CHAPTER 1

INTRODUCTION

1.1. Theoretical Principles of Nonlinear Optics

Before the advent of lasers, transparent optical materials were assumed to be essentially passive, unaffected by light travelling through them. The high powers of laser beams made it possible for the first time to observe that the presence of light can indeed affect the optical properties of the medium.\(^1\)

The interaction of the electric field of an electromagnetic radiation with any material polarizes that material.\(^2\) This induced polarization results in charge separation i.e., positive and negative charges in the constituent molecules are moved in opposite directions, inducing an oscillating dipole in the medium. An oscillating dipole emits electromagnetic radiation. The secondary radiation combines with the original incident radiation to produce the characteristic optical properties.

The induced dipole per unit volume is called polarization, \(P\), and to a very good approximation, it is linearly proportional to the strength of the applied field \(E\),

\[
P = \chi E
\]

where the constant, \(\chi\) is the linear susceptibility of a collection of molecules and is related to the dielectric constant and refractive index of the material.

When the electronic charge in the optical material is displaced by the electric field of the applied electromagnetic radiation and polarization takes place, the total electric field, \(D\), which is the sum of the electric fields due to
the electromagnetic radiation and that generated due to polarization of the material, becomes 5

\[ D = E + 4\pi P = (1 + 4\pi \chi)E \quad 1.2 \]

where, \(4\pi \chi E\) is the internal electric field created by induced polarization.

The dielectric constant, \(\varepsilon\) in a given direction is defined as the ratio of the total internal field to the applied field in that direction,

\[ \varepsilon = \frac{D}{E} = 1 + 4\pi \chi \quad 1.3 \]

The frequency dependence of dielectric constant provides insight into the mechanism of charge polarization. At optical frequencies, in the absence of absorption or dispersion of electromagnetic radiation by the material, the square of the refractive index equals the dielectric constant.

\[ n^2(\omega) = \varepsilon(\omega) \quad 1.4 \]

Consequently, we can relate the refractive index to the bulk susceptibility of the material as,

\[ n^2(\omega) = 1 + 4\pi \chi(\omega) \quad 1.5 \]

In general, equation 1.5 relates the property of light to the property of electron density distribution (polarizability). From this equation, it is clear that the optical properties of a material depend on electron density distribution, which is dictated by the chemical structure of the material.

When the material is subjected to laser light of high intensity, the polarizability can change and be driven beyond the linear limit. The polarizability can now be expressed as a power series (equation 1.6), 2-4, 6.
where, \( P_0 \) is the static dipole of the sample, \( \chi^{(n)} \) is the \( n \)th order susceptibility of the material. The \( \chi^{(1)} \) term is responsible for linear optical properties such as light reflection and refraction. The terms beyond \( \chi^{(1)} \) are not linear in \( E \). They are referred to as nonlinear polarization and give rise to nonlinear optical (NLO) effects. At low field strengths, the polarization will approximately show a linear response, since the higher order terms become negligible and can be ignored. With increasing field strength however, nonlinear effects become more important.

The odd terms (\( \chi^{(1)}, \chi^{(3)} \) etc.) in equation 1.6 contribute to the polarization of all materials, but the values of the even coefficients (\( \chi^{(2)}, \chi^{(4)} \) etc.) are restricted by a symmetry requirement. These terms are non-zero only if the material lacks a center of symmetry, i.e., non-zero even order coefficients will be found only in crystals having a noncentrosymmetric space group. In amorphous solids, in liquids and gases and in solids in which the molecules are related by a center of symmetry, the even terms are always zero. The coefficient \( \chi^{(2)} \) is used below to illustrate the nature of induced nonlinear polarization. The coefficient is often written as,

\[
\chi^{(2)}_{ijk} (-2\omega; \omega, \omega) \tag{1.7}
\]

where, \( i, j, k \) refer to the principal axes of the medium and indicate tensorial characteristics of \( \chi^{(2)} \). \( 2\omega \) represents the frequency of the resultant field for the input frequencies \( \omega \). The minus sign is a convention indicating momentum conservation given by the vector sum,

\[
k_1 + k_2 + k_3 = 0 \tag{1.8}
\]
where, \( k_1, k_2 \) and \( k_3 \) are the wave vectors (2\( \omega \), \( \omega \) and \( \omega \) in this case) given by \( k_i = 2\pi/\lambda \) and points in the direction of propagation of the wave.

A variety of nonlinear optical effects can occur through \( \chi^{(2)} \) and \( \chi^{(3)} \) depending on the exact nature of the input frequencies, the proximity of molecular vibration or resonance to the input frequencies or frequency combinations and phase matching conditions. Some of the observable optical effects and applications are listed in Table 1.1 for \( \chi^{(2)} \) and \( \chi^{(3)} \).

### Table 1.1. Various NLO effects and possible applications

<table>
<thead>
<tr>
<th>Susceptibility</th>
<th>Effect</th>
<th>Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \chi^{(2)}(0; \omega, -\omega) )</td>
<td>optical rectification</td>
<td>hybrid bistable device</td>
</tr>
<tr>
<td>( \chi^{(2)}(-\omega; \omega, 0) )</td>
<td>electro-optic (Pockels) effect</td>
<td>modulators, variable phase retarders</td>
</tr>
<tr>
<td>( \chi^{(2)}(-2\omega; \omega, \omega) )</td>
<td>frequency doubling</td>
<td>second harmonic generation (SHG)</td>
</tr>
<tr>
<td>( \chi^{(3)}(-\omega; \omega, \omega, -\omega) )</td>
<td>AC-Kerr effect degenerate four-wave mixing</td>
<td>optical bistability, phase conjugation, real-time holography</td>
</tr>
<tr>
<td>( \chi^{(3)}(-3\omega; \omega, \omega, \omega) )</td>
<td>frequency tripling</td>
<td>deep UV conversion</td>
</tr>
</tbody>
</table>

The coefficient \( \chi^{(2)} \) leading to frequency doubling consists of a new component, \( 2\omega \). This is called a “three-wave mixing” process, since two photons with frequency \( \omega \) have combined to generate a single photon with frequency \( 2\omega \). This analysis can be extended to third and higher order terms, thus, third-order processes involve “four-wave mixing.”

