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MOLECULAR MATERIALS FOR NONLINEAR OPTICS

An overview of our recent advances in the investigation of molecular materials for nonlinear optical applications is presented. Applications of these materials include optically bistable devices, optical limiters, and harmonic generators.

INTRODUCTION

Organic molecular materials are a class of materials in which the organic molecules retain their geometry and physical properties when crystallization takes place. Changes occur in the physical properties of individual molecules during crystallization, but they are small compared with those that occur in ionic or metallic solids. The energies binding the individual molecules together in organic solids are also relatively small, making organic molecular solids mere aggregations of molecules held together by weak intermolecular (van der Waals) forces. The crystalline structure of most organic molecular solids is more complex than that of most metals or inorganic solids;[1] the asymmetry of most organic molecules makes the intermolecular forces highly anisotropic.

Owing to the electronic structure of organic molecular solids, their optical properties are often much more nonlinear than those of inorganic solids. Organic molecular materials exhibit many types of nonlinear optical properties, but three types are of interest in our investigations: optical bistability, excited-state absorption, and second-harmonic generation. There are many more nonlinear optical properties, such as sum-difference frequency generation, third-harmonic generation, and intensity-dependent index of refraction, but these are not included in our present investigation.

Current materials research is centered in three areas: (1) molecular crystals, including compounds such as urea, 2-methyl-4-nitroaniline (MNA), organic dyes, and organic charge-transfer complexes (including organometallics); (2) natural products such as proteins, lipids, and alkaloids; and (3) organic polymers, including substituted polydiacetylenes, polypyrroles, and liquid crystals.

Since structural modifications in the individual molecules lead to changes in the bulk properties of the solid, techniques known as "molecular engineering" have been developed. By molecular engineering deliberate chemical modifications are made on the individual molecules to effect changes in the bulk solid so that a desired optical property is enhanced. Such modifications simplify device processing technology by locking the optical properties of the device into the molecular structure itself, thus reducing the number of fabrication steps.

Only recently have optical devices been based on organic single crystals and polymers exhibiting a variety of potentially important optical qualities and capabilities such as optical bistability, optical threshold switching, photoconductivity, harmonic generation, optical parametric oscillation, and electro-optic modulation. A sample of various applications for several optical materials is shown in Table 1.

The optical effects so far observed in many organic materials result from the interaction of light with bulk materials such as solutions, single crystals, polycrystalline films, and amorphous compositions. In these materials, each molecule in the solid responds identically, so that the response of the bulk material is the sum of the responses of the individual molecules. That effect suggests that it may be possible to store and process optical signals or to exploit nonlinear properties at the molecular level. The branch of science investigating such possibilities is called "molecular optics."

The overview we present here is limited to the three research projects undertaken at APL in the field of organic molecular materials: optical bistability, optical limiting, and harmonic generation.

MATERIALS FOR OPTICAL COMPUTING

Basic Elements of Optical Computing

The basic functions of a computer are information processing and information storage. In serial-type computers (von Neumann architecture) the required arithmetic, logic, and memory operations are performed by devices that can switch reversibly between two states often referred to as "0" and "1". The semiconductor devices that enable the computer to perform its complex functions must be able to switch between the two states at a very high speed while requiring minimal electrical energy. The electronic semiconductor device used as the basic building block in the modern computer is the transistor.

It has been proposed that the electronic transistor be replaced by an optical counterpart.[2] An optical transistor, for example, would perform the same operations as its electronic analog, but it would modulate light rather than control an electrical signal.

The use of optical beams instead of electrical signals offers several advantages in the design of computer circuit elements. First, an optical transistor can operate at a much higher speed (in picoseconds instead of nanoseconds) because, unlike the conventional semiconductor

Table 1—Applications of molecular optical materials.

Application	Materials	Significance
Optical display devices	Conducting polythiophene complexes	Produces colored displays having fast switching times and better viewing geometry (no polarizing element) than liquid crystal devices.
	Tetrathiafulvalene or pyrazoline in poly-methacrylonitrile doped with $LiClO_4$	
	Poly(3-bromo-N-vinylcarbazole) N,N′-di(n-heptyl)-4,4′-bypyridinium dibromide	Very fast (<200 ms) photochromic changes observed
		High speed, reversible, and exhibits memory effects.
Electrophotography	Poly(vinyl carbazole)-trinitrofluorenone CuTCNQ + poly(N-vinyl carbazole)-trinitrofluorenone Polycarbonate-triphenylalanine N,N′-diphenyl-N,N′-bis(3-methyl phenyl)-[1,1′-biphenyl]-4,4′-diamine in polycarbonate	High quantum efficiency. Charged by halogen lamp, multiduplication up to 50 copies.
Optical information storage (optical recording)	Metal-TCNQ complexes	Erasable, high-contrast media.
	Photochromic dyes	High sensitivity, stable, and erasable.
	Liquid crystalline polymers	Liquid crystal polymers provide high contrast and high resolution with high sensitivity.
	1,4-dihydroxyanthraquinone	Used in amorphous SiO_2 matrix as frequency-domain storage media; requires cryogenic temperatures.
Photovoltaics	Polyacetylene/n-ZnS	Used in Schottky barrier configuration; polyacetylene bandgap matches solar spectrum well.
	Electrochemically doped poly(N-vinyl carbazole) merocyanine dyes	Conversion efficiencies from 0.015 to 2.00%.
Optoelectronic devices	Metal-TCNQ complexes	Electrical switching behavior occurs in conjunction with applied optical field.
Photonic devices (solid-state optical switching elements)	Electrochemically doped polythiophenes	Optoelectronic switching accompanied by optically induced doping; subsequent undoping occurs electrochemically.
	Urea	Used in optical parametric oscillator; conversion efficiencies approach 20%; tunable through visible and infrared.
	Methylnitroaniline	Used as frequency-doubling material.
	1:1 copolymer of methylmethacrylate and glycidilmethacrylate polyphenyl-syloxane polydiacetylene	Used as optical waveguide in integrated optics.
	Liquid crystalline polymers	Used as light valve in optical logic networks.

device, electron flow through it is not severely limited by fundamental physical considerations. In the all-optical device, the operating speed is limited only by the switching time and relaxation time of the material. Second, the all-optical device does not present the disadvantage of the electronic device in which the resistance to electron flow increases power consumption, thus producing heat that tends to retard the operation of densely packed electron circuits. Third, since interconnecting wires are not used for optical components, there is the possibility that computer architectures can be enhanced for parallel processing of information and images. Direct optical processing of images in parallel with data is a requirement of future computing that cannot be easily met by conventional electronic systems.

Electro-optical Devices

Several types of electro-optical device are being studied for possible application in optical computing. These devices are combinations of lasers, detectors, and transistors integrated into single monolithic packages. Such devices provide direct electronic-to-optic interfaces with digital and analog integrated circuits. Because of the extraordinary properties of the hybrid devices, they are also being considered for use in optical data communications and for the direct optical processing of visual images.

