clusters of great versatility and structural diversity in both symmetry and size, and when prepared with the appropriate counter-ion, will form ionic liquids with very unique properties. POMs have applications in many fields of science because of their wide variety of properties, which include electrochromism, photochromism, conductivity, redox activity, syntheses, catalysis, antimicrobial and antitumor properties. The properties of the POMs can be easily tuned by varying the size of the cluster, substitution of the heteroatoms, or by synthesizing different organic-inorganic hybrids. Typical inorganic POM salts have little or no solubility in organic solvents. However, utilizing organic-based ammonium and phosphonium cations can promote the solubility of POMs into a variety of organic solvents. Utilizing the larger, bulkier cations also result in hybrid organic-inorganic room temperature ionic liquids. Recently, Rickert et al. described the synthesis and characterization of trihexyl(tetradecyl) phosphonium salt of the Linqvist isopolyoxoanion, $[W_6O_{19}]^{-2}$.[1,2] This hexatungstopolyoxoanion hybrid exhibits a melting point of -48 °C and improved thermal stability compared to previously described POM ionic liquid hybrids.

It has been demonstrated that surfactants can significantly improve the chemical properties of POMs, and make POM anions soluble in organic solvents. Monomer-encapsulated POMs in where the POM anion is coupled with a monomeric surfactant can also be synthesized using counter-ions containing polymerizable functional groups. Monomer-encapsulated POMs can be used to form clusters-containing polymeric materials, or composites. This methodology is an effective technique for the introduction of polyoxometalates into polymer matrices. Recently, Lixin Wu reported the encapsulation of $[EuW_{10}O_{36}]^{-9}$ by dodecyl(11-methacryloyloxyundecyl)dimethyl-ammonium cation.[3] This polyoxometalate contains nine polymerizable groups that can be copolymerized with methyl methacrylate to yield a polymer containing Eu-substituted POM.

Polyoxometalates have the ability of accepting electrons or energy and emitting with little or no structural changes. This property makes POMs attractive clusters for energy transfer into luminescent centers for optical applications. Energy transfer occurs in POMs upon irradiation when there is an $O \rightarrow M$ ligand to metal charge transfer (LMCT) in where electrons are promoted from the low energy state of oxygen to the high energy electronic states of the metal. This energy is trapped into electron traps or hole traps and can be released by optical stimulation through an intramolecular energy transfer leading to a charge transfer emission.[4]

Tungsten polyoxometalates have an $O \rightarrow W$ excitation at approximately 270 nm but exhibit very weak or often no emission at room temperature. The tungsten, as well as molybdate, POMs only emit at cryogenic temperatures under irradiation,[5] as well as under x-ray excitation (radioluminescence, RL) (Figure 1). In the presence of the right luminescent center, however, excitation of the POM LMCT band can result in energy transfer to, and emission from, the luminescent site. Energy transfer from POMs to lanthanides incorporated into the cluster, e.g. Eu^{3+} and Gd^{3+}, are very well known.[3,6-9] As lanthanides are also often used in luminescent materials and are known to have enhanced emission when the emission results from energy transfer, we have synthesized lanthanide-containing POM ionic liquids and polymeric materials. The structural and optical properties of these materials are described.

