

## Small molecule supramolecular assemblies for third-order nonlinear optics

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**Abstract:** This chapter discusses organic molecules for third-order nonlinear optics – responsible for effects such as self- and cross-phase modulation, and all-optical switching – and the issues related to using such molecules to create a solid-state material. The chapter will review the figures of merit that help determine the potential of a small molecule, and discuss the problem of obtaining a bulk material with a large third-order nonlinearity that at the same time possesses a high optical quality compatible with photonic applications. As a concluding example, the chapter will end with a review of recent progress in optimizing the third-order optical nonlinearity of small molecules and in using those molecules to fabricate dense supramolecular assemblies for integrated nonlinear optics.

**Key words:** organic molecules, third-order nonlinear optics, self-assembly, small molecules, donor–acceptor substitution.

### 5.1 Introduction

The polarization induced in matter by the electric field of an optical wave has nonlinear components that depend on higher powers of the optical electric field. A second-order response leads to the linear electro-optic (Pockels) effect and to the generation of new optical frequencies through processes such as difference frequency or second harmonic generation. A third-order response allows the interaction between different optical waves and many other phenomena that can be seen in general as the combination of three photons with frequencies  $\omega_1$ ,  $\omega_2$ ,  $\omega_3$ , to generate a fourth one, with frequency  $\omega_4 = \omega_1 + \omega_2 \pm \omega_3$ . This process is described by the frequency-dependent third-order nonlinear optical susceptibility  $\chi^{(3)}(-\omega_4, \pm\omega_3, \omega_2, \omega_1)$  (Hellwarth, 1977), which is in general a complex function that gives the strength of the third-order response as a function of the wavelength of the interacting optical waves. Third-order nonlinear optical effects could enable a wide variety of applications that require light–light interaction. Examples include self-action phenomena such as self-focusing and nonlinear transmission (optical limiting), information transfer from one optical wave to another, and in general all optical switching fabrics that would route and process information without the need for electronic intermediaries.

The challenge to actually realize devices for these all optical switching applications is not only that of creating materials that possess a large third-order susceptibility, but also that such materials must at the same time have a very high optical quality and be compatible with integrated optics technology.

When working towards a larger nonlinear optical response, it is useful to consider the fact that both linear and nonlinear polarizabilities often grow hand in hand because of their fundamental microscopic origins. For materials that have a similar number density of polarizable units, linear and third-order susceptibilities are approximately related by

$$\frac{\chi^{(3)}(-\omega, -\omega, \omega, \omega)}{[\chi^{(1)}(-\omega, \omega)]^4} = \text{const} \quad [5.1]$$

a quantity that will retain its order of magnitude among different materials of the same class. As an example, some chalcogenide glasses with a refractive index of  $\sim 2.7$  reach a third-order susceptibility that is about three orders of magnitude larger than that of silica glass and share the same ratio of Eq. 5.1 with silica glass with a refractive index of 1.5 (Jin *et al.*, 2010). Thus, in these glasses high third-order nonlinearities are simply connected to high refractive indices.

A disproportionate increase in third-order susceptibility with respect to the linear susceptibility can be obtained in molecular materials, where the units responsible for the linear and nonlinear optical response are molecules with extended  $\pi$ -electron conjugation. From an ultra-simplified physics point of view, such molecules allow the wavefunction of the electron that interacts with the light to have a large volume, in some cases essentially as large as the molecule itself. The larger wavefunction raises the target area for interaction with a photon and consequently the linear and nonlinear optical polarizabilities. Because higher-order nonlinearities are proportional to higher-order powers of the volume of the wavefunction (see, e.g., Armstrong *et al.*, 1962, for the sum-over states expansion of nonlinear optical susceptibilities), it is possible for the ratio of Eq. 5.1 to become much larger in organic materials when compared with typical values for inorganic materials without delocalized electrons, such as oxide or chalcogenide glasses. This is one key basic advantage of organic molecular materials for applications in nonlinear optics.

In addition to this, organic molecules are attractive because their nonlinearities remain relatively large for off-resonant excitation. Their response is then electronic in origin and practically instantaneous. This is in contrast to other effects, like molecular reorientation, photorefraction based on photoinduced charge transport, or resonant carrier excitation in semiconductors, where strong optical nonlinearities can be obtained, but only at the expense of relatively long exposure times or relaxation times. Finally,

organics are also of major interest because of their large flexibility for fine-tuning their chemical structure and properties towards the optimization of a given effect.

## 5.2 Fundamental principles of the third-order nonlinear optical response

The third-order nonlinear optical effects responsible for self-phase modulation, cross-phase modulation, and degenerate four-wave mixing are described by a frequency dependent third-order susceptibility  $\chi^{(3)}(-\omega, -\omega, \omega, \omega)$  that gives the amplitude of the third-order polarization created at the same frequency by the interaction of up to three other optical waves. In the most general case, three optical fields with three different wavevectors and vectorial amplitudes  $\mathbf{E}^a$ ,  $\mathbf{E}^b$ ,  $\mathbf{E}^c$  can create a nonlinear optical polarization at the same frequency that has an amplitude given by

$$P_i^{(3)} = \frac{3}{2} \epsilon_0 \chi_{ijkl}^{(3)}(-\omega, -\omega, \omega, \omega) E_j^a E_k^b E_l^c \quad [5.2]$$

where  $\epsilon_0$  is the electric constant, and the amplitudes are defined so that the corresponding time-dependent field is given by  $\mathbf{E}(t) = \text{Re}[\mathbf{E}e^{-i\omega t}]$ . The third-order susceptibility is also responsible for the change in the refractive index seen by an optical wave as a function of its intensity. When this change is expressed as  $n(I) = n(0) + n_2 I$ , with  $I$  the optical intensity, then the value of the nonlinear refractive index  $n_2$  is

$$n_2 = \frac{3}{4\epsilon_0 c n^2} \chi_{1111}^{(3)}(-\omega, -\omega, \omega, \omega) \quad [5.3]$$

where  $\epsilon_0$  is the electric constant,  $c$  the speed of light, and  $n$  is the linear refractive index of the nonlinear optical material.

