

REF

AD-A281 283

Form Approved
GSA FPMR (41 CFR) 101-11.6

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, reviewing and collecting the data, and reviewing and editing the collection of information. Send comments to Washington, DC 20543.

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1. AGENCY USE ONLY

6/1/94

3. REPORT TYPE AND DATES COVERED

Final 12/1/92 - 2/28/94

4. TITLE AND SUBTITLE

Rational Design, Construction, and Processing of High-Performance Nonlinear Optical Materials

5. FUNDING NUMBERS

61102F 2303 A3

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8. PERFORMING ORGANIZATION REPORT NUMBER

FA9620 -
AFOSR-93-1-0114

AFOSR-TR- 94 04 16

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

AFOSR/NC-MC
Building 410, Bolling AFB DC
20332-6448
D. Lee

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

DTIC
ELECTE
S F D
JUL 11 1994

12a. DISTRIBUTION/AVAILABILITY STATEMENT

APPROVED FOR PUBLIC RELEASE; DISTRIBUTION IS UNLIMITED.

12b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)

This project consists of a collaborative synthetic, processing, physical characterization, and theoretical program aimed at the rational design, construction, evaluation, and fundamental understanding of new types of maximum-performance molecule/polymer-based materials exhibiting high second-order ($\chi^{(2)}$) optical nonlinearities. Areas of emphasis include poled chromophore-functionalized glassy polymers, poled chromophore-embedded crosslinkable matrices, chromophoric self-assembled superlattices, the theoretical design and analysis of novel chromophores and chromophore environments, theoretical studies of poling dynamics, studies of optical damage phenomena, and fabrication of new types of NLO waveguides. Each research component of this highly interactive effort builds upon work already in progress as well as upon strong on-going collaborations in laser optics and quantum theory.

DTIC QUALITY INSPECTED 2

14. SUBJECT TERMS

Nonlinear optical material, polymer, chromophore, cross-linking, self-assembly, second harmonic generation.

15. NUMBER OF PAGES

14

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT

UNCLASSIFIED

18. SECURITY CLASSIFICATION OF THIS PAGE

UNCLASSIFIED

19. SECURITY CLASSIFICATION OF ABSTRACT

UNCLASSIFIED

20. LIMITATION OF ABSTRACT

NSN 7540-01-280-5500

Standard Form 298 (Rev. 2-89)
Prescribed by ANSI Std. Z39-18

Final Technical Report 12/1/92-2/28/94

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Rational Design, Construction, and Processing of
High-Performance Nonlinear Optical Materials
AFOSR-93-1-0114
Northwestern University

The past year saw dramatic progress in several interconnected areas related to the design of polymeric NLO materials with optimized properties. Key goals have been to create and understand the properties of processable polymeric materials having maximum chromophore number densities and, for $\chi^{(2)}$ materials, having maximum chromophore alignment and alignment temporal stability. Closely interfaced theoretical work has focused on developing computationally efficient and chemically-oriented descriptions of organic and organometallic molecular NLO phenomena. These are extremely useful in designing new chromophores with maximum efficiency and in understanding what molecular properties give rise to the most efficient chromophores. Results are briefly summarized by category below.

1. CROSSLINKING CHROMOPHORE-FUNCTIONALIZED POLYMERS

The goal of this effort has been to determine whether it was possible to *simultaneously* pole and thermally crosslink NLO chromophore-functionalized polymers. We demonstrated that this is indeed possible using several complementary systems, each chosen to provide key aspects of the required knowledge base. Synthesis and processing have been closely interfaced with a battery of incisive structural and NLO measurements. The major achievements of this effort are described below.

A. Poled, Chromophore - Functionalized Poly(*p*-hydroxystyrenes)

Poly(*p*-hydroxystyrene) is a robust, easily processable industrial polymer that is amenable to a variety of straightforward functionalization and crosslinking modifications. We have prepared chromophore-functionalized polymers with chiral, prolinol-derived high- β nitroaniline

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and nitroaminostilbene substituents. Levels of chromophore functionalization as high as 90% (~ 60% of the chromophore number density of a molecular crystal), T_g values as high as 176°C, and $\chi^{(2)}$ values as high as 3.2×10^{-7} esu at $\hbar\omega = 1.17\text{eV}$ have been achieved. In regard to the temporal stability of poling-induced chromophore alignment, SHG decay constants on the order of several years at room temperature (before crosslinking -- see below) have been achieved. Analysis of SHG (t) as a function of microstructure, poling field, processing, and chromophore number density indicate reasonable correspondence to the Singer-Kucyzk "chromophore gas" model. KWW parameters reveal striking differences from guest-host systems and classify these materials as Angell "intermediate glasses".

