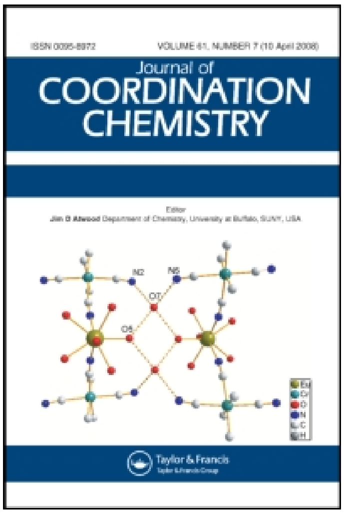

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

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To cite this Article Robinson, L. M. and Shriver, D. F.(1996) 'SYNTHESIS AND PHOTOPHYSICAL PROPERTIES OF POLYMER-BOUND HEXANUCLEAR MOLYBDENUM CLUSTERS', Journal of Coordination Chemistry, 37: 1, 119 — 129
To link to this Article: DOI: 10.1080/00958979608023545
URL: http://dx.doi.org/10.1080/00958979608023545

J. Coord. Chem., 1996, Vol 37, pp. 119–129
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SYNTHESIS AND PHOTOPHYSICAL PROPERTIES OF POLYMER-BOUND HEXANUCLEAR MOLYBDENUM CLUSTERS‡

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(Received January 26, 1995; Accepted February 20, 1995)

The coordination of $[Mo_6Cl_8{}^i(SO_3CF_3)_6{}^a]^{2-}$ (**1**) and $[Mo_6Cl_8{}^iCl_4{}^a(EtOH)^a{}_2]$ (**2**) to poly(e-vinylpyridine) (PVP) produces crosslinked materials. Formation of these materials occurs by displacement of axial ligands ((**a**) in Fig. 1) $SO_3CF_3{}^-$ or EtOH on the clusters by the vinylpyridine moieties. The availability of six coordination sites in **1** and two coordination sites in **2** offers control over the degree of crosslinking and solubility of the materials. Similarly, varying the ratio of cluster coordination sites (C) to polymer-pendant pyridine ligands (P) yields materials with a wide range of solubilities and glass transition temperatures (T_g). Materials with C:P ratios of 1:100 are highly soluble in CH_2Cl_2 and MeOH, with T_g values slightly higher than that of pure PVP. Unswellable materials with no discernible T_g are obtained with C:P ratios of 1:5 and lower, indicating a high degree of crosslinks. Transient emission spectroscopy reveals that polymer-bound cluster **1** lacks the luminescent properties characteristic of many $[Mo_6Cl_8]^{4+}$ based clusters. Conversely, polymer-bound cluster **2** displays intense luminescence and retains the unusually long-lived excited-state observed for the free clusters in solution. The emission lifetime of PVP-bound **2** fits a biexponential decay, with τ_1 = 90 μs (60 %) and τ_2 = 8 μs (40 %), while $[Mo_6Cl_8{}^iCl_6{}^a]^{2-}$ has a uniexponential decay of τ = 156 μs in CH_2Cl_2 solution.

KEYWORDS: molybdenum cluster, polymers, poly(4-vinylpyridine), metallopolymer

INTRODUCTION

Polymer-bound complexes are currently being investigated for applications in molecular electronics, chemical sensors, and catalysis.[1] Polymer-supported photochemical systems are of particular interest because they offer potential advantages over traditional solution-based systems, including increased ease of separation of photosensitizer and photo-products, the flexibility to employ a broad range of solvents, and possible steric or electrostatic effects that may reduce the rate of back electron transfer reactions between photo-intermediates.[1,2]

Many catalytically and photo-active transition metal complexes have been immobilized on polymers.[1-6] For example, films of poly(4-vinylpyridine) and modified polystyrene with polymer-pendant derivatives of $[Ru(bpy)_3]^{2+}$ have been employed in photoinduced charge separation and photocatalytic water-splitting experiments.[3] Inorganic or organometallic *clusters* incorporated into polymers are

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less common; however, $[SiW_{11}O_{40}(SiR)_2]^{4-}$ (R = vinylic substituent)[4] and a vinyl substituted derivative of $[Cp_4Fe_4(CO)_4]$[5] have been successfully polymerized, and the resulting immobilized clusters retain the redox and photochemical properties of the parent clusters. After the present work was completed, we discovered a brief report of the reaction of Mo_6Cl_{12} with polyvinylpyridine in the thesis literature.[6]

