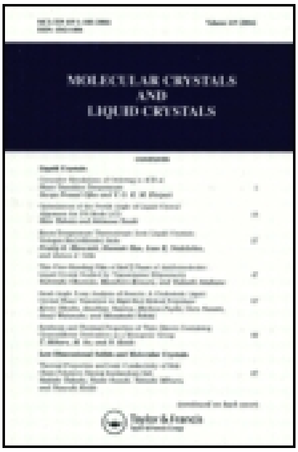

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Guest-Host Molecular Ensembles for Nonlinear Optics

David F. Eaton [a], Albert G. Anderson [a], Wilson Tam [a], Walter Mahler [a] & Ying Wang [a]

[a] The Du Pont Company, Central Research and Development, Experimental Station, PO Box 80356, Wilmington, Delaware, 19880-0356, USA

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GUEST-HOST MOLECULAR ENSEMBLES FOR NONLINEAR OPTICS

DAVID F. EATON*, ALBERT G. ANDERSON, WILSON TAM, WALTER MAHLER AND YING WANG
The Du Pont Company, Central Research and Development,
Experimental Station, PO Box 80356, Wilmington, Delaware, USA
19880-0356

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Abstract. This paper discusses structural strategies for assembling bulk materials for nonlinear optics. In part one, we review a strategy, based on the concepts of guest-host inclusion complexation. We incorporate molecules into crystalline environments in which molecular dipoles are assembled into materials for second harmonic generation by polar alignment of the dipoles. In part two, we review the fabrication and properties of optical quality materials for third order nonlinear optics based on nanoscale particles of semiconductors included in polymer media.

Keywords: nonlinear optics, inclusion complex, dipole organization, thiourea inclusion compound, nanoscale semiconductor particles

INTRODUCTION

Integrated optical devices promise to increase the data transfer bandwidth of switching and communications systems. A major need before practical implementation can occur is the realization of practical materials[1] for both the passive, waveguiding functions of such integrated devices and for the active, switching, amplification and logic functions which will also be required.

Passive regions can be delineated using photopolymer technology to prepare holographic optical elements or channel waveguide structures to guide light in two-dimensional planar devices. Active regions will be produced with electro-optic (EO) or all-optical (nonlinear, NLO) materials.

Second order EO or NLO materials, which rely on $\chi^{(2)}$ properties for the expression of their nonlinearity, must have specific symmetry properties relative to the light propagating through them. This need restricts the materials available and places constraints on the design of systems. No such symmetry restrictions apply to third order ($\chi^{(3)}$) systems.

This paper describes two materials technologies for integrated optics. Both technologies rely on the paradigm of guest-host inclusion chemistry to provide the molecular architecture necessary to express the desired NLO property. In the first, molecular inclusion compounds are described for second order NLO. By the techniques of inclusion chemistry, we have prepared crystalline complexes capable of second harmonic generation (SHG) from components that individually are incapable of SHG. The second technology marries small semiconductor cluster science to polymer science to yield monolithic optical glasses with $\chi^{(3)}$ properties.

Both of these technologies have been described in detail in previous publications from our laboratories.[2, 3, 4] It is our purpose here to review the materials principles involved and to place the technolgies in perspective.

INCLUSION COMPOUNDS FOR SHG

Our goal has been to devise methods to align polar organic and organometallic molecules, chosen because of their potentially large hyperpolarizabilities, in three-dimensional space in such a way that there is no center of symmetry in the material. At the time we began our work, several methods were known by which one could align molecules: Electric fields could be used to align materials, especially in polymer films.[5] This is also the principle behind the determination of dipole moments by classical methods and the determination of molecular hyperpolarizabilities by the so-called EFISH technique (electric field induced second harmonic generation). Dipolar materials can be adsorbed at a surface to break local symmetry. This is the principle behind surface enhanced Raman spectroscopy. Various Langmuir-Blodgett film-forming techniques can also be used to form ordered mono- or multi-layers with polarity. Also, chiral auxilliaries can be attached to the "nonlinear optiphore" to ensure that crystalline materials will be acentric, though this technique does not guarantee that a high degree of orientational order will be present.

We desired to devise a technique that would be relatively rapid and accessible to most chemists without the need for elaborate equipment. Our goal was to provide chemists (who might have had a shelf-full of favorite materials that they judged might be attractive for NLO) a simple way to test their materials for efficacy.