Eq. 5.2 is in SI units, which will be used throughout in this chapter. This expression goes over to its equivalent in electrostatic units (esu) used by Maker and Terhune (1964), Hellwarth (1977), and a relevant part of the literature, with the substitution  $\epsilon_0 \chi_{ijkl}^{(3)} \leftrightarrow 4c_{ijkl}$ . Numerical values can then be converted using the rule

$$\chi_{ijkl}^{(3)}[\text{m}^2 \text{V}^{-2}] = 4 \frac{4\pi}{(10^{-4} c)^2} c_{ijkl}[\text{esu}] \quad [5.4]$$

where  $c$  is the speed of light in vacuum in m/s and the first factor of four after the equal sign takes into account the factor of four that was originally included in the definition of their third-order susceptibilities  $c_{ijkl}$  by Maker and Terhune (1964). Not everyone in the 'esu world' uses this factor of 4, in which case it should be dropped from Eq. 5.4. But it is very important to

be aware of it and consider its possible existence when comparing results from different authors.

The focus of this chapter is on *off-resonant* third-order effects, described by third-order susceptibilities that are real-valued. In this *zero frequency limit* the third-order susceptibilities do depend on the energy of the excited states, but their frequency dependence becomes negligible. In addition, the susceptibilities describing different nonlinear optical processes such as self phase modulation or third-harmonic generation – described by  $\chi^{(3)}(-\omega, -\omega, \omega, \omega)$  and  $\chi^{(3)}(-3\omega, \omega, \omega, \omega)$ , respectively – become equal in the zero-frequency limit (see, e.g., Hellwarth, 1977). These facts mean values for off-resonant susceptibilities are the simplest way to compare different materials for their nonlinear optical performance.

What should the magnitude of the third-order susceptibility be in order to enable the use of third-order nonlinear optical effects in applications? One way to answer this question is to consider a light intensity of 1 GW/cm<sup>2</sup>, which corresponds to a 30 W peak power focused on a circular surface with a 1 μm radius. Such a peak power is found in a 30 ps pulse at an energy of 1 nJ, and it can also be obtained in a train of 10 ps pulses at a repetition rate of 10 GHz with an average power of 3 W. This is the kind of power that one can reach at the output of a standard fiber amplifier. In a material with a real third-order susceptibility  $\chi^{(3)} = 2 \times 10^{-19} \text{ m}^2 \text{ V}^{-2}$ , which is 1000 times larger than that of fused silica, a light intensity  $I = 1 \text{ GW/cm}^2$  induces a  $\pi$  phase shift in a probe wave after a propagation length

$$L = \frac{\epsilon_0 c n^2 \lambda}{3 \text{Re}[\chi_{1111}^{(3)}] I} = 1.5 \text{ mm} \quad [5.5]$$

An off-resonant third-order susceptibility 1000 times larger than the one of silica glass can thus allow one wave to switch another one on and off by phase shifting the light traveling in one branch of a Mach Zehnder interferometer that is only a few millimeters long. It is reasonable to consider this third-order susceptibility value as the value that would enable practical nonlinear optical devices in integrated optics.

### 5.3 Macroscopic susceptibilities and microscopic polarizabilities

In the organic molecules of interest to this chapter, the  $\pi$ -electron wavefunction strongly couples to an optical electric field, dominating the nonlinear response in the visible and near-infrared. The way light–matter interaction happens can be tuned by modifying the  $\pi$ -electron wavefunction in various ways, e.g. by chemical substituents conjugatively attached elsewhere on a molecule. By changing the shape of the  $\pi$ -electron system and

the substituents attached to it, the physical properties of the molecule, and in particular its linear and nonlinear optical properties, can be tuned with great flexibility.

Microscopically, the third-order susceptibility  $\chi^{(3)}$  of a molecular material depends on the third-order polarizability (or second *hyper*polarizability)  $\gamma$  that describes the molecular polarization induced by the local optical electric field. The relationship between third-order susceptibility and polarizability is

$$\chi_{ijkl}^{(3)} = f_i f_j f_k f_l N \gamma_{ijkl} \quad [5.6]$$

where the susceptibility and polarizability tensors are understood to be in the same reference frame,  $f_i$  are local field factors that assume the values  $f_i = (n_i^2 + 2)/3$  in the Lorentz approximation ( $n_i$  is the refractive index for light polarized along the coordinate axis  $i$ ), and  $N$  is the number density of molecules. Over the past few decades, lots of work has focused on understanding and optimizing the third-order polarizability  $\gamma$ . This has resulted in well-understood key principles that determine a larger nonlinear optical response. Typical examples are longer paths for  $\pi$ -electrons and the use of donor and acceptor groups (Brédas *et al.*, 1994; Marder *et al.*, 1997). It has also been shown that in general molecular hyperpolarizabilities are connected to the difference in average length between single and double bonds in a conjugated path, i.e. bond length alternation (Marder *et al.*, 1993; Meyers *et al.*, 1994). General principles for optimizing molecular third-order polarizabilities have also been established when studying resonant two-photon absorption, which is connected to the imaginary part of the third-order polarizability, but a review of this work is outside the scope of this chapter.

