

Third-Order Nonlinear Optical Properties of Complexes with MM Triple and Quadruple Bonds (M = Mo, W) at 1064 nm by Degenerate Four-Wave Mixing

Brian D. Pate,[†] Jonathan R. G. Thorne,[‡] Damon R. Click,[†] Malcolm H. Chisholm,^{*,§} and Robert G. Denning^{*,‡}

Department of Chemistry, Indiana University, 800 East Kirkwood Avenue, Bloomington, Indiana 47405, Inorganic Chemistry Laboratory, Oxford University, South Parks Road, Oxford OX1 3QR, U.K., and Department of Chemistry, The Ohio State University, 100 West 18th Avenue, Columbus, Ohio 43210

Received November 28, 2001

Measurements of the third-order nonlinear optical responses of solutions of the metal–metal multiply bonded complexes $\text{Mo}_2(\text{OPr})_6$, $\text{W}_2(\text{O}i\text{Bu})_6$, $\text{M}_2(\text{NMe}_2)_6$, $\text{M}_2(\text{O}_2\text{C}i\text{Bu})_4$, and $\text{M}_2\text{Cl}_4(\text{PMe}_3)_4$ (M = Mo, W), using picosecond degenerate four-wave mixing at 1064 nm, are reported. These complexes display only very small instantaneous electronic polarizations when excited with cross-polarized beams. When the excitation beams are similarly polarized, a significant third-order optical response is detected, which is attributable to the formation of bulk thermal excitation gratings. Time-dependent measurements support this view.

Introduction

The nonlinear optical responses of a variety of organo-metallic and coordination compounds have been examined.^{1,2} Large second-order susceptibilities have been reported for compounds showing charge separation in the excited state.² Much of this work seems to have been inspired by a report by Green et al. on substituted ferrocenyl compounds.³ Alkynes and conjugated organic molecules show large third-order nonlinear susceptibilities,⁴ and we have for some time wondered whether M–M multiple bonds might show similarly large responses. We were thus particularly interested in the 1997 report by Mashima et al. of the large third-order nonlinear optical susceptibilities of quadruply and triply bonded M_2L_4 and $\text{M}_2\text{L}_4\text{Pd}_2\text{Cl}_2$ (M = Mo, Cr; L = 6-diphe-

nylphosphino-2-pyridonate) complexes, as dichloromethane solutions, by picosecond degenerate four-wave mixing (DFWM).⁵ These measurements were conducted at 532 nm, with supporting measurements of the femtosecond optical Kerr effect (OKE) of one complex ($\text{Mo}_2\text{L}_4\text{Pd}_2\text{Cl}_2$) at 790 nm. The reported microscopic hyperpolarizabilities, γ_{ijkl} ($-3\omega; \omega, \omega, \omega$), were (Mo_2L_4) 6.9×10^{-31} esu, (Cr_2L_4) $\leq 10^{-33}$ esu, ($\text{Mo}_2\text{L}_4\text{Pd}_2\text{Cl}_2$) 1.5×10^{-30} esu, and ($\text{Cr}_2\text{L}_4\text{Pd}_2\text{Cl}_2$) 5.2×10^{-31} esu. The study was conducted exclusively using like-polarized excitation beams,⁶ with no supporting time-dependent measurements. On the basis of the agreement in magnitude of the OKE (790 nm) and DFWM (532 nm) results, the authors suggested that the 532 nm hyperpolarizability was primarily due to nonresonant nonlinearity (instantaneous electronic polarization). The authors mentioned that the lowest energy electronic absorption band of $\text{Mo}_2\text{L}_4\text{Pd}_2\text{Cl}_2$ peaked at 640 nm.

* To whom correspondence should be addressed. E-mail: chisholm@chemistry.ohio-state.edu.

[†] Indiana University.

[‡] Oxford University.

[§] The Ohio State University.

