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13. ABSTRACT *(Maximum 200 words)*

The work support by the AASERT award has accomplished the following. 1) It has resulted in the development of syntheses for useful precursors to nonlinear optical materials. In particular extended donor substituted aldehydes have been synthesized. 2) It has yielded new chromophores with large second order nonlinear optical properties. 3) It has explored the utility of synthesizing donor-acceptor substituted thiophene vinylene oligomers for second order nonlinear optical applications. 4) It has studies the application of the two level models derived values of molecular nonlinearities to predict the electro-optical coefficient of poled polymer films containing the same chromophores. 5) It is lead to the development of a new class of highly polarized chromophores by incorporation of a new, very strong acceptor. 6). It has demonstrated that phthalocyanine molecules with heavy metals such as lead can leads to efficient optical limiting in the visible region of the electromagnetic spectrum. Finally it has provided a unique opportunity to provided undergraduate students with a background in chemical research and the fundamental ingredients required for approaching scientific problems.

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FINAL TECHNICAL REPORT

2. Objectives.

The primary objectives of this work were to train undergraduate students to perform chemical research and motivate them to enter graduate school in chemistry. Additionally, we sought to develop a variety of molecules whose second-order nonlinearities had been optimized, develop techniques to efficiently synthesize these molecules, and develop second-order molecules that could be covalently attached to polymers. Finally phthalocyanine molecules for optical switching were to be developed.

3. Status of the research effort

The work supported by the AASERT award has accomplished the following. 1) It has resulted in the development of syntheses for useful precursors to nonlinear optical materials. In particular, extended donor substituted aldehydes have been synthesized. 2) It has yielded new chromophores with large second-order nonlinear optical properties. 3) It has explored the utility of synthesizing donor-acceptor substituted thiophene vinylene oligomers for second-order nonlinear optical applications. 4) It has studied the application of the two level models derived values of molecular nonlinearities to predict the electro-optical coefficient of poled polymer films containing the same chromophores. 5) It has led to the development of a new class of highly polarized chromophores by incorporation of a new, very strong acceptor. 6) It has demonstrated that phthalocyanine molecules with heavy metals such as lead can lead to efficient optical limiting in the visible region of the electromagnetic spectrum. Finally, it has provided a unique opportunity to provide undergraduate students with a background in chemical research and the fundamental ingredients required for approaching scientific problems.

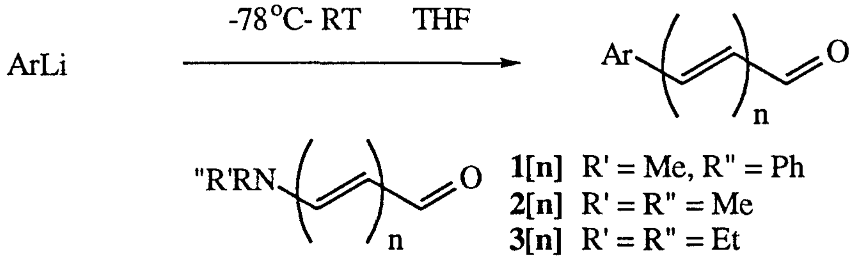
4. Accomplishments/ New Findings.

This AASERT award was geared specifically towards undergraduate training and as such the implementation of the grant is different than most where, one or two graduate students received long-term support. In contrast, here several undergraduates (all US citizens, and some under-represented minorities) performed the research integrated into but distinct from the group's work funded by the parent AFOSR grant . Accordingly, since several students worked part time and over summers, we were able to make an impact on a variety of areas summarized in the six projects below. With few exceptions the student did first-rate work and greatly benefited from their participation in the AASERT program. Several have gone on to graduate school at universities such as Cornell (Cummins), Berkeley (Choong), U of Colorado at Boulder (Kuhout and Niessink). Two are currently applying to medical schools (M. Perry and Yang) or graduate school (Kustedjo). The rest are still completely their course work, required to obtain the undergraduate degrees. Thus, it is my opinion that, this award has been successful in both training and inspiring students whilst producing research that is of benefit to the Air Force. What follows are short summaries of each of the six projects.

Project 1. Convenient Syntheses of Aldehyde Precursors for Nonlinear Optics

Often, the key carbon-carbon bond forming steps in the syntheses of nonlinear optical materials necessitate a variety of polyene aldehyde precursors. Current approaches to polyenal compounds include extensions of shorter aldehydes by either one or two double bonds. We have found a convenient route to convert aromatic halide and heteroaromatic compounds to aromatic polyenals with up to three ethylene repeat units in a reasonably general one-pot process. The procedure was then used to synthesize a variety of precursor aldehydes in order to explore the nonlinear optical properties of variable-length donor-acceptor polyenes.

The key sequence in the general reaction scheme below in Fig. 1 is reminiscent of the synthetic method of Jutz, using Grignard reagents which were treated with N-methyl, N-phenylpropen-1-al (**1[1]**) or its higher vinylog, **1[2]** in yields of 5-95%. In our procedure, we used a wide variety of organolithium reagents available from lithium-halogen exchange of t-butyllithium with aryl bromides or heteroaromatic compounds. The bromides were commercially available or could be synthesized from a facile high yield procedure for bromination of julolidine. Here we demonstrated that organolithium reagents add to known ω–N,N-dialkylaminopolyenals **2[n]** and **3[n]** (n=1-3) to make substituted polyenals or polyene-dialdehydes. The method provides a one-pot synthesis of short (n=2,3) polyenals **4[n]** in as much as 64% yield.



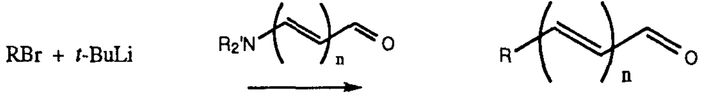
1[n] R' = Me, R" = Ph
2[n] R' = R" = Me
3[n] R' = R" = Et

Fig. 1. Synthesis of vinylogous aryl aldehydes by attach of a aryl lithium reagent on a vinylogous amide.

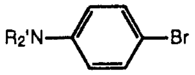
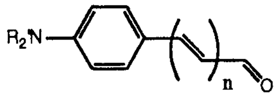
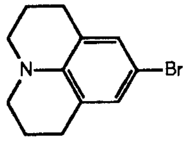
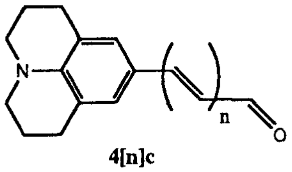
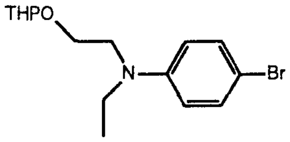
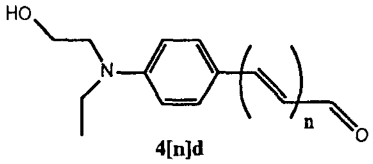
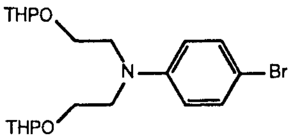
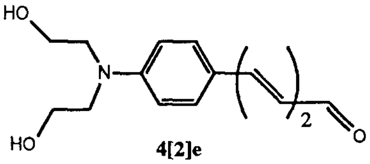
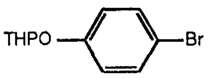
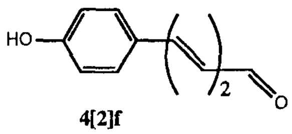
Several families of donor-substituted aldehydes were synthesized and characterized. The structures of the reagents and products as well as yields are given in Table 1. It is especially useful to make comparisons of reactivity and yield based on amide lengths and donor identities in the series **4[n]a** and **4[n]c**. Polyenals containing the commonly-utilized donor group (N,N-dimethylamino)phenyl were obtained in the highest overall yields, probably due to the fact that they are relatively stable under reaction conditions and thus easily isolated in pure form. Interestingly, **4[1]a** and **4[1]c** were formed in substantially lower yields than **4[n]a** and **4[n]c** (n=2 and 3). This is in contrast to the behavior reported for reactions using amides **1[n]**, where yields up to 95% were obtained with n=1 and up to 60% with n=2.