Even though such structure–property relationship studies are very interesting, considering the problem of the nonlinear optical response of a molecule from a much more fundamental and simplified point of view can also be very valuable. One way of doing this that provides a good review of the efficiency and potential of the nonlinear optical response is to evaluate the fundamental quantum limit to the higher order polarizabilities of a molecule (Kuzyk, 2000a, 2000b, 2003a, 2003b, 2003c). For third-order nonlinear optics, Kuzyk showed that there is an upper limit to the molecular third-order polarizability that is basically given by the upper limit to the square of the dipole transition matrix element as determined through sum rules, which is  $e^2 \hbar^2 N_\pi / (2mE_{01})$ , where  $e$  is the unit charge,  $\hbar$  is Planck's constant divided by  $2\pi$ ,  $N_\pi$  is the number of delocalized electrons (estimated as twice the number of multiple bonds in the conjugated system), and  $E_{01}$  is the excitation energy to the lowest optically accessible state (Kuzyk, 2000a). For the zero-frequency limit of the third-order polarizability, its fundamental limit depends on the fourth power of the dipole transition

matrix element – which is limited by the square of  $e^2\hbar^2N_\pi/(2mE_{01})$  – divided by the third power of the optical excitation energy (Armstrong *et al.*, 1962). These arguments are a summary explanation of the following expression (in SI units) for the fundamental limit, which applies to a centrosymmetric molecule (Kuzyk, 2000b, 2003a),

$$\gamma_{1111}^c = \gamma_c = \frac{e^4\hbar^4}{\epsilon_0 m_e^2} \frac{N_\pi^2}{E_{01}^5} \quad [5.7]$$

where  $\epsilon_0$  is the electric constant that appears in the SI definition of the photoinduced microscopic dipole. While the limit to the off-resonant third-order polarizability can theoretical reach  $4\gamma_c$  for a noncentrosymmetric object that is an ideal two-level system (Kuzyk, 2000b), the quantity in Eq. 5.4 can serve as a useful guideline when evaluating the efficiency of a molecule (May *et al.*, 2005), and can be used to define an *intrinsic nonlinear polarizability* that is a scale-invariant measure of a molecule's non-linear optical properties (Zhou and Kuzyk, 2008). Here, we use Eq. 5.7 to define an intrinsic third-order polarizability  $\gamma^l = \gamma_{\text{rot}}/\gamma_c$ , where  $\gamma_{\text{rot}}$  is the experimental value for the rotational average of the third-order polarizability, defined in the next paragraph.

One simple case of molecular material is that in which the component molecules are randomly oriented with respect to each other, like for molecules in solution or diluted in a polymer matrix. Then, the effective third-order polarizability per molecule that determines the molecular contribution to the nonlinearity is obtained by an orientational average of the molecular third-order polarizability tensor  $\gamma_{ijkl}$ . The interaction between linearly polarized waves with the same polarization is then described by the rotational average  $\gamma_{1111}^{\text{rot}}(-\omega, -\omega, \omega, \omega)$  (Andrews, 2004)

$$\gamma_{1111}^{\text{rot}} = \gamma_{\text{rot}} = \frac{1}{15} \sum_{j,k=1}^3 (\gamma_{jjkk} + \gamma_{jkkj} + \gamma_{jkjk}) \quad [5.8]$$

where the  $\gamma_{ijkl}$  are the individual components of the third-order polarizability tensor of a molecule in the molecule's reference frame. What is important to note here is that for similar values of the tensor elements of the third-order polarizability a one-dimensional molecule will have a significantly smaller  $\gamma^{\text{rot}}$  than a molecule that extends into two or three dimensions. Specifically, for a molecule with a one-dimensional conjugated system,  $\gamma^{\text{rot}} \sim \gamma_{1111}/5$ , while for a planar molecule with similar values of the tensor elements  $\gamma^{\text{rot}}$  would automatically become almost four times larger, and even better for non-planar molecules. In fact, broken conjugation in a non-planar molecule would not necessarily be a problem when considering orientational averaging because it would simply create partially independent, but potentially equally large, molecular tensor components that would efficiently contribute to  $\gamma^{\text{rot}}$ . In order to maximize the third-order

susceptibility of amorphous assemblies of randomly oriented molecules it is better to have molecules where the conjugated system responsible for the nonlinearity extends in two or three dimensions, even if the individual tensor elements of the third-order polarizability are not expected to grow just because of that. Another reason to use non-planar molecules is that this characteristic tends to reduce intermolecular interactions, which would help avoid the occurrence of microcrystals in dense supramolecular assemblies. This will be discussed later on, in the next section.

The orientational average  $\gamma_{1111}^{\text{rot}}(-\omega, -\omega, \omega, \omega)$  determines the bulk third-order susceptibility contributed by the individual molecules to a molecular assembly in a manner equivalent to Eq. 5.6:

$$\chi_{1111}^{(3)} = f^4 N \gamma_{1111}^{\text{rot}} \quad [5.9]$$

with the local field factor  $f$  and the number density  $N$ . For a weak concentration of molecules in solution, the above expression can be re-written as

$$\chi_{1111}^{(3)} = f^4 C N_A \frac{\rho_s}{M} \gamma_{1111}^{\text{rot}} \quad [5.10]$$

where  $C$  is the mass concentration of the molecule (as an example,  $C$  would be of the order of 0.01 when preparing solutions for nonlinear optical measurements),  $N_A$  is Avogadro's number,  $\rho_s$  is the density of the solvent, and  $M$  is the molar mass of the molecule. The total third-order susceptibility of the solution is then the sum of Eq. 5.10 and of the third-order susceptibility of the solvent.

