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Recent development in the design of organic materials for optical power limiting

Charles W. Spangler

Department of Chemistry and Biochemistry, Montana State University, Bozeman, MT 59717, USA. E-mail: uchcs@montana.edu

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During the past five years there has been considerable progress in the design of organic materials for optical power limiting. Among the more promising of the new material approaches are new reverse saturable absorbers (RSA) which derive their limiting capability on the photogeneration of highly absorbing charge states. Equally intriguing are the new approaches to designing chromophores with large two-photon cross-sections which give access to highly absorbing transient excited states. It now seems possible to combine these two new optical limiting paradigms in single structures which may therefore be considered as bimechanistic optical power limiters.

Introduction

Rapid advances in laser technology have resulted in new and improved laser systems that are compact, efficient, and operate at a variety of wavelengths. Indeed, several common applications are ubiquitous in everyday life, such as CD players, price and inventory scanners and lecture presentation laser pointers. However, military applications have also kept pace, as evidenced by the marketing of a portable laser system by Norinco, Inc.[1] (PRC) capable of inflicting severe eye damage, and having a maximum range of 2–6 miles depending on atmospheric conditions. This increased presence of lasers in 'friendly' applications and in potential enemy weapons systems presents significant hazards to the eyesight of ground based military personnel, optical sensors and both military and commercial aircraft pilots. The military potential of laser weaponry has been discussed in detail in a recent publication by Anderberg and Walbarsht,[2] and most recently, Miller *et al.* have reviewed the general requirements for optical limiters from the military perspective.[3] In this review we will attempt to address the rapidly escalating need for protection from laser devices by both civilian and military sectors, and the current state of the art in designing optical power limiting (OPL) materials. Potentially, there are a large number of wavelengths that could be generated in laser weapons systems, and protection schemes must also cover a wide range of response times, from sub-nanosecond to block lasers with short pulse durations, to tens of microseconds to block quasi-CW sources. Military requirements are currently focused primarily on pulsed laser weapons, while most civilian applications involve CW sources. This combination of requirements places severe restrictions on materials, which must respond quickly, provide protection from a variety of pulse durations, and be frequency agile.

The magnitude of the problem

A recent excellent review highlights the need for laser safety in the laboratory, highlighting the myriad accident types that can occur, and resultant damage to human tissue, even death.[4] However, reviews such as this cover only accidents that can be prevented, such as using proper eyewear designed specifically for the laser lines one could encounter in a specific laboratory application. At the current time, little can be done to protect against any and all unknown laser frequencies that one could encounter by accident or deliberate attack. It is important to note at this time that laser 'weapons' can be primarily viewed as falling into two distinct categories: (1) those primarily designed to 'dazzle' rather than blind, and (2) those designed to permanently disable humans by blinding, or to destroy sensors. Pulsed laser weapons are designed to blind, while CW or quasi-CW lasers tend to dazzle for varying time periods. Several recent examples illustrate the scope and magnitude of the problem. The Federal Aviation Administration is currently investigating at least four reports of pilots being temporarily blinded by lasers while flying aircraft in the Los Angeles area, the most recent being a United Air Lines pilot, flying a Boeing 737 near Ontario, CA. Airport, being blinded by a green flash. In this, as well as other cases, the copilot had to land the airplane.[5] It is not known what type of laser was employed in these attacks. In November, 1998, two US helicopter pilots received minor corneal burns from a ground-based laser while on routine patrol near the town of Zenica in Bosnia-Herzegovina.[6] What is even more disturbing is a rash of reported store robberies in the UK in which hand-held laser pointers were used to temporarily blind or 'dazzle' the counter clerks. Even in the author's hometown of Bozeman, MT, there have been several reports of automobile drivers flashing lasers at oncoming traffic, dazzling the oncoming drivers for several seconds, as well as students bringing laser pointers to school for personal protection.[7] Obviously, the need for optical limiters is not limited to the military, but is rather a growing societal problem that can only escalate. While it is possible to protect the human eye from laser pointers with proper filtering, assuming one can anticipate the frequency, static filters are not appropriate for frequency-agile pulsed lasers. What is needed is the development of 'smart' materials that are transparent under ordinary ambient light conditions, but can rapidly undergo structural modification (<1 ps) to absorb or block intense laser light over a broad frequency range extending into the NIR for various sensors, and for specific time intervals. At the current time no such universal frequency agile OPL materials exist, with the exception of carbon black suspensions in carbon disulfide which can provide broadband protection between 400 and 700 nm. However, such liquid suspensions are cumbersome in actual field use. To protect against both pulsed and CW lasers simultaneously with one material is problematic, and will probably require a tandem limiter employing both filters and smart materials. In all probability, effective OPL devices, whatever their final design, will also require focusing optics to be effective.

Prevalent mechanisms for optical power limiting

This review is not intended to be comprehensive with respect to the historical development of organic OPLs. Several excellent reviews covering the background of OPL development have appeared recently,[8–11] so this current review will focus only on recent developments in two general areas: (1) OPLs that rely on reverse saturable absorption (RSA) from rapidly photogenerated transient states, and (2) OPLs that rely on two-photon absorption (TPA) that can give access to similar large transient absorption effects. Further, this review will limit its discussion to OPLs that operate in the visible region of the electromagnetic spectrum (400–800 nm), and which are primarily designed to afford eye protection. In general, in the visible region organic chromophore RSAs tend to have their primary absorption, $\lambda_{\max}$ (π–π^*), at 400 nm, or below, to give reasonable transmission for solution or thin film measurements. Two-photon absorbers, on the other hand, would tend to depend on absorption in the 600–800 nm region to give rise to OPL effects in the visible. A variety of schematic energy diagrams have been presented to represent the pathways giving rise to OPL *via* either RSA or TPA. In their simplest form, they can be represented as illustrated in Fig. 1 for both mechanisms.