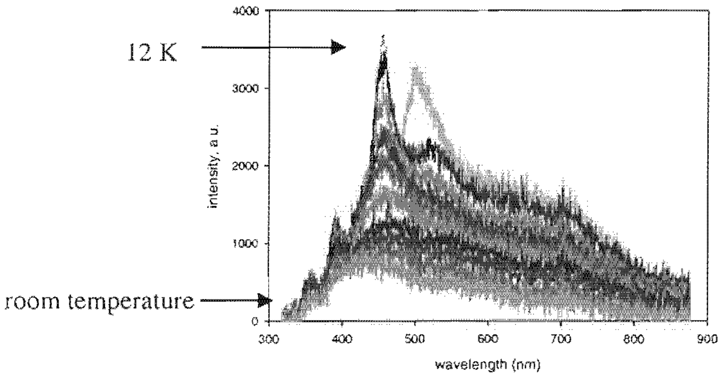


Figure 1. Temperature dependent radioluminescence of $[W_{10}O_{32}]^{-4}$

Experimental

Materials

Sodium tungstate was used as obtained from Fisher. Acryloyl chloride was used as obtained from Alfa Aesar. Tetradecyl(trihexyl)phosphonium chloride was obtained from Cytec (Canada) and was cleaned prior to use via extraction from hexane/water. All other reagents were obtained from Acros and were used without further purification. ^{1}H-NMR spectra were recorded in $CDCl_3$ at 25 °C in a Bruker Avence 300 Spectrometer (^{1}H at 300 MHz and ^{13}C and 75 MHz). Fluorescent studies were performed in a PTI Photon Technology International instrument containing a motor driver MD-5020, lamp power system LPS 220B, and a Bryte box.

$Na_9EuW_{10}O_{36} \cdot 32H_2O$

$Na_2WO_4 \cdot 2H_2O$ (8.3g, 25 mmol) was dissolved in 20 mL of water. The pH was adjusted to pH= 7.0-7.5 by slow addition of acetic acid. The solution was heated to 90 °C. Then, a solution containing $Eu(NO_3)_3 \cdot 6H_2O$ (1.1g, 2.47 mmol) in 2 mL of water was added to the hot tungsten solution with stirring. A cloudy solution formed that cleared instantly. After 10 minutes, the reaction mixture was allowed to cool to room temperature and crystallized by slow evaporation of the solvent. It was obtained 7.27 g of the product.

$Na_9TbW_{10}O_{36} \cdot 32H_2O$

$Na_2WO_4 \cdot 2H_2O$ (8.3g, 25 mmol) was dissolved in 20 mL of water. The pH was adjusted to pH= 7.0-7.5 by slow addition of acetic acid. The solution was heated to 90 °C. Then, a solution containing $TbCl_3 \cdot 6H_2O$ (0.92g, 2.47 mmol) in 2 mL of water was added to the hot tungsten solution with stirring. A cloudy solution formed that cleared instantly. After 10 minutes, the reaction mixture was allowed to cool to room temperature and crystallized by slow evaporation of the solvent. It was obtained 6.86 g of the product.

(tetradecyl(trihexyl)phosphonium)$_9EuW_{10}O_{36}$ (POM-1)

Tetradecyl(trihexyl)phosphonium chloride (1 g, 1.93 mmol) was dissolved in 20 mL of CH_2Cl_2. $Na_9EuW_{10}O_{36}$ (0.726 g, 0.22 mmol) was dissolved in 20 mL of water. The solutions were mixed together and vigorously stirred for 1 h. Then, the phases were separated. The organic phase was concentrated under reduced pressure to obtained 1.31 g of (Cyphos)$_9EuW_{10}O_{36}$.

(tetradecyl(trihexyl)phosphonium)$_9TbW_{10}O_{36}$ (POM-2)

Tetradecyl(trihexyl)phosphonium chloride (1 g, 1.93 mmol) was dissolved in 20 mL of CH_2Cl_2. $Na_9TbW_{10}O_{36}$ (0.727 g, 0.22 mmol) was dissolved in 20 mL of water. The solutions were mixed together and vigorously stirred for 1 h. Then, the phases were separated. The organic phase was concentrated under reduced pressure to obtained 1.34 g of (Cyphos)$_9TbW_{10}O_{36}$.