One example of the integrated electro-optical device is the electro-optical switch in which the nonlinear properties of the material are modulated by an applied electrical signal to gate the switching of an optical signal. This kind of electronic switching capability has been reported for several types of devices. Some, like the liquid-crystal light valve,[3] are made of organic and polymeric material. It must be noted, however, that the operating speed of the device, like that of other integrated electro-optical devices using electrical inputs to gate optical signals, is limited by the effects of capacitance and electron transit time.

All-Optical Logic Devices

All-optical devices are switches controlled by the intensity of the incident optical beam. Two basic types of all-optical switching devices, classified by their functional applications to information processing, are proposed for digital optical computing: the single-threshold bistable optical device and the double-threshold bistable optical device. In Fig. 1, the intensity of the optical output signal is plotted as a function of the intensity of the optical input signal for idealized devices of both systems.

For the single-threshold device, the characteristic operating curve (Fig. 1a) is that of output intensity increasing linearly as a function of input intensity until a critical threshold is reached. At that threshold, the output intensity rises sharply from the low output regime to a high output regime. As the input intensity is decreased, the optical output returns by the same path to the low output regime. The two linear regions of the "S" curve represent the two states of the optical device, namely, the "off" and "on" (or "0" and "1") states. A single-threshold device can perform signal amplification and the basic logic operations such as analog-to-digital conversion and logic AND and OR functions by simply se-
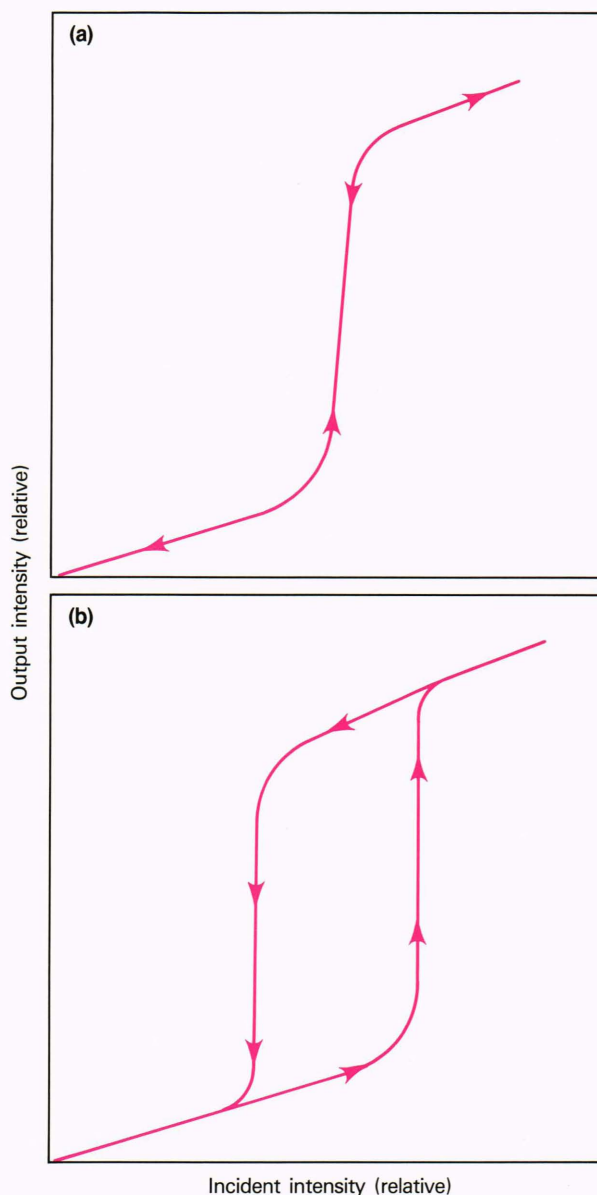

Figure 1—Representative input–output characteristics of bistable optical devices: (a) single-threshold device, (b) double-threshold device.

lecting the appropriate incident beams supplied to it. An all-optical logic device of this type is represented in Fig. 2.

The optical characteristics of a double-threshold bistable optical device (Fig. 1b) are similar to those of the single-threshold bistable optical device (Fig. 1a) because it can also have two stable states for a given set of input signals. For the double-threshold device, however, a decrease in the intensity of the input signal when the device is operating in the high-output regime does not immediately cause a decrease in the output to the low output regime. This resultant hysteresis loop can be used to add a short-term memory function to the operation of these devices.

An optical transistor can function as either type of all-optical device by combining two optical beams at its
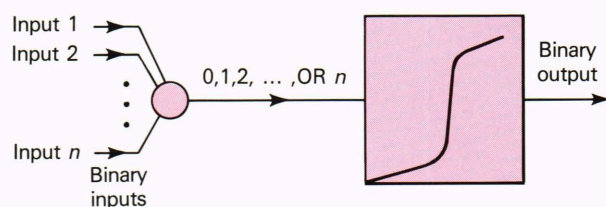
Figure 2—Representative *n*-input binary logic OR gate.

Figure 3—Typical spectrum of optical transmission in (a) unswitched and (b) switched gel-derived silica glass containing AgTCNQ.

input to produce a single output beam. Combining the input beams is accomplished by adjusting the two beams so that the intensity of one beam is close to, but not exceeding, the input threshold of the device, while the second beam, which is of much lower intensity, is added to the first so that the input threshold is exceeded, resulting in an optical output signal. By this combining of input signals, a weak beam is effectively amplified by the nonlinearity in the response of the device material.

Advantages of Molecular Materials

Organic, biological, and polymeric materials are being investigated for application in all-optical processing. Many organic materials, especially polymers, because of their abundant crosslinking, are often more resistant to laser damage than are ionic crystalline materials. Also, many organic molecular materials are more transparent at certain frequencies than inorganic materials, and the wavelength-dependent transparency can be controlled by synthetic design to match specific laser frequencies. Finally, it appears that organic materials can be made capable of storing and processing information at the molecular level. Development of this capability is supported in recent reports describing voltage-tunable optical data storage that uses persistent spectral hole burning[4] and reversible multiple-state optical recording that uses organic charge-transfer complexes.[5]

Organic Photochromics

Organic compounds that exhibit distinct optical states are being studied for application in optical storage (e.g., in optical memories and optical data processing). The reversible photochemical reaction in this class of materials can convert a single chemical structure alternately between two stable isomers that often exhibit two distinct absorption maxima. Organic photochromic compounds such as spyropyrans and aberchrome dyes are being developed for use in reversible optical memories. In addition to use in optical memories, these materials are now used for optical data processing, for spatial light modulation, and in optical waveguide devices.

