Efficient Singlet Oxygen Generation from Polymers Derivatized with Hexanuclear Molybdenum Clusters

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Received September 19, 1995. Revised Manuscript Received November 13, 1995[⊗]

The molybdenum(II) chloride cluster Mo_6Cl_{12} has been immobilized on 2% cross-linked poly(4-vinylpyridine) (PVP-Mo_6Cl_{12}) by the axial ligation of two pendant pyridines of the polymer to the hexanuclear metal core. Polymers with different cluster loadings exhibit the characteristic broad band emission of Mo_6Cl_{12} at $\lambda_{max} = 765 \pm 3$ nm, and luminescence decays are composed of short- and long-lifetime components, which are consistent with the presence of cis- and trans-disubstituted cluster species, respectively. The lifetime of the cis form is too short to permit its bimolecular reaction with oxygen. However, the long-lifetime component is quenched efficiently by O_2, and Stern−Volmer analyses of emission lifetimes yield quenching rate constants of $(2-10) \times 10^5$ M^{-1} s^{-1} for cluster loadings in the range $(3.5-0.3) \times 10^{-3}$ g/g of PVP, respectively. The quenching rate constant increases to $\sim 50 \times 10^5$ M^{-1} s^{-1} for all polymers in MeOH regardless of cluster loading. In aqueous solutions (pH 3−6) intermediate quenching rate constants are observed. These results correlate with the swelling properties of the PVP polymer in various solvents where greater swelling is manifested in greater accessibility of oxygen to the cluster active site and hence increased quenching rate constants. Oxygenated solutions of PVP-Mo_6Cl_{12} and alkenes photoreact to yield oxidized olefins. The products and product distributions indicate an energy transfer quenching reaction between oxygen and electronically excited polymer-bound clusters to produce singlet oxygen.

Introduction

Polymers capable of light-initiated physical or chemical responses have emerged prominently as important new materials for photo- and electrochemical energy conversion schemes,[1−4] molecular electronics,[5−7] heterogeneous catalysis,[8] and chemical sensing.[9,10] A common approach to the design of light-sensitive polymers is to electrostatically or covalently associate a chromophore to a polymer backbone to yield materials with targeted photochemical reactivity. Nowhere is this better demonstrated than with the synthesis of polymers that can photosensitize the production of singlet oxygen. The importance of singlet oxygen as a therapeutic reagent for the destruction of cancerous tumors,[11−14] an oxidant in degradation pathways of polychlorinated aromatics[15−17] and organic effluents,[18,19] an algaecide[20] and pesticide,[21] and its role in commercial applications to improve self-adhesion properties of rubbers and plastics[22−25] and in paper bleaching processes,[26−28] has evoked a need for what some[29] have called "sensitizers of choice" by systematically coupling

[⊗] Abstract published in *Advance ACS Abstracts,* January 1, 1996.

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photosensitizers to insoluble polymers by using solid phase synthetic methodologies. The presence of the photosensitizer in the heterogeneous polymer environment may diminish troublesome side reactions, abate sensitizer depletion by self-quenching owing to site isolation of the chromophore on the polymer backbone, increase the range of environments in which singlet oxygen can be photosensitized, and afford the facile isolation of reaction products from the polymer-bound photosensitizer.

Nevertheless the efficient photosensitized production of singlet oxygen requires the polymer material to meet several criteria. The excited state properties of the photosensitizer must be retained when appended to the polymer backbone. Specifically, the long lifetime required for the bimolecular reaction between oxygen and the electronic excited state cannot be significantly perturbed by immobilization. Additionally, inasmuch as the energy transfer process for oxygen production is collisional in nature, oxygen diffusivities through the polymer must be high and the photosensitizer must be accessible. Yet the most severe limitation of an efficient singlet oxygen material is its chemical stability within the severely oxidizing singlet oxygen environment. Although tethering a singlet oxygen photosensitizer to a polymer backbone can enhance stability, most materials are typically subject to long-term degradation resulting from the chemical oxidation of the photosensitizer and/or polymer. The electrostatic association of sensitizer dyes to silica gel by Kautsky et al.,[30] was followed by the covalent attachment of rose bengal (a uranine dye) to poly(styrene-*co*-vinylbenzyl chloride) some 40 years later.[31] Since these benchmark studies, a variety of organic and inorganic photosensitizers have been electrostatically or covalently appended to polymers in recent years.[32−34] The transition-metal-based systems have proven to be particularly versatile because they tend to absorb and luminesce intensely, can be tuned over a wide range of excited-state energies by small variations in the ligation coordination sphere, and above all generally show diminished bleaching resulting from greater chemical stabilities.

