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Artificially Structured Nonlinear Optical and Electro-Optic Materials

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Artificially Structured Nonlinear Optical and Electro-Optic Materials

Robert Donohoe*, Alan Bishop, C. Buscher, Jan Gammel, Dequan Li, Duncan McBranch,
Avadh Saxena, and Xiaoguang Yang

Abstract

This is the final report of a three-year, Laboratory-Directed Research and Development (LDRD) project at the Los Alamos National Laboratory (LANL). Emerging electro-optic technologies, including optical signal processing, switching, and data manipulation, require high performance, processable nonlinear optical (NLO) and electro-optic (EO) materials for their success. The aim of this project is to combine physical characterization and materials modelling to guide a rational synthesis of artificially structured materials optimized for NLO and EO applications. New materials consisting of chromophores optimized for the red and near-infrared spectral region, directly attached to optical substrates using covalent bonding of self-assembled (CBSA) mono- and multi-layers, have been produced and their NLO response measured. A second strategy, based on the construction of multiple heterojunctions of one-dimensional solids, is also being explored through fundamental physical characterization combined with detailed modeling. The results of CW and ultrafast optical and Raman spectroscopy of these materials demonstrate the highly polarizable nature of the junctions, confirming the NLO potential of the materials. The overall goal was to develop these synthetic approaches through a combined synthesis, characterization, and theoretical effort where materials modeling, benchmarked by observed physical properties, is used to guide rational synthesis of advanced electronic materials.

1. Background and Research Objectives

Emerging electro-optic technologies, including optical signal processing, switching, and data manipulation, require high performance, processable nonlinear optical (NLO) and electro-optical (EO) materials for their success. The aim of this project was to combine physical characterization and materials modeling to guide a rational synthesis of artificially

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structured materials optimized for NLO and EO applications. New materials consisting of chromophores optimized for the red and near-infrared spectral regions, directly attached to optical substrates using covalent bonding of self-assembled (CBSA) mono- and multilayers, have been produced and their NLO response measured. In addition, we have demonstrated a novel route to ordered materials through the design and synthesis of new molecular building blocks, templates, or substructures that can be organized into supramolecular assemblies. The synthetic approach here is to fix dipole orientation by structural interlocking of NLO chromophores into cone-shaped "supermolecules," and then to utilize them to build polar self-assembled monolayers. We have designed calixarene-based NLO molecular "pyramids," demonstrated self-assembly on oxide surfaces, and determined their spectroscopic second order NLO properties. We have performed measurements of the coverage and molecular orientation in polar self-assembled monolayers. The ordering in these materials arises from the competition of bonding to the surface and mutual steric effects that force alignment of the dipolar chromophores.

2. Importance to LANL's Science and Technology Base and National R&D Needs

The development of new NLO and EO materials is a major driving force behind the effort in advanced materials throughout the world. Our in-house making-measuring-modeling capability makes this project uniquely capable of rapid and important advances in this field. Our approaches have the potential for providing robust, highly processable materials for device applications. This project supports a LANL core competency in nuclear and advanced materials.

The Nation's future technologies depend on a vigorous effort to develop advanced materials. This need has been recognized as one of the key areas to be addressed by the Department of Energy (DOE) and the Laboratory; success in several major programs in the civilian and DOE business sectors depends on the production of new materials with novel properties. Our expertise in materials synthesis and modeling has repeatedly been identified as one of this Laboratory's strengths in the advanced materials and new technology arenas. In addition to NLO applications, the versatile synthetic strategies developed in this project are applicable to chemical sensors for in situ environmental monitoring, solar energy storage, and nanotechnology.