Our ability to optimise the NLO properties of organic materials relies on a fundamental understanding of the interrelationship between chemical structure and molecular nonlinearities. At a molecular level, the induced dipole
generated by the interaction of electric field of electromagnetic wave with molecule can be represented by equation 1.9 which is analogous to equation 1.6, \[ \mu = \mu^0 + \alpha E + \beta E^2 + \gamma E^3 + \ldots \] where, \( \mu^0 \) is the static dipole of the molecule in the absence of any external field, \( \alpha \) is the linear polarizability and \( \beta \) and \( \gamma \) are the first and second hyperpolarizabilities of the molecule, respectively. The molecular coefficients, \( \alpha, \beta \) etc. are analogous to the susceptibility of the material (\( \chi^{(n)} \)) except that for the \( \chi \) terms, local field factors arising from the surrounding medium are taken into account.

Design of materials possessing second order NLO effects relies on the relationship between molecular structures and property. The basic strategies accepted for designing SHG materials should take into account factors such as (i) the material should be polarizable, (ii) there should be asymmetric charge distribution, (iii) contain a \( \pi \)-conjugated electron pathway and (iv) possibility of eccentric crystal packaging.

1.2. Organic Materials for Second Harmonic Generation

Second-order effects are associated with the third term in the polarization equation (equations 1.6 and 1.9). Molecules containing a conjugated \( \pi \)-electronic system with charge asymmetry exhibit extremely large values of \( \beta \). To induce charge asymmetry, donor and acceptor groups are substituted on opposite ends of a conjugated molecule which lead to low-lying charge transfer resonance states. The common donor groups are characterised by predominant \( p \) character (\( sp^3 \) bonding) and often have available electron pairs on a \( p \) orbital and the common acceptor groups are characterised by the possession of more \( s \) character (\( sp^2 \) or \( sp \) bonding), or vacant orbitals (as in certain boron compounds).
1.2.1. Early Studies

The first generation of materials used for SHG were inorganics such as ammonium dihydrogen phosphate (ADP), potassium dihydrogen phosphate (KDP), and β-barium borate (BBO). These materials possess only moderate nonlinear coefficients. However, they have relatively large transparency ranges from UV to IR and high optical damage thresholds. Organic materials were initially assumed to be fragile, less easily processed and also less physically and chemically stable. However, the unique electronic properties of organic materials impart them with much higher second order nonlinearities and shorter switching times than the known inorganic materials.

In the early 1960s very little was known about the requisite structural features to be present in organic molecules to have NLO properties and hence compounds were examined on the basis of their ready availability. Some of these compounds are listed in Table 1.2.

An interesting aspect of all these compounds is that although they are nonchiral they crystallise in noncentrosymmetric space groups.

The SHG properties of urea were first reported by Kurtz and Perry. Urea is considered as the first potentially useful organic nonlinear material although it has only a moderate nonlinear coefficient (χ(2) = 3 x KDP). It is however transparent down to 200 nm and has fairly large birefringence.

1.3. Molecular Engineering of NLO Materials

Molecular engineering is “the planned synthesis of materials possessing desired bulk properties.” In the present context, it is the synthesis of organic materials which possess efficient SHG properties at both the molecular and material level. The observed nonlinear response of a material is governed by the optical characteristic of constituent molecular chromophores, the frequencies of the input radiation and the overall spatial orientation that can be imposed.
<table>
<thead>
<tr>
<th>Compound</th>
<th>Structure</th>
<th>Space group</th>
<th>NLO efficiency</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td><img src="image1.png" alt="Structure 1" /></td>
<td>$I\bar{4}3m$</td>
<td>$10 \times \text{KDP}$</td>
<td>18</td>
</tr>
<tr>
<td>2</td>
<td><img src="image2.png" alt="Structure 2" /></td>
<td>$P2_12_12_1$</td>
<td>$6 \times \text{KDP}$</td>
<td>19</td>
</tr>
<tr>
<td>3</td>
<td><img src="image3.png" alt="Structure 3" /></td>
<td>$P3_2$</td>
<td>$9 \times \text{KDP}$</td>
<td>20</td>
</tr>
<tr>
<td>4</td>
<td><img src="image4.png" alt="Structure 4" /></td>
<td>$P2_1$</td>
<td>$10 \times \text{KDP}$</td>
<td>21</td>
</tr>
<tr>
<td>5</td>
<td><img src="image5.png" alt="Structure 5" /></td>
<td>$P\text{ca}$</td>
<td>$3 \times \text{KDP}$</td>
<td>22</td>
</tr>
<tr>
<td>6</td>
<td><img src="image6.png" alt="Structure 6" /></td>
<td>$P\text{bc}2_1$</td>
<td>$51 \times \text{KDP}$</td>
<td>23</td>
</tr>
<tr>
<td>7</td>
<td><img src="image7.png" alt="Structure 7" /></td>
<td>$P\text{na}2_1$</td>
<td>$29 \times \text{KDP}$</td>
<td>24</td>
</tr>
</tbody>
</table>

upon large ensembles of these constituents. The spatial organization is important for second order NLO properties, because in order for $\beta$ (or $\chi^{(2)}$) to be nonzero, the molecules (or material) used have to be noncentrosymmetric. Regrettably, as one modifies the molecular properties it becomes more difficult
to simultaneously obtain the desirable absorption and optical properties such as transparency in the near UV to visible range and low scattering. Furthermore, they must be orientationally, environmentally, and photochemically stable.

