

집적광학과 광통신을 위한 비선형광학 유기물질

Organic nonlinear optic materials for integrated
optics and optical telecommunications

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New nonlinear organic materials have been developed for all-optical signal processing. The organic materials possess many interesting features for this purpose. Unlike inorganic molecules the delocalized π -electron distribution and intramolecular charge transfer mechanism allows certain organic molecules to respond highly anharmonically to an external field. In the present paper the origins of nonlinear phenomena, advantages of organic materials and structures of organic devices will be discussed.

I. Introduction

The fast growing development of optical communication systems has stimulated the wider search for materials with highly nonlinear optical properties capable of forming the basis of devices for the efficient processing of optical signals.^[1]

The operation of such devices is based on the variation of the dielectric polarization $P(t)$ of the solid in an intense optical field $E(t)$. The electric charges in solids are held in equilibrium by atomic fields of the order of $10^8 \sim 10^9 \text{V/cm}$, and the nonlinearity in their motion can only be observed by using perturbing fields that are not negligible compared to these values. Most of the nonlinear effects in condensed matter can be observed at intensities in the kilowatt to megawatt per square centimeter range which corresponds to electric fields of the order of $10^3 \sim 10^4 \text{V/cm}$, which are small compared to atomic fields. However, because of coherence of laser beam, the efficiency of a nonlinear optical process reaches from 10^{-3} to 10^{-1} .

The nonlinear response of the macroscopic

polarization is represented as

$$P(t) = \chi^{(1)}E(t) + \chi^{(2)}E^2(t) + \chi^{(3)}E^3(t) + \dots \quad (1)$$

Here the coefficients $\chi^{(1)}$ is linear susceptibility, $\chi^{(2)}$ and $\chi^{(3)}$ are second and third order nonlinear susceptibility respectively. The coefficients become decreasingly smaller with increasing order and in most materials terms beyond the third can be neglected.

The first and third coefficients are common to all materials and give rise to linear optical processes and third order nonlinear processes respectively. The second term $\chi^{(2)}$, the second order response, occurs only in non-centrosymmetric structure. Where strong, these various contributions can be used in a variety of potential devices, some examples of which are shown in Table 1.

II. Organic materials

In the search for suitable materials with strong nonlinear responses, interest has focussed principally on inorganic substances. This is an avenue dictated

Table 1. Effects and application of electric susceptibility function χ .

Order	crystal	Molecule	Effects	Possible utilization
1	$\chi^{(1)}$	α	refraction	optical fibres
2	$\chi^{(2)}$	β	generation of second harmonic $\omega + \omega \rightarrow 2\omega$	frequency doublers
			frequency mixing $\omega_1 \pm \omega_2 \rightarrow \omega_3$	optical mixers
			parametric amplification $\omega_3 \rightarrow \omega_1 + \omega_2$	optical parametric oscillators
3	$\chi^{(3)}$	γ	Pockels effects $\omega + 0 \rightarrow \omega$	electro optical spectroscopy
			4-wave mixing	Raman coherent spectroscopy
			phase gratings	real time holography
			Kerr effect	ultra high speed optical gates
		optical bistability	amplifiers, amplitude choppers, logical gates etc . . .	

macroscopic polarization

$$P = P_0 + \chi^{(1)}E + \chi^{(2)}EE + \chi^{(3)}EEE + \dots$$

molecular dipole

$$p = p_0 + \alpha E + \beta EE + \gamma EEE + \dots$$

principally by habit ; device physicists being more conditioned to accept that these materials are rugged and easily processible. Organic materials are usually discounted on the basis that they are fragile, less easily processible and less chemically and physically stable than inorganic counterparts. In general terms, such criticisms are rational. However in recent yeas much efforts have been made to overcome these difficutties and open the way to explore the superlative potential of organic materials.^[1]

Organic materials are known, the structures of some of which are shown in Fig. 1, which

- a) Have second order nonlinear properties which far surpass those of inorganic materials.
- b) Show far greater radiation damage threshold in the regimes of operation than do the best inorganic materials.
- c) Have faster response time than inorganic materials.
- d) are transparent in visible and infrared region.

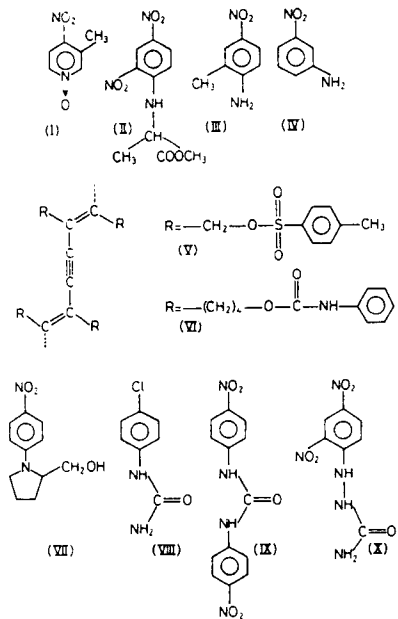


Figure 1. Various molecular structures of current materials.