11-bromoundecylacrylate

11-bromoundecanol (97%, 10 g, 39 mmol) was dissolved in 100 mL of CH_2Cl_2. Then, Na_2CO_3 (4.1 g, 39 mmol) was added to the solution. Acryloyl chloride (96%, 3.6 mL, 42 mmol) was dissolved in 25 mL of CH_2Cl_2 and was added dropwise to the solution. The reaction mixture was stirred at room temperature for 4 days. Then, the reaction mixture was washed 3x 50 mL of water. The organic phase was dried over $MgSO_4$ and gravity filtered to remove the $MgSO_4$. The volatiles were removed under reduced pressure. The product oil was obtained in 91% yield (10.8g). ^{1}H-NMR (cdcl$_3$, 300 MHz): 1.2-1.5 m, 14H), 1.6-1.7 (m, 2H), 1.8-1.9 (m, 2H), 3.41 (t, 2H, J= 6.6 Hz), 4.15 (t, 2H, J= 6.9 Hz), 5.82 (dd, 1H, J=1.8, 10.5 Hz), 6.12 (dd, 1H, J= 10.5, 17.4 Hz), 6.40 (dd, 1H, J=1.5, 17.4 Hz). ^{13}C-NMR (cdcl$_3$, 75 MHz): 25.9, 28.1, 28.6, 28.7, 29.2, 29.36, 29.39, 29.41, 32.8, 34, 64.7, 128.6, 130.4, 166.3.

dodecyl(11-acryloyloxyundecyl)dimethylammonium bromide

11-bromoundecylacrylate (10.8 g, 36 mmol) and *N,N*-dimethyldodecylamine (95%, 7.98g, 36 mmol) were dissolved in 40 mL of acetone. The reaction mixture refluxed for 24h. Acetone was removed under reduced pressure and a solid was obtained. The solids were washed with diethyl ether and dried under vacuo. The reaction proceeded quantitatively. ^{1}H-NMR (cdcl$_3$, 300 MHz): 0.85 (t, 3H, J= 6.9 Hz), 1.2-1.33 (m, 30H), 1.6-1.67 (m, 6H), 3.40 (m, 10H), 4.11 (t, 2H, J= 6.6 Hz), 5.79 (dd, 1H, J= 1.5, 10.5 Hz), 6.09 (dd, 1H, J= 10.5, 17.4 Hz), 6.37 (dd, 1H, J= 1.5, 17.4 Hz). 13C-NMR (cdcl$_3$, 75 MHz):

[dodecyl(11-acryloyloxyundecyl)dimethylammonium]$_9$EuW$_{10}$O$_{36}$ (POM-3)

dodecyl(11-acryloyloxyundecyl)dimethylammonium bromide (2 g, 3.9 mmol) was dissolved in 20 mL of CH_2Cl_2. $Na_9EuW_{10}O_{36}$ (1.44 g, 0.43 mmol) was dissolved in 20 mL of water. The solutions were mixed together and stirred for 1 h. Then, the phases were separated. The organic phase was concentrated under reduced pressure to obtained 2.66 g of the SEC-$EuW_{10}O_{36}$ cluster.

[dodecyl(11-acryloyloxyundecyl)dimethylammonium]$_9$TbW$_{10}$O$_{36}$ (POM-4)

dodecyl(11-acryloyloxyundecyl)dimethylammonium bromide (2 g, 3.9 mmol) was dissolved in 20 mL of CH_2Cl_2. $Na_9TbW_{10}O_{36}$ (1.44 g, 0.43 mmol) was dissolved in 20 mL of water. The solutions were mixed together and stirred for 1 h. Then, the phases were separated. The organic phase was concentrated under reduced pressure to obtained 1.80 g of the SEC-$TbW_{10}O_{36}$ cluster.

