

# Molecules To Materials

## 4. Molecular Nonlinear Optical Materials

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**Design of molecular nonlinear optical materials is presented; their inherent advantages are highlighted and their current status appraised.**

### Introduction

In this article, we first consider the emerging scenario of photonic technology. A brief description of the basic concepts behind the design of molecular nonlinear optical materials is provided. We focus attention on quadratic nonlinear optical applications, second harmonic generation in particular, where molecular design has been most effective. Finally an appraisal of the status of molecular materials in the fast growing and technologically significant area of nonlinear optics is presented.

### Nonlinear Optical Effects

Reflection, refraction, diffraction and absorption are commonly observed interactions of light with matter. During these processes the optical properties of the material such as the refractive index and the absorption coefficient remain unaffected by the electromagnetic radiation. However when the light used is in the form of powerful laser beams, some materials manifest marked changes in their optical properties as a result of the interaction with the strong electromagnetic field of the radiation. This in turn effects a modification of the frequency, phase or amplitude of the light transmitted through the material. Such interactions arising out of multiphoton effects are known as nonlinear optical (NLO) processes (*Box 1*) and the materials in which such processes can be carried out efficiently are called NLO materials.

Previous articles of this series were on:

1. Design and fabrication of functional molecular solids, Vol.3, April 1998.
2. Liquid crystals and molecular conductors, Vol.3, May 1998.
3. Molecular magnetic materials, Vol.3, July 1998.

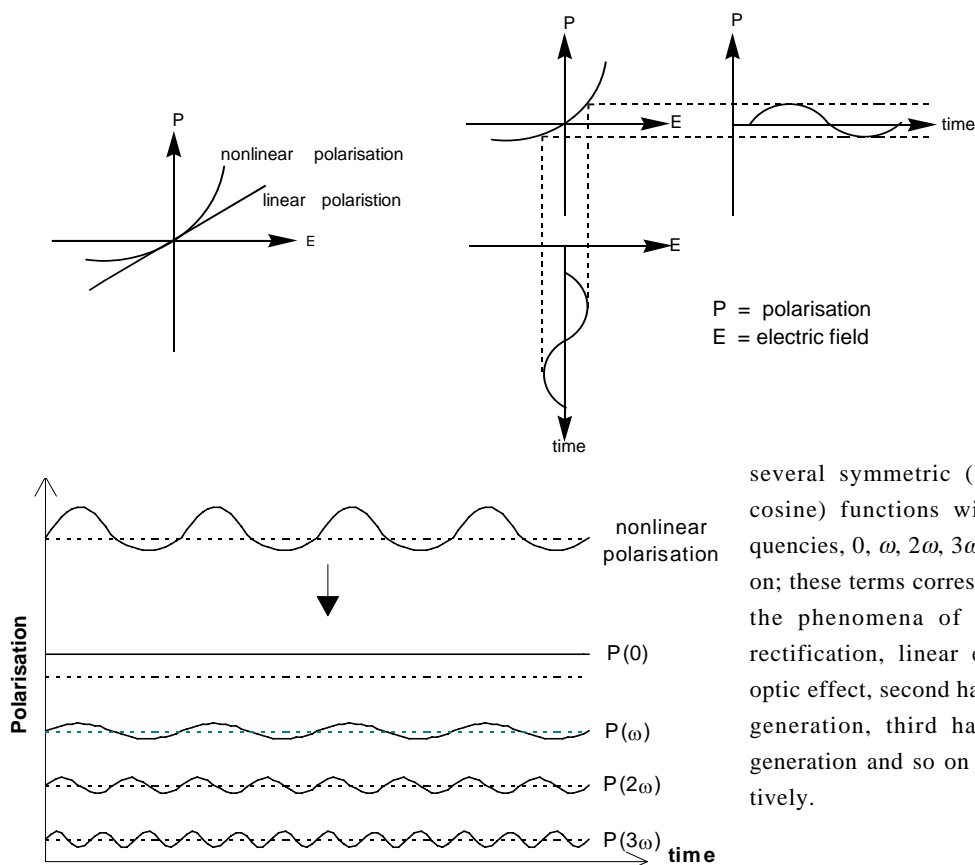
#### Please Note in part 2.

