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13. ABSTRACT (Maximum 200 words)

We have synthesized two new chrom ophore series whose bipolaron absorptions are in the spec tral region 600-900 nm, an area of extreme interest for eye protection from laser attacxk. These chromophore series were derivatized for attachment to 3,5-dihydroxybenzyl alcohol to form dendrons, which were then attached to a core molecule, bis-phenol A, to form G-0 dendrimers. We were also successful in preparing several dendrimers based on bis-(diphenylamino)stilbene repeat units by divergent methodology. These new dendrimers not only form highly absorbing charege states, but also display very large two-photon absorption cross-sections. When the dendrimers are irradiated in the presence of strong elec tron acceptors, such as fullerene, photo-induced absorption occurs, and highly absorbing transient species are formed. In solution these photo-induced species appear to be polaronic rather than bipolaronic. These results offer the possibity that eiher polaronic radical-cations or bipolaronic dications might be accessible by photo-induced electron-transfer processes. When these reverse saturable absorption processes occur in the same chromophores that have large two-photon absorption, optical power limiting can observed from either or both mechanisms, depending on the excitation wavelength. Thus these new materials may be considered to be bimechanistic in an optical limiting sense.

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14. SUBJECT TERMS polaron, bipolaron, optical limiting, photo-induced absorption, two-photon absorption	15. NUMBER OF PAGES 07
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OBJECTIVES:

The original proposal was to study approaches to the design and synthesis of new dendritic macromolecules whose surface functionalities would have unique electronic and nonlinear absorption characteristics which may make them effective optical power limiters . This ASSERT project was linked to our main program (F49620-96-1-0440) whose goal was not only to synthesize new limiting materials, but also to develop unique methods of spectroscopic characterization of the species giving rise to the nonlinear absorption events responsible for any observed optical limiting. This program was further enhanced by a DURIP award from AFOSR which allowed the development and implementation of these new spectroscopic techniques. This combination allowed us to focus a critical mass of synergistic talents on an area of current intense interest to the Air Force Research Laboratories.

RESEARCH ACCOMPLISHMENTS:

A. Synthesis of New Chromophores, Dendrons and Dendrimers for OPL

As we have outlined in our previous Progress Reports, We have completed the syntheses of two new chromophore series whose bipolaron absorptions are in the spectral region 600-900 nm, an area of extreme interest to the Air Force Research Laboratories (WPAFB-MLPJ) for eye protection from laser attack. These two chromophore series were derivatized for attachment to 3,5-dihydroxybenzyl alcohol to form dendrons for convergent dendrimer synthesis. Dendrons for all five chromophores were obtained in good yield (50-80%). Oxidative doping of the chromophores and dendrons in solution ($SbCl_5$ / CH_2Cl_2) confirmed that all five chromophore moieties can be converted to the bipolaron, and that the dendron bipolarons have essentially the same absorption characteristics as the free chromophores. The derivatized dendrons were, in turn, coupled to a typical core molecule (bisphenol A) to form model G-0 dendrimers in excellent yield (ca. 70-80%). As in the dendrons, the absorption characteristics of both the neutral dendrimers and the dendrimer bipolarons indicate that all four chromophore moieties can be converted to the bipolaron form upon oxidative doping, and that the dendrimer bipolaron absorptions were identical to the corresponding dendron and chromophore bipolaron absorptions. It should also be noted that the dendrons and G-0 dendrimers were quite soluble and processible, and could be easily purified by standard column chromatography. The chromophore, dendron and dendrimer structures are illustrated in Figure 1. The syntheses of the chromophores, dendrons and dendrimers were reported at a series of meetings during the past year, notably the SPIE meeting (July, 1999, Denver, CO), the Materials Research Society Fall Meeting (December, 1999, Boston, MA) and the American Chemical Society Spring Meeting (April, 2000, San Francisco, CA). The SPIE and ACS papers have been published, while the MRS papers are In Press at the current time and will be published in the next few months. During the past six months we have initiated a "scale-up" synthetic effort for the chromophores, dendrons and dendrimers in Figure 1 in collaboration with Scientific Materials Corp. (see INTERACTIONS/TRANSITIONS Section). This collaboration is part of a unique interaction between Montana State Universitry (C. Spangler and L. Spangler Research

