REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY *(Leave blank)*	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED FINAL 30 Sep 91 TO 29 Sep 94

4. TITLE AND SUBTITLE

NONLINEAR OPTICAL PROCESSES IN POLYMER FILMS

5. FUNDING NUMBERS

F49620-91-C-0100
61101E
8103/04

6. AUTHOR(S)

Dr A.F. Garito

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

Dept of Physics
University of Pennsylvania
David Rittenhouse Laboratory
Philadelphia PA 19104-3246

8. PERFORMING ORGANIZATION REPORT NUMBER

AFOSR-TR-95-025[illegible]

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

AFOSR/NL
110 Duncan Ave Suite B115
Bolling AFB DC 20332-0001

Dr Charles Y-C. Lee

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

DTIC
S ELECTE D
APR 1 9 1995
C

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION / AVAILABILITY STATEMENT

Approved for public release;
distribution unlimited.

12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*

Electrooptic organic polymer thin films show great promise for applications in integrated optoelectronic devices. These materials are usually formed as guest-host polymer systems that exhibit large second order nonlinear optical coefficients, low DC and microwave dielectric constants, and broad optical transparency ranges. The major obstacle to the development of practical polymer optoelectronic devices has been the thermal stability of the electrooptic coefficients of the guest-host polymer films. Current research has focused on finding new guest dye chromophores that possess large nonlinear optical coefficients and thermal stabilities greater than 300 degree. We summarize our recent development of a new class of high termal stability fused-ring chromophores, 1,8-naphthoylene benzimidazoles, based on computer aided molecular design and experimental measurements of microscopic second order optical coefficients. The new chromophores were designed for their structural similarity to polyimide repeat units and consequent easy incorporation into high temperature host polyimides. They are highly colored, comparatively soluble in common organic solvents, and very stable in polyamic acid solutions. They possess relatively large second order optical coefficients and thermal stabilities exceeding 340 degree.

14. SUBJECT TERMS	15. NUMBER OF PAGES
	16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT

NSN 7540-01-280-5500

Standard Form 298 (Rev 2-89)
Prescribed by ANSI Std Z39-18
298-102

Abstract

Electrooptic organic polymer thin films show great promise for applications in integrated optoelectronic devices. These materials are usually formed as guest-host polymer systems that exhibit large second order nonlinear optical coefficients, low DC and microwave dielectric constants, and broad optical transparency ranges. The major obstacle to the development of practical polymer optoelectronic devices has been the thermal stability of the electrooptic coefficients of the guest-host polymer films. Current research has focused on finding new guest dye chromophores that possess large nonlinear optical coefficients and thermal stabilities greater than 300°C.

We summarize our recent development of a new class of high thermal stability fused-ring chromophores, 1,8-naphthoylene benzimidazoles, based on computer aided molecular design and experimental meaurements of microscopic second order optical coefficients. The new chromophores were designed for their structural similarity to polyimide repeat units and consequent easy incorporation into high temperature host polyimides. They are highly colored, comparatively soluble in common organic solvents, and very stable in polyamic acid solutions. They possess relatively large second order optical coefficients and thermal stabilities exceeding 340°C. Fluorine substitution raises the nolinear optical coefficients while the thermal stability increases to greater than 420 °C.

FINAL TECHNICAL REPORT

30 September 93 - 29 September 94

Nonlinear Optical Processes in Polymeric Films

PRINCIPAL INVESTIGATOR:	Professor Anthony F. Garito	(215) 898-5810
PROGRAM MANAGER:	Dr. Charles Lee	(202) 767-4960

ARPA ORDER: 8103 PROGRAM CODE: 0D10

CONTRACTOR: University of Pennsylvania

EFFECTIVE DATE: 30 September 91 EXPIRATION DATE: 29 September 94

CONTRACT NUMBER: F49620-91-C-0100 AMOUNT: $1,880,090

Sponsored by
Advanced Research Projects Agency
DARPA Order No. 8103

Monitored by
AFOSR Under Contract # F49620-91-C-0100

Table of Contents

1. Overview and Summary of New High Thermal Stabilty Electrooptic Chromophore Research

Electrooptic organic polymer thin films show great promise for applications in integrated optoelectronic devices. These materials exhibit large second order nonlinear optical coefficients, low DC and microwave dielectric constants, and broad optical transparency ranges extending from near infrared to visible wavelengths. The amorphous polymer films are formed by spin-coating, spraying, or dipping, and then aligned in the presence of a DC electric field, a procedure called electric field poling that induces the required macroscopic asymmetry. These material processing steps require much less time and effort than the single crystal growth and polishing procedures used for inorganic systems such as lithium niobate and gallium arsenide.