- (1) Zuo, J.; You, X. *Chin. Soc. Bull.* **2001**, *46*, 178. Goovaerts, E.; Wenseleers, W. E.; Garcia, M. H.; Cross, G. H. *Handb. Adv. Electron. Photonic Mater. Devices* **2001**, *9*, 127. Long, N. J. *Optoelectron. Prop. Inorg. Compd.* **1999**, 107. Heck, J.; Dabek, S.; Meyer-Friedrichsen, T.; Wong, H. *Coord. Chem. Rev.* **1999**, *190–192*, 1217.
- (2) Lacroix, P. G. *Eur. J. Inorg. Chem.* **2001**, 339. Qin, J.; Liu, D.; Dai, C.; Chen, C.; Wu, B.; Yang, C.; Zhan, C. *Coord. Chem. Rev.* **1999**, *188*, 23. Whittall, I. R.; McDonagh, A. M.; Humphrey, M. G.; Samoc, M. *Adv. Organomet. Chem.* **1998**, *43*, 349. Bildstein, B. *Coord. Chem. Rev.* **2000**, *206–207*, 369.
- (3) Green, M. L. H.; Marder, S. R.; Thompson, M. E.; Bandy, J. A.; Bloor, D.; Kolinsky, P. V.; Jones, R. J. *Nature* **1987**, *330*, 360.

- (4) Luh, T.-Y.; Chen, R.-M.; Hwu, T.-Y.; Basu, S.; Shiau, C.-W.; Lin, W.-Y.; Jin, B.-Y.; Hsu, C.-C. *Pure Appl. Chem.* **2001**, *73*, 243. Jiang, M.-H.; Fang, Q. *Adv. Mater.* **1999**, *11*, 1147. Jenkins, I. H.; Lindsell, W. E.; Murray, C.; Preston, P. N.; Woodman, T. A. *J. ACS Symp. Ser.* **1998**, *704*, 321. Yamamoto, T.; Hayashida, N. *React. Funct. Polym.* **1998**, *37*, 1. Nalwa, H. S. *Nonlinear Opt. Org. Mol. Polym.* **1997**, 611. Nalwa, H. S.; Watanabe, T.; Miyata, S. *Nonlinear Opt. Org. Mol. Polym.* **1997**, 89.
- (5) Mashima, K.; Tanaka, M.; Kaneda, Y.; Fukumoto, A.; Mizomoto, H.; Tani, K.; Nakano, H.; Nakamura, A.; Sakaguchi, T.; Kamada, K.; Ohta, K. *Chem. Lett.* **1997**, 411.
- (6) Kleinman, D. A. *Phys. Rev.* **1962**, *126*, 1977.

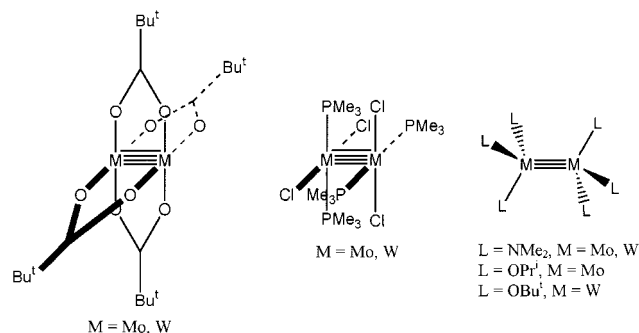


Figure 1. Structural representations of the investigated dimetal complexes.

We decided to investigate the mechanism of the reported nonlinearity by studying a series of multiply bonded metal dinuclear compounds⁷ (see Figure 1) in which the bond order and ligand sets were systematically varied. We employed picosecond DFWM at 1064 nm, a position far from the visible absorption maxima. We tested both *yyyy* and *xyyx* beam polarizations (see the Experimental Section), with additional time-dependent measurements in the former configuration.

