Synthesis of dendrons and dendrimers incorporating diphenylamino-N-ethyl-N-hydroxyethylaminodiphenylpolyenes for photonic applications

by Kimba Lee Ashworth

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Chemistry
Montana State University

Abstract:
With the recent advances in laser technology, a need for protection from their potential damage is imperative. This problem requires the development of new optical power limiting materials to offer protection for eyes and optical sensors.

In this research, diphenylamino-N-ethyl-N-hydroxyethylamino-diphenylpolyene chromophores with up to three double bonds have been synthesized and incorporated into dendrons and generation-0 dendrimers. The convergent dendrimer synthesis was successfully used in the conversion of chromophores to dendrons and dendrimers.

The chromophores were also tested for their photoluminescence for organic light emitting diode and hole transport materials. The evaluation of the dendrons and dendrimers for these applications is currently being carried out in other collaborating laboratories.

The absorption characteristics of the three chromophores and their respective dendrons and dendrimers were examined to assess their optical power limiting performance. ll three chromophores and their dendrons and dendrimers form stable, highly absorbing bipolaronic charge states showing promise for reverse saturable absorption optical power limiting. The possibility also exists that these materials will show optical power limiting by two photon absorption. The compounds are currently being evaluated as bimechanistic optical limiting materials operating by both reverse saturable absorption and two photon absorption.

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APPROVAL

of a thesis submitted by

Kimba Ashworth

This thesis has been read by each member of the thesis committee and has been found to be satisfactory regarding content, English usage, format, citations, bibliographic style, and consistency, and is ready for submission to the College of Graduate Studies,

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

Figure Page

LIST OF SCHEMES

Scheme Page

ABSTRACT

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In this research, diphenylamino-N-ethyl-N-hydroxyethylamino-diphenylpolyene chromophores with up to three double bonds have been synthesized and incorporated into dendrons and generation-0 dendrimers. The convergent dendrimer synthesis was successfully used in the conversion of chromophores to dendrons and dendrimers.

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CHAPTER 1

INTRODUCTION

With the recent advances in laser technology, a need for protection from their potential damage is imperative. Military needs include protection for eyes and optical sensors against lasers with a wide range of wavelengths and response times. Norinco, Inc. (PRC) has already marketed a portable laser system capable of inflicting damage from up to six miles away.[1] The design of new optical power limiting (OPL) materials has become a progressing field in answer to this need for laser protection.

Optical power limiting is demonstrated when a material can limit the transmittance or output of energy at high energy input. Figure 1 shows a general graph of this process. There are some important parameters to be considered when designing effective optical power limiters for laser protection. The material should transmit light under ambient conditions allowing the eye or sensor to function normally, as indicated by the linear region of the curve, but then the material absorbs most of the intense laser light when needed. The limit goal value is the maximum energy that the eye or sensor can withstand without damage, so the plateau value is set below the limit goal to ensure protection.

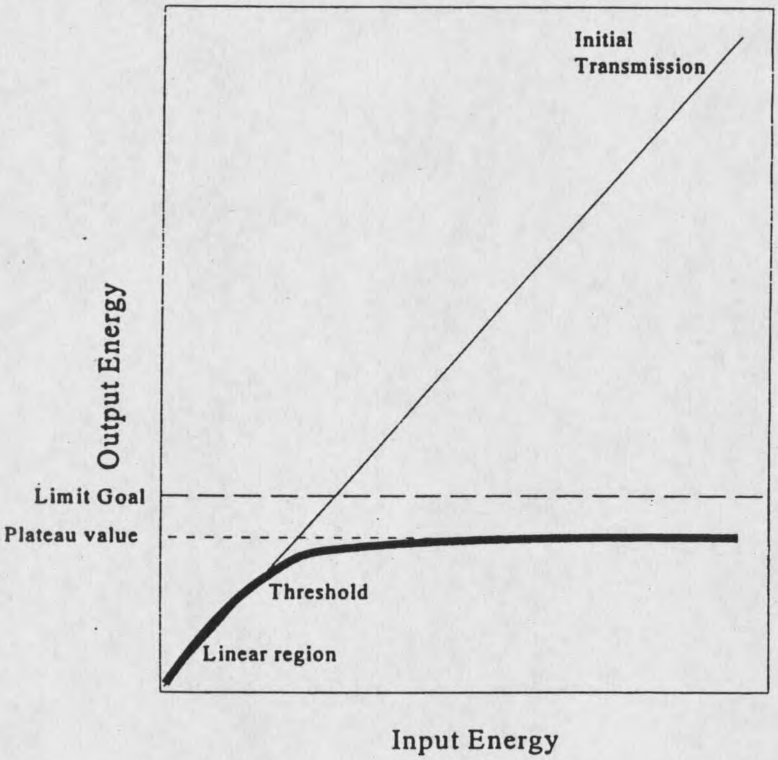


Figure 1. Optical Power Limiting Curve

There is a need to protect against different types of lasers, different wavelengths and different pulse durations. If optical power limiting materials are to be used as a defense, they must be designed to respond quickly and protect a wide frequency range of the spectrum. There are different types of optical power limiting materials being researched at the current time, including reverse saturable absorbers, two photon absorbers, photorefractive materials, photochromic materials and sacrificial materials. Organic materials that exhibit either reverse saturable absorption

(RSA) or two photon absorption (TPA) have the most potential for being effective optical power limiters in laser defense.

Simple forms of schematic energy level diagrams have been presented to represent the pathways giving rise to optical power limiting via either RSA or TPA. Figure 2 illustrates the pathway for RSA. After the S_0 to S_1 transition, then either S_1 to S_n or intersystem crossing (ISC) to another transient state (TS) can occur. The transient states could be triplet, or photogenerated charge states. If the absorptions for S_1 to S_n or TS_1 to TS_n are strong then optical limiting is possible.