Bistable Optical Switching of Organometallic Materials in Gel-Derived Silica Glasses

Bistable optical switching is known to occur in the organometallic compound silver tetracyanoquinodimethane (AgTCNQ) when it is exposed to incident laser radiation above a characteristic power threshold.[5-10] It has been postulated that the effect of the applied optical field on the initial charge-transfer complex is to cause a phase transition induced by an electric field, resulting in the formation of a nonstoichiometric complex salt containing neutral TCNQ, as shown in the reaction
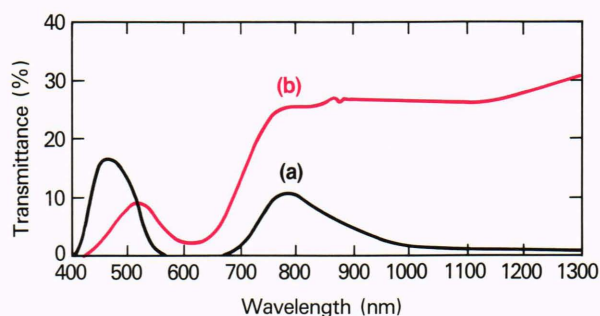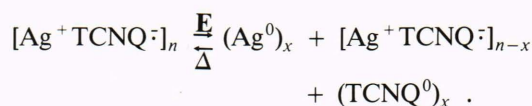
$$[Ag^+TCNQ^{\dot{-}}]_n \xrightarrow{\mathbf{E}}{\Delta} (Ag^0)_x + [Ag^+TCNQ^{\dot{-}}]_{n-x} + (TCNQ^0)_x \ .$$

The original charge-transfer complex can be reformed by heating the complex salt in its solid phase. The changes observed in the optical properties of AgTCNQ result directly from the electric-field-induced effect that breaks the weak ionic bond between the metal cation and the organic-radical anion (an excited state electron-transfer reaction). Switching times from the simple charge-transfer complex containing neutral molecules is less than 4 ns.

This effect in AgTCNQ suspended in a matrix of gel-derived silica glasses formed at low temperature is described in Ref. 11. The changes in the optical absorption by AgTCNQ in the silica matrix were used to demonstrate optical logic operations by moderate-power continuous or pulsed laser radiation.

AgTCNQ was prepared in colloidal form, with particle sizes ranging from 0.22 to 2.50 μm, by the aqueous reaction of LiTCNQ and AgNO$_3$ according to the original procedure described by Melby et al.[12] Monolithic gate-array processors were prepared from gel-derived glass containing AgTCNQ by hydrolyzing and polymerizing tetramethyl orthosilicate (TMOS). Typical disks of the finished material were 2.5 cm in diameter by 1 mm thick. The AgTCNQ particles remained uniformly dispersed during formation of the glass. The spectrum of optical transmission in a gel-derived glass containing AgTCNQ is shown in Fig. 3a. Three absorption peaks have been identified and are interpreted in reports that deal with the optical spectra of powder TCNQ compounds suspended in potassium bromide pellets.[13,14]

The disk was then irradiated by a Nd:YAG laser at 1060 nm, pulsed at a 10-Hz rate, delivering 200 mW average power, with a beam 6 mm in diameter. The beam raster scanned over a 1 × 1 cm area. The irradiation caused the blue color of AgTCNQ to transform rapidly into the pale yellow that is characteristic of the formation of neutral TCNQ, as indicated by curve b in Fig. 3. Because of the great change in the transmission spectrum, this material may be useful in high-speed optical logic devices.

Because of the threshold characteristics of these gel-derived glasses containing AgTCNQ, they have also been used to demonstrate analog-to-digital conversion and various logic operations. Samples were irradiated with various combinations of two laser beams, and changes in the output transmission were monitored. A logic AND-gate function and an optical transistor were demonstrated in concept by using beams from two Nd:YAG lasers (1060 nm), each operating below the switching threshold. Irradiation from only one of the beams, operated below threshold, resulted in minimal output transmission. When the combined power of the two beams exceeded the threshold (≈ 2000 mW in glass) of the organic complex, the optical transmission through the irradiated area to the output increased significantly, corresponding to a decrease in the charge-transfer band centered near 1300 nm. The output signal increased by as much as ten times.

A similar method was used with this material to perform the logic OR-gate function. The intensity of each laser beam was set above the 2000-mW (average power) threshold. Irradiation from either or both of the laser beams resulted in a rapid increase in transmission, just as it did for the logic AND-gate function.

By irradiating the AgTCNQ at a wavelength that is transmitted less in the switched state than in the unswitched state (i.e., using the Nd:YAG 532-nm laser line or the 488-nm argon-ion laser line), an Exclusive OR (XOR) function was demonstrated. Below the threshold, either beam was transmitted equally well, but when the combined power of the two exceeded the threshold, the material became more absorptive in the green spectral region, owing to the formation of neutral TCNQ, which has an absorption peak at about 400 nm. The measured output intensity decreased by as much as one half.

The reversal of the process in these materials is limited: the donor and acceptor species are segregated, owing to the large thermal energy flux during laser exposure. Work to reduce the optical threshold of the switching process and to increase the number of cycles of operation with these materials is continuing, however.

EXCITED-STATE PHOTOPHYSICAL PROPERTIES OF MOLECULAR MATERIALS

We are now studying several classes of organic-dye macromolecular systems in hopes of developing an all-optical "real-time" threshold logic element based on excited-state photophysical properties. Several critical prerequisites must be satisfied before a material having nonlinear optical properties can be used in real-time optical processing or switching applications. They include optically induced nonlinearity, fast switching and recovery times, immunity to thermal and laser damage, optical activity at common laser wavelengths, low optical power thresholds, and processability into device structures.

Table 2 is a compilation of the basic photochemical events and processes that commonly take place in organic molecules. Events requiring the least time are listed first, followed by those requiring progressively more time. For a photochemical process to be considered for use in optical processing, the time required for the event must be

Table 2—Time scale of molecular processes.

Time Scale (s)		Photochemical Event
Femto	(10^{-15})	Electronic motion Electron orbital jumps Electron transfer Proton transfer Vibrational motion
Pico	(10^{-12})	Bond cleavages (weak) Rotational and translational motion (molecules are small and fluid) Bond cleavages (strong) Spin-orbit coupling
Nano	(10^{-9})	Rotational and translational motion (molecules are large and fluid) Hyperfine coupling
Micro	(10^{-6})	"Ultrafast" chemical reactions
Milli	(10^{-3})	Rotational and translational motion (molecules are large and/or very viscous)
—	(10^{0})	"Fast" chemical reactions
Kilo	(10^{3})	"Slow" chemical reactions
Mega	(10^{6})	

less than 10^{-9} s. On this basis, Table 2 shows that almost all chemical reactions involving the formation of an actual product are too slow to meet the prerequisites, but the events that do meet them are dynamic ones such as electronic motion, electron orbit hopping, electron or proton transfer, rotational and translational motion of small molecules, and bond cleavage.

