Organic materials for nonlinear optics Part 1

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In glancing through a flat windowpane we confront light's interaction with glass, but ignore it. We assume that the world's image is not perceptibly altered when light passes through the glass. Yet glass does play tricks with light: A penny viewed through a variety of lenses may appear the same size, magnified, reduced, or blurred. The shape *of* glass dictates the distortion of the image. The 14th century craftsmen who first formed lenses from glass to aid those with deteriorating vision progressed by trial and error. Even Galileo used the exacting labor of grinding glass, without benefit of a practical theory of optics, to improve his pioneering telescope. The optics industry flourished for centuries before theory could minutely chart the interaction between light and glass.

Contemporary optics research is distant from common experience, seeking clues far more subtle than the shape of a piece of glass, with techniques more esoteric than abrasive polishing of a glass lens. The traditional dominance of glass in optics is now challenged by a host of synthetic materials that exhibit unusual optical behavior. Laser light of unmatched brilliance both probes and incites these novel effects. A detailed understanding of the nature of light, and how it interacts with matter, is essential to evince these effects. Although everyday optical tools- windowpanes and eyeglasses-may remain unaffected, such delicate engineering has thrust optics along routes far removed from the crudely empirical development of geometrical optics.

In this paper we will follow some of the newly laid routes into the domain of organic materials-materials that have such unusual responses to light that they undermine some of our intuitive assumptions about optics. The molecular structure of these organic materials can be custom designed to amplify their optical properties.

Novel devices based on the optical phenomena manifested by organic materials may change communications and information processing.

Refraction and linear optics

Both familiar and novel optical properties of materials depend intimately on the character of light. A beam of light can be simply modeled as a stream of many packages, all moving in a straight line at the same speed. Each package, or photon, is a self-propelled carrier of energy and momentum. The package is composed of a pair of perpendicular electric and magnetic field vectors whose magnitudes and directions oscillate periodically. The frequency of this oscillation dictates the "color," momentum, and energy content of the package; higher frequencies correspond to greater energy and momentum. The oscillations of different photons are in phase if their magnitudes peak simultaneously. If the peaks are asynchronous, the field vectors cancel and the light disappears.

When light in air enters a denser, transparent material such as glass, its electric field induces a slight separation between the positive and negative charges on each molecule in the material. Negative charges attempt to orient toward the instantaneous positive direction of the field of light, and vice versa. The dielectric constant, e, is a measure of this response of charges in a material to an applied electric field (usually de). A small electric field, which reflects the spatial arrangement of the molecules, is created by the polarization of charge. Its direction opposes the incident field; it oscillates asynchronously with light. This small electric field, induced by light, in turn alters the direction and diminishes the magnitude of the field of light. As a consequence, the speed of light is reduced within the material. The fields of light perturb charges in the material, which in turn perturb light through an induced field. Although this interaction occurs microscopically, it has a familiar macroscopic effect: refraction. When a pencil partially immersed in water appears crooked or a lens focuses a bright spot of light, we observe refraction.

The index of refraction, n, is the ratio of the speed of light in free space to its speed in a material. The value of n is characteristic of the material. Although light of all "colors" travels at the same speed in free space, its speed inside a material varies slightly with color, or frequency; the index of refraction is frequency

dependent. A prism sorts white light into a rainbow by deflecting the higher frequency, bluer "colors" farther from the path of the incoming beam. When the frequency of light approaches one of the material's built-in natural frequencies, the molecules oscillate sympathetically, absorbing more of light's energy. Ordinarily, the index of refraction of a material is not affected by the brightness of the light shining on it, a quality that enables us to use the same pair of binoculars to focus on a faint star at night and a bird in daylight (1, 2).

 Intensity-dependent nonlinear effects

   However, when laser light is directed on a material, entirely different properties-microscopically sensitive to a precise match between light and the material-can be evoked. The high intensity of a laser beam can produce an electric field that rivals and disrupts the internal electric field of atoms in the material. The closely correlated oscillation phases, or coherence, of a laser beam produce a well-defined field pattern, persistent in space and time. This can evoke complex, collective behavior in an ordered material system. Through interaction, light and the material can drastically alter each other in a uniquely interrelated fashion.

