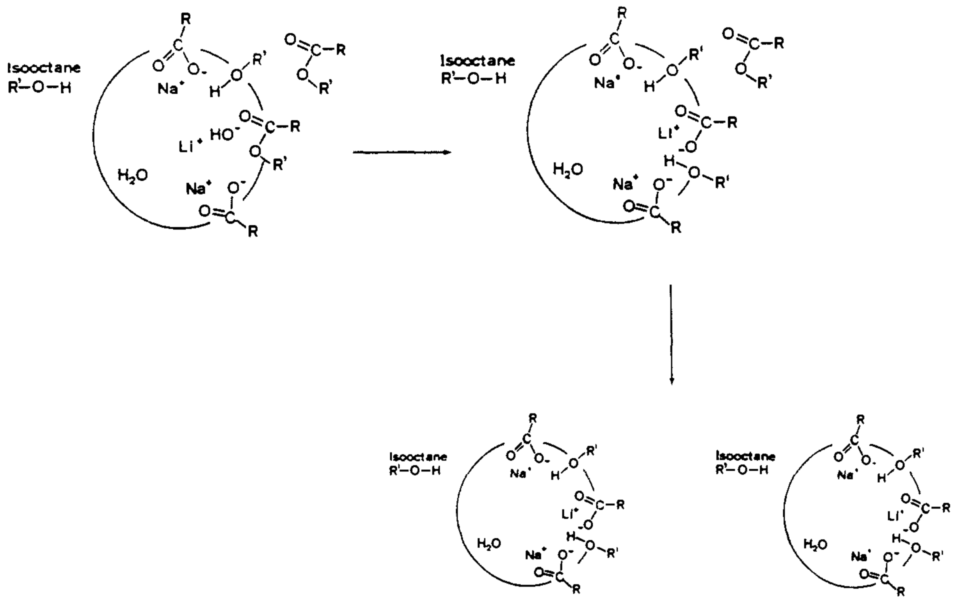


Figure 1. Schematic representation of the reverse micellar reaction system used; R = $(CH_2)_6CH_3$ and R' = $(CH_2)_7CH_3$.

a homogeneous distribution of all materials among all micelles.

There is no reaction in a control experiment carried out by suspending the same amount of LiOH in the organic mixture without octanoic acid sodium salt, i.e., there is no reaction in the absence of micelles. The situation in the micellar system can therefore be pictured as shown in Figure 1.

The reaction has been monitored by FTIR, by following the decrease of the ester band at 1744 cm^{-1} and the parallel increase of the band of the octanoic acid sodium salt at 1570 cm^{-1}.[16]

After ca. 100 h (close to equilibrium), 18 mM "fresh" octanoic acid salt has been produced, with a corresponding increase in the concentration of reverse micelles. Representative kinetic data are reported in Table I.

Since the "newly born" micelles can only be built at the expense of the preexisting ones, the average w_0 value will decrease during time. If for example the surfactant concentration would increase by a factor of 2, the final w_0 would decrease by a factor of 2, leading to a decrease in the water pool radius, the volume of the micelles, and the aggregation number.[4]

We have used the technique of time-resolved fluorescence quenching to directly determine the concentration change of micelles.[17,18] The fluorescent probe 1-pyrenesulfonic acid sodium salt and the quencher sodium iodide are ions localized in the water pool. Since the magnitude of the intramicellar quenching of the probe is proportional to the quencher concentration and inversely proportional to the micelle concentration,[17,18] the method allows the determination of the concentration of the reverse micelles.[19]

Results are given in Table I. It can be seen that the concentration of the micelles [M] increases by ca. 60%, whereas R_w decreases by 14%.

The value for the final micellar radius has been determined by quasielastic light scattering, which is also reported in Table I, and found to be in good agreement with that determined by fluorescence.

In conclusion, this work confidently demonstrates that the reverse micellar system presented here is endowed with the property of self-replication. Since the reaction is localized within the boundary of the structure itself, and since the reaction leads to the production of the components of the boundary which in terms define the identity of the structure, this work also provides the first chemical example of autopoietic organization. The fidelity of self-replication is not perfect, as the dimensions of the micelles become smaller from generation to generation; however, this "single-phase autopoietic cycle" can in principle be amended by a continuous supply of water.[4,20] More generally, micellar systems appear as suitable model systems for autopoiesis; and we are presently pursuing this work with a CTAB-based micellar aqueous system and with a lecithin-based liposomal system.