- 1) Page 17 last line was inadvertently omitted, the same is given below: '...  $6.3 \times 10^5 \text{ Scm}^{-1}$  and  $2.2 \times 10^6 \text{ Scm}^{-1}$ . However, at lower ...'
- 2) Figure 5: The structure on the right is  $\text{TTF}^{+}$  (and not  $\text{TTF}^{++}$ ).
- 3) Figure 6: Read 'unpaired  $e^-$ ' instead of unpaired  $\bar{e}$ .



**Box 1. Basic Aspects of Nonlinear Optical Phenomena**

When electromagnetic radiation is incident on matter, a variety of polarisations are induced depending on the frequency of the radiation. When the frequencies are relatively low (radiowave and microwave) three contributions to the total polarisation occur, orientation polarisation, vibrational polarisation and electronic polarisation. The first one involves reorientation of molecules in a field, whereas the second one is associated with the deformation of the nuclear framework of the molecule by the applied field. When the radiation has wavelengths in the optical range, only electronic polarisation occurs because of the higher frequencies involved. When the electric field associated with the electromagnetic radiation is small, as is usually the case with ordinary light, the polarisation varies linearly with the electric field and the constant of proportionality is the familiar polarisability,  $\alpha$  in the case of molecules and the linear electric susceptibility  $\chi^{(1)}$  in the case of bulk solids. However when laser light is used, the associated electric fields are very large and the induced polarisation is usually nonlinear. In such a case, a symmetrically varying electromagnetic radiation, say a sinusoidal wave with frequency  $\omega$ , can induce an unsymmetrically fluctuating polarisation in a noncentrosymmetric material. Such a periodic, but unsymmetrical function can be decomposed into



several symmetric (sine or cosine) functions with frequencies,  $0, \omega, 2\omega, 3\omega$  and so on; these terms correspond to the phenomena of optical rectification, linear electro-optic effect, second harmonic generation, third harmonic generation and so on respectively.

*continued...*

The total nonlinear polarisation,  $\mathbf{P}$  can be related to the permanent polarisation  $\mathbf{P}_0$  and the applied electric field,  $\mathbf{E}$ , for the case of molecules and for bulk materials using the following equations respectively.

$$\mathbf{P}_{\text{microscopic}} = \mathbf{P}_0 + \alpha \cdot \mathbf{E} + \beta \cdot \mathbf{E} \cdot \mathbf{E} + \gamma \cdot \mathbf{E} \cdot \mathbf{E} \cdot \mathbf{E} + \dots$$

$$\mathbf{P}_{\text{macroscopic}} = \mathbf{P}_0 + \chi^{(1)} \cdot \mathbf{E} + \chi^{(2)} \cdot \mathbf{E} \cdot \mathbf{E} + \chi^{(3)} \cdot \mathbf{E} \cdot \mathbf{E} \cdot \mathbf{E} + \dots$$

$\alpha$ ,  $\beta$  and  $\gamma$  are the molecular polarisability, first hyperpolarisability and second hyperpolarisability and  $\chi^{(n)}$  are the electric susceptibilities of order  $n$ . The magnitude of these tensorial nonlinear coefficients are quite small and decrease with increasing order. It is due to this reason that the nonlinearities show up only at high electric fields. The quadratic term gives rise to phenomena such as second harmonic generation (wherein two photons of frequency  $\omega$  give rise to one photon of frequency  $2\omega$ ) and the linear electro-optic effect. The cubic term leads to effects such as third harmonic generation and the quadratic electro-optic effect.