Previous discussions of optical limiting have relied on the most prevalent transition states being formed during optical pumping of the ground state singlet (S_0) to be triplets, usually represented as T_1, formed by intersystem crossing (ISC) from the S_1 excited state. In Fig. 1, the T_1 to T_n transitions are replaced by TS_1 to TS_n where TS represents all possible transient states. In particular, the possibility of the formation of photogenerated charge states, both polaronic radical-ions and bipolaronic diions, will be discussed in later sections. Reverse saturable absorber chromophores display excited state absorption cross-sections which are larger than the S_0 to S_1 cross-section at the excitation wavelength. Thus, in general, as the intensity of the laser irradiation increases, the population of the S_1 and T_1 states (*via* ISC) increase, the more light is absorbed. The kinetics and population dynamics for several absorbers have been discussed in detail by Perry,[9] and Miles[12] has extended this discussion to the use of 'bottleneck' device design to obtain the maximum OPL efficiency from typical RSA chromophores. He has pointed out that optical limiting has been achieved for high f# optics, but is inadequate for eye protection at the current time, while low f# optics may result in damage to the limiter. The use of multiple plate arrays can be used to avoid material damage at high input levels. Thus, in principle, for any given conjugated chromophore system, the possibility exists for tuning the excited state absorption by preferentially forming triplets (T), polaron-like radical-ions (P) or bipolaron-like diions (BP), all of whom would exhibit characteristic, but different, absorption.

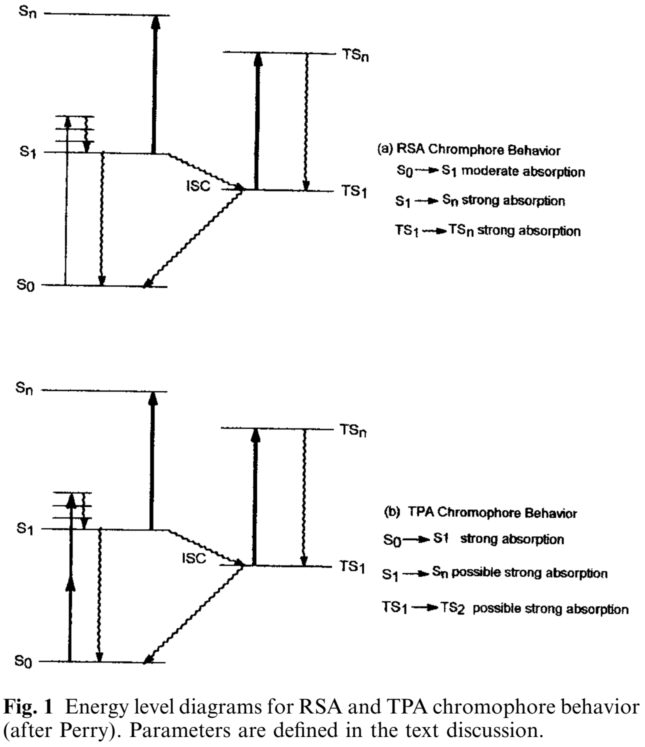


Fig. 1 Energy level diagrams for RSA and TPA chromophore behavior (after Perry). Parameters are defined in the text discussion.

In a similar fashion one could envision designing chromophores which function as optical limiters by TPA. Inherent in this approach to OPL is that adequate structure–property relationships could be established that would allow rational new chromophore design with greatly enhanced two-photon cross-sections. Such structure–property relationships can be inferred from several recent papers.[13–15] Ideally, one can imagine chromophores that might function in a bimechanistic fashion: (1) RSA behavior at the high energy end of the visible, and (2) TPA behavior at the low energy end of the visible. In the following sections, an attempt will be made to establish such a structure–property paradigm for optical limiter design.

The design of efficient reverse saturable absorption chromophores

The reverse saturable absorption phenomena offers exciting possibilities for the design of 'smart' passive limiters. Nonlinear absorption of light was experimentally observed in the late 1960s,[16] and reverse saturable absorption described for solutions of anthracene in 1974.[17] Since that time, a number of other structural families have been studied and shown to exhibit RSA, and a wide variation in structural types can be briefly characterized as follows: indanthrones,[18] metal cluster compounds,[19–21] porphyrins,[22–25] phthalocyanines[26–33] and fullerenes.[34–37] While the large majority of RSA characterizations of these materials has been carried out in solution, studies have also focused on guest–host films, such as C_{60} in PMMA,[38] as well as sol–gel materials and polymers.[39–41] Of particular note for these latter studies is that there is very little change in the optical limiting ability in going from solution to PMMA or ORMOSILS, and the photophysics is largely unaffected by choice of host material. However, it should also be noted that degradation of the polymer host is possible, particularly if repeated pulses hit the same spot causing thermal degradation or ablation, which is much less likely for the liquid samples. This observation is important for the design of OPL materials from an actual device design perspective, where the processing advantages of polymers over liquid solutions is obvious.