Acknowledgment. We thank Peter Schurtenberger for carrying out the quasielastic light scattering measurements, Francisco Varela, Ulrich Müller-Herold, and Peter Schmidli for helpful discussions, and Claudio Nastruzzi for technical advice.

---

[16] Further details about the general principle of the method have been described earlier: Walde, P.; Luisi, P. L. *Biochemistry* **1989**, *28*, 3353-3360.

[17] Lang, J.; Jada, A.; Malliaris, A. *J. Phys. Chem.* **1988**, *92*, 1946-1953.

[18] Verbeeck, A.; De Schryver, F. C. *Langmuir* **1987**, *3*, 494-500.

[19] With this method, the ratio of the concentration of quencher molecules to the concentration of reverse micelles, [Q]/[M], is determined. Since [Q] is known, [M] can be calculated, and by knowing [M], the radius of the micelle water pool, R_w, can be calculated from simple geometrical considerations by assuming sphericity of the reverse micelles.[17]

[20] Note that in ref 4, where the "single-phase" and the "two-phase autopoietic cycle" are theoretically presented, the text of figures 2 and 3 has been mistakenly exchanged.

Rapid Deactivation of Mustard via Microemulsion Technology

F. M. Menger* and A. R. Elrington

Department of Chemistry, Emory University
Atlanta, Georgia 30322

Received July 11, 1990

Notable progress in the destruction of nerve agents has been reported by Moss[1] and ourselves.[2] Recently, our attention has turned to another family of loathsome compounds, the mustards. Mustards are environmentally persistent cytotoxic alkylating agents that are manufactured with low technology and are used in chemical warfare.[3] Their detoxification is hampered by an extreme insolubility in the solvent where they are potentially most reactive, water. We have oxidized mustard simulants (e.g., "half-mustard") to nontoxic sulfoxides[3] on a reasonable scale with

$ClCH_2CH_2SCH_2CH_2Cl$ mustard

$CH_3CH_2SCH_2CH_2Cl$ half-mustard

---

[1] Moss, R. A.; Kim, K. Y.; Swarup, S. *J. Am. Chem. Soc.* **1986**, *108*, 788.

[2] Menger, F. M.; Gan, L. H.; Johnson, E.; Durst, H. D. *J. Am. Chem. Soc.* **1987**, *109*, 2800. Menger, F. M.; Tsuno, T. *J. Am. Chem. Soc.* **1989**, *111*, 4903.

[3] Jackson, K. E. *Chem. Rev.* **1934**, *15*, 425.

0002-7863/90/1512-8201$02.50/0 © 1990 American Chemical Society

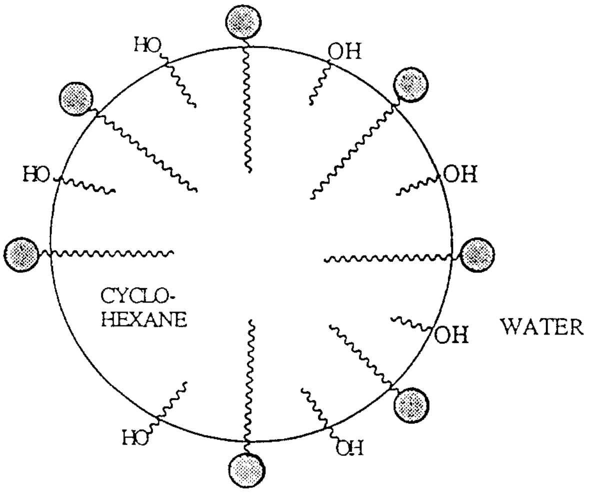


Figure 1. Schematic of an oil-in-water microemulsion where the surfactant head-groups (shaded circles) and the hydroxyls of the cosurfactants lie at the oil/water interface.

a microemulsion-based method that is simple, cheap, mild, and rapid. The strategy would appear to have general utility in organic chemistry.[4]

A microemulsion is an isotropic and optically transparent dispersion of oil in water (O/W) or water in oil (W/O) where "oil" is a hydrocarbon.[5,6] Such chemical systems form spontaneously when water, a hydrocarbon, a surfactant, and a "cosurfactant" (generally a low molecular weight alcohol) are mixed in specific proportions. Microemulsions, with dispersed droplets averaging 50–500 Å in diameter, remain clear indefinitely. Figure 1 shows schematically the structure of an O/W microemulsion.