Materials having a centre of inversion symmetry will have their induced polarisation exactly reversed in direction when the electric field of the electromagnetic radiation is reversed *i.e.*  $\mathbf{P}(-\mathbf{E}) = -\mathbf{P}(\mathbf{E})$ . The quadratic and higher even order products of  $\mathbf{E}$  which contribute to the polarisation are unchanged by the change of direction of  $\mathbf{E}$ , whereas the cubic and other odd order terms are reversed by the reversal of  $\mathbf{E}$ . Hence in centrosymmetric systems, the even order terms vanish completely and the nonlinear effects arise exclusively from cubic and higher order odd terms. On the other hand, in a noncentrosymmetric system there are no symmetry constraints which relate the polarisations in opposite directions and hence NLO effects of any order can be observed.

A typical second harmonic generation process consists of conversion of the invisible 1064 nm (near infra red) radiation from a Nd:YAG laser to the visible 532 nm (green) using an NLO active material. The linear electro-optic effect can be demonstrated by determining the change in refractive index of a second order NLO material on application of strong electric fields. Experiments designed along these lines can be used to evaluate the hyperpolarisabilities of molecules and the second order NLO susceptibility of materials.

The discovery of semiconductors earlier in this century created a revolution in science and technology that ushered in the present 'electronic age'. Speculation is rife that a second revolution is in the making. The next revolution is expected to take us into the 'photonic age' when photons don the role that electrons play in the present day technology. Considering the higher speeds they possess and the larger range of frequencies they cover, photons should prove to be the superior carriers of information; 'light' after all 'is Nature's fastest messenger' (Einstein). Study of



nonlinear optics helps us learn the rules of the game that photons play in the world of photonics. Though significant advances have been made in the understanding of nonlinear optical phenomena and major breakthroughs have been achieved in the design of laser systems and nonlinear optical materials and devices, there is a considerable way to go before we can fully realise the 'photonic age' in practical terms. At present practical application has been achieved at an intermediate level, in the area of the so-called electro-optics which utilises the services of electrons and photons. Effect of applied electric field on the optical properties of nonlinear optical materials is exploited here. Electro-optic devices have made considerable impact in the area of telecommunication. Pundits predict that this happy marriage of photons and electrons is likely to go a long way; meanwhile the purists are hard at work to develop 'all-photonic' systems.

Whichever way one looks at it, these new developments in the area of nonlinear optics fueled by the tremendous advances in the field of laser technology, calls for a parallel progress in the field of materials. Inorganic materials having good crystal quality and strong nonlinear optical responses have been the choice so far. For example, commercial laser systems employ crystals of potassium dihydrogen phosphate (KDP) and  $\beta$ -barium borate to double the frequency of the fundamental beam, a process known as second harmonic generation (SHG). Lithium niobate is used in electro-optic devices. However, of late there has been an increasing recognition of the potential of molecular and polymeric materials for nonlinear optical applications.

The efficiency with which a material can carry out nonlinear optical processes is controlled primarily by its nonlinear susceptibilities of various order, denoted as  $\chi^{(2)}$ ,  $\chi^{(3)}$  and so on. A crucial distinction between the traditional inorganic materials and the molecular materials is revealed when one tries to analyse the origin of their nonlinear susceptibilities. In the case of the latter, the bulk nonlinear susceptibility can be understood in terms of (i) the contribution of the individual molecules (known as the molecular hyperpolarisabilities,  $\beta$ ,  $\gamma$  etc.) and (ii) the