Our concept was to use guest-host inclusion chemistry to organize dipolar materials in three dimensional space. Commonly, when dipolar species in isotropic media interact at high concentrations they are found to dimerize in a head-to-tail motif. This centrosymmetric orientation denies any SHG capability. Many polar organic materials crystallize in centrosymmetric space groups. Since it is polar (often dipolar) compounds that possess the highly mobile electron distributions (for example, in donor-acceptor, or charge-transfer compounds) that have been shown to be needed for high second order polarizability (high β), many natural candidates for SHG have zero SHG capability. Our hope was to use the guest-host paradigm to direct the solid state growth of bulk crystals in polar orientations.

The concept is shown schematically in Figure 1. In the figure, the dipolar arrow is meant to convey the dipole direction of the nonlinear optiphore which we wish to align. We prevent the formation of centrosymmetric dipole dimers by ensuring that the dimensions of our inclusion cavity (the thick black wavy lines represent the cavity boundaries) are smaller than about two times the smallest dimension of the guest. In this way, only one guest can occupy a cavity. Once this single occupation is assured, then simple electrostatic principles dictate that the minimum energy arrangement within a single channel will be as shown in the figure, with the dipoles aligned. In the three-dimensional structure of the complex, however, there is no certainty that the alignment will persist across channels. That is, if alternate channels run in the opposite sense, a center of symmetry results, and electrostatic energy is in fact minimized. We reasoned, however, that a second possiblity was potentially feasible. If each channel motif is translated one-half a crystallographic unit and then displaced one unit in another direction, then the arrangement shown in Figure 1 results in which a

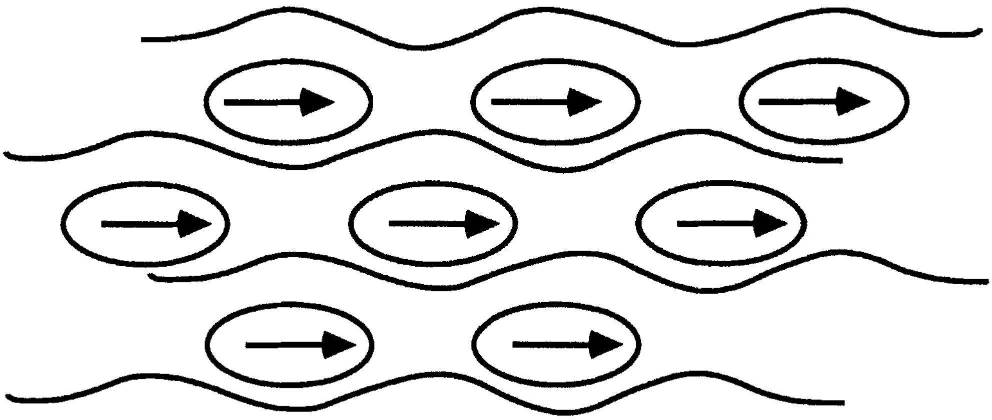

FIGURE 1. A depiction of the guest-host paradigm as applied to induced SHG in solid inclusion complexes.

staggered, totally aligned bulk structure becomes an electrostatic minimum arrangement. This occurs because of the half-step displacement, which produces a charge neutralization across channels.

In experimental studies involving six different hosts and some 28 different organic and organometallic guests (chosen because they possessed low-lying charge-transfer transitions which we judged would provide hyperpolarizability), we have produced approximately 45 different crystalline inclusion complexes of defined stoichiometry.[6] In almost every case, the complexes exhibited SHG as a microcrystalline powder by the Kurtz-Perry powder test.[7] Yet in almost every case, neither the host nor the guest were themselves capable of SHG in their pure states. That is, the inclusion complexation induced SHG activity in the materials. X-ray crystallographic studies of 12 of the complexes established the packing motif shown schematically in Figure 1 to be the most frequent packing pattern among the complexes. For a full discussion of the crystallography, including coordinate information, see reference 2. Reference 6 contains several color plates that show the packing motif well.