Up to the present time, the major obstacle to the development of practical polymer optoelectronic devices is the thermal stability of the electrooptic coefficients of the aligned polymer films. Initial research efforts have often involved polymethyl methacrylate (PMMA), whose low glass transition temperature leads to a loss of macroscopic alignment and a resulting decrease in the electrooptic coefficient at device fabrication and operating temperatures.

High thermal stability polyimides are well known in the microelectronics industry for their ease of thin fim processing, low thermal expansion coefficients, and high chemical stability at high temperatures.Recent research has shown that polyimides are well suited to the role of polymer host in guest-host systems. Poled guest-host thin film systems using polyimide have exhibited electrooptic coefficients that remain stable up to 300°C.

The focus of current research in the field has shifted towards finding guest dye molecules that possess large nonlinear optical coefficients, yet at the same time retain high thermal stability greater than 300°C. We summarize here our recent development of a new class of high thermal stability fused-ring chromophores based on computer aided molecular design and experimental meaurements of microscopic second order optical coefficients.

The new chromophores were designed for their structural similarity to polyimide repeat units and consequent easy incorporation into host polyimides. Members of this class are highly colored, comparatively soluble in common organic solvents, and very stable in polyamic acid solutions. The thermal stabilities of the pure chromophores have been studied and found to exceed temperatures beyond 340°C. By substituting fluorine for hydrogen in the new chromophores, the thermal stability was found to increase to greater than 420 °C.--the highest thermal stabilty achieved so far.

During the present funded research period, a new tunable laser source was designed and implemented to carry out measurements aimed toward understanding of the nonlinear optical processes at microscopic molecular levels in the new high temperature stable chromophores. The chromophores possess comparatively large second order nonlinear optical coefficients, comparable to those of well-studied dye molecules such as DCM or DR1. Significantly, excellent agreement was achieved between theory and experiment, demonstrating our depth of understanding of this new materials class.

Our understanding of the microscopic features of the new high thermal stability chromophores was achieved through computer simulations of nonlinear optical processes occuring in organnic structures. We used unique Cray supercomputer source code that we have developed over the years. The new chromophore structures were actually developed by molecular computer aided design following structural guidelines that simulate basic features of the host polyimde repeat units. A large number of molecular structures were simulated prior to actual synthesis, illustrating many advantages provided by the combination of computer simulation and material synthesis, especially in terms of time, labor, and materials.

Importantly, the new high thermal stability chromophores are the first realization of large elecrooptic guest molecules to qualify under semiconductor fabrication conditions.

2. Newly Designed EO Chromophores in Fluorinated Polyimides

As new electrooptic(EO) materials are being developed for applications in integrated optic devices, an important phase will be a variety of qualifying tests under conditions simulating the fabrication, assembly, and end-use device conditions. New high perfomance optical grade fluorinated polyimides have been developed to act both as passive waveguides and as hosts for electooptic chromophores in active regions of devices. Oftentimes in evaluation tests, new chromophores cannot withstand the stringent thermal and chemical stabilty conditions required in polyimide-based fabrication processes and device assembly steps.

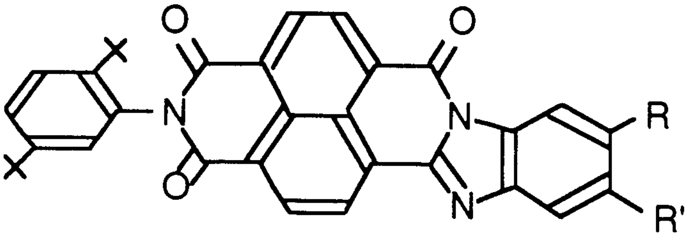


Fig. 1

Earlier, we had reported the development of a new class of high thermal stability fused-ring chromophores (Figure1) designed for their structural similarity to polyimide repeat units and eventual incorporation into host polyimides[1]. Recently, the first results from successful qualifing tests in the optical polyimides have been obtained. The example of testing under different polyimide cure conditions is illustrated by the refractive index data in Figure 2. In contrast to the severe sublimation/diffusion of DCM dye at nominally low polyimide processing temperatures, the newly designed EO chomophores retain their optical properties to greater than 365°C as illustrated by the case for R=N(CH_3)$_2$ and R'=H.

