Clearly, cycloisomerization is a powerful tool for construction of polycycles in which the nature of the polycycle depends only upon the juxtaposition of the unsaturation.

Acknowledgment. We thank the National Science Foundation and the General Medical Sciences Institute of the National Institutes of Health for their generous support of our program. We thank the UC-San Francisco Mass Spectrometry Facility supported by the NIH Division of Research Resources for obtention of mass spectra.

Supplementary Material Available: Characterization data for **1-12**, **14-17**, **19**, and **22-27** (6 pages). Ordering information is given on any current masthead.

Nonlinear Optical and Excited-State Properties of Conjugated One-Dimensional $[\mathrm{N{\equiv}M(OR)_3}]_n$ Polymers

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Conjugated organic molecules and polymers have long been the subjects of extensive study, in part because their delocalized π-electron systems endow these materials with enhanced electrical conductivities[1] and nonlinear optical[2] responses. We have been interested in the comparatively small and unexplored class of transition-metal complexes and polymers that are structurally and, in a formal sense, electronically analogous to such conjugated organic materials, on the basis of our expectation that the incorporation of optically tunable and redox-tunable unsaturated metal centers into conjugated structures should further augment their physical properties.[3] This has led us to investigate the class of one-dimensional polymers of the type $[\mathrm{N{\equiv}M(OR)_3}]_n$ (M = Mo, W).[4,5] The structures of these[5] and related[6] metal-nitrido polymers differ from those typical of linear-chain transition-metal compounds[7] in that they display a distinct bond-length alternation along the polymer backbone; band-structure calculations[8] and qualitative bonding considerations suggest that these species may be viewed as analogues of hydrocarbon polyenes and polyynes. Herein we report that these metal-nitrido polymers represent a new class of highly optically transparent inorganic nonlinear-optical materials and that they possess unusual photophysical properties.[9]

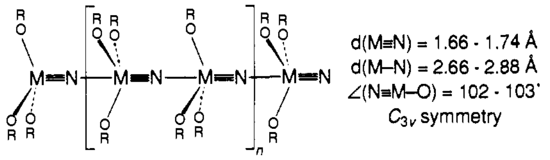

Table I. Photophysical and Second-Harmonic Generation Data for $[\mathrm{MN(OR)_3}]_n$

polymer	SHG efficiency[a]	emission $\tilde{\nu}_{max}$ (fwhm),[b] cm^{-1} [c,d]	emission τ, μs[c,e]
$[\mathrm{WN(OCMe_3)_3}]_n$	0.20	19 490 (4980)	60
$[\mathrm{MoN(OCMe_3)_3}]_n$	0.25	18 000 (4920)	750
$[\mathrm{MoN(OCMe_2CF_3)_3}]_n$	0.35	18 890 (5160)	*f*
$[\mathrm{MoN(OCMe_2Et)_3}]_n$	*g*	18 050 (4930)	760

[a] Efficiency (urea = 1) of unsized powders (λ_{ex} = 1064 nm). [b] Fwhm = full width at half maximum. [c] Crystalline sample, T = 77 K. [d] Corrected for spectrometer response. [e] λ_{ex} = 266 nm (Nd:YAG fourth harmonic, 5-ns fwhm pulse width, power < 100 μJ/pulse). Single-exponential emission decays were observed over at least five emission lifetimes. [f] Reproducible and single-exponential emission decays were not observed due to photodecomposition. [g] No signal observed.

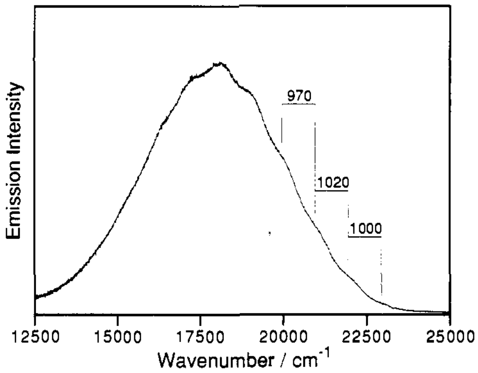

Figure 1. Emission spectrum (corrected for spectrometer response) of crystalline $[\mathrm{MoN(OCMe_2Et)_3}]_n$ at 77 K. Spacings (±50 cm^{-1}) of the ν(Mo≡N) vibronic progression are indicated.