Although we have examined over two dozen microemulsions (both O/W and W/O of widely differing compositions), we will for brevity focus on two particularly efficacious O/W recipes (given here in weight percent): (a) 3% cyclohexane in 82% water stabilized by 5% sodium dodecyl sulfate and 10% 1-butanol and (b) 4% *n*-hexadecane in 60% water stabilized by 24% Brij-96[7] and 12% 1-butanol.

Half-mustard (0.18 mL) was dissolved in 15 mL of microemulsion. When 5% aqueous hypochlorite was then added to the system in a 2-fold excess over half-mustard, the latter was, according to NMR and TLC, converted at room temperature into sulfoxide instantaneously. Thus, the reaction was complete before we could quench it (ca. 15 s). In contrast, mustard present in the environment can persist for months (a property utilized in the recent Iran–Iraq war in which mustard was spread on moats surrounding military installations).

Several features of the mustard oxidation in the microemulsion media should be emphasized:

1. Reaction capacity is excellent, 15 mL of microemulsion being capable of oxidizing as much as 1 mL of sulfide in a homogeneous mixture. This represents a decided advantage over reactions promoted by micelles, cyclodextrins, and synthetic hosts that typically employ substrate levels of 1 mM or less.[8] Oil droplets in an O/W microemulsion can obviously solubilize large amounts of water-insoluble organic reactants.

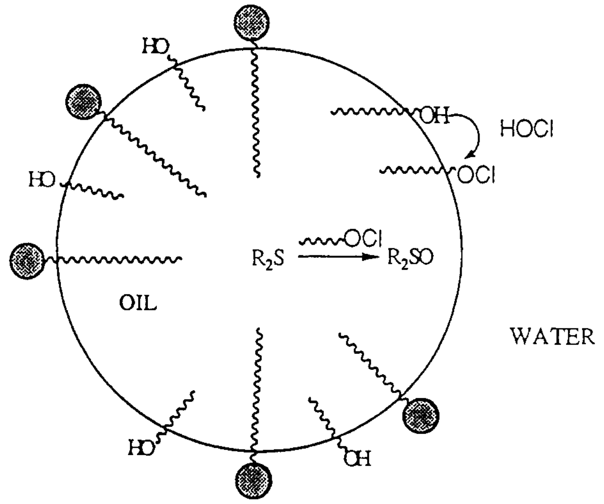


Figure 2. Proposed mechanism for oxidation of an oil-soluble mustard by water-soluble hypochlorite mediated by a cosurfactant. The extremely fast rate is related in part to the large interfacial contact area between the oil droplet and the continuous aqueous phase.

2. Since oxidation of the sulfide to sulfoxide consumes hypochlorite stoichiometrically, the reaction is not truly catalytic. Hypochlorite is, however, so cheap (we used grocery store bleach) that operating in a "turnover mode" (as was done with nerve agent hydrolysis[2]) is not a pressing issue.

3. According to NMR, sulfoxide is formed quantitatively with no evidence of sulfone production. This selectivity is important because mustard sulfone is an irritant[3] (although not as dangerous as mustard itself).

4. Last year, Drago et al.[9] published in this journal a kinetic study of sulfide oxidation by sodium hypochlorite using phase-transfer catalysis. Our microemulsion method seems more serviceable for two reasons: (a) Their phase-transfer catalysis was much slower, requiring at least 20 min for complete oxidation. (b) Phase-transfer catalysis entails continuous stirring, a disadvantage for applications in the real world.

5. Microemulsions (15 mL) were prepared from anionic, non-ionic, and cationic surfactants (sodium dodecyl sulfate, Brij-96, and cetyltrimethylammonium bromide, respectively). Half-mustard (0.18 mL) reacted instantaneously regardless of the surfactant charge. It was critical, however, to have an alcohol present as a cosurfactant. Thus, a cosurfactant-free microemulsion was formulated according to the following recipe: 15% water in 68% n-heptane stabilized with 17% Aerosol-OT (an oil-soluble anionic surfactant[10]). Sulfide oxidation within this microemulsion was incomplete even after 5 h. On the other hand, reaction was over in less than 15 s with a microemulsion consisting of 56% water, 24% n-heptane, 8% Aerosol-OT, and 12% 1-butanol as the cosurfactant.[11]

The most reasonable explanation for our results is that an alkyl hypochlorite[12,13] forms at the oil/water interface where the cosurfactant is known to reside[5] (Figure 2). Subsequent oxidation of the half-mustard then proceeds either in or on the oil droplet. The speed of the sulfide oxidation can be attributed to a large hydrocarbon/water contact area that permits "communication" between the water-soluble HOCl and the oil-soluble sulfide with interfacial cosurfactant serving as an intermediary.