Groups), Scientific Materials Corp., and the Air Force Research Laboratory at WPAFB (MLPJ) funded through a special appropriation and managed by Technical Management Concepts, Inc. This program goal is the design, synthesis, and characterization of a composite organic/inorganic optical limiter, and for prototype construction of an actual working device to Air Force specifications. The dendritic materials described and developed as part of this AASERT program will be the basis for the organic component of this prototype design

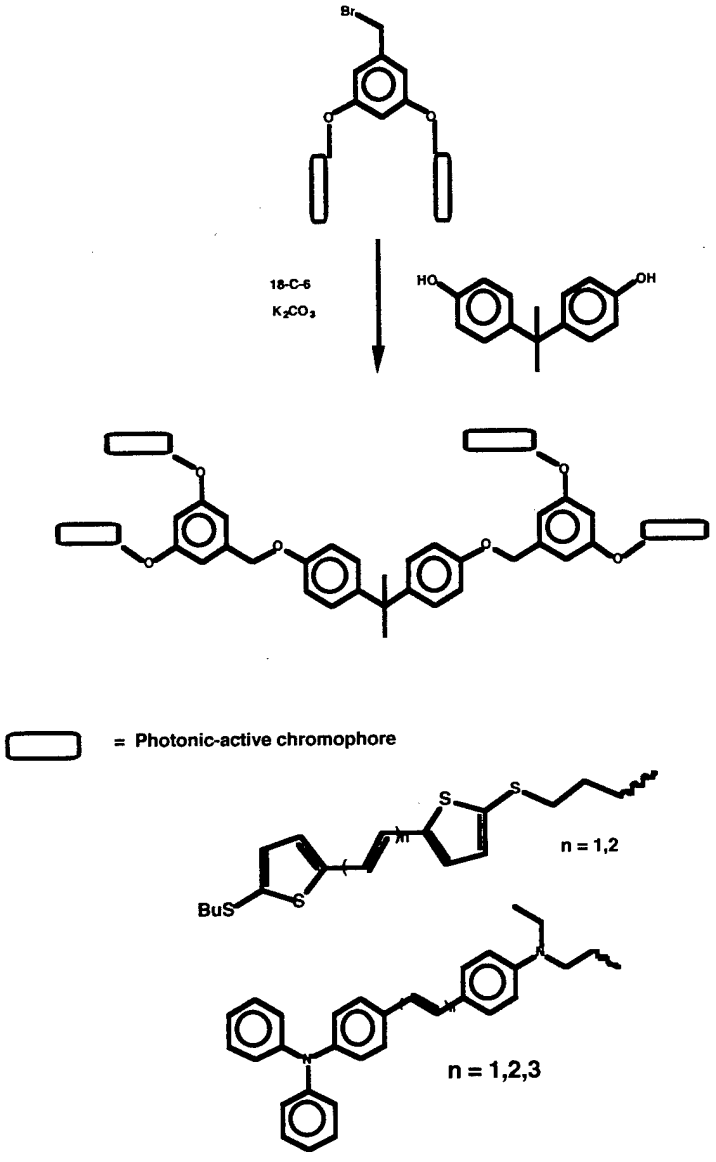

Figure 1. Chromophores, dendrons and dendrimers for OPL applications.

We have also been successful in preparing several dendrimers based on bis-(diphenylamino)-E-stilbene repeat units. These dendrimers form exceptionally stable bipolarons upon oxidative doping as illustrated below:

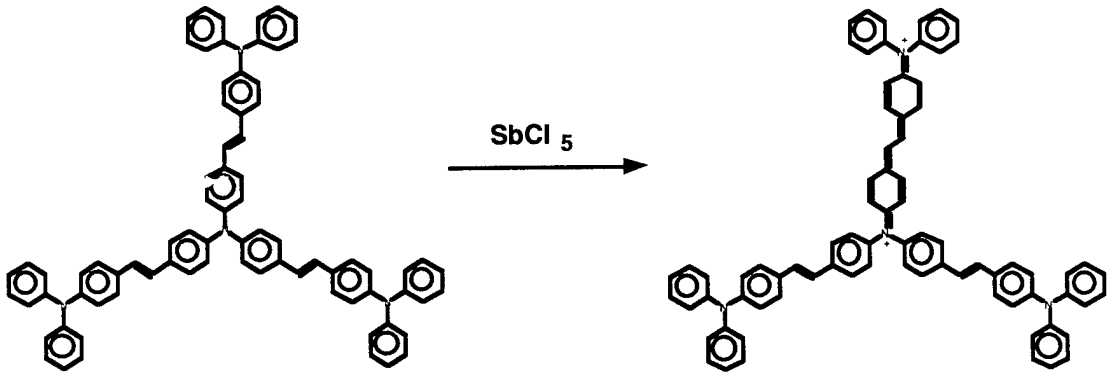

Figure 2. Bipolaron delocalization in model three-arm dendrimer

We also synthesized a model four-arm dendrimer based on the same repeat units, wherein the delocalization can be even more pronounced. This is illustrated below in Figure 3, which also illustrates the two-photon absorption capability of these materials in comparison to an Air Force Research Lab standard, AF-50:

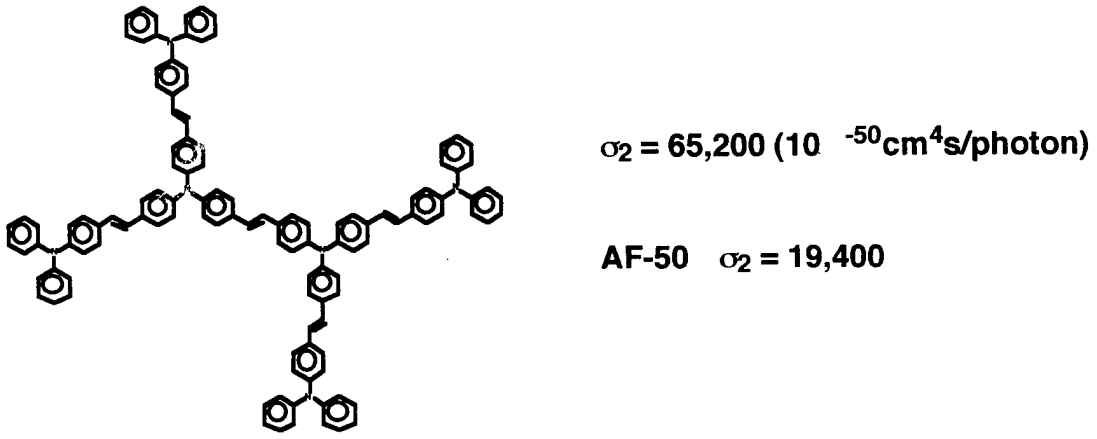

Figure 3. Four-arm dendrimer model.

The two-photon cross-section illustrated in Figure 3 was measured at 810 nm for 8 ns pulses. The actual maximum for the intrinsic two-photon absorption has been recently measured at MSU with 180 fs pulses and found to be at 760 nm. This research is being carried out in collaboration with Prof. Alex Rebane in the Physics Department, and has suggested several new possible research direction s which will be explored in the next

few years. These new materials are also being investigated in collaboration with the Air Force Research Labs at WPAFB which will be explained in greater detail below.

B. Spectroscopic Characterization of New OPL Materials

We have performed photo-induced absorption (PIA) and time-resolved photo-induce absorption (TRPIA) experiments on all compounds synthesized for this project. Spectra were obtained using a nanosecond pulsed laser system and a step-scan interferometer. Experiments were performed in dilute solution using C_{60} as the photo-induced acceptor to initiate the electron transfer process.

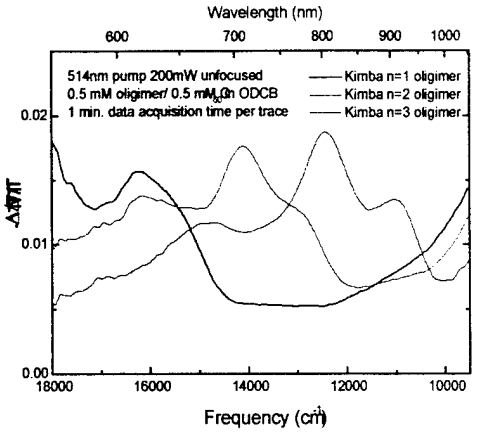

Figure 4. Continuous PIA spectra of functionalized diphenylamino polyene oligimers synthesised in this project.