B. An Epoxy-Based High- β Difunctional Chromophoric Co-Monomer

We have achieved the synthesis of the high- β chromophoric co-monomer 3-aminomethyl-4-(3-aminomethyl-2-methyl-4-nitrophenylazo)-N,N-dimethylaniline for use as a component in crosslinkable, NLO-active epoxy matrices. After concurrently corona poling and thermally crosslinking with a Bisphenol A diglycidyl ether diepoxide or (preferentially) a polyepoxide, thin films of such crosslinked matrices exhibit high second harmonic generation efficiencies ($\chi^{(2)} = 1.4\text{--}4.1 \times 10^{-8}$ esu at $\hbar\omega = 1.17$ eV). These poled, crosslinked matrices exhibit excellent SHG temporal stability, with the long term decay time constant of the polyepoxide-based material exceeding 1 year at room temperature. The polyepoxide crosslinker imparts far higher SHG temporal stability -- an important clue for designing the next generation of crosslinked NLO materials.

C. Probing SHG Temporal Characteristics Via Site-Selective Crosslinking/Hydrogen Bonding

The phenyl hydroxyl-functionalized high- β NLO chromophore N-(3-hydroxy-4-nitrophenyl)-(S)-prolinol (HNPP) has been synthesized. Appending this and the protected 3-benzyloxyl analogue (BNPP) to poly(*p*-hydroxystyrene) (PHS) via ether linkages at the prolinol


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oxygen yields a series of chromophore-functionalized glassy polymers specifically designed for hydrogen-bonding and/or 1,2,7,8-diepoxyoctane thermal crosslinking at either backbone (PHS) or chromophore sites. For 35% chromophore functionalization, T_g values follow the ordering: crosslinked HNPP-PHS > HNPP-PHS > (88% chromophore-functionalized HNPP-PHS) > crosslinked BNPP-PHS > BNPP-PHS. Corona-poled (and simultaneously crosslinked where applicable) thin films exhibit high SHG efficiencies ($\chi^{(2)} = 1.5 - 3.5 \times 10^{-8}$ esu at $\hbar\omega = 1.17$ eV) and SHG temporal stability that follows the ordering: crosslinked HNPP-PHS > crosslinked BNPP-PHS > HNPP-PHS > BNPP-PHS > 88% functionalized HNPP-PHS. The $d_{33}(t)$ data can be fit to a biexponential function, and the long-term decay time constants for the crosslinked materials exceed 1 year at room temperature. From this work, we have learned a great deal about the architecturally most effect places to attach crosslinkers. Applying these ideas to PHS systems functionalized with nitrostilbene chromophores and crosslinking with a *polyfunctional* epoxy yields materials with $\chi^{(2)} \sim 2.0 \times 10^{-7}$ esu and with $\leq 5\%$ decay in SHG efficiency over 2000 h at 100°C in air.

D. Exceptional Second Harmonic Generation Temporal Stability of a Chromophore-Functionalized Polyimide

Robust, processable polyimides are the polymeric materials of choice for a wide variety of electrical and optical functions under extreme environmental conditions. They are the logical building blocks with which to construct the next generation of second-order NLO polymers. We have achieved the synthesis of the robust nonlinear chromophoric co-monomer 3,5-diamino-4'-nitrodiphenylamine for use as a reactive component in combination with a bismaleimide monomer in an NLO-active polyimide matrix. After concurrent corona poling and thermal polymerization, thin films of these chromophoric polyimides exhibit high non-resonant efficiencies ($\chi^{(2)} = 1.5-6.0 \times 10^{-8}$ esu at $\hbar\omega = 1.17$ eV) and DSC-determined glass transition temperatures as high as 236°C. These poled polyimides also exhibit excellent SHG temporal

stability, retaining 90-95% of the initial SHG efficiency after more than 1000 h in air at 85°C, and 90% of the initial SHG efficiency after more than 500 h in air at 120°C. This work is now being extended to chromophores with larger β values and to polyimides produced via "ene" reactions.