---

(4) For previous studies of reactions in microemulsions, see: Bunton, C. A.; de Buzzaccarini, F. *J. Phys. Chem.* **1982**, *86*, 5010. Bunton, C. A.; de Buzzaccarini, F.; Hamed, F. H. *J. Org. Chem.* **1983**, *48*, 2461. Blandamer, M. J.; Burgess, J.; Clark, B. *J. Chem. Soc., Chem. Commun.* **1983**, 659. Martin, C. A.; McCrann, P. M.; Ward, M. D.; Angelos, G. H.; Jaeger, D. A. *J. Org. Chem.* **1984**, *49*, 4392. Mackay, R. A.; Longo, F. R.; Knier, B. L.; Durst, H. D. *J. Phys. Chem.* **1987**, *91*, 861. Erra, P.; Solans, C.; Azemar, N.; Parra, J. L.; Clausse, M.; Touraud, D. *Prog. Colloid Polym. Sci.* **1987**, *73*, 150. Garlick, S. M.; Durst, H. D.; Mackay, R. A.; Haddaway, K. G.; Longo, F. R. *J. Colloid Interface Sci.* **1990**, *135*, 508.

(5) Prince, L. M., Ed. *Microemulsions. Theory and Practice*; Academic Press: New York, 1974.

(6) Kahlweit, M.; Strey, R.; Busse, G. *J. Phys. Chem.* **1990**, *94*, 3881.

(7) Brij-96 is a non-ionic, poly(oxyethylene) ether surfactant obtained from Sigma. $CH_3(CH_2)_7CH{=}CH(CH_2)_8(OCH_2CH_2)_{10}OH$.

(8) Dugas, H.; Penney, C. *Bioorganic Chemistry. A Chemical Approach to Enzyme Action*; Springer-Verlag: New York, 1981; Chapter 5.

(9) Ramsden, J. H.; Drago, R. S.; Riley, R. *J. Am. Chem. Soc.* **1989**, *111*, 3958.

(10) Aerosol-OT, 1,4-bis(2-ethylhexyl) sodium sulfosuccinate, was supplied by Fisher.

(11) The difference between 15 s and 5 h cannot be attributed to the type of microemulsion because both O/W and W/O formulations were found to react instantly when an alcoholic cosurfactant was present.

(12) Anbar, M.; Dostrovsky, I. *J. Chem. Soc.* **1954**, 1094.

(13) In Brij-96-based microemulsions, both the surfactant and cosurfactant are capable of forming hypochlorites.

Acknowledgment. This work was supported by the Army Research Office. We are also grateful to LASPAU (Latin American Scholarship Program of American Universities) for a fellowship.

Description of Quadratic Optical Nonlinearities for Transition-Metal Organometallic Chromophores Using an SCF-LCAO MECI Formalism

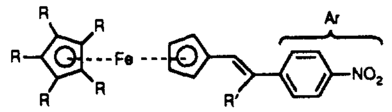
David R. Kanis, Mark A. Ratner,* and Tobin J. Marks*

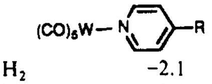
Department of Chemistry and the Materials Research Center
Northwestern University, Evanston, Illinois 60208

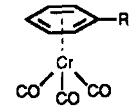
Received June 6, 1990

While current activity in molecular and macromolecular nonlinear optical (NLO) materials has focused predominantly on organic π-electron chromophores,[1] recent results suggest that organometallic chromophores may also hold promise.[2,3] In particular, low-lying strongly allowed one-photon metal-to-ligand and ligand-to-metal charge transfer (MLCT, LMCT) transitions[4] could conceivably give rise to large microscopic second-order nonlinearities (β_{ijk}) via a mechanism analogous to the charge-transfer excitations in organic NLO chromophores.[1] The understanding and rational design of organic chromophores has benefitted significantly from efficient, chemically oriented quantum chemical descriptions of π-electron NLO processes.[5-7] We communicate here the first SCF-LCAO approach to describing the second-order NLO characteristics of transition-metal organometallic molecules[8] and report some initial mechanistic observations.