We describe here the derivitization of poly(4-vinylpyridine) with the photosensitive hexanuclear molybdenum chloride cluster, Mo_6Cl_{12}. The cluster is composed of an octahedral core of molybdenum with eight face bridging chlorides and four axial chlorides, which are shared among neighboring cluster subunits. The extended cluster array is broken by donor ligands, L, to give $Mo_6Cl_{12}L_2$ species. The clusters are extremely versatile sensitizers for polymer modification since any nucleophilic ligand can serve to axially coordinate the hexanuclear core including amine,[35] phosphine,[36−38] alcohol,[39] triflate,[40] and alkoxide donor ligands.[41] Indeed, the axial coordination sites have been used to covalently attach the cluster core to the siloxide backbone of sol−gel glasses[42] and recently to silica gel[43] and poly(vinylpyridine).[44]

Regardless of the nature of the axial substituent, the excited states of these hexanuclear clusters are intensely luminescent. The triplet character of the excited state gives rise to intense red emission that is long lived, approaching 200 μs for the hexamolybdenum chloride family of compounds. As we have shown previously, the excited state is highly energetic and able to participate in a variety of electron-[45,46] and energy transfer reactions;[47] this class of compounds is especially effective in producing singlet oxygen by intermolecular energy transfer.[47] We now report the photophysical properties and singlet oxygen reactivity of the Mo_6Cl_{12} cluster covalently bound to poly(4-vinylpyridine). Unprecedented stabilities of the materials for the photosensitized production of singlet oxygen is observed.

Experimental Section

Materials. Mo_6Cl_{12} was prepared according to the method of Dorman and McCarley[48] with appropriate modifications.[46b] Reillex 402 (Aldrich), poly(4-vinylpyridine) that is 2% crosslinked with divinylbenzene, was modified with Mo_6Cl_{12}. The polymer was heated to 120 °C for several days in an oven, and 100 mg of the dried polymer was added to refluxing methanol or ethanol under an argon atmosphere. Alcohol solutions of Mo_6Cl_{12} were added dropwise to the polymer solution, which was allowed to reflux for several hours. The resulting polymer-bound cluster material was filtered under air and washed with copious amounts of MeOH, ensuring that no free Mo_6Cl_{12} remained admixed with the polymer. As an added precaution, Mo_6Cl_{12}-modified polymer was refluxed for 24 h in MeOH to ensure that the sensitizer was chemically bound to the polymer backbone and not simply trapped in the polymer matrix. The amount of cluster covalently bound to the polymer was determined by monitoring the absorbance of the cluster solution at 340 nm before and after polymer addition. Electronic absorption spectra of the filtered supernatant liquid indicated a maximum binding of 3.5×10^{-3} mol of cluster/g of polymer. Typical experiments employed derivatized polymer containing 0.31, 0.84, 1.9, and 3.5×10^{-3} mol of cluster/g of polymer, depending on the initial Mo_6Cl_{12} concentration of the alcohol solution.

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Attachment of the hexanuclear cluster to the polymer backbone is not limited to the pyridine anchor. Triphenylphosphine polymers are also readily derivatized by the cluster core. Mo_6Cl_{12} was covalently bound to 2% and 20% cross-linked, styrene−divinylbenzene copolymer beads with pendant triphenylphosphine groups (Aldrich). Polymer (0.5 g) and Mo_6Cl_{12} (0.3 g) were added to 10 mL of ethanol, and the solution was allowed to reflux for several hours. The cluster derivatized polymer was filtered and washed with copious amounts of ethanol. The amount of cluster bound to the polymer (determined by the same procedure employed for poly(4-vinylpyridine)) was 1.1×10^{-4} and 2.6×10^{-4} mol of cluster/g of polymer for the 2% and 20% cross-linked polymers, respectively. The photophysical properties and singlet oxygen chemistry of the triphenylphosphine polymer was similar to the 4-vinylpyridine polymer; accordingly for the sake of brevity, the chemistry of latter is only presented.

Toluene, obtained from Burdick and Jackson Laboratories (distilled-in-glass grade), was subjected to seven freeze−pump−thaw cycles and vacuum distilled onto 4 Å molecular sieves contained in a 1-L flask equipped with a high-vacuum Teflon valve. Methanol and ethanol, used for polymer syntheses, were refluxed over sodium for no less than 6 h and freshly distilled prior to use.