For certain classes of dye chromophores, called reverse saturable absorbers,[15] the excited-state absorption cross section σ_2 resulting from photoinduction is higher than the ground-state absorption cross section σ_1. The ground-state absorption cross section is determined from the ratio of the monochromatic beams incident on and emerging from a dye sample, according to the relation

$$I = I_0 R \exp(-N_0 \sigma_1 L) , \qquad (1)$$

where I_0 is the intensity of the beam before it impinges on the dye sample, R is the reflection loss at the sample, N_0 is the number of absorbing molecules per unit volume, and L is the sample length. The increase in the excited-state absorption cross section results in an increase in absorption by the dye sample as the intensity of the incident beam is increased, according to the relation

$$I_{ex} = I_0 R \exp[-(N_1 \sigma_1 + N_2 \sigma_2)L] , \qquad (2)$$

where N_2 is the number of molecules in the excited state per unit volume. The excited-state absorption coefficient σ_2 is determined by[16]

$$\sigma_2 = \sigma_1 + (1/N_2 L)\ln(I/I_{ex}) , \qquad (3)$$

assuming $N_1 + N_2 = N_0$. We are attempting to determine the constant σ_2 for a variety of laboratory-synthesized materials.

It is difficult to describe the exact mechanism of reverse saturation because the organic structures are complex, but an energy diagram does provide a simple model to illustrate the effect. (Figure 4 is such an energy-level diagram for an idealized saturable absorber.) At low optical intensities, the optical transparency of the material does not change appreciably, but as the incident intensity increases, the population of the first excited state S_1 also increases. This population increase is accompanied by nonradiative decay from the vibrationally excited states to the lowest vibrational manifold of the first excited state. The population of the ground state becomes increasingly depleted at moderate intensity levels. At those moderate intensities, the ground-state absorption coefficient σ_1 of the saturable absorber would begin to decrease and the material would become increasingly transparent, but, at the higher intensities, the first excited state becomes populated, acting as a trap, and excitation from the first excited state to higher excited states S_2 begin to dominate the photophysical behavior of the material. In this regime, σ_2 becomes significant and the material behaves as a reverse saturable absorber and will remain in the highly absorbing state as long as the metastable excited state remains heavily populated. Depopulation of state S_2 is believed to be caused by a complex relaxation mechanism.

We started our investigation by studying a molecular system in which electronic transitions to excited states produce nonlinar optical phenomena. The reported nonlinear absorption characteristic of the indanthrone dye chromophore (Fig. 5) provided the reason to choose it for our investigation. In an organic dye chromophore, the absorption time of visible light and the subsequent electronic motions in the chromophore's π-electron system can be on the order of 10^{-12} s. The indanthrone system is known to exhibit reverse saturable absorption when it is irradiated by short-duration pulses at high peak power.[15]

A typical input–output curve for a 4.5×10^{-5} M aqueous solution of indanthrone is shown in Fig. 6. Observe that at 300 mW average power (corresponding to about 2.1×10^{17} W/m^2 peak power) the transmittance at 532 nm drops from 32.2% to about 0.9%. Note also that very little degradation occurs during irradiation, because the input–output curve follows the same path whether the power is increasing or decreasing.

We have also synthesized three compounds based on the indanthrone chromophore (Fig. 7): oxidized indanthrone, chloroindanthrone, and an indanthrone ladder oligomer.[17,18] All three are effective reverse saturable absorbers.
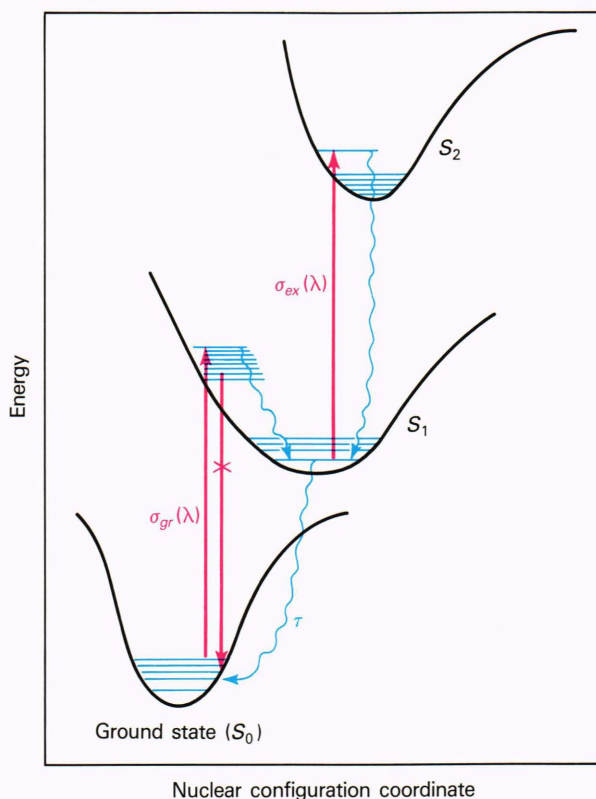

Figure 4—Electronic energy levels in an idealized saturable absorber. (From D. J. Harter, M. L. Shand, and Y. B. Band, "Power/Energy Limiter Using Reverse Saturable Absorption," *J. Appl. Phys.* **23**, 865–868 (1984). Reproduced by permission, Am. Inst. Phys.)
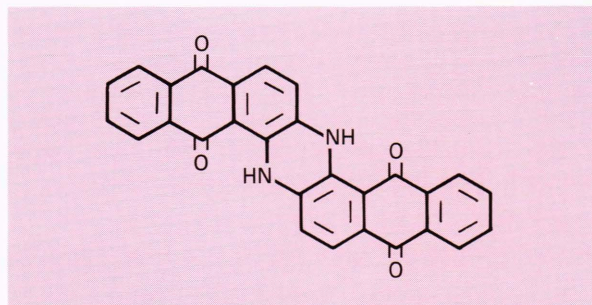

Figure 5—Chemical structure of the indanthrone molecule.

Data were obtained (Fig. 8) by directing focused Q-switched pulses from a Nd:YAG laser into a cell containing the dye. Part of the incident light, proportional to the incident power on the cell, was directed into a power meter. The light passing through the cell, proportional to the transmitted power, was directed into a second power meter. In most cases, average powers were measured and the pulse energies were inferred from the measured average power.