Table I. Comparison of Calculated and Experimental Molecular Quadratic Hyperpolarizability Data in Units of 10^{-30} cm^5 esu^{-1} ($\hbar\omega$ = 0.65 eV)

no.	R	R′	$\beta_{vec}^{exp\,a}$	$\beta_{vec}^{calcd\,b}$	$\beta_{tot}^{calcd\,b}$
					
1	H	H(cis)	14	29.0	29.1
2	H	H(trans)	34	41.0	41.0
3	H	CN	22	31.9	37.1
4	CH_3	H	40	45.4	45.5
5	CH_3	CN	35	35.3	40.4
6[d]	H	H	21	51.0	56.4
7[e]	H	H	52	73.7	73.8

no.	R	$\beta_{vec}^{exp\,a}$	$\beta_{vec}^{calcd\,b,c}$
			
8	NH_2	−2.1	−3.60
9	*n*-butyl	−3.4	−5.91
10	H	−4.4	−7.66
11	phenyl	−4.5	−5.28
12	$COCH_3$	−9.3	−16.80

no.	R	$\beta_{vec}^{exp\,a}$	$\beta_{vec}^{calcd\,b}$	$\beta_{tot}^{calcd\,b}$
				
13	NMe_2	−0.4	−0.51	−3.0
14	NH_2	−0.6	−1.1	−1.9
15	$COOCH_3$	−0.7	−3.1	−4.8
16	H	−0.8	−1.9	−1.9
17	OCH_3	−0.9	−1.5	−1.6
18	*trans*-styryl	−2.2	−4.0	−4.8

[a] Experimental EFISH data of ref 3a. [b] ZINDO-derived parameters defined in footnotes 14, 16, and 17. [c] See footnote 16. [d] Ar = 2,4-dinitro. [e] Ar = 4-(4-nitrophenyl)-*trans*-butadienyl.

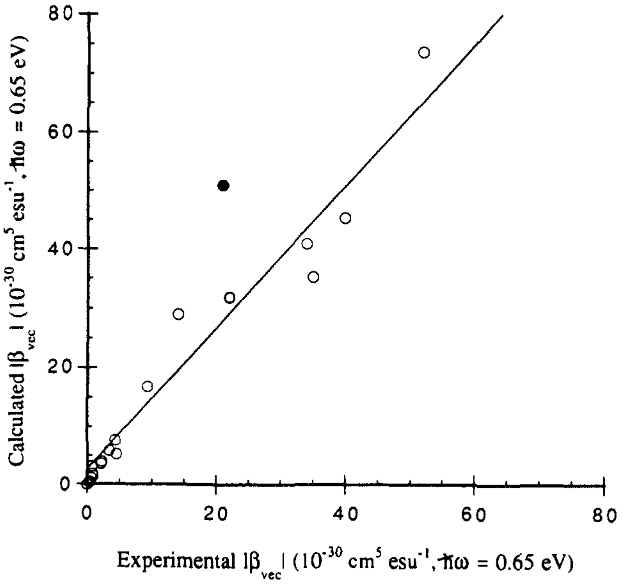


Figure 1. Plot of organometallic chromophore β_{vec} values calculated by the present ZINDO model versus experimental values from ref 3a; $\hbar\omega$ = 0.65 eV. The solid line is a least-squares fit to the data points and is drawn as a guide to the eye. The anomalously small β_{vec}^{exp} noted for chromophore **6** (filled circle) is thought to arise from nonplanarity in the stilbene part of the molecule (see footnote 18).

The ZINDO (INDO/S) electronic structure formalism[9,10] provides an accurate depiction of *linear* optical phenomena for

---

(1) Messier, J., Kajar, F., Prasad, P., Ulrich, D., Eds.; *Nonlinear Optical Effects in Organic Polymers*; Kluwer Academic Publishers: Dordrecht, 1989. (b) *Nonlinear Optical Properties of Organic Materials*; Khanarian, G., Ed. *Proc. SPIE*—Int. Soc. Opt. Eng. **1989**, *971*. (c) *Nonlinear Optical Properties of Polymers*; Heeger, A. J., Orenstein, J., Ulrich, D. R., Eds. *Mater. Res. Soc. Symp. Proc.* **1988**, *109*. (d) Chemla, D. S., Zyss, J., Eds. *Nonlinear Optical Properties of Organic Molecules and Crystals*; Academic Press: New York, 1987; Vols. 1 and 2. (e) Zyss, J. *J. Mol. Electron.* **1985**, *1*, 25–56. (f) Williams, D. J. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 690–703.