A typical SHG material consists of an electron accepting group, a conjugated bridge, and an electron donating group. The conjugated bridge allows for good communication between the donor and acceptor groups. Changing a donor (D) or an acceptor (A) group alone on the π system will perturb the electron density of the molecule. The most dramatic effect is found when both D and A groups interact in a mesomeric fashion (Figure 1.1).

![Figure 1.1. Substituent-induced electronic perturbations. Substitution of benzene by a donor-acceptor pair results in ground-state mesomeric charge redistribution](image)

This analogy is illustrated by Asato et al. by synthesizing a series of compounds that contain substituted azulenes as donor. A representative example (8) is shown in Scheme 1.1.
The disruption of aromaticity of azulene on going to the zwitterionic state is more than compensated by the gain of resonance energy upon formation of the aromatic azulenylium carbocation.\textsuperscript{28} The $\mu\beta$ value of compound 8 is $1323 \times 10^{-48}$ esu at 1907 nm, which is comparable to that of the diethylaniline derivative 9 ($\mu\beta = 1400 \times 10^{-48}$ esu),\textsuperscript{13} shown in Chart 1.1.

Drost \textit{et al.} have reported that the introduction of electron rich five membered heteroaromatics such as thiophene as part or all of the $\pi$-conjugation between the donor and acceptor increases the hyperpolarizability of the molecule (Table 1.3).\textsuperscript{29} These results were supported by molecular orbital calculations.\textsuperscript{30} From Table 1.3 it is clear that substituting a phenyl group by thiophene brings about a significant enhancement of the $\mu\beta$ value. The enhancement in $\mu\beta$ values on thiophene substitution has been attributed to the
lower resonance energy (117 kJ/mol) compared to that of benzene (151 kJ/mol).

Table 1.3. Thiophene-based donor-acceptor compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>Structure</th>
<th>$\lambda_{\text{max}}$ (nm) in dioxane</th>
<th>$\beta\mu$, $10^{-48}$ esu, at $\lambda = 1907$ nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>(CH$_3$)$_2$N-(\ Noon)-(\ Noon)-NO$_2$</td>
<td>424</td>
<td>580</td>
</tr>
<tr>
<td>11</td>
<td>(CH$_3$)$_2$N-(\ Noon)-(\ Noon)-NO$_2$</td>
<td>478</td>
<td>600</td>
</tr>
<tr>
<td>12</td>
<td>(\ Noon)-(\ Noon)-(\ Noon)-NO$_2$</td>
<td>460</td>
<td>660</td>
</tr>
<tr>
<td>13</td>
<td>(\ Noon)-(\ Noon)-(\ Noon)-NO$_2$</td>
<td>516</td>
<td>1040</td>
</tr>
<tr>
<td>14</td>
<td>(CH$_3$)$_2$N-(\ Noon)-(\ Noon)-(\ Noon)-CN</td>
<td>468</td>
<td>1100</td>
</tr>
<tr>
<td>15</td>
<td>(CH$_3$)$_2$N-(\ Noon)-(\ Noon)-(\ Noon)-CN</td>
<td>513</td>
<td>1300</td>
</tr>
<tr>
<td>16</td>
<td>(\ Noon)-(\ Noon)-(\ Noon)-CN</td>
<td>584</td>
<td>2600</td>
</tr>
</tbody>
</table>
A number of new organic compounds have been synthesized in order to find the optimum features of donor and acceptor groups for generating new materials with efficient SHG properties. The relationship between donor and acceptor strengths and $\mu\beta$ value are not straightforward. For example, a recent study has shown that increasing acceptor strength does not necessarily lead to increase in the values of $\mu\beta$ (Table 1.4).\textsuperscript{31}

Table 1.4. Nonlinear optical coefficient of donor-acceptor substituted chromophores of the form $D(CH\equiv CH)_nA$

<table>
<thead>
<tr>
<th>Compound</th>
<th>D</th>
<th>A</th>
<th>n</th>
<th>No. of conjd. atoms</th>
<th>$\lambda_{max}$ (nm)</th>
<th>$\mu\beta$ x $10^{48}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>17</td>
<td>Me$_2$N</td>
<td>CHO</td>
<td>0</td>
<td>3</td>
<td>&lt;240</td>
<td>1.8</td>
</tr>
<tr>
<td>18</td>
<td>Me$_2$N</td>
<td>CHO</td>
<td>1</td>
<td>5</td>
<td>284</td>
<td>21</td>
</tr>
<tr>
<td>19</td>
<td>Et$_2$N</td>
<td>CHO</td>
<td>2</td>
<td>7</td>
<td>363</td>
<td>130</td>
</tr>
<tr>
<td>20</td>
<td>Me$_2$N</td>
<td>CHO</td>
<td>3</td>
<td>9</td>
<td>422</td>
<td>366</td>
</tr>
<tr>
<td>21</td>
<td>Me$_2$N</td>
<td>CH=C(CN)$_2$</td>
<td>0</td>
<td>5</td>
<td>352</td>
<td>7.6</td>
</tr>
<tr>
<td>22</td>
<td>Me$_2$N</td>
<td>CH=C(CN)$_2$</td>
<td>1</td>
<td>7</td>
<td>374</td>
<td>54</td>
</tr>
<tr>
<td>23</td>
<td>Et$_2$N</td>
<td>CH=C(CN)$_2$</td>
<td>2</td>
<td>9</td>
<td>476</td>
<td>482</td>
</tr>
<tr>
<td>24</td>
<td>Me$_2$NC$_6$H$_4$</td>
<td>CH=C(CN)$_2$</td>
<td>3</td>
<td>11</td>
<td>550</td>
<td>2089</td>
</tr>
<tr>
<td>25</td>
<td>Me$_2$NC$_6$H$_4$</td>
<td>CHO</td>
<td>0</td>
<td>7</td>
<td>326</td>
<td>32</td>
</tr>
<tr>
<td>26</td>
<td>Me$_2$NC$_6$H$_4$</td>
<td>CHO</td>
<td>1</td>
<td>9</td>
<td>384</td>
<td>168</td>
</tr>
<tr>
<td>27</td>
<td>Me$_2$NC$_6$H$_4$</td>
<td>CH=C(CN)$_2$</td>
<td>0</td>
<td>9</td>
<td>420</td>
<td>250</td>
</tr>
<tr>
<td>28</td>
<td>Me$_2$NC$_6$H$_4$</td>
<td>CH=C(CN)$_2$</td>
<td>1</td>
<td>11</td>
<td>486</td>
<td>689</td>
</tr>
</tbody>
</table>