We began our study by reexamining the electronic absorption of these series (see Figure 2).⁷ The lowest energy band of the $\text{Mo}_2(\text{O}_2\text{CR})_4$ compounds, which peaks at 430 nm, has been assigned to a $^1(\delta^2 \rightarrow \delta\delta^*)$ (metal-based) electronic transition. The lowest energy band of the analogous tungsten species peaks at 360 nm, and is assigned to two coincident electronic transitions, a $^1(\delta^2 \rightarrow \delta\delta^*)$ transition which is masked by a much more intense metal–ligand charge transfer. The $^1(\delta^2 \rightarrow \delta\delta^*)$ band of $\text{Mo}_2\text{Cl}_4(\text{PMe}_3)_4$ peaks at 585 nm. A less intense, higher energy $^1(\delta^2 \rightarrow \pi\delta^*)$ band peaks at 435 nm. The analogous tungsten complex has low-energy maxima at 660 and 500 nm (again, the former is more intense). The lowest energy UV/vis absorption maxima of the triply bonded complexes fall at the following wavelengths: $\text{Mo}_2(\text{OR})_6$, 360 nm; $\text{W}_2(\text{OR})_6$, 420 nm; $\text{Mo}_2(\text{NMe}_2)_6$, 360 nm; $\text{W}_2(\text{NMe}_2)_6$, 330 nm. The lowest energy band of all of the above complexes has a tail that extends into the near-IR region and is responsible for a small amount of absorption even at wavelengths as long as 1064 nm.

Experimental Section

Sample Preparation. Dichloromethane and hexane were distilled over the appropriate drying agents under nitrogen and degassed

(7) See the following for preparations and electronic absorption spectroscopy. $\text{Mo}_2(\text{O}_2\text{CCMe}_3)_4$: Stephenson, T. A.; Bannister, E.; Wilkinson, G. *J. Chem. Soc.* **1964**, 2538. $\text{W}_2(\text{O}_2\text{CCMe}_3)_4$: Santure, D. J.; Huffman, J. C.; Sattelberger, A. P. *Inorg. Chem.* **1985**, *24*, 371. $\text{Mo}_2\text{Cl}_4(\text{PMe}_3)_4$: Cotton, F. A.; Extine, M. W.; Felthouse, T. R.; Koltammer, B. W. S.; Lay, D. G. *J. Am. Chem. Soc.* **1981**, *103*, 4040. $\text{W}_2\text{Cl}_4(\text{PMe}_3)_4$: Schrock, R. R.; Sturgeooff, L. G.; Sharp, P. R. *Inorg. Chem.* **1983**, *22*, 2801. $\text{Mo}_2(\text{NMe}_2)_6$: Chisholm, M. H.; Cotton, F. A.; Frenz, B. A.; Reichert, W. W.; Shive, L. W.; Stults, B. R. *J. Am. Chem. Soc.* **1976**, *98*, 4469. $\text{W}_2(\text{NMe}_2)_6$: Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Stults, B. R. *J. Am. Chem. Soc.* **1976**, *98*, 4477. $\text{Mo}_2(\text{OPr}^t)_6$: Chisholm, M. H.; Cotton, F. A.; Murillo, C. A.; Reichert, W. W. *Inorg. Chem.* **1977**, *16*, 1801. $\text{W}_2(\text{OBu}^t)_6$: Akiyama, M.; Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Haitko, D. A.; Little, D.; Fanwick, P. E. *Inorg. Chem.* **1979**, *18*, 2266. Chisholm, M. H.; Clark, D. L.; Kober, E. M.; Van Der Sluys, W. G. *Polyhedron* **1987**, *6*, 723.