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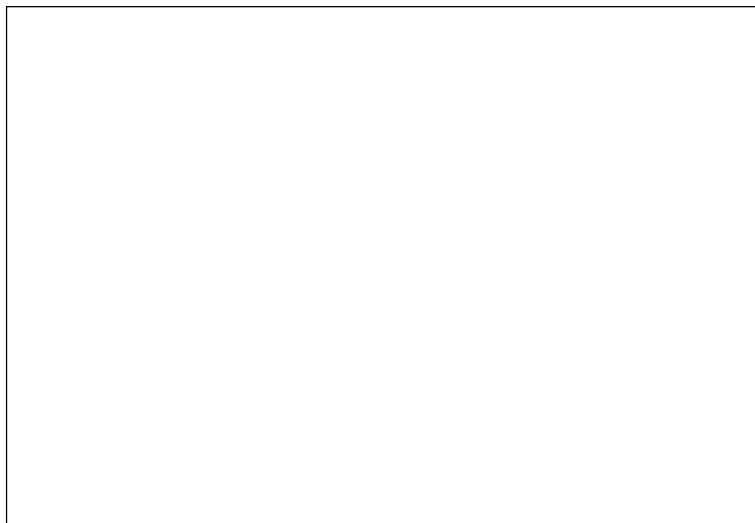
cumulative impact of their contributions determined by the way the molecules are arranged in the bulk. In the case of the former such a dissection of the bulk nonlinear susceptibility is not possible, since the material property arises from the mutual disposition of the constituent atoms and ions and is much more complex to picture. Herein lies one of the advantages of molecular materials in this field.

## Second Order NLO Materials

We pointed out in Part 1 of this series, that the preparation of molecular materials goes through two stages: optimising the molecule and the material fabrication by assembly of the molecular units. In the context of quadratic nonlinear optical applications such as second harmonic generation, the first problem has been tackled fairly successfully; practical guidelines are available to tailor molecular systems to achieve high hyperpolarisabilities. Simple theoretical considerations indicate that noncentrosymmetric molecules having low energy electronic excitations with large oscillator strengths and large dipole moment change on excitation have enhanced hyperpolarisabilities. However, if the excitation energies are close to the energy of either the exciting or the transmitted radiation, absorption will lead to impaired efficiency of the NLO process.

As shown in *Box 1* quadratic or other even order NLO effects can be observed only in noncentrosymmetric systems. Several  $\pi$ -conjugated molecules with unsymmetric electron distribution due to electron-donating and accepting groups possess large first hyperpolarisabilities,  $\beta$ . These molecules are sometimes described as push-pull systems. The criteria listed above show that  $\beta$  can be enhanced by increasing the extent of conjugation; however, an optimum level is desirable to avoid the problem of the energy gaps coming close to the energies of the electromagnetic radiations involved in the NLO applications. The unsymmetric polarisation induced in these molecules which gives rise to the second order NLO effects is schematically illustrated in *Figure 1* for the case benzene substituted with donor (D) and acceptor (A) groups