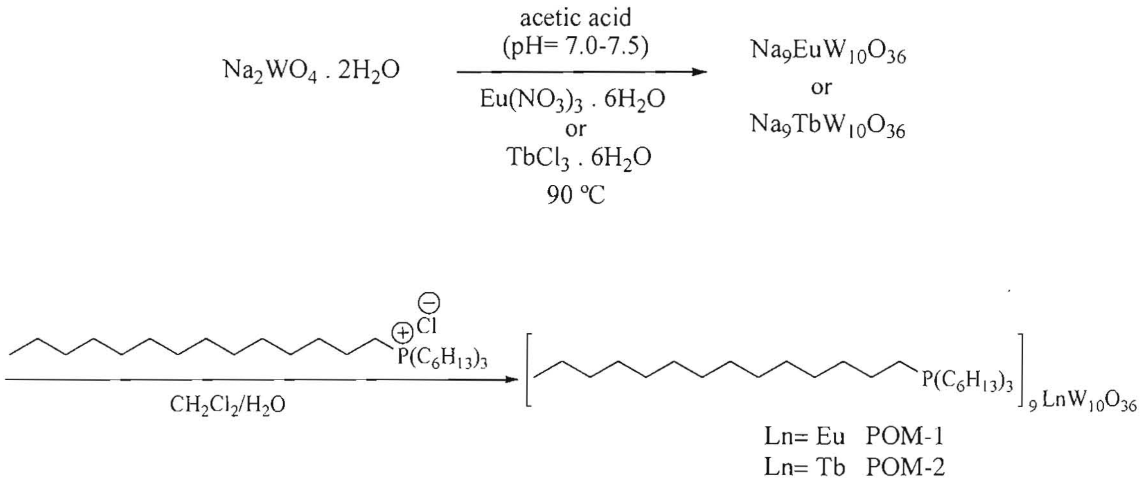
Poly(methyl methacrylate)-co- POM-3 or POM-4

[dodecyl(11-acryloyloxyundecyl)dimethylammonium]$_9$LnW$_{10}$O$_{36}$ (0.5 g) was dissolved in 4.5 g of methyl methacrylate. AIBN (0.2 mg) was added and the mixture was sealed and degassed with argon for 15 min. The mixture was heated at 65 °C for 24 h.

Results and Discussion

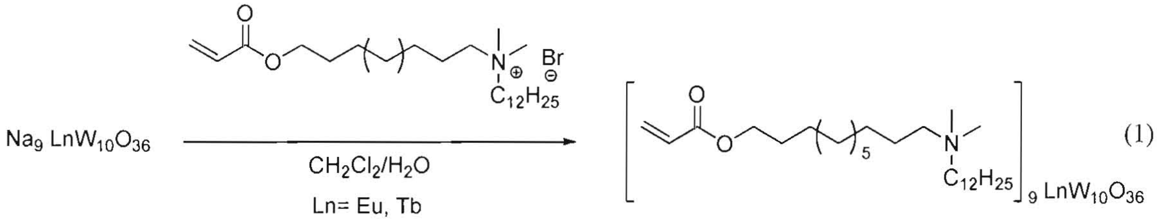
Previously, Gianellis et al. showed that the replacement of the protons in $H_3PW_{12}O_{40}$ with PEGylated quaternary ammonium cations yields a POM ionic liquid with a glass transition temperature, T_g, of -35 °C as determined by DSC. Additional effort has been put into the development of other polyoxometalate ionic liquids as well. Rickert et al. demonstrated that using tetradecyl(trihexyl)phosphonium as the cation you can obtain POM ionic liquids with melting points below 65 °C. Following similar procedures we produced POMs that contain a luminescent center as room temperature ionic liquids.

We chose to synthesize sandwich POMs where two W_5O_{18} clusters are coordinated to a lanthanide ion. For the synthesis of IL sandwich clusters we chose tetradecyl(trihexyl)phosphonium as the counter-ion because of its known ability to produce liquid salts.[1,2] $Na_9EuW_{10}O_{36}$ and $Na_9TbW_{10}O_{36}$ were synthesized following a known procedure.[10] Each salt was then dissolved in 20 mL of water and mixed with tetradecyl(trihexyl)phosphonium chloride dissolved in 20 mL of dichloromethane. After vigorous stirring the two phases were separated. The solvent of the organic phase was removed under reduced pressure and residual water removed via freeze drying. The products obtained were room temperature ionic liquids [trihexyl(tetradecyl)phosphonium]$_9EuW_{10}O_{36}$ (POM-1) and [trihexyl(tetradecyl)phos-phonium]$_9TbW_{10}O_{36}$ (POM-2). ICP analyses of POM-1 and POM-2 showed no residual Na^+ after the extraction of the Na-POM cluster into the organic phase with the phosphonium salt. POM-1 and POM-2 have good miscibility in most organic solvents, such as toluene, dichloromethane, chloroform, methanol, and acetonitrile.