Experiments with continuous excitation allowed rapid identification of PIA bands and quick confirmation that electron transfer occurred with the new compound. High quality data with excellent S/N could be obtained in as little as 1 min. at low excitation powers see Figure 4). The peaks shown are due to the bipolaron state and show the expected red shift with increasing conjugation length. The same bands were observed in the TRPIA spectra of these compounds.

In the dendritic compounds, a change in the intervalence transition (5000 - 7000 cm^{-1}) was observed indicating a difference in how the hole can move between nitrogen sites in the molecule (Figure 5). These spectra were extracted from the TRPIA data set for each molecule to compare the spectral differences in the mid IR range.

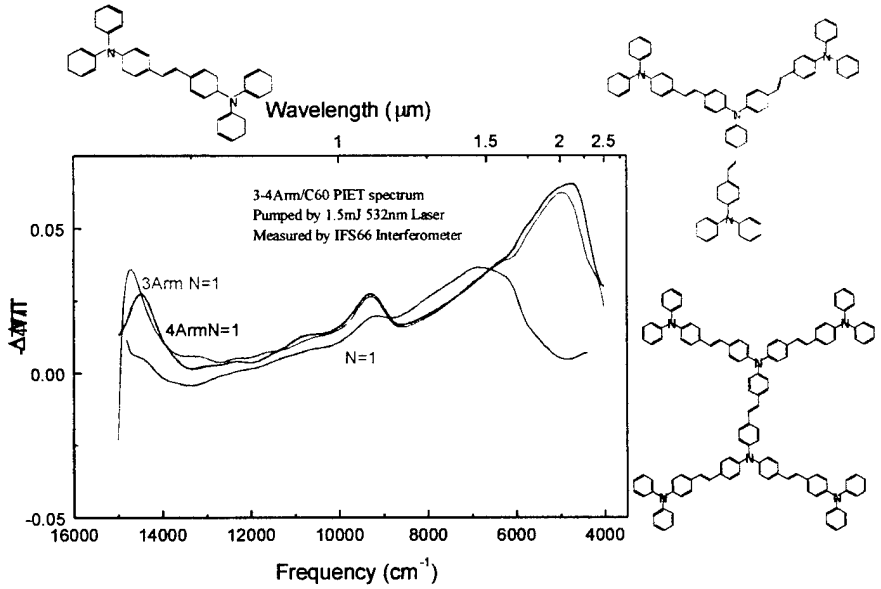

Figure 5. Comparison of the intervalence band for bis(diphenylaminostilbene) and three and four arm dendrimers based on the same moeity.

Figure 6 shows a full TRPIA spectrum for one of the three compounds, a comparison of the decay curves, and a second order kinetics plot for the charge recombination process.