Results presented here demonstrate that an array of aryl-capped polyenals and polyenedials of various conjugation lengths may be produced using a one-pot general synthetic route in satisfactory yield for materials applications. Starting materials are either commercial or synthesized using literature procedures. The method is compatible with protected protic or carbonyl functionalities. Once rapidly produced with the general procedure described here, these versatile aldehydes may be condensed or polycondensed using conventional chemistry.

Table 1. Labeling scheme and yield for aldehydes prepared in this study.



4[n]

RBr	Amide	Product	Yield
	3[2]	 **4[n]a** R' = Me **4[2]b** R' = Bu	n = 2 64%
	2[1] 3[2] 2[3]	 **4[n]c**	n =1 31% n = 2 58% n = 3 51%
	3[2] 2[3]	 **4[n]d**	n = 2 58% n = 3 34%
	3[2]	 **4[2]e**	48%
	3[2]	 **4[2]f**	29%

Project 2. Large First Hyperpolarizabilities of Push-Pull Polyenes with Strong Acceptors

In our attempts to understand the chemical factors leading to large β, we found that in conjugated donor-acceptor molecules, β could be correlated with bond length alternation (BLA), defined as the average difference between the lengths of adjacent carbon-carbon bonds in the polymethine chain. In particular, it was found that a plot of β versus BLA for a simple donor-acceptor polyene exhibits peaks at $\approx |0.04$ Å$|$ of BLA. The BLA of a neutral donor-acceptor molecule can be related to the relative contribution of neutral and charge-separated resonance forms to the ground-state structure. If the neutral form dominates then the molecule will have a low mesomeric dipole moment and have a large magnitude of BLA (|BLA|). If the two forms contribute equally then the molecule will have a rather large mesomeric dipole moment and exhibit a cyanine-like geometry, with essentially no |BLA|. Both theoretical and experimental studies suggest that chromophores that lose substantial aromaticity upon charge separation tend to have |BLA| that are too large for β to be optimized. This is because the aromatic stabilization energy that is lost upon charge separation, raises the energy of that form relative to the neutral form, and therefore diminishes its contribution to the ground-state. By utilizing acceptors such as N,N'-diethylthiobarbituric acid and 3-phenyl-5-isoxazolone, that gain aromaticity upon charge separation, we have shown that very large values of β can be realized relative to the conventional stilbene-type chromophores that possess two phenyl rings in the neutral resonance form. Similar to N,N'-diethylthiobarbituric acid, the N,N'-diethylbarbituric acid acceptor also gains aromaticity upon charge separation (Fig. 1c), and so we hypothesized that chromophores containing this acceptor could have large β as well. In addition, we examined indandione based derivatives. Although the acceptor in these compounds do not gain aromaticity upon charge separation, the benzene ring in the acceptor of indandione based compounds may be brought into more complete conjugation with the rest of the π-electron system (Fig. 1e). This increased conjugation may be thought of as a topological driving force for charge-separation and could therefore lead to a decreased |BLA| relative to stilbene compounds. Accordingly we report the nonlinear optical properties compounds incorporating the N,N'-diethylbarbituric acid acceptor, as well as indandione based acceptors.

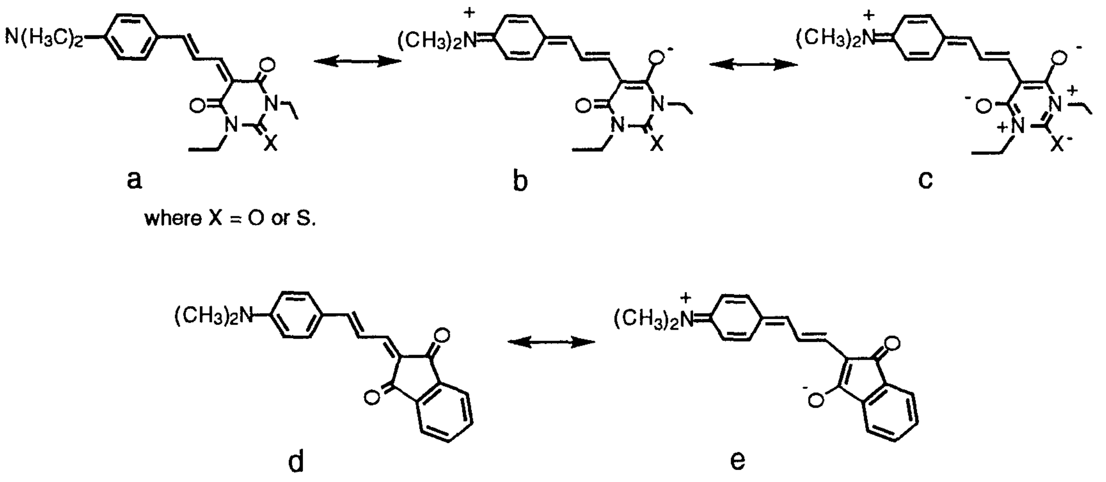
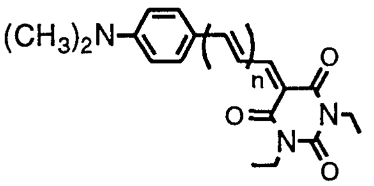
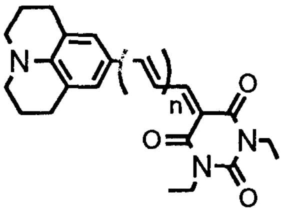


Fig. 1. For a N, N'-diethylbarbituric acid or N, N'-diethylthiobarbituric acid containing compound a: neutral resonance form, b: one of the charge-separated resonance forms, and c: a charge- separated resonance form in which the acceptor ring has aromatic character. For an indandione containing compound d: neutral resonance form and e: a charge-separated resonance form in which the benzene ring of the indandione acceptor is brought into full conjugation with the rest of the π-system.

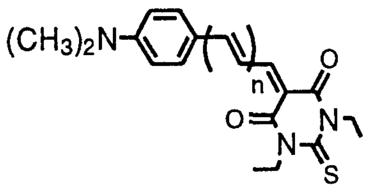
The compounds in this report and their labeling scheme are shown in Fig. 2. All compounds were synthesized by the Knoevenagel condensation of a donor-substituted aldehydes and an active methylene acceptor. For the N,N'-diethylbarbituric acid derived compounds **1[n]** and **2[n]**, and the mono(dicyanomethylidene)indandione derived compounds **8[n]** and **9[n]**, the reactions proceeded acceptably. However, the syntheses of the indandione derivatives, **6[n]** and **7[n]** and the bis(dicyanomethylidene)indandione adducts **10[n]** and **11[n]** were typically troubled with side products that could not be easily separated from the desired product. In the case of the n = 2 and 3 derivatives for series **6[n]** and **7[n]**, a competitive reaction of the active methylene of indandione with a carbonyl of another molecule of indandione leads to significant formation of the known, commercially available, compound, bindone as identified by ^{1}H and ^{13}C NMR spectroscopies. For series **10[n]** and **11[n]**, although it was possible to synthesize most of the compounds with n = 1-3, purification was frustrated by decomposition upon chromatography on silica or upon recrystallization in polar, organic solvents (in particular, the elemental analyses for carbon differed from the theoretical values by as much as 2% even after repeated recrystallizations). Furthermore, for an isolated sample of **11[1]** that was >80% pure by ^{1}H NMR, the observed spectrum was not consistent with an all trans isomer. Accordingly these compounds were not pursued further.