(2) (a) Green, M. L. H.; Marder, S. R.; Thompson, M. E.; Bands, J. A.; Bloor, D.; Kolinsky, P. V.; Jones, R. J. *Nature* **1987**, *330*, 360–362. (b) Frazier, C. C.; Harvey, M. A.; Cockerham, M. P.; Hand, H. M.; Chauchard, E. A.; Lee, C. H. *J. Phys. Chem.* **1986**, *90*, 5703–5706. (c) Eaton, D. F.; Anderson, A. G.; Tam, W.; Wang, Y. *J. Am. Chem. Soc.* **1987**, *109*, 1886–1888. (d) Calabrese, J. C.; Tam, W. *Chem. Phys. Lett.* **1987**, *133*, 244–245. (e) Anderson, A. G.; Calabrese, J. C.; Tam, W.; Williams, I. D. *Chem. Phys. Lett.* **1987**, *134*, 392–396. (f) Tam, W.; Calabrese, J. C. *Chem. Phys. Lett.* **1988**, *144*, 79–82. (g) Coe, B. J.; Jones, C. J.; McCleverty, J. A.; Bloor, D.; Kolinsky, P.V.; Jones, R. J. *J. Chem. Soc., Chem. Commun.* **1989**, 1485–1487. (h) Bandy, J. A.; Bunting, H. E.; Garcia, M. H.; Green, M. L. H.; Marder, S. R.; Thompson, M. E.; Bloor, D.; Kolinsky, P. V.; Jones, R. J. In *Organic Materials for Non-linear Optics*, Hann, R. A., Bloor, D., Eds.; Royal Soc. Chem. Monograph 69; Burlington House: London, 1989; pp 225–231.

(3) (a) Cheng, L.-T.; Tam, W.; Meredith, G. R.; Marder, S. R. *Mol. Cryst. Liq. Cryst.*, in press. (b) Park, J.; Firestone, M. A.; Marks, T. J.; Yang, J.; Wong, G. K.. unpublished observations.

(4) See, for example: (a) Lever, A. B. P. *Inorganic Electronic Spectroscopy*, 2 ed.; Elsevier: Amsterdam, 1984; Chapter 5. (b) Geoffroy, G. L.; Wrighton, M. S. *Organometallic Photochemistry*; Academic Press: New York, 1979; Chapter 1.

(5) (a) Lalama, S. L.; Garito, A. F. *Phys. Rev.* **1979**, *20*, 1179–1194. (b) Garito, A. F.; Teng, C. C.; Wong, K. Y.; Enmmankahamiri, O. *Mol. Cryst. Liq. Cryst.* **1984**, *106*, 219–258. (c) Docherty, V. J.; Pugh, D.; Morley, J. O. *J. Chem. Soc., Faraday Trans. 2* **1985**, *81*, 1179–1192. (d) Morley, J. O. *J. Am. Chem. Soc.* **1988**, *110*, 7660–7663.

(6) (a) Li, D.; Marks, T. J.; Ratner, M. A. *Chem. Phys. Lett.* **1986**, *131*, 370–375. (b) Dirk, C. W.; Twieg, R. J.; Wagniere, G. *J. Am. Chem. Soc.* **1986**, *108*, 5387–5395. (c) Li, D.; Ratner, M. A.; Marks, T. J. *J. Am. Chem. Soc.* **1988**, *110*, 1707–1715. (d) Ulman, A. *J. Phys. Chem.* **1988**, *92*, 2385–2390.

(7) (a) Li, D.; Marks, T. J.; Ratner, M. A. *Mater. Res. Soc. Symp. Proc.* **1989**, *134*, 665–672. (b) Wu, J. W.; Heflin, J. R.; Norwood, R. A.; Wong, K. Y.; Zamani-Khamiri, O.; Garito, A. F.; Kalyanaraman, P.; Sounik, J. *J. Opt. Soc. Am. B.* **1989**, *6*, 707–720. (c) Li, D.; Ratner, M. A.; Marks, T. J., submitted for publication.

(8) Communicated in part: Kanis, D. R.; Firestone, M. A.; Ratner, M. A.; Marks, T. J. *Abstracts of Papers*, 199th National Meeting of the American Chemical Society, Boston, MA; American Chemical Society: Washington, DC, 1990; INOR 472.

(9) (a) Anderson, W. P.; Edwards, W. D.; Zerner, M. C. *Inorg. Chem.* **1986**, *25*, 2728–2732. (b) Anderson, W. P.; Cundari, T. R.; Drago, R. S.; Zerner, M. C. *Inorg. Chem.* **1990**, *29*, 1–3.

0002-7863/90/1512-8203$02.50/0