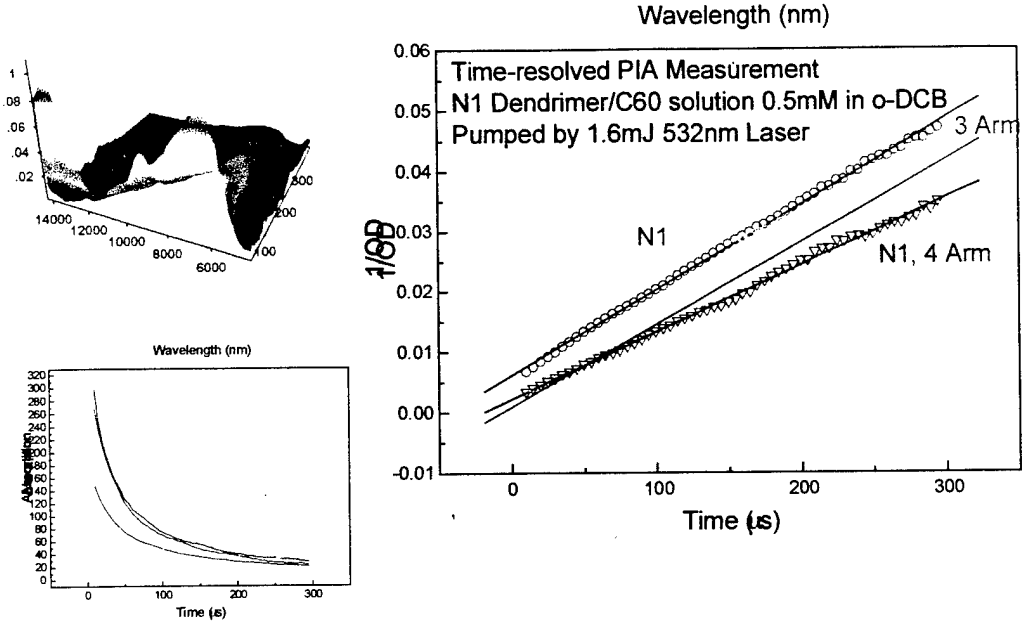

Figure 6. TRPIA spectrum(upper left) for one of the three compounds shown in the previou figure; decay of the charge states obtained from the TRPIA data for each compound (lower left); and a second order kinetics plot for the charge recombination(right).

SUMMARY:

We have synthesized five new chromophores, five new dendrons and five new G-0 dendrimers that are capable of reverse saturable absorption by photogeneration of polaronic (or bipolaronic) charge states in the presence of electron aceeptors. We have demonstrated that optical pumping of a C_{60} acceptor results in fast electron transfer from the donor chromophore, dendron or dendrimer to yield highly absorbing charge states in solution. In all probability, polaronic charge states resulting from a single electron transfer from donor to acceptor are the dominant species formed under these experimental conditions. Irradiation of either the three-arm or four-arm dendrimers based on bis-(diphenylamino)-E-stilbene repeat units display similar behavior. We are currently synthesizing dendrons and dendrimers with both donors and acceptors covalently attached within the same moiety. This should facilitate more efficient e-transfer, and possibly shift the e-transfer mechanism to bipolaron formation instead of the observed polarons.

PERSONNEL SUPPORTED:

The ASSERT Fellow has been supported for three years (Mr. Anthony Smith). At the current time he has not completed his dissertation. Several under graduate research assistants have also been supported at various times during this program. The most

productive of these assistants, Mr. Benjamin Reeves, is currently pursuing his doctoral degree under the direction of Prof. John Reynolds at the University of Florida. Ben also completed a departmental Honors B.S. thesis, and was recognized as the Outstanding Senior in his graduating class.

PUBLICATIONS:

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3. C. W. Spangler, T. Faircloth, E. H. Elandaloussi and B. Reeves, "Synthesis of New Multifunctional Polymers Incorporating Bis-(diphenylkamino)diphenylpolyene Moieties", Mat. Res. Soc. Symp. Proc. **488**, 283 (1998).
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9. A. Hyfield, K. Short, L. Spangler, C. Spangler, "Excited State Absorption In Dendrimers Incorporating Diphenylaminodiphenylpolyene Moieties Via Photo-Induced Electron Transfer" W. Sonnenberg, A. Hyfield, K. Short, L. Spangler, C. Spangler, *Materials Research Society Fall 1999 Conference Symposium Proceedings* v597, p363.

INTERACTIONS/TRANSITIONS:

The chromophores, dendrons and dendrimers described in this Final Report are currently being evaluated as optical power limiters using an Air Force test protocol (WPAFB-MLPJ) in collaboration with Scientific Materials Corp. (Bozeman, MT) (Randy Equall, 406-585-3772) as part of our SBIR Phase II/III funded through Wright Labs and administered by Technical Management Concepts, Inc. (Beavercreek, OH). The goal of this interaction is to supply the Air Force an optical limiting prototype system for field

testing and possible deployment within 1-2 years. All of the materials described in the AASERT program, as well as our parent grants (e.g. F49620-96-1-0440), are being tested as part of this effort. We are also funded for optical limiting materials and characterization development by both BMDO (administered by the Army Research Office – Doug Kiserow, Program Officer) and ARO (Doug Kiserow and Michael Cifton). Our primary contact at the Air Force Research Laboratories for sample submission is Dr. Paul Fleitz, and we have also had a continuing collaboration with Dr. Tom Cooper for several of these compound series (as well as others not covered in this report).

NEW DISCOVERIES, INVENTIONS or PATENT DISCLOSURES

One of the PIs (CWS) has filed a Provisional Patent Application (co-Inventor, Alexsander Rebane) for a "Mode-Locked laser infrared deection card and method". CWS acknowledged partial support from our parent grant, F49620-96-1-0440.

HONORS/AWARDS:

During the tenure of this grant, Prof. Lee Spangler (co-PI) was awarded a Teaching/Research Excellence Award by Montana State University.