The highest pulse energy delivered to the cell was approximately 100 mJ. The near-zero transmittance was set at 55% for each dye (see Fig. 9) by adjusting the con-
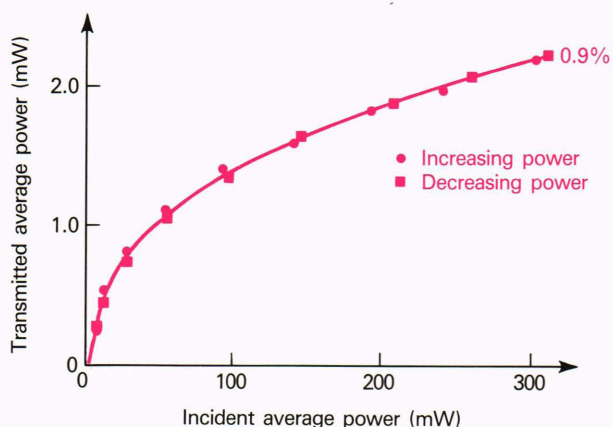
Figure 6—Input–output characteristics of a 4.5×10^{-5} M aqueous solution of indanthrone, illustrating the nonlinear optical properties of the indanthrone molecule. Transmittance at zero power is 32.2%; wavelength of incident beam is 532 nm.
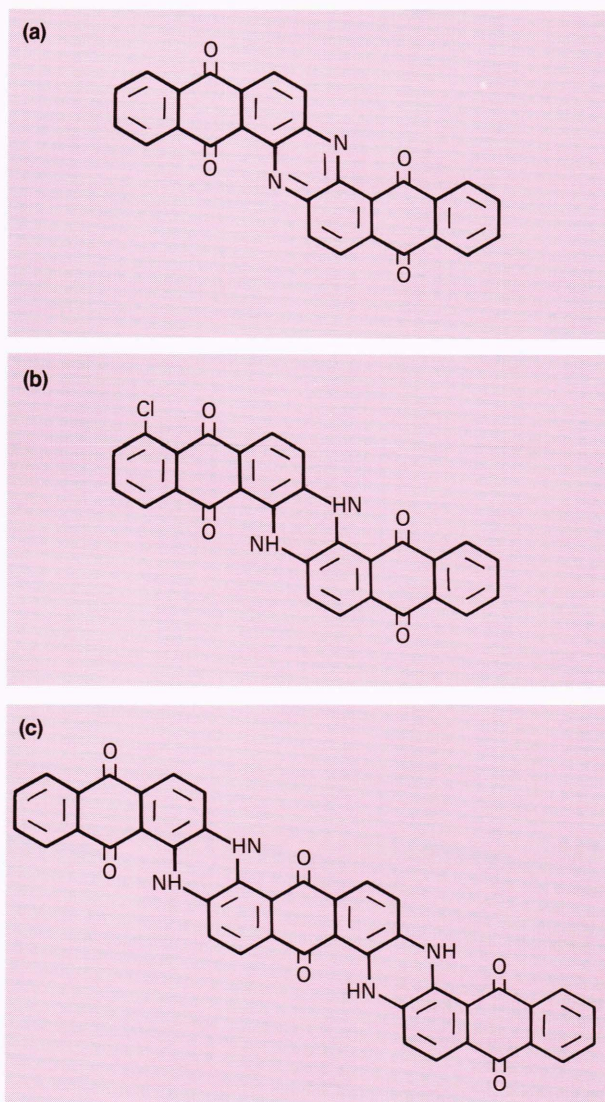

Figure 7—Chemical structure of (a) oxidized indanthrone, (b) chloroindanthrone, and (c) indanthrone ladder oligomer.

centration in an isopropanol suspension. At relatively low input levels at 1064 nm, the response of each compound to increasing intensity is linear, because of the intrinsic linear absorption by the dye chromophore. The onset of the nonlinearity observed for each compound at higher input levels is due to excited-state absorption. This highly absorptive state becomes dominant at levels of about 10^{15} W/m^2. The 8 to 30% drop in transmittance at an incident irradiance of 10^{16} W/m^2 was dependent on the electronic environment of the chromophore in the excited state. In all experiments, the temporal distribution and transverse mode profile were approximately Gaussian. The pulse duration was held constant at 10 ns and the nonlinear effect was not polarization dependent.

Although indanthrone is reported to exhibit reverse saturable absorption at 532 nm, it is essentially a linear absorber at 1064 nm. For the indanthrone structure modified by chemical oxidation, the nonlinearity at 1064 nm increases in comparison with the nonlinearity of unoxidized indanthrone (Fig. 9). Possibly the oxidized form of indanthrone, with its increased π-electron density, aids in stabilizing the electronic dipole moment in the excited state by increasing the contribution of the excited-state resonance form. This addition to the conjugated π-system may also account for the shift to greater nonlinearity for this molecule at longer wavelengths.

Adding a chlorine atom to the basic indanthrone system (Fig. 9) increases the excited-state absorption cross section and reduces the power density required for nonlinear behavior. The halogenation of the indanthrone chromophore probably increases the rate of intersystem crossing to the excited state, thus increasing the excited-state absorption.

Extending the indanthrone chromophore by adding an aminoanthraquinone subunit to form the ladder oligomer (Fig. 9) shifts the absorption maximum toward the infrared, because conjugation of the molecule is increased. The excited-state absorption cross section for the ladder oligomer at 1064 nm is higher than for indanthrone, oxidized indanthrone, or chloroindanthrone.

The transmittance versus log irradiance at 532 nm for the four compounds studied is plotted in Fig. 10. The parent indanthrone molecule exhibits the greatest nonlinearity, followed by oxidized indanthrone, chloroindanthrone, and the ladder oligomer. Thus, the experimental results show that modifying the chemical structure of a known nonlinear optical material can predictably control the optical properties with respect to wavelength dependence and changes in optical density. Developing this technology of modifying materials having nonlinear optical properties can lead to applications in nonlinear image processing, optical limiting, and optical pulse compression.

ORGANIC MATERIALS FOR SECOND-HARMONIC GENERATION

Second-harmonic generation (SHG) in organic materials (see Table 3) has been known for many years, especially in materials such as MNA (2-methyl-4-nitroani-

Figure 8—Experimental apparatus for measuring nonlinear absorption in indanthrone and its derivatives.
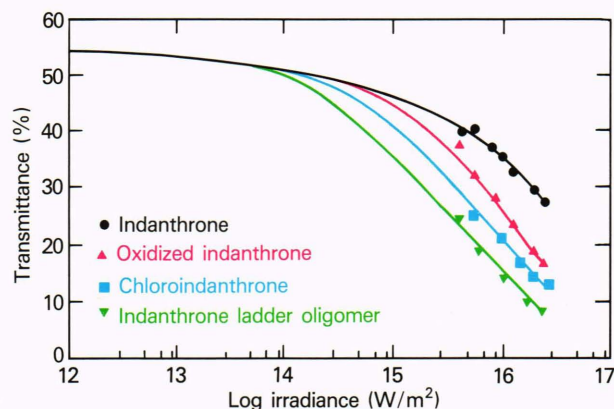

Figure 9—Transmittance plotted as a function of log irradiance for indanthrone and indanthrone-based reverse saturable absorbers. Wavelength of incident beam is 1064 nm.

