Second-order nonlinear optical materials: recent advances in chromophore design

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This paper deals with recent and important developments in the field of organic materials for second-order nonlinear optics. Attention is drawn to current trends in chromophore design with a discussion of current progress and problems in this field. A number of important classes of chromophores, such as one-dimensional charge-transfer molecules, octopolar compounds, ionic materials, multichromophore systems and organometallics, are discussed.

Nonlinear optics has been recognized for several decades as a promising field with important applications in the domain of opto-electronics and photonics.[1,2] High performance electro-optic switching elements for telecommunications and optical information processing are based on materials with high nonlinear optical (NLO) properties. Hence, a variety of materials have been investigated for their nonlinear optical properties, *e.g.* inorganic materials,[2] organometallic compounds,[3] liquid crystals,[4] organic molecules and polymers.[5] Inorganic crystals, such as lithium niobate, have been used as nonlinear optical materials for several decades, and electro-optic devices that use lithium niobate are already on the market. However, these crystals have several drawbacks: high quality single crystals are difficult to grow, are expensive, and not easy to incorporate into electronic devices.

During the 1980s it became clear that organic materials might be a better choice for use in nonlinear optical applications.[5,6] A lot of organic chromophores exhibit extremely high and fast nonlinearities, much better than those observed in inorganic crystals. In addition, due to the versatility of organic synthesis, their nonlinear optical properties can be custom-tailored depending on the desired application. The chromophores can be incorporated into a variety of macroscopic structures such as crystals, Langmuir–Blodgett (LB) films, self-assembled films and poled polymers.[5] At this moment, poled polymers seem to be closest to commercial applications due to the several advantages that this approach offers.[7,8] Such materials are cheap, easy to fabricate, have good film-forming properties for making waveguides, and are compatible with existing semiconductor technologies. It has already been demonstrated that high performance electro-optic devices based on poled polymers can be made.[9–13] At present, several organic systems (molecular as well as macroscopic) with sufficiently high nonlinearities have been developed. The focus of the research in this area seems to be shifting to the optimization of a variety of other parameters, *i.e.* thermal stability, chemical stability and optical loss.[14] Also, completely new approaches to design efficient nonlinear optical materials have lately emerged.

In this review, we will give an overview of recent and what we believe to be major advances in organic nonlinear optics. It is not an exhaustive discussion of all the work that has been done in this field. Instead, this paper is focussed towards recent developments and current trends in NLO chromophore design.

Theoretical background and experimental techniques

The first step in designing second-order nonlinear optical materials is the identification of suitable molecules or chromophores with high nonlinear optical properties. These chromophores can later be incorporated into a variety of macroscopic assemblies such as poled-polymer films, LB films or single crystals. The key property that determines the magnitude of the molecular second-order nonlinear response is the first hyperpolarizability β. When a molecule is subjected to an intense light field, the induced dipole moment is given by eqn. (1),

$$\mu_i = \alpha_{ij}E_j + \beta_{ijk}E_jE_k + \gamma_{ijkl}E_jE_kE_l + \dots \qquad (1)$$

where summation over repeated indices is implied. μ_i is the ith component of the induced dipole moment and E_i are components of the applied electro-magnetic field. The coefficients α_{ij}, β_{ijk} and γ_{ijkl} are components of the linear polarizability the first hyperpolarizability, and the second hyperpolarizability tensor, respectively. The terms beyond the first on the right hand side of eqn. (1) describe a nonlinear response to the incident electric field. The β tensor is responsible for second-order nonlinear optical effects such as second-harmonic generation (frequency doubling), frequency mixing, optical rectification and the electro-optic effect (Pockels effect). Since β is a second-order polar tensor, it vanishes in a centrosymmetric environment. Therefore, most second-order nonlinear optical materials have been composed so far from non-centrosymmetric one-dimensional charge-transfer molecules. Typically, they contain a conjugated π-electron system, asymmetrically substituted by electron donor and acceptor groups (a so called DπA system). Such systems can be described by one dominant hyperpolarizability component lying in the direction of charge transfer. The simplest theoretical description of the hyperpolarizability of one-dimensional charge transfer molecules is the two-level model of Oudar and Chemla.[15] The model holds quite well for many organic chromophores but fails for octopolar compounds, certain organometallics and some recently developed unconventional chromophores (as discussed briefly in the corresponding paragraphs). With this model it is possible to establish trends in the nonlinearity–molecular structure relationship in terms of relatively simple physical properties. It describes the nonlinear response in terms of an electronic charge transfer excitation between the ground and excited state. For second-harmonic generation, the dominant β component is given by eqn. (2),

$$\beta(-2\omega;\omega,\omega)=\frac{3}{2\varepsilon_0\hbar^2}\frac{{\omega_{ge}}^2\Delta\mu_{ge}{\mu_{ge}}^2}{\left[(\hbar\omega_{ge})^2-(\hbar\omega)^2\right]\left[(\hbar\omega_{ge})^2-(2\hbar\omega)^2\right]}$$

$$=\beta(0)\frac{{\omega_{ge}}^4}{\left[(\hbar\omega_{ge})^2-(\hbar\omega)^2\right]\left[(\hbar\omega_{ge})^2-(2\hbar\omega)^2\right]} \quad (2)$$

with $\hbar\omega_{ge}$ the energy difference of the charge transfer between the ground and excited state, $\hbar\omega$ the energy of the incident photon, $\Delta\mu_{ge}$ the difference in the dipole moments of the ground and excited states and μ_{ge} the transition dipole moment between the ground and excited states. It is clear from this equation that the hyperpolarizability will be enhanced whenever the fundamental frequency ($\hbar\omega$) and/or the doubled frequency ($2\hbar\omega$) is close to the charge transfer absorption band. $\beta(0)$ is the dispersion free (or static) hyperpolarizability. Therefore, $\beta(0)$ is the relevant parameter in comparing the nonlinearity of different molecules.

For organic molecules, the experimental determination of the hyperpolarizability is usually carried out in solution using either the traditional EFISHG (Electric Field Induced Second-Harmonic Generation) technique or the recently developed hyper-Rayleigh scattering technique. In EFISHG,[16,17] a strong static electric field is applied to a solution of NLO chromophores. The interaction of the field with the permanent dipoles (μ) of the molecules causes a bias in the average orientation of the molecules. The partial removal of the isotropy allows second-harmonic generation to occur. From the intensity of the detected second-harmonic light the quantity $\mu\beta$ is determined. It represents the scalar product of the permanent dipole moment and the vectorial part of the hyperpolarizability. A separate measurement of the permanent dipole moment is necessary to extract β. A disadvantage is that due to the application of a *dc* electric field, only polar and nonionic molecules can be measured.

Recently, a new technique based on hyper-Rayleigh scattering (HRS) was developed to measure hyperpolarizabilities of molecules in solution.[18–23] Since its development in 1991, HRS has become a standard technique to evaluate the nonlinear optical properties of unconventional (*e.g.* ionic and apolar compounds) nonlinear molecules. A HRS measurement is conducted by focussing an intense laser beam on an isotropic solution containing nonlinear molecules and measuring the intensity of scattered frequency-doubled light. The fact that second-order optical processes can occur in an isotropic centrosymmetric solution is due to fluctuations in molecular orientations that instantaneously break the centrosymmetry of the solution. The advantage of this technique, as compared to EFISHG, is the absence of an orienting electric field. Therefore, ionic and apolar molecules are also accessible for measurement. In addition, it is possible to determine several components of the β tensor of nonlinear molecules.[24] A disadvantage is that multiphoton fluorescence often interferes with the hyper-Rayleigh signal and this can lead to serious experimental errors.[25] However, approaches to avoid interference from multiphoton fluorescence have been developed.[26,27]

For an ensemble of molecules, the macroscopic polarization is given by eqn. (3),

$$P_i=\chi_{ij}{}^{(1)}E_j+\chi_{ijk}{}^{(2)}E_jE_k+\chi_{ijkl}{}^{(3)}E_jE_kE_l+\ldots \quad (3)$$

where the χs are the macroscopic susceptibilities. They can be directly related to the molecular nonlinearities by local field factors, the density of chromophores and an appropriate coordinate transformation. Note that the noncentrosymmetry requirement for second-order processes needs to be fulfilled also on a macroscopic level. In addition, several other properties are required in order for a material to qualify for practical applications, *e.g.* phase-matching possibilities (for SHG applications) and mechanical strength, as well as environmental and thermal stability.