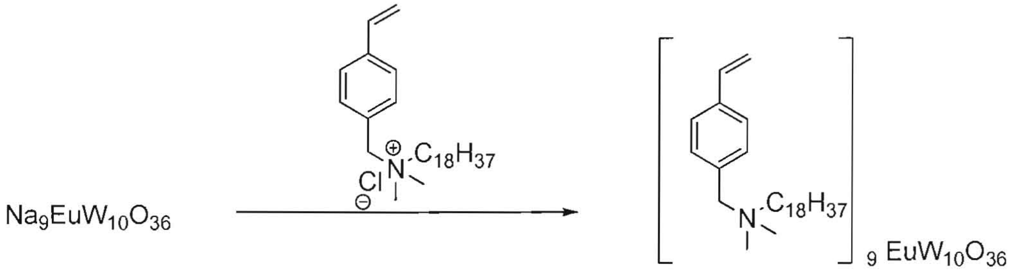
Scheme 1. Synthesis of [tetradecyl(trihexyl)phosphonium]$_9EuW_{10}O_{36}$.

Following the same procedure [dodecyl(11-acryloyloxyundecyl)dimethyl-ammonium]$_9$EuW$_{10}$O$_{36}$ (POM-3) and [dodecyl(11-acryloyloxyundecyl)dimethylammonium]$_9$ TbW$_{10}$O$_{36}$ (POM-4) were synthesized (eq. 1). Monomer-encapsulated POM-3 and POM-4 are liquid at room temperature and have great miscibility in common organic solvents. A similar POM was previously reported by Haolong Li et al.[3] Haolong Li reported the synthesis of [dodecyl(11-methacryloyloxyundecyl)dimethylammonium]$_9$ EuW$_{10}$O$_{36}$ and its copolymerization with methyl methacrylate. We also synthesized a different monomer encapsulated [EuW$_{10}$O$_{36}$]$^{-9}$ using octadecyl(styryl)dimethyl-ammonium chloride as the surfactant (eq. 2). [Octadecyl(styryl)dimethylammonium]$_9$EuW$_{10}$O$_{36}$ (POM-5) is solid a room temperature and polymerizes when heated to approx. 115 °C.



(1)

POM-3: Ln= Eu
POM-4: Ln= Tb



(2)

POM-5

The miscibility of POM-3 and POM-4 in common organic solvents and in methyl methacrylate makes them suitable for their copolymerization with methyl methacrylate. The poly(methyl methacrylate) (PMMA) composites, PMMA/POM-3 and PMMA/POM-4, were obtained as transparent hybrids (Figure 2a and b). POM-5 has also great miscibility in methyl methacrylate. However, the copolymerization of POM-5 with methyl methacrylate yield a composite that has better transparency in the visible region than PMMA/POM-3 and PMMA-POM-4 (Figure 2c). The better transparency obtained in PMMA/POM-5 demonstrate that POM-5 has more compatibility with the polymer matrix than POM-3 and POM-4. PMMA/POM composites showed strong emission bands that were retained from their corresponding monomer-encapsulated POMs. PMMA/POM-3 and PMMA/POM-5 showed strong emission at 592 and 615 nm corresponding to the Eu^{3+} emission. PMMA/POM-4 showed strong emission bands at about 550 nm corresponding to a Tb^{3+} emission band.

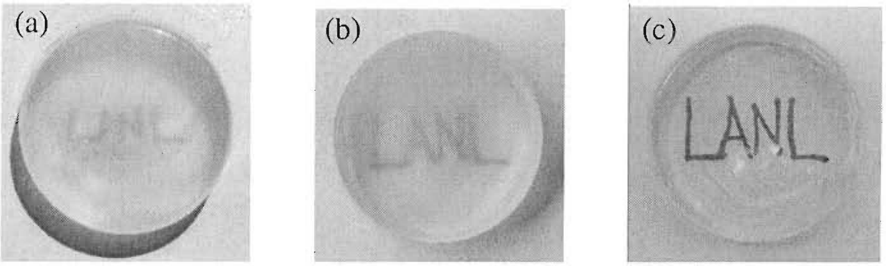


Figure 2. PMMA/POM-3 (a), PMMA/POM-4 (b), and PMMA/POM-5 (c).