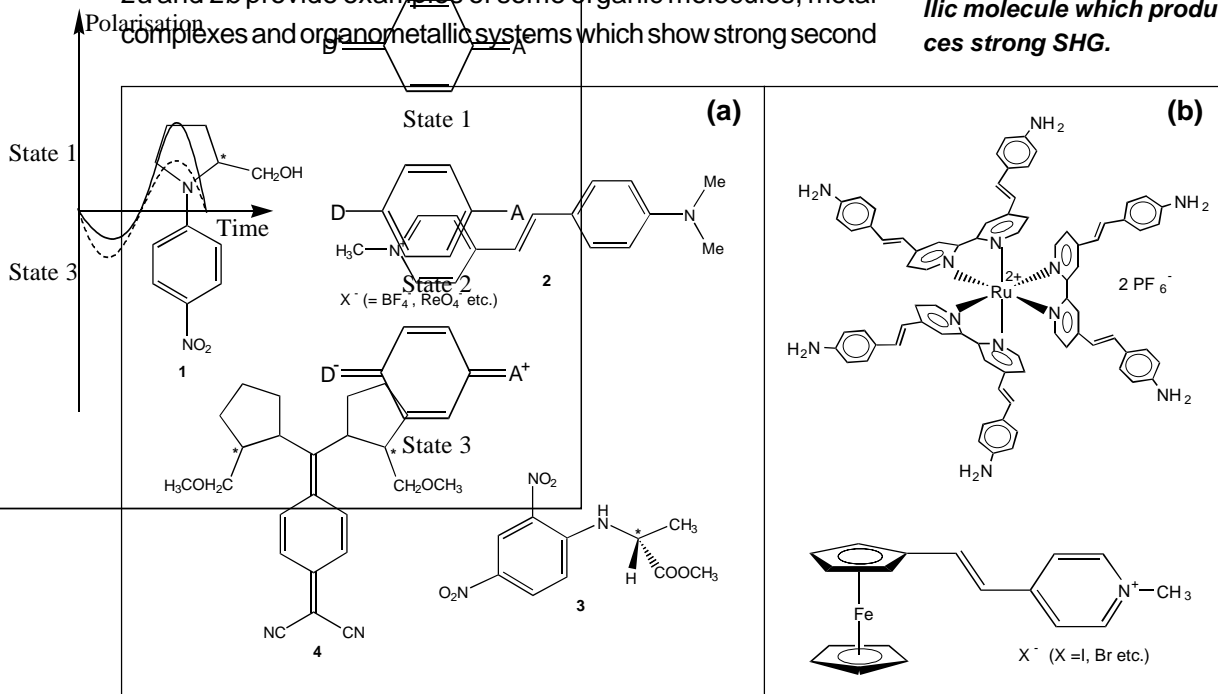


**Figure 1.** Schematic representation of the origin of asymmetric polarisation in donor-acceptor substituted benzene; the broken line represents the symmetric response of unsubstituted benzene.

(compare with the *Figure in Box 1*). The ease with which the  $\pi$ -electrons in these systems can be polarised leads to nonlinear responses which are stronger and faster than that of most inorganic materials. Organic materials also possess the advantage of having smaller refractive indices compared to inorganic crystals. *Figures 2a and 2b* provide examples of some organic molecules, metal complexes and organometallic systems which show strong second

**Figure 2a.** Some organic molecules which exhibit strong SHG; asterisk indicates chiral centre.

**2b.** A coordination complex with large hyperpolarisability and an organometallic molecule which produces strong SHG.



At this stage the subtle tools of weak interactions are brought to bear on the problem.

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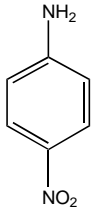
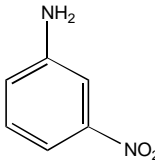
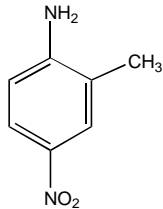
Turning to the problem of assembling molecules to fabricate molecular materials for second order NLO applications, we find that the situation is more complicated. Once we generate noncentrosymmetric molecules with large  $\beta$  values, they have to be assembled into a noncentric bulk material. For improved bulk  $\chi^{(2)}$  values, the molecules must be aligned appropriately so that their hyperpolarisabilities add up constructively. Several of the types of molecules we discussed above having large  $\beta$  values, also possess appreciable ground state dipole moments. Crystallisation of such molecules often leads to centrosymmetric lattices to maximise the dipole-dipole attractive interactions. At this stage the subtle tools of weak interactions are brought to bear on the problem. Some of the commonly used features are intermolecular H-bonding, steric factors and molecular chirality. Symmetry considerations alone ensure that a pure enantiomer will form a noncentric lattice. Features such as H-bonding and steric factors are often utilised to steer the molecules into appropriate alignment so that a large bulk NLO susceptibility is built up from the molecular hyperpolarisabilities.

Urea is a particularly enlightening example to describe the role of intermolecular interaction that leads to an efficient NLO material. The crystal structure of urea was illustrated in Part 1 of this series. The molecules are arranged in such a way that the strongest dipole components along the carbonyl bond are aligned antiparallel. However, to accommodate the extensive intermolecular H-bonding the molecular planes in adjacent arrays orient themselves orthogonal to each other. This leads to a noncentric lattice and hence SHG capability. Urea is perhaps the simplest molecular material capable of efficient SHG; it is used as a reference for comparing the SHG of other organic compounds, expressed in units of U.