Next, it is interesting to consider the case of a single-component dense supramolecular assembly of randomly oriented molecules. Such a structure is very similar to a glass made up of molecules. In such a case the number density of molecules  $N$  that appears in Eq. 5.6 is essentially determined by the space taken up by a single molecule in the assembly. In this context, obtaining a large third-order susceptibility for the bulk supramolecular assembly means that the third-order polarizability of a molecule must not only be large, but it must be large compared to the molecular volume, which determines how densely the molecules can be packed together. Since determining the average volume taken up by a molecule in a dense supramolecular assembly can be cumbersome, this point can be most easily expressed by defining a *specific third-order polarizability*  $\tilde{\gamma} = \gamma_{1111}^{\text{rot}} / m$ , where  $m = M/N_A$  is the mass of the molecule. Eq. 5.6 can then be written as

$$\chi_{1111}^{(3)} = f^4 \rho \tilde{\gamma} \quad [5.11]$$

where  $\rho$  is the density of the supramolecular assembly. This is useful because it allows deriving an estimate for the third-order susceptibility of a dense single-component assembly from the molecular third-order



polarizability as it can be determined, e.g., for molecules in solution. Using  $f^4 = 10$  (refractive index of  $\sim 1.8$ ) and  $\rho = 1000 \text{ kg/m}^3$  (density of water) one finds the simple rule of thumb that to obtain a third-order susceptibility of the order of  $\chi^{(3)} \sim 2 \times 10^{-19} \text{ m}^2 \text{ V}^{-2}$ , which is 1000 times larger than the  $\chi^{(3)}$  of fused silica, one needs a specific third-order polarizability  $\tilde{\gamma} \sim 2 \times 10^{-23} \text{ m}^5 \text{ V}^{-2} \text{ kg}^{-1}$ .

When characterizing a nonlinear optical molecule it is useful to evaluate the magnitude of its third-order polarizability with respect to absolute quantities that give an idea of how efficient a given molecular design is. In this respect the *specific third-order polarizability*  $\tilde{\gamma}$  discussed above is useful because it relates the size of the third-order polarizability to the size of the molecule. On the other hand, the discussion above also showed that the efficiency of a particular molecular design can additionally be judged from the proximity of a molecule's nonlinearity to the fundamental limit, i.e. by the dimensionless *intrinsic third-order polarizability*  $\gamma^I$ . For clarity, it is worthwhile to repeat here together the definition of these two figures of merit:

$$\tilde{\gamma} = \frac{\gamma_{1111}^{\text{rot}}}{m} \quad [5.12]$$

$$\gamma^I = \frac{\gamma_{1111}^{\text{rot}}}{\gamma_C} \quad [5.13]$$

where  $m = M/N_A$  is the mass of the molecule and  $\gamma_C$  is the quantum limit given in Eq. 5.4. The specific and the intrinsic third-order polarizability offer complementary ways to assess how efficient the nonlinear optical response of a molecule is, and it is very informative to use them both when assessing the third-order response of a new molecule. Currently, good values for the intrinsic third-order polarizability in highly nonlinear molecules are of the order of 0.02, while good values for the specific third-order polarizability should be of the order of  $10^{-23} \text{ m}^5 \text{ V}^{-2} \text{ kg}^{-1}$ .

The interplay of intrinsic and specific third-order polarizabilities in different kinds of molecules is highlighted in Table 5.1. The first interesting observation derived from Table 5.1 is that the fundamental limit can indeed be almost reached in the smallest, simplest substances, like the helium atom and the hydrogen molecule, which have a nonlinearity within a factor of three of the fundamental limit (intrinsic third-order polarizability of the order of 0.3–0.4). Next,  $C_{60}$  represents a relatively large molecule with a sizable third-order nonlinearity, but its intrinsic and specific third-order polarizabilities remain relatively weak. Finally, the last two entries in the table are two recently developed small molecules with exceptionally high intrinsic and specific third-order polarizabilities. More details on the compounds in the last two rows of the table can be found in the literature (May



**Table 5.1** Comparison of fundamental limit  $\gamma_c$  (from Eq. 5.9), experimental rotational average, and specific and intrinsic values of the third-order polarizability (see Eqs. 5.12–5.13) for some representative compounds.  $\lambda_{\max}$  is the wavelength corresponding to the lowest energy optical excitation.  $N_e$  is an estimation for the number of electrons in the conjugated system. In the case of the ‘DDMEBT’ molecule (see text), which has a broken conjugation because of its non-planar structure,  $N_e$  is the sum of the number of electrons for the two conjugated systems contained in the molecule.

Molecule	$m$ [ $10^{-23}$ kg]	$N_e$	$\lambda_{\max}$ [nm]	$\gamma_c$ [ $10^{-48}$ m <sup>5</sup> V <sup>-2</sup> ]	$\gamma_{\text{rot}}$ [ $10^{-48}$ m <sup>5</sup> V <sup>-2</sup> ]	$\tilde{\gamma}$ [ $10^{-23}$ m <sup>5</sup> V <sup>-2</sup> kg <sup>-1</sup> ]	$\gamma'$
<b>He</b>	0.66	2	62	$1.3 \times 10^{-4}$	$0.5 \times 10^{-4}$	(a) $7.5 \times 10^{-4}$	0.38
<b>H<sub>2</sub></b>	0.33	2	110	$23 \times 10^{-4}$	$8 \times 10^{-4}$	(a) $2.39 \times 10^{-4}$	0.35
<b>C<sub>60</sub></b>	119.7	60	465 <sup>(*)</sup>	2807	4.6	(b) 0.38	$1.6 \times 10^{-3}$
<b>TDMEE</b>	40.89	16	591	662	7	(c) 1.96	0.012
<b>DDMEBT</b>	69.16	26	527	985	6	(d) 0.87	0.006

(a) Zero-frequency limit from Shelton and Rice (1994), converted into SI units from atomic units, taking into account an additional factor of 6 stemming from a difference in the definition of third-order terms.