Quenching Experiments. Quenching rate constants were determined by using the Stern−Volmer[49−51] method of luminescence intensities and lifetimes. Steady-state and time-resolved luminescence spectra were recorded on previously described[52] emission and Nd:YAG laser ($\lambda_{exc} = 355$ nm, fwhm = 8 ns) instruments. Stern−Volmer experiments were conducted over a quencher concentration range of 10^{-5}−10^{-2} M in specially constructed high-vacuum cells, consisting of a 1 cm quartz cuvette attached to a sidearm terminating with a 10 mL round-bottom flask. The cuvette was isolated from the round-bottom chamber by a high-vacuum Teflon valve.

Oxygen was added to the cell by employing high-vacuum manipulations. The concentration of oxygen dissolved in solvent, C_g(M), was calculated according to Henry's law,[53]

$$C_g = 1000X_g r/M_1(1 - \chi_g) \quad (1)$$

where r is the density (g/mL) of solvent, M_1 is the molecular weight of solvent, and X_g is the mole fraction solubility of oxygen in the solvent:

$$X_g = P_g/K_H \quad (2)$$

P_g, the pressure (mmHg) of oxygen added to the system, was determined by mercury manometry. The Henry's law constant, K_H, was calculated from the following:[53]

$$K_H = 760 \text{ mm} + \frac{170.33r \text{ mm mL mol}^{-1}}{\alpha M_1} \quad (3)$$

$$\alpha = L(273.15 \text{ K}/T) \quad (4)$$

where α is the Bunsen coefficient, L is the Ostwald coefficient, and T is the temperature of measurement.

Photochemistry. The photosensitized oxidations of 2×10^{-2} M acetonitrile solutions of 2,3-diphenyl-*p*-dioxene, 1-methylcyclohexene, and 1,2-dimethylcyclohexene by PVP−Mo_6Cl_{12} ($\lambda_{exc} \geq 436$ nm), $Mo_6Cl_{14}^{2-}$ (1×10^{-5} M), and polymer-derivatized rose bengal ($\lambda_{exc} \geq 590$ nm) were performed with procedures previously developed in our laboratories.[47] Photolyzed solutions were treated with excess triphenylphosphine, which reduced the initially formed hydroperoxide to its corresponding alcohol. Products were analyzed by gas chromatography and GC/MS.

Results

Alcohol solutions of Mo_6Cl_{12} react readily with Reillex 402 to yield a yellow polymeric material. The Mo_6Cl_{12}-derivatized poly(4-vinylpyridine) polymer (PVP−Mo_6Cl_{12}) is extremely stable and no evidence of leaching of the Mo_6Cl_{12} cluster unit from polymer is observed after several years. The Reillex 402 polymer has a high density of pyridyl binding sites (8 mequiv/g of polymer), which are readily accessed by the cluster core. Since this material is only 2% cross-linked, it exhibits properties of both a gel and a macroreticular polymer. Thus, for our studies, this support is ideal because it is structurally well-defined yet exhibits sufficient flexibility to allow oxygen to permeate the polymer and come in contact with immobilized cluster.

Photophysical Properties. The excited-state properties of the poly(4-vinylpyridine)-bound cluster are very similar to the model monomer complex, $Mo_6Cl_{12}(py)_2$ (py = pyridine). The molecular compound exhibits broad, featureless emission ($\lambda_{max} = 766$ nm), and the decay profile of the emission fits a biexponential rate law with short- and long-lifetime components of $\tau_1 = 8$ μs (39%) and $\tau_2 = 55$ μs (61%), respectively, where the relative contributions of the lifetimes to the overall decay curve were obtained from the A factors of the biexponential fit. Similarly, polymers with different cluster loadings possess the characteristic broad band emission of Mo_6Cl_{12} at $\lambda_{max} = 765 \pm 3$ nm and the luminescence decays are also composed of long- and short-lifetime components. The luminescence decay lifetimes for the polymer at the different cluster loadings are graphically illustrated in Figure 1 for solid PVP−Mo_6Cl_{12}, and for PVP−Mo_6Cl_{12} suspended in toluene and MeOH. The overall behavior of the polymers in the absence of oxygen is similar, irrespective of cluster loading: the decay lifetimes of the long and short components are roughly invariant with the only exception observed for PVP−Mo_6Cl_{12} at highest cluster loadings; and across a solvent series, the lifetime varies marginally. In each system, the relative contributions of the short- and long-lifetime components varied between 30 and 70%. Whereas the photophysical behavior of solids in vacuum and nonpolar solvents such as toluene are very similar, polymers swelled in polar solvents such as MeOH exhibit attenuated lifetimes, approaching that of the $Mo_6Cl_{12}(py)_2$ model compound. The observed decay kinetics are not specific to the Reillex polymer or method of introduction of the Mo_6Cl_{12} moiety onto a PVP. Shriver et al. have recently replaced the axial alcohol ligands of $Mo_6Cl_{12}(EtOH)_2$ molecular subunit on PVP.[44] Here too biexponential behavior is observed with lifetimes ($\tau_1 = 90$ μs (60%) and $\tau_2 = 8$ μs (40%)) commensurate with those observed by us for the Reillex-bound cluster.