   In conventional circumstances, when two light beams cross each other the departing photons in one beam appear unaffected by the other beam. But if two light beams. coincide while traversing certain special materials, the departing photons may become distinguishable from the incident photons. The first beam alters the material's optical behavior; the second beam, arriving while the

   Table 1. Second-order nonlinear optical properties*

Table 1. Second-order nonlinear optical properties[a]

Material	n	ε	$d_{ij} \times 10^{-12}$ m/v
KDP (KH_2PO_4)	1.47	42	$d_{36} = 0.45$
LiNbO$_3$	2.3	78	$d_{22} = 2.3$
		32	$d_{33} = 40$
MNA (2-Methyl-4-nitroaniline)	1.8	4	$d_{11} \sim 250$
DANS (4-N,N-dimethylamino-3-acetamonitrobenzene)	1.71	4	$d_{eff} \simeq 27$

[a] n is the real part of the index of refraction, ε is the dielectric constant, d_{ij} is a second-order nonlinear coefficient in the direction ij.

   influence of the first is still in sway, "sees" a different material. Its future course diverges from that observed in the absence of the first beam. Once the optical field has departed, the material gradually reverts to its unperturbed state. The duration of this relaxation is the material's characteristic response time. A light beam emerging from such an interaction is often qualitatively changed (e.g., in frequency

or intensity) or refracted from the incident beam. This behavior is termed nonlinear optics; the input and output beams cannot be related by a simple proportionality (3).

A myriad of events occurring at the intimate scale of local interaction between light and the material can induce large-scale nonlinear effects. The electric field of the laser beam can contort the shape of atoms by drawing the electrons toward its direction or by inciting electrons to jump to a different electronic orbit. The arrangement of atoms in the three-dimensional matrix of the material can shift, as the field pulls oppositely on the positively and negatively charged atoms. The field can induce an array of randomly oriented molecules to align uniformly along its direction. Bonds between atoms can be stretched or even broken by the electric field. If the beam's intensity is increased, its electric field also increases, evincing more pronounced distortions in the material. Yet a twofold increase in light intensity will not induce a twofold increase in distortion. The extent of distortion is contingent upon the material's inherent electronic properties. Any disruption of the charge configuration of the material will be macroscopically observable as a change in the speed and refraction of light.

A century ago researchers found that strong electric fields could alter the optical properties of materials. Ordinarily, glass is isotropic: It exhibits the same refraction no matter what the angle of incident light. Kerr showed that the refraction of light passing through glass along the direction of an applied electric field is different from the refraction along a perpendicular (4). Pockels discovered the same behavior in crystals that lack a center of symmetry (5). However, it was not possible to use the electric field of light to change the way materials refract light-until the laser was invented.

Light-induced optical effects can be more dramatic than the processes observed by Kerr and Pockels. An intense laser beam can induce a discontinuity in the way the material-both within and outside the beam's path- refracts light. This discrepancy, for example, may create a lens that is embedded in the material and that focuses the beam to a remarkable bright, narrow spot. The energy of the laser beam, focused by the lens to a point, can even damage the material. In optical fibers, uncontrolled "self- focusing" of light, caused by the nonlinearity of the materials, can

disrupt both the transmission and the fiber.

Optical harmonics

The seminal experiment in nonlinear optics was conducted by Franken in 1961 (6). A beam of red light from a ruby laser was directed through a quartz crystal, and the light emerging from the crystal included both a red and an ultraviolet component. Franken found that the frequency of the UV component was precisely double that of the incoming red light. This doubled frequency is called the second harmonic, in analogy with acoustics, where the higher harmonics of a fundamental tone are integer multiples of the frequency of the fundamental. The rich quality of musical sound derives from the simultaneous vibration of an instrument's string or air column at the fundamental and its harmonics; however, the world would look quite different if optical harmonics were commonplace. Light photons ordinarily do not interact with each other to change frequency. White light that passes through a piece of blue grass appears blue only because the glass absorbs all but the blue light; the glass did not transform photons from one "color" to another.