The inclusion paradigm does not insure that complexes will be acentric. Our success rate for preparation of polar structures is about 65%. The "errors" occur for a variety of reasons. The most common is that other forces come into play which counteract the electrostatic forces that tend to enforce polarity. For example, we find that hydrogen bonding can alter the structure of even closely homologous solids. An example, discussed in reference one in detail, compares the behavior of two nearly isostructural (from a shape perspective) metal carbonyls - benzene chromium tricarbonyl and cyclohexadiene iron tricarbonyl. While the two have similar shapes, the former has a strong dipole moment (4.8 D) and the latter has nearly none (0.4 D). The benzene chromium tricarbonyl complex with the host thiourea is polar, with an R3c crystal structure in which dipoles line up conforming to the motif of Figure 1. The complex exhibits modest SHG (2.3x urea standard). The thiourea complex of cyclohexadiene iron tricarbonyl is only weakly polar (0.4x urea) and has a different crystal sturcture in which two polar orientations of the host are found. The structure is dominated by strong hydrogen bonds from the thiourea amide hydrogens to the carbonyl oxygen atoms, and this H-bonding is apparently able to overwhelm the weaker dipolar forces in this structure.

Still, the 65% success ratio we experience is diametrically opposed to nature's 65% rate of formation of centrosymmetric structures, so our paradigm has value. We believe it represents a valuable method of solid state engineering applicable to the preparation of polar solids.

SEMICONDUCTOR CLUSTER POLYMER COMPOSITES

Size-quantized semiconductor particles posses extremely interesting structural, electronic and optical properties. In such nanoscale materials, the physical size of the particle matches or is less than the Bohr radius of the exciton, the primary excitation particle produced when light is absorbed by the material. Materials in this size regime have been produced and studied by a variety of researchers.[8] The properties of clusters identical to those described here are reported in more detail in a paper by Wang and Herron.[9] The optical nonlinearities of semiconductors have been known for some time.[10] We have employed the third order nonlinearitites of a variety of nanoclusters of the II-VI and III-V classes in a series of unique polymer composite structures which provide another example of the inclusion paradigm in preparing new materials for nonlinear optics.

A major problem encountered in using nanoscale particles of semiconductors is the coalescence of particles to form larger particles. Most preparative routes to nanoparticles involve elaborate methods to protect the colloidal particles, kinetically, from interacting to form particles larger than those desired. We developed a technology which prevents agglomeration of particles and produces optical quality thin films containing modest amounts of inlcuded semiconductor material.[11] The optical nonlinearity of the films is comparable to that of other materials, but the films have all advantages of polymer processibility not available to bulk semiconductors.

It is not sufficient to disperse a colloidal supsension of nanoclusters in a polymer film. Aggregation can still occur over time since the films, while viscous, still flow, and the particles are kinetically unprotected. We have devised a chemical route to polymer composites in which the nanocluster is prepared inside a cavity which acts as a protective shield against agglomeration. The technology is illustrated schematically in Figure 2.

Copolymers of ethylene and methacrylic acid are melt-formable, transparent thermoplastics. The carboxylic phase forms micelles (hydrogen bonded networks very similar to the structure of aqueous soaps formed by fatty acid salts in water) dispersed in the polyethylene phase. The micelles can be saponified by treatment in the melt at about 250° C with metal salts, for example lead acetate ($PbAc_2$). This forms lead "soaps" and liberates acid vapors (in the case described, acetic acid is driven off). The lead carboxylate salt containing polymers form high quality thin films containing

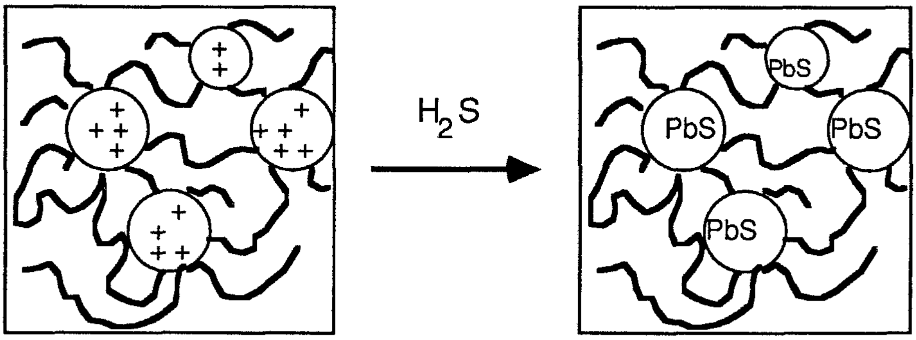

Figure 2. Schematic of precipitation of nanoparticles of PbS in the pores of co-poly(ethylene-methacrylic acid) after ion exchange with $PbAc_2$.