Nonlinear optical chromophores can be incorporated into a macroscopic environment in a variety of ways. Probably the most important and most widely used is the incorporation of dipolar chromophores into a polymer host by simply dissolving the chromophore into a polymeric material (guest–host systems), by covalently attaching the chromophores to a polymeric backbone (side-chain polymers) or by incorporating the chromophores into the backbone of the polymer (main-chain polymers).[14] To achieve the necessary noncentrosymmetry, the chromophores in the polymer matrix need to be poled. This is done by aligning the dipolar chromophores with a strong orienting electric field (electric field poling), while heating the polymer to near its glass transition temperature where it becomes rubbery. Cooling the systems in the presence of the field freezes the orientation of the chromophores. Since the chromophores are oriented by means of their static dipole moment, the macroscopic nonlinearity is proportional to the product $\mu\beta$. Therefore, this quantity is often referred to as the molecular figure of merit for chromophores incorporated into poled polymer films. Note that due to the presence of the orienting electric field, only polar and neutral chromophores can be electric-field poled. Advantages of the poled polymer approach are the relative ease of thin film making by spin coating and its compatibility with existing semiconductor technology. A disadvantage of the poled polymer approach is that it represents a thermodynamically unstable system. The chromophores in the polymer matrix tend to relax with time, eventually leading to a centrosymmetric system.[14,28] Methods to suppress relaxation processes include crosslinking and the use of polymers with high glass transition temperatures. Over the last few years, the poled polymer approach has matured significantly and is almost ripe for electro-optic market applications. The development of polymeric materials for SHG applications has been less successful, in particular because of low nonlinearities, absorption losses and phase-matching problems. Achieving phase-matched frequency doubling in polymeric films or waveguides is usually done by (i) quasi phase-matching in a periodically poled polymer film, (ii) launching the fundamental and second-harmonic signals into different waveguide modes, (iii) Cerenkov SHG, and (iv) anomalous dispersion phase-matching.[14,29]

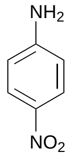
A second approach to organize molecules has been to incorporate NLO chromophores into noncentrosymmetric LB films.[29] This approach offers the advantage of much greater chromophore alignment and chromophore density. However, LB films are often of poor optical quality due to microdomain formation, have poor temporal stability and are often very fragile. On the other hand, some encouraging results have been obtained where films of good optical quality showed high nonlinearities.[30–33]

A related approach is based on covalent self-assembly techniques to make artificial superlattices.[28] The problem of fragility is solved here by covalently linking different layers of the superlattice. Recent results suggest that very large nonlinearities can be achieved. However, since each layer of the superlattice involves a chemical reaction, it still remains a question if sufficiently thick layers with good optical quality can be obtained.

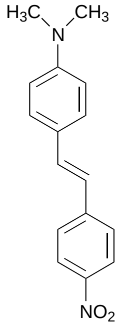
A fourth approach is the formation of crystals.[29,34] Single crystals may provide a high degree of ordering as well as a large concentration of chromophores per unit volume, together with a stable structure. In addition, phase-matching can be achieved using birefringence (type I and type II, critical and noncritical phase-matching). However, the fabrication of single crystals of good quality is often a very tedious and time consuming procedure and the fabrication of waveguide structures might be difficult. In addition, only a few nonlinear chromophores crystallize into noncentrosymmetric space groups. On the other hand, Hulliger *et al.* discovered new single crystalline inclusion compounds with nonlinear optical properties. Channel type inclusion complexes formed by perhydrotriphenylene and several NLO molecules (that otherwise crystallize centrosymmetrically) yielded materials with macroscopic second-order NLO properties.[35]

Traditional DπA chromophores

Inspired by the two-level model and the development of the EFISHG technique, several one-dimensional charge transfer systems with good NLO properties were developed during the 1980s. Typical examples of such molecules are *p*-nitroaniline (PNA) and dimethylaminonitrostilbene (DANS). DANS was considered to be quite nonlinear at that time and is still being used as a typical benchmark to evaluate NLO properties of other molecules.[36] Attempts to further increase the nonlinearity were usually aimed at increasing the donor and acceptor strength or increasing the length of the conjugation bridge.[37] In addition, chromophores with other types of conjugation bridges have been investigated. Many of these systems fall into the category of substituted benzenes, biphenyls, stilbenes, azostilbenes and tolanes.[38,39] All these systems have a predominantly aromatic ground state and a corresponding charge transfer state that is quinoidal in nature (Fig. 1).



PNA



DANS

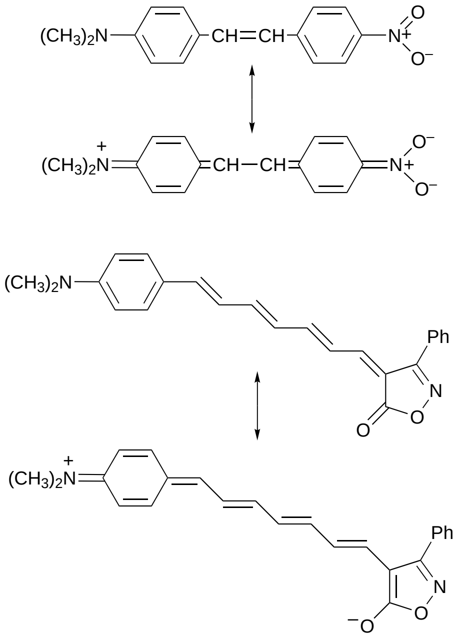
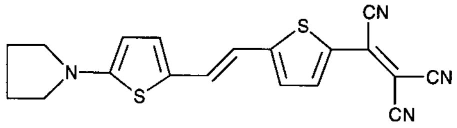
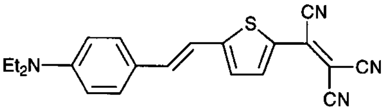
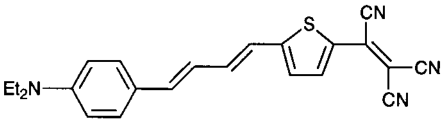
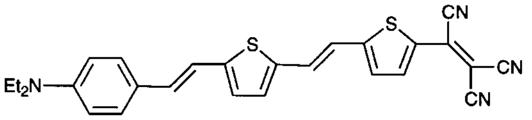
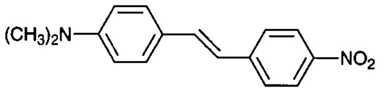