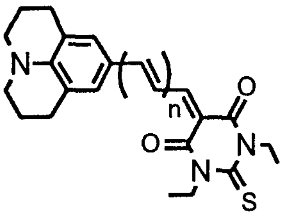
1[n] where n = 0, 1, 2, 3



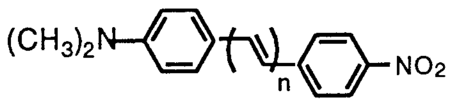
2[n]where n = 0



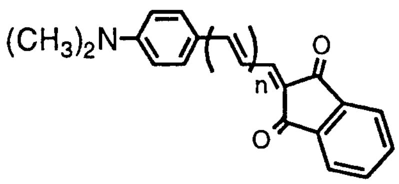
3[n] where n = 0, 1, 2, 3



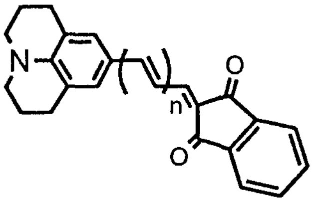
4[n]where n = 0, 1, 2, 3



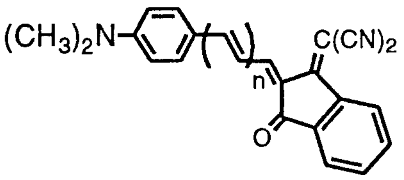
5[n] where n = 1, 2, 3, 4



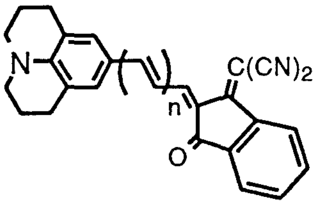
6[n] where n = 0, 1



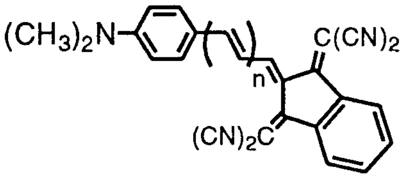
7[n]where n = 0



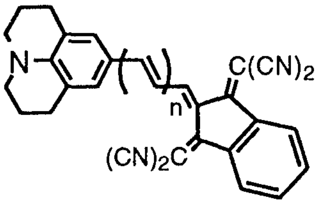
8[n] where n = 0, 2, 3



9[n]where n = 0, 1, 2



10[n]where n = 0



11[n]where n = 0

Fig. 2. Structure and labeling scheme for compounds investigated in this study.

The hyperpolarizabilities of the compounds in series **1[n]**-**11[n]** were measured by electric-field-induced-second-harmonic-generation (EFISH) in chloroform, with 1.907 μm as fundamental radiation. Table 1 summarizes the optical properties for the N,N'-diethylbarbituric acid derivatives, as well as a series of N,N'-diethylthiobarbituric acid and nitrophenyl containing derivatives for comparison.

Table 1. Selected linear and nonlinear optical data for compounds in series **1[n]**-**5[n]**.

Cmpd #	$\mu/10^{-18}$ *(esu)*^{a}	$\beta/10^{-30}$ *(esu)*^{a}	$\beta(0)/10^{-30}$ *(esu)*^{a}	$\mu\beta/10^{-48}$ *(esu)*^{a}	$\mu\beta(0)/10^{-48}$ *(esu)*^{a}
1[0]	5.1	47	34	240	170
1[1]	5.1	170	110	880	560
1[2]	5.8	340	210	1960	1120
1[3]	5.3	660	385	3500	2040
2[0]	5.7	64	45	370	260
3[0]	5.4	70	48	370	260
3[1]	5.7	260	150	1460	860
3[2]	6.2	640	347	3950	2150
3[3]	6.6	1490	772	9830	5100
4[0]	7.0	90	60	610	390
4[1]	6.6	360	190	2210	1160
4[2]	6.3	1140	490	7150	3070
4[3]	8.8	2170	910	19100	8020
5[1]	6.6	73	55	480	360
5[2]	7.6	110	80	810	610
5[3]	8.2	130	95	1070	780
5[4]	9	190	130	1700	1200

a: The error in the measurements is estimated to be ±20%. The β values have not been corrected for the electronic deformation contribution to the EFISH signal.

Table 2 summarizes the optical data for compounds with indandione based acceptors. We report "dispersion-corrected" $\beta(0)$ and $\mu\beta(0)$ values as well, obtained by using a two-level model. As is routinely done, the energy corresponding to the absorption maximum rather than the more correct electronic origin was used as the resonance energy for the two-level model correction. For molecules that absorb at energies corresponding to wavelengths greater than 600 nm, this protocol may lead to significantly overestimated "$\beta(0)$" values (even with the assumption that the two-level model is valid for these compounds). With these caveats in mind, there are still several points that can be inferred from the data in the Tables 1 and 2.

Table 2. Selected linear and nonlinear optical data for compounds in series **6[n]-11[n]**.

Cmpd #	$\mu/10^{-18}$ *(esu)*[a]	$\beta/10^{-30}$ *(esu)*[a]	$\beta(0)/10^{-30}$ *(esu)*[a]	$\mu\beta/10^{-48}$ *(esu)*[a]	$\mu\beta(0)/10^{-48}$ *(esu)*[a]
6[0]	3.7	58	40	220	150
6[1]	3.6	190	120	690	430
7[0]	4.0	100	70	410	270
8[2]	6.9	470	210	3202	1420
8[3]	6.5	750	320	4875	2060
9[0]	6.3	120	70	780	430
9[1]	6.1	270	110	1630	690
9[2]	6.8	530	170	3630	1130
10[0]	6.7	95	50	640	330
11[0]	8.0	90	40	720	320

a: The error in the measurements is estimated to be ±20%. The β values have not been corrected for the electronic deformation contribution to the EFISH signal.

For a given conjugation length, the $\mu\beta$ values for the compounds in Table 1 and those in series **6[n]** and **7[n]**, suggest a relative ordering of the acceptor strength as follows: N,N'-diethylthiobarbituric acid > N,N'-diethylbarbituric acid > indandione> nitrophenyl. The larger nonlinearities in compounds derived from N,N'-diethylthiobarbituric acid relative to those derived from N,N'-diethylbarbituric acid may result from an increased contribution of an aromatic charge-separated, resonance form (Fig. 1c) in the former compounds leading to a more optimal BLA.

The increased contribution of the aromatic resonance form (Fig. 1c) could be due to a more polarized carbon-sulfur bond in the N,N'-diethylthiobarbituric acid acceptor relative to the carbon-oxygen bond in the N,N'-diethylbarbituric acid acceptor. We are currently performing molecular orbital calculations to probe this issue more fully.