The contribution to the molecular hyperpolarizability, $\beta$ can be resolved into two components, an additive term and a charge transfer term.\textsuperscript{32,33}

$$\beta = \beta_{add} + \beta_{CT}$$

1.10
Of these $\beta_{add}$ is the additive part due to substituent-induced asymmetry in the charge distribution and $\beta_{CT}$ is the charge transfer term.

The charge transfer term, $\beta_{CT}$ can be described in terms of ground and first excited states having charge transfer character and is related to the energy of the optical transition $W$, its oscillator strength $f$, and the difference between excited and ground state dipole moments, $\Delta \mu_{c,g}$ by equation 1.11,\textsuperscript{34}

$$\beta_{CT} = \frac{3e^2 \hbar^2}{2m} F(\omega)f \Delta \mu_{c,g}$$  \hspace{1cm} 1.11

$$F(\omega) = \frac{W}{[W - (2\hbar \omega)^2][W^2 - (\hbar \omega)^2]}$$  \hspace{1cm} 1.12

$$\Delta \mu_{c,g} = \mu_c - \mu_g$$  \hspace{1cm} 1.13

Clearly, to maximise $\beta$, it is favourable to seek molecules that have an electronic transition with a small energy gap near $2\omega$ accompanied by a large oscillator strength and dipole moment change. The spectroscopic energy gap $W$ is related to the frequency (or wavelength, $\lambda$) of absorptions found in the UV-Vis spectra of the molecules and the oscillator strength is related to the extinction coefficient $\varepsilon$ of the absorption. From equation 1.11, it is clear that $\beta$ will be maximum when the value of $W$ is moderate and $\Delta \mu$, the difference in dipole moment between the excited and ground state is maximum. Good agreement was obtained between the value of $\beta_{CT}$ predicted by this expression and $\beta_{exp}$ (assuming that $\beta_{exp} = \beta_{CT}$) for a series of disubstituted benzene and stilbene derivatives. Table 1.5 lists experimentally determined values of $\beta$ for various nitroanilines and monosubstituted compounds.\textsuperscript{34}
Table 1.5. Charge-transfer contribution, $\beta_{\text{CT}}$, calculated from the two level model, and experimental values $\beta_{\text{exp}}$ for a series of benzene and stilbene derivatives

<table>
<thead>
<tr>
<th>Compound</th>
<th>Structure</th>
<th>$\beta_{\text{CT}} \times 10^{-30}$ (esu)</th>
<th>$\beta_{\text{exp}} \times 10^{-30}$ (esu)</th>
</tr>
</thead>
<tbody>
<tr>
<td>29</td>
<td>O$_2$N-</td>
<td>19</td>
<td>34.5</td>
</tr>
<tr>
<td></td>
<td>NH$_2$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>O$_2$N-</td>
<td>227</td>
<td>260</td>
</tr>
<tr>
<td></td>
<td>NH$_2$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>31</td>
<td>O$_2$N-</td>
<td>383</td>
<td>450</td>
</tr>
<tr>
<td></td>
<td>N($\text{CH}_{3}$)$_2$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>32</td>
<td>H$_2$N-</td>
<td>217</td>
<td>220</td>
</tr>
<tr>
<td></td>
<td>NO$_2$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>33</td>
<td>H$_2$N-</td>
<td>715</td>
<td>650</td>
</tr>
<tr>
<td></td>
<td>NO$_2$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

A significant enhancement of polarizability has been demonstrated by extending the conjugation length between donor and acceptor. This generally results from decreasing the energy gap and increasing the transition dipole moment between the relevant states. The quantitative relationship between hyperpolarizability and chain length of a conjugated system has been derived by various groups $^{35-37}$ (equations 1.14 – 1.16).
This strategy is applicable to conjugated systems, except for molecules with strong aromatic bridges, such as stilbenes. This is due to the loss of aromaticity on going from the ground state to charge-separated excited state in the case of systems with aromatic bridges. Table 1.6 illustrates the effect of chain length on the first hyperpolarizability of some conjugated systems.\(^\text{38,39}\)

However, even if a molecule has a large $\beta$ value, it might fail to exhibit SHG activity. Crystallization in a noncentrosymmetric fashion is also required, and since about 70% of all nonchiral molecules crystallize in centrosymmetric space groups, this is a major problem. To counter this, many strategies for forming accentric crystals capable of showing SHG activity have been employed and some of these include (i) incorporation of chiral groups,\(^\text{40,41}\) (ii) hydrogen bonding,\(^\text{40,42-44}\) (iii) ionic chromophores,\(^\text{45,46}\) (iv) steric hindrance,\(^\text{47}\) (v) inclusion phenomena,\(^\text{48-51}\) (vi) Langmuir-Blodgett techniques,\(^\text{52}\) (vii) cocrystallization,\(^\text{53}\) and (viii) reduction of dipole-dipole interaction.\(^\text{54}\) These methods have met with varying degrees of success in ensuring a dipolar alignment favourable for SHG. The influence of some of these effects on NLO properties of materials are described in following sections.
Table 1.6. Second-order hyperpolarizabilities of some conjugated chromophores