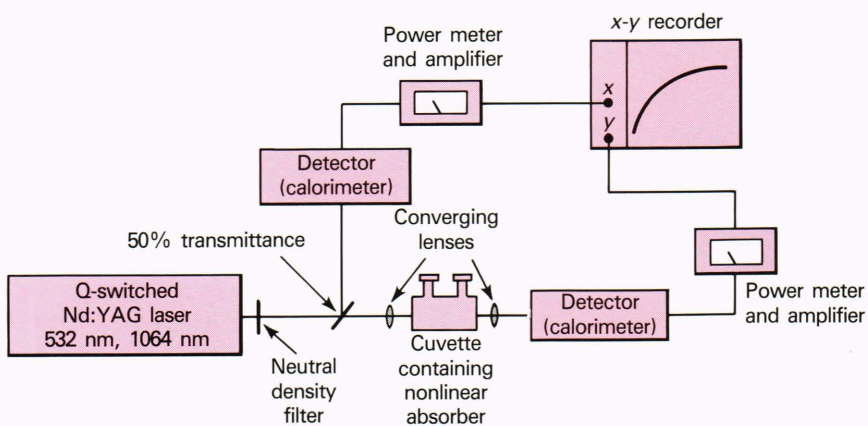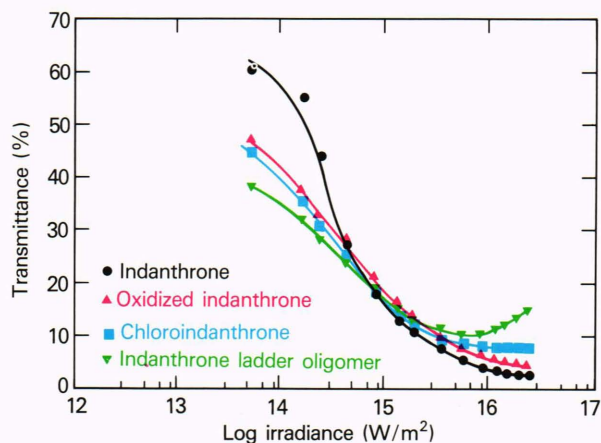**Figure 10**—Transmittance plotted as a function of log irradiance for indanthrone and indanthrone-based reverse saturable absorbers. Wavelength of incident beam is 532 nm.

line)[19] and urea.[20,21] SHG takes place in these materials because of the highly nonlinear polarizabilty of the π-bond structure and the asymmetrical charge distribution associated with donors and acceptors in the molecule. The polarizability for any substance is

$$\mathbf{P} = \epsilon_0 \chi_1 \mathbf{E} + \epsilon_0 \chi_2^2 \mathbf{E}^2 + \epsilon_0 \chi_3^3 \mathbf{E}^3 + \dots , \qquad (4)$$

where $\mathbf{P}$ is the macroscopic polarization. The first term on the right is the linear polarizability associated with linear refraction; the second (which vanishes for optically isotropic materials) is responsible for SHG in anisotropic crystals; and the third is responsible for four-wave mixing effects, photorefraction, and optical bistability. In these terms, ϵ_0 is the permittivity of free space, $\mathbf{E}$ is the electric field strength, and χ is the dielectric susceptibility. For SHG, χ_2^2 is a third-rank tensor of the form $\chi_{ijk}^{(2\omega)}$. The second-order nonlinear term then takes the form

$$\mathbf{P}_i^{(2\omega)} = \epsilon_0 \chi_{ijk}^{(2\omega)} \mathbf{E}_j^{(\omega)} \mathbf{E}_k^{(\omega)}, \quad j,k = 1,2,3 . \qquad (5)$$

The numerical values of the tensor coefficients are usually represented by the letter d and are functions of frequency and temperature. The units of $\chi_{ijk}^{(2\omega)}$ are different from those of the first-order linear susceptibility term $\chi_{ij}^{(\omega)}$. The first-order term is a dimensionless ratio, whereas the second-order susceptibility tensor has units of inverse electric field strength (meters per volt in the meter-kilogram-second system).[22]

Organic molecules can be adapted to molecular engineering. An example of such a molecule is 2-methyl-4-nitroaniline (Fig. 11a), which consists of a nitro (NO_2) acceptor group and an amino (NH_2) donor group separated by a conjugated ring system. This molecule is easily polarized, has a high degree of charge transfer, and is thus an excellent material for SHG. Presence of the methyl group was necessary to assure a noncentrosymmetric crystal structure.

Another well-known material that has received considerable attention for some time is urea, which has the structure shown in Fig. 11b. Urea is often the efficiency standard against which other organic compounds having nonlinear optical characteristics are compared—a convention we retain here.

The potential SHG materials were tested using the well-known powder-susceptibility measurements first used by Kurtz and Perry.[20] In their technique a powdered sample is placed in a cuvette and irradiated by pulses from a Nd:YAG laser operating at a wavelength

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Table 3—Organic materials for second-harmonic generation.

Chemical Name	Structure	SHG Efficiency Relative to Urea
2-nitrobenzaldehyde	[structure: benzene ring with CHO and NO₂]	*
3-nitrobenzaldehyde[†]	[structure: benzene ring with CHO and NO₂]	~1×
4-nitrobenzaldehyde[†]	O₂N–[ring]–CHO	~2×
3-cyanobenzaldehyde	[structure: benzene ring with CHO and CN]	0.3×
4-cyanobenzaldehyde	NC–[ring]–CHO	~1×
4-nitrobenzaldehyde hydrazone[†]	O₂N–[ring]–CH=N–NH₂	10×
3-nitrobenzaldehyde hydrazone	[ring]–CH=N–NH₂ with NO₂	0.1×
2-nitrobenzaldehyde hydrazone	[ring]–CH=N–NH₂ with NO₂	0.001×
4-nitorbenzaldehyde phenylhydrazone	O₂N–[ring]–CH=N–NH–[ring]	0.5×
3-nitrobenzaldehyde phenylhydrazone	[ring]–CH=N–NH–[ring] with NO₂	0.001×
2-nitrobenzaldehyde phenylhydrazone	[ring]–CH=N–NH–[ring]	0.001×
1-naphthaldehyde phenylhydrazone	[naphthalene]–CH=N–NH–[ring]	~5×
1-pyrenecarboxaldehyde phenylhydrazone	[pyrene]–CH=N–NH–[ring]	~4.0×
1-naphthaldehyde hydrazone	[naphthalene]–CH=N–NH₂	0.001×
benzaldehyde hydrazone	[ring]–CH=N–NH₂	*
3-cyanobenzaldehyde phenylhydrazone	[ring]–CH=N–NH–[ring] with CN	0.002×
3-nitrobenzaldehyde methylhydrazone	[ring]–CH=N–NHCH₃ with NO₂	0.001×
4-nitrobenzaldehyde dimethylhydrazone	O₂N–[ring]–CH=N–N(CH₃)₂	0.05×
4-nitrobenzaldehyde methylhydrazone	O₂N–[ring]–CH=N–NHCH₃	0.001×

*Only preliminary data are available for these compounds.
[†]See Ref. 1.