Time-resolved spectroscopic analysis of the light emitted by powdered samples of $[\mathrm{MN(OR)_3}]_n$ (M = Mo, R = CMe$_3$, CMe$_2$CF$_3$; M = W, R = CMe$_3$)[4,5b] upon irradiation with the 1064-nm output of a pulsed Nd:YAG laser reveals a line at the frequency-doubled wavelength of 532 nm whose width and temporal profile are comparable to those of the excitation pulse. The observation of this second-harmonic generation (SHG) for $[\mathrm{MoN(OCMe_3)_3}]_n$ and $[\mathrm{WN(OCMe_3)_3}]_n$ is consistent with the fact that they crystallize in noncentrosymmetric space groups ($P6_3cm$, $P6_3$),[5] thus fulfilling a prerequisite for possessing bulk second-order susceptibilities ($\chi^{(2)}$).[2c,10,11] In contrast, the compound $[\mathrm{MoN(OCMe_2Et)_3}]_n$ displays no SHG signal. Given the

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otherwise very similar electronic properties of this polymer (vide infra) relative to those that are SHG active, we presume that this as yet structurally uncharacterized material crystallizes in a centrosymmetric space group.

Determination of the relative yield of SHG using standard techniques[13] shows that these polymers are 0.20–0.35 times as efficient as urea[14] (Table I). These efficiencies are surprisingly modest, in view of the facts that these compounds should, in principle, possess large molecular hyperpolarizabilities (β), as predicted from the $\beta \propto L^3$ dependence of this property on the conjugated chain length (L), and that, as d^0-configured species, their lower lying electronic excited states (including those of the $[\pi\pi^*]$ type) will be necessarily charge transfer in nature, which is important since the virtual excitation of such states induces large optical nonlinearities in conjugated organic species.[2c,10] The efficiencies do not appear to be intrinsically limited by crystallographic factors,[15] since the polymer dipoles are aligned parallel to one another in the solid state.[5]

In order to develop an electronic-structural framework through which to interpret the SHG properties of these polymers, and for the purpose of comparison to their calculated[8a] band structures, we have probed their lowest energy electronic excited states and found them to be highly emissive at low temperature. Crystals of all derivatives display broad and, for the molybdenum polymers, vibronically structured emission at 77 K (Figure 1). The extremely long excited-state lifetimes (Table I)—those for the molybdenum polymers are among the longest known for transition-metal complexes—indicate that the emission is a spin-forbidden process. In accord with this assignment, the emission excitation spectra of all polymers display a weak (and unstructured) band as the lowest energy feature.[16]