The vast majority of the above examples of RSA behavior have focused on the triplet states resulting from fast, efficient intersystem crossing from the S_1 state initially populated by the incident pulsed laser irradiation. For example, the heavy atom effect in metallophthalocyanines and metalloporphyrins, which magnifies the OPL behavior, can be attributed to the enhancement of the ISC from S_1 to T_1, thereby giving greater access to the highly absorbing triplet state manifold.[25,27,30,31] However, much less attention has been paid to other possible nonlinear absorption transient states. For several years our research group has been studying the formation and stabilization of polaron-like radical-cations and bipolaron-like dications by oxidative doping of series of polyenylic oligomers.[42–47] In solution the dication appears to be the predominant species, particularly if mesomerically stabilized by electron-donating substituents. The spectra of both the neutral and bipolaronic dications formed from α,ω-diphenyl and α,ω-dithienylpolyene series with up to ten double bonds (Fig. 2) are red-shifted by such substitution, and the shift in oscillator strength correlates well with the electron-releasing ability of the substituent groups. Typical polaron-like radical-cation and bipolaron-like dication structures are illustrated in Fig. 3 for a dithienylpolyene.

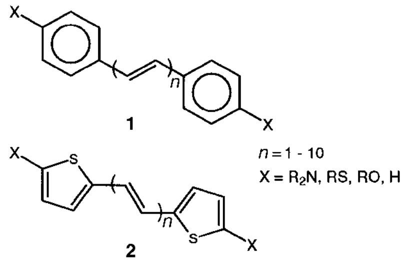


Fig. 2 α,ω-Diphenyl- and α,ω-dithienylpolyenes which form stable bipolaron-like dications upon oxidation with $SbCl_5$ in solution.

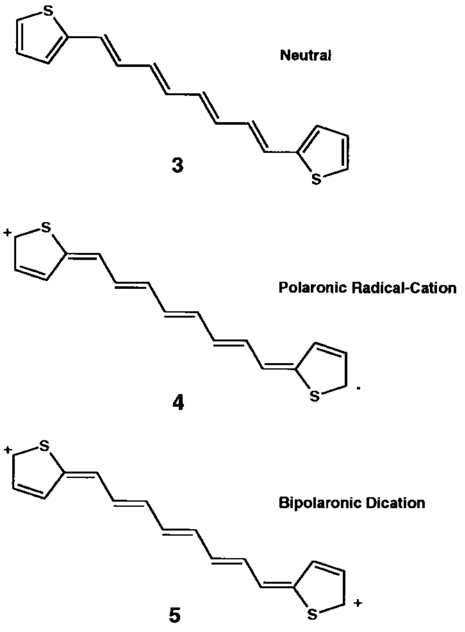


Fig. 3 Typical stuctures for neutral, polaron-like radical-cation and bipolaron-like dication for 1,8-bis(2′-thienyl)octa-1,3,5,7-tetraene.

In Table 1 the absorption spectra λ_{max} for several series of dithienylpolyenes and their respective $P(+^{\bullet})$ and $BP(++)$ are listed. As can be readily seen, by varying the conjugation length and nature of the substituents, the absorption characteristics of polaronic and bipolaronic species can be fine-tuned over a wide range of the visible. It should be noted here that most reported studies of P or BP formation in polyenes focused on their nonlinear optical properties, particularly as a function of increasing conjugation length. For polaron or bipolaron absorptions to be observed in the 400–700 nm region, shorter conjugation lengths would need to be employed (enes and dienes). The linear absorptions for these shorter conjugation lengths are below 400 nm, thus imparting little or no color to the sample. In almost all cases studied, the polaronic and bipolaronic charge states are more highly absorbing than the S_0 to S_1 initial one-photon process. Thus, if these charge states could be photo-generated from the neutral species on the ps time scale, they could be effective optical limiting materials. It has been previously predicted that the incorporation of polaronic or bipolaronic charge states in the π-conjugation sequences (*e.g.* polyenes) should lead to greatly enhanced third-order optical nonlinearity.[48,49] This has been confirmed experimentally for bipolaron formation in both bis(anthracenyl)polyenes,[50] and for α,ω-dithienylpolyenes.[51] The question, then, is not whether such charge states would lead to enhanced nonlinear absorption, but whether they can be formed in significant amounts, and on an appropriate time scale, to afford protection from either or both ns and ps laser pulses.

Cao *et al.*[52] were able to show that oligomers of ladder polymers formed photogenerated species on the picosecond time scale that were highly absorbing, and whose $\mathrm{Im}[\chi^{(3)}]$ response correlated closely with the photo-induced absorption spectrum. When the PIA spectrum was compared to that of the chemically produced bipolaron, the correspondance was dramatic. These workers concluded the bipolaronic charge state could be produced directly from the structural relaxation of the initially formed exciton, and also that bipolaron formation correlated with large increases in the $\mathrm{Im}[\chi^{(3)}]$ response. These conclusions were confirmed by more detailed pump-probe experiments with other ladder oligomers by Sapochak *et al.*[53] which also demonstrated that structural relaxation to a transient charge state was faster than the excitonic electron–hole recombination, and that the transient charge state was relatively long-lived on the ps timescale. Current studies in our laboratory have shown that the photo-induced charge states in fact can survive for milliseconds.