Photophysical differences among the polymers are accentuated by the presence of oxygen. As clearly shown in Figure 1, the short lifetime component is only slightly attenuated in oxygen atmospheres, whereas the lifetime of the long component is reduced significantly. The effect of oxygen on polymer photophysics may be quantified with measurements of the quenching rate

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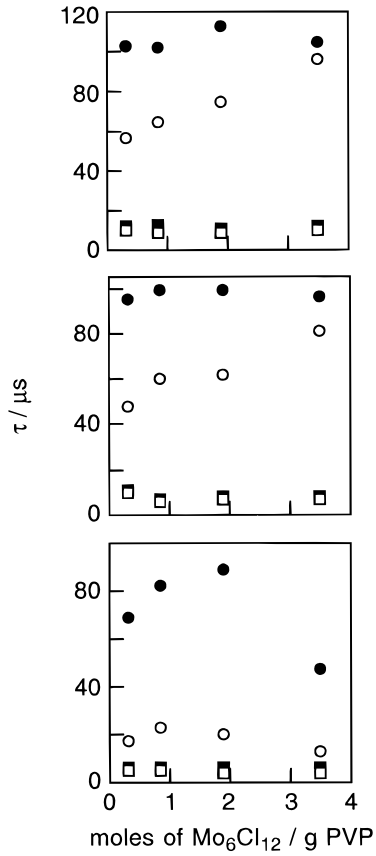


Figure 1. Long (circles) and short (squares) lifetime components of luminescence decay of Mo_6Cl_{12}-derivatized poly(4-vinylpyridine) polymer in the presence (open) and absence (filled) of oxygen as (top) a solid, (middle) in toluene, and (bottom) in MeOH.

Table 1. Oxygen Quenching Rate Constants of Mo_6Cl_{12}-Derivatized Poly(vinylpyridine) Polymers

PVP-Mo_6Cl_{12} (moles cluster/g of PVP)	$k_q/10^5$ M^{-1} s^{-1} in toluene	$k_q/10^5$ M^{-1} s^{-1} in MeOH
3.1×10^{-4}	10.1	43
8.4×10^{-4}	6.4	31
1.9×10^{-3}	5.9	38
3.5×10^{-3}	1.9	54

constants. Table 1 lists the oxygen quenching rate constants derived from the long lifetime component for the different derivatives in toluene and MeOH. In the nonpolar toluene solvent, the excited state reaction between the cluster and oxygen monotonically decreases with increasing loading, spanning 1 order of magnitude in reaction rate. Differences among the polymers are virtually eliminated in MeOH where the quenching rate constant is large and similar ($k_q = 4.2(1.1) \times 10^5$ M^{-1} s^{-1}) for all polymer derivatives. In aqueous solutions, the oxygen quenching chemistry exhibits behavior intermediate between MeOH and toluene. Figure 2 plots $k_q(O_2)$ for PVP−Mo_6Cl_{12} in aqueous solutions over a pH range 1−6. Within our experimental error, the oxygen quenching rate constant is invariant from $1 <$ pH < 6, but decreases at pH = 1.

Singlet Oxygen Chemistry. Substituted cyclohexenes react with oxygen radicals and $^1O_2$ to yield characteristic products and product distributions.[54] Photolyzed acetonitrile solutions of PVP-Mo_6Cl_{12} and

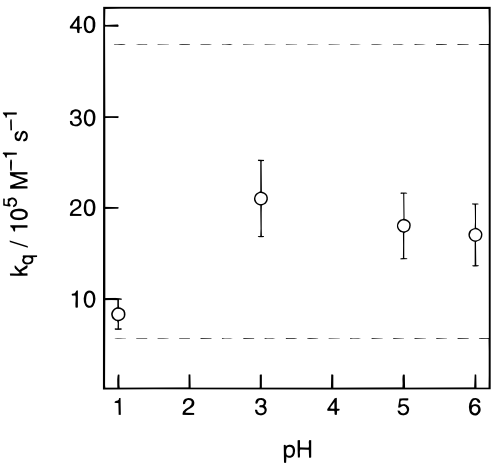
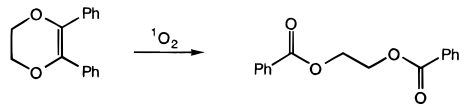


Figure 2. pH dependence of oxygen quenching rate constants of Mo_6Cl_{12}-derivatized poly(4-vinylpyridine) polymer (1.9×10^{-3} mol of Mo_6Cl_{12}/g of PVP) in H_2O.