Fig. 1 Structure of ground state and charge separated state for DANS and **2b**

In the early nineties, the pioneering work of Marder and co-workers paved the way for the development of highly advanced NLO chromophores.[40,41] He showed that for a given conjugation bridge there is an optimal combination of donor and acceptor strengths (or ground state polarization) to maximize $\mu\beta$, and that beyond this point, increased donor–acceptor strength (or further ground state polarization) will attenuate $\mu\beta$. More recently, it was shown that bond length alternation, *i.e.* the average difference in length between single and double bonds in the molecule, is the relevant parameter in the optimization of the hyperpolarizability of molecules.[42–44] Most of the existing molecules were shown to have too much bond length alternation to maximize $\mu\beta$. For example, molecules with aromatic ground states (like DANS) tend to be more bond length alternated (less polarized) for a given combination of donor–acceptor than a simple polyene chain of comparable length. The high degree of bond length alternation in such molecules is indicative of an insufficient contribution of the charge separated resonance form to the ground state configuration of the molecules and is a direct consequence of the loss of aromatic stabilization in the charge separated form (Fig. 1). Therefore attempts were made to design molecules with less aromatic character in the ground state or systems where loss of aromaticity in the ground state is compensated by a gain in aromaticity in the charge separated form (**2b** Fig. 1). For example, replacing benzene rings in stilbene derivatives by heterocyclic rings like thiophene or furan decrease the aromatic character of the ground state and leads to extremely high hyperpolarizabilities, especially with very strong electron acceptors such as tricyanovinyl.[45–49] Examples of such optimized molecular structures are shown in Table 1, together with their hyperpolarizabilities, dipole moments and absorption characteristics. For comparison, we have also included the structure and data of DANS. Note that some of the systems shown have a nonlinearity that is an order of magnitude higher than that of DANS. Consequently, incorporation of compound **1c** into a polyquinoline matrix resulted in a material with an electro-optic coefficient of 26 pm V^{-1}, comparable to that of lithium niobate.[50] Compounds that can gain aromaticity in their charge separated form, such as the systems shown in Table 2, also show extremely enhanced nonlinearities.[51,52] One of these compounds was successfully incorporated as a guest into a polycarbonate matrix at a 20 wt% loading level. This guest–host system exhibited an electro-optic coefficient of 55 pm V^{-1}, almost twice that of lithium niobate. This is the highest value ever achieved with a poled polymer.[52]

Materials to be used for electro-optic and frequency doubling applications must not only have high nonlinearities, but also require good thermal and chemical stability and low optical loss (high transparency). Unfortunately, organic materials synthesized for incorporation into nonlinear optical polymers typically exhibit tradeoffs between nonlinearity and each of the other properties.[53–56] For example, all of the systems discussed in the previous paragraphs have extremely high optical nonlinearities, but only limited thermal stabilities (decomposition temperatures $<250\,^{\circ}$C). In order for the nonlinear response to be stable during processing and operation, the chromophores need to be chemically stable at all temperatures that the system encounters. Typically, organic molecules for nonlinear optical applications will have to endure extremely high temperatures during fabrication processes (sometimes as high as 300 °C).[14] Achieving thermal stabilities of this kind has proven to be extremely difficult without compromising the molecules' nonlinearity. Addition of thermal stability in chromophores can in principle be achieved by replacing aliphatic structures by aromatic ones along the conjugation path of the molecules. However, as indicated above, additional aromaticity tends to decrease the hyperpolarizability. Moylan and co-workers circumvented this dilemma by replacing aliphatic dialkylamino donor groups with diarylamino groups,

Table 1 Absorption maxima (λ_{max}) and the scalar product [$\mu\beta(0)$] of dipole moment and static hyperpolarizability for a series of conjugated donor–acceptor compounds containing heterocyclic rings. DANS (**1e**) has been included in the table for comparison. Data taken from refs. 45 and 51

compound	λ_{max}/nm	$\mu\beta(0)/10^{-48}$ esu
 **1a**	718	2564
 **1b**	640	3023
 **1c**	662	4146
 **1d**	653	3469
 **1e**	430	363

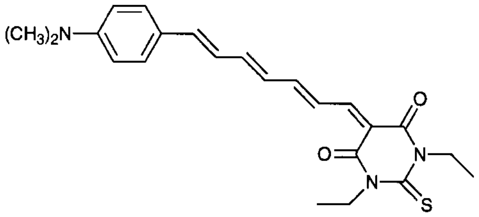
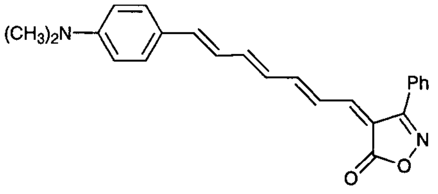
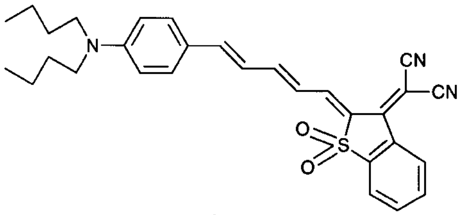
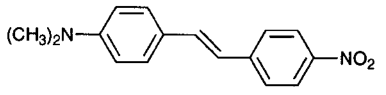
which results in a substantial increase in thermal stability of a wide range of chromophores without compromising the nonlinearity of the chromophore.[53,57] Because the aryl groups are not required to adopt a quinoidal configuration during intramolecular electron transfer, transfer is not impeded and the hyperpolarizability can be large. Therefore, a class of compounds that was expected to be very thermally stable turned out to be highly nonlinear as well. Some of the investigated systems showed thermal stabilities as high as 400 °C. One of these compounds (Table 3, **3a**) was successfully incorporated into a polyimide matrix. The electron donor group of the chromophore was incorporated directly into the polyimide backbone (donor-imbedded).[58] Glass transition temperatures and chemical stabilities as high as 350 °C were obtained. The electro-optic response (about 7 pm V^{-1}) was shown to have long term stability at 225 °C and short term stability up to 300 °C, due to the high glass transition temperature (T_g) of the polymer.

Other chromophores with thermal stabilities exceeding 300 °C have been developed.[59,60] For example, certain naphthalene benzimidazoles show good nonlinearity and thermal stabilities in excess of 350 °C (Table 3, **3b**). These systems are based on a fused ring system that is structurally similar to polyimide, which would make them very soluble in high T_g polyimides.[61,62] Rao *et al.* replaced the most reactive CN group in the tricyanovinyl group with aryl units in tricyanovinylthiophenes and was able to raise their chemical and thermal stability considerably (Table 3, **3c**).[48] Also, the thermal instability associated with the olefinic linkages in tricyanovinylthiophenes was removed by designing a set of compounds based on bithiophenes and fused thiophenes lacking such linkages (Table 3, **3d**).[63] Another class of extremely thermally stable chromophores with good nonlinearities are symmetrical analogues of the commercially available 4-(dicyanomethylene-2-methyl-6-(4-dimethylaminostyryl)-4-pyran (DCM) laser dye (Table 4, **4a**).[64,65] These donor–acceptor compounds are based on a dicyanomethylenepyran acceptor attached to two carbazole donors, with thermal stabilities of *ca.* 350 °C (Table 4, **4b**). An additional advantage of such two-dimensional 'lambda-shaped' molecules is that they may be less susceptible to loss of nonlinearity in poled polymer films.[66]

Another important issue is the nonlinearity–transparency trade-off. From the two-level model it is clear that the hyperpolarizability is a strong function of the absorption maximum. Furthermore, the low energy tails of the electronic absorption bands can extend several hundreds of nanometres into the long wavelength region. Because even a small absorption at the operating wavelength of electro-optic devices (typically 1.3 or 1.5 μm) can be detrimental, it is important to make NLO chromophores as transparent as possible without compromising the molecule's nonlinearity. Furthermore, for frequency doubling applications one would require materials that are simultaneously transparent at the fundamental and second-harmonic wavelength. Some progress has been made in designing molecules with good transparency and high nonlinearity.