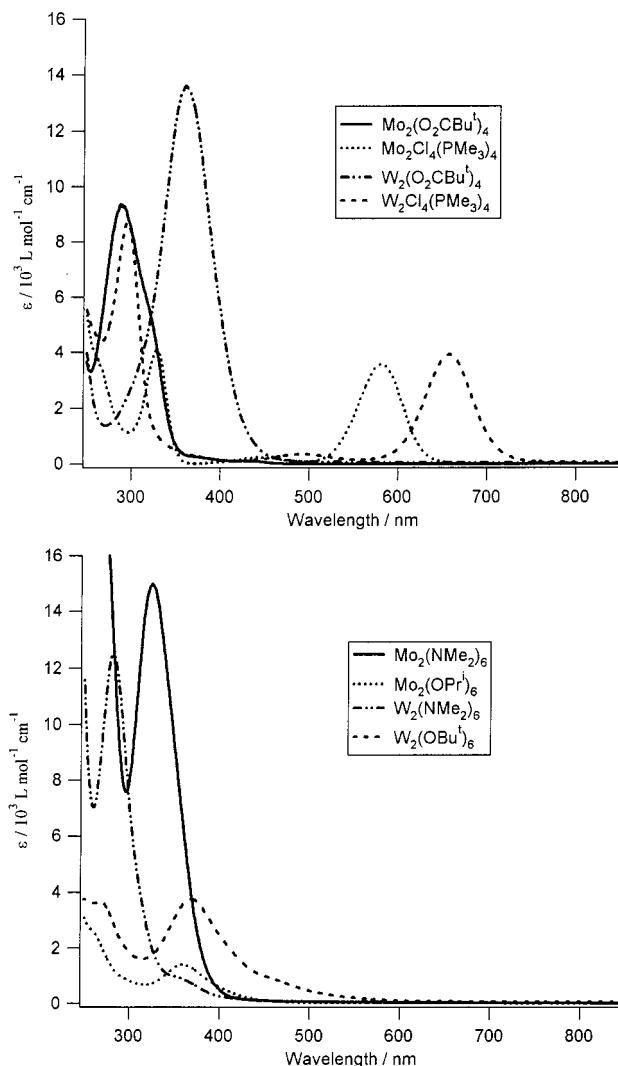


Figure 2. Electronic absorption spectra of the investigated dimetal complexes: top, quadruply bonded compounds; bottom, triply bonded compounds.

under reduced pressure prior to use. Solutions of the dimetal complexes (in dichloromethane or hexane) were prepared in a nitrogen-filled glovebox. Each was passed by syringe through a 0.1 Å filter, transferred into a dry cuvette, and capped with a greased Teflon stopper.

Laser Characteristics and DFWM Configurations. DFWM susceptibilities were measured in the forward scattering folded box geometry using an active passive mode-locked YAG laser at 1064 nm with a temporal resolution of 50 ps and a repetition rate of 4 Hz, as described in detail in previous work.⁸ Quartz cuvettes of 1 mm path length were employed. Measurement of the (reference) signal from the pure solvent was performed in tandem with the measurement of each solution. Measurements were made using both the *xyyx* and *yyyy* beam polarizations. (Here *x* and *y* are orthogonally polarized beams.) In each case, two beams (*xy* or *yy*) create a grating across which a third beam (*y*) diffracts, leading to the production of the nonlinear signal (of *x* or *y* polarization). The intensity of the diffracted beam provides information on the amplitude of the optical

(8) Kuebler, S. M.; Denning, R. G.; Anderson, H. L. *J. Am. Chem. Soc.* **2000**, *122*, 339. Kuebler, S. M. D. Phil. Thesis, University of Oxford, Oxford, 1997. Kuebler, S. M.; Denning, R. G. *Chem. Phys. Lett.* **1996**, *250*, 120.