2,3-diphenyl-*p*-dioxene, **1**, yield the carbonyl-containing



(5)

1 **2**

product, ethylene glycol dibenzoate, **2**, in 100% yield as determined by NMR. The product derives directly from the dioxetane, which is produced by the reaction of **1** with $^1O_2$. The photooxidation reaction is catalytic in PVP-Mo_6Cl_{12}, and it is limited only by our patience in carrying out the experiments (several hundred equivalents of substrate per equivalent of polymer-bound cluster photosensitizer). Absorption spectra of the reaction solution before and after photolysis shows that no Mo_6Cl_{12} leaches into solution during reaction.

The photosensitized production of singlet oxygen by the polymers is further supported by the photoreaction of PVP-Mo_6Cl_{12} and **1** in the presence of 1,4-diazobicyclo-[2.2.2]octane (DABCO) and 2,6-di-*tert*-butylphenol (DTBP). Both traps possess specific oxygen chemistry. DABCO inhibits $^1O_2$ reaction by returning it to ground state via a charge transfer complex ($k = 5.2 \times 10^7$ M^{-1} s^{-1}).[55,56] Conversely, DTBP is an efficient free radical inhibitor, capable of scavenging superoxide but completely inert to $^1O_2$.[57] Both traps are unreactive toward the excited state of Mo_6Cl_{12} with no quenching observed to the detection limits of our instrumentation ($k_q < 10^4$ M^{-1} s^{-1}). Thus for a $^1O_2$ reaction pathway, there should be no appreciable reaction of **1** in the presence of DABCO whereas the product yield should be unaffected by DTBP. As shown in Table 2, this is the case. The photooxidation of **1** is inhibited markedly by DABCO and unaffected by the presence of the free radical inhibitor DTBP. These results are consistent with the oxidation of **1** by an authentic singlet oxygen reaction, sensitized by PVP-Mo_6Cl_{12}.

These photooxidation results are paralleled by olefin product distribution studies. Reaction of 1-methylcy-

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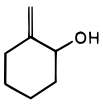
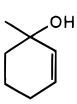
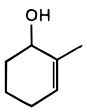
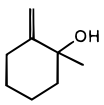
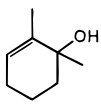
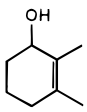
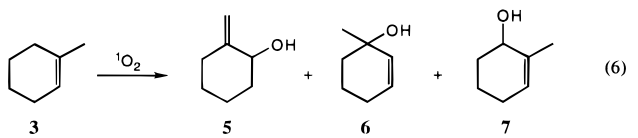
Table 2. Products of Reaction of 1-Methylcyclohexene, 3, and 1,2-Dimethylcyclohexene, 4, with Oxygen under Photosensitized and Radical Oxidation Conditions[a]

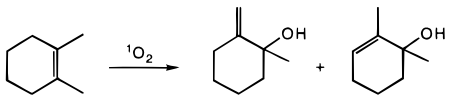
Photosensitizer	Products of 			Products of 		
						
PVP-Mo_6Cl_{12} [b]	77%	23%	0%	85%	15%	0%
$Mo_6Cl_{14}^{2-}$ [c]	64%	24%	2%	90%	10%	0%
P-Rose Bengal [b]	45%	41%	14%	86%	14%	0%
Auto-oxidation [d]	36%	12%	40%	7%	39%	54%
Reillex 402™	0%	0%	0%	0%	0%	0%

[a] Products are defined in eqs 6−9. [b] Polymer-bound cluster sensitizer irradiated ($\lambda_{exc} \geq 436$ nm) in O_2-saturated acetonitrile solutions containing [olefin] = 2×10^{-2} M. [c] Irradiated ($\lambda_{exc} \geq 436$ nm) O_2-saturated acetonitrile solutions containing $[Mo_6Cl_{14}^{2-}] = 1 \times 10^{-5}$ M and [olefin] = 2×10^{-2} M. The photosensitized reaction of **3** yielded 10% unidentified products. [d] Product distributions reported in ref 54. Radical autooxidation of **3** yields 12% unidentified products.