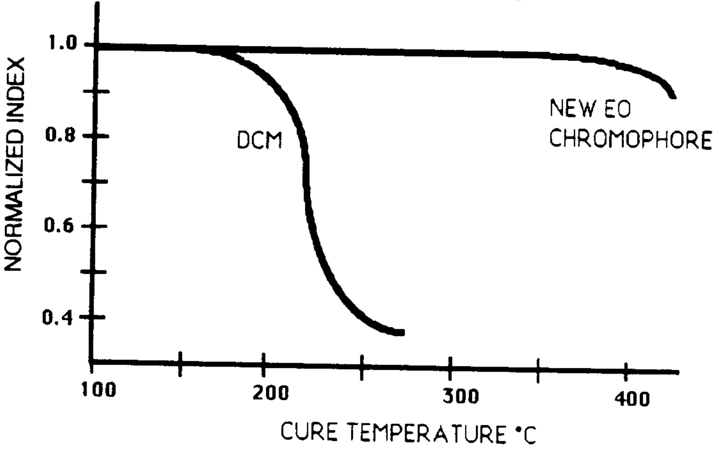


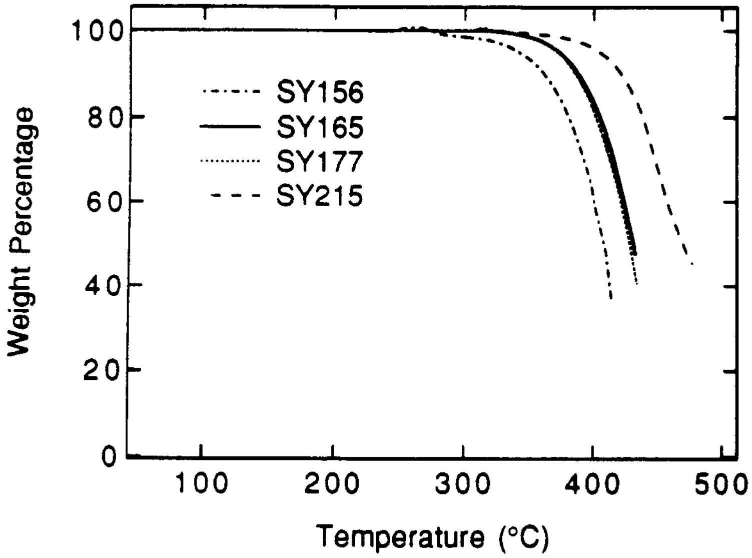
Fig. 2

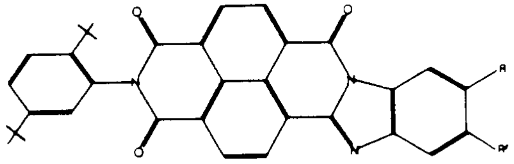
---

[1] R.F. Shi, M.H. Wu, S. Yamada, Y.M. Cai, and A.F. Garito, App. Phys. Lett. **63**, 1173(1993).

3. High Temperature Chromophore Thermal Analysis

In the search of new nonlinear optical materials suitable for integrated device applications, one important criterion is the thermal stability of the materials to satisfy conditions in polyimide-based fabrication processes and device assembly steps. Earlier, we had reported the development of a new class of high temperature fused-ring chromophores, 1,8-naphthoylene-benzimidoles. Here we summarize our recent systematic thermogravimetric analysis (TGA) of this new class.





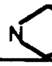
R	R'	Material	3% DT(°C)
H	H	SY156	325
H	OCH_3	SY165	365
NH_2	H	SY177	360
	H	SY215	385

Figure 1

Shown in Figure 1 are the TGA data of the new series indicating the weight percentage of the original sample in pure form as a function of temperature in flowing Argon environment. We notice that for the parent compound (SY156), the decomposition temperature is very high, reaching 340°C for the 5% weight loss. As the H groups are substituted with various donor groups, not only do we gain enhanced second order responses, we also have increased thermal stabilities. The most interesting feature lies with the arcylated amino compound (SY215), which has the standard $\mu\beta$ of $(1500\pm150)\times10^{-48}$ esu in solution with CH_2Cl_2 at λ=1.908 μm (to be reported), the pure sample achieves the best thermal stability so far, with the 5% weight loss temperature in excess of 398°C. This excellent thermal behavior, combined with large molecular second order responses, and good solubility and uniformality in polyimides, should lead to the realization of high EO coefficient polymer systems to qualify under real semiconductor fabrication conditions, thereby representing a critical step in the progress towards a true optical device technology.