In series **1[n]**, **3[n]**, **4[n]** and **6[n]** there is an anomalously large increase in the β values between the n = 0 and n = 1 entries. For the n = 0 derivatives, there are steric interactions between a carbonyl oxygen of the N,N'-diethylbarbituric acid, N,N'-diethylthiobarbituric acid and indandione moieties and one of the ortho hydrogens of the aromatic donor ring. These interactions likely lead to twisting about the bond between the aromatic ring and the central methylidene carbon, thereby reducing the electronic coupling between the donor and acceptor and consequently leading to somewhat diminished nonlinearity. However, upon insertion of an additional double bond in the n = 1 compounds, the molecules can adopt a planar conformation, and we believe that this is responsible in part for the significantly enhanced nonlinearities relative to the n = 0 compounds.

Simple comparisons of effective acceptor strength for "homologous" compounds in series **8[n]**, **9[n]**, **10[n]** and **11[n]** in Table 2, relative to the compounds in Table 1, and those in series **6[n]** and **7[0]** are complicated by concomitant changes in the conjugation length as well as the orientation of the dipole moment vector with respect to β (since EFISH measures the projection of the β tensor on the molecular dipole moment). Thus, we believe that it may not be particularly meaningful to rank the acceptors in compounds series **8[n]**, **9[n]**, **10[n]** and **11[n]** relative others in this study by this means. It is clear however, that for a given value of n, the compounds in Table 2 are not as nonlinear as those in either series **3[n]** or **4[n]**. It is interesting to note that if one compares the β(0) values for **8[2]** to **9[2]**, or **10[0]** to **11[0]**, in each case the compound with the weaker donor (N,N-dimethylaminophenyl) has a *larger* value than the compound with the stronger donor (julolidinyl). Although it is possible that for each pair, a conformational difference could account for the unusual reversal in the normal structure-property trends, it should also be noted that the data is consistent with both compounds **9[2]** and **11[0]** being on the region of the β versus BLA curve, for molecules of that length, where increasing either donor or the acceptor strength should lead to a diminution of the nonlinearity.

The results presented here confirm our hypothesis that molecules with acceptors that can gain aromaticity upon charge separation can have very large second-order nonlinearities relative to compounds with nitrophenyl acceptors. The larger dipole moments and nonlinearities for series **3[n]** and **4[n]**, relative to the others considered in this study and reported elsewhere, suggest that compounds based upon substituted thiobarbituric acids may be promising chromophores for infrared electrooptic poled polymer modulators.

Project 3. Materials with Thiophene Bridges for Second -Order Nonlinear Optical Applications

As noted in Project 2, we have found that compounds containing the N,N' diethythiobarbituric acid and 3-phenyl-5-isoxazolone acceptors can have unprecedented nonlinearities. The N,N'-diethythiobarbituric acid and 3-phenyl-5-isoxazolone compounds with the largest nonlinearities also contain extended polyene chains. Such polyene chains are excellent bridges for charge transport, but compromise the high temperature stability required for poled polymer applications. Jen *et al.* have synthesized and characterized several alkyl amino donor thiophene stilbene compounds with a range of acceptors including nitro, dicyanovinyl and tricyanovinyl. Their results indicate that the thiophene compounds have much greater nonlinearities than the analogous compounds containing phenyl rings. In this proposal, we seek to determine whether it is possible to simultaneously achieve large nonlinearities excellent thermal stability by adding an extra thiophene to the conjugated chain and by using acceptors which gain aromaticity upon charge -separation. We will present the syntheses and electro-optic coefficients of three compounds.

The extensions and addition of the acceptor groups are shown in Fig. 1. The compounds were purified by chromatography on silica, recrystallized and then characterized by UV-visible, ^{1}H and mass spectroscopy, as well as elemental analysis. β values were measured in dioxane solution by EFISH using 1.907 μm fundamental radiation. Non-resonant r_{33} values of a 1 μm thick film with 2 mol % of the chromophore in a PMMA host matrix were obtained by the reflection measurement technique using a 1.3 μm laser diode source.

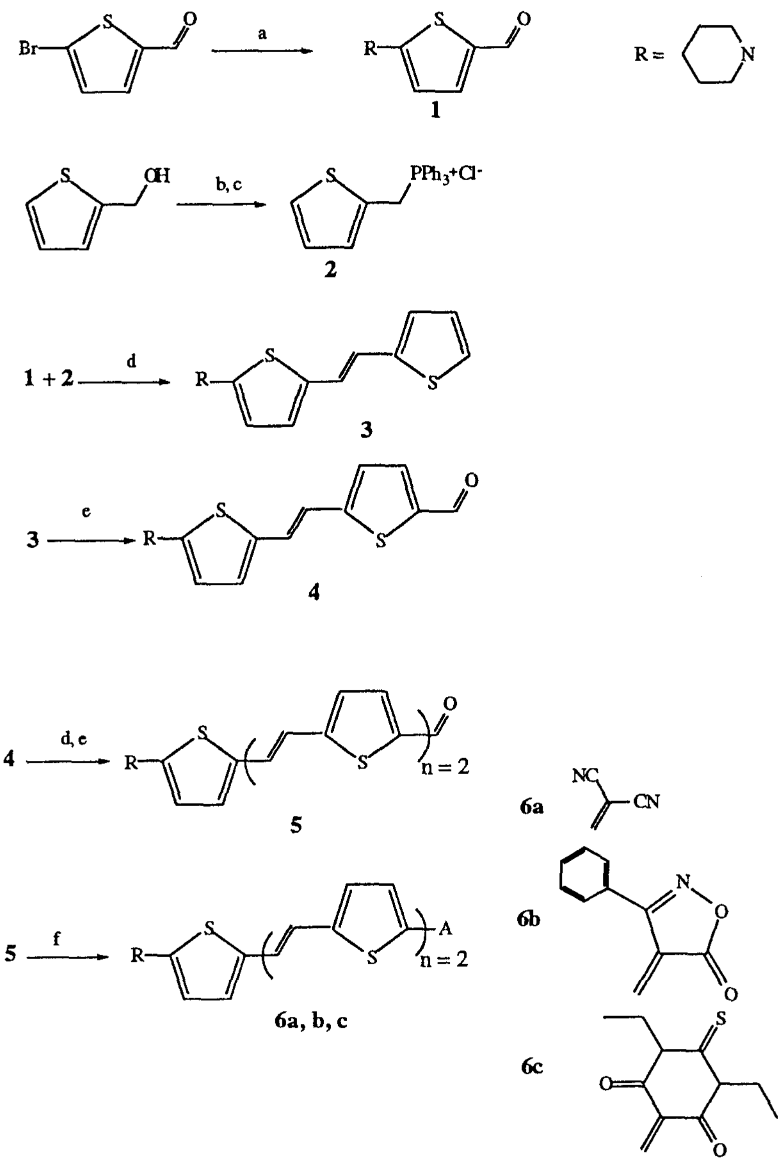
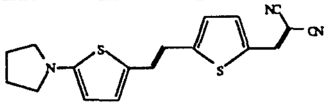
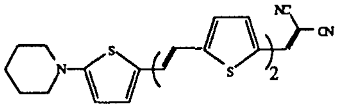
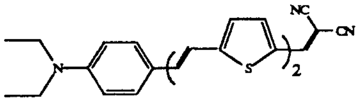
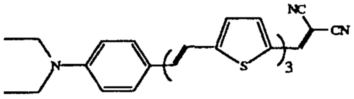
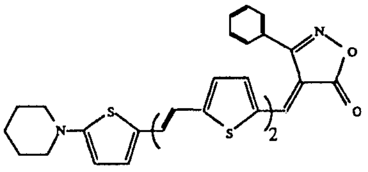
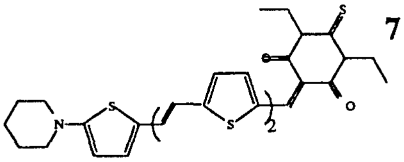