clohexene, **3**, and 1,2-dimethylcyclohexene, **4**, with $^1O_2$ yields characteristic products[54] derived from allylic hydroperoxide intermediates (ene reaction[58,59]):

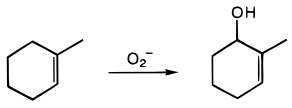


3 **5** **6** **7** (6)

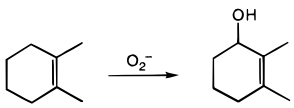


4 **8** **9** (7)

Conversely, reactions of **3** and **4** with superoxide ion yield oxygenated products corresponding to the radical autooxidation of the olefin:



3 **7** (8)



4 **10** (9)

For **3**, the ene products are distinct from the product generated by radical autooxidation. Table 2 reproduces the product distributions for the photooxidation of **3** and **4** sensitized by PVP-Mo_6Cl_{12}; for purposes of comparison, the product distributions for the photochemistry of these substrates in homogeneous solutions of $Mo_6Cl_{14}^{2-}$ and rose bengal are also shown. The product distributions of the photosensitized oxidations in homogeneous solution and for PVP-Mo_6Cl_{12} are nearly identical.

(58) Frimer, A. A. *Chem. Rev.* **1979**, *79*, 359.
(59) Turro, N. J. *Modern Molecular Photochemistry;* Benjamin/Cummings: Menlo Park, CA, 1978; Chapter 14.

Discussion

The Mo_6Cl_{12}-derivatized poly(4-vinylpyridine) polymer exhibits the intense luminescence that is characteristic of the $[Mo_6Cl_8]^{4+}$ cluster core axially ligated by chloride and pyridine. The energy and lifetime of PVP−Mo_6Cl_{12} and the $Mo_6Cl_{12}(py)_2$ model complex are nearly identical, though distinguished from the $Mo_6Cl_{14}^{2-}$ parent cluster (λ = 760 nm; τ_0 = 160 μs in CH_2Cl_2) by a slight red shift in the emission energy and shorter luminescence decays. This concomitant shift of emission to lower energy with shorter lifetime follows the predictions of the energy gap law.[60] The relatively small perturbation of the cluster's excited state energy and relative magnitude of lifetimes upon substitution of chloride by pyridine is consistent with the electronic structure of this family of cluster compounds. The e_g HOMO and a_{2g} LUMO orbitals, formed from linear combinations of d_{xy} orbitals of adjacent metal atoms,[61] are confined to a cube that inscribes the octahedral metal atoms of the cluster unit. In this orientation, the metal orbitals are directed toward the eight face-bridging halides situated at the vertexes of this cube, and hence mixing is extensive, as verified by photophysical and spectroscopic studies.[62,63] Conversely, the axial ligands are juxtaposed over the faces of the cube where σ-orbital mixing is symmetry forbidden and where the parallel disposition of π orbitals leads to only weak overlap between the metal and ligand frontier orbitals. Hence, as observed here, the overall excited state properties of these clusters are generally invariant with axial ligand substitution.

Whereas the luminescence energy and overall magnitude of emission lifetimes are affected little by axial ligation, the excited state dynamics are decidedly distinct from the $Mo_6Cl_{14}^{2-}$ parent cluster. Inasmuch as the same behavior is observed for PVP−Mo_6Cl_{12} and

(60) Kober, E. M.; Caspar, J. V.; Lumpkin, R. S.; Meyer, T. J. *J. Phys. Chem.* **1986**, *90*, 3722.
(61) Hughbanks, T.; Hoffman, R. *J. Am. Chem. Soc.* **1983**, *105*, 1150.
(62) Zietlow, T. C.; Nocera, D. G.; Gray, H. B. *Inorg. Chem.* **1986**, *25*, 1351.
(63) Newsham, M. D. Ph.D. Thesis, Michigan State University, 1988.