The opportunity of form crosslinked polymer materials incorporating photoactive hexanuclear molybdenum clusters is afforded by the recent synthesis of the substitutionally labile cluster, $[Mo_6Cl_8{}^i(SO_3CF_3)_6{}^a]^{2-}$ (**1**), by Johnston *et al.*, (Figure 1).[7] Recently, the reaction of **1** with n-vinylimidazole (NVI) was shown to yield $[Mo_6Cl_8{}^i(NVI)_6{}^a]^{4+}$, which undergoes AIBN initiated copolymerization with NVI to form a highly crosslinked polymer matrix.[8]

In the present work, we employed hexanuclear molybdenum clusters, $[Mo_6Cl_8{}^i(SO_3CF_3)^a{}_6]^{2-}$ (**1**) and $[Mo_6Cl_8{}^iCl_4{}^a(EtOH)^a{}_2]$ (**2**), to modify poly(4-vinylpyridine), because the variation in the number of potential coordination sites (six for complex **1**, and two for complex **2**) provides potential control over the degree of crosslinking and solubility of the polymer/cluster material. The unusual photophysical properties of the molybdenum clusters afford the opportunity to synthesize polymers with interesting redox and photophysical properties. Upon absorption of visible or near-UV light, the clusters display unusually long excited-stage lifetimes (τ = 160 μs for $[Mo_6Cl_8{}^iCl_6{}^a]^{2-}$ in CH_2Cl_2 solution),[9a] which are among the longest known for any transition metal complex. The electronically excited cluster can undergo electron transfer with electron acceptors to generate $[Mo_6Cl^i{}_8Cl^{a_6}]^{1-}$, a powerful oxidant, or electron donors to generate $[Mo_6Cl^i{}_8Cl^a{}_6]^{3-}$, a powerful reductant (Figure 2).[9] The behavior of the clusters in solution has been studied extensively, and they have been examined as possible

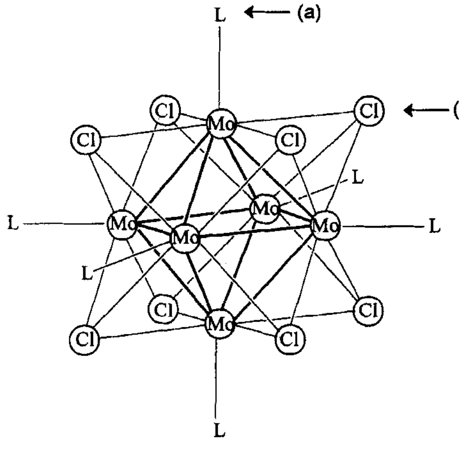

Figure 1 Representation of the $[Mo_6Cl_8{}^i(SO_3CF_3)_6{}^a]^{2-}$ cluster. Six molybdenum atoms form an octahedral metal core. Eight face-bridging (inner) chlorides, designated by the **i** superscript, cap the faces of the metal octahedron. Six additional $SO_3CF_3{}^-$ (triflate) ligands occupy the axial positions, which are designated by superscript **a**.

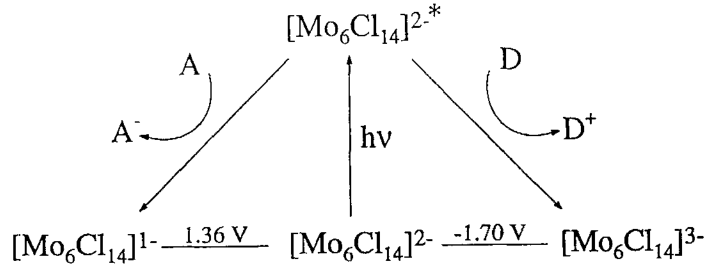

Figure 2 Redox and photochemistry of the $[Mo_6Cl_8{}^iCl_6{}^a]^{2-}$ cluster. Reduction potentials are reported vs. SCE in dichloromethane. Data from ref. 9e.

candidates for use in catalytic and photo-catalytic redox cycles.[9] Recently, we reported that $[Mo_6Cl_8{}^i(SO_3CF_3)_6{}^a]^{2-}$ ca be covalently bound to silica gel to yield photo- and redox-active materials.[10]

In the present work, we investigated how coordination to poly(4-vinylpyridine) affects the photophysical properties of molybdenum clusters **1** and **2**. The effect of varying the crosslinking agent (**1** or **2**) and the ratio of cluster coordination sites to polymer-pendant pyridine groups (C:P) upon the solubility and glass transition temperature of the polymer/cluster materials is also presented.