Over the past few years, other research groups have addressed the problem of the efficiency of photo-generated charge state formation in conjugated molecules and polymers. Of particular interest to the problem of optical limiting is a recent review by Sariciftci and Heeger[54] on the photophysics of charge separation between conjugated polymers and fullerenes. C_{60} is a recognized optical limiter based on reverse saturable absorption from the excited state manifold.[34–38] Sariciftci and coworkers have also demonstrated that a photo-induced electron transfer can occur between a conducting polymer, such as MEHPPV or poly[3-alkylthiophene], and C_{60}, which produces different transient absorption species than either component irradiated individually.[54,55] Light-induced electron spin resonance studies indicate formation of both $D(+\cdot)$ and $A(-\cdot)$ polarons. Photoluminescence is also quenched. The proposed mechanism[54] can be briefly illustrated as in eqn. (1)–(5):

$$\mathrm{D}+\mathrm{A}\rightarrow{}^{1,3}\mathrm{D}^{*}+\mathrm{A}\quad\text{D Excited}\tag{1}$$

$${}^{1,3}\mathrm{D}^{*}+\mathrm{A}\rightarrow{}^{1,3}(\mathrm{D}\cdots\mathrm{A})^{*}\quad\text{Excitation delocalized over D–A complex}\tag{2}$$

$${}^{1,3}(\mathrm{D}\cdots\mathrm{A})^{*}\rightarrow{}^{1,3}(\mathrm{D}^{\delta+}\cdots\mathrm{A}^{\delta-})^{*}\quad\text{Charge transfer initiated}\tag{3}$$

$${}^{1,3}(\mathrm{D}^{\delta+}\cdots\mathrm{A}^{\delta-})\rightarrow{}^{1,3}(\mathrm{D}^{+}\cdots\mathrm{A}^{-})\quad\mathrm{D}(+)\text{ and }\mathrm{A}(-)\text{ begin to form}\tag{4}$$

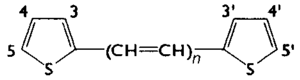
$${}^{1,3}(\mathrm{D}^{+}\cdots\mathrm{A}^{-})\rightarrow\mathrm{D}(+)+\mathrm{A}(-)\quad\text{Polarons formed}\tag{5}$$

Eqn. (1) and (3) represent singlet or triplet states.

In this proposed mechanism, the D and A moieties can be either a guest–host ensemble, or they can be covalently attached within the same molecules, separated by some defined distance. Relaxation can occur at any time during the mechanism, either by releasing heat to the lattice or by some allowed radiative pathway. Ideally, pumping the acceptor could lead to the same excited states manifold, thus providing reverse saturable absorption *via* either photo-induced electron transfer or photo-induced hole transfer.[54]

Janssen and coworkers[56] were able to demonstrate PIA in a series of oligothiophenes (nT, $n = 6,7,9,11$) in solution. Both metastable triplet and oligothiophene radical cations (polarons) were identified, and the nature of the transient species formed appeared to be solvent dependent. Addition of an acceptor, TCNE, quenches the triplet state formation and efficiently produces the radical-cations. Thus, to a certain degree, the absorption characteristics of the transient species can be controlled by both solvent and the presence of e-accepting species. It was also shown in subsequent studies that various conjugated polymers (as donors) formed long-lived charge-separated states in the presence of a series of TCNQ derivatives as acceptors.[57] The photo-induced appearance of the polaron bands again correlated with the loss of photoluminesence observed in the pristine polymer. And finally, composite films of C_{60} and oligothiophenes display PIA spectra

Table 1 P (+ •) and BP (+ +) formation in dithienylpolyenes



Substituents	n	λ_{max} π–π*/nm[a]	λ_{max} P(+ •)/nm	λ_{max} BP(+ +)/nm
None	5	*416*, 443	*705*, 797, 1084	653, *713*
None	6	*432*, 461	*760*, 853, 1154	713, *776*
5,5′-(Me)$_2$	5	*425*, 450	[808][b]	660, *710*
5,5′-(Me)$_2$	6	*441*, 469	*888*, 1167, 1580	720, *776*
3,3′-(Me)$_2$	5	*422*, 449	[795][b]	650, *699*
3,3′-(Me)$_2$	6	*440*, 469	*881*, 1154, 1574	713, *769*
5,5′-(OMe)$_2$	3	*398*, 420	[*731*, 1076][b]	*520*, (545)[d]
5,5′-(OMe)$_2$	4	*416*, 442	*806*, 1103, 1299	*577*, (605)[d]
5,5′-(SMe)$_2$	3	404	*792*, 1009, 1240	610, (643)[d]
5,5′-(SMe)$_2$	4	*422*, 444	*859*, 1114, 1348	663, (702)[d]
5,5′-(SMe)$_2$	5	*434*, 460	*c*	717, (775)[d]
5,5′-(SMe)$_2$	6	*451*, 478	*c*	773, (835)[d]
5,5′-(SC$_{10}$H$_{21}$)$_2$	7	*462*, 493	*c*	834, (905)[d]
5,5′-(SC$_{10}$H$_{21}$)$_2$	8	*475*, 507	*c*	884, (970)[d]
3,4,3′,4′-(Bu)$_4$	3	422, *399*, 380	*c*	593, *655*
3,4,3′,4′-(Bu)$_4$	4	443, *418*, 396	*c*	600, *661*
3,4,3′,4′-(Bu)$_4$	5	462, *435*, 412	*c*	679, *715*
3,4,3′,4′-(Bu)$_4$	6	480, *450*, 426	*c*	*719*, 809
3,4,3′,4′-(Bu)$_4$	7	496, *464*, 439	*c*	790, *849*
3,4,3′,4′-(Bu)$_4$	8	510, *477*, 450	*c*	855, *914*
3,4,3′,4′-(Bu)$_4$	9	521, *489*, 461	*c*	892, *971*
3,4,3′,4′-(Bu)$_4$	10	534, *499*, 471	*c*	950, *1022*
3,4,3′,4′-(Bu)$_4$; 5,5′-(BuS)$_2$	3	424	*c*	643
3,4,3′,4′-(Bu)$_4$; 5,5′-(BuS)$_2$	4	439	*c*	657
3,4,3′,4′-(Bu)$_4$; 5,5′-(BuS)$_2$	5	451	*c*	705
3,4,3′,4′-(Bu)$_4$; 5,5′-(BuS)$_2$	6	466	*c*	754
3,4,3′,4′-(Bu)$_4$; 5,5′-(BuS)$_2$	7	476	*c*	801
3,4,3′,4′-(Bu)$_4$; 5,5′-(BuS)$_2$	8	488	*c*	849