In the year following Franken's discovery, Bloembergen explicitly derived these optical effects by incorporating perturbing motions of electrons and charged atoms into the quantum mechanical model of light's interaction with matter. His study became the theoretical foundation of nonlinear optics, for which he was awarded a Nobel Prize in 1981 (7, 8).

A material exhibiting optical nonlinearities can override the noninteracting nature of photons. The material mediates the interaction; the energies of two incident photons may be added, producing a new photon at the combined energy. When the new photon is released, the difference in momentum between the incoming and the outgoing photons may be absorbed by the matrix of the material. If two laser beams of different frequencies impinge on a material, a light output of more diverse frequencies is possible. A material interacting with photons of unequal energy may emit that energy either in a single photon at the total combined energy or as several photons that split the total energy between them. The material facilitates these transformations without being affected itself; it acts as a catalyst.

When photon energies are combined to create photons of a new color, the

Table 2. Third-order nonlinear optical properties[a]

Material	n	n_2 esu (10^{-11})	Response time, s
GaAs ⟨100⟩	3.20	14.1	$<10^{-12}$
Si ⟨111⟩	3.44	8.8	$<10^{-12}$
CS_2	1.59	1.1	$<10^{-11}$
Fused silica	1.46	0.0095	$\sim10^{-14}$
PTS polydiacetylene	1.88	80.0	$\sim10^{-14}$
MNA	1.8	25.0	$\sim10^{-14}$
p-Nitroaniline	—	14.0	$\sim10^{-14}$

[a] n_2 is a measure of the intensity-dependent index of refraction.

refractive speed of the light beam changes, for the speed depends on frequency. The incident and resultant beams each travel at different speeds because of their different frequencies. At its creation, each new photon oscillates in phase with its parent photons. However, because the pace of the child beam differs from its parent, the oscillation phases of photons emitted by widely separated atoms will fall out of synchronization. These out-of-phase oscillations will cancel, diminishing the intensity of the new beam. For optical harmonics and mixture frequencies to be observable, the material's refractive properties must be manipulated to prevent phase cancellation. Sometimes by either heating or rotating the material, the speed of the incoming light traveling along one direction can be matched to that of the outgoing beam, traveling along a perpendicular. Then the phases of the newly created photons will remain synchronized. An even more stringent condition governs the combination of two photons with different frequencies to produce a third, or more. If the speeds of all three beams are not matched, phase cancellation will negate the effect (9-11).

Materials and nonlinear optics

Light and material must be tailored to precisely complement each other before these unusual effects can arise. The electric field of light interacts with and disrupts the electrical environment internal to the material. By systematically tweaking the molecular structure of a material, its interaction with light can be analyzed. Insights derived from these studies of light and matter can shape the design of new materials with an enhanced nonlinear response to light.

The detection of nonlinear optical behavior in ordinary materials is elusive; ideally the material must possess superior optical quality-transparency, freedom from defects

that scatter light, uniformity, a polished surface- in addition to sustaining the matching of light's refractive speeds. Inorganic materials traditionally associated with optics (e.g., quartz and the new semiconductors) initially received the most attention. For example, lithium niobate, which can be grown as single crystals, satisfies many of these criteria; however, further enhancement of these properties is desirable. Several organic materials match and may even exceed the efficiency of lithium niobate in generating optical harmonics. However, deficiencies in other properties such as phase-matching ability may hinder their practical use *(12)*.

Results of some comparative studies of the nonlinear optical behavior of inorganic and organic materials are summarized in the two tables. Table 1 lists parameters relevant to the production of second-order optical harmonics: the index of refraction, n; the dielectric constant, e; and a directionally dependent measure of the second-order effect, d*.* Materials with a high & respond sluggishly to the stimulus of light's electric field. In this respect, 2-methyl-4-nitroaniline (MNA) with a 5% lower dielectric constant and a 100-fold higher second-order coefficient than lithium niobate, would be preferable for applications in which a quick response time is critical to the operation of a device. (We will describe the nature of these devices in Part 2 of this series.)