EXPERIMENTAL

General Experimental

The syntheses of tetrabutylammonium salts of $[Mo_6Cl_8{}^i(SO_3CF_3)_6{}^a]^{2-}$ (**1**) and $[Mo_6Cl_8{}^iCl_6{}^a]^{2-}$, anhydrous Mo_6Cl_{12} (which forms $[Mo_6C_8{}^iCl_4{}^a(EtOH)^a{}_2]$ (**2**) upon dissolution in ethanol), and $[Mo_6Cl_8{}^iCl_4{}^a(py)_2{}^a)$ were performed by methods described in the literature.[7,11,12] Poly(4-vinylpyridine) (M.W. = 50,000), supplied by Polysciences, was dried under high vacuum for 24 h at 50°C. All reactions were conducted under prepurified dinitrogen to exclude moisture. The solvents (dichloromethane, acetone, methanol, ethanol and pentane) were dried and freshly distilled. Moisture-sensitive reactants were stored in a dry box.

Synthesis of Poly(4-vinylpyridine) Supported $[Mo_6Cl_8{}^i(SO_3CF_3)_6{}^a]^{2-}$, **1**

A 0.300 g (1.34×10^{-4} mol) or 0.050 g (2.23×10^{-5} mol) sample of **1** was dissolved in 20 mL CH_2Cl_2 and added dropwise to a 20 mL stirred solution of 0.42 g or 1.40 g PVP in CH_2Cl_2, yielding 1:5 and 1:100 ratios of cluster coordination sites (C) to polymer-pendant pyridine groups (P), respectively. The reaction flasks were covered in foil because the cluster is photosensitive, and the reaction stirred approximately 12 h to promote complete substitution of triflate ligands with pyridine groups. The 1:5 ratio reaction yielded an orange powder, which was isolated by filtration through a glass frit, washed with 3×10 mL portions of CH_2Cl_2 and dried under vacuum for several hours. The reaction carried out at a C:P ratio of 1:100 yielded an orange solution, which was reduced to approximately 10 mL and layered with 30 mL pentane to precipitate the polymer, while leaving the highly soluble $Bu_4NSO_3CF_3$ byproduct in solution. The pentane/CH_2Cl_2 solution was decanted, leaving a sticky orange polymer film that was dried under vacuum for approximately 12 h.

Synthesis of Poly(4-vinylpyridine) Supported $[Mo_6Cl_8{}^iCl_4{}^a(EtOH)_2{}^a]$, **2**

A 0.050 g (5.0×10^{-5} mol) sample of Mo_6Cl_{12} was dissolved in 10 mL EtOH and added dropwise to a stirred solution of 0.016 g, 0.105 g or 1.00 g PVP (yielding C:P ratios of 1:1.5, 1:10 and 1:100, respectively) in 20 mL EtOH. After approximately 12 h reaction, the products were isolated by removing solvent and drying the polymers for 12 h under vacuum.

Electronic Spectra

UV-vis spectra were acquired on a Varian Cary IE spectrophotometer. Spectra of soluble samples were measured in CH_2Cl_2, using matched cells of 1.0 cm pathlength, or as films cast on quartz plates from CH_2Cl_2 or MeOH solution. Insoluble samples were analyzed in nujol mulls pressed between quartz plates, with neat nujol as the reference. Fluorescence measurements were performed on a Photon Technology International (PTI) QM-2 fluorimeter equipped with a 75 W Xenon lamp. Solution fluorescence spectra of **1**, **2** and soluble polymers were determined in 1.0 cm quartz cells in rigorously degassed CH_2Cl_2 or MeOH. Front-scattering fluorescence spectra were acquired using a triangular front-face quartz cell. Uncorrected emission wavelengths are reported.