4. Nonlinear Optical Properties of High Temperature EO Chromophores

Electrooptic (EO) organic polymer films show great promise for integrated optoelectronic device applications. Molecules used in these films must possess both large nonlinear optical coefficients and sufficient thermal stability to withstand the high temperatures required by the poling and device fabrication processes.[1] Recent thermal gravimetric analysis experiments have shown that a new fused-ring guest molecule designed for incorporation into host polyimides, 1,8-naphthoylene-(3'-pyrrolidino)-benzimidazole-4,5-dicarbox-N-(2,5- di-tert-butyl) phenylimide (hereafter SY215, shown in Fig. 1 along with its linear absorption spectrum), exhibits less than 5% weight loss until approximately 400°C in its pure form.[2] We report here measurements of the dispersion of the second order optical susceptibility β of SY215 in the near infrared region. The experimental results are compared to calculations using multiple-excited configuration interaction theory.

The second order nonlinear optical properties of SY215 in liquid CH_2Cl_2 solution were characterized using DC-field induced second harmonic generation (DCSHG). The probe beam was supplied by a tunable source based on optical parametric generation and amplification in KTP crystals.[3] DCSHG measurements were made at seven wavelengths in the near infrared region ranging from 1600 nm to 1960 nm. Values of $\mu_x\beta_x(-2\omega;\omega,\omega)+5kT<\gamma(-2\omega;\omega,\omega,0)>$ extracted from the data are shown as points in Fig. 2.

Calculations of the nonlinear optical properties reveal the origin of the large nonlinear optical response. The largest contribution to $\beta_{xxx}(-2\omega;\omega,\omega)$, the dominant component of $\beta_x(-2\omega;\omega,\omega)$, arises from the virtual excitation sequence $S_0 \rightarrow S_1 \rightarrow S_1 \rightarrow S_0$, where S_0 denotes the ground state and S_1 the first excited state.

---

[1] R.F. Shi, M.H. Wu, S. Yamada, Y.M. Cai, and A.F. Garito, App. Phys. Lett. **63**, 1173(1993).

[2] S. Yamada, Y.M. Cai, R.F. Shi, M.H. Wu, and A.F. Garito, Mat. Res. Soc. Proc., 1993 (to be published).

[3] M.H. Wu, Y.M. Cai, and A.F. Garito, in *Quantum Electronics and Laser Science Conference*, 1993 OSA Technical Digest Series, Vol. 3 (Optical Society of America, Washington, DC, 1993), pp. 59-60.

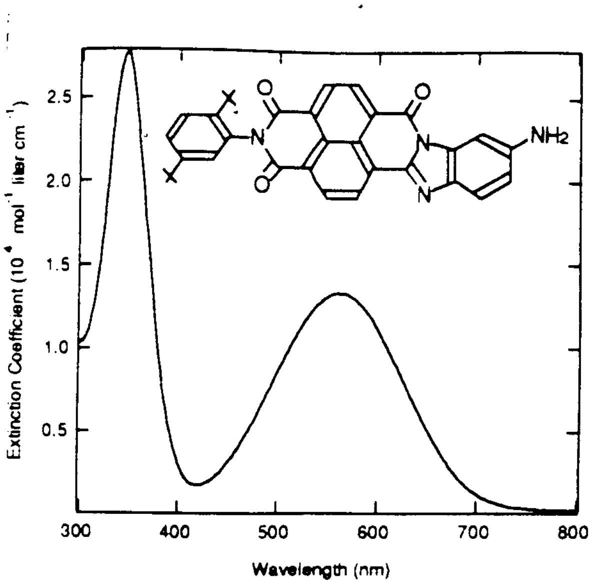


Fig. 1. Ground state linear absorption spectrum of SY215 in solution with dichloromethane (CH_2Cl_2). Inset: Schematic molecular structure diagram of SY215.