(b) Corresponds to  $\tilde{\gamma}_{111}$  calculated using Eq. 5.6 and a refractive index of 2 from the bulk third-order susceptibility determined in the zero-frequency limit by Strohkendl *et al.* (1997).

(c) From May *et al.* (2005) but corrected for a calibration error that inflated the third-order polarizability values of May *et al.* (2005) by a factor 1.5.

(d) From Michinobu *et al.* (2005), but corrected for the same calibration error mentioned in footnote (c) above, and lowered by an additional 25% to reflect recent measurements (Beels *et al.*, 2012).

<sup>(\*)</sup> The wavelength of maximum absorption for C<sub>60</sub> was taken to correspond to the energy of the lowest lying electronic state that can only be accessed by a two-photon transition. This state is found at an energy of 2.67 eV (Strohkendl *et al.*, 1997), corresponding to a wavelength of 465 nm.

*et al.*, 2005, 2007; Esembeson *et al.*, 2008; Koos *et al.*, 2009; Scimeca *et al.*, 2009; Beels *et al.*, 2012). In addition, DDMEBT will be discussed later on in this chapter. For our purposes in the present discussion, they serve as good examples of the kind of nonlinearities that can be obtained in relatively small organic molecules when they are optimized.

## 5.4 From molecules to bulk solid-state materials

While it is possible to develop and synthesize a large variety of molecules for nonlinear optics, a key challenge towards any application is the ability to create a solid-state material where the nonlinearity of a molecule can be efficiently expressed. One such example is the single crystal of poly(2,4-hexadiyne-1,6-diol di-*p*-toluenesulfonate) (PTS). The nonlinear refractive index of PTS is  $2.2 \pm 0.3 \times 10^{-12} \text{ cm}^2 \text{ W}^{-1}$  at a wavelength of  $1.6 \mu\text{m}$  (Lawrence *et al.*, 1994). Using Eq. 5.3 and a refractive index of 1.75 for PTS (Feldner *et al.*, 2001) one obtains a third-order susceptibility of  $\sim 2.4 \times 10^{-18} \text{ m}^2 \text{ V}^{-1}$ , which is four orders of magnitude larger than fused silica. This is a very good value, but it should be noted that it is observed only for light polarized along the crystallographic axis corresponding to the orientation of the essentially one-dimensional polymer chains that make up the crystal. And while this third-order polarizability is relatively high, such a single-crystalline material is generally difficult to fabricate and to integrate with photonic circuitry.

One big advantage of third-order nonlinear optics is that no molecular ordering is necessary to translate the molecular nonlinearities into the bulk nonlinear susceptibility of a solid-state material. This facilitates the use of nonlinear optical molecules to create appropriate bulk materials: the molecules do not need to have any defined orientation when they are assembled together. One possibility to translate molecular nonlinearities into a bulk material is therefore to disperse nonlinear optical molecules in a polymer matrix. The resulting bulk susceptibility is then determined by Eq. 5.10, from the polarizability of the active molecules multiplied by their density. The general applicability of this technique combined with the many molecules that have been developed over the years has led to a large body of literature. A review of some of the results has been provided by Hales and Perry (2008).

The nonlinearity of a solid-state material obtained by dispersing nonlinear optical molecules in a polymer matrix is limited both by the maximum number density of molecules that can be reached and by the magnitude of their third-order polarizability. The practical maximum density that can be reached is limited by the necessity to avoid aggregation effects. Most of the work on third-order nonlinear optical molecules in the literature has until now focused on obtaining larger and larger third-order polarizabilities,

which grow with molecular size. While this will increase the nonlinearity in a polymer matrix if the number density of the molecules can be maintained, it is important to ask if this is the optimum route towards obtaining the best bulk material. When molecules with stronger nonlinearity are embedded inside a polymer, their nonlinearity is always diluted, and the question then becomes whether the dilution effect of the nonlinearity can be compensated by a large third-order polarizability. If it cannot, then one has to look at other ways to combine molecules together that have the potential to deliver a larger number density.

An alternative to embedding into polymers is to create a dense supramolecular assembly where the nonlinear molecules are closely packed together in an essentially amorphous phase, with each molecule randomly oriented with respect to the others. In such a material there is no dilution effect and its maximum susceptibility would be directly determined by the nonlinearity of the molecule relative to its size (the *specific* third-order polarizability mentioned earlier). The ability to have a larger number density of molecules should allow such a dense single-component supramolecular assembly to display a third-order susceptibility that is competitive or larger than for the case of molecules embedded in a polymer matrix. Since bigger molecules are more difficult to handle, a natural idea is to use smaller molecules. Smaller molecules may not be able to compete with the 'best' absolute third-order polarizabilities, but larger third-order polarizabilities in larger molecules that are more difficult to handle and need to be diluted into polymers are also not useful.

The question for single-component assemblies is whether it is possible to obtain molecules with a *specific* third-order polarizability that is large enough to deliver the required third-order susceptibility in the bulk (see previous section). The focus is no longer on large third-order polarizabilities alone.

## 5.5 Small molecules with large third-order nonlinearities

Research on third-order nonlinear optics over the years has striven to make the third-order polarizability of individual organic molecules as large as possible. The result has often been relatively large molecules because the third-order polarizabilities increase rapidly with size. However, larger molecules are generally more difficult to combine into a dense solid state where their nonlinearity is not diluted and which is homogeneous with a good optical quality. This is a fundamental issue that has historically made it difficult to transfer high nonlinearities from molecules to solid state and to integrate organic third-order elements in integrated optics or other applications. Large molecules with large nonlinearities are only of academic inter-

est if they cannot be combined in a bulk material that actually allows their use in practical applications.