Emission lifetimes were determined by transient emission spectroscopy with pulsed N_2 laser excitation (λ_{exc} = 337 nm) or PTI pulsed Xe lamp (λ_{exc} = 330 nm). Luminescence was monitored at 700 nm. Lifetimes were derived using standard least-squares linear regression statistics for single exponential decays. Multiexponential decay curves were fit to the equation $y = A_1e^{-1/\tau 2} + A_2e^{-t/\tau 2}$ where τ_1 and τ_2 are the excited-state lifetimes of fractional populations A_1 and A_2, respectively. Samples in a specially constructed 1.0 cm pathlength fluorescence cell with a vacuum-line adapter and 20 mL side-arm flask were exposed to high vacuum for at least 1 h. Rigorously degassed CH_2Cl_2 or MeOH (subjected to six freeze-pump-thaw cycles) was then vacuum transferred into the sample cell.

IR spectra were acquired on a Bomem MB-100 FT-IR at 2 cm^{-1} resolution. Samples were analyzed in nujol mulls pressed between KBr plates or as films. Far-IR spectra were acquired on a Digilab Model FTS-40 at 2 cm^{-1} resolution on nujol mulls of the sample pressed between polyethylene plates.

Determination of Glass Transition Temperature (T_g)

The T_g values of pure PVP and polymer-bound **1** and **2** were measured on a Perkin-Elmer DSC 7 differential scanning calorimeter at four different heating rates (80, 60, 40 and 20°C/min). The midpoint of the transition at each heating rate was graphed and extrapolated to a 0°C/min heating rate to yield the reported T_g value. Naphthalene and indium were employed as calibration standards.

RESULTS

Reaction of $[Mo_6Cl_8^i(SO_3CF_3)_6^a]^{2-}$ with Poly(4-vinylpyridine)

Upon addition of a CH_2Cl_2 solution of **1** to a solution of poly(4-vinylpyridine) in a C:P ratio of 1:5, an orange precipitate forms. After several hours of stirring, no color was evident in solution, indicating complete coordination of **1** to the pyridine groups on the polymer backbone had occurred. The dark orange powder isolated from the reaction does not dissolve or swell in CH_2Cl_2, MeOH, CH_3CN, or acetone, and no cluster appears to leach from the support when suspended in these solvents. Infrared spectra reveal intense bands at 1030 and 640 cm^{-1} characteristic of uncoordinated $SO_3CF_3^-$ (triflate) ligand.[13] The triflate groups serve as counterananions for the polymer-bound cluster, ideally $[Mo_6Cl_8^i(VP)_6^a]^{4+}$, where VP represents a vinylpyridine group in poly(4-vinylpyridine). The presence of triflate groups may also be due to excess $Bu_4NSO_3CF_3$ formed as a by product that is trapped in the polymer matrix even after multiple washings with solvent. Infrared spectra showed none of the characteristic features of cluster-coordinated triflate ligand (ν(S-O) = 997 cm^{-1}). As summarized in Table 1, the IR spectrum reveals new peaks which are distinctly shifted from those associated with the uncoordinated pyridine groups. Far-IR analysis also indicates changes in the cluster coordination environment have occurred. Bands attributed to $\nu(Mo\text{-}Cl^i)$, $\nu(Mo\text{-}Cl^a)$ and ν(Mo-Mo) at 330, 247 and 221 cm^{-1}[1,14] respectively, shift to 352, 311, and 213 cm^{-1}. In addition, a weak band at approximately 435 cm^{-1} may be attributable to an out-of-plane ring deformation of pyridine, which shifts from 405 cm^{-1} upon complex formation.[15a] A similar band occurs at 428 cm^{-1} for the model complex $[Mo_6Cl_8^iCl_4^a(py)_2^a]$. The UV-vis profile of the polymer/cluster material in a nujol mull shows the onset of absorption at approximately 450 nm, as observed for other clusters with the $[Mo_6Cl_8]^{4+}$ core. While$[Mo_6Cl_8Cl_6^a]^{2-}$ and $[Mo_6Cl_8^i(SO_3CF_3)_6^a]^{2-}$ have distinct absorption maxima at 313 nm and 297 nm, respectively, the polymer-bound cluster has a very broad absorption, with maxima at approximately 265 nm and 230 nm associated with the pyridine groups on the polymer. The model compound $[Mo_6Cl_8^iCl_4^a(py)_2^a]$ displays a similar absorption profile. Front-scattering fluorescence experiments reveal peaks at 475 and 520 nm, which are characteristic of the pyridine groups of the polymer. Interestingly, the strong luminescence in the 680 nm region characteristic of other cluster derivatives with the $[Mo_6Cl_8]^{4+}$ core (λ_{em} = 675 nm for **1** and 685 nm