[a] CH_2Cl_2 solution. [b] Absorption spectra decay to BP (+ +) very fast; only unambiguous assignable absorption. [c] Not observed on spectrometer scanning time scale. [d] Absorptions shown in parentheses represent shoulders. Note: peaks in italics represent peaks of maximum absorption. Portions of this table are reprinted with permission from *Molecular Electronics and Molecular Electronic Devices*, Vol. III, (ed K. Sienicki) copyright CRC Press, Boca Raton, Florida.

characteristic of the polymer radical-cations and fullerene radical-anions.[58] Examples of donor polymers and TCNQ derivatives that show this behavior are shown in Fig. 4.

Over the past five years, we have established a program whose goal has been the design of fast, efficient OPLs *via* RSA from photo-generated charge states (either polaronic radical-cations or bipolaronic dications).[15,59] We have described how a systematic study of chromophore RSA in polymers can be accomplished *via* covalent attachment to a PMMA backbone (pendant) in which the chain lengths and polydispersity are invariant.[60] This scheme is illustrated in Fig. 5. This approach allows for the study of electron transfer to acceptors such as

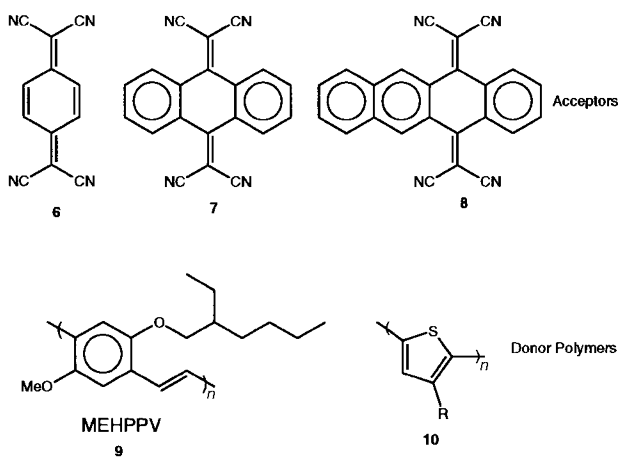


Fig. 4 Typical acceptors and donor conjugated polymers in photo-generated charge transfer.

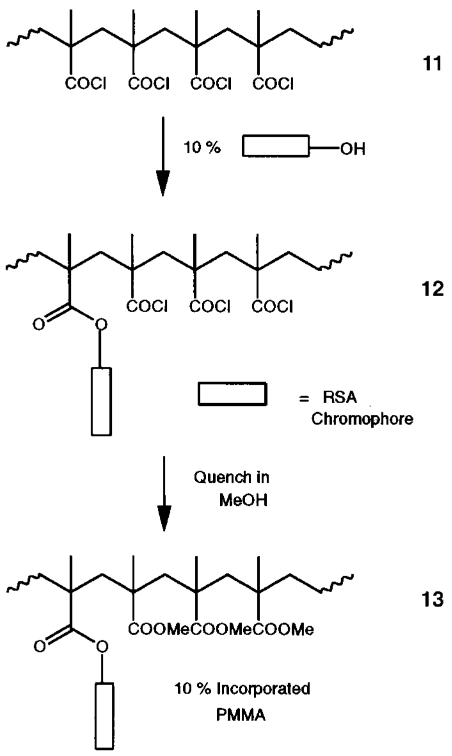


Fig. 5 Incorporation of typical RSA-OPL chromophore into a PMMA backbone.

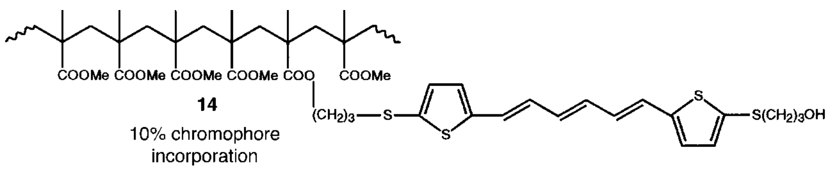


Fig. 6 Typical RSA-OPL chromophore (DT3SP) substituted onto a PMMA backbone.

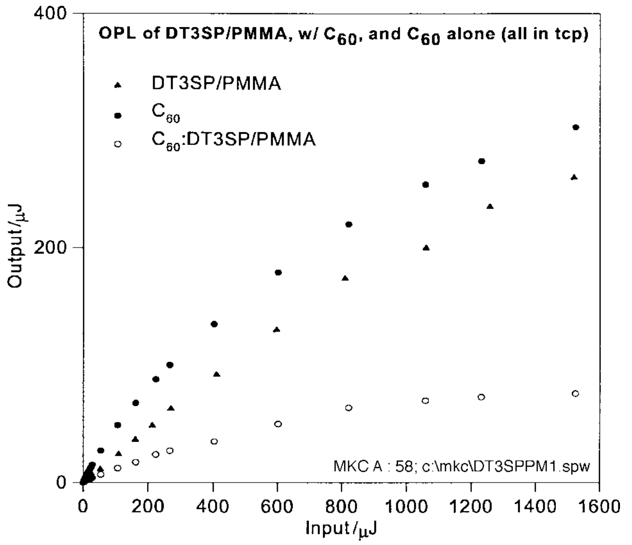


Fig. 7 Optical limiting for DT3SP/PMMA, C_{60}, and DT3SP/PMMA+C_{60}. A laser beam of 7 mm was focused 1 cm onto the rear of a 3 mm long path length cuvette containing the solutions (increasing fluence through solution) using a 10 cm focal length lens (open aperture). The energy of the incident and transmitted laser beams were compared with a pyroelectric detector at the back of the cuvette.