- I 3-methyl-4-nitropyridine-1-oxide(POM)
- II methyl-(2,4-dinitrophenyl)-aminopropanoate (MAP)
- III 2-methyl-4-nitroaniline (MNA)
- IV meta-nitroaniline (mNA)
- V polydiacetylene with diacetylene monomer : bis (p-toluene sulphonate) 2,4-hexadiyne-1,6-diol (PTS)
- VI idem with monomer : bis-(phenylurethane) of 5,7-dodecadiyne-1,2-diol(TCDU)
- VII N-(4-nitrophenyl)-(L)-prolinol (NPP)
- VIII para-chlorophenylurea (PCPU)
- IX di-(p-nitrophenyl)-urea (DNPU)
- X 1-(2,4-dinitrophenyl)-semicarbazide (DNP-SC)

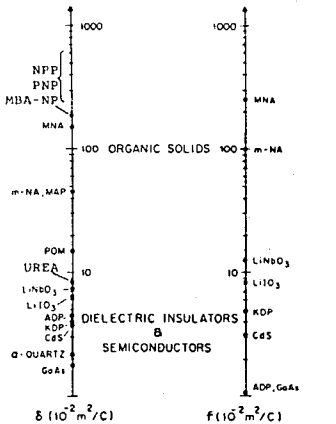
The properties are quantified in Table 2 which shows both the second harmonic generation coefficients and the optical damage thresholds for a number of organic materials relative to those of the best inorganic material lithium niobate.[2] Such improvements must evoke interest.

This interest is sustained to a greater degree when one considers that often quoted advantage of organic materials ; that if the molecular basis for the nonlinear behaviour can be defined then materials with much improved properties can be predicted by theoretical quantum mechanical calculation. Subsequent synthesis and molecular engineering can then be used to yield non-centrosymmetric crystals of the material. The prospect is endless.

Organic nonlinear optical material consists of ;

- a) Molecular crystals
- b) Polymers
- c) Liquid crystals
- d) Organometallic compounds

(a) SECOND HARMONIC LINEAR ELECTRO-OPTIC



$$\gamma_{ijk} = \epsilon_0(\epsilon_k - 1)f_{ijk}$$

$$\chi_{ijk}^{(2)} = 2\epsilon_0\chi_{ii}^{(1)}\chi_{jj}^{(1)}\chi_{kk}^{(1)}\delta_{ijk}$$

(b) LASER DAMAGE THRESHOLD ($MW \text{ cm}^{-2}$)

	0.53 μm	1.06 μm
MAP	150	3000
POM	50	-
MBA-NP	-	300
LINDO ₃	20	50

Table 2. Optical properties of organic and inorganic materials, (a) Miller's delta function and (b) laser damage threshold .

III. Molecular nonlinear optic properties

The crystal properties of a molecular solid primarily reflect a combination of the molecular contributions. In the present case the molecular contribution is via the induced molecular dipole moment.

$$\mu(t) = \alpha E(t) + \beta E^2(t) + \gamma E^3(t) + \dots \quad (2)$$

where α is the molecular polarizability and β and γ are the first and second order hyperpolarizabilities. The crystal polarization is then the sum of the molecular contributions plus structural contributions due to the influence of intermolecular forces on the electronic structure of the molecules combined in the solid state. The molecular contribution dominates and hence a high value of β should contribute to a high $\chi^{(2)}$ provided that a non-centrosymmetric structure results.

The high nonlinear response in organic molecules comes from delocalized distribution of π -electron system. By introducing strong donor and acceptor groups into the π -electron, symmetric distribution of delocalized electrons is distorted and the nonlinear hyperpolarizabilities are to be greatly enhanced.

Theoretical quantum mechanical approaches lead to empirical ground rules for material selection. These are that the molecule should have

- a) A high polarizability
- b) Delocalized electrons
- c) Low energy excited states

Thus a simple aromatic molecule such as p-nitroaniline which has all these attributes should have a relatively high β which in fact is the case (Fig. 2). Unfortunately, p-nitroaniline crystallizes in a centrosymmetric crystal structure and $\chi^{(2)}$ is zero i. e. all the molecular dipole moments sum to zero. This problem can be rectified by simple 2-methyl substitution. This yields sufficient molecular asymmetry to allow the molecules to form a crystal with a non-centrosymmetric space group and which has an exceptionally high $\chi^{(2)}$ value.