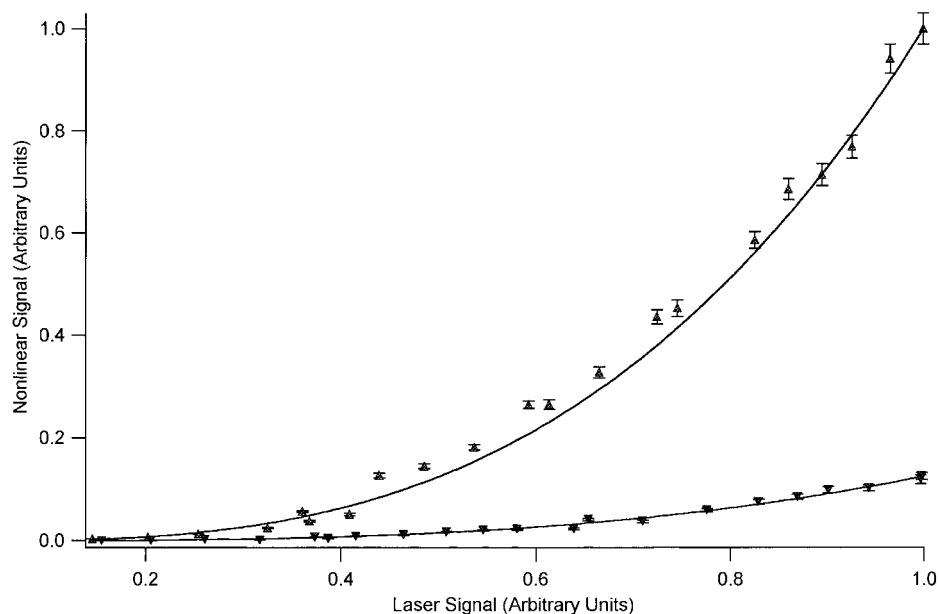


Figure 3. Normalized nonlinear optical response of a 28 mM solution of a representative dimetal complex, $\text{Mo}_2(\text{O}_2\text{CBu})_6$ (upper data), together with the response of the solvent, CH_2Cl_2 , and cubic fits to both data sets.

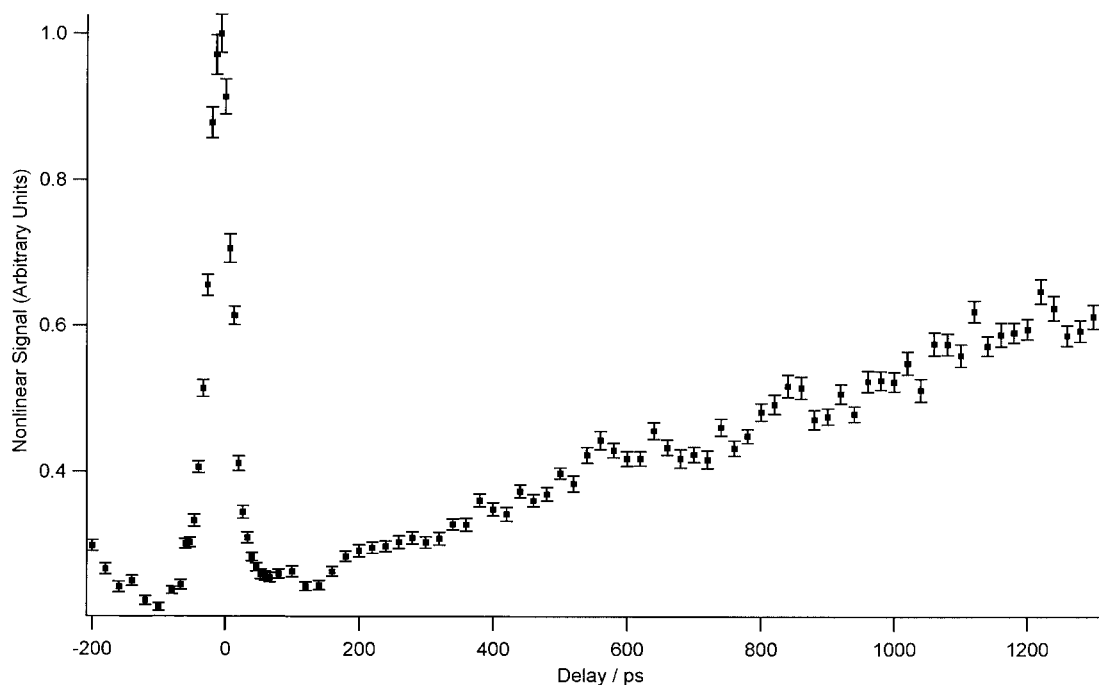


Figure 4. Time dependence of the nonlinear optical response of a 20 mM solution of a representative dimetal complex, $\text{Mo}_2(\text{O}_2\text{CBu})_6$. The delay time of one of the excitation beams was varied.

grating and thus the magnitude of the induced nonlinearity. Time-dependent data were obtained by delaying one of the pump beams.