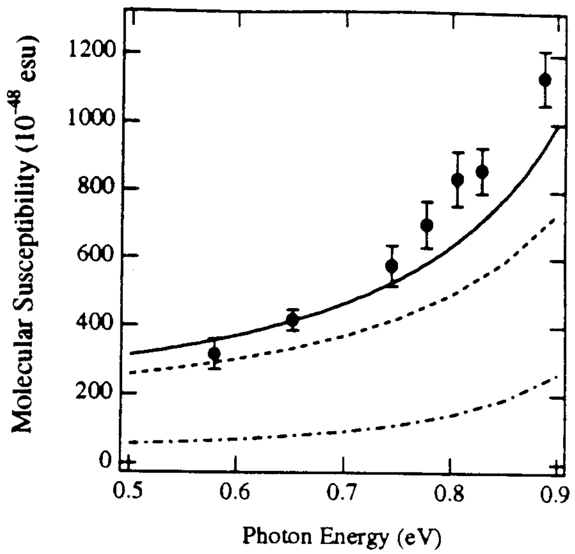


Fig. 2 Experimental (points) and theoretical (solid line) values for $\mu_x\beta_x(-2\omega;\omega,\omega)$ $+<\gamma(-2\omega;\omega,\omega,0)>5kT$ as a function of photon energy. μ_x is measured to be 4.4 D. The room temperature T is taken to be 300 K.

The charge separated nature of the first excited state results in both a large dipole moment difference and a large transition moment between S_0 and S_1 states. The contour diagram of the difference in the charge density distribution between the S_0 and S_1 states shown in Fig. 3(a) clearly illustrates the transfer of π electrons from the donor substituted imidazole ring to the naphthoylene moiety, and consequent large charge separation. The contour diagram of the transition density matrix between S_0 and S_1 shown in Fig. 3(b) exhibits similar features. Contributions due to virtual excitation sequences involving higher lying excited states not considered in the standard two-level model decreased the value of $\beta_{xxx}(-2\omega;\omega,\omega)$ by 27%.

Direct comparison of the theoretical and experimental values obtained from DCSHG measurements, which include a contribution from $<\gamma(-2\omega;\omega,\omega,0)>$, entails the calculation of $<\gamma(-2\omega;\omega,\omega,0)>$. The calculated dispersion of $\mu_x\beta_x(-2\omega;\omega,\omega)+5kT<\gamma(-2\omega;\omega,\omega,0)>$ is shown as the solid line in Fig 2. Both the theoretical and experimental results, which are fairly well matched in the entire region, show the dispersion resulting from the 2ω resonance due to the $S_0 \rightarrow S_1$ transition at 1.86 eV. The value of β_x can be estimated by subtracting the calculated third order contribution (23%) from the total, resulting in a value of 268×10^{-30} esu for $\beta_x(-2\omega;\omega,\omega)$ at $h\omega=0.65$ eV. SY215, with its high thermal stability and large nonlinear susceptibility, which is larger than that of the commonly studied EO dye, dimethylamino-nitrostilbene (DANS), is thus an excellent candidate material for optoelectronic device applications.