Fig. 1: Reactions schemes for synthesis of the thiophene chromophores. Steps: (a) 1.3 eq. piperidine/DMSO/aliquat/110°C/48 hrs. (b) HCl/-10°C/1 hr. (c) 2 eq triphenyl phosphine/Ethanol/RT/18 hrs. (d) Equimolar **1** + **2** / ethanol / NaOEt/ Argon / 1 hr. (e) i) 1.1 eq. butyl lithium / THF / argon / -50 - RT / 1 hour ii) 1.6 eq. dimethyl formamide / -70°C / argon / 5 mins. iii) 10% HCl. (f) For the dicyanovinyl acceptor **6a**: 1.1 eq. malononitrile/1.5 eq. triethylamine/ $CHCl_3$/reflux/30 mins. For the phenyl isoxazolone acceptor **6b**: 1.5 eq phenyl isoxazolone / 1.5 eq. piperidine / ethanol/ reflux / 30 mins. For the thiobarbituric acid acceptor **6c**: 1.5 eq thiobarbituric acid/ 1.5 eq. piperidine / ethanol/ reflux / 30 mins.

Table 1. Values of the optical absorption maxima (λ_{max}), the dipole moment (μ), the first hyperpolarizability (β) and r_{33}.

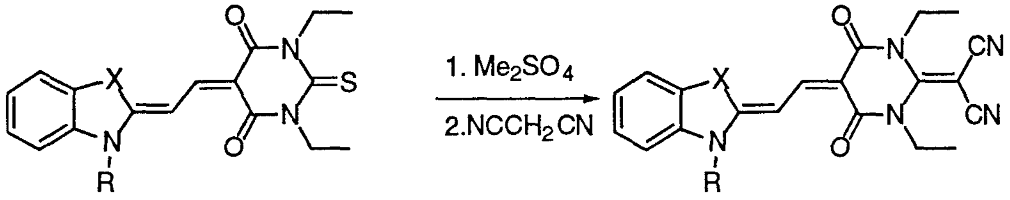
Compound	Cmpd #	λ_{max} (nm)	$\beta\mu/10^{-48}$ (esu)	loading (mol%)	r_{33} (pmV^{-1})
	**9**	584	2680	2.0[a]	2.7[a]
	**6**		4450	1.0	1.1
	**10**	547	2370	-	-
	**11**	556	3910		
	**8**			0.5	0.7
	**7**		5220	1.0	1.7

a: the electro-optics polymers actually have piperdine donor, not pyrollidine.

As can be seen from the table, large nonlinearities are compared to molecules such as dimethylaminonitrostilbene, DANS ($\mu\beta$ = 480) are observed for the thiophene containing chromophores. On comparing the $\mu\beta$ value of compound **6** versus **10** and 11 it can be shown that incorporating a phenyl ring in the chromophore actually decreases the nonlinearity. On comparing the three compounds, **6**, **7** and **8** which contain three thiophene rings only it appears that the $\mu\beta$ values of **7** and **8** which contain acceptors which gain aromaticity have higher nonlinearities.

Project 4. Design and Synthesis of Optimized Nonlinear Optical (NLO) Compounds

In attempt to increase the acceptor strength and group dipole of the thiobarbituric acid acceptors we have explored the synthesis series of dyes incorporating a dicynomethylidenylthiobarbituric acid acceptor. The dyes containing the dicynomethylidenylthiobarbituric acid should be highly polarized and the alignment of dicynomethylidenyl group along the charge transfer axis of the molecule should result in large and negative μβ products. The molecules under study and the basic synthetic scheme is shown in Fig. 1



1a. X = S

2a. X = O

3a. X = $\overset{H_3C\;CH_3}{C}$

1b. X = S

2b. X = O

3b. X = $\overset{H_3C\;CH_3}{C}$

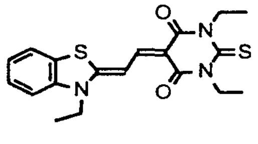
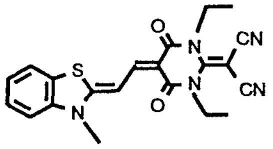
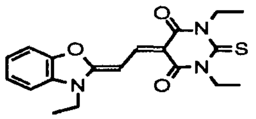
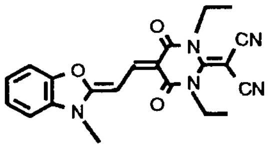
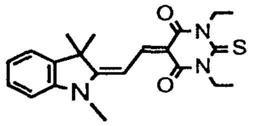
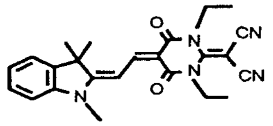
Fig. 1 Synthesis of NLO dyes containing the dicynomethylidenylthiobarbituric acid acceptor.

The first step of the conversion activated the thioketone functionality of the thiobarbituric acid to create an electrophile more suitable for a modified Knoevenagel condensation with malononitrile. The reaction conditions had to be optimized for each type of donor. Structural proof and proof of purity was obtained by the following forms of characterization: IR, NMR, TLC, elemental analysis, mass spectroscopy, and UV-Vis. By these methods the successful synthesis of **1b, 2b,** and **3b** were confirmed.

In an effort to establish a general procedure a number of experimental conditions were attempted. Variables that were controlled include: solvent conditions for the second step, temperature, duration of each step, amounts of reactants, and type of methylating agent. We suspect that the reactivity of the thioketone or its methyl salt is strongly coupled to the strength of the donor. There also were many possible side reactions that were postulated for loss of product. Conversion of the thiobarbituric acid to barbituric acid was observed for reaction conditions where there was competition for an oxygen-containing nucleophile (e.g. water, alcohols) with the malononitrile to displace the intermediate thioketone salt with oxygen. The malononitrile itself was also susceptible to oxidation, especially when the second step was conducted overnight and exposed to air. Polymerization of the starting material was suspected when several times no precipitate was observed but rather a black tar was observed.

The UV/vis spectra and ^{1}H NMR of the compounds support the hypothesis that the dicyanomethylidenylthiobabituric acid is a stronger acceptor than the thiobarbituric acid acceptor. (Table 1). The coupling constants of the olefinic protons on the 2 carbon bridge all became greater after conversion which suggests that the ground state polarization is greater in the dicyanomethylidenylthiobabituric acid chromophores. The small bathochromic shift of λ_{max} suggests that the transparency of molecules remained constant while $|\beta|$ increased (*vide infra*).

Table 1. Characterizing data for compounds **1a-3a** and **1b-3b**

Structure	#	$^3J_{HH}$	λ_{max}	Structure	#	$^3J_{HH}$	λ_{max}
	**1a**	13.8	504		**1b**	14.2	510
	**2a**	14.1	468		**2b**	14.3	476
	**3a**	14.6	494		**3b**	14.9	504

One unexpected observation of these compounds is that they are intensely fluorescent. Currently, the possibility of a two-photon fluorescence effect that may govern this property of these compounds is being explored through fluorimetry and quantum yield measurements with Dr. Joe Perry at the Jet Propulsion Laboratory. The compounds are currently being studied by EFISH by Marguerite Barzoukas in Strasbourg.