Table 2 gives characteristics pertinent to the third-order harmonics: index of refraction, n; a third-order index, ng; and the response time. Again the organic materials excel both in rate of response and in magnitude of the third- order effect. Inorganic materials typically must compensate for changes in their electrical environment by shifting the position of atomic nuclei, a slower process than the electronic motions that perform the same function in organics. The inherently rapid electronic perturbations in organics-orders of magnitude faster than switching times in electronic devices-have potential for inclusion in information processing systems. The optical and electrical properties of a material proceed directly from the identity of its component parts-atoms and molecules-and from the arrangement of these parts into a superstructure. Inorganic materials constitute a limited range of atomic species; improvement of nonlinear performance must be sought through a change in crystal structure rather than by subtle modifications to the molecule. This is a daunting prospect, for the material may exist only in a specific crystal form. Even if other structures exist, the effort to grow a new

form of crystal is typically laborious and protracted. Organic molecular structure, however, can be modified incrementally by making small changes in the backbone or substituents. In this way the chemist can fine- tune the material's response to light as well as its other chemical and mechanical properties.
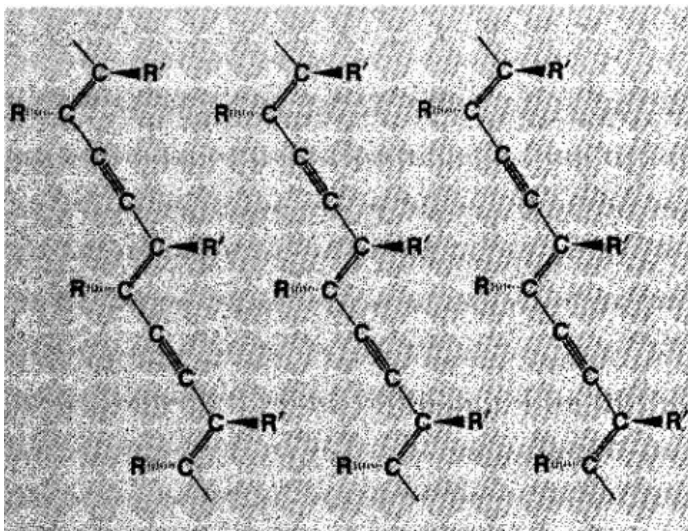

Figure 1. Polydiacetylene chains in a crystal. R is an electroactive side group and R' is a surfactive group
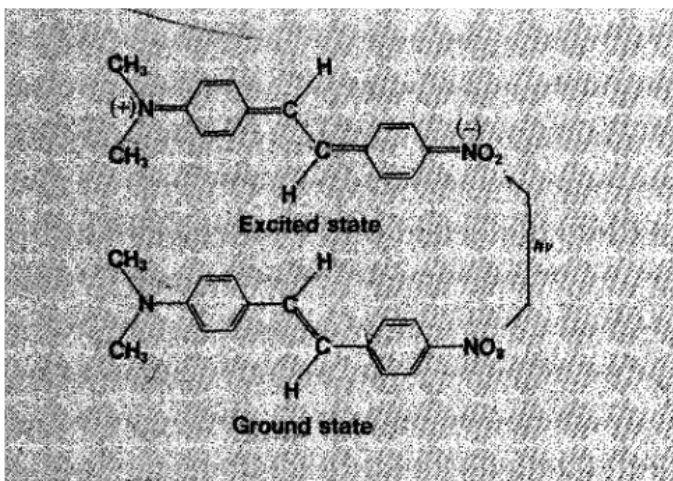

Figure 2. Molecular structures of the ground and resonance excited states for 4-dimethylamino-4'nitrostilbene (DANS). $N(CH_3)_2$ Is the electron donor and NO_2 is the electron acceptor

A conjugated backbone appears to be crucial to the ability of polymeric molecules to generate third harmonics. The electrons, distributed along the backbone, react quickly when the electrical environment is changed by another molecule, an electric field, or light. This quick response and the extensive spreading of the cloud is the

source of a sizable, fast, third-order response in these quasi one-dimensional systems.