<table>
<thead>
<tr>
<th>Compound</th>
<th>Structure</th>
<th>$\beta \times 10^{-30}$ esu</th>
</tr>
</thead>
<tbody>
<tr>
<td>34</td>
<td>O$_2$N―arah―NH$_2$</td>
<td>34.5</td>
</tr>
<tr>
<td>35</td>
<td>O$_2$N―arah―arah―NH$_2$</td>
<td>260</td>
</tr>
<tr>
<td>36</td>
<td>PhO$_2$S―arah―arah―NMe$_2$</td>
<td>59</td>
</tr>
<tr>
<td>37</td>
<td>PhO$_2$S―arah―arah―NMe$_2$</td>
<td>145</td>
</tr>
<tr>
<td>38</td>
<td>Me$_2$N―arah―SO$_2$CH$_3$</td>
<td>26</td>
</tr>
<tr>
<td>39</td>
<td>arah―arah―SO$_2$CH$_3$</td>
<td>573</td>
</tr>
</tbody>
</table>

1.3.1. Effect of Chirality on SHG

Enhancement of the SHG properties of materials by introducing chiral moieties such as amino acids and sugars has been studied extensively. Several naturally occurring amino acids and sugars which contain chiral centers were found to be SHG active. Recognising the role of chirality in
enhancing the SHG properties of molecules, several polarizable donor-acceptor systems attached to chiral groups have been examined. For example, the 2,4-dinitroaniline derivative, MAP (40), containing the methyl ester of the active amino acid (S)-(+-)alanine showed SHG efficiency 14 times that of urea (Chart 1.2).

![Chart 1.2](image)

To date, only the chirality of the tetrahedral carbon has been utilized in this fashion. The five other general chirality types (asymmetric heteroatom, asymmetric octahedral center, restricted rotation of dissymmetric planes, helical dissymmetry, and dissymmetric knots and braids) remain to be exploited.

Although chirality guarantees a noncentrosymmetric molecular structure, this may not ensure noncentrosymmetric packing of the molecules in the crystal. Dipolar forces will tend to favour the head-to-tail antiparallel dimerization of molecules, and chirality may not significantly modify this tendency. The dipolar interactions can however be surpassed by the effect of intermolecular hydrogen bonds, since these bonds are one or two orders of magnitude more energetic than van der Waals and dipole-dipole interactions. Furthermore, hydrogen bonds, as opposed to dipolar potentials, are not predisposed towards generating centro- or noncentrosymmetric crystal structures. The combination of chirality and hydrogen bonding potential can thus promote a greater number of interesting structures.
Zyss et al. have demonstrated the effect of chirality and hydrogen bonding in N-(4-nitrophenyl)-(L)-prolinol (NPP, 41). This compound is 10 times more active than MAP (40).

![Chart 1.3](image)

The simultaneous chiral and hydrogen-bonding character of electron donating prolinol group enhances the nonlinear response of this molecule. In another example, replacement of dimethylamino group by prolinol in the stilbene derivative increases the $\beta$ value by about two times (Chart 1.4).

![Chart 1.4](image)

Molecules containing cyclobutanedione acceptor moiety substituted by chiral groups have been reported. The presence of both chirality and hydrogen bonding properties leads to materials with large SHG efficiencies (Table 1.7).
The high SHG efficiencies of these compounds is due to several factors such as (i) the strong electron accepting property of cyclobutanedione, (ii) their high molecular absorption coefficient, (iii) hydrogen bonding properties, and (iv) chirality. Powder SHG measurements indicate that compound 45 is inactive (Table 1.7) probably due to electrostatic interactions between the adjacent molecules predominating over hydrogen bonding interactions in this case.

A squaraine dye with extended conjugation possessing a large molecular hyperpolarizability ($\mu\beta = 481 \times 10^{-30}$ esu) has been reported by Chen et al. (Chart 1.6). Although it has a strong absorption in the near IR

<table>
<thead>
<tr>
<th>Compound</th>
<th>$X$</th>
<th>$Y$</th>
<th>$Z$</th>
<th>SHG</th>
</tr>
</thead>
<tbody>
<tr>
<td>44</td>
<td>Me</td>
<td>H</td>
<td>OH</td>
<td>2.5</td>
</tr>
<tr>
<td>45</td>
<td>Me$_2$N</td>
<td>H</td>
<td>OH</td>
<td>0.0</td>
</tr>
<tr>
<td>46</td>
<td>Me$_2$N</td>
<td>H</td>
<td>NHCH$_2$CH(OH)Me</td>
<td>64.0</td>
</tr>
<tr>
<td>47</td>
<td>Me$_2$N</td>
<td>H</td>
<td>NHCH(Et)CH$_2$OH</td>
<td>6.0</td>
</tr>
<tr>
<td>48</td>
<td>Me$_2$N</td>
<td>H</td>
<td>NHCH(CH$_2$Ph)CH$_2$OH</td>
<td>8.0</td>
</tr>
<tr>
<td>49</td>
<td>Me$_2$N</td>
<td>Et</td>
<td>NHCH(Et)CH$_2$OH</td>
<td>26.0</td>
</tr>
<tr>
<td>50</td>
<td>MeO(CH$_2$)$_3$(Me)$_2$N</td>
<td>H</td>
<td>NHCH$_2$CH(OH)Me</td>
<td>58.0</td>
</tr>
</tbody>
</table>
region (732 nm) it possess a large transparency window in the range of 260 to 680 nm, making it highly suited for SHG applications.

![Chemical structure](image)

**Chart 1.6**

### 1.3.2. Role of Hydrogen Bonding for SHG Materials

Hydrogen bonds most often found in SHG materials involve interaction between a hydrogen bound to $sp^3$ nitrogen or oxygen and an oxygen atom with more $s$ character.

Hosseini et al. have synthesized 1,6-diazacyclodecane derivative 52 in which the donor and acceptor moieties are attached to the nitrogen atoms on either side of the diaza compound (Chart 1.7).