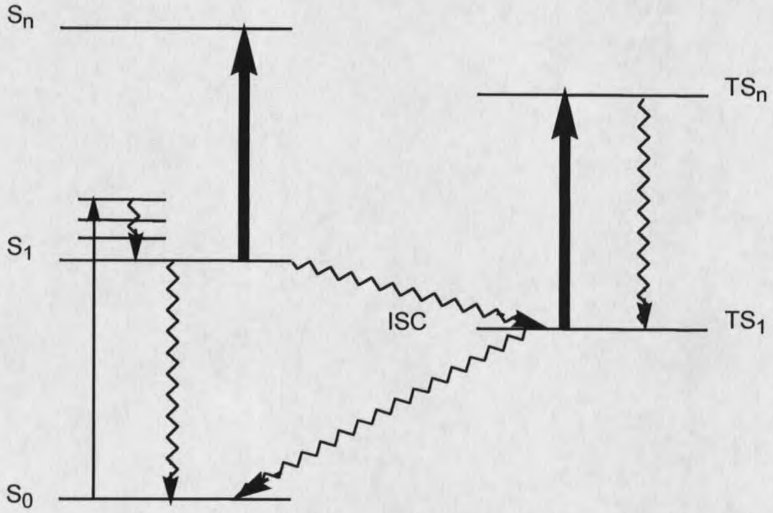


Figure 2. Energy Level Diagram for RSA Optical Power Limiting

There are a variety of materials that have been studied as reverse saturable absorbers, including indanthrones[2], phthalocyanins[3], porphyrins[4], and fullerenes[5]. These materials have RSA behavior based on formation of triplet states resulting from intersystem crossing from the first excited state that has been populated by laser irradiation. The Spangler research group has been studying the RSA behavior of organic chromophores that upon oxidative doping form polaron-like radical-cations and bipolaron-like dications as stable, highly absorbing transient states.[6] These chromophores have transient state absorption cross-sections which are larger than the ground state absorption cross-section. Therefore, as the intensity of the laser irradiation increases, it might be possible for the transient state (TS) transitions via intersystem crossing to become dominant, allowing more light to be absorbed.

Two photon absorbing chromophores have also been a focus of the research in the Spangler group. Figure 3 represents the pathway of TPA. Two photons at half the energy of the excitation wavelength are simultaneously absorbed, populating the S_1 or S_2 levels giving access to the excited state manifold.

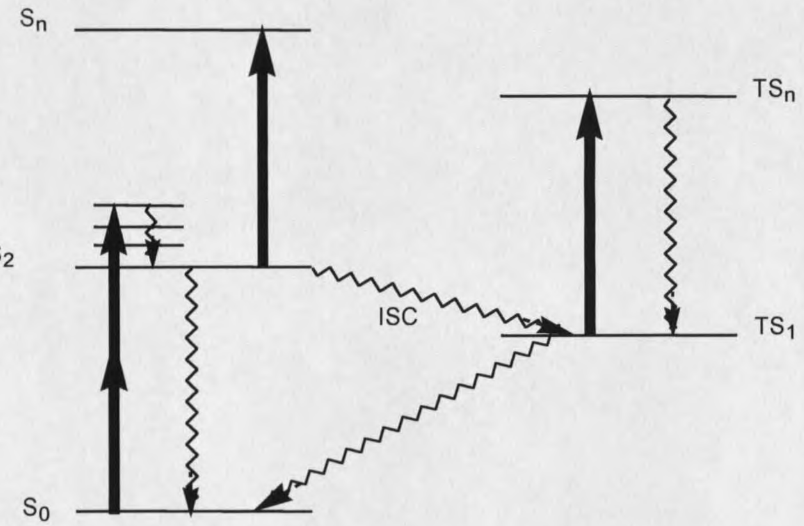


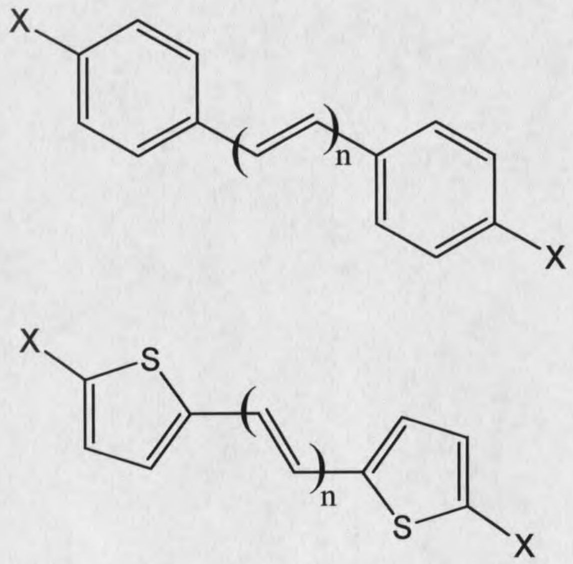
Figure 3. Energy Level Diagram for TPA behavior.

CHAPTER 2

HISTORICAL SECTION

Design of RSA and TPA Chromophores

The Spangler research group has been synthesizing and studying optical power limiting chromophores that operate by RSA or TPA for the past few years, specifically α,ω-dithienyl- and α,ω-diphenylpolyenes with up to ten double bonds.[6-11] Figure 4 shows the general structures for these chromophores.



(1)

n = 1 - 10

X = R_2N, RS, RO, H

(2)

Figure 4. α,ω-Diphenyl- and α,ω-Dithienylpolyenes.