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The case of nitroanilines provides a graphic demonstration of how subtle molecular modifications change drastically, the solid state NLO property. The three nitroanilines shown in *Figure 3*



	pNA	mNA	MNA
			
$\beta/10^{-30}$ esu	20	6	17
SHG/U	0	40	80

**Figure 3. Hyperpolarisabilities and SHG capabilities of nitroanilines.**

have comparable  $\beta$  values implying that their molecular NLO responses are similar. Note that *m*-nitroaniline has the lowest  $\beta$ ; this may be attributed to the fact that the electron donating and accepting effects do not act along the same axis. More importantly, dramatic differences are observed in the SHG capabilities of their crystals. *p*-Nitroaniline goes into a centrosymmetric lattice and shows zero SHG in spite of having an appreciable  $\beta$  value. In *m*-nitroaniline the ground state dipole moment is considerably smaller and a noncentric crystal lattice is formed. Even though the  $\beta$  of *m*-nitroaniline is smaller than that of *p*-nitroaniline, it shows appreciable solid state second harmonic generation. The minor modification on *p*-nitroaniline in terms of adding a single methyl group at the *ortho* position provides enough steric bulk to screen most of the dipolar forces and facilitate a noncentric crystal structure with improved alignment of the push-pull chromophores leading to a strong SHG of  $\sim 80$  U.

A wide variety of modifications on the nitroaniline framework have been explored in the search for molecular materials capable of strong SHG. *p*-Nitrophenylprolinol, NPP (**1** in *Figure 2a*) is one of the most efficient molecular material for SHG that has been characterised in great detail. NPP has a chiral carbon centre that ensures noncentrosymmetry of the lattice and the H-bonding present leads to a nearly optimal arrangement of molecular dipoles giving rise to an SHG capability of 150 U. For the sake of



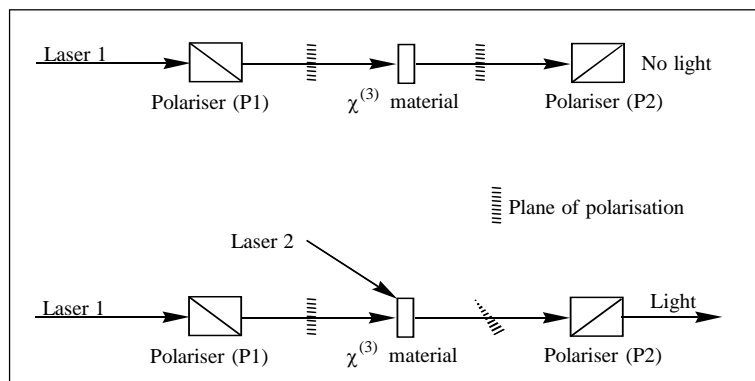


comparison we note that KDP, a standard inorganic crystal used for SHG shows an efficiency of  $\sim 0.3$  U.

Besides second harmonic generation, the large quadratic NLO susceptibilities of molecular materials may be utilised in electro-optic devices. Molecular crystals and poled polymeric materials are being investigated for electro-optic applications such as guided wave modulators and switches. This will be discussed further in Part 5 of this series on molecular devices.