II. CHROMOPHORIC SELF-ASSEMBLED NLO SUPERLATTICES

We have developed a new approach to the construction of robust, intrinsically acentric second-order nonlinear optical (NLO) materials with exceptionally high frequency doubling efficiencies. The approach involves the sequential construction of covalently self-assembled chromophore-containing multilayer structures. Noteworthy features include a stilbazole, alkynyl, or related chromophore precursor in which layer-building quaternization affords both an anchored high- β chromophore center and diagnostic changes in the optical spectrum. In addition, soft polymeric layers can be introduced transverse to the stacking direction to promote structural stability. The course of multilayer evolution on clean SiO₂ and other substrates (Si, Ge, ITO) is readily characterized by optical spectroscopy, XPS spectroscopy, advancing contact angle measurements, null ellipsometry, and grazing angle X-ray reflection. These multilayer films adhere tenaciously to glass, are insoluble in common organic solvents and strong acids, and can only be effectively removed by diamond polishing or HF etching. They exhibit high thermal stability. *Importantly, the high SHG efficiencies of such materials are achieved without electric field poling.* Key accomplishments of this effort are described below.

A. Stilbazolium Systems

We have demonstrated an approach to the synthesis of thin-film second-order nonlinear optical (NLO) materials in which self-assembled chromophore-containing multilayer structures are built up in the repeating reaction sequence: I₃Si(CH₂)₂C₆H₄CH₂I (Cp), 4-[N,N-bis(3-hydroxypropyl)amino]styryl-4'-pyridine (Ch), Cl₃SiOSiCl₂OSiCl₃ (Si), polyvinylalcohol (PVA).

The multilayer structures have been characterized by optical and XPS spectroscopy, advancing contact angle measurements, null ellipsometry, and NLO properties. The latter measurements reveal multilayer superlattices with good structural uniformity and that $\chi^{(2)} = 2 \times 10^{-7}$ esu at $\hbar\omega = 1.17$ eV for bulk samples ($\chi^{(2)} = 6 \times 10^{-7}$ esu for an individual CpCh monolayer of 22 Å estimated thickness). Good structural regularity has been achieved over 5 multilayers. We also find that the second-order response can be significantly manipulated via simple ion exchange reactions.

B. Synthesis, Properties, and Structural Interconversions of Assemblies with Rod-Like Alkynyl Chromophores.

We have developed an approach to the synthesis of thin-film second-order nonlinear optical (NLO) materials in which self-assembled chromophore-containing multilayer structures are built up on clean glass or quartz surface in the repeating reaction sequence: $p\text{-Cl}_3\text{Si}(\text{CH}_2)_2\text{C}_6\text{H}_4\text{CH}_2\text{Cl}$ (coupling layer), 4-[N,N-bis(3-hydroxypropyl)amino]phenylethynyl-4'-pyridine (chromophore layer), $\text{Cl}_3\text{SiOSiCl}_2\text{OSiCl}_3$ (capping layer). The multilayer structures have been characterized by optical (the maxima are blue-shifted compared to the aforementioned stilbazolium analogues) and XPS spectroscopy, advancing contact angle measurements, and polarized second harmonic generation (SHG) properties. It is found that the initially formed coupling-chromophore monolayer exhibits a rather weak SHG response which increases substantially upon capping with the Si reagent. The proposed structural reorganization of the chromophore dipoles (β_{zzz} direction) to an average orientation more coincident with the surface normal is supported by optical spectroscopy. The square root of the SHG intensity scales linearly with the number of chromophore layers up to 9 layers. For a single coupling-chromophore layer nonlinearities as high as $\chi^{(2)} = 5 \times 10^{-7}$ esu at $\hbar\omega = 1.17\text{eV}$ have been achieved.

C. **Observation of Film Growth and Microstructural Evolution by *In Situ* second Harmonic Generation Techniques**

To better understand and to optimize the efficiency of the self-assembled chromophoric film growth process, the self-assembling adsorption/quaternization of a dialkylaminostilbazole nonlinear optical chromophore precursor onto benzyl chloride-prefunctionalized surfaces has been studied *in situ* by polarized second harmonic generation techniques. The measurements reveal that the self-assembly kinetics are approximately biexponential $\left(I_{2\omega}^{1/2} \sim (1 - \alpha_1 e^{-k_1 t} - \alpha_2 e^{-k_2 t})\right)$ with a rapid initial phase, followed by a slower second phase. The *in situ* measurements also indicate that the average tilt angle of the chromophore dipole moment direction with respect to the surface normal increases significantly ($\sim 20^\circ \rightarrow 42^\circ$) in the initial phases of chromophore adsorption, then remains nearly constant. These results suggest substantial chromophore-chromophore electrostatic and steric repulsion as monolayer growth proceeds. The maximum chromophore coverage observed corresponds to $\sim 49 \text{ \AA}^2/\text{molecule}$ and $\chi^{(2)} = 3 \times 10^{-7}$ esu at $\hbar\omega = 1.17$ eV.