On the other hand, molecules that do not necessarily have very large third-order polarizabilities in an absolute sense, but that have a large specific polarizability and can be more easily manipulated to obtain dense supramolecular assemblies, should be the focus of increased attention because of their potential to form bulk materials that reflect the nonlinearity of the constituent molecules while at the same time having a high optical quality.

Fortunately, investigations into the optimization of the third-order polarizability of smaller molecules with a compact conjugated system have revealed that a relatively high third-order polarizability can be maintained while reducing the size of the molecule if donor–acceptor substitution is used to control the relative energies of ground and excited states. While donor–acceptor substitution is well known for optimizing the second-order nonlinear optical response, it also plays a very simple and important role in increasing the third-order polarizability in small molecules.

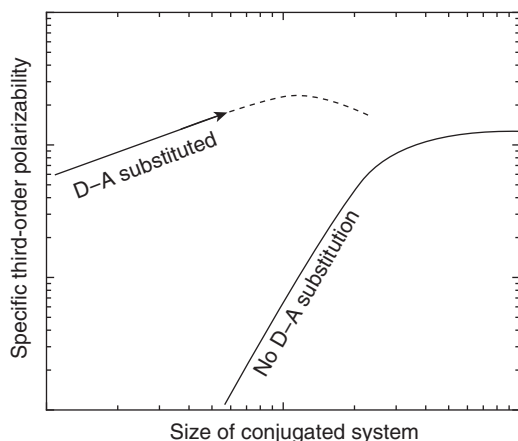
In small molecules with donor–acceptor substitution, the wavefunction of the ground state is mostly centred on the donor-group(s), while the wavefunction of the first excited state is mostly centred on the acceptor-group(s) (Moonen *et al.*, 2003; Fernandez and Frenking, 2006). It is then the chemical structure of the substituents, in addition to the size of the molecule, which sets the difference between the energies of the highest occupied molecular orbital (HOMO) and of the lowest unoccupied molecular orbital (LUMO) (Fernandez and Frenking, 2006; May *et al.*, 2007). As the size of the conjugated system decreases, donor–acceptor substitution keeps the HOMO–LUMO gap smaller than what would be otherwise expected from a fundamental ‘particle in a box’ effect. As an example, for the polyynes studied by Slepko *et al.* (2004), a linear conjugated system consisting of six consecutive triple bonds has a first optical transition from the ground state at  $\sim 4.08$  eV (corresponding to a wavelength of 304 nm). Similarly, in the poly(triacetylene) wires investigated by Gubler *et al.* (1999), a linear conjugated system consisting of six double or triple bonds has a first optical transition at  $\sim 3.3$  eV (wavelength of 377 nm). On the other hand, the TDMEE molecule (May *et al.*, 2005; see also Table 5.1) arguably has a smaller conjugated system than these compounds, but it has a first optical excitation energy of  $\sim 2.1$  eV (591 nm wavelength). Finally, in another family of donor–acceptor substituted molecules the HOMO–LUMO gap has been shown to remain practically unchanged while the size of the conjugated system between donors and acceptor was varied (Bures *et al.*, 2007; May *et al.*, 2007).

Since the transition dipole matrix element between ground and excited state remains high in small donor–acceptor substituted molecules, the

smaller HOMO–LUMO gap directly leads to a larger off-resonant third-order polarizability (Armstrong *et al.*, 1962). The importance of the excited state transition energies is also evident from the fact that the quantum-limit to the third-order polarizability is inversely proportional to the fifth power of the first optical excitation energy for a conjugated system of fixed size (see Section 5.3).

From the expression for the fundamental limit (Eq. 5.7), one sees that if excited state energies remain constant while the number of conjugated electrons increases, then the maximum third-order polarizability grows as the square of the number of delocalized electrons, but not faster (May *et al.*, 2007). Such an increase is less steep than what is generally observed in other molecular systems (Slepkov *et al.*, 2004), where the third-order polarizability vs. size of the conjugated system follows a much steeper power law that is caused by the simultaneous increase in transition dipole moment and decrease in HOMO–LUMO gap. The latter remained practically invariant for the molecules of May *et al.* (2007), as forced by the presence of the donors and acceptors, and kept the nonlinearity high as the size of the molecule shrank.

In summary, the effect of donor–acceptor substitution on the HOMO–LUMO gap leads to a much less steep decrease of the third-order polarizability as the size of a molecule shrinks (May *et al.*, 2007) when compared with unsubstituted molecules (Slepkov *et al.*, 2004; Gubler *et al.*, 1999). Clearly, the increase in third-order polarizability with donor–acceptor substitution can only be explained in such a straightforward way as long as the overlap between the HOMO and the LUMO can be maintained. As the size of the molecule increases past an optimum value, the centering of HOMO and LUMO on donor and acceptor groups should lead to smaller transition dipole matrix elements and the specific third-order polarizability should stop growing. This effect is different in physical origin from the saturation of the specific third-order polarizability with molecular size that is observed in unsubstituted compounds (Gubler *et al.*, 1999), which is more related to the transition from a molecular excitation to a localized excitation in what becomes increasingly like a polymer chain. A semi-quantitative summary and illustration of these principles is shown in Fig. 5.1. Donor–acceptor substituted molecules are able to maintain a large third-order nonlinearity at small sizes while unsubstituted molecules suffer a steep decrease of the third-order nonlinearity with molecular size. The dashed line that continues the trend of the donor-substituted systems towards larger sizes is a qualitative extrapolation that is as yet unsupported by direct experimental data but that is expected because of the decrease in the transition dipole moment for increasing space between donor and acceptor groups, towards which HOMO and LUMO gravitate.



