LA-UR-96- 3069

Title: **Artificially-Structured Photorefractive and Biomimetic Materials**

Author(s): **Duncan McBranch, CST-6
Alan Bishop, T-11
Robert Donohoe, CST-4
Eric Maniloff, CST-6
Xiaoguang Yang, CST-1**

**RECEIVED
SEP 23 1996
OSTI**

Submitted to: **DOE Office of Scientific and Technical Information (OSTI)**

Los Alamos
NATIONAL LABORATORY

Los Alamos National Laboratory, an affirmative action/equal opportunity employer, is operated by the University of California for the U.S. Department of Energy under contract W-7405-ENG-36. By acceptance of this article, the publisher recognizes that the U.S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or to allow others to do so, for U.S. Government purposes. The Los Alamos National Laboratory requests that the publisher identify this article as work performed under the auspices of the U.S. Department of Energy.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

MASTER

Form No. 836 R5
ST 2629 10/91

DISCLAIMER

**Portions of this document may be illegible
in electronic image products. Images are
produced from the best available original
document.**

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Artificially-Structured Photorefractive and Biomimetic Materials

Duncan McBranch*, Alan Bishop, Robert Donohoe, Alan Heeger (University of California Santa Barbara), Dequan Li, Eric Maniloff, Fred Wudl (University of California Santa Barbara), and Xiaoguang Yang

Abstract

This is the final report of a one-year, Laboratory-Directed Research and Development (LDRD) project at the Los Alamos National Laboratory (LANL). Organic materials have shown great promise for near-term applications in electro-optic, photorefractive, and electroluminescent devices. Electro-optic materials are useful for fast optical switching; photorefractive materials are essential for optical computing and information storage; electroluminescence is the basis for light-emitting diodes (LED's). Existing organic electro-optic and photorefractive materials require a breakthrough in techniques to control the microscopic molecular orientation while maintaining economical processing. Our unique approach addresses this problem by building ordered superlattices by molecular engineering. Existing organic LED's suffer from device breakdown, probably catalyzed by interfacial defects. Our approach allows molecular-level control of the electronic properties of the polymer interfaces by designing charge-transport layers to isolate the active polymer layer. This project sought to create new electro-optic and photorefractive materials by engineering rationally-designed nonlinear molecular building blocks into multilayer thin films using self-assembly techniques.

1. Background and Research Objectives

Organic materials have shown great promise for near-term applications in optoelectronic devices. Photo-induced charge transfer in nonlinear optical organic materials leads to photorefractive phenomena, which are useful for optical computing and information storage. These same effects can be tailored to optimize directed energy transfer along molecular structures, which can be applied to light harvesting and energy storage. The potential market

* Principal investigator, e-mail: mcbranch@lanl.gov

for these devices is vast. Commercialization of these materials would allow faster and cheaper routing of information along fiber-optic networks, enable computers that process information in parallel holographically, and represent a new generation of materials for energy storage and conversion.

Existing organic photorefractive materials require a breakthrough in techniques to control the microscopic molecular orientation while maintaining economical processing and stability. Our unique approach utilizes self-assembly, a process in which molecules self-organize to form ordered multilayers. Molecular systems based on light-absorbing chromophores linked to fullerenes can be designed for ultrafast photo-induced intermolecular charge transfer, leading to subpicosecond changes in the polarizability. This response is many orders of magnitude faster than in conventional photorefractive materials, which rely on charge diffusion across micron-length scales. In each case, a new approach in materials development is required to solve existing problems.

Another novel class of materials is based upon one- and two-dimensional oligomers of biological molecules used for energy and electron transport. The basic molecular unit of these systems is the porphyrin moiety, which is ubiquitous in biological photosynthetic and energy transport systems because of its excellent energy- and electron-transfer properties, chemical robustness, and tunability. The excited state energy and the redox potentials can be tuned both by organic substitution around the porphyrin ring and varying the central metal ion. This tunability, combined with the variability of geometric structures in both one and two dimensions, offers a flexible approach to directed electron or energy transport.

Interconnected efforts in materials synthesis, characterization, and theoretical modeling are essential to the development of these new materials. Our synthesis effort is integrated with spectroscopic and structural studies aimed at materials characterization and delineation of underlying photophysical properties. The materials theory component is focused on development of new models, benchmarked by physical measurements, that will guide synthetic refinements and give a predictive approach to materials and device properties. This research approach takes advantage of unique capabilities in each of these areas at Los Alamos and Santa Barbara.

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

The project impacts several Laboratory core competencies and will increase Laboratory visibility in an area of advanced materials development. It brings together expertise in materials synthesis, characterization and photophysical measurements, and electronic materials

modeling. Specific Laboratory core competencies include nuclear and advanced materials; theory, modeling, and high-performance computing; and bioscience and biotechnology. In addition, the program contains elements of key thrust areas for the Laboratory including broad collaboration across traditional boundaries, novel synthetic chemistry, ultrafast spectroscopy, advanced materials modeling, and research guided by industrial needs.

3. Scientific Approach and Results to Date

We have designed several candidate molecular systems, tested the transient optical properties of these molecules, and designed self-assembly routes to thin film formation. We have set up the transient absorption experiments, which can probe subpicosecond charge transfer, and set up transient holography experiments to measure changes in polarizability following photoexcitation.

With the aim of understanding (i) charge transfer across C₆₀-conjugated polymer interfaces, (ii) the relaxation ensuing the charge transfer, and (iii) mechanisms that inhibit back-transfer of charge, and to calculate molecular hyperpolarizability (β) and $\chi^{(2)}$ in the relaxed photoexcited geometry, we have first studied separately the PPV-like polymers, oligomers and C₆₀ molecules and have attained quantitative understanding of their ground states [e.g., bond-order-wave (BOW), etc.] and excitations (polarons, excitons) using tight-binding formalism. We calculated the relaxed geometry of two coupled PPV chains self-consistently in a Coulomb field (electrostatics) and found that the charge transfer between the chains delocalizes the polaron on both chains. An analogous calculation on two coupled C₆₀ molecules showed similar effect: charge transfer across the molecules with delocalization of the equatorial polarons. We then computed the molecular hyperpolarizabilities in PPV oligomers and C₆₀ separately. This understanding based on the adiabatic relaxation technique has now been combined to assess geometry relaxation subsequent to electron transfer from the PPV chain to the C₆₀ molecule resulting in hole polaron formation on the PPV chain and the electron polaron formation on the C₆₀ molecule.

The investigation of biomimetic light harvesting pigments has focused upon development of a collaborative effort with the National Renewable Energy Laboratory (NREL) and Lawrence Berkeley National Laboratory (LBNL). Our strengths, including developmental synthetic chemistry and application of time-resolved spectroscopy, complement the strengths at NREL (light energy conversion) and LBNL (electrochemistry). We have measured the energy transfer rates of soluble oligomers of porphyrin and polypyridyl inorganic charge transfer complexes using transient absorption spectroscopy. Figure 1 demonstrates the transient bleach of a zinc porphyrin pigment at short times (1 ps) near 550 nm, which evolves into a transient

bleach near 520 nm associated with a covalently attached free base porphyrin. This shows that the energy transfer in this "dimer" transpires with a 20 picosecond lifetime, indicative of a through-bond mechanism, even though the electronic coupling of the two associated pigments is small in the ground state.

Figure 1. Evolution of transient absorption showing signature of a zinc porphyrin at short time (1 ps, 550 nm), with energy transfer to a free-base porphyrin (20 ps, 520 nm).