

Nonlinear Optical (NLO) Properties of Organometallic Molecules and Polymers

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The study of nonlinear optical (NLO) properties concerns the interaction of intense electromagnetic fields with materials to produce modified fields that are different from the input fields in terms of phase, frequency, or amplitude. This talk will focus on recent studies of the ability of organometallic molecules and polymers to affect the frequency of the input field. One interesting feature of NLO materials is that they can convert an input optical wave into an output wave of doubled or tripled input wave frequency. This process is known as Second-Harmonic Generation (SHG) or Third-Harmonic Generation (THG) [1].

Upon exposure to intense electric fields, materials can be polarized, and the induced polarization can be described in terms of an expansion series, both at the molecular level and the bulk material level. The expansion coefficients at the molecular level (α , β , γ) are known as the polarizability, and the second- and the third-order nonlinearities, while at the bulk level, the coefficients ($\chi^{(1)}$, $\chi^{(2)}$, $\chi^{(3)}$) are the first-, second-, and third-order susceptibilities.

Since SHG was first observed in single-crystal quartz by Franken and co-workers [2] in 1961, the search for materials that have large NLO coefficients has been carried out due to their applications in the areas of telecommunication, optical computing and storage, optical switches and waveguides, optical amplifiers, and image processing. Although thorough study during the past decades has shown that organic conjugated systems can provide much larger NLO coefficients [3] than typical inorganic compounds, inorganic compounds (such as LiNbO_3) are preferred for practical applications due to their superior mechanical and physical properties [4]. In recent years, organometallic molecules and polymers have come under scrutiny in the search for new NLO materials [3, 5-13].

A simple theoretical model calculation shows that the second-order nonlinearity, β , of a molecule is mainly determined by intramolecular charge-transfer processes, such that:

$$\beta_{\text{tot}} \approx \beta_{\text{CT}} = \frac{3e^2h^2}{8\pi\pi^2} * \frac{W}{(W^2-4h^2v^2)(W^2-h^2v^2)} * f * \Delta\mu_{\text{ex}}$$

where $\Delta\mu_{\text{ex}}$ is the difference of dipole moments between the ground and excited states, W is the energy gap, f is the oscillator strength of the transition, and $h\nu$ is the fundamental energy. This equation indicates that large dipole moment changes between the ground and excited states, high oscillator strengths, and low energy gaps will give large β values.

Systematic studies of the metallocene derivatives $(\text{C}_5\text{X}_5)\text{M}(\text{C}_5\text{H}_4)-(\text{CH}=\text{CH})_n\text{-p-C}_5\text{H}_4\text{Y}$ ($\text{M} = \text{Fe}, \text{Ru}$) [5-7] and pyridine tungsten carbonyl complexes $\text{W}(\text{CO})_5(\text{NC}_5\text{H}_4\text{-4-X})$ [5] show that the presence of intense low energy charge-transfer absorptions, strong push-pull effects, the right choice of the metal centers, proper molecular configurations, and large ground state/excited state overlaps all favor large β values. Extended Hückel molecular orbital calculations have been carried out for the metallocene derivatives in order to better understand these effects [6].

Due to the vector nature of the molecular second-order nonlinearity β , a non-centrosymmetric space group is required to obtain bulk materials that have non-zero $\chi^{(2)}$ values. A study of the packing diagrams of the salts of ferrocene derivatives $(E)-(\eta-C_5H_5)Fe(\eta-C_5H_4CH=CH(4-C_5H_4N-1-CH_3))^+X^-$ shows that the proper alignment of the dipolar molecules in the solid state is also necessary to obtain a large $\chi^{(2)}$ value [8,9]. The importance of efficient conjugation is illustrated by the one-dimensional $[N\equiv W(OR)_3]_n$ polymer [10].