Table 1 Comparison of IR Spectral Peaks of Pyridine Groups for Poly(4-vinylpyridine) and Polymer-Supported Cluster $[Mo_6Cl_8(VP)_6]^{4+}$.[a]

Poly(4-vinylpyridine)	$Mo_6Cl_8(VP)_6]^{4+}$	Assignment[b]
1596(s)	1637(s)	Ring-breathing band.
1555(s)	1615(s)	Ring-breathing band.
1491(m)	1505(s)	Ring-breathing band.
1413(s)	1413(m)	Ring-breathing band.
820(s)	825(m)	Out-of-plane C-H deformation.
567(m)	558(m)	In-plane C-H deformation.

[a] Idealized formula where VP represents a pyridine group on polyvinylpyridine.
[b] Assignments based on reference 15b.

for $[Mo_6Cl_8{}^iCl_6{}^a]^{2-}$ in CH_2Cl_2 solution) is not observed for polymer-bound **1**, Figure 3.

Reaction of **1** with PVP in a C:P ratio of 1:100 yields a yellow polymer soluble in CH_2Cl_2 and MeOH. The UV-vis spectrum of a polymer film cast from CH_2Cl_2 and fluorescence measurements of a rigorously degassed CH_2Cl_2 solution of the polymer are similar to those described above for the 1:5 product.

Reaction of $[Mo_6Cl_8{}^iCl_4{}^a(EtOH)_2{}^a]$ with Poly(4-vinylpyridine)

The reaction of $[Mo_6Cl_8{}^iCl_4{}^a(EtOH)_2{}^a]$ with a variety of neutral ligands, including pyridine, pyrazine and tri-alkyl phosphines, yields only disubstituted species,[11,12] and therefore, the reaction of $[Mo_6Cl_8{}^iCl_4{}^a\,(EtOH)_2{}^a]$, with PVP is expected to yield the polymer-bound cluster $[Mo_6Cl_8{}^iCl_4{}^a(VP)_2{}^a]$, where VP represents a vinylpyridine group in poly(4-vinylpyridine).

Upon reaction of poly(4-vinylpyridine) with **2** in a C:P ratio of 1:1.5, a suspension of bright yellow particles forms. No color is apparent in the supernatant solution after the particles settle, indicating that the reaction has gone to completion. The yellow powder obtained after removing the solvent does not dissolve or swell in CH_2Cl_2, MeOH or acetone. The IR spectrum of the product reveals peaks for coordinated pyridine groups as described for the reaction of poly(4-vinylpyridine) and **1**, and the UV-vis spectrum is also similar.

Reaction of C:P ratios of 1:100 or 1:10 yields viscous orange solutions. The dry polymers are glassy, dark-orange materials. The 1:100 polymer readily redissolves in CH_2Cl_2 and MeOH, and swells significantly in acetone, while the 1:10 polymer redissolves only in MeOH or EtOH. The excess of uncoordinated pyridine groups in this material leads to strong IR bands that mask the region characteristic of coordinated pyridine. The UV-vis spectra are similar to those of the 1:1.5 polymer-bound **2** described above. Steady state fluorescence measurements reveal two peaks: an emission at 675 nm that is characteristic of other $[Mo_6Cl_8]^{4+}$ based

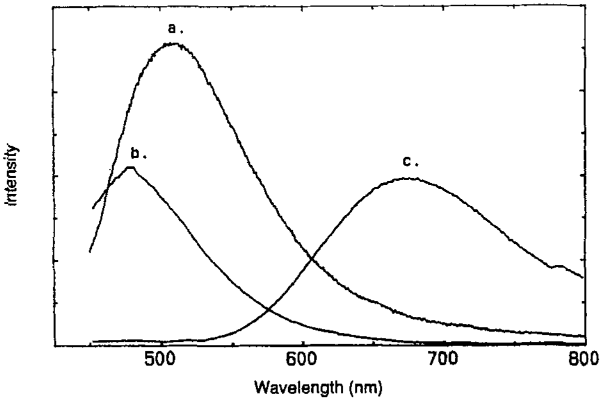

Figure 3 Comparison of fluorescence spectra of $[Mo_6Cl_8{}^i(VP)_6{}^a]^{4+}$ (VP = pyridine group on polyvinylpyridine) (a), pure poly(4-vinylpyridine) (b), and starting material $[Mo_6Cl_8{}^i(SO_3CF_3)_6{}^a]^{2-}$ (c). Samples were run in CH_2Cl_2 solution (λ_{exc} = 420 nm). Peak intensities are not representative of emission quantum yields, as samples are of different concentrations (λ_{exc} = 420 nm).