The electronic communication between donor and acceptor groups is achieved by transannular hydrogen bond as shown in Scheme 1.2.

![Chemical structure](image)

**Chart 1.7**
Intermolecular hydrogen bonding induced by attaching a highly polar group to the conjugated backbone of the nonchiral molecule can make the crystal noncentrosymmetric resulting in high SHG coefficients (Table 1.8). 60

![Chart 1.8](image)

**Table 1.8. SHG efficiency of nonchiral 4-nitroaniline derivatives**

<table>
<thead>
<tr>
<th>Compound</th>
<th>D</th>
<th>R</th>
<th>R'</th>
<th>SHG (x SHG_{urca})</th>
</tr>
</thead>
<tbody>
<tr>
<td>53</td>
<td>HO—NH−</td>
<td>H</td>
<td>H</td>
<td>80</td>
</tr>
<tr>
<td></td>
<td>CF₃</td>
<td></td>
<td></td>
<td>30</td>
</tr>
<tr>
<td>54</td>
<td>HO₂C—NH−</td>
<td>H</td>
<td>CF₃</td>
<td>80</td>
</tr>
<tr>
<td></td>
<td>CF₃</td>
<td></td>
<td></td>
<td>115</td>
</tr>
<tr>
<td>55</td>
<td>NC—N</td>
<td>H</td>
<td>H</td>
<td>140</td>
</tr>
<tr>
<td>56</td>
<td>NC—N</td>
<td>H</td>
<td>H</td>
<td>85</td>
</tr>
</tbody>
</table>

Intermolecular hydrogen bonding can also help in bringing about cocrystallization of two different chromophores. Pan et al. have reported the cocrystallization of a merocyanine dye 57 with nitrophenol derivatives 58 and
59, which involve short hydrogen bonding (R-OH...O ca. 2.46 Å) between the phenolic groups, whereas they could not get cocrystals of 57 and nitroaniline derivatives.

![Diagram of 57a and 57b](image)

Short hydrogen bonds have several advantages in that they are characterized by high bonding strengths and higher degree of flexibility which can adapt their bonding directions to fit the three dimensional packing for stabilization of the crystal.

1.3.3. Metallic Complexes

In addition to conventional organic end groups, transition metal moieties have been examined as donors and acceptors. Incorporation of metals into SHG systems introduces a new dimension with possibilities of many new
variables. The metals can have a large diversity of oxidation states and ligand environments, and due to their polarizable $d$ electrons are likely to possess greater nonlinear activity.

The first report on organometallic compounds for SHG came in 1987 by Green et al.$^{62}$ The cis-ferrocene derivative, 60 (Chart 1.10) was analyzed, since it crystallizes in noncentrosymmetric space group. The trans-isomer shows no SHG signal, because of its center of symmetry. Kurtz powder measurements at 1064 nm for the compound gave SHG efficiency 62 times larger than that of urea. The facile redox ability exhibited by the metallocene derivatives leads to large value of $\beta$ by charge transfer through the $\pi$-conjugation system.

![Chart 1.10](image)

Other than ferrocene derivatives, metal carbonyls,$^{63}$ octahedral metal complexes,$^{64}$ square-planar metal complexes,$^{65}$ and silicon complexes$^{66}$ were extensively studied by different groups. The largest SHG values for organometallic compounds, reported to date, are for a series of salts of the type shown in Chart 1.11 and the results are summarised in Table 1.9.
The values of the powder SHG signals depend on the counter ions. Compound 61, which possess $\Gamma$ as the counter ion, for example showed SHG efficiency 220 times than that of urea, whereas 63 and 68 possessing $\text{Cl}^-$ and $\text{CF}_3\text{SO}_3^-$ as the counter ions were inactive. \(^{67}\)

Large $\mu\beta$ values can also be obtained for molecules that do not possess a dipole moment. Trisubstituted ruthenium complexes in spite of having zero...
dipole moments, show SHG efficiency due to multidirectional metal-to-ligand charge transfer.\textsuperscript{68} Ruthenium complexes also exhibit excellent thermal and photochemical stability.\textsuperscript{69} An example is the tris-bipyridine ruthenium complex 70, which has a $\beta$ value of $2200 \times 10^{-30}$ esu. This value is comparable to those of long dipolar donor-acceptor conjugated molecules.\textsuperscript{69,70}

![Chart 1.12]

1.3.4. Polymeric Systems

Polymers embedded or chemically bonded with a nonlinear chromophore comprise a very promising class of NLO materials due to their processibility, which can give large-area high-quality films for integrated optical applications. As mentioned earlier, for even-order NLO interactions, materials possessing centrosymmetries result in vanishing macroscopic nonlinear response. Different poling techniques have been invented for the removal of the centrosymmetry in polymers. These techniques consist of the use of an
external force to align the NLO chromophore by means of a mechanical stress, a magnetic field, an electric field, or polarized laser beam.

Electric field poling techniques are most often used for second-order NLO applications. This technique allows the alignment of polar components of a thin film of a polymeric material. The different steps involved are indicated in the following sequence.\textsuperscript{71}

**Poling steps**

1. Heat thin film of the polymeric material above its glass transition temperature (Tg)
2. Switch on the electric field
3. Cool
4. Switch off the electric field

![Diagram of alignment of chromophore moieties](image)

(a) Random orientation

(b) Aligned orientation

**Figure 1.2. Schematic representation of alignment of chromophore moieties (a) before and (b) after poling**

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There are two types of electric field poling, namely electrode poling and corona discharge. In the case of electrode poling a strong DC electric field (permanent or pulsed, of the order of $10^6$ V/cm) is applied to a pair of electrodes sandwiching a NLO material composing a host material and chromophore to be oriented, above the glass-transition temperature ($T_g$) of the host material. The orientation is then frozen by cooling while keeping the electric field on. Corona discharge is carried out by charging the surface of a film under a strong potential. This method is more flexible with fewer limitations on the geometry of the electrodes.