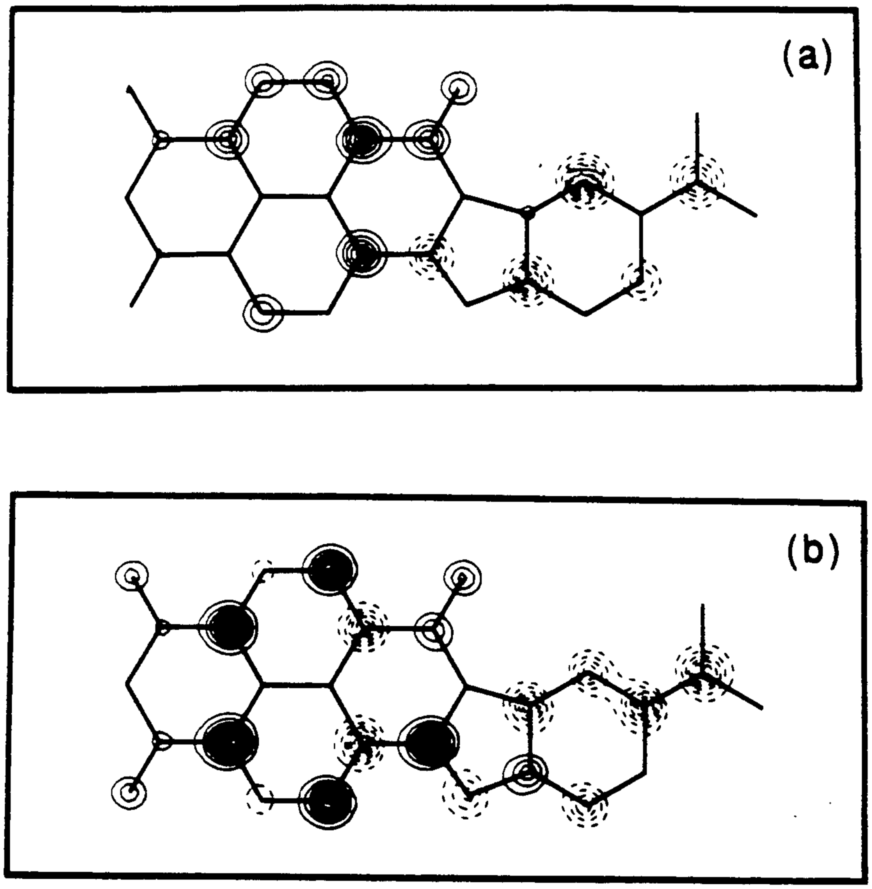
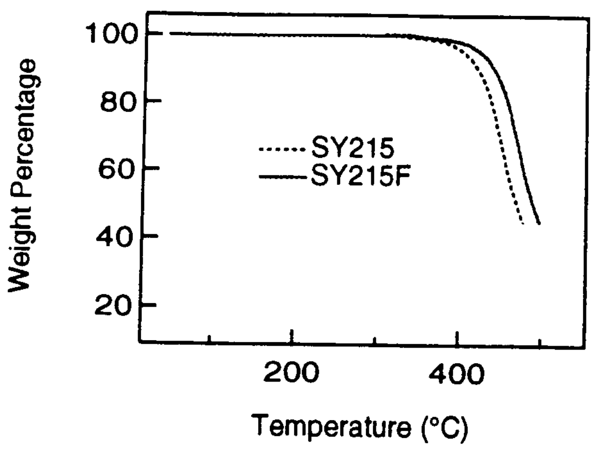
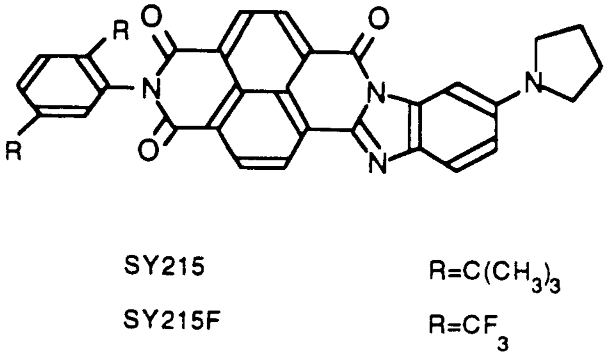


Fig. 3. Contour diagrams of (a) the transition density matrix $\rho_{0,1}$ between the ground state S_0 and the first excited state S_1.and (b) the corresponding difference in the electron charge density distribution. Solid lines and dashed lines correspond to increased and decreased charge density, respectively, and the contour cut is taken at 0.4Å above the molecular plane. The dipole moment difference and the transition moment between the S_1 and S_0 states are found to be 16.8 D and 7.6 D, respectively.

5. Properties of High Thermal Stability Fluorinated EO Chromophores

In previous studies, we showed how to reduce optical attenuation in high thermal stability EO chromophores by substituting hydrocarbon t-butyl groups of the SY series with CF_3 groups as in SY215 (see figure below), a typical example of the new chromophore class. We reported then that the linear optical properties of the hydrocarbon and new fluorinated chromophores are essentially the same. Here we describe initial results in the comparison of the thermal and second order optical properties of the two EO chromophore series.





Thermal analyses, as illustrated by the TGA data above, reveal that compared to the t-butyl substituted SY215, which retains 5% weight loss at 398°C, the new CF_3 substituted chromophore SY215F possesses an even higher decomposition temperature. The thermal stability of SY215F is enhanced by about 20°C compared to SY215. Accompanying the increased thermal stability is an increased second order optical response for the new fluorinated series. DCSHG measurements show that $\mu\beta$ increases by about 40%. For example, at $\lambda = 1800$ nm, values of $\mu\beta + \langle\gamma\rangle 5kT$ for SY215 and SY215F are found to be 1850×10^{-48} and 2600×10^{-48} esu, respectively.