C_{60} incorporated either as a guest in the OPL-PMMA host, or covalently attached. This also allows the percentage incorporation of both D and A, and thus the D/A ratio, to be varied independently and over a wide range. Since C_{60} can accept more than one electron (up to a maximum of 6), close covalent attachment offers the possibility of either donor chromophore polaron or bipolaron formation. Optical power limiting studies have been carried out for a typical dithienylpolyene OPL chromophore as a 10% incorporated PMMA polymer, C_{60}, and the polymer–C_{60} guest–host in collaboration with workers at Laser Photonics Technology, Inc. (Amherst, NY). Optical limiting is observed in each case, with the guest–host polymer system exhibiting the best limiting behavior.[60] The structure of the polymer is illustrated in Fig. 6, while the OPL behavior is illustrated in Fig. 7.

Further studies are currently being carried out in collaboration with LPT with similar chromophore-incorporated PMMA with covalently attached C_{60} derivatives to determine optimal D and A loading and D/A ratio. It is clear that this approach will allow some control of the optical region afforded RSA protection since the chromophore identity, conjugation length, substituent effects, acceptor identity and D/A ratio can all be independently controlled. Although these results are very preliminary, what is not clear is whether charge-transfer is responsible for the observed limiting behavior, or if the D and A effects are additive. However, the results are encouraging progress towards the goal of less than 1 microjoule of transmitted intensity.

The design of efficient two-photon absorption chromophores

While two-photon absorption has been studied for a number of years, detailed structure–property relationships which might permit the design of new chromophores with enhanced two-photon cross-sections have been lacking.[13,14,61] However, in the last few years two groups have attempted to address the lack of such design paradigms. Reinhardt and coworkers have proposed two classes of chromophores that might give rise to enhanced two-photon absorption 1,[4,62–64] as illustrated in Fig. 8.

The design concept is based on the relationship between the molecular two-photon cross-section and the Im component of the third-order NLO susceptibility [eqn. (6)]:

$$\sigma_2=\frac{8\pi^2 h\nu}{n^2c^2N}\mathrm{Im}[\chi^{(3)}] \qquad (6)$$

where h = Planck's constant, ν = frequency of incident light, n = index of refraction, c = speed of light in vacuum and N = number of absorbing molecules.

Reinhardt's group designed series of molecules for use at 800 nm, and recognized the salient problem of how to increase the two-photon cross-section while maintaining $\lambda_{\max}$ of the chromophores constant. Some important design parameters became apparent during these studies, and a series of general rules for increasing the molecular two-photon cross-sections emerged:

(1) Extend the conjugation length
(2) Change the identity of the conjugated bridge
(3) Increase the π-donor strength
(4) Incorporate more polarizable double bonds
(5) Increase planarity of the chromophore

By applying these design concepts, the best compounds to come out of these studies are illustrated below. However, it should be recognized that these workers carried out their measurements at only one wavelength, and only with nano-

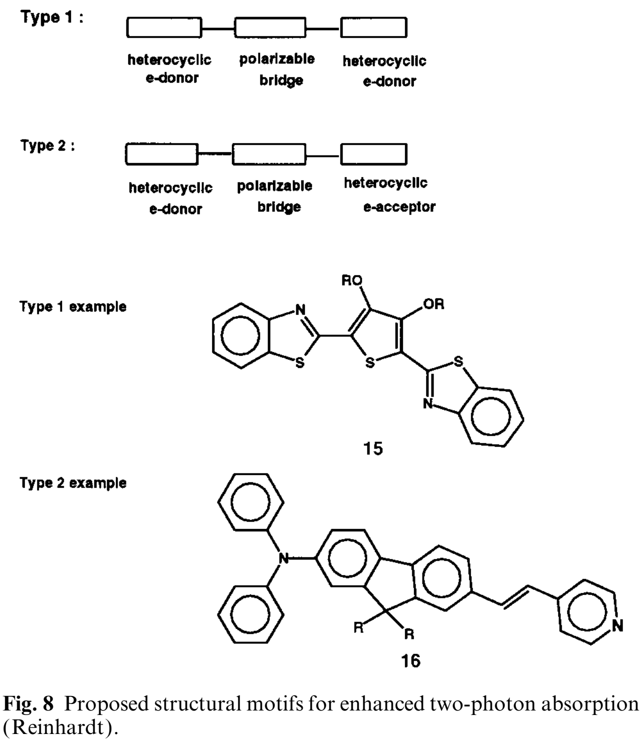
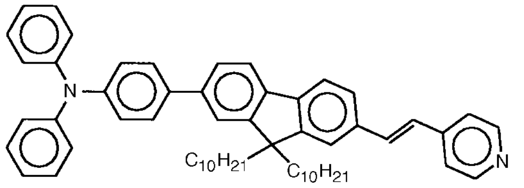


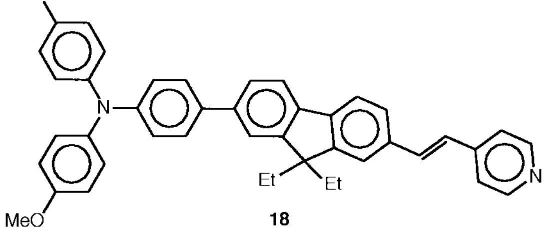
Fig. 8 Proposed structural motifs for enhanced two-photon absorption (Reinhardt).

second pulses. Therefore, it is most probable that the cross-sections reported are enhanced by excited state absorption.