Besides the good miscibility of the POM containing Eu^{3+} luminescent center, all POMs show a bright photoluminescence under UV excitation. Figure 3 shows the luminescence of PMMA/POM-3 and PMMA/POM-5 during exposure to ultraviolet light at 254 nm. POM-1, PMMA/POM-3, and PMMA/POM-5 fluorescent spectra exhibit strong emission bands when exciting the O→W LMCT of the POM. Therefore, excitation of the strong LMCT transition at about 270 nm yields strong emission of Eu^{3+} at 580 and 615 nm (Figure 4). Excitation of Eu^{3+} could not be detected indicating that the emission of Eu^{3+} results from effective intramolecular energy transfer from the O→W band to the Eu^{3+} site. The Eu^{3+} emission bands at 592 nm and 615 nm corresponds to a $^5D_0 \rightarrow {}^7F_1$ transition and a $^5D_0 \rightarrow {}^7F_2$ transition, respectively.[3,10]

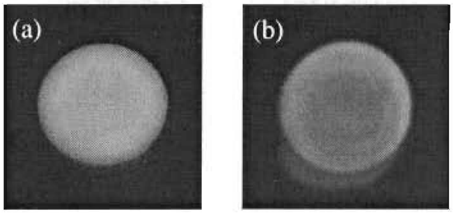


Figure 3. PMMA/POM-3 (a), and PMMA/POM-5 (b) under UV light at 254 nm.

The microenvironment of Eu^{3+} can be determined and is influenced by external components. The $^5D_0 \rightarrow {}^7F_1$ transition peak at around 592 nm represents the magnetic dipole transition of Eu^{3+}, and it is not affected by external components. The $^5D_0 \rightarrow {}^7F_2$ transition peak at 615 nm corresponds to the electric dipole transition and it is greatly sensitive to the environment. The emission spectra shown in Figure 4 show the dependence of the Eu^{3+} electric dipole transition on the microenvironment. It is observed that the $^5D_0 \rightarrow {}^7F_2$ transition for PMMA/POM-5 is of higher intensity than for PMMA/POM-3. This observation suggests that changing the cation of the POM from dodecyl(11-acryloyloxyundecyl)dimethyl-ammonium to octadecyl(styryl)dimethylammonium cation changes the dielectric microenvironment of the Eu^{3+} and affects it electric dipole transition $^5D_0 \rightarrow {}^7F_2$. POM-1 cannot be directly compared with the polymer composites because its luminescence was obtained from a diluted solution of POM-1 in dichloromethane. Dichloromethane also influences the dielectric environment of the Eu^{3+}.