The major drawback of polymer films is that $\chi^{(2)}$ is perpendicular to the film surface. For bulk electro-optic applications it is desirable to have a film with $\chi^{(2)}$ parallel to the film surface to achieve electro-optic modulation for two-dimensional device applications. This drawback is yet to be overcome. One of the main problems with polymers loaded with NLO active molecules is that chromophores cannot be introduced into the polymer at high concentrations. With increasing concentration of the guest molecules, the polymer tends to crystallize causing problems of light scattering. The other major problem is the loss of alignment of the chromophores on removal of the poling field even in the frozen state of the molecule. One method of overcoming these problems is to covalently link optically active chromophores as pendent groups on to the polymer backbone. In this manner quite high chromophore concentrations can be obtained and the alignment in such systems also tends to be retained for much longer times. In this context methacrylate copolymers with side chains containing aminonitrostilbene moieties, 71 (Chart 1.13) have been studied. Such polymers typically have refractive indices in the range of 1.5-1.7 and dielectric constant of about 3.
Debye units which is constant over a very wide frequency range. Better orientational stability was also observed.

![Polymer backbone]

Another type of NLO polymers are those that contain active chromophores in the main-chain.\textsuperscript{76} Most of the reported main chain polymers are head-to-tail polymers in which all the chromophore dipole moments point in the same direction along the polymeric main chain.\textsuperscript{76,77} Zhang et al. have reported the synthesis and SHG properties of a main-chain diacceptor substituted carbazole derivative 72 in which the chromophores are aligned in a shoulder-to-shoulder arrangement (Chart 1.14).\textsuperscript{78}
The use of polymers which are simultaneously liquid crystals enhances the net guest alignment achievable with an applied field by the inherent axial alignment properties of the liquid crystals through intermolecular interactions between the host and the guest. However, the scattering texture found in liquid crystals is problematic and limits the use of such liquid crystalline polymers as host materials.

1.3.5. Supramolecular Systems

Supramolecular chemistry, the chemistry of the intermolecular bond, involves both organization and function, depending, in particular, on molecular recognition events. It extends towards the design of molecular devices that operate on photon, electron or ion control modes and which can be formed through self-assemblying of their components. It has been pointed out by Lehn that by molecular recognition or complex formation various types of molecular systems can be organized to a high degree, to generate materials possessing NLO properties. This may be achieved by introducing the
molecules into organized phases such as molecular films, liquid crystals or solid state structures, by suitable derivatization or mixing with host substances.

In the Langmuir-Blodgett film technique,\textsuperscript{79} for example, monolayers of molecules containing a hydrophilic group at one end and hydrophobic tail on the other are spread over the surface of water in an appropriate fixture. By controlling the surface pressure the molecules can be made to organize into highly oriented structures at the air water interface. It is also possible to transfer the monolayers on to a substrate of appropriate polarity. Subsequent deposition cycles can be employed to fabricate multilayer films of macroscopic dimensions. With appropriate choices of head and tail units noncentrosymmetric films with polar cylindrical symmetry can be fabricated (Figure 1.3).

LB film formation and SHG studies of three polysiloxanes (Chart 1.15) were reported by Kalita et al. in 1992.\textsuperscript{80} All these compounds form Z-type layers on a variety of substrates. Monolayers of 74 were found to possess a nonlinear optical susceptibility, $\chi^{(2)} (-\omega; \omega, \omega)$ of 10.6 pm/V. For multilayer films, the SHG intensity was found to increase with the thickness of the LB structure.

\begin{center}
\includegraphics[width=0.5\textwidth]{figure13.png}
\end{center}

\textbf{Figure 1.3.} Schematic representation of a noncentrosymmetric LB film. The nonlinear chromophores represented by squares is incorporated into alternate layers.
Prasad et al. have shown that the SHG intensity from multilayer LB films of polymers of the type shown in Chart 1.16 increases quadratically, with increasing number of bilayers, indicating that $\chi^{(2)}$ of the bilayer is a linear sum of the macroscopic optical nonlinearities of the individual monolayers (Table 1.10). The multilayer LB film of each polymer was made by alternate deposition with a spacer polymer, poly(tert-butyl methacrylate).
Table 1.10. SHG intensities of different bilayer samples measured at an incident angle of 45°

<table>
<thead>
<tr>
<th>Type of bilayer</th>
<th>$I^2\omega$ (10 layers)</th>
<th>$I^2\omega$ (20 layers)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymers N and R</td>
<td>$0.148 \pm 0.024$</td>
<td>$0.425 \pm 0.097$</td>
</tr>
<tr>
<td>Polymers N and P</td>
<td>$0.037 \pm 0.006$</td>
<td>$0.112 \pm 0.021$</td>
</tr>
<tr>
<td>Polymers R and P</td>
<td>$0.034 \pm 0.007$</td>
<td>$0.128 \pm 0.018$</td>
</tr>
</tbody>
</table>
Ashwell et al. have made an interesting observation that centrosymmetric molecules can exhibit SHG if they aggregate in a noncentrosymmetric manner, and there is a contribution to the bulk susceptibility from intermolecular charge transfer. For example, monolayers of centrosymmetric squaraine dyes deposited by LB technique possess SHG properties. The X-ray crystal structure of a representative example of this series, 2,4-bis(4-(N,N-dibutylamino)phenyl) squaraine, 79, has confirmed that the chromophore is planar and centrosymmetric. The bulk material does not exhibit SHG because of the centrosymmetry of the molecule, whereas the LB films of this compound are SHG active.

![Chart 1.17](image)

An alternative to LB film techniques would be the construction of covalently linked molecular layer structures. The key assembly step is effected in either a solvent-free solid state or chemical vapour deposition mode, which allows the assembly of chromophoric groups with high structural regularity and large NLO responses. An illustrative example of such a system is shown in Scheme 1.4.