$Mo_6Cl_{12}(py)_2$, the biexponential decay of the time-resolved cluster luminescence within the polymer environment appears to be intrinsic to the hexanuclear metal core and its primary coordination sphere, and it is not particular to the polymer environment. Saito[37] and more recently DiSalvo[38] and co-workers have shown that reaction of donor ligands with Mo_6Cl_{12} leads to both the cis and trans forms of $Mo_6Cl_{12}L_2$. We find that the mixture of cis and trans isomers of $Mo_6Cl_{12}[P(n\text{-propyl})_3]_2$ in the solid state exhibit pronounced biexponential lifetime behavior with the smaller fraction of material, known to be the cis form, exhibiting a lifetime of 11 μs and the greater fraction of material, known to be the trans form, exhibiting a lifetime of 86 μs. Axial substitution in a cis configuration significantly lowers the symmetry of the HOMO and LUMO orbital manifolds, and we suspect, as is usually the case, that the lower symmetry leads to a higher density of states and more efficient nonradiative decay to the ground state. Because we have no control of the substitution of the two pendant pyridines of the polymer backbone to the hexanuclear metal core in our synthesis, cis and trans forms of the substituted cluster in the polymer matrix are present, and consequently we observe biexponential decay kinetics for our samples.

The different time scales for the biexponential decay engender different efficiencies for excited state reactivity. The short lifetime decay is fast enough to prevent reaction between Mo_6Cl_{12} and oxygen within the polymer. If we assume that the quenching rate constants for the cis-derivatized species are intrinsically similar to the trans species (see Table 1), then Stern−Volmer analysis of the short-lifetime component reveals that only ∼5% quenching can be expected in oxygen-saturated solutions. Hence there does not appear to be any chemically distinguishing feature of the polymer that obviates the reaction of oxygen at the cluster active sites. Rather, the lifetime of the derivative is simply too short to prevent its efficient reaction with oxygen. This is not the case, however, for the trans-derivatized cluster active sites. As shown in Table 1, the long-lived excited state is efficiently quenched by oxygen; the quenching rate constants were determined by Stern−Volmer analysis of the long lifetime component. The $\sim 10^3$ decrease in the bimolecular rate constants for the quenching of PVP−Mo_6Cl_{12} vs free cluster in homogeneous solution ($k_q(O_2) = 10^9$ M^{-1} s^{-1} for $Mo_6Cl_{14}^{2-}$ in solution) can be attributed to the hindered ability of the oxygen to diffuse through the polymer matrix.

The quenching reactivity of the cluster-derivatized polymer in different solvents can be correlated directly to the swelling behavior of the polymer matrix. In toluene, all derivatives exhibit the same degree of oxygen quenching as observed in the solid state. This is not surprising since the polymer swells only 8−10% in toluene relative to the dry state.[64] In addition, the oxygen diffusivity within the polymer decreases with increasing cluster loading as reflected by the order of magnitude decrease in the oxygen quenching rate constant for the polymer exhibiting the highest cluster loading. This result is consistent with the increased cross-linking of the polymer as the extent of cluster derivatization increases. Conversely the degree of cross-linking has little effect on polymer photophysics and reactivity in MeOH where the polymer is able to swell by ∼70%, relative to the dry state.[63] The open structure of the swelled polymer in MeOH is in evidence by the large increases in the oxygen quenching rate constant. In addition, the oxygen quenching rate constant is invariant for the range of cluster loadings used in our study (Table 1). Presumably, the fully extended structure of the polymer matrix in alcohol is sufficiently voluminous to permit oxygen to diffuse freely to the cluster active sites within the polymer network.

The pH dependence of the quenching rate constant summarized in Figure 2 is also accounted for by the swelling properties of the polymer. The oxygen quenching behavior for all cluster derivatives of the polymer in water (pH 3−6) is intermediate with respect to that observed in toluene and methanol, as expected, since the polymer swells by 33−37% in water over this pH range.[64] This behavior changes at pH 1, where the oxygen quenching of the long lifetime component is reduced. Although the polymer swells to 130% vs the dry state in 5% HCl (∼pH 1), the hydrochloride is formed with the presence of hydrophilic and hydrophobic domains.[65] These domains will segregate in ionic polymers, and the transport of substrate through the polymer will be retarded owing to cross-phase exchange.[66] In the case here, the isolation of the active sites within islands surrounded by the hydrophilic domains of the pyridinium hydrochloride might significantly slow the overall diffusion of oxygen through polymer thereby accounting for the decreased quenching rates at pH = 1.