Interesting candidates to defeat the nonlinearity–transparency trade-off (for electro-optic applications) are the previously mentioned symmetrical DCM derivatives. Most of these compounds perform rather well in the nonlinearity–transparency trade-off. They are about twice as nonlinear as one would expect them to be, given their absorption characteristics. This is due to the presence of two charge-transfer states

Table 2 Absorption maxima (λ_{max}), dipole moments (μ), static hyperpolarizabilities [$\beta(0)$] and the static scalar product [$\mu\beta(0)$] of a series of conjugated donor–acceptor compounds with extremely high nonlinearities. DANS (**1e**) has been included in the table for comparison. Data taken from refs. 51, 52 and 57

compound	λ_{max}/nm	$\mu/10^{-18}$ esu	$\beta(0)/10^{-30}$ esu	$\mu\beta(0)/10^{-48}$ esu
 **2a**	624	6.6	772	5095
 **2b**	582	8.9	528	4696
 **2c**	770	—	—	3900
 **1e**	430[a] 438[b]	6.6 6.69	55 42.1	363 282

[a] Ref. 51. [b] Ref. 57.

lying close to each other in energy, each of which can contribute to the hyperpolarizability.[65] According to the authors, these compounds represent the best progress to date in defeating the nonlinearity–transparency–thermal stability trade-off.

Less success has been achieved in the development of chromophores for frequency doubling applications. Some transparent chromophores have been incorporated into single crystals. For example, 8-(4-acetylphenyl)-1,4-dioxa-8-azaspiro-[4,5]decane was used to frequency double the 810 nm output of a diode laser in a ring resonator under noncritical phase-matching conditions. The molecule is transparent up to 384 nm.[67] An organic crystal of 4-(isopropylcarbamoyl)nitrobenzene (transparent up to 420 nm) was able to convert Ti–sapphire laser light (930 nm) into 465 nm blue light with high conversion efficiency under type II noncritical phase-matching conditions.[68]

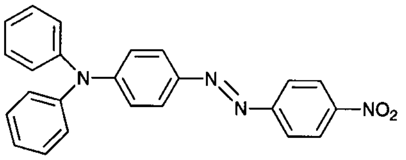
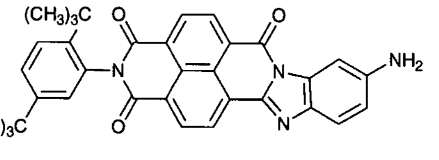
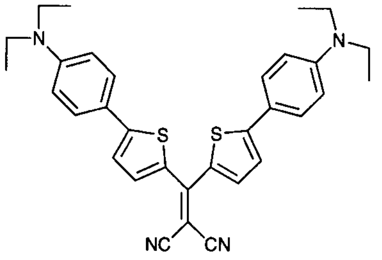
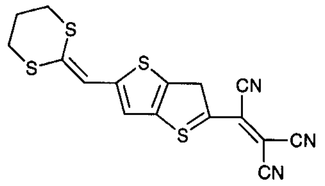
Octopolar molecules

In the early nineties, Zyss and co-workers introduced octopolar molecules for second-order nonlinear optics. Octopolar molecules are nonpolar molecules that combine second-order nonlinear optical properties with a strict cancellation of all vector-like observables, including the ground- and excited-state dipole moment.[69–72] Hence, such systems cannot be described by the two-level model because $\Delta\mu_{ge}=0$. Instead, the two-level model must be extended to a three level model in the octopolar case. The advantages of using such nonpolar species for NLO applications have been discussed. They include easier (noncentrosymmetric) crystallization, no dipolar (aggregate) interaction, better ratio of off-diagonal versus diagonal β tensor components, and improved efficiency–transparency trade-off.

Due to the development of hyper-Rayleigh scattering techniques it soon became possible to experimentally evaluate the hyperpolarizability of octopolar molecules. For example, the hyperpolarizability of the tricyanomethanide ion, tetraorganotin compounds, symmetrically substituted benzenes and triazines and tertiary amines have been evaluated.[73–78] Recently, a number of efficient octopolar structures have been identified. For example, the octopolar crystal violet cation (Table 5, **5b**) was shown to be considerably nonlinear, with hyperpolarizabilities comparable to traditional dipolar compounds.[22,26,74] Octopolar structures currently displaying the largest hyperpolarizabilities appear to be tri-substituted ruthenium complexes (Table 5, **5a**).[79] An intense multidirectional metal-to-ligand charge transfer leads to a significant enhancement of the hyperpolarizability.

The finding that compounds other than one-dimensional dipolar systems are capable of exhibiting significant nonlinearities is one of great importance and can considerably increase our understanding of molecular nonlinear optical processes. In addition, two- and three-dimensional stereochemistry offers new possibilities for the design and synthesis of optically nonlinear molecules. On the other hand, due to the absence of a permanent dipole moment, octopolar chromophores incorporated in a polymer matrix cannot be poled by

Table 3 Absorption maxima (λ_{max}), the scalar product [$\mu\beta(0)$] of dipole moment and static hyperpolarizability, and decomposition temperature (T_d) of a number of thermally stable chromophores with good nonlinearity. Data taken from refs. 48, 57, 61, 62 and 63

compound	λ_{max}/nm	$\mu\beta(0)/10^{-48}$ esu	T_d/°C
 **3a**	486	319	393
 **3b**	562	199	360
 **3c**	513	854	354
 **3d**	570	1281	310

a static electric field. Therefore, a current challenge is the macroscopic organization of octopolar molecules in a noncentrosymmetric environment. Besides the formation of single crystals, the recently developed method of all-optical poling might be useful in obtaining the required macroscopic noncentrosymmetry. All optical poling is based on the fact that combinations of certain light fields can exhibit polarity. For example, the coherent superposition of a field at frequency ω [$E(\omega)$] and one at frequency 2ω [$E(2\omega)$] leads to a nonzero time-averaged cubic interference term $<E^3>$ where $E = E(\omega) + E(2\omega)$. In addition, its irreducible tensor decomposition has a component with octopolar symmetry. Therefore coupling of this field is permitted even in the absence of a dipole.[80] Recently, the octopolar molecule ethyl violet was oriented in a sol–gel matrix by all-optical poling.

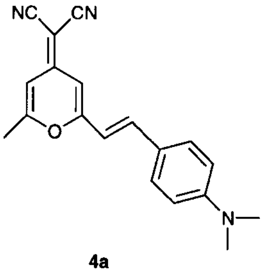
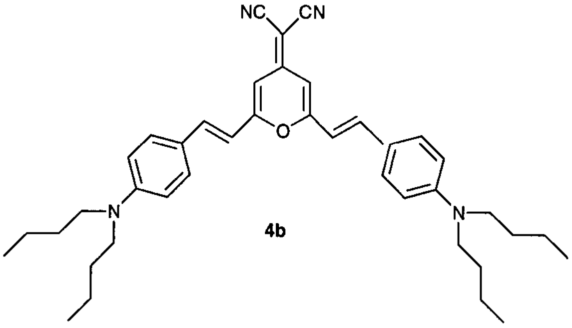
Charged organic compounds

Charged organic compounds have been known for several years as an interesting class of materials for second-order nonlinear optics, especially for the development of single crystals and LB films with high NLO properties. This is due to the high nonlinearity of some ionic compounds and the fact that single crystals with different structures can be grown simply by changing the counterions.