For third-order NLO properties ($\gamma/\chi^{(3)}$), study of Pt poly-yne complexes [11] indicates that for low levels of conjugation, extending the conjugation length will increase the γ value dramatically, while at high levels of conjugation, this increase is not that dramatic; and that the molecular configuration, as well as the nature of the substituents present in the molecules, can also affect the γ values. Studies of the Group 3 metal bis(phthalocyanine) compounds MPc_2 demonstrate that the $\gamma/\chi^{(3)}$ values are dependent on the choice of the metal M [12]. All these factors are also exhibited by the Group 4 metallocene halide and acetylide complexes Cp_2MX_2 [13].

Overall, organometallic compounds provide opportunities for developing new NLO materials. Future work on new metal-containing and more efficiently conjugated systems should provide better understanding of the relationship between nonlinear optical properties and the molecular design. Furthermore, applying the understanding of the origin of NLO properties of typical inorganic compounds to organometallic systems will provide another approach to new NLO materials.

References

1. For general background information about NLO effects, see:
 - (a) Prasad, P. N.; Williams, D. J. *Introduction to Nonlinear Optical Effects in Molecules and Polymers*; John Wiley & Sons, Inc., 1991.
 - (b) Bredas, J. L.; Chance, R. R., Eds.; *Conjugated Polymeric Materials: Opportunities in Electronics, Optoelectronics, and Molecular Electronics*; NATO ASI Series, Series E: Applied Sciences, 1990, Vol. 182.
 - (c) Marder, S. R.; Sohn, J. E.; Stucky, G. D., Eds.; *Materials for Nonlinear Optics*; ACS Symposium Series, 1991, Vol. 455.
 - (d) Prasad, P. N.; Ulrich, D. E., Eds.; *Nonlinear Optical and Electroactive Polymers*; Plenum Press, 1988.
2. Franken, P. A.; Hill, A. E.; Peters, C. W.; Weinreich, G., "Generation of Optical Harmonics," *Phys. Rev. Lett.* **1961**, 7, 118.
3.
 - (a) Hann, R. A.; Bloor, D., Eds.; *Organic Materials for Non-linear Optics*; The Royal Society of Chemistry, 1989.
 - (b) Hann, R. A.; Bloor, D., Eds.; *Organic Materials for Non-linear Optics II*; The Royal Society of Chemistry, 1991.
 - (c) Messier, J.; Kajzar, F.; Prasad, P., Eds.; *Organic Molecules for Nonlinear Optics and Photonics*; NATO ASI Series, Series E: Applied Sciences; 1991, Vol. 194.
 - (d) Chemla, D. S.; Zyss, J., Eds.; *Nonlinear Optical Properties of Organic Molecules and Crystals*; Academic Press, Inc., 1987, Vol. 1.
4. Eaton, D. F., "Nonlinear Optical Materials," *Science* **1991**, 253, 281.