The photochemistry of olefins in the presence of PVP−Mo_6Cl_{12} clearly identifies the oxygen quenching reaction to be energy transfer to yield singlet oxygen. As observed previously for the $[M_6X_8]Y_6^{2-}$ (M = Mo or W; X, Y = halide) parent species,[47] generation of singlet oxygen by energy-transfer between one-electron-oxidized cluster and superoxide ion is efficiently circumvented by the competitive energy transfer process, despite the high free energy driving force associated with the former pathway. The reaction of olefins **1**, **3**, and **4** in the presence of PVP-Mo_6Cl_{12} yields products and product distributions that parallel that of the native cluster ion and rose bengal, which are known to be efficient $^1O_2$ generators.[46] Distributions characteristic of radical autooxidation chemistry are not observed. For **3**, addition of $^1O_2$ to the olefinic bond, with subsequent abstraction of the sterically accessible allylic hydrogen, produces the appropriate hydroperoxide, which undergoes ensuing decomposition to give **5** and **6** in eq 6 in highest yields. Owing to the steric congestion of the "ene" transition state, **7** is produced in the lowest yield. This result is noteworthy because this latter species is the autooxidation product of **3**, therefore suggesting that the photochemically generated oxidant is $^1O_2$ and not O_2^-. Along this line, photooxidation studies employing **4** as a chemical trap are even more compelling. The symmetric disposition of the methyl groups about the double bond in **4** is manifested in the generation of only two products, **8** and **9**, from the ene reaction; production of **10** is unique to the radical autooxidation pathway.

(64) Data courtesy of Reilly Tar and Coal Company.

(65) Muller, G. In *Polyelectrolytes;* Selegny, E., Ed.; Reidel: Dordrecht, Netherlands, 1974; p 195.

(66) Buttry, D. A.; Anson, F. C. *J. Am. Chem. Soc.* **1983**, *105*, 685.

As summarized in Table 2, the products formed in the cluster photosensitized oxidation of **4** can be exclusively accounted for by **8** and **9**, and **10** is not detected as an oxidation product.

The relationship between polymer swelling properties and oxygen diffusivity is also manifested in the singlet oxygenation photochemistry. The photoxidations of **1** in toluene and MeOH directly parallel the extent of the swelling of the polymer matrix by solvent. During a 3 h period, the quantity of **2** oxidized increases with the degree of polymer swelling. These results of the oxidations in MeOH and toluene are particularly appealing, given that the lifetime of singlet oxygen is shorter in MeOH than in toluene. The congruence between the trend in photooxidation product yield with the singlet oxygen quenching rate constant indicates that the swelling behavior of the polymer matrix regulates the diffusion of oxygen in PVP−Mo_6Cl_{12} sensitizers.

The PVP−Mo_6Cl_{12} polymer is a useful oxygen sensor and solid state singlet oxygen photocatalyst owing to the material's remarkable photostability. Solutions of the polymer generate singlet oxygen over the course of months with no perceptible loss of activity. Even more striking, solids are indefinitely stable with no significant degradation of photoreactivity. After several years of storage, the polymers exhibit similar lifetimes and the efficiency for singlet oxygen reactivity is preserved. The stability of the photosensitizer in a singlet oxygen environment results from the thermodynamically stable metal−metal and metal−chloride bonds composing the cluster active site. Of course, for oxygen sensing and singlet oxygen applications, optimized function will be obtained for polymer supports exhibiting high oxygen permeabilities. To this end, on the basis of the work described herein, this family of cluster active sites has been tethered to highly oxygen permeable polymers via amine linkages to produce very stable and technologically relevant materials[67] for oxygen sensing applications.

Conclusion

The molybdenum(II) chloride cluster Mo_6Cl_{12} has been immobilized on 2% cross-linked poly(4-vinylpyridine) and the resulting PVP−Mo_6Cl_{12} retains the photophysics and oxygen reactivity of the parent cluster core. The quenching of PVP−Mo_6Cl_{12} excited states by molecular oxygen is slower than that of the free cluster in homogeneous solution (10^6 in polymer vs 10^9 M^{-1} s^{-1} in solution) and can be attributed to the hindered ability of the oxygen to diffuse through the polymer matrix. The accessibility of the cluster can be controlled by adjusting the physical structure of the matrix using preferential solvation. On a microscopic level, lifetime studies suggest that both the cis and trans forms of the cluster bind to the polymer. The longer lived trans form reacts with oxygen whereas the cis form is too short-lived to permit similar reactivity. The stability of the all-inorganic cluster active site in the singlet oxygen environment makes the PVP−Mo_6Cl_{12} system an exemplary material for oxygen sensing and photooxidation applications.

Acknowledgment. Financial support provided by the Air Force Office of Scientific Research (F49620-94-1-0170) and the National Science Foundation Materials Research Science and Engineering Center (DMR-9400417) are gratefully acknowledged. We thank Professor D. F. Shriver for providing us with a reprint of ref 44.

CM950443F

(67) Lekowitz, S. M.; Webb, S. P.; Paquette, M. S. U.S. Patent 4,-994,396, 1991.