5.1 Qualitative representation of how the specific third-order polarizability (Eq. 5.12) of molecules is expected to vary with molecular size for the case of donor–acceptor substituted compact molecules and for other non-substituted conjugated systems such as those presented by Slepko *et al.* (2004) and Gubler *et al.* (1999). Donor–acceptor substitution in smaller molecules keeps the variations of the HOMO–LUMO gap with size small, leading to a slower decrease of the third-order polarizability for shrinking size when compared to unsubstituted systems, where a combination of an increasing HOMO–LUMO gap and a smaller transition dipole moment leads to a steeper decrease for smaller molecules. The thick solid curves in the figure are obtained by interpolating and smoothing out the data published by May *et al.* (2005, 2007) for the donor–acceptor substituted small molecules, and by Slepko *et al.* (2004) and Gubler *et al.* (1999) for the more extended systems without donor–acceptor substitution. The dashed curves represent a trend that is not yet supported by data, but that is expected because of HOMO and LUMO becoming increasingly separated for large distances between donor and acceptor groups.

Figure 5.1 shows that the bulk nonlinearity that can potentially be produced using small molecules (the specific third-order polarizability) can be as large as the best that can be expected for the largest molecules (assuming it was possible to combine them in a dense assembly with the required optical quality). In fact, small donor–acceptor substituted organic molecules were the first that clearly approached the fundamental quantum limit within less than two orders of magnitude, similar to what is observed in second-order nonlinear optics (Clays, 2001; Kuzyk, 2003c; May *et al.*, 2005, 2007). In addition, this relative closeness to the fundamental limit was accompanied by a large specific third-order polarizability and by the ability of many

molecules, which can sublime without decomposition, to create dense supramolecular assemblies by vapor deposition.

In summary, donor–acceptor substitution has been observed earlier to have an effect on third-order nonlinearities, but it plays a uniquely simple and important role in increasing the third-order response of small molecules; an effect that can be best visualized by the tuning of the HOMO–LUMO gap. This understanding of the effects of donor–acceptor substitution in small molecules directly connects to the fundamental sum-over-states expansion of the third-order polarizability in perturbation theory (Armstrong *et al.*, 1962), and to the fundamental limit developed by Kuzyk. Such a view delivers a particularly simple and direct guiding principle for understanding and optimizing the nonlinear optical response of small molecules.

## 5.6 Small molecule supramolecular assemblies with high optical quality and large third-order susceptibility

The key point of the previous section is that small molecules can deliver the same (or better) performance as large molecules from the point of view of creating a bulk nonlinear optical material, and as seen from the two figure of merit that describe the efficiency of the nonlinear optical response of a molecule, the intrinsic and the specific third-order susceptibility  $\gamma^l$  and  $\tilde{\gamma}$  (see Eqs. 5.12 and 5.13). Two examples of such high performance small molecules have been presented in Table 5.1.

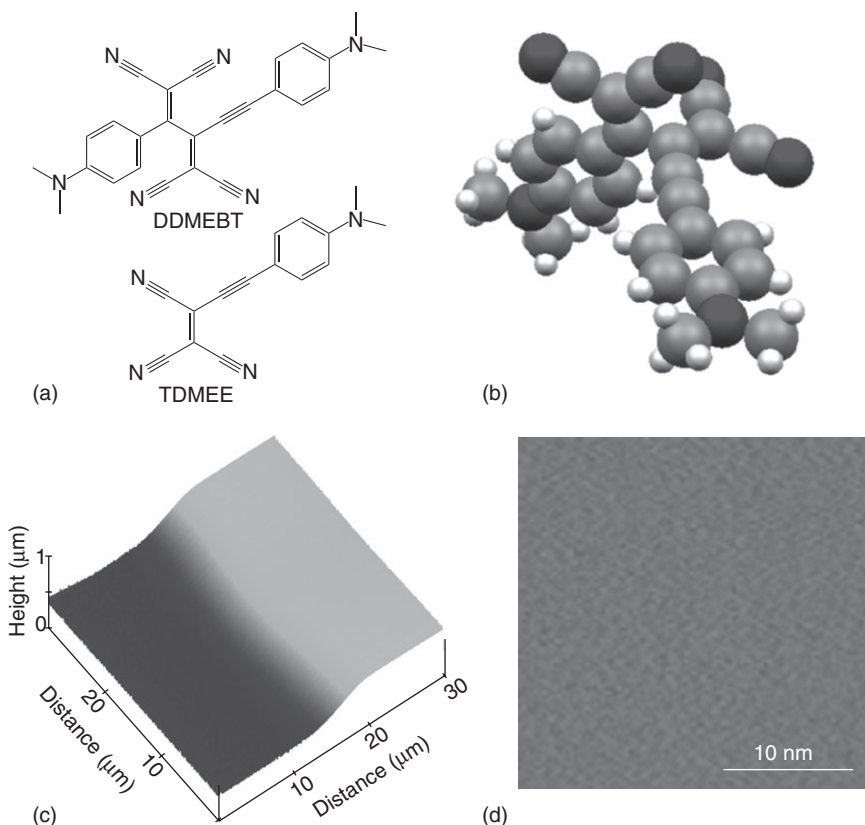
The next challenge once such molecules have been identified is to use them to create dense supramolecular assemblies. Molecules with a relatively small molecular mass that can sublime without decomposition open up the possibility of creating supramolecular assemblies by physical vapor deposition or molecular beam deposition. These techniques have unique advantages. They operate in a clean environment (high vacuum), they do not need solvents, they can provide precise and *in situ* control of growth rate, substrate temperature, and film thickness, and are also fully compatible with vapor-phase microelectronic fabrication techniques that involve masking and dry-etching. The main issue to solve in order to obtain high-quality thin films in this way is the tendency of the molecules to crystallize. This is particularly a problem for planar molecules with donor–acceptor substitution where  $\pi$ – $\pi$  stacking interactions and antiparallel molecular dipole alignment can be powerful forces towards forming crystals. In the case of molecular beam deposition on a substrate, such crystals would start growing independently at different locations on the substrate and lead to microcrystalline materials with too much light scattering to be used in applications. In fact, the TDME molecule (May *et al.*, 2005) has very