Results and Discussion

Values of γ_{eff} , measured using the yyyy configuration, are collected in Table 1. These were calculated as described in previous work,⁹ employing corrections for solution absorption and assuming equal refractive indices of the solution and solvent. Although there is some overlap among the two sets of compounds, in general the quadruply bonded complexes

Table 1. Effective Third-Order Optical Responses at 1064 nm Measured Using yyyy Polarized Beams

	$\gamma_{\text{eff}}/10^{-33}$ esu		$\gamma_{\text{eff}}/10^{-33}$ esu
$\text{Mo}_2(\text{O}_2\text{CCMe}_3)_4$	13	$\text{Mo}_2(\text{NMe}_2)_6$	2.7
$\text{W}_2(\text{O}_2\text{CCMe}_3)_4$	5.6	$\text{W}_2(\text{NMe}_2)_6$	8.8
$\text{Mo}_2\text{Cl}_4(\text{PMe}_3)_4$	2.6	$\text{Mo}_2(\text{OPr}^i)_6$	2.4
$\text{W}_2\text{Cl}_4(\text{PMe}_3)_4$	5.2	$\text{W}_2(\text{OBu}^i)_6$	2.1

had higher responses. We were unable to detect a nonlinear signal above that of the solvent for any of these complexes using the xyxx configuration. This indicates¹⁰ that instanta-

(9) Thorne, J. R. G.; Kuebler, S. M.; Denning, R. G.; Blake, I. M.; Taylor, P. N.; Anderson, H. L. *Chem. Phys.* **1999**, *248*, 181.

(10) Andrews, J. R.; Hochstrasser, R. M. *Chem. Phys. Lett.* **1980**, *76*, 207.
Andrews, J. R.; Hochstrasser, R. M. *Chem. Phys. Lett.* **1980**, *76*, 213.

neous electronic polarization makes a negligible contribution to the (yyyy) observed nonlinear responses. It should be emphasized, then, that the values of γ_{eff} reported in Table 1 are not true molecular hyperpolarizabilities, but are rather bulk phenomena due to spatial modulation of the linear susceptibility.^{10,11} Such grating formation can occur by a number of mechanisms, including (1) molecular orientation,¹² (2) formation of excited electronic states,¹³ (3) thermal effects (formation of thermal and thermal acoustic gratings),¹⁴ and (4) electrostriction.¹⁵ Studies of the nature of the time-dependent response facilitate differentiation between these various mechanisms.

A representative plot of input laser intensity versus generated nonlinear signal intensity is presented in Figure 3. Fits of both the solution and solvent data to $y = mx^3$ are also shown, confirming the cubic dependence of the measured signal on the input laser intensity. The concentration dependence of this nonlinear signal confirms that it is real and positive, with two-photon absorption making a negligible contribution.⁹

Time-dependent data for these solutions, as shown in Figure 4, consists of two components, an initial pulse-width-limited spike, attributable to the solvent response, and a longer lived signal which grows over a nanosecond time scale. The simplest means to account for this latter signal is to attribute it to the buildup of a thermal grating during the nonradiative decay of an excited electronic state. (A thermal background is also generally present, with an intensity of about 15% of the solvent spike.)

We detected fifth-order behavior for one of the dimetal complexes, $\text{Mo}_2(\text{OPr}^i)_6$. This seems to suggest that two-photon absorption makes a significant contribution to the

measured optical nonlinearity in this case, although why this particular complex should be more prone to this response mechanism than the other dimetal species is unclear.

Conclusions

This study casts doubt on claims of an especially high nonresonant nonlinearity (instantaneous electronic hyperpolarizability) of simple group 6 dimetal derivatives. It is far more likely that measured nonlinearities of such simple molecular species are due to resonant contributions, such as the formation of excited-state gratings and subsequent thermal effects. Only a very small absorption cross-section is needed to produce such gratings. (The authors of the 1997 report⁵ drew their conclusions from studies conducted relatively close to the absorption maxima, only employed the yyyy beam configurations, and did not include time-dependent information. The noted nonlinearities almost surely result from resonant effects such as the ones suggested here.)