D. **Dispersion of Second-Order Optical Nonlinearity in Chromophoric Self-Assembled Films by Optical Parametric Amplification. Experiment and Theory.**

The dispersion of the second-order optical nonlinearity in chromophoric self-assembled stilbazolium films has been characterized in detail as a function of fundamental wavelength from 800 to 1600 nm using an optical parametric amplifier-based measurement system. The second harmonic generation (SHG) spectrum exhibits a distinctive two-photon resonance at $\hbar\omega = 1.3$ eV (960 nm). The maximum in the second-order susceptibility coincides with a low energy chromophore-centered charge-transfer one-photon excitation at 480 nm (2.6 eV). The experimental SHG dispersion values compare favorably with theoretical results computed using a semi-empirical sum-over-states formalism. These indicate that the $\chi^{(2)}$ response is dominated by an excitation along the long axis of the stilbazolium chromophore from the highest occupied

to the lowest unoccupied molecular orbital.

III. THEORETICAL STUDIES ENABLING THE RATIONAL DESIGN, CONSTRUCTION, AND PROCESSING OF HIGH-PERFORMANCE MOLECULAR/MACROMOLECULAR NONLINEAR OPTICAL MATERIALS

Experience has shown that research progress in the molecular/macromolecular NLO area can be most effectively achieved via an integrated, multidisciplinary attack that involves a close interplay of theory, synthesis, processing, and physical characterization. Just such a program has been in operation at Northwestern University. Our theoretical effort has been focussing on the development of "user-friendly," chemically-oriented quantum chemical techniques for understanding chromophore second- and third-order NLO response, for designing completely new types of organic, metal-organic, and inorganic chromophores, for understanding chromophore-chromophore and chromophore-environment interactions, for examining new mechanisms of nonlinearity, and for understanding the polymer dynamics phenomena which governing the response of chromophore/polymer ensembles to the application as well as cessation electric poling fields. Key elements of progress in this effort are summarized below.

A. Calculation and Electronic Description of Molecular Quadratic Hyperpolarizabilities Employing the Zindo-SOS Quantum Chemical Formalism

To understand the second-order nonlinear optical response of molecular chromophores, we have developed and applied a formalism based on the use of perturbation theoretic (sum-over-states) methods using an uncorrelated (single determinant) ground state. When this method is used with a semiempirical INDO/S hamiltonian, it affords calculational results that are in excellent systematic agreement with experimental observations on a wide variety of organic and organometallic chromophores. Perhaps more important, the sum-over-states formulation permits understanding of the nonlinear response in terms of the nature of the excited states, interstate transitions, and changes in localization, and dipole moment character.

This study carried out calculations on a series of substituted organics, revealing several important regularities:

- 1) Nonlinear response increases substantially with increasing size of conjugating groups between donor and acceptor ends.
- 2) Generally, increased polarity in the ground state results in increased nonlinear response.
- 3) Two-level models offer qualitative guidance in many, but not all, situations. Three-level corrections to two-level terms generally scale straightforwardly, being roughly $-1/2$ the value of the two-level terms.

B. Calculation and Electronic Description of Quadratic Hyperpolarizabilities. Toward a Molecular Understanding of NLO Responses in Organo-Transition Metal Chromophores

We have explored the use of the computationally efficient, chemically oriented INDO-SOS electron model (ZINDO) in concert with perturbation theory to relate molecular quadratic hyperpolarizabilities to molecular architecture and electronic structure in transition-metal chromophores. The ZINDO-derived second-order nonlinear optical responses are found to be in excellent agreement with the experiment for a variety of ferrocenyl and arene chromium tricarbonyl derivatives. The assumptions needed to describe nonlinear optical response in simple molecular orbital terms are presented and their reliability analyzed in a quantitative fashion. All of the ferrocenyl chromophores examined are found to closely resemble traditional organic π -electron chromophores in that intense MLCT transitions dominate the second-order response. A detailed examination of the modest second-order nonlinearities of the chromium arenes identifies two shortcomings that may be characteristic of many organometallic architectures: the intrinsic hyperpolarizability may be far greater than the experimentally accessible vectorial component of β (that directed along the dipole moment direction), and the electronic distribution about the metal centers in many organometallic structures is pseudo-centrosymmetric. This

explains the relatively low nonlinearities of a number of recently reported organometallic chromophores. The design utility of the present computational formalism is illustrated by the calculation of the second-order response of a hypothetical organometallic chromophore having a very acentric electron distribution and correspondingly a large calculated second-order response than any measured to date for a proposed organometallic chromophore.