attractive properties from the nonlinear optical point of view (see Table 5.1) but forms very bad films (Esembeson *et al.*, 2008).

The breakthrough towards obtaining the first dense, homogeneous supramolecular assemblies for nonlinear optics that had a very high optical quality was a modification of the TDMEE molecule that consisted in making it non-planar (Esembeson *et al.*, 2008). This new molecule was the DDMEBT molecule also presented in Table 5.1, above. DDMEBT ([2-[4-(dimethylamino)phenyl]-3-([4-(dimethylamino)phenyl]ethynyl)buta-1,3-diene-1,1,4,4-tetracarbonitrile]) may surprise because it has a broken conjugation, but contains almost the complete TDMEE molecule as a conjugated sub-unit, which is the part most responsible for its nonlinearity. The rotational average of its third-order polarizability is only slightly smaller than that of TDMEE, but the non-planar structure of DDMEBT reduces intermolecular interactions in such a way that vapor depositing it on any substrate leads to a homogeneous bulk material with very high optical quality (Fig. 5.2).

The DDMEBT material has very attractive properties. It combines a high optical quality with a high third-order nonlinearity three orders of magnitude larger than fused silica, it has a relatively low refractive index of 1.8 at 1.5  $\mu\text{m}$ , it has been found to be quite stable with a shelf life of years (Beels *et al.*, 2012), and it can be vapor deposited on any substrate. In order for it to be used in applications, it is necessary to control its interaction with light signals. While it would be possible to define waveguides out of the DDMEBT material alone, its properties render it quite attractive for integration with well-established integrated optics technologies. In particular, DDMEBT has been found to create thin homogeneous cover layers on top of nanostructured substrates and to be the ideal material to combine with silicon-on-oxide technology to create hybrid devices (Koos *et al.*, 2009; Scimeca *et al.*, 2009). Its use in so-called silicon-organic-hybrid (SOH) devices was the first demonstration of a practical device that combined organics and state-of-the-art silicon and optical telecom technology to create new functionalities that have never been possible before (Koos *et al.*, 2009; Leuthold *et al.*, 2009; Scimeca *et al.*, 2009; Vallaitis *et al.*, 2009). In particular, it was found that the DDMEBT material added only negligible losses to a slot-waveguide consisting of nanoscale silicon ridges  $\sim 200$  nm tall and  $\sim 200$  nm apart (Koos *et al.*, 2009), and that its nonlinearity created a waveguide with a record-high nonlinear parameter of  $100 \text{ W}^{-1} \text{ m}^{-1}$ . This SOH device underwent state-of-the-art testing in a telecommunication setting, and it was successfully used for time-division demultiplexing of a 170 Gbit/s data stream using nonlinear optical frequency conversion in a 4 mm long SOH waveguide (Koos *et al.*, 2009). But since the nonlinear optical response of the organic material is electronic and off-resonant, much higher speeds are in principle possible (Vallaitis *et al.*, 2009).



5.2 (a) The DDMEBT molecule compared to TMEE, (b) a spatial model of the DDMEBT molecule, (c) atomic force microscopy (AFM) picture of the edge of a thin film obtained by molecular beam deposition of DDMEBT that shows the homogeneity and flatness of the film, and (d) SEM picture highlighting the homogeneity of the film on the nanoscale (adapted from Esembeson *et al.*, 2008).

## 5.7 Conclusion

In conclusion, dense small molecule supramolecular assemblies are the realization of a new paradigm for nonlinear optics, where the focus has been moved away from molecules that have higher and higher third-order polarizabilities and towards smaller molecules that have an optimized third-order polarizability closer to the quantum limit. Large molecules with large absolute third-order polarizabilities cannot necessarily be combined into a useful bulk material with correspondingly high nonlinearity, while the smaller molecules can be assembled into a dense, essentially amorphous material that optimally reflects the molecular properties, has a high optical

quality, and can produce (by vapor deposition) wide area films (many square centimeters) that can be combined with any substrate or passive guided-wave technology. In this way it is possible to obtain a successful translation of the molecular properties to a stable bulk solid-state material with high optical quality, and to combine this material with existing passive integrated optic technology. This led to the first demonstration of ultrafast all-optical switching based on an organic supramolecular assembly and silicon-on-oxide technology, and to the realization of a new nonlinear optical functionality for the silicon photonics platform.

The outlook for the future is, as usual, not clear. Telecommunication technologies are evolving at a rapid rate and it is difficult to predict the role that organics-based systems might play in photonics platforms that in the second decade of this century are quickly moving towards coherent communication systems that rely heavily on electronic processing. Still, the variety of applications of optical systems is also increasing at a rapid pace, and the availability of new nonlinear optical organic materials compatible with integrated optics technologies is yet another tool in the photonics toolbox, there to be picked up when needed.

## 5.8 References

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