The polydiacetylene class of polymers has emerged as one of the more promising prospects for third-order nonlinear effects. The third-order index, n2, of polydiacetylenes (Figure 1) is one of the larger indices demonstrated to hold within the range of the transparent frequencies of a material. The response time of polydiacetylenes is predicted to be in the subpicosecond range (Table 2).

Organic molecules with other nonlinear behavior, such as second-order effects, can be integrated into the diacetylene through the side groups. The electrons are polarizable along the length of the macromolecular backbone. This extensive conjugation-in the substituents, in the backbone, and in their interplay together-may be responsible for a broad range of nonlinear phenomena not possible in a single monolithic inorganic system. The side groups R and R' can be varied and modified to optimize optical, mechanical, and processing properties (*13*).

Molecular hyperpolarizability, ß, is a measure of the tendency of a molecule to exhibit second harmonics. Two terms contribute to the hyperpolarizability: an asymmetry term, *Bas*, and a charge-transfer term, *Bet* A greater asymmetry in the way charge is distributed along a molecule will induce a more pronounced interaction with the electric field *of* light. Second harmonics, however, will not occur at all if the molecule crystallizes or assembles with a center of symmetry. The charge-transfer term describes the extent to which the field of light induces transitions from the molecule's ground state to its excited, or resonance, state. Because a crystal lattice of organic molecules is stabilized primarily by weak van der Waals forces, its macroscopic second-order behavior can be regarded as an averaged sum of these molecular hyperpolarizabilities.

This correlation between structural and optical properties can be demonstrated by the behavior of 4- dimethylamino-4'-nitrostilbene (DANS) (Figure 2). The C-C-bridging group confines the molecule to a plane, extending conjugation from end to end and stabilizing its resonance structure. In the resonance structure shown, positive and negative charges are maximally separated, producing a large internal electric field. The electron- donating (dimethylamino) and electron-withdrawing (nitro) groups create an asymmetry in charge. In this case, the charge-transfer term dominates: For DANS the estimated value of *Bet* 3.8 X 10-32 esu is very close to the

experimental determination of Btotal 4.5 x 10-32 esu.

Key parameters extracted from the UV and visible spectrum of DANS confirm these results. The calculated probability of a transition from ground to resonance state (related to *Bet)* is very high. In addition, the polarization of the molecule in its resonance state is 4 times greater than in the ground state. This suggests that a molecule that admits a large charge separation in converting to its resonance state will possess a substantial hyperpolarizability. This observation is a possible blueprint for the design of molecules with enhanced nonlinear behavior that may assist in the selection of optimum molecular structures from the large palette of organic molecular structures available.

Organic materials satisfy other practical requirements for nonlinear optics. They may be selected and tailored to be transparent to light of frequencies convenient for experimentation and applications. In addition, light usually travels at markedly disparate refractive speeds when it is directed along different axes in organic crystals; this phenomenon is termed birefringence. This facilitates the effort to match the phases of the incident beam with the optical harmonic, which is necessary to prevent cancellation of the harmonic (14). Although organic molecules such as DANS can be designed with an asymmetric structure, they often crystallize in a symmetric configuration. This precludes production of second harmonics. Alternative techniques for crystal growth must be devised to circumvent this drawback. A recently developed technique embeds active molecules within a polymer host in which, following alignment in an electric field, they are available for use in nonlinear experiments. This remarkable approach bypasses the stringent demands of crystal growing.

In Part 2 our attention shifts from the theoretical foundations of nonlinear optical behavior in polymers to the more practical agenda of processing these materials and incorporating them into optical devices. The techniques of casting, crystallization, and thin-film multi- layer growth are adapted for the production of the appropriate form of the polymer that retains its nonlinear function. Through the active component of an optical device (i.e., the nonlinear material), a light beam or imposed electric field operates on the incident light by either switching or altering its information content. The emergent light beam bears the imprint of the nonlinear interaction as a change in its frequency, direction, or intensity.

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