3. Scientific Approach and Results to Date

3.1 Development of New Self-Assembled NLO Chromophores

Organic NLO chromophores are typically π -conjugated molecules with a D- π -A structure, where D and A are electron donor and acceptor, respectively, and π is a π -conjugated segment or sensitizer. This structural feature has been widely used to attain large values of the molecular second-order nonlinear susceptibility, β . By tethering these linear molecular units together through methylene bridges, a calixarene-based NLO chromophoric pyramid is derived [1]. To achieve optimum molecular β , the orientation of each D- π -A unit should be fixed in nearly the same direction. Therefore, our approach involves the synthesis of a calix[4]arene with a frozen "cone" conformation by substitution at the lower rim with ethoxyethyl groups [2,3]. The upper rim of the calixarene was then functionalized for the incorporation of pyridyl units. It was demonstrated by ^1H NMR and IR that the resulting calixarene precursor has a rigid structure and fixed dipole orientation; self-assembled monolayers (SAMs) of this compound should show higher alignment, better thermal and structural stability than SAMs using a single chromophoric unit.

The construction of covalently bonded self-assembled monolayers of the pyramid-like imine derivative of calix[4]stilbazole is based on the methodologies reported by Li, *et al.* [4]. A space filling model on the surface is shown in Figure 1 [5]. In order to study the molecular orientation and the NLO response on the surface, spectroscopic second harmonic generation (SHG) was measured [5]. The angular dependence of SHG using femtosecond pulses to generate p-polarized SHG from both p- and s-polarized fundamental are shown in Figure 2 for a fundamental wavelength of 862 nm. An average molecular orientation of $\psi \sim 37 \pm 3^\circ$ was deduced by modeling the angular dependent SHG response ($n_{\text{film}} = 1.7$); an absolute magnitude of $d_{33} \sim 60$ pm/V was deduced by calibrating to reference Y-cut quartz. The solid lines in Figure 2 are best fits to an expression developed [6] and modulated by an interference term, which has the same physical origin and angular dependence as the well-known Maker fringes in bulk samples [7]. The wavelength dependence (fundamental $\lambda = 890$ -750 nm; harmonic $\lambda = 445$ -375 nm) indicates a gradual increase of d_{33} as the fundamental moves to shorter wavelength, consistent with normal refractive index dispersion in this spectral region approaching the charge transfer resonance at 390 nm. The longest wavelength (890 nm) is well off the charge transfer resonance, and the value quoted for d_{33} is largely nonresonant (60 pm/V). We find a value of $d_{33} \sim 90$ pm/V at $\lambda = 750$ nm, indicating a slight two photon enhancement at shorter wavelengths.

We have made a significant step forward in construction of supramolecular architecture by demonstrating the formation of self-assembled monolayers with "pyramid"-like molecular

building blocks. Structural interlocking via the bridging methylene groups among the D- π -A units yields films with exceptionally large second-order nonlinearities (d_{33} ~60 pm/V; λ = 890 nm), and robust molecular dipole alignment. It is expected that the multilayer films fabricated from "pyramid"-like molecules would have similarly attractive properties.

3.2 Understanding Ordering and Coverage in Polar SAMs

Most current strategies to SAMs are *ad hoc* with little understanding of structure-function relationship and mesoscale ordering. The key fundamental issues are (1) what is the surface coverage monolayers vs. aggregates; (2) what is the mesoscale structure ordering vs. random; and (3) what is the intrinsic relationship between molecular orientation and surface coverage. We have demonstrated that the formation of molecular self-assemblies on surfaces results from a complex interplay between chemical bonding to the surface, and steric interactions of adjacent molecules [8].

We have employed a zirconium-sulphonate linkage that allows the convenient quantitative exchange with phosphate salts upon exposure. The zirconated surfaces were "developed" by anchoring various sulfonate chromophores including tetrasulphonic phthalocyanine nickel (NiPc), 1,4-bis(hydroxy-1,1'-azobenzene-4'-sulfonic acid, sodium salt (Tropaeolin), 4-amino-1,1'-azobenzene-3,4'-disulfonic acid sodium salt (AABDS), 4-(4-hydroxy-1-naphthylazo)benzenesulfonic acid, sodium salt (Orange I), 4"-nitrobenzene-1",4-diazoamino-1,1'-azobenzene-2"-arseno-4'-sulfonic acid, sodium salt (Sulfarsazene). These chromophores (except NiPc) can be considered as rigid rod-like sensitizers with a charge transfer state in the blue to red region of the optical spectrum. The average angle $\langle\psi\rangle$ of the transition moments with respect to the surface normal, can be derived by comparing the absorbance of the thin-film for light polarized parallel to the surface against that for the same number of identical species in solution [8].