clusters, and an intense fluorescence at 510 nm attributed to the pyridine groups of the polymer. The latter is slightly shifted from the emission at 480 nm observed for the pure polymer in CH_2Cl_2 solution, Figure 4. Transient emission experiments reveal that the decay of the excited-state fits a biexponential decay rate. The emission lifetimes (τ) are presented in Table 2.

Glass Transition Temperatures

The glass transition temperature (T_g) of the polymer-bound clusters increases significantly as crosslinking increases, as presented in Table 3. The most heavily crosslinked materials, with C:P ratios of 1:5 and 1:1.5 for polymer-bound **1** and **2**, respectively, display no well-defined T_g.

DISCUSSION

Reaction of **1** and **2** with poly(4-vinylpyridine) affords materials with interesting photophysical properties and a controllable degree of crosslinking and solubility as the ratio of cluster coordination sites to polymer-pendant pyridine ligands (C:P) is varied. Very high loadings of **1** and **2** on the polymer (*i.e.*, 1:1 and 1:5 ratios of C:P) lead to unswellable materials. Soluble polymers can be obtained for ratios of 1:100 with **1** (six coordination sites available) and 1:10 with **2** (two coordination sites available).

The relative solubilities of the polymers correlate well with the measured glass transition temperatures (T_g). As summarized in Table 3, the most soluble polymers, with C:P ratios of 1:100, display T_g values only slightly above that of the pure polymer. Interestingly, PVP crosslinked with **1** has a slightly higher T_g than that of the analogous 1:100 material crosslinked with **2**. This difference in T_g may be due to the fact that six pyridine ligands anchored to a single crosslinking cluster site (**1**)

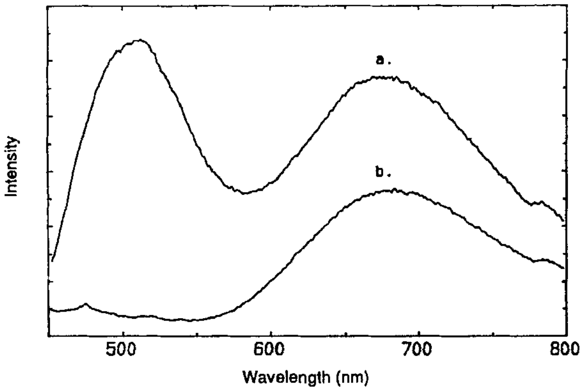

Figure 4 Comparison of fluorescence spectra of $[Mo_6Cl_8{}^iCl_4{}^a(VP)^a]$ (VP = pyridine group on polyvinylpyridine) in CH_2Cl_2 (a) and $[Mo_6Cl_8{}^iCl_4{}^a(MeOH)_2{}^a]$ in MeOH solution (b). Peak intensities are not representative of emission quantum yields, as samples are of different concentrations (λ_{exc} = 420 nm).

Table 2 Comparison of Emissive Lifetimes (τ) of Free and Polymer-Supported $[Mo_6Cl_8]^{4+}$ Based Clusters

Cluster[a]	$\tau(\mu s)$[b]
$[Mo_6Cl_8{}^iCl_4{}^a(VP)_2{}^a]$ 1:100 ratio	$\tau_1 = 90$ (60%) $\tau_2 = 8$ (40%)
$[Mo_6Cl_8{}^iCl_4{}^a(VP)_2{}^a]$ 1:10 ratio	$\tau_1 = 61$ (48%)[c] $\tau_2 = 9$ (52%)[c]
$[Mo_6Cl_8{}^i(VP)_6{}^a]^{4+}$ 1:100 ratio	---[d]
$[Mo_6Cl_8{}^iCl_4{}^a(MeOH)_2{}^a]$	$\tau_1 = 39$ (68%)[c] $\tau_2 = 5$ (32%)[c]
$[Mo_6Cl_8{}^iCl_6{}^a]^{2-}$	156
$[Mo_6Cl_8{}^i(SO_3CF_3)_6]^{2-}$	110