5. Cheng, L.-T.; Tam, W.; Meredith, G. R.; Marder, S. R., "Quadratic Hyperpolarizabilities of Some Organometallic Compounds," *Mol. Cryst. Liq. Cryst.* **1990**, *189*, 137.
 6. Calabrese, J. C.; Cheng, L.-T.; Green, J. C.; Marder, S. R.; Tam, W., "Molecular Second-Order Optical Nonlinearities of Metallocenes," *J. Am. Chem. Soc.* **1991**, *113*, 7227.
 7. Bandy, J. A.; Bunting, H. E.; Green, M. L. H.; Marder, S. R.; Thompson, M. E.; Bloor, D.; Kolinsky, P. V.; Jones, R. J., "The Synthesis of Ferrocenyl Compounds with Second-order Optical Nonlinearities" In *Organic Materials for Nonlinear Optics*; Hann, R. A.; Bloor, D., Eds.; The Royal Society of Chemistry, 1989, p 219.
 8. Marder, S. R.; Perry, J. W.; Tiemann, B. G.; Schaefer, W. P. "Organometallic Salts with Large Second-Harmonic-Generation Powder Efficiencies: (E)-1-Ferrocenyl-2-(1-methyl-4-pyridiniumyl)ethylene Salts," *Organometallics* **1991**, *10*, 1896.
 9. Suslick, K. S.; Chen, C.-T.; Wilson, S. R., "Metalloporphyrin Coordination Polymers as Field Responsive Materials," *J. Am. Chem. Soc.*, submitted.
- 4
10. Pollagi, T. P.; Stoner, T. C.; Dallinger, R. F.; Gilbert, T. M.; Hopkins, M. D., "Nonlinear Optical and Excited-State Properties of Conjugated One-Dimensional $[N\equiv M(OR)_3]_n$ Polymers," *J. Am. Chem. Soc.* **1991**, *113*, 703.
 11. Porter, P. L.; Guha, S.; Kang, K.; Frazier, C. C., "Effects of Structural Variations of Platinum and Palladium Poly-ynes on Third-Order Nonlinearity," *Polymer* **1991**, *32*, 1756.
 12. Shirk, J. S.; Lindle, J. R.; Bartoli, F. J.; Boyle, M. E., "Third-Order Optical Nonlinearities of Bis(phthalocyanines)," *J. Phys. Chem.* **1992**, *96*, 5847.
 13. Myers, L. K.; Langhoff, C.; Thompson, M. E., "Cubic Nonlinear Optical Properties of Group 4 Metallocene Halide and Acetylide Complexes," *J. Am. Chem. Soc.* **1992**, *114*, 7560.
 14. For other studies on organometallic systems, see:
 - (a) Frazier, C. C.; Harvey, M. A.; Cockerham, M. P.; Hand, H. M.; Chauchard, E. A.; Lee, C. H., "Second-Harmonic Generation in Transition-Metal-Organic Compounds," *J. Phys. Chem.* **1986**, *90*, 5703.
 - (b) Shirk, J. S.; Lindle, J. R.; Bartoli, F. J.; Hoffman, C. A.; Kafafi, Z. H.; Snow, A. W., "Off-Resonant Third-Order Optical Nonlinearities of Phthalocyanines," *Appl. Phys. Lett.* **1989**, *55*, 1287.
 - (c) Ghosal, S.; Samoc, M.; Prasad, P. N.; Tufariello, J. J., "Optical Nonlinearities of Organometallic Structures: Aryl and Vinyl Derivatives of Ferrocene," *J. Am. Chem. Soc.* **1990**, *94*, 2847.
 - (d) Kanis, D. R.; Ratner, M. A.; Marks, T. J., "Description of Quadratic Optical Nonlinearities for Transition-Metal Organometallic Chromophores Using an SCF-LCAO MECI Formalism," *J. Am. Chem. Soc.* **1990**, *112*, 8203.
 - (e) Blau, W. J.; Byrne, H. J.; Cardin, D. J.; Davey, A. P., "Nonlinear Optical Properties of Group 10 Metal Alkynyls and Their Polymers," *J. Mater. Chem.* **1991**, *1*, 245.

- (f) Copley, R. C. B.; Lamberth, C.; Machell, J.; Mingos, D. M. P.; Murphy, D. M.; Powell, H., "Second-Harmonic Generation Properties of Some Coordination Compounds Based on Pentanedionato Ligands," *J. Mater. Chem.* **1991**, *1*, 583.
- (g) Hosoda, M.; Wada, T.; Yamamoto, T.; Kaneko, A.; Garito, A. F.; Sasabe, H., "Enhancement of Third-Order Optical Nonlinearities of Soluble Vanadyl Phthalocyanines in Doped Polymer Films," *Jpn. J. Appl. Phys.* **1992**, *31*, 1071.
- (h) Spotts, J. M.; Schaefer, W. P.; Marder, S. R., "The Synthesis and Spectroscopic Properties of Organometallic Cyanine Analogues," *Adv. Mater.* **1992**, *4*, 100.
- (i) Winter, C. S.; Oliver, S. N.; Rush, J. D.; Hill, C. A. S.; Underhill, A. E., "Third-Order Optical Nonlinearities in Metal Dithiolate Complexes," In *Organic Molecules for Nonlinear Optics and Photonics*; Messier, J.; Kajzar, F.; Prasad, P., Eds.; NATO ASI Series, Series E: Applied Sciences, 1991, Vol. 194, p 383.