Figure 3 shows that the formation of SAMs can be divided into three categories: partially ordered sub-monolayers, well-ordered monolayers, and randomized aggregates. When the surface coverage was low, sub-monolayers were formed with some net alignment. As the surface coverage increased, highly ordered mesoscale structures started to organize and the optimized alignment, $\langle\psi\rangle = 32\pm3^\circ$, was achieved while the surface coverage approached a close packed state of ~2.0-4.0 molecules per nm². Aggregation forms on surfaces when the surface coverage is greater than a monolayer and the orientation is random. This shows that the average molecular orientation is a complex function of the surface coverage and resulting steric interactions of adjacent rod-like molecules. The optimum surface coverage (minimum points in Fig. 3) is governed by the cross sectional area of the molecule on surfaces. For example, the optimum coverage of AABDS and Sulfarsazene is approximately 1.6 times that of Orange I (3.7 molecules/nm² vs. 2.3 molecules/nm²), consistent with the molecular cross-

section ratio of 1.5, due to the bulky naphthanyl group, and its steric hindrance effect. Second harmonic generation was carried out to verify the chromophoric alignment. Values of the second-order nonlinear susceptibility d_{33} relative to crystalline quartz were obtained for SAMs of Orange I, AABDS, Tropaeolin, and Sulfarsazene, respectively [7]; these values were 6.56, 3.88, 6.04, and 1.17 pm/V, respectively. The values obtained for $\langle\psi\rangle$ from these measurements were similar for all of the compounds, within the experimental resolution: $\langle\psi\rangle=35^\circ\pm5^\circ$. These results support the formation of oriented, polar monolayer films.

3.3 Modeling

We have used a combination of many-body techniques, using both high-performance computing and analytical methods, to address the following issues:

1. We have estimated hyperpolarizability factors for a sequence of organic molecules, and within MNDO accuracy identified polarizable regions and sensitivities to side groups. These systematics can now be incorporated into models including anisotropic polarizability for self-assembly and macroscopic nonlinear optics coefficients.
2. We have calculated electroabsorption spectra, and $\chi^{(2)}$ and $\chi^{(3)}$, in extended conjugated organic systems based on excitons, including the effect of lattice relaxation in the photoexcited states. We have used configuration interaction, coupled exciton-phonon (Condon-Herzberg-Teller), and sum-over-states techniques to study geometries of 1Bu and mAg1 states. We have determined the systematic dependence of spectra and Huang-Rhys factors on the strength of electron-electron and electron-lattice coupling.
3. We have used fully nonadiabatic numerical quantum mechanical methods to explore "breather" excitations in nonlinear coupled electron-phonon lattices. These bound multiphonon states and their associated electronic properties will be fundamental to the interpretation of time-resolved spectroscopy under development at Los Alamos.

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Figure 1: A space filling model of a robust self-assembled, calix[4]arene-based monolayer on an idealized silica surface.

$I^{2\omega}$ (Arb. Units)

Figure 2: Femtosecond SHG signal vs. incident angle for p-polarized SHG from both p- (solid circles) and s-polarized (open circles) fundamental at a wavelength of 862 nm, plotted together with best theoretical fit (solid line).

Figure 3: Plot of molecular orientation (optical transition moment) in degree with respect to surface normal versus chromophoric monolayer coverage in unit of molecules per nm² for AABDS (solid circles), Sulfarsazene (open circles), and Orange I (solid squares). The solid lines serve as visual aid only.