(a) 2-methyl-4-nitroaniline (MNA)

(b) Urea

(c) 4-nitrobenzaldehyde hydrazone

(d) 4-nitrobenzaldehyde methylhydrazone   4-nitrobenzaldehyde dimethylhydrazone

(e) 4-nitrobenzaldehyde phenylhydrazone

(f) 1-naphthaldehyde phenylhydrazone   1-pyrenecarboxaldehyde phenylhydrazone
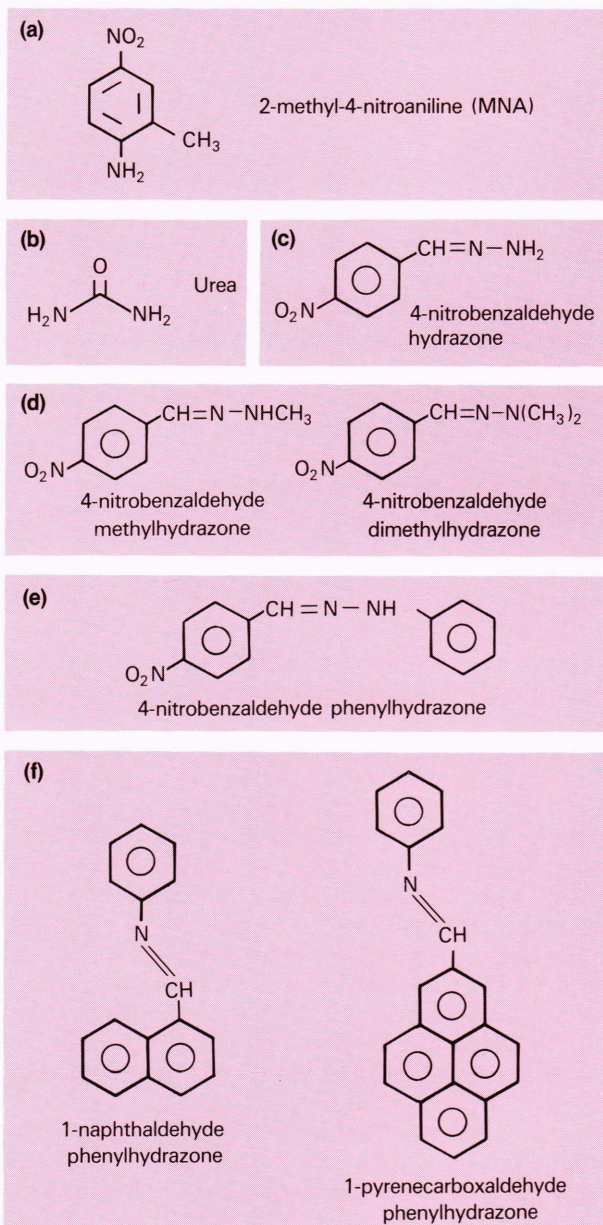
Figure 11—Chemical structure of several organic materials used for second-harmonic generation.

of 1064 nm (ω). If the powdered sample is a material suitable for SHG, light at twice the fundamental frequency (2ω) will be emitted by the sample (i.e., wavelength of 532 nm). Because the powdered sample contains crystalline grains that are randomly oriented crystallographically, the emitted second harmonic is weak but easily detectable by electron-multiplier phototubes.

Efficient SHG requires large biaxial or triaxial crystals so oriented that the fundamental frequency propagates as an o-ray and the harmonic propagates as a e-ray, or vice versa. (An o-ray, or ordinary ray, is the ray where the refractive index does not vary with crystallographic direction; an e-ray, or extraordinary ray, is the ray where the refractive index varies with crystallographic direction.) The crystal orientation is adjusted so that the o-ray (1064 nm) and e-ray (532 nm) propagate at the same

speed. Thus, power is coupled from the fundamental to the harmonic as the two waves propagate in phase through the crystal. Meeting this condition is known as phase matching. The powder method is also used to test whether a material can be phase matched by measuring the total second-harmonic output (532 nm) while the crystallite size of the powdered sample is varied. Phase-matchable materials will show an increase in the second-harmonic output with crystallite size that saturates once the coherence length of the fundamental and harmonic frequencies is exceeded. Materials that cannot be phase matched show an increase in second-harmonic output as crystallite size is increased toward the coherence length, and then show a sharp decrease in second-harmonic output as crystallite size is increased beyond the coherence length. The crystallite size at which the decrease occurs is typically a few micrometers. Some materials, even though they have acentric electron distributions and net dipole moments, often crystallize in a centrosymmetric crystal system. Despite the centrosymmetry in such instances, these molecules can be "poled" or aligned by an electric field in a polymer that has been heated above the glass transition temperature (T_g) to produce a noncentrosymmetric solid that, when cooled below T_g, will exhibit SHG.[23]

We have also investigated a class of compounds that has received little attention since the initial investigation in 1977 by Davydov et al.[24] The prototype compound of the series is 4-nitrobenzaldehyde hydrazone (NBAH), shown in Fig. 11c. The compound, synthesized by reaction of 4-nitrobenzaldehyde with hydrazine, was first reported by Davydov et al. to have a powder efficiency 2.5 times that of urea. Unexpectedly, we observed much higher powder efficiencies, up to 10 times that of urea. As a result, we synthesized derivatives of NBAH to determine whether the SHG powder efficiency could be enhanced and whether there are similar molecules with high SHG powder efficiencies. The methyl and dimethyl derivatives of NBAH (shown in Fig. 11d) were synthesized in much the same way as the NBAH. Although these materials are chemically similar to NBAH, they exhibited lower SHG powder efficiencies that are 0.001 to 0.05 times that of urea. Experiment thus shows that minor chemical changes can result in significant changes in the arrangement of molecules within the crystal, often resulting in decreased SHG powder efficiency. The compound 4-nitrobenzaldehyde phenylhydrazone was synthesized by the same method and has the structure shown in Fig. 11e, but this compound showed an SHG powder efficiency about 0.5 times that of urea. The efficiency would be much greater except that the compound is significantly absorptive at 532 nm.

We have also made hydrazone derivatives of large conjugated ring systems such as naphthalene and pyrene (Fig. 11f). These compounds do not exhibit much charge transfer, because their aromatic ring systems donate weakly, but both have greater SHG powder efficiencies than urea. Table 3 lists many of the hydrazone derivatives of various aromatic aldehydes that have been synthesized along with their respective SHG powder efficiencies referenced to that of urea.

CONCLUSION

Our research is continuing in an effort to synthesize, modify, and characterize new organic molecular materials for nonlinear optical applications that include bistable optical switching, using an organometallic complex; optical limiting and processing, using organic dyes that exhibit reverse saturable absorption; and second-harmonic generation, using organic crystalline materials. The results of our research should provide new materials that will significantly advance the field of nonlinear molecular materials.