Until the development of HRS, the hyperpolarizability of charged ionic compounds was not directly accessible for measurement. Therefore, not much research has been done to carefully study the nonlinearity–structure relationship in such compounds. Only recently have some groups started to evaluate the molecular nonlinearities of ionic compounds using HRS. For example, Duan *et al.* investigated sodium toluene-*p*-sulfonate and found an off-resonant hyperpolarizability of 22×10^{-30} esu, comparable to that of *p*-nitroaniline but with much better transparency.[81] Chauchard *et al.* also found that polyaryl salts combine good hyperpolarizabilities with good transparency.[82] Kang *et al.* studied diazonium compounds having hyperpolarizabilities much larger than typical nonionic azobenzene dyes.[83]

Stilbazolium dyes (Table 6, **6a** and **6b**) have also received a lot of interest lately, especially because of their extremely high nonlinearities[84] and the possibilities of incorporating them into a variety of macroscopic structures. For example, intercalated layered materials comprising a stilbazolium dye and an inorganic material were shown to exhibit large nonlinearities due to the spontaneous poling induced by the intercalation process.[85] Kim *et al.* included a stilbazolium dye into the helical cavity of amylose, forming a rigid rod supramolecular complex. Spin coated thin solid films of the material were shown to exhibit self-poling of the chromophore leading to a respectable nonlinearity.[86] Ashwell and co-workers used stilbazolium chromophores in Langmuir–Blodgett films and Lin *et al.* were

Table 4 Absorption maxima (λ_{max}), the scalar product [$\mu\beta(0)$] of dipole moment and static hyperpolarizability, and decomposition temperature (T_d) of laser dye DCM and a symmetrical analogue of DCM. Data taken from ref. 65

compound	λ_{max}/nm	$\beta(0)/10^{-30}$ esu	T_d/°C
 **4a**	468	646	332
 **4b**	496	1688	348

able to create self-assembled films containing a related aminophenylazopyridinium chromophore of good quality and extremely high nonlinearity.[87–89]

The hyperpolarizability of the chromophore-containing protein bacteriorhodopsin was recently evaluated using HRS. The extremely high hyperpolarizability was shown to be due to the presence of the protonated Schiff base of the retinal chromophore (Table 6, **6c**).[90–93]

Rigid multichromophore systems

An extremely interesting approach to optimize the vector product $\mu\beta$ is to make use of rigid molecular structures containing several orientationally correlated chromophores. In such structures, the total hyperpolarizability and dipole moment are obtained as coherent superpositions of the individual chromophores and can lead to enhanced nonlinear optical properties.

The dipole moment of a rigid structure containing n nonlinear chromophores can be written as a vector sum of the individual chromophores. In the limit where the total dipole moment is solely due to the chromophores, we have eqn. (4),

$$\mu = n\mu_{chrom}\langle \cos\theta \rangle \qquad (4)$$

where θ is the angle between the chromophoric dipole moment and the net dipole moment of the superstructure. The angular brackets refer to an average over the distribution of polar angles θ of the chromophores (Fig. 2). For the common case of one-dimensional charge-transfer molecules, the dominant component of the hyperpolarizability β_{chrom} is along the dipole moment μ_{chrom} and the vectorial part of the entire structure is given by eqn. (5).

$$\beta = n\beta_{chrom}\langle \cos\theta \rangle \qquad (5)$$

This analysis implies that the hyperpolarizability per chromophore of the multichromophore structure is actually reduced compared to the individual chromophores. However, the vector product $\mu\beta$ of the superstructure is given by eqn. (6),

$$\mu\beta = n^2\beta_{chrom}\mu_{chrom}\langle \cos\theta \rangle^2 \qquad (6)$$

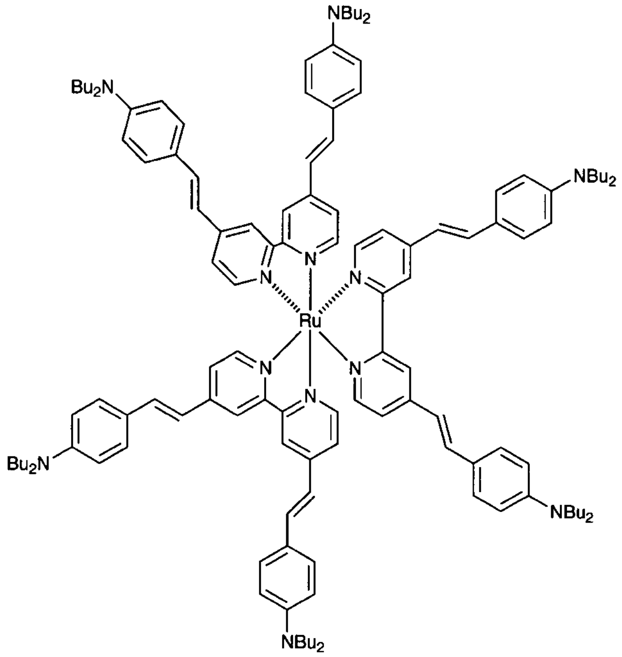
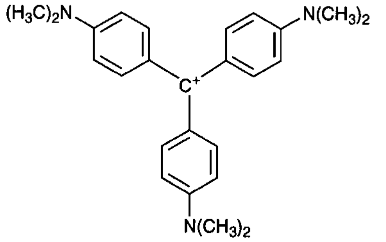
and hence, $\mu\beta$ per chromophore ($\mu\beta/n$) will be enhanced whenever $n\langle \cos\theta \rangle > 1$. Consequently, the nonlinear response of the structure can be enhanced by either increasing the number of chromophores or by improving the alignment. Therefore, this approach may prove extremely useful in designing improved nonlinear materials for incorporation in polymer matrices, especially because of the possibility of optimizing the nonlinear response without sacrificing transparency (and thermal stability).

Enhancements of $\mu\beta$ in multichromophore systems have been experimentally observed, for example in main-chain polymers.[14] Also, Duan *et al.* observed enhancements in $\mu\beta$ for a series of oligomeric methyl methoxybenzoates.[94] A very elegant and successful approach was the synthesis of calix[4]arenes combining up to four nonlinear optical chromophores in one calixarene molecule. Enhancements in $\mu\beta$ per chromophore (as compared to the free chromophore) of more than a factor of 2 where observed,[95,96] as shown in Table 7. Recently, it was shown that nonlinear optical chromophores can be organized as orientationally correlated side groups of rigid helical polymers.[97] The nonlinearity of such a structure can be significantly enhanced. For example for helical poly(isocyanide)s that contain nonlinear chromophores as side groups an enhancement in $\mu\beta$ per chromophore of 1.5 was observed (Table 8). Enhancements in the nonlinearity of chromophore functionalized poly(glutamate)s have also been observed. This was attributed to the supramolecular helix structure of the polyglutamate. The extremely high dipole moment of the poly(glutamate) backbone in combination with the noncentrosymmetric alignment of the chromophores in the supramolecular structure gave rise to a 35-fold enhancement in $\mu\beta$ per chromophore (Table 9).[98]

Other unconventional organic chromophores

Besides the systems mentioned in the previous paragraphs, some unconventional chromophores have appeared to show promising properties. For example, some of these systems perform rather well in the efficiency–transparency trade-off.

Table 5 Absorption maxima (λ_{max}) and static hyperpolarizability [$\beta(0)$] of a tri-substituted ruthenium complex and crystal violet. Data taken from refs. 22, 74 and 79

compound	λ_{max}/nm	$\beta(0)/10^{-30}$ esu
 **5a**	513	1200
 **5b**	588	470[a] 290[b]

[a]Ref. 74. [b]Ref. 22.