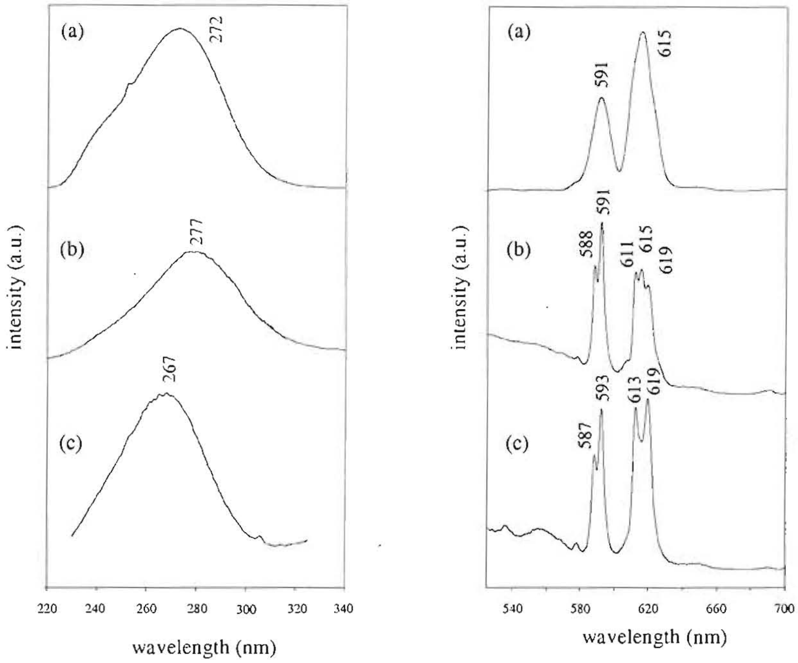


Figure 4. The excitation (left) and emission (right) spectra of a solution of 10^{-4}M POM-1 in CH_2Cl_2 (a), PMMA/POM-5 (b), and PMMA/POM-3 (c).

PMMA/POM-4 also shows strong luminescence when exposed to UV light at 254 nm, as it is shown in Figure 5. The excitation of Tb^{3+} appears in the region of 285-305 nm, and resembles the $^7F_6 \rightarrow {}^5H_5$ terbium transition. The excitation band observed for POM-2 and PMMA/POM-4 appear at about 270 nm suggesting that the excitation occurs in the polyoxometalate cluster and the energy is transfer to the Tb^{+3} ion giving emission in the green region at about 550 nm (Figure 6). The emission of the Tb^{3+} at about 550 nm corresponds to the $^5D_4 \rightarrow {}^7F_6$ transition.[11]

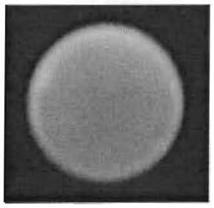


Figure 5. PMMA/POM-4 under UV light at 254 nm.

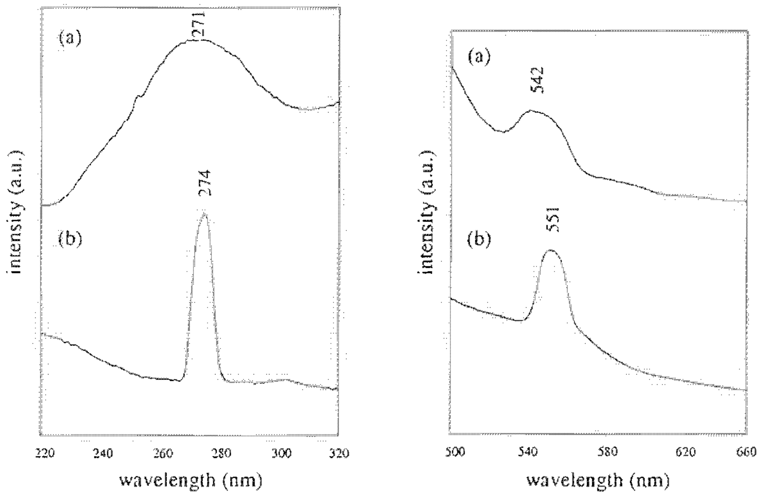


Figure 6. Excitation (left) and emission (right) spectra of POM-2 (a) and PMMA/POM-4 (b).

Conclusion

We have synthesized a number of POM clusters that can be used as light emitting materials. We were able to produce polyoxometalate sandwich clusters containing Eu^{3+} and Tb^{3+} as luminescent centers. These clusters are liquid at room temperature and exhibit strong emission of the lanthanide when the excitation occurs in the O→W LMCT suggesting that energy transfer occurs from the polyoxometalate to the lanthanide trivalent cation. We have also demonstrated that POMs can be easily introduced into polymer matrices by using appropriate monomeric surfactants. Monomer-encapsulated POMs can be copolymerized with methyl methacrylate to yield transparent hybrid composites. The polymer composites retained the luminescence properties of the monomer-encapsulated POM starting materials.

Acknowledgments

DOE-LANL LDRD - Postdoctoral Research and Development.

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