The luminescence lifetimes (upon excitation of the low-energy visible band) of the $\text{M}_2\text{Cl}_4(\text{PMe}_3)_4$ species have been previously measured to be 140 ns for $\text{M} = \text{Mo}$ (in 2-methylpentane, $\phi = 0.26$)¹⁶ and 41 and 50 ns for $\text{M} = \text{W}$ (in dichloromethane and benzene, respectively),¹⁷ while we suspect that the electronic excited states of the other dimetal complexes decay at a faster rate.¹⁸ The data presented above do not distinguish between these two classes of compounds, and suggest that all these dimetal complexes have a significant nonradiative (thermal) contribution to their (1064 nm generated) excited-state decay.

To obtain a pure molecular electronic hyperpolarizability, it would be useful to study a neat material. Clearly, such a study would be advantageous in that the detected nonlinear signal would be due entirely to the compound of interest; solvent responses would not be present. Our initial studies indicate that 1 mm thick (solid-state) samples of these species absorb too strongly at 1064 nm to permit the collection of meaningful data. To pursue this work further, thin films of a high degree of homogeneity and of well-defined density and thickness would be needed. On the basis of our study, however, we expect that the measured nonlinear responses would be fairly small.

IC0112138

- (11) Beddard, G. S.; McFadyen, G. G.; Reid, G. D.; Thorne, J. R. G. *Chem. Phys.* **1993**, *172*, 363. Heilweil, E. J.; Hochstrasser, R. M.; Souma, H. *Opt. Commun.* **1980**, *35*, 1429.
- (12) Nunzi, J.; Charra, F.; Fiorini, C. *Condens. Matter News* **1993**, *2*, 6. Newell, A. C.; Moloney, J. W. *Nonlinear Optics*; Addison-Wesley: Redwood City, CA, 1992. McGraw, D. J. Siegman, A. E.; Wallraff, G. M.; Miller, R. D. *Appl. Phys. Lett.* **1989**, *54*, 1713.
- (13) Vauthey, E.; Henseler, A. *J. Phys. Chem.* **1995**, *99*, 8652. Laudereau, A. In *Ultrashort Laser Pulses: Generations and Applications*, 2nd ed.; Kaiser, W., Ed.; Topics in Applied Physics; Springer: Berlin, 1993; Vol. 60, p 35. Cui, Y.; Zhao, M.; He, G. S.; Prasad, P. N. *J. Phys. Chem.* **1991**, *95*, 6842.
- (14) Brédas, J.-L.; Adant, C.; Tackx, P.; Persoons, A.; Pierce, B. M. *Chem. Rev.* **1994**, *94*, 243. McEwan, K. J.; Madden, P. A. *J. Chem. Phys.* **1992**, *97*, 8748. McEwan, K. J.; Harrison, K. J.; Madden, P. A. *Mol. Phys.* **1990**, *69*, 1025. Genberg, L.; Bao, Q.; Gracewski, S.; Miller, R. J. D. *Chem. Phys.* **1989**, *131*, 81. Fayer, M. D. *IEEE J. Quantum Electron.* **1986**, *22*, 1437.
- (15) Yariv, A. *Quantum Electronics*, 3rd ed.; Wiley: New York, 1989. Trebino, R.; Gustafson, E. K.; Siegman, A. E. *J. Opt. Soc. Am. B* **1986**, *3*, 2195. Trebino, R.; Barker, C. E.; Siegman, A. E. *IEEE J. Quantum Electron.* **1986**, *22*, 1413. Kerr, E. L. *IEEE J. Quantum Electron.* **1970**, *6*, 616.

- (16) Hopkins, M. D.; Gray, H. B. *J. Am. Chem. Soc.* **1984**, *106*, 2468.
- (17) Hsu, T.-L. C.; Engebretson, D. S.; Helvoigt, S. A.; Nocera, D. G. *Inorg. Chim. Acta* **1995**, *240*, 551.
- (18) Unpublished work.