The emission energy of the $[MN(OR)_3]_n$ polymers is only moderately dependent upon the nature of the alkoxide ligand (Table I), which suggests that the orbital character of the emissive state derives largely from within the $[MN]_n$ backbone. This view is supported by the nature of the vibronic structure that is observed in the emission spectra of the molybdenum compounds. Although the vibronic transitions are irregularly spaced at higher quanta, the separation of the transitions near the electronic origin (where line broadening and coalescence effects are minimized) is ca. 1000 cm^{-1} (Figure 1), which is attributable to $\nu(\mathrm{Mo}\equiv\mathrm{N})$ ($\bar{\nu}$ = 1020 cm^{-1}).[5b] A simple Franck–Condon simulation of the vibronic intensity profile indicates that a ca. 0.2-Å distortion along the M≡N coordinate is associated with the population of the emissive state, from which we infer that the orbital transition producing this state is strongly M≡N bonding to antibonding in nature; by comparison, a 0.1-Å elongation of the M≡N bond has been calculated for the $^3[\pi\pi^*]$ states of d^2 $[OsNX_4]^-$ (X = Cl, Br) ions).[17] Our interpretation of these data is consistent with the results of a band-structure calculation for $[WN(OH)_3]_n$,[8a] which indicates that the valence and conduction bands are $[WN]_n$ localized and correlate, respectively, with the $\pi(\mathrm{W}\equiv\mathrm{N})/\sigma(\mathrm{W}\equiv\mathrm{N}{:})$ and the $\pi^*(\mathrm{W}\equiv\mathrm{N})$ orbitals of monomeric $WN(OH)_3$.[18] That such a large distortion should be associated with the band-gap excitation of an electron from the least $[MN]_n$-bonding orbital of the filled band to the least $[MN]_n$-antibonding orbital of the empty band indicates that the electron is not extensively delocalized along the polymer chain, in accord with the small dispersion calculated[8a] for these bands.[19]

In view of these findings, we suggest that the effective conjugated chain length that controls the emission and SHG properties of these polymers is considerably less than the structural chain length. While this undoubtedly serves to limit $\chi^{(2)}$ for these materials, it also endows them with far greater optical transparency than more highly conjugated compounds, such that the 532-nm second-harmonic line in our SHG measurements is still ca. 1 eV below the onset of absorption. This contrasts with a number of recently reported transition-metal SHG complexes, which possess larger efficiencies but also strongly absorb visible light.[20] Optimizing this efficiency/transparency tradeoff is central to improving SHG materials and could be accomplished for these polymers by tuning the covalency of the polymer backbone through replacement of the nitrido bridges with other atoms or groups. We have succeeded in preparing complexes derived from these archetypal metal–nitrido polymers and will report on them shortly.

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(18) The location of the Fermi level for $[WN(OH)_3]_n$ is not apparent from ref 8a, since the calculated energies of the tops of the *z* and *x,y* bands are nearly identical. The large M≡N distortion of the emissive state favors assignment of the band-gap excitation as $\pi \rightarrow \pi^*$; a $^3[e \rightarrow e]$ orbital transition such as this yields $^3A_1$, $^3A_2$, and ^3E excited states, for which there are two A_1, two A_2, and four E spin–orbit components. Although a detailed assignment of the emissive state is not available at present as a result of this complexity, the long emission lifetimes of $[MoN(OR)_3]_n$ may indicate that emission from an A_2 spin–orbit state predominates at 77 K, since the $A_2 \rightarrow A_1$ transition is dipole forbidden.

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Crystallographic Evidence for Multiple Coordinating Conformations in a Family of Macrocyclic Chelators

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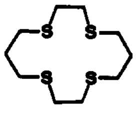
Elucidating the relationship between a chelator's covalent structure and the strength with which that molecule binds metal ions remains an important goal in the domain of molecular recognition. A detailed mechanistic picture of the complexation process requires, among other things, information on the chelator's conformation in the final coordination complex. The most precise structural data are provided by single-crystal x-ray or neutron diffraction, but the binding processes of interest generally occur in solution, and the validity of extrapolation from the solid state to solution is unclear. In some cases, the relevance of crystallographically observed ligand conformations to solution behavior may be evaluated by NMR, but experimental parameters (e.g., paramagnetic ions or inconvenient exchange rates) are often not conducive to NMR spectroscopy. Even when NMR analysis is possible, this approach may provide only limited insight on ligand conformation.

Ni(II) complexation by **1**–**3** provides an example of divergent structural information obtained from crystallographic and solution spectroscopic studies. The X-ray crystal structure of **1**-Ni(BF$_4$)$_2$



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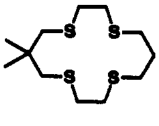

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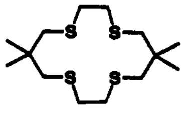

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