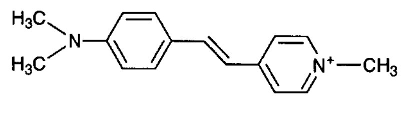
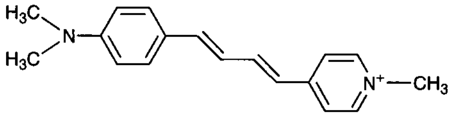
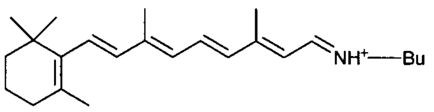
Bahl *et al.* showed that 1,8-diarylnaphthalenes exhibit remarkable NLO-active, combined with thermal stability and high transparency (Table 10, **10a**). In these systems, direct conjugation between donor and acceptor is avoided. Instead, non-covalent through-space interactions are responsible for the material's nonlinear properties.[99] Lambert *et al.* studied ammonium–borate zwitterions and found that these systems were significantly more transparent than traditional DπA systems (*e.g.* DANS) but with improved transparency (Table 10, **10b**).[100]

Unsymmetrical squaraine dyes are currently being investigated as a new class of nonlinear optical molecules.[101–103] One squaraine dye with an extended conjugated system was shown to have a $\mu\beta$ value of roughly eight times that of DANS. Although one would not expect to observe second-order nonlinear effects from centrosymmetric squaraine dyes, Ashwell and co-workers showed that such systems exhibit strong second-order nonlinearities in Langmuir–Blodgett samples of the material.[104,105] This was attributed to an intermolecular charge transfer in noncentrosymmetric aggregates of the molecules in the LB films.

Recently, the hyperpolarizability of two tautomeric forms of nitrobenzyl derivatives were investigated by HRS.[106] Switching between both forms can be performed by a photo-induced proton transfer. Large differences were found between the two forms which suggests that these systems can be used to optically modulate second-harmonic generation through a photo-induced proton transfer process.

Highly chiral molecules also seem to show extremely interesting NLO properties. It was shown theoretically that isotropic media composed of chiral molecules can possess an electro-optic response.[107] This is related to the inherently low symmetry of chiral materials: even isotropic materials consisting of chiral molecules are noncentrosymmetric. The predicted effect relies on material damping and was estimated to be of the order of that of the inorganic crystal potassium dihydrogen phosphate (KDP). The theoretical results also suggest that it is possible to design an experimental arrangement that could lead to gain for the incident light field. Such an effect would be of considerable importance for the amplification of optical signals in polymeric fibers. Furthermore, the nonlinear optical properties of chiral molecules and polymers can be significantly enhanced by optimizing magnetic dipole contributions to the nonlinearity, in addition to the usual electric dipole contributions. For example, in a Langmuir–Blodgett film of a chromophore functionalized chiral poly(isocyanide), magnetic dipole nonlinearities were estimated to be of the order of 10–20% of the electric dipole nonlinearity.[108]

Table 6 Absorption maxima (λ_{max}) and static hyperpolarizability [$\beta(0)$] of charged organic compounds. Data taken from refs. 84 and 92

compound	λ_{max}/nm	$\beta(0)/10^{-30}$ esu
 **6a**	474	363
 **6b**	492	624
 **6c**	513	900

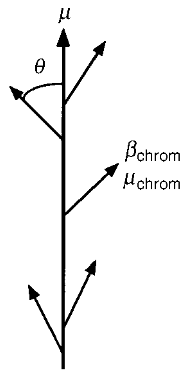


Fig. 2 Schematic representation of individual chromophores along the net dipole moment of a rigid multichromophore structure. The small arrows represent individual chromophores with hyperpolarizability β_{chrom} and dipole moment μ_{chrom} that make an angle θ with respect to the net dipole moment μ (big arrow).

Organometallic compounds

Compared to organic nonlinear optics, the field of organometallic nonlinear optics is relatively young and unexplored. In the last decade, researchers have sporadically investigated the NLO properties of organometallic compounds, and only recently have they begun a systematic investigation of the molecular properties that determine the NLO response of organometallic compounds. Organometallics are potentially interesting candidates for NLO purposes. They show very strong absorption bands [metal-to-ligand charge-transfer (MLCT) and ligand-to-metal charge-transfer (LMCT)] in the UV–VIS region which are related to high transition dipole moments and low transition energies. As a consequence, the two-level model predicts large hyperpolarizabilities. A more important issue is that next to a larger hyperpolarizability, the insertion of a metal group introduces other geometries as a palette of coordination patterns is available for metals. Other than dipolar species can be synthesized and/or the hyperpolarizability can be fine-tuned by small changes in ligands other than the NLO active ones. Moreover, the possibility of chirality, which may induce a non-centrosymmetrical crystallization, can lead to a useful macroscopic arrangement. Good summaries of the NLO work performed on organometallic compounds can be found in several recent review articles.[3,109–111]

Although in 1986 Frazier *et al.* investigated the second-harmonic efficiencies of over 60 transition metal–organic compounds, attention to organometallic species was mainly drawn in 1987 by Green *et al.* when they revealed a SHG efficiency as high as 62 times that of a urea reference sample for *cis*-[1-ferrocenyl-2-(4-nitrophenyl)ethylene].[112,113] A profound EFISHG study of the molecular properties governing the hyperpolarizability of metallocenes was performed three years later (Table 11, **11a**).[114,115] As for organic systems, elongation of the conjugated bridge, as well as the addition of electron donating substituents to the metallocene donor group, was shown to increase the hyperpolarizability. However, in contrast to most organic compounds, two optical transitions [a π–π^* charge transfer (CT) transition analogous to the CT transition in substituted benzenes and a MLCT] were suggested to contribute to the hyperpolarizability, which prohibits the use of the two-level model for metallocene compounds. On the other hand, a theoretical evaluation (ZINDO-SOS) of the hyperpolarizability of metallocene complexes suggest the hyperpolarizability to be dependent on only one MLCT transition,[116–118] and that the two-level model still holds for this class of materials. Both experiment and theory agree that the donor strength of ferrocene is comparable to that of the organic methoxyphenyl donor. Yet ferrocenes were expected to be stronger donors based on binding energies and redox potentials. It is suggested that poor coupling between the metal and the organic π-system reduces the donor properties of the metal centre.

Recently, a series of conjugated ferrocene compounds with heterocyclic acceptors were evaluated for their nonlinear optical properties.[119] Resonantly enhanced $\mu\beta$ values up to 3000×10^{-48} esu were found and the increase of conjugation length or acceptor strength clearly led to increased hyperpolarizabilities (Table 11, **11b**). No problems unique to ferrocene were seen upon incorporation into poled polymer films and electro-optical coefficients were found consistent with the $\mu\beta$ values.

Using the HRS technique, partially oxidized ferrocenyl (donor–acceptor motif) and bisferrocenyl (donor–acceptor–donor motif) compounds have been investigated.[120] Upon the addition of the second ferrocene group an increase of *ca.* 50% was observed. Partial oxidation of the complexes led to a substantial increase in the resonant enhanced hyperpolarizability. This enhancement is attributed to a differential electron transfer mechanism from the metal complex to the oxidant, resulting in a large dipole moment difference between ground and excited state.