In the new fluorinated EO chromophores, the CF_3 substitution has led to higher thermal stability, improved second order optical properties, and enhanced compatibility with host optical polyimides. These important features, combined with reduced optical loss in the near infrared region, hopefully will provide yet another major step in the development of organic materials suitable for real device applications.

6. Third Harmonic Generation Dispersion Study of Squaraine Dyes

Earlier, we had reported the experimental observation of high-lying two-photon states that are critical to the negative third order optical responses in squaraine dyes using femtosecond pump-probe techniques[1]. In this section, we discuss results from our recent full third harmonic dispersion measurements on squaraine dyes.

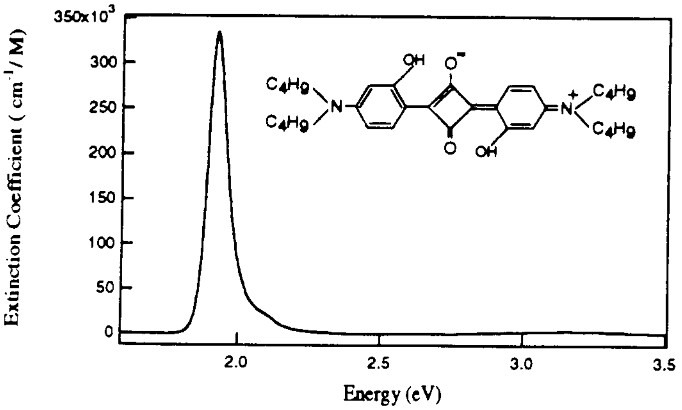


Fig. 1

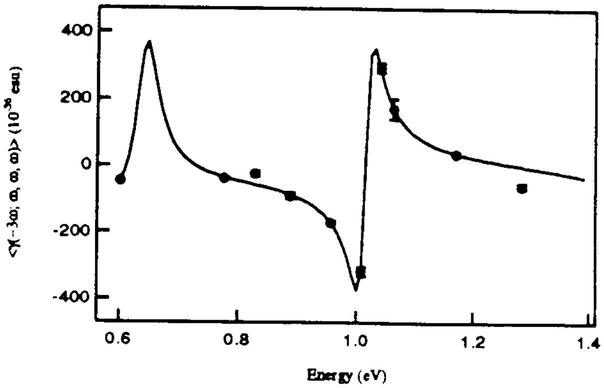


Fig. 2

	$1^1A_g \rightarrow 1^1B_u$	$1^1B_u \rightarrow 2^1A_g$	$1^1B_u \rightarrow n^1A_g$
μ (D)	12.4	2.05 ± 0.05	14.5 ± 0.1
E(eV)	1.92	2.03 ± 0.01	3.62 ± 0.03
Γ (eV)	0.067	0.026 ± 0.004	0.030 ± 0.015

Fig. 1 shows the linear optical spectrum of BSQ squaraine dye in chloroform solution with a sharp major absorption peak at 1.92 eV (647 nm). The large transparency window is ideally suited for third harmonic generation (THG) dispersion measurements. Fig. 2 shows the full dispersion results for the real part of the isotropically averaged $<\gamma(-3\omega;\omega,\omega,\omega)>$ for BSQ in chloroform as a function of the fundamental input photon energy. Points are from measurements and the curve is from a four-level fit with the parameters illustrated in the above table. The results clearly demonstrate that below all electronic resonances, $<\gamma(-3\omega;\omega,\omega,\omega)>$ is negative. In addition, the fit shows the high-lying two-photon state (n^1A_g) is critical to understanding the features of the dispersion result. Interestingly, the sign change for $<\gamma(-3\omega;\omega,\omega,\omega)>$ at $\hbar\omega = 1.01$ eV indicates that the low-lying two-photon state (2^1A_g) has a non-negligible contribution to γ, which confirms the independent finding by Singer and coworkers[2].

[1] Y.Z. Yu, R.F. Shi, A.F. Garito, and C.H. Grossman, Opt. Lett. **19**, 786(1994).

[2] J.H. Andrews, J.D.V. Khaydarov, and K.D. Singer, *ibid.* **19**, 984(1994).