[a]Polymer-supported clusters are presented as idealized formulas, where VP represents a pyridine group on polyvinylpyridine. Ratios refer to cluster coordination sites (C) to polymer-pendant pyridine groups (P). [b]Measured in CH_2Cl_2 solution unless otherwise noted. Error limits estimated as ±5%. [c]Measured in MeOH solution. [d]No luminescence attributable to the cluster is observed.

form knots in the polymer matrix, decreasing flexibility and yielding a slightly higher T_g. Polymer-bound **2** with C:P ratio of 1:10 (soluble only in MeOH) displays a significantly higher T_g than the CH_2Cl_2 soluble (1:100) polymers. The most highly crosslinked, unswellable materials display no discernible T_g, as is often the case for heavily crosslinked polymers.[16]

The effect of the polymer matrix on the photophysical properties of the cluster is particularly interesting. Polymers that range from lightly to highly crosslinked with **1** or **2** retain UV-vis profiles that are similar to the spectra of other compounds with the $[Mo_6Cl_8]^{4+}$ core; however, the luminescence behavior and excited-state lifetimes of the polymer-bound and free clusters vary significantly. Polymer-bound **1** displays no luminescence in the 680 nm region that is characteristic of $[Mo_6Cl_8]^{4+}$ based clusters ($\lambda_{em} = 675$ nm and 685 nm for $[Mo_6Cl_8{}^i(SO_3CF_3)_6{}^a]^{2-}$ and $[Mo_6Cl_8{}^iCl_6{}^a]^{2-}$, respectively). It is possible that coordination of **1** to the polymer through six pyridine ligands establishes additional non-radiative decay pathways that are not present in $[Mo_6Cl_8{}^i(SO_3CF_3)^a{}_6]^{2-}$ or $[Mo_6Cl_8{}^iCl^a{}_6]^{2-}$, and that compete effectively with luminescent decay. In general, for a given chromophore, non-radiative decay rates increase when high frequency ground state "acceptor" vibrational states are available, or the energy gap (ΔE) between the excited and ground states decreases.[17] Trends in non-radiative decay rates have been studied for a series of osmium coordination complexes. In these systems, it was established that the C-C modes of 2,2'-bipyridine (bpy) ligands vibronically couple to the excited state, leading to efficient non-radiative decay and decreased quantum yields (Φ_{em}).[17b] For example, $[Os(bpy)(dppy)_2]^{2+}$ (dppy = *cis*-1,2-bis-(diphenylphosphine)ethylene) has a lifetime of 1684 ns and $\Phi_{em} = 0.382$, while $[Os(bpy)_3]^{2+}$ displays $\tau = 60$ ns and $\Phi_{em} = 0.005$.[17b] The latter complex has a non-radiative decay rate that is approximately 60 times that of the former, and has a smaller ΔE value. In the case of polymer-supported **1**, the pyridine ligands may provide similar vibrational acceptor modes, thus increasing non-radiative decay and decreasing Φ_{em} so dramatically that the luminescence is not detectable above the fluorescence background of the polymer pyridine groups. This premise is further

Table 3 Glass Transition Temperatures.

Polymer:[a]	PVP	$[Mo_6Cl_8{}^iCl_4{}^a(VP)_2{}^a]$ 1:100 ratio	$[Mo_6Cl_8{}^i(VP)_6{}^a]^{4+}$ 1:100 ratio	$[Mo_6Cl_8{}^iCl_4{}^a(VP)_2{}^a]$ 1:10 ratio
T_g(°C):[b]	138	144	152	186

[a]Ratios refer to cluster coordination sites (C) to polymer-pendant pyridine groups (P). [b]Extrapolated to 0°C/min heating rate. Error limits estimated at ±2°C.

supported by the fact that no luminescence characteristic of the cluster is observed upon addition of a slight excess of pyridine to a soluion of **1** in CH_2Cl_2. Similarly, a solution of **1** in MeOH, which readily displaces the axials triflate groups,[7] exhibits no luminescence.

