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13. ABSTRACT (Maximum 200 words) The goal of the research in this grant is to optimize metal-organic complexes for nonlinear optical (NLO) applications, by determining how variations in the metal centers and types of ligands will affect the NLO properties of the complexes. We studied a number of Pd (II) and Pt(II) complexes of phosphine ligand, and we found that these complexes exhibit both NLO refraction and NLO absorption that depends both on the nature of the phosphine ligand and on the nature of the metal center and its coordination geometry. We also observed large optical nonlinearities in Mo(CO) ₄ complexes. We performed extensive studies of these complexes and we observed strong optical limiting in these complexes for 5.8 ns laser pulses at 532 nm. Finally, we began to explore a series of asymmetric pentaazadentate porphyrin-like metal complexes ((R-APPC) _n MJCl _n). These complexes show strong reverse saturable absorptions on a picosecond time scale. The optical nonlinearities are dependent on the conjugated R group and the metal center, so that complexes with even better optical nonlinearities might be obtained in the future by a judicious choice of ligands and metals. Hence, this class of asymmetric pentaazadentate porphyrin-like metal complexes shows great promise for optical power limiting applications.				
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STATEMENT OF THE PROBLEM STUDIED

The Department of Defense (DoD) has a fundamental need for nonlinear optical (NLO) materials that can be used in optics-based applications such as switching, computing, information processing, and power limiting for sensor protection. Materials that satisfy all optical device requirements for the applications listed above are generally unavailable. We have discovered that transition metal complexes are extremely promising materials for these applications. These complexes have very high, non-resonant laser-induced optical nonlinearities that are comparable to those of conjugated polymers. In addition, these complexes have very low absorption losses, are stable and are easily prepared.

To optimize transition metal complexes with phosphorus-donor ligands for DoD applications, we have performed a research effort to investigate in detail the factors that lead to the large optical nonlinearities in these materials. We have studied how variations in the metal centers and numbers and types of phosphorus-donor ligands affect the NLO properties of the complexes. These studies were performed with degenerate four wave mixing (DFWM) experiments, Z-Scan experiments, and power limiting experiments using picosecond and nanosecond Nd:YAG laser pulses, as well as, nanosecond wavelength tunable color center laser pulses.

The most immediate DoD applications for these materials are in optical power limiting for the hardening of eyes and sensor systems against frequency agile laser threats, against which spectral rejection filters are ineffective. Solutions of these complexes would appear to be ideal for these applications because they have very low linear absorptions (so that no optical loss penalty is suffered) and many have exhibited extremely high NLO responses in our preliminary studies.

SUMMARY OF THE MOST IMPORTANT RESULTS

Our preliminary studies had demonstrated that $\text{Mo}(\text{CO})_4$ complexes with phosphine ligands could exhibit large third-order nonlinearities. These results were surprising because the $\text{Mo}(\text{CO})_4$ complexes did not have the high degrees of conjugation normally associated with large third-order nonlinearities in organic compounds. To better understand this phenomenon, we explored the relationship between the structures and third-order nonlinearities of a number of Pd(II) and Pt(II) complexes of phosphine ligands using Z-scan experiments (See Papers 8, 9, and 11). These Pd(II) and Pt(II) complexes have a low linear absorption at the working wavelength of 532 nm and exhibit both NLO refraction and NLO absorption effects. Our studies indicated that the NLO properties of these complexes depended both on the nature of the phosphine ligand and on the nature of the metal center and its coordination geometry, but the third-order nonlinearities for the Pd(II) and Pt(II) complexes were significantly lower than were those for $\text{Mo}(\text{CO})_4$ complexes with similar phosphine ligands.

The difference between the third-order nonlinearities of the Pd(II) and Pt(II) complexes and those of the $\text{Mo}(\text{CO})_4$ complexes with similar phosphine ligands prompted us to study in more detail the factors that give rise to the large optical nonlinearities of the $\text{Mo}(\text{CO})_4$ complexes. These studies demonstrated that the third-order nonlinearities for solutions of the $\text{Mo}(\text{CO})_4$ complexes correlate with the degree to which these solutions have been exposed to oxygen (See Papers 1, 5, 6, 9, 11,12, and 13). Further, we observed

that the rate at which oxidation occurs depends on the nature of the solvent and, in certain solvents such as dichloromethane, the oxidation can be stopped, at least temporarily, by the addition of excess of the phosphine ligand. This allows the preparation of solutions with large optical nonlinearities and low linear absorption, as is required for optical power limiting applications.

Because the increases in the third-order nonlinearities for solutions of the $\text{Mo}(\text{CO})_4$ complexes paralleled the increases in the linear absorptions of the solutions, we explored the mechanism that contributes to the enhancement of the third-order nonlinear response of oxidized solutions of $\text{cis-Mo}(\text{CO})_4(\text{PPh}_3)_2$. We found that the mechanism by which the oxidized species enhanced the third-order nonlinear response was not dominated by thermal effects, but was instead due to the strong nonlinear absorption and nonlinear refraction of the oxidized species. We also demonstrated strong optical limiting by solutions of oxidized $\text{cis-Mo}(\text{CO})_4(\text{PPh}_3)_2$ for 5.8 ns laser pulses at 532 nm. Hence, these complexes have many attractive properties for optical power limiting applications.