IV. Organic devices

Organic nonlinear optical devices take two forms ; bulk structure and waveguide structure. Bulk materials are suitable for use with high-power lasers, while relatively low power semiconductor laser-driven system requires fully optimized waveguide structure. Theoretical calculation[3] shows that the ratio of second harmonic conversion rate, $\eta = P^{(2\omega)}/P^{(\omega)}$ in the bulk and in the planar waveguide would be of the order of 10^4 in the

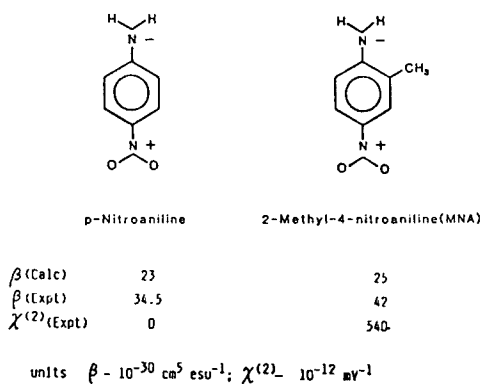


Fig. 2 Comparison of p-nitroaniline with 2-Methyl-4-nitroaniline (MNA).

case where the crystalline length is 1cm and the wavelength is 1 μm . In the calculation the assumption of no pump depletion was made. However in practice a ratio of the order of 10^2 can be reasonably expected. This is one of advantages of waveguided structure for use with a low-power laser. For example a c.w. pump power of 100 mW, which corresponds to currently available GaAlAs laser emission, is equivalent to a power density of the order of 10 MWcm^{-2} when confined along a guide of average cross-sectional area $1\mu\text{m} \times 1\mu\text{m}$. This power density comes close to the optical damage threshold of LiNbO_3 , which partially accounts for the demand of new materials which are able to sustain higher power densities. A second advantages of waveguided configuration is to achieve phase matching condition by using velocity-frequency dispersion of the different eigenmodes.^[4] Mode dispersion can be taken advantage of to compensate for the effective index dispersion, very much as birefringency is used to compensate index dispersion in bulk anisotropic media. In Fig. 3 a number of waveguiding configurations are shown, which are fairly general. It should be noted that stringent thickness control is very important in waveguide structure. The techniques of solution deposition, spinning, plasma polymerization, vacuum evaporation and Langmuir-Blodgett deposition^[5,6] are used to control the film thickness. Another problem with the waveguide configurations is how to orient the crystal. Several attempts, including application of dc field, have been made to control the orientation, but it is yet to be found the proper solution.

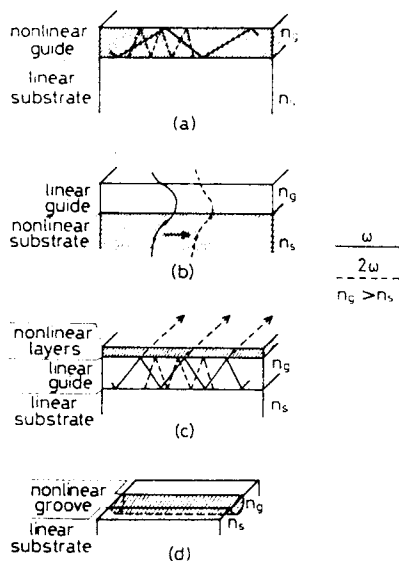


Fig. 3 Examples of waveguiding nonlinear structures.

V. Conclusion

Earlier work on bulk crystalline nonlinear materials has conclusively established the relevance of some specifically tailored organic compounds for efficient second and third order nonlinear interactions. There exists a considerable background know-how in both the fabrication and use of nonlinear organic materials for integrated optics,^[5,7] and in understanding of the origin of the higher nonlinear efficiencies of organic compounds.^[1,2]

Referencers

- [1] D. S. Chemla and J. Zyss, ed., 'Nonlinear Optical Properties of Organic Molecules and Crystals', Academic Press, Orlando, 1987.
- [2] D. J. Williams, ed., 'Nonlinear Optical Properties of Organic and Polymeric Matenals', Am. Chem. Soc., Washington D. C., 1983.
- [3] A. Az é ma, J. Bontineau, F. Gires and A. Saissy, SPIE 213, 26 (1979).
- [4] P. K. Tien, Applied Optics, 10, 2395 (1971).
- [5] C. W. Pitt, J. Non Cryst. Solids, 47, 159 (1982).
- [6] C. W. Pitt and F. Grunfeld, SPIE 401, 156 (1983).
- [7] H. P. Weber, W. J. Tomlinson and E. A. Chandros, Opt. and Quant. Electron. 7, 465 (1975).