A different approach has been attempted by Cao *et al.* using the ferrocenyl group as a bridge, constructing a donor–switch–acceptor structure wherein the metal moiety acts as an electro-

Table 7 Absorption maxima (λ_{max}), dipole moment (μ), static hyperpolarizability [$\beta(0)$] and scalar product [$\mu\beta(0)$] of a calix[4]arene derivative and a reference compound. For the calixarene, $\beta(0)$ and $\mu\beta(0)$ are given per calixarene molecule (calix) and per individual chromophore (chrom). Data taken from ref. 96

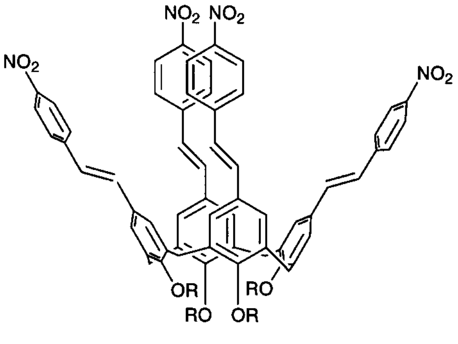
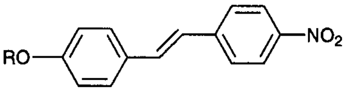
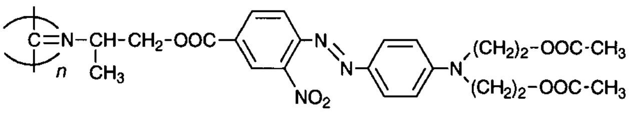
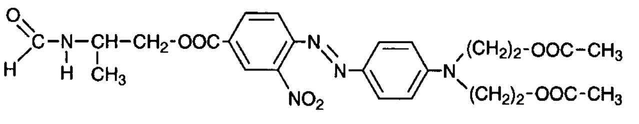
compound	λ_{max}/nm	$\mu/10^{-18}$ esu	$\beta(0)/10^{-30}$ esu	$\mu\beta(0)/10^{-48}$ esu
 **7a** R = Pr	370	15.3	127 (calix) 32 (chrom)	1943 (calix) 486 (chrom)
 **7b** $R = CH_3$	377	4.5	44	198

Table 8 Absorption maxima (λ_{max}), static hyperpolarizability [$\beta(0)$] and scalar product [$\mu\beta(0)$] of a chromophore functionalized poly(isocyanide) (with $n = 97$) and a corresponding reference compound. For the poly(isocyanide), $\beta(0)$ and $\mu\beta(0)$ are given for the entire polymer (polymer) and per individual chromophore (chrom). Data taken from ref. 97

compound	λ_{max}/nm	$\beta(0)/10^{-30}$ esu	$\mu\beta(0)/10^{-48}$ esu
 **8a**	438	810 (polymer) 8.4 (chrom)	35 200 (polymer) 363 (chrom)
 **8b**	457	165	239

optical switch. Measurements on LB films of the amphiphilic ferrocene derivative yielded a hyperpolarizability of 180×10^{-30} esu.[121]

Molecular hyperpolarizabilities of bimetallic compounds have been studied using the HRS technique.[122–124] For example, a bimetallic (Fe–Cr) sesquifulvalene complex was shown to exhibit static hyperpolarizabilities up to 105×10^{-30} esu, the largest measured to date for ferrocene derivatives (Table 12, **12b**).[123,124] Monometallic manganese(I) sesquifulvalene complexes on the other hand showed only modest hyperpolarizabilities.[125]

Next to ferrocene derivatives, organoruthenium complexes have also been the subject of a number of NLO investigations. In 1988, Richardson an co-workers demonstrated that the addition of a (η^5-cyclopentadienyl)bis-triphenylphosphine)ruthenium group to the liquid crystal molecule 4-cyano-4″-pentyl-*p*-terphenyl increases the second-order NLO efficiencies of the corresponding LB films. In addition, EFISHG studies have been performed on several cyano(cyclopentadienyl)bis(triphenylphosphine)ruthenium terminated aromatic compounds and the effect on the hyperpolarizability of the type of π-conjugated bridge has been assessed.[126,127] Sakaguchi *et al.* prepared LB films of amphiphilic tris(2,2′-bipyridine)ruthenium(II), Maker fringes were observed and a hyperpolarizability was determined of 70×10^{-30} esu.[128,129] Moreover, light-induced modulation of the SHG efficiency was demonstrated. Upon UV irradiation, a decrease of the SHG signal proportional to the intensity of the UV pulses was observed. The switching is ascribed to differences in the hyperpolarizability of the ruthenium ground state and (MLCT) excited state.[130–132] The transient absorption spectrum showed the formation of Ru^{III} and the bipyridine anion radical upon excitation. Chemical oxidation of Ru^{II} complexes also results in a clear decrease of the hyperpolarizability for the Ru^{III} complexes in respect to the Ru^{II} compounds,[133] which is in agreement with the results of the optical modulation experiment.[130–132] Octopolar Ru complexes were also investigated and have already been discussed previously.[79,133,134]

Extremely high hyperpolarizabilities were found for some mixed-valence bimetallic ruthenium complexes (Table 12, **12a**).[135] The intervalence charge transfer (IVCT) transition was suggested to account for the augmented hyperpolarizability. However, later corrections assigned a more modest hyperpolarizability for these complexes (*i.e.* reduced by a factor of 6).[22,136]

Table 9 Absorption maxima (λ_{max}), static hyperpolarizability [$\beta(0)$] and scalar product [$\mu\beta(0)$] of a chromophore functionalized poly(γ-methyl-L-glutamate) (16 mol% functionalized) and a corresponding reference compound. For the polyglutamate, $\beta(0)$ and $\mu\beta(0)$ are given for the entire polymer (polymer) and per individual chromophore (chrom). Data taken from ref. 98

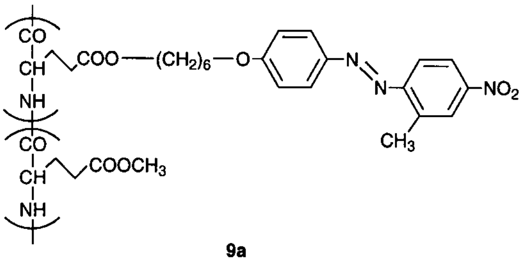
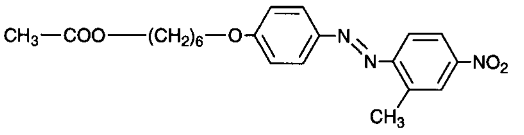
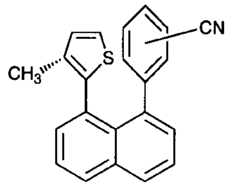
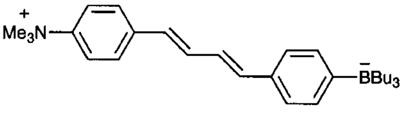
compound	λ_{max}/nm	$\mu/10^{-18}$ esu	$\beta(0)/10^{-30}$ esu	$\mu\beta(0)/10^{-48}$ esu
 **9a**	365	460	259 (polymer) 21.1 (chrom)	119 000 (polymer) 9 690 (chrom)
 **9b**	369	9.6	28.8	277

Table 10 Absorption maxima (λ_{max}) and static hyperpolarizability [$\beta(0)$] of 1,8-diarylnaphtalene (**10a**) and an ammonium–borate zwitterion (**10b**). Data taken from refs. 99 and 100

compound	λ_{max}/nm	$\beta(0)/10^{-30}$ esu
 **10a**	296	24
 **10b**	341	69

A systematic study of gold(I), nickel(II) and ruthenium(II) σ-arylacetylide complexes has been performed by Whittal and co-workers. The hyperpolarizabilities were found to increase from the 14-electron gold complexes to the 18-electron nickel complexes and further to the 18-electron, more oxidizable ruthenium compounds (Table 11, **11c**).[137–140] Moreover, the influences of different types of π-systems, chain lengthening, acceptor and ligand have been investigated.[138–142] Heterobimetallic complexes with a ruthenium bis(triphenylphosphine)(indenyl)acetylide donor were reported that exhibit the largest hyperpolarizabilities to date for bimetallic systems (Table 12, **12c**).[111,141,142]