C. Design of Chromophoric Molecular Assemblies with Large Second-Order Optical Nonlinearities. A Theoretical Analysis of the Role of Intermolecular Interactions

The role and nature of intermolecular interactions in determining quadratic nonlinear optical macroscopic hyperpolarizabilities has been investigated using the INDO/S (ZINDO) sum-over-excited particle-hole-states formalism on clusters (dimers and trimers) of archetypical donor/acceptor organic π -electron chromophore molecules. It is found that the calculated aggregate hyperpolarizability depends strongly on relative molecular orientations, exhibiting the largest values in slipped cofacial arrangements, where the donor substituent of one molecular unit is in close spatial proximity to the acceptor substituent of the nearest neighbor. These results convey important suggestions for the design of multichromophore assemblies having optimum $\chi^{(2)}$ values. For example, cofacial assembly of chromophores having low ground state dipole moments should maximize molecular contributions to the macroscopic susceptibility. The classical "two-level" model is a good approximation for estimating the hyperpolarizability in such cluster systems, although at larger distances it yields overestimated β_{ijk} values. Other cases where the two-level model breaks down more significantly are also identified.

D. Electron Donor-Acceptor Complexes as Potential High-Efficiency Second-Order Nonlinear Optical Materials. A Computational Investigation

The second-order nonlinear optical response of model molecular 1:1 and asymmetric 2:1 organic π electron donor-acceptor (EDA) complexes has been investigated using the INDO/S sum-over-excited particle-hole-states formalism. It is found that intermolecular charge-transfer

transitions in EDA complexes represent a promising approach to achieving sizable second-order optical nonlinearities. Calculated hyperpolarizabilities may be generally related to the strength of the donor-acceptor interaction in the complex, affording for a given acceptor, the largest values in the case of aminoarene donors. The large change in dipole moment that accompanies intermolecular charge-transfer transitions and the relatively low-lying charge-transfer excitation energies are the major sources of the large calculated second-order nonlinearities. The relative orientation of donor and acceptor components is also an important feature, leading to stabilization of the ground state as well as to maximization of the oscillator strength of the lowest energy charge-transfer excitation, and in turn, the NLO response. In the case of asymmetric 2:1 EDA complexes, calculated hyperpolarizability enhancements over the 1:1 complexes can be related to the red-shift of the charge-transfer excitation, as well as to an increase in dipole moment change between ground and excited states. The perturbation theoretical "two-level" model is a useful first approximation for predicting the second-order nonlinear response of such complexes.

E. Nonlinear Optical Characteristics of Novel Inorganic Chromophores Using the ZINDO Formalism

We have successfully demonstrated the application of perturbation theory and the ZINDO (INDO/S) LCAO-SCF formalism for calculating the molecular second-order nonlinear optical properties of organic and main group inorganic chromophores. Good agreement is found between the ZINDO-derived vector components for frequency doubling ($\beta_{vec}(\omega, \omega, 2\omega)$) and experimental data for a series of conventional π -organic chromophores. Frequency doubling efficiencies are then calculated for several classes of inorganic chromophores containing unusual substituents and conjugation pathways.

F. The Role of Intermolecular Interactions in Molecular Electronics. Computational Design of Architectures with Large Second-Order Optical Nonlinearities

The role of intermolecular interactions in determining quadratic nonlinear optical macroscopic hyperpolarizabilities is investigated using the INDO/S (ZINDO) sum-over-excited particle-hole-states formalism on clusters (dimers and trimers) of archetypical donor-acceptor π -electron chromophores. The calculated aggregate hyperpolarizability depends strongly on relative molecular orientations, exhibiting the largest values in slipped cofacial arrangements, where the donor substituent of one unit is in close proximity to the acceptor substituent of the nearest neighbor. These results argue that cofacial assembly of chromophores having low dipole moments should maximize molecular contributions to the macroscopic susceptibility. The classical "two-level" model is generally a good approximation for estimating hyperpolarizabilities in such systems. The second-order response of model molecular 1:1 and asymmetric 2:1 electron donor-acceptor (EDA) complexes is also investigated using the INDO/S formalism. Intermolecular charge-transfer in EDA complexes represent a promising approach to achieving sizable second-order optical nonlinearities. Calculated hyperpolarizabilities reflect the strength of the donor-acceptor interaction in the complex, affording for a given acceptor, the largest values in the case of the strongest donors. The large change in dipole moment accompanying intermolecular charge-transfer transitions and low-lying charge-transfer excitation frequencies are major sources of the large calculated second-order nonlinearities. The "two-level" model is again a useful first approximation for predicting the nonlinear response of such complexes.

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