Finally, we have explored the relationship between chemical structures and NLO properties of a series of asymmetric pentaazadentate porphyrin-like metal complexes ($[(\text{R-APPC})\text{M}]\text{Cl}_n$) (See Papers 2, 3, 4, 7, 12, and 13). These complexes have a low linear absorption at the working wavelength of 532 nm and exhibit high molecular second-order hyperpolarizabilities, as well as, strong reverse saturable absorptions that are sufficiently fast to provide optical limiting on a nanosecond time scale. The NLO properties of these complexes depend both on the nature of the ligand and on the nature of the metal center. This is an important result, because it means that the NLO properties of these complexes can be tailored or "engineered" to optimize their optical properties, unlike other excited state absorbing materials that are candidates for optical power limiting.

In addition, we performed a systematic degenerate four wave mixing (DFWM) study of a series of expanded porphyrin-like metal complexes using 40 ps laser pulses at 532 nm. The molecular second-order hyperpolarizabilities for these complexes range from 1.1×10^{-31} to 1.2×10^{-30} esu, which are 2-7 times larger than those of PbPc and SiNc, which are excited state absorbing materials that had previously exhibited some of the best optical power limiting characteristics. The nonlinearities of these complexes are predominantly electronic in origin over the ps time scales. The γ values can be significantly enhanced by altering of the conjugated R group and the metal center. This suggests that complexes with even larger γ values can be obtained by a judicious choice of ligands and metals. Thus, this class of asymmetric pentaazadentate porphyrin-like metal complexes shows unparalleled promise for optical power limiting applications.

LIST OF ALL PUBLICATIONS AND TECHNICAL REPORTS PUBLISHED UNDER GRANT

Journal Articles Published Under Grant

1. W. Sun, C. Lawson, and G. Gray, "Third Order Nonlinearity and Optical Limiting of Dichloromethane Solutions of $\text{cis-Mo}(\text{CO})_4(\text{PPh}_3)_2$ ", *Opt. Commun.* Vol. **180**, pp. 361-366 (2000).

2. W. Sun, C. Byeon, C. Lawson, G. Gray, D. Wang, "Third Order Susceptibilities of Asymmetric Pentaazadentate Porphyrin-Like Metal Complexes", *App. Phys. Lett.* **74**, pp. 3254-3256 (1999).
3. W. Sun, C. Byeon, M. McKerns, C. Lawson, G. Gray, and D. Wang, "Characterization of the Third Order Nonlinearity of $[(CH_3-TXP)Cd]Cl$ ", in *Power Limiting Materials and Devices*, (edited by C. Lawson), SPIE Vol. **3798**, pp. 107-116 (1999).
4. W. Sun, C. Byeon, M. McKerns, C. Lawson, G. Gray, and D. Wang, "Optical Limiting Performance of Asymmetric Pentaazadentate Porphyrin-Like Cadmium Complexes", *Appl. Phys. Lett.* Vol. **73**, pp. 1167-1169 (1998).
5. W. Sun, C. Byeon, M. McKerns, C. Lawson, J. Dunn, M. Hariharasarma, and G. Gray, "Oxidative Enhancement of the $\chi^{(3)}$ Values of Solutions of *cis*- $Mo(CO)_4L_2$ ($L=PPh_3, AsPh_3, PPh_2Np$) Complexes As Measured By DFWM", *Optical Materials* Vol. **11**, pp. 87-93 (1998).
6. W. Sun, C. Byeon, M. McKerns, C. Lawson, J. Dunn, H. Hariharasarma, and G. Gray, "Enhancement of the Third-Order Susceptibility of *cis*- $Mo(CO)_4(PPh_3)_2$ Solution By Oxygen In Different Solvents", in *Nonlinear Optical Liquids for Power Limiting and Imaging*, (edited by C. Lawson), SPIE Vol. **3472**, pp. 108-115 (1998).
7. W. Sun, C. Byeon, M. McKerns, G. Gray, D. Wang, and C. Lawson, "Investigation of Relationship Between Chemical Structures and Optical Limiting Properties of Pentaazadentate Porphyrin-Like Metal Complexes", in *Nonlinear Optical Liquids for Power Limiting and Imaging*, (edited by C. Lawson), SPIE Vol. **3472**, pp. 127-134 (1998).
8. D. Gale, G. Gray, and C. Lawson, "Nonlinear Optical Properties Of Metal-Organic Complexes with Phosphorous-Donor Ligands", in *Nonlinear Optical Liquids and Power Limiters*, (edited by C. Lawson), SPIE Vol. **3146**, pp. 54-60 (1997).

Books/Book Chapters Published Under Grant

9. *Structure-Property Relationships In Transition Metal-Organic Third-Order Nonlinear Optical Materials*, G. Gray and C. Lawson, pp. 1-27, Chapter I of ***Opto-Electronic Properties of Inorganic Compounds***, edited by M. Roundhill & J. Fackler (Plenum Publishing Co., N.Y., N.Y., 1998).

Yearly Reports for Grant

10. Annual Report #1 for Grant DAAH04-96-1-0400, "New Metal Organic Complexes", UAB Report Number UABOPTICS123096, (1996).
11. Annual Report #2 for Grant DAAH04-96-1-0400, "New Metal Organic Complexes", UAB Report Number UABOPTICS123097, (1997).
12. Annual Report #3 for Grant DAAH04-96-1-0400, "New Metal Organic Complexes", UAB Report Number UABOPTICS123098, (1998).
14. Annual Report #4 for Grant DAAH04-96-1-0400, "New Metal Organic Complexes", UAB Report Number UABOPTICS123099, (1999).

LIST OF ALL PARTICIPATING SCIENTIFIC PERSONNEL

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REPORT OF INVENTIONS

No inventions on this grant.

BIBLIOGRAPHY/REFERENCES

The references are the same as the previously listed Publications and Technical Reports Published under the grant.

APPENDIXES

The book chapter and eight journal articles that were published under this grant are attached, in order to provide technical details.