### Third Order NLO Materials

For applications related to third order nonlinearity,  $\pi$ -conjugated polymers are the materials of choice since they possess large second hyperpolarisabilities,  $\gamma$  leading to the largest  $\chi^{(3)}$  values presently known. Extensive research is under way to realise practical applications of polymers such as polyacetylene, polydiacetylene and polyphenylenevinylene. Fullerenes like  $C_{60}$  and  $C_{70}$  (again!) have also been shown to have large  $\gamma$  values. Some of the applications that are being actively pursued are third harmonic generation (THG), photorefractivity and light intensity dependent refractive index changes. THG is useful in laser systems to generate new frequencies. Photorefractive materials have applications in areas such as high density optical data storage. Change of refractive index induced in a  $\chi^{(3)}$  material by means of a laser pulse can be used to produce all-photon switches for optical communication devices. The principle of such an all-photon device, the Kerr gate is illustrated in *Figure 4*. No light comes through when laser



**Figure 4. Principle of operation of a Kerr gate.**

beam 1 polarised at P1 is stopped at the cross polariser P2. When the NLO active material in the path is subjected to an intense pulse of laser beam 2, its refractive index is changed by virtue of its large  $\chi^{(3)}$  value. If the refractive index is anisotropic it effects a change in the polarisation state of laser beam 1. This in turn leads to transmission of light through P2. Thus the third order NLO material facilitates the use of laser beam 2 to open the gate for laser beam 1.

## Status of Molecular NLO Materials

One may wonder why organic molecular materials with their superior second and third order NLO properties have not surpassed the traditional inorganic solids in technological and commercial applications. One of the basic problems is the lack of robustness of molecular materials. Molecular crystals in general are fragile and brittle. They have relatively low thermal stability and low damage thresholds under laser irradiation. Large, optically clear crystals are difficult to grow and for specialised applications the crystals have to be large enough to cut and polish. Good transparency of the material at the operating frequencies is essential and several organic compounds with large hyperpolarisabilities absorb visible light making NLO applications at these wavelengths inefficient.

One of the approaches employed to get around the problem of poor crystal characteristics of molecular materials is to adopt novel techniques of bulk material assembly. Polymeric thin films are becoming increasingly popular since they combine the superior NLO activity with the useful mechanical properties of polymers. Techniques such as poling in polymer films and Langmuir – Blodgettry described earlier (Part 1 of the series) can be used to obtain suitable aligned states of the molecular dipoles for quadratic NLO applications. Another approach is to chemically attach the molecular entity to polymer backbones and align them under electric field poling conditions. Problems of depoling of the chromophores upon removal of the poling field has to be circumvented by cross-linking techniques subsequent to electric field poling which locks the aligned chromophores into position.

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Self-assembly techniques involving layer-by-layer growth of the NLO active molecules achieved by appropriate chemical reactions is another approach being developed. Since symmetry constraints are not present in the case of third order NLO applications a wide choice of material fabrication techniques can be utilised. Organic  $\pi$ -electron conjugated polymers offer excellent opportunities in this area.

### Concluding Remarks

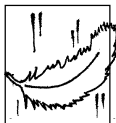
We have taken a brief look at the emerging possibilities of photonics technology and considered potential nonlinear optical applications of molecular and polymeric systems. In the case of quadratic NLO applications such as second harmonic generation, the way the molecular hyperpolarisabilities add up is the point of interest. First, molecular systems with large hyperpolarisability have to be identified. The units have to be assembled to obtain optimum macroscopic nonlinear optical response. In the next part of this series we will look at several examples of molecular material devices and later molecular scale devices.

### Suggested Reading

- [1] P Day, D C Bradley, D Bloor (eds.). *Molecular Chemistry for Electronics. Proceedings of the Royal Society Discussion Meeting*. Royal Society, London, 1990.
- [2] D S Chemla and J Zyss (Eds.) *Nonlinear Optical Properties of Organic Molecules and Crystals*. Academic Press. Orlando, 1987.
- [3] H S Nalwa and S Miyata (Eds.). *Nonlinear Optics of Organic Molecules and Polymers*. CRC Press. Boca Raton, 1997.

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When the layman says 'reality' he usually thinks that he is speaking about something which is a self-evident known; while for me working on the elaboration a new idea of reality seems to be precisely the most important and extremely difficult task of our time.

— Wolfgang Pauli in a letter to Markus Fierz  
dated August 12, 1948