By contrast, polymer-supported **2**, ideally $[Mo_6Cl_8{}^iCl_4{}^a(VP)_2{}^a]$, where VP represents a vinylpyridine group on the polymer, luminesces at 675 nm and retains a rather long-lived excited-state upon coordination to PVP. Comparison of the emission lifetimes (τ) of polymer-bound **2** and several related clusters with the $[Mo_6Cl_8]^{4+}$ core raises several interesting issues (Table 2). First, the emission lifetime of $[Mo_6Cl_8{}^iCl_4{}^a(VP)_2{}^a]$ is significantly shorter than that of $[Mo_6Cl_8{}^iCl_6{}^a]^{2-}$ or $[Mo_6Cl_8{}^i(SO_3CF_3)_6{}^a]^{2-}$. Similarly, model compound $[Mo_6Cl_8{}^iCl_4{}^a(py)_2{}^a)$, which is only sparingly soluble in MeOH, has a shortened emission lifetime, with $\tau_1 = 39$ µs (63%) and $\tau_2 = 19$ µs (37%). These results again indicate that coordination of the cluster to pyridine sites in the polymer affects the electronic structure of the cluster, leading to a more rapid decay rate, as discussed above.

As summarized in Table 2, the emission lifetimes of $[Mo_6Cl_8{}^iCl_4{}^a(VP)_2{}^a]$, $[Mo_6Cl_8{}^iCl_4{}^a(py)_2{}^a]$, and $[Mo_6Cl_8{}^iCl_4{}^a(MeOH)_2{}^a]$ fit a biexponential decay rate, while $[Mo_6Cl_8{}^iCl_6{}^a]^{2-}$ and $[Mo_6Cl_8{}^i(SO_3CF_3)_6{}^a]^{2-}$ display single exponential decays. The biexponential decay indicates that two species, possessing different lifetimes, contribute to the overall decay profile. Given that both *cis* and *trans* isomers of $[Mo_6Cl_8{}^iCl_4{}^a(PR_3)_2{}^a]$ (R = alkyl group) have been isolated,[18] it is reasonable to assume that both *cis* and *trans* coordinated species of $[Mo_6Cl_8{}^iCl_4{}^aL_2{}^a]$(L = VP, py, MeOH) are present in the products, and that these two species have different lifetimes. It has been observed that differences in symmetry can result in different emission lifetimes for isomers of simple metal complexes. For example, *cis* and *trans*-$[Cr(cyclam)(NH_3)_2{}^+$ (cyclam = 1,4,8,11-tetraazacyclotetradecane) have lifetimes of 116 and 175 µs, respectively.[19]

The emission lifetime of polymer-bound **2** is somewhat attenuated in MeOH relative to CH_2Cl_2 solution. (The solvent dependency is similar to that of $[Mo_6Cl_8{}^iCl_6{}^a]^{2-}$, with $\tau = 156$ µs in CH_2Cl_2 and 41 µs in MeOH.) The solvent dependency of polymer-bound **2** indicates that the polymer matrix does not completely shield the cluster from interaction with solvent or other molecules in solution. Additional evidence that the cluster is accessible to solution species is provided by quenching experiments with oxygen. In solutions of CH_2Cl_2 or MeOH saturated with oxygen, the luminescence of polymer-bound **2** is significantly quenched, and a large decrease in the emission lifetimes of the cluster occurs, with $\tau_1 = 14$ µs and $\tau_2 = 3$ µs. This behaviour parallels that observed for $[Mo_6Cl_8{}^iCl_6{}^a]^{2-}$ in solution. It has been reported that quenching of the $[Mo_6Cl_8{}^iCl_6{}^a]^{2-}$ excited-state by oxygen occurs via energy transfer.[9f]

CONCLUSION

The use of $[Mo_6Cl_8{}^i(SO_3CF_3)_6{}^a]^{2-}$ (**1**) and $[Mo_6Cl_8{}^iCl_4{}^a(EtOH)_2{}^a)$ (**2**) to modify poly(4-vinylpyridine) yields materials of varying solubilities and photophysical properties. Polymer-bound **2** retains the interesting luminescence and long excited-state lifetime displayed by other $[Mo_6Cl_8]^{4+}$ based compounds. In solution, the polymer-bound cluster appears to be accessible and reactive to species such as O_2, which may render these materials useful for photochemical or photocatalytic applications.

Acknowledgement

This research was supported by the U.S. Department of Energy Award No. DE-FG02-ER13640. This work made use of MRL Central Facilities supported by the National Science Foundation, at the Materials Research Center of Northwestern University, under Award No. DMR-9120521. Laura Robinson was recipient of a predoctoral NSF fellowship. The authors thank Professor J.T. Hupp for use of the transient emission spectroscopy instrumentation.

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