REFERENCES

[1] F. Nicoud and R. J. Tweig, "Organic SHG Powder Test Data," in *Nonlinear Optical Properties of Organic Molecules and Crystals,* Vol. 2, D. S. Chemla and J. Zyss, eds., Academic Press, Ltd., London, p. 221 (1987).
[2] J. A. Neff, "Major Initiatives for Optical Computing," *Opt. Eng.* 26, 2 (1987).
[3] E. Marom, "Real-Time Image Subtraction Using a Liquid Crystal Light Valve," *Opt. Eng.* 25, 274 (1986).
[4] A. Szabo, "Frequency Selective Optical Memory," U.S. Patent 3,896,420 (1975).
[5] R. S. Potember, R. C. Hoffman, and T. O. Poehler, "Molecular Electronics," *Johns Hopkins APL Tech. Dig.* 7, 129–141 (Apr–Jun 1986).
[6] R. S. Potember, T. O. Poehler, and R. C. Benson, "Optical Switching in Semiconductor Organic Thin Films," *Appl. Phys. Lett.* 41, 548 (1982).
[7] R. C. Benson, R. C. Hoffman, R. S. Potember, E. Bourkoff, and T. O. Poehler, "Spectral Dependence of Reversible Optically Induced Transitions in Organometallic Compounds," *Appl. Phys. Lett.* 42, 855 (1983).
[8] R. S. Potember, R. C. Hoffman, R. C. Benson, and T. O. Poehler, "Erasable Optical Switching in Semiconductor Organic Charge-Transfer Complexes," *J. Phys.* 44, C3-1597 (1984).
[9] T. O. Poehler, R. S. Potember, R. Hoffman, and R. C. Benson, "Optical Phase Transitions in Organic Charge-Transfer Complexes," *Mol. Cryst. Liq. Cryst.* 107, 91 (1984).
[10] R. S. Potember, T. O. Poehler, R. C. Hoffman, K. R. Speck, and R. C. Benson, "Reversible Electric Field Induced Bistability in Carbon-Based Radical-Ion Semiconducting Complexes: A Model System Molecular Information Processing," in *Molecular Electronics,* F. L. Carter, ed., Marcel Dekker, Inc., New York, p. 91 (1986).
[11] K. R. Speck, T. O. Poehler, A. A. Burk, C. A. Viands, and R. S. Potember, "Bistable Optical Switching of Organometallic Doped Gel-Derived Silica Glasses," *Proc. 5th Int. Congress on Applications of Lasers and Electro-Optics,* C. M. Penney and H. J. Caulfield, eds., Springer-Verlag, New York, p. 243 (1987).
[12] L. R. Melby, R. J. Harder, W. R. Hertler, W. Mahler, R. E. Benson, and W. E. Mochel, "Substituted Quinodimethans. II. Anion-Radical Derivatives and Complexes of 7, 7, 8, 8-Tetracyanoquinodimethane," *J. Am. Chem. Soc.* 84, 3374 (1962).
[13] K. Kamaras, G. Gruner, and G. A. Sawatzky, "Optical Absorption in Complex TCNQ Salts," *Solid State Commun.* 27, 1171 (1978).
[14] J. B. Torrance, B. A. Scott, and E. B. Kaufman, "Optical Properties of Charge-Transfer Salts of Tetracyanoquinodimethane (TCNQ)," *Solid State Commun.* 17, 1369 (1975).
[15] C. R. Guiliano and L. D. Hess, "Nonlinear Absorption of Light: Optical Saturation of Electronic Transitions in Organic Molecules with High Intensity Laser Radiation," *IEEE J. Quantum Electron.* QE-3, 358 (1967).
[16] M. L. Shand, J. C. Walling, and R. C. Morris, "Excited-state Absorption in the Pump Region of Alexandrite," *J. Appl. Phys.* 52, 953 (1981).
[17] M. K. Shah and K. H. Shah, "Indanthrones from 1-Amino-Anthraquinones: Part I-Studies of Variables in the Preparation," *Indian J. Technol.* 13, 312 (1975).
[18] M. C. Clark, "Chemistry of Indanthrone. Part XII. Some Properties of the Dinaphthophenazinediquinones and Their NN'-Dihydro-derivatives," *J. Chem. Soc. (C),* 2090 (1966).
[19] B. F. Levine, C. G. Bethea, C. D. Thurmond, R. T. Lynch, and J. L. Bernstein, "An Organic Crystal With an Exceptionally Large Optical Second Harmonic Coefficient: 2-methyl-4-Nitro Aniline," *J. Appl. Phys.* 50, 2523 (1979).
[20] S. Kurtz and T. T. Perry, "A Powder Technique for the Evaluation of Nonlinear Optical Materials," *J. Appl. Phys.* 39, 3798 (1968).
[21] D. Bauerle, K. Betzler, H. Hesse, S. Kappan, and P. Loose, "Phase-Matched Second Harmonic Generation in Urea," *Phys. Status Solidi (A)* 42, K119, (1977).
[22] G. C. Baldwin, *An Introduction to Nonlinear Optics,* Plenum Press, New York, p. 81 (1969).
[23] K. D. Singer, J. E. Sohn, and S. J. Lalama, "Second Harmonic Generation in Poled Polymer Films," *Appl. Phys. Lett.* 49, 248 (1986).

[24]B. L. Davydov, S. G. Kotochshchikov, V. A. Nefedov, "New Nonlinear Organic Materials for Generation of Second Harmonics of Neodymium Laser Radiation," *Sov. J. Quantum Electron.* (*Eng. Trans.*) **7**, 129 (1977).

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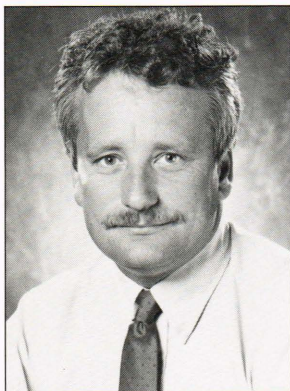
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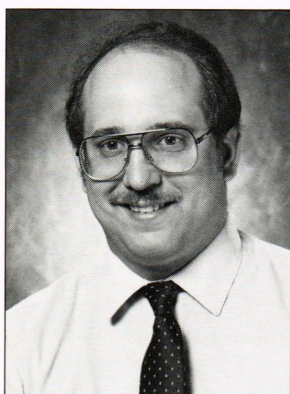
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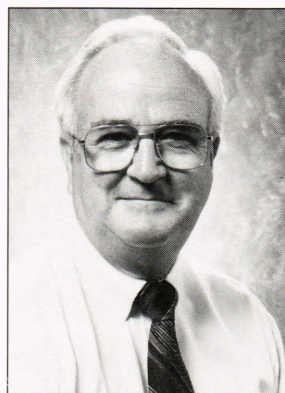
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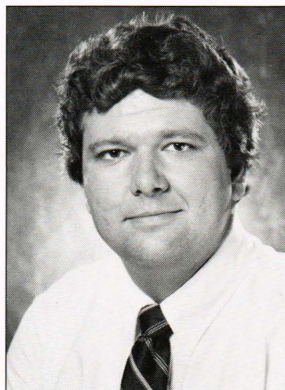
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