Project 5. Preparation and Characterization of Electro-Optic Polymer Films Containing Chromophores with Large Hyperpolarizabilities

Electro-optic polymer films containing chromophores with large molecular hyperpolarizabilities are of current interest for application in electro-active polymer waveguide devices, such as modulators and directional couplers. We have synthesized a large number of dyes with nonlinear optical properties, in particular, a series of extended conjugated dyes that are highly polarized and possess large first hyperpolarizability, β, have recently become available. Studies have been performed earlier on the molecular nonlinear optical properties. In this project, we sought to incorporate a number of such dyes into glassy polymers and to conduct poling and electro-optic studies with the goal of trying to realize large electro-optic coefficients in poled polymer thin films.

A variety of dye polymer systems have been prepared and examined, including several dialkylaminophenyl polyenes and polyenylthiophenes with thiobarbiuturic acid, phenylisoxazolone, and tricyanovinyl acceptors, as well as a potent new acceptor [3-(dicyanomethylidene)-2,3-dihydrobenzothiophen-2-ylidene-1,1,-dioxide] which we will refer to as the Sandoz or SZ acceptor. Films have been prepared using polymethylmethacrylate (PMMA), polycarbonate (PC)and polyimide (PI). The following is a summary of a recent examination of the electro-optic (E/O) coefficients of several dyes, including the "ROITech" dye [((Butyl)$_2$N)Phenyl-(C=C)-ThienylTricyanovinyl] in PMMA. The solutions were prepared using the following procedure. Chlorobenzene was the solvent for spin-coating the dye/polymer films. Samples were baked out on a hot stage for a total of 1 hr, with 1/2 hour at 60°C and 1/2 hour at 80°C. Spinning rates of 0.8-1.5 Krpm were used, yielding films of about 1μm thickness.

Table 1 shows the results of the determination of the dye concentration in the PMMA films, as determined using the absorbance, thickness and the ε_{max} for the dye in CH_2Cl_2 solution. Although solutions were prepared to yield ~ 2 mol % of dye in polymer, the actual concentrations varied down to 0.94%. Table 2 shows the results from the E/O measurements, which were performed using modulated ellipsometry. The values obtained for the first two dyes are lower than theoretically predicted from the EFISH μβ values by a factor of ~2-3. However, the values for the "ROITech" dye and the "Sandoz" dye are higher and in better agreement with prediction, both being only 1.5 times lower than the calculated value. The value r_{33} of 10.5 pm/V for the "Sandoz" dye in PMMA at a loading of only 2 mol% is a rather large electro-optic coefficient and suggests that this dye could yield poled polymers with unprecedented nonlinearity at high loading levels. Polymer films of PC containing the "Sandoz" dye at 20 wt.% were prepared by our collaborators in Switzerland and samples were sent to us for characterization. We performed modulated ellipsometric measurements on these films in the usual manner, wherein the phase shift between polarization components was AC modulated electro-optically in the film and DC modulated with a Soliel-Babinet compensator. These measurements allowed us to assess the relative values of the real and imaginary parts of the electro-optic coefficient. After poling the PC/"Sandoz" film at only 50V/µm poling field (1/2 the value for the samples above) we obtained a very large electro-optic coefficient of 17 pm/V, consistent with the value of 55 pm/V obtained in Switzerland with a poling field of 150V/µm. Furthermore, our measurements show that the imaginary part of the electro-optic coefficient was very small, being < 1% of the real part, consistent with a pure refractive index modulation and no absorption modulation component.

In conclusion, the efforts in the past year have allowed us to reach our goal of obtaining large electro-optic coefficients in poled polymer films. Efforts are underway to incorporate highly nonlinear dyes with high thermal stability in polymers with high glass transition temperatures, in order to realize polymer thin films with large electro-optic coefficients and long term thermal stability.

Table 1. Assessment of dye concentration in polymer.
ε_{max} values are for CH_2Cl_2 solutions.

Dye	λ_{max} CH2Cl2	λ_{max} PMMA	Abs.	thickness µm	ε_{max} $M^{-1}cm^{-1}$	mol % from Abs.
MeNPh-3-TB	610	588	0.996	1.15	69,100	1.25
MeNPh-3-Isoxaz	579	578	0.534	0.92	61,900	0.94
BuNPh-1-ThTCV	706	660	0.901	0.82	48,350	2.3
BuNPh-3-SZ	773	704	1.19	0.89	96,350	1.39

Note on labeling scheme: Me and Bu refers to dialkyl substitution on amino group, Ph = phenyl, the number after the Ph indicates the number of double bonds in the polyene segment, Th = thiophene, TB = thiobarbituric acid, Isoxaz = phenylisoxazolone, TCV = tricyanovinyl, and SZ = 3-(dicyanomethylidene)-2,3-dihydrobenzothiophen-2-ylidene-1,1,-dioxide].

Table 2. ELECTRO-OPTIC Results.

$\lambda = 1300$ nm, $\theta_{inc} = 48.8^{o}$, V_{ac}(rms) = 20, r_{33} calc value obtained using $\mu = 10D$.

Dye	mol % from Abs.	thickness μm	Poling V	r_{33} exp.	μβ EFISH	r_{33} calc. (λ_s,λ_p)
MeNPh-3-TB	1.25	1.15	100	5.2	9,800	10.8
MeNPh-3-Isoxaz	0.94	0.92	100	3.1	8,200	9.7
BuNPh-1-ThTCV	2.3	0.82	100	8.6	6,200	13.0
BuNPh-3-SZ	1.39	0.89	120	10.5	13,500	15.9

r_{33} is in units pm/V.

Project 6. Enhanced Reverse Saturable Absorption and Optical Limiting in Heavy-Atom Substituted Phthalocyanines

Materials that exhibit reverse saturable absorption are currently of interest for use in optical limiting devices for protection of sensors and eyes from energetic light pulses. Reverse saturable absorption (RSA) can occur when states with absorption cross sections (σ_e) in excess of the ground-state cross section (σ_g) are produced. RSA in the visible spectrum due to electronic excitation has been reported for several classes of organic chromophores.[1-7] The effectiveness of RSA molecules for optical limiting is determined mainly by the ratio of cross sections (σ_e/σ_g), which is function of wavelength, and the populations of the states that evolve in time during the pulse. There is considerable interest in approaches to enhancing the performance of RSA chromophores.

RSA and optical limiting in metallophthalocyanines (MPc) such as chloroaluminum phthalocyanine (CAP) and bis(tri-(n-hexyl)siloxy) silicon naphthalocyanine (SiNc) has been investigated[4,7] on picosecond and nanosecond timescales at 532-nm. Picosecond experiments[7] showed that σ_s/σ_g , where s refers to the excited -singlet state, were 10.5 and 14, for CAP and SiNc, respectively. Nanosecond measurements on CAP[8] and SiNc[9] indicate that σ_t/σ_g values (t $\equiv$ triplet state) are about 20 to 50. However, the triplet populations achievable during nanosecond pulses are limited by the small intersystem crossing rates, k_{isc}, for these molecules.[9] These observations suggested to us the use of the "heavy-atom" effect as an approach to enhancing the optical limiting performance of phthalocyanines. By increasing the atomic number of the central metal atom, k_{isc} for the π-electronic states can be increased, allowing more efficient population of the triplet state.

We have examined the RSA performance of MPc's containing metals from groups IIIA (Al, Ga, In) and IVA, (Si, Ge, Sn and Pb). For the Al, Ga and InPc's the molecular structures were of the form (tri-(n-hexyl)siloxy) MPc, whereas the Si, Ge, and SnPc's, of the form bis(tri-(n-hexyl)siloxy) and PbPc was of the form Pbtetra(t-butyl)Pc. These molecules were synthesized according to literature methods.[10] The electronic absorption spectrum of SnPc is shown in Fig. 1, which reveals a strong "Q-band" absorption at 678 nm and a region of weak absorption from ~ 450 to 600 nm. Also shown is the transient triplet-triplet absorption spectrum, which shows a maximum at 510 nm and a bandwidth of ~ 130 nm. The ground-state and triplet-triplet spectra for the other molecules were quite similar, with a slight red shift of the Q-band as the metal becomes heavier.