Construction of such superlattices involves the basic siloxane technology developed by Sagiv et al. and refined by Ulman and others. These steps can be repeated to get multilayers with net chromophore alignment. These materials offer greater number densities than poled films and
Scheme 1.4

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far greater structural control and stability than LB films. The course of multilayer evolution can be monitored by following the growth of absorption of the chromophore (in this case at 510 nm), XPS spectroscopy, contact angle measurements and NLO characteristics. These films adhere strongly to glass, and are insoluble in common organic solvents and strong acids. The SHG efficiency of the monolayer film of 80 with 22 Å thickness was found to be \( \sim 700 \times 10^9 \) esu, which is considerably higher than that of typical poled polymers and compares well with the best LB films.\(^{88,89}\)

### 1.3.6. Molecular Recognition Induced Self-Organization and NLO Effects

Molecular recognition process is based on selective intermolecular interactions between complementary components. They may affect the properties of the system at the molecular, supramolecular and material levels by (i) perturbing the electronic and optical properties of the component, (ii) generating supramolecular species, and (iii) inducing organization in condensed phase, respectively. All these effects are of importance with respect to the NLO properties of the material and its constituents.\(^ {90} \)

The binding of two complementary components of donor D and acceptor A type yields a push-pull supramolecular species in which the interaction may be expected to modify the initial donor and acceptor features of the isolated species (Scheme 1.5).

![Scheme 1.5](image)
Molecular recognition directed self-assembling of organized phases has been described in the formation of mesophases by association of complementary molecular components, supramolecular liquid crystalline polymers, and ordered solid state structures. In all these cases, the incorporation of NLO active groups may be expected to produce materials whose SHG properties would depend on molecular recognition induced self-organization.

1.3.7. Liquid Crystals

Another class of orientationally ordered assembly is liquid crystalline systems. They are often inhomogeneous, a property which arises from the phase of the liquid crystal such as helical structure of cholesteric liquid crystals and chiral phase in smectic liquid crystals.

The bulk susceptibilities of liquid crystals are related to the orientational order of the molecules in the material. Due to this orientational anisotropy, liquid crystals experience body torque in the presence of applied fields, which may give rise to director (unit vector describing the average direction of the molecular long axis) reorientation. This leads to large changes in dielectric tensor. Therefore directional reorientation is responsible for extremely large nonlinear susceptibilities in liquid crystals. NLO effects can also exist without director reorientation. In these cases the nonlinearities originate from changes in the degree of orientational order, changes in density due to the action of the optical field, and may involve laser heating or other mediating mechanisms.

Liquid crystals may be obtained from suitably modified molecules having NLO properties. Various liquid crystalline azobenzene derivatives of the general structure shown in Chart 1.18 have found applications in image storage and optical switching.

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Although SHG was observed in aligned samples of MBBA\textsuperscript{95} (Chart 1.19), these types of compounds were assumed to possess center of symmetry.

Various push-pull stilbene and diacetylene derivatives bearing long alkyl chains have also been shown to display nematic and smectic mesophases (Chart 1.20).\textsuperscript{96}

These compounds are highly polarizable and possess nonlinear optical properties.
Kauranen et al. have reported the synthesis of orientationally ordered side chain polymers with a rigid back bone (85-88, Chart 1.21). Here, poling of the chromophore is achieved by chemical synthesis, without applying any external field.
The very large permanent dipole moment observed for such systems can be due to two reasons: (i) addition of dipole moments of the chromophores, or (ii) dipole moment associated with the supramolecular structure itself.\textsuperscript{98}

The hyperpolarizabilities of the polymer compounds were much larger than those of the respective chromophores (Table 1.11). This shows that the chromophores are arranged in a noncentrosymmetric fashion in the polymer chain and each chromophore contributes coherently to the hyperpolarizability of the polymer.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\lambda_{\text{max}}$ (nm)</th>
<th>$\beta \times 10^{30}$ esu</th>
</tr>
</thead>
<tbody>
<tr>
<td>85</td>
<td>457</td>
<td>774</td>
</tr>
<tr>
<td>86</td>
<td>438</td>
<td>3020</td>
</tr>
<tr>
<td>87</td>
<td>448</td>
<td>564</td>
</tr>
<tr>
<td>88</td>
<td>435</td>
<td>5150</td>
</tr>
</tbody>
</table>

Ferroelectric liquid crystals (FLC) are distinguished by spontaneous polarization, and hence do not possess inversion symmetry. They are known to exhibit relatively low SHG coefficients. However in 1991, Walba \textit{et al.} synthesized a low molar mass compound (89) specially designed for second order nonlinear optics, and this compound showed a second harmonic coefficient ($d_{22}$) of 0.6 $\pm$ 0.3 pm/V in the chiral smectic C (Sc*) phase.\textsuperscript{99,100}

The NLO chromophores aligned in the direction of the polarization, perpendicular to the long axis direction of the molecule, were later improved by Schmitt \textit{et al.} by the addition of an electron donating amino group in the \textit{para} position to the electron accepting nitro group (compound 90, Chart 1.22).\textsuperscript{101}
Hult et al. in 1996 reported NLO studies of the polymer obtained by the photopolymerization of the ferroelectric monomer 91.\textsuperscript{102} The monomer was poled and subsequently cross-linked by \textit{in-situ} photopolymerization. The cross-linked pyroelectric polymer exhibited an electro-optical coefficient of 15 - 35 pm/V.

1.4. Summary

This Chapter covers some of the salient aspects of NLO materials and their properties. However, we have not covered the entire spectrum of compounds synthesized for nonlinear optics. Excellent reviews and texts\textsuperscript{103-104} are available in
the literature on organic,\textsuperscript{105-110} organometallic,\textsuperscript{9} polymeric,\textsuperscript{111, 112} and liquid crystalline materials.\textsuperscript{113-116}

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