17

$\sigma_2 = 11560 \times 10^{-50}$ cm^4 s photon^{-1}



18

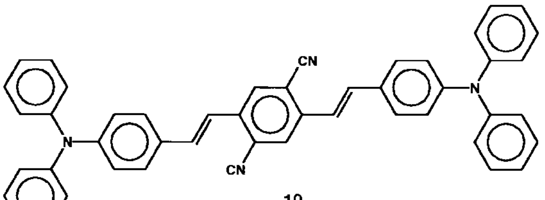
$\sigma_2 = 11480 \times 10^{-50}$ cm^4 s photon^{-1}

Perry, Marder and coworkers have identified similar design parameters, but based on their observation of the effect of strong donor substitution on stilbene derivatives.[13,65,66] These workers originally noted that bis(di-*n*-butylamino)-(*E*)-stilbene had a two-photon cross-section almost 20 times that of (*E*)-stilbene itself, which they have related to increased electron delocalization in the first excited state, and subsequent increases in the S_1 to S_2 transition dipole moments. This, and similar observations in PPV dimer (oligomer) models, has led to design criteria for enhancement of the two-photon cross-sections. Two distinct chromophore types emerge from these studies:

Type 1: D–A–D

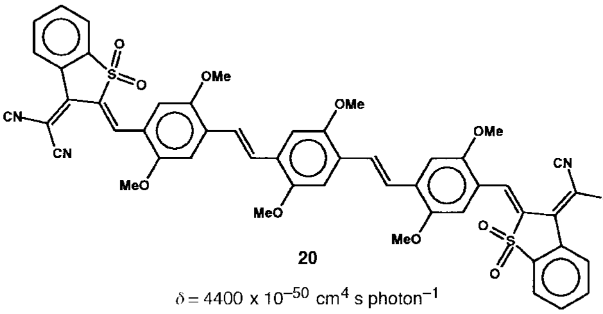
Type 2: A–D–A

Type 1 is typified by a PPV dimer with dibutylamino end groups and CN substitution on the central ring, *e.g.* compound **19**, and Type 2 chromophores are typified by reversing the positions of the D and A groups, *e.g.* compound **20**.



19

$\delta = 1940 \times 10^{-50}$ cm^4 s photon^{-1}

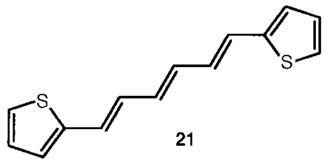


20

$\delta = 4400 \times 10^{-50}$ cm^4 s photon^{-1}

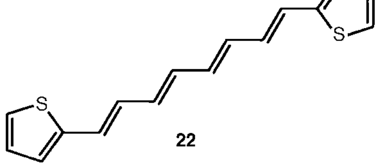
These workers also note that the peak of two-photon absorption occurs at wavelengths significantly shorter than 2 times the one-photon absorption maximum, thus indicating that the two-photon state is energetically above the lowest B_u one-photon state. They also note that two-photon excited state absorption generates a larger 'effective' two-photon absorptivity when ns pulses are compared to ps pulses. Thus, there is an entry into the same excited state manifold as for one-photon optical limiting, but at a lower entry energy. This may have a profound influence on design criteria and/or the possibility that one chromophore may provide OPL throughout the visible region, but by two different mechanisms (bimechanistic OPL).

During the past few years, in collaboration with Science Applications International Corp. and the Materials Directorate at Wright Laboratories (MLPJ) (WPAFB, OH), we have shown *via* fluoresence studies that α,ω-dithienylpolyenes have two-photon absorption states that can provide optical limiting.[67,68] Dithienylpolyenes *e.g.* **21** and **22** can exhibit significantly enhanced two-photon cross-sections for ns pulses, and as such display bimechanistic OPL (RSA and TPA):



21

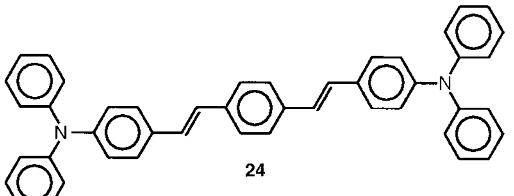
$\sigma_2 = 2500 \times 10^{-50}$ cm^4 s photon^{-1}
(24 ps pulse)



22

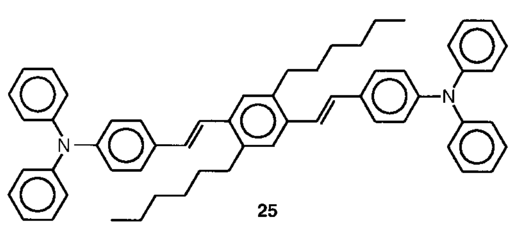
$\sigma_2 = 20000 \times 10^{-50}$ cm^4 s photon^{-1}

We have also recently designed several new TPA chromophores as part of a collaboration with scientists at Laser Photonics Technology, Inc. (Amherst, NY) whose goal is to produce highly efficient molecules with large two-photon cross-sections prone to further excited state absorption.[69] Following similar reasoning to that developed by Perry and Marder,[13] we chose to independently examine the PPV oligomer series. To date we have synthesized several dozen new chromophores with varying structural motifs. We have found large effective two-photon cross-sections for ns pulses, indicative of further induced excited state absorption. Two such examples are compounds **24** and **25**.