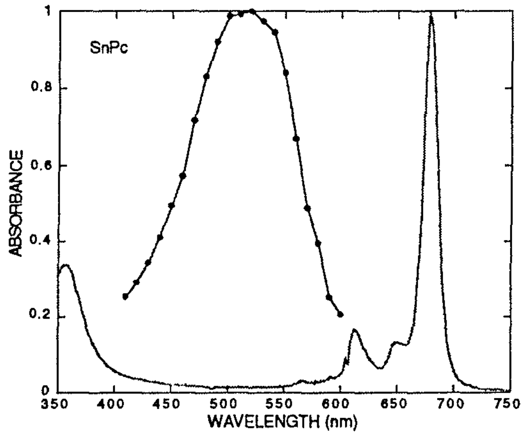


Fig. 1. Electronic absorption spectrum of bis(tri-(n-hexyl)siloxy)SnPc in toluene solution, at 7.1 x 10^{-6} mol/L. Also shown (connected dots) is the transient absorption spectrum (arb. units) of SnPc in toluene obtained 100 ns after excitation at 355 nm.

The triplet quantum yields (Φ_t) and the first excited-singlet lifetimes (τ_s) are given, in Table 1, for the group IIIA and IVA MPc's. Indeed, the τ_s values decrease and the Φ_t values increase as the metal becomes heavier. Thus, the triplet population achievable during a Q-switched laser pulse (e.g 8 ns) is significantly enhanced for the molecules with large Φ_t values. To the extent that the σ_g, σ_s and σ_t values are each similar for the different molecules, one would expect trends of increased nonlinear absorption for the heavier metal Pc's, for pulse widths between ~ 0.5 and 25 ns.

Table 1. Photophysical properties for group IIIA and IVA metal phthalocyanines.

Metal	τ_s (ns) [a]	ϕ_t [b]	f_t (8 ns)
Al	6.9	0.35	0.18
Ga	3.3	0.51	0.42
In	0.3	0.88	0.95
Si	4.5 [c]	0.35 [d]	0.25
Ge	4.2 [c]	0.37 [d]	0.28
Sn	2.0 [c]	0.62	0.63
Pb	0.35	0.92	0.95

a) Determined by picosecond pump/probe measurements at 700 nm, uncertainty is ± 10%.
b) Determined from ground-state bleaching recovery at 700 nm, uncertainty is ± 0.10.
c) Determined using time-correlated photon counting.
d) Estimated from fluorescence quantum yields.

Nanosecond nonlinear transmission measurements were performed using a frequency-doubled Q-switched Nd:YAG laser operating in a near Gaussian transverse mode with an 8-ns (FWHM) multimode pulse envelope. The laser pulses were focussed at the center of 1-cm pathlength solution cells by a 15-cm focal length, 2.5 cm diameter "best form" lens (f/40 geometry) giving a waist spot size of ~13 μm (HW1/e^2M) and a cell entrance spot size of ~63 μm. The transmitted energy was collected by a 2.5 cm diameter, 15 cm focal length lens located to relay the collected energy to a nominal spot size of ~2.0 mm on a photodiode of 1 cm diameter. This geometry afforded essentially total integrated energy detection, as was verified by the following experiment. Measurements with a 50% transmitting aperture stop in front of the detector performed on SiNc in a series of solvents with varying thermal refractive index coefficients (i.e., nitrobenzene to carbon disulfide) showed different transmission responses, whereas without the aperture the responses were the same, thus demonstrating the insensivity of the unapertured detection to refractive spot size changes for pulse energies up to the highest values used.

Nonlinear transmission data obtained with 532-nm, 8-ns laser pulses, for the two series of MPc's are shown in Fig. 2. At incident fluences below about 2 mJ/cm^2, the transmittance coincides with that measured using a spectrophotometer. The nanosecond pulse data for the two series of molecules show the trend of increased nonlinear absorption as the metal becomes heavier, consistent with an enhanced triplet contribution. Measurements on the group IVA MPc's were also performed using 70-picosecond pulses, which are short compared to the timescales for triplet formation in these molecules. The Si, Ge and SnPc's showed the opposite trend of the nonlinear transmittance compared to that for the nanosecond pulses. Since the σ_g values are all about ~ 2.3×10^{-18} cm^2 for these molecules, the picosecond results show that the relative strength of the excited -singlet absorption is opposite to the apparent absorption observed on the nanosecond timescale. These results are consistent with enhanced triplet populations for the heavier-metal molecules during the longer pulses.

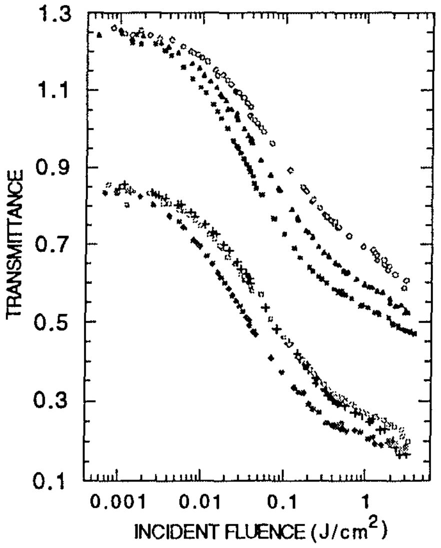


Fig. 2. Nonlinear transmittance of group IIIA (upper set: Al, o; Ga, ▵, In,) and IVA (lower set: Si, +; Ge, ; Sn, •).. Solutions had 84% linear transmission at 532 nm for a 1-cm pathlength which corresponds to a concentration of ~$1.4\mathrm{x}10^{-4}$ mol/L for IIIA and IVA metal Pc's, respectively. The upper curves have been displaced vertically by 0.4, for presentation.

The nonlinear transmission functions for reverse saturable absorbers are expected to range from $T_{lin} = \exp(-\sigma_g \mathrm{No}\ L)$, for low incident fluences, to a saturated transmission, $T_{sat} = \exp(-\sigma_e N_O L)$, for high degrees of excitation. When the pulse width is short compared to the excited-state (say the triplet) lifetime, we can define a saturation fluence, $F_{sat} = h\nu/\sigma_g\Phi_t$. At such high fluences, the ground-state population is largely depleted and excited-state population is distributed between the first excited -singlet and lowest-triplet states. A figure of merit for RSA molecules involving excited -singlet and triplet states can be defined as

$$\sigma_{eff} / \sigma_g = \ln T_{sat} / \ln T_{lin} \approx (\sigma_s f_s + \sigma_t f_t) / \sigma_g$$

where σ_{eff} is an effective excited-state cross section and f_s and f_t are average fractional populations of the excited -singlet and triplet states during the pulse.

From Fig. 2, we estimate that $T_{sat} \sim 0.07$ for InPc. For this molecule f_t (Table 1) is ~ 0.95 , so we can ignore f_s. Using a typical value of σ_t for MPc's of $50\mathrm{x}10^{-18}$ cm^2, we calculate

$T_{sat} = 0.02$. This value is smaller than that observed, yet the fluence exiting the sample was about equal to F_{sat} (0.24 J/cm^2 for InPc), suggesting that uniform on-axis saturation was being approached. In any case, we can use the high fluence transmittance to place a lower bound on σ_{eff}/σ_g for the various molecules. The cross section ratios range from 10 to 16 for the group IIIA MPc's and from 10 to 18 for the group IVA MPc's as the metal becomes heavier.