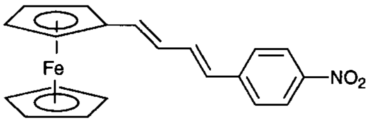
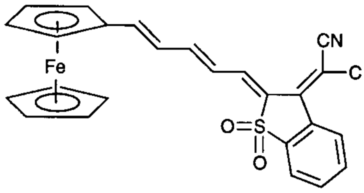
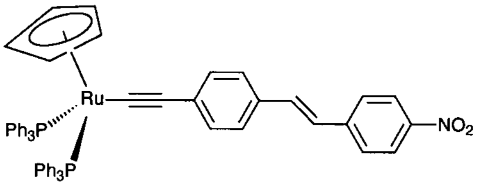
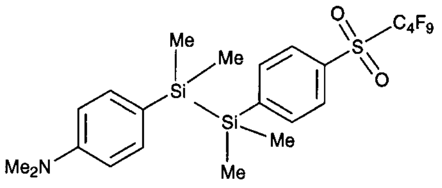
Ruthenium has not only been studied as a possible acceptor or donor, but its ability to act as a bridge was also assessed. Donor/acceptor-substituted *trans*-tetraamineruthenium(II) complexes that show coplanarity of the axial ligands which can allow π–π coupling through the polarizable ruthenium centre, exhibit large, however resonant enhanced, hyperpolarizabilities.[143] Silicon can be incorporated as a donor, bridge or even as an acceptor into an organic system (Table 11, **11d**).[144–146] Studies report rather moderate quadratic hyperpolarizabilities, the largest efficiency found for the silicon donor. The main advantage of these systems compared to other metallic complexes is their transparency in the visible region.

Recently, a new type of planar transition metal complex, namely metal Schiff base complexes, has been investigated for its second-order NLO properties.[147–149] For (*N,N′*-disalicylidenephenylene-1,2-diaminato)M^{II} (M = Co, Ni, Cu), the hyperpolarizability as measured with EFISHG, as well as the calculated values, increased on going from the closed shell d^8 Ni^{II} to the open-shell d^9 Cu^{II} and d^7 Co^{II} analogues.[147] Computations on the positively charged open-shell $(DANS)_2{}^+$ dimer showed an enhanced hyperpolarizability for the open-shell dimer compared to the DANS monomer or the closed-shell $(DANS)_2$ dimer.[149] Both reports were consistent with an increased molecular hyperpolarizability for the open-shell systems. Improved accessibility of lower-lying excited states in the case of the open-shell complex was suggested to account for the larger hyperpolarizability. As a consequence, the two-level model does not hold for open-shell complexes, in contrast to the closed-shell ones. However, results on a similar Schiff base metal complex present a similar hyperpolarizability for both the open shell Cu^{II} and the closed-shell Ni^{II} complex, thus undermining the previous conclusions.[148]

The largest hyperpolarizability reported to date for an organometallic compound is that of the push-pull {5-[4-(dimethylamino)phenylethynyl]-15-(4-nitrophenylethynyl)-10,20-diphenylporphinato}Zn^{II} complex (Table 13).[150,151] Compared to acetylenyl-bridged D–porphyrin–A systems, phenyl-bridged metalloporphyrins exhibit rather small hyperpolarizabilities.[151,152] In the absence of the acetylenyl bridge, electronic communication between donor and acceptor through the porphyrin bridge is strongly reduced as a consequence of the dihedral angle between the phenyl rings and the porphyrin base. The open-shell–closed-shell model suggested by Di Bella *et al.* seems to hold for the phenylporphyrins that show larger hyperpolarizabilities for the open-shell Cu^{II} complexes than for the closed-shell Zn^{II} porphyrines;[152] the results for arylacetylporphyrins, however, are not consistent with the proposed model.[150]

In general, the addition of the metal leads to an increased hyperpolarizability compared to that of the free ligand. However, the use of organometals in applications will probably suffer from the nonlinearity–transparency trade-off. As mentioned, the MLCT/LMCT transitions that are responsible for the hyperpolarizabilities are very strong and lie in the visible region, especially in the case of the most promising organometallic complexes such as tris(bipyridine)ruthenium, ruthenium σ-arylacetylide or zinc arylacetyporphyrins.

Table 11 Absorption maxima (λ_{max}), the scalar products [$\mu\beta$ and $\mu\beta(0)$] and the static hyperpolarizabilities [$\beta(0)$] of some organometallic compounds. Data taken from refs. 115, 119, 138 and 146

compound	λ_{max}/nm	$\mu\beta/10^{-48}$ esu	$\mu\beta(0)/10^{-48}$ esu	$\beta(0)/10^{-30}$ esu
 **11a**	382/500	297[a]	200	45
 **11b**	516/745	3000[a]	—	—
 **11c**	460	9660[b]	1545	234
 **11d**	277	228[b,c]	14	

[a] Measurements performed at the fundamental wavelength of 1.9 μm. [b] Measurements performed at the fundamental wavelength of 1.06 μm. [c] Calculated using a theoretical (AM1) dipole moment.

Table 12 Absorption maxima (λ_{max}) and the static hyperpolarizabilities [$\beta(0)$] of bimetallic compounds. Data taken from refs. 123, 136 and 141

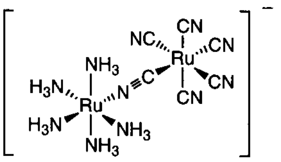
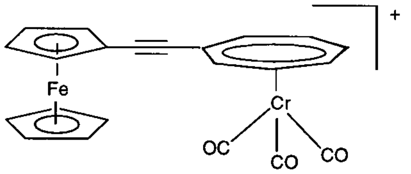
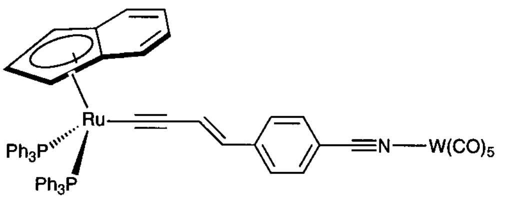
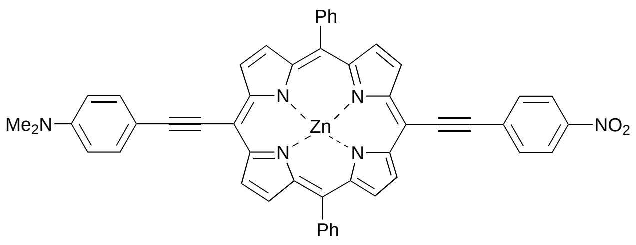
compound	λ_{max}/nm	$\beta(0)/10^{-30}$ esu
 **12a**	684	81
 **12b**	600	105
 **12c**	456	150

Table 13 Absorption maxima (λ_{max}), static hyperpolarizability [$\beta(0)$] and scalar product [$\mu\beta(0)$] of a push-pull arylethynyl zinc phorphyrin. Data taken from ref. 150



λ_{max}/nm	$\beta(0)/10^{-30}$ esu	$\mu\beta(0)/10^{-48}$ esu
475	800	9840

Conclusion

We have given an overview of recent and important developments in the field of organic and organometallic chromophores with nonlinear optical properties. It is clear from this overview that there are two main activities in this field.

First, we have the further improvement of the nonlinearity of traditional nonlinear optical molecules and the optimization of secondary properties like transparency and thermal stability. From the applications point of view, we think it is safe to conclude that the nonlinearity of some of the investigated traditional chromophores are sufficiently high to develop electro-optic materials that can compete with inorganic materials like lithium niobate. However, better combinations of nonlinearity–stability–transparency are needed in order to really outperform the inorganics. For frequency doubling applications, on the other hand, we still have a long way to go. Some chromophores show potential when incorporated into organic crystals, but polymeric materials for frequency doubling applications are still far off.

Second, we see a tendency to develop completely new NLO systems with interesting properties, such as octopolar compounds, ionic chromophores, multichromophore systems and organometallic compounds. Some interesting results were obtained, but this field is still in its infancy. Problems related to stability and optical loss remain to be resolved. On other hand, the search for nonlinear optical properties in completely new materials can only increase our understanding of the mechanisms responsible for NLO effects.

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