up to 20 weight percent lead. Treatment of these films with vapors of weak acids such as H_2S regenerate the carboxylic acid unit and forms a new inorganic salt, in the case described, lead sulfide, PbS. This molecular PbS is formed within the micelle. It can combine with other PbS units formed by reaction within the same micelle to form a small agglomerate, $(PbS)_n$, but the agglomerate can not become larger than the number of lead ions originally present in each micelle. Therefore the size of the PbS particle can be kept very small even though the concentration of PbS in the polymer is quite high. Further particle growth can only occur if micelles merge. Studies by Mahler[10] show that the projected half-life for particle growth is 10^5 years at room temperature because the viscosity of the polyethylene phase is very high. The net result is a technology that allows preparation of a variety of small semiconductor particles in a medium that will stabilize them.

Particles in the polymeric media can be characterized by a variety of techniques. X-ray powder spectroscopy determines that they are crystalline down to about 25Å sizeand the broadening of the x-ray lines can be used to calculate their size. Below 25Å the particles become indistinguishable form amorphous material at least by x-ray criteria. The absorption spectra of the particles are shifted to the blue in accordance with the quantum size effect. Because the particles are much smaller than the wavelength of light, the films do not scatter and are transparent. The particles exhibit interesting emission spectra which are dominated by defect centers. Wang and Herron have reviewed the general properties of the particles both in the polymer glasses and within other encapsulating media such as zeolites and porous glasses.[9]

The nonlinear optical properties of films of chalcogenide semiconductor polymer composites were studied by four-wave mixing[3] and time resolved picosecond spectroscopy.[12] In this way a measure of the optical nonlinearity can be obtained which can be compared directly to the nonlinearity of other semiconductor materials studied by others. Table I lists the nonlinear absorption coefficients determined for a CdS cluster 55 Å in size embedded in polymer to the nonlinearity of a commercial borosilicate glass containing small clusters of the doped semiconductor $CdS_xSe_{(1-x)}$. Also shown are values for the best organic material known to date, polydiacetylene, and also the quantum well semiconductor structure GaAs/GaAlAs.

TABLE I. Nonlinear Absorption Coefficients of Several Third Order Materials.

Material	α_2/α_0 (cm^2/W)	λ (nm)	τ (ps)
55 Å CdS	-6.1×10^{-7}	480	55
Corning Glass (3-69)	-1×10^{-7}	500	10
Polydiacetylene	-7×10^{-8}	621	2
GaAs/GaAlAs	$< 10^{-6}$	850	>32000

The results shown in Table I confirm the high nonlinearity of semiconductor clusters as had been demonstrated earlier by Jain and Lind[13] for the commercial glasses such as the Corning 3-69 filter glass listed in the Table. The polymer supported clusters are in fact modestly better than the borosilicate glasses, as fact which may reflect the more modest temperatures used to fabricate the polymer clusters which avoids the oxidative degradation of clusters formed under high temperature glass-forming conditions. The best material, that which requires the least power, is the quantum well structure, but it is very slow (nearly three orders of magnitude slower that the cluster materials). The organic material is the fastest, since it is a true resonant π-polarization electronic response, but it requires 10x the power needed by the clusters. The main conclusion we draw from the comparison is that the cluster materials are comparable to the best known materials. The advantage, we believe is in the fabricability of the polymer medium and its compatibility with optical technology as a thin film medium. Also, since the electronic and optical properties are dictated by the surface properties of the cluster, we beileve that our technology offers ways to modify the surface chemistry at the cluster-micelle interface. By such modification we hope to improve, or tailor, the overall photophysical properties of the material.

CONCLUSIONS

This paper has reviewed two strategies for the preparation of materials for nonlinear optical applications. Both strategies rely on the concepts of inclusion chemistry and encapsulation to effect the assembly process or to protect the guest. Application of nonlinear optics to real world situations will require materials with improved physical and optical properties compared to those described here. The paradigms of guest-host chemistry provides a framework for experimenting with new materials.

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