24

$\sigma_2 = 6670 \times 10^{-50}$ cm^4 s photon^{-1}
(8ns pulse)



25

$\sigma_2 = 8180 \times 10^{-50}$ cm^4 s photon^{-1}

Chromophore **25** shows excellent optical limiting potential in the range 800–675 nm with a maximum OPL effect at 675 nm ($CHCl_3$ solution, 8 ns pulses, 10 Hz). We are currently focusing on design features which will blue shift the wavelength maximum of two-photon absorption to the 500–600 nm range, and several chromophores are currently under testing with Laser Photonics Technology, Inc. which may satisfy this requirement. TPA chromophores which limit between 500 and 700 nm *via* enhanced two-photon absorption would complement chromophores which limit between 400 and 600 nm by RSA.

One problem that currently plagues the field of two-photon chromophore design is that the various groups involved seldom use the same characterization protocol to define the measured two-photon cross-section. Thus one finds a variety of experimental set-ups, types of focus, and particularly pulse duration. Groups that are primarily interested in the intrinsic cross-section (subsequent transient absorption minimized or eliminated) use shorter pulses (ps or fs) and measure two-photon fluorescence. However, groups that are primarily interested in using two-photon absorption for optical power limiting tend towards encouraging transient state absorption following the initial two-photon absorption process thus inflating the apparent cross-section value. This can be accomplished by using ns pulses, which is germane to the current state-of-the-art in deployed military weapons. Thus, it is important to know the pulse durations when comparing results from different laboratories, since ns cross-sections will almost always appear larger than their ps counterparts. In this review, as far as possible, the pulse durations are indicated for each σ or δ reported value. One additional problem with optical limiters based on two-photon absorption is the caveat that they will in all probability be ineffective against lasers employing microsecond pulses. Most of the chromophores recently reported as effective OPLs *via* TPA employed ns pulses, typically 8–10 ns in duration. The more effective chromophores should, indeed, be tested in the μs time domain, to determine how much, if any, excited state absorption occurs.

Bimechanistic optical power limiter design

It is clear that a great deal of progress has been made over the past decade in the design of organic optical power limiters. It is equally clear that much work remains to be done. We now understand how to generate highly absorbing transient charge states; however, we do not yet know how to simultaneously generate broad band coverage which can counter frequency-agile lasers. While it is true that increased broad band coverage accompanies large increases in the P or BP charge state absorptivities, the magnitude of the increase is hard to predict at the present time. Marder, Perry and coworkers have suggested[66] that broad band coverage might be accomplished by matching two or more two-photon absorbers to cover much of the visible region. However, this approach may sacrifice some ambient transparency. The same may be said of combining two or more RSA chromophores whose excited state transient absorptions may both be of comparable intensities. We also must learn a great deal more about how RSA chromophores can be pumped to yield these transient species, whether PIA *via* photo-induced hole and electron transfer are equally attractive routes, and how to design chromophores (both D and A) whose excited states are even more highly absorbing and convey broad band coverage.

One intriguing possibility is designing chromophores that can provide eye and/or sensor protection by more than one mechanism, as has been mentioned previously. For example, bis(diphenylamino)-(*E*)-stilbene forms highly absorbing bipolarons, as illustrated in Fig. 9, and also exhibits enhanced two-photon absorption on the ns time scale. Dithienylpolyenes show similar behavior. Although the overlap of the maximum bipolaron absorption and the maximum two-photon absorption are still not ideal and do not at the current time provide coverage for the whole visible region, these chromophores may be regarded as prototypical bimechanistic OPLs, providing optical limiting by charge state formation in the high energy end (400–600 nm) and by two-photon absorption at the low energy end (600–800 nm). Detailed studies of the formation of highly absorbing triplets, polarons and bipolarons may provide an even greater understanding of how to provide protection for specific wavelength bands by having more than one transient species present at any given time. When this is coupled with our increasing understanding of design structure–property relationships for large two-photon cross-sections, the combination holds the promise of providing commercially viable optical limiting polymers in the near future.

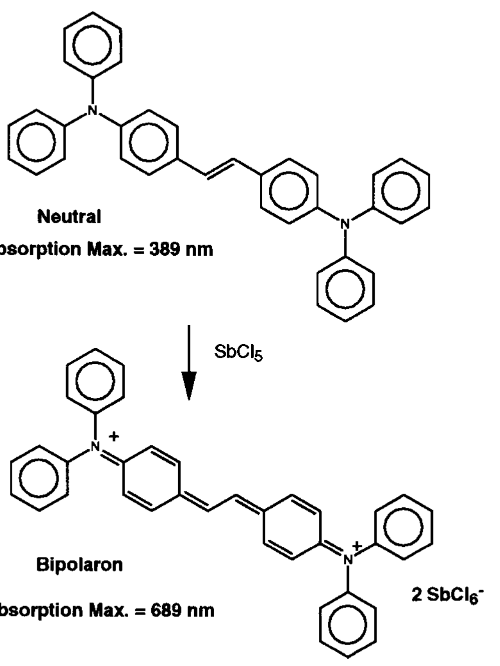


Fig. 9 Formation of bipolaron in bis(diphenylamino)stilbene.

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