We have investigated the performance of the heavy-atom phthalocyanines in a simple optical limiting geometry. Figure 3 shows the optical limiting response in an f/8 geometry of PbPc compared with those of the CAP and SiNc, which was previously, to our knowledge, the strongest known absorptive optical limiting dye for nanosecond 532-nm pulses. The strong signal output of the PbPc is lower by factor of 4 and 1.5 compared to CAP and SiNc, respectively. More importantly, the maximum allowable input energy for 3 microjoules output energy, i.e. the energy corresponding to 50% probability for retinal damage to eyes, is a factor of 16 and 2 higher than for CAP and SiNc, respectively. These results demonstrate the enhanced capability (i.e., nonlinear suppression of nanosecond 532 nm pulses by a factor of 81 for a limiter with a linear transmission of 30%, in a f/8 optical system) of the heavy-atom phthalocyanines for optical limiting applications. It should be emphasized that the optical limiting geometries utilized are far from optimal.

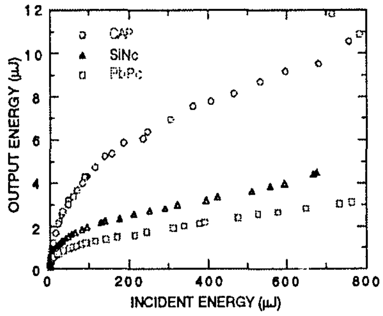


Fig. 3. F/8 optical limiting response of PbPc and SiNc in toluene and CAP in methanol, at 532 nm. Solutions had a linear transmittance of 0.3 at 532 nm; concentrations were 7 x 10^{-4} M for SiNc, 9 x 10^{-4} M for CAP, and 1.3 x 10^{-3} M for PbPc.

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5. Undergraduates who were supported either directly by salary or support for laboratory expenses were:

Graham Cummins
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A Jennifer Niessink
Suzy Kuhout
Karen Kustedjo
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6. Cumulative list of publications (with acknowledgment of funds from AFOSR AASERT award):

1. Mansour, K.; Alvarez, D.; Perry, K.J.; Choong, I.; Marder, S.R.; Perry, J.W. "*Dynamics of Optical Limiting in Heavy-Atom Substituted Phthalocyanines.*" Proc. SPIE, **1853**, (1993), 132.

2. Gilmour, S; Jen, A.; Marder, S. R.; Niessink, A. J.; Perry, J. W.; Skindhøj, J.; Cai, M. " *Second-order Nonlinear Optical Properties of Thiophene Containing Chromophores with Extended Conjugation* ." in Materials Research Society Symposium Proceedings Vol. 328, Garito, A. F.; Jen, A.K.-Y.; Lee, Y.-C.; Dalton, L. R. eds, Materials Research Society, Pittsburgh, 1994. p. 485

3. Bourhill, G.; Cheng, L.-T.; Lee, G.; Marder, S. R.; Perry, J. W.; Perry, M. J.; Tiemann, B. G. "*The Relationship Between Second-Order Nonlinear Optical Properties and Ground-State Polarization.*" in Materials Research Society Symposium Proceedings Vol. 328, Garito, A. F.; Jen, A.K.-Y.; Lee, Y.-C.; Dalton, L. R. eds, Materials Research Society, Pittsburgh, 1994. p. 625.

5. Perry, J.W.; Mansour, K.; Marder, S.R.; Alvarez, Jr., D.; Perry, K.J.; Choong, I. "*Enhanced Reverse Saturable Absorption and Optical Limiting in Heavy-Atom Substituted Phthalocyanines.*" Optics Letters, **19**, 625 (1994).

6. Marder S.R.; Cheng, L.-T.; Tiemann, B.G.; Friedli, A.C.; Yang, E. "*Large First Hyperpolarizabilities in Push-Pull Polyenes with Strong Acceptors.* " Nonlinear Optics, **9**, 213 (1995).

7. Friedli, A.C.; Yang, E.; Marder, S.R. "*A Convenient Synthesis of Polyenals with Extended Conjugation.*" submitted.

8. Skindhøj, J.; Bourhill, G.; Gilmour, S.; Tiemann, B. G.; Mansour, K; Perry. K. J.; Cheng, L.-T.; Marder S. R.; Perry, J. W. "*Electro-Optics Coefficients of Guest -Host Polymers Containing Chromophores with Large First Hyperpolarizabilities: A Test of the Two-State Oriented Gas Model.*" in preparation.

7. Interactions:

a. Papers presented at scientific conferences (not AASERT funds were used to support travel by non AASERT personnel):

1. Marder S.R.; Cheng, L.-T.; Gorman, C.B.; Murdoch, J.; Tiemann, B. G. "*Optimizing the Second-Order Optical Nonlinearities of Organic Molecules: Asymmetric cyanines and highly polarized polyenes.*" Presented at Society for Photooptical and Instrumentation Engineers National Meeting, San Diego, CA, July 20-25, 1992. (Invited Lecture).
2. Mansour, K.; Alvarez, D.; Perry, K.J.; Choong, I.; Marder, S.R.; Perry, J.W. "*Dynamics of Optical Limiting in Heavy-Atom Substituted Phthalocyanines.*" Presented at Organic and Biological Optoelectronics: Electro-Optics and Lasers Applications in Science and Engineering 93. Los Angeles, CA, January 16-23, 1993.
3. Mansour, K.; Alvarez, D.; Perry, K.J.; Choong, I.; Marder, S.R.; Perry, J.W. "*Dynamics of Optical Limiting in Heavy-Atom Substituted Phthalocyanines.*" Presented at Organic and Biological Optoelectronics: Electro-Optics and Lasers Applications in Science and Engineering 93. Los Angeles, CA, January 16-23, 1993.
4. Mansour, K.; Alvarez, Jr., D.; Choong, I.; Perry, K.J.; Marder, S.R.; Perry, J.W. "*Nonlinear Absorption in Metallophthalocyanines.*" Presented at CLEO/QELS. Baltimore, MD, May 2-7, 1993.
5. Cheng, L.-T. Friedli, A.C.; Gilmour, S.; Gorman, C. B.; Marder, S. R.; Perry, J.W.; Perry, K. J.; Skindhøj, J.; Tiemann, B. G., Yang, E. "*The Effect of Bond Length Alternation on The Molecular Hyperpolarizabilities of Polymethine Dyes*" Presented at, The International Conference on Organic Nonlinear Optics, Val Thorens, (France) January 9-13, 1994.
6. Gilmour, S.; Perry, J.W.; Skindhøj, J.; Marder, S. R.; Niessink, A. J.; Cheng, L.-T. "*Second-Order Nonlinear Optical Properties of Polymers Containing Polyene and Thiophene Based Dyes*" Presented at, OL/ LASE Conference, Los Angeles, CA, January 23-29, 1994.

b. Consultative and advisory functions. None.

c. Transitions.

The work performed in this project has in large part been performed in collaboration with Alex Jen of ROITech who is exploring the potential of molecules synthesized by the undergraduates, for incorporation into second-order nonlinear optical polymers. In addition, samples of metal substituted phthalocyanines synthesized as part of the project have been transitioned to Wright Laboratory for systems testing as optical limiting materials.

8. New discoveries, inventions or patent disclosures. None

9. Honors/Awards. None