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Multipolar engineering of molecules and materials for quadratic nonlinear optics

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Abstract

The first generation of molecular engineering studies whereby a one-dimensional bipolar donor–acceptor conjugated system had served, since the early 1970s, as a quasi-exclusive template, had failed to take into account the tensorial dimension attached to the β quadratic hyperpolarizability tensor. We review here the outgoing second generation of molecular design studies based on three-dimensional multipolar charge transfer which reflects on enhanced values for all β_{ijk} coefficients, then opening-up the possibility of polarization-independent nonlinear interactions. This can be ensured by more isotropic crystalline lattices or statistical polymer-based orientational distribution out of reach for the cruder one-dimensional systems. A particular challenge which has in fact triggered this domain in the early 1990s to this day has been set by octupolar systems whereby the symmetry-imposed cancellation of the dipole moment precludes the utilization of an electric field coupling scheme to orient molecules into a noncentrosymmetric order. We will review this new domain, encompassing both physical and chemical considerations, all the way from new molecular engineering techniques, with associated quantum modeling, to advanced characterization methods and macroscopic ordering schemes jointly aiming at promoting and exploiting the so far largely ignored tensorial dimension of nonlinear light–matter coupling schemes in molecules. *To cite this article: I. Ledoux, J. Zyss, C. R. Physique 3 (2002) 407–427.* © 2002 Académie des sciences/Éditions scientifiques et médicales Elsevier SAS

molecular engineering / nonlinear optics / octupoles / multipoles / polymers / molecular crystals / dendrimers

Ingénierie moléculaire de molécules et matériaux multipolaires pour l'optique non linéaire quadratique

Résumé

Une première génération de recherche en ingénierie moléculaire fondée quasi-exclusivement, depuis les années 70, sur le modèle de la diode moléculaire bipolaire à transfert de charge, ne prenait pas en compte la dimension tensorielle intrinsèquement attachée à la susceptibilité optique quadratique β . Nous faisons ici le point sur une deuxième génération d'études en cours depuis le début de la décennie précédente, qui se traduit

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en particulier par des valeurs accrues de tous les coefficients β_{ijk} , et ouvre la voie à la possibilité d'interactions non linéaires insensibles à la polarisation. De telles configurations sont le résultat de modes d'organisation macroscopique de natures cristalline ou statistique (polymères fonctionnels) plus isotropes et hors de portée des systèmes unidimensionnels moins élaborés. Les systèmes octupolaires, pour lesquels des contraintes strictes de symétrie imposent l'annulation du moment dipolaire, ont posé un défi particulier dans ce contexte, en interdisant le recours aux méthodes traditionnelles d'orientation sous champ électrique pour lever la centrosymétrie au niveau macroscopique. Nous passerons en revue ce nouveau domaine, qui mêle étroitement les considérations physiques et chimiques, en allant des nouveaux schémas d'ingénierie moléculaire et de leurs modèles quantiques associés aux méthodes de caractérisation et d'orientation macroscopiques visant à mettre en valeur la dimensionnalité tensorielle, jusqu'ici largement ignorée, des phénomènes de couplage non linéaire en milieu moléculaire. *Pour citer cet article : I. Ledoux, J. Zyss, C. R. Physique 3 (2002) 407–427. © 2002 Académie des sciences/Éditions scientifiques et médicales Elsevier SAS*

ingénierie moléculaire / optique non linéaire / octupôles / multipôles / polymères / cristaux moléculaires / dendrimères

1. Introduction

Significant advances have been reported lately in the field of nonlinear molecular optics in the critical area of material engineering towards optoelectronics device technologies [1–3] which is currently experiencing a revival of both a practical and conceptual nature. Strong leverage from the optoelectronic and telecommunication industries, together with motivations of a more fundamental nature, are strongly pushing forward this domain, to which a broad community of physicists, chemists and electrical engineers provides a distinctive and rather unique cross-disciplinary culture and methodology. As far as applied motivations are concerned, a major driving force is the necessity to fulfill the needs for key signal processing functions such as modulation, routing or switching to meet the ever increasing demands of Dense Wavelength Division Multiplexing (DWDM) networks in terms of bandwidth, low energy consumption and innovative functionalities, so as to disseminate new services down to the end-users. In this domain the limits of current III–V semiconductors or lithium niobate technologies are being increasingly reached, especially when it comes to low-cost, high-volume production requirements, whereby the exploration and demonstration of alternative solutions, such as those proposed by organic materials, has become a priority.

The requirements of nonlinear material engineering are primarily governed by nonlinear figures of merit directly attached to the desired functionality, whereas equally stringent requirements apply to the optical quality and robustness of the materials. Organic materials for quadratic nonlinear optics have been traditionally following the now well-established traditional pattern of a strongly dipolar quasi one-dimensional intramolecular charge transfer molecule, sometimes referred to as the bipolar 'molecular diode'. The resulting molecular hyperpolarizability β tensor is then dominated by a single diagonal β_{xxx} coefficient, where x is the molecular charge transfer axis. This restricted template has been subsequently generalized by the proposition and demonstration of the broader class of multipolar materials [4,5] whereby efficient two- and three-dimensional molecules are able to match a more diversified range of optical polarization configurations in self-assembled or externally engineered multipolar macroscopic structures. In that respect, early studies based on group theory and quantum mechanics [4–7] have helped set conceptual foundations to the domain of non-dipolar molecules for nonlinear optics which became known as *octupolar* and more generally *multipolar* molecules, and thus designate new directions in molecular engineering beyond the boundaries of quasi-one-dimensional rod-like dipolar systems.

At the macroscopic level, besides the earlier and successful development of a dipolar crystalline engineering route in the 1970s and the 1980s with such milestones as POM [8], NPP [9] and DAST [10],

most research teams concentrate on the optimization of poling conditions and long-term stability of electro-optic polymers [11]. Noncentrosymmetry is traditionally obtained by electric field orientation techniques in a viscous phase, either by a corona needle or between electrodes [12]. This method is based on the coupling of preferably large molecular dipoles to an externally applied electric field, and is therefore not applicable as such to octupolar molecules which are intrinsically deprived of dipole moments. Permanent orientation of functionalized materials such as guest–host polymers with an octupolar guest in solid solution or in tethered configuration remains, however, an essential prerequisite towards further practical development of multipolar materials. This requirement triggered the search for an original poling method that would not depend on the availability of a permanent dipole. It is indeed possible to imprint transient as well as permanent noncentrosymmetric order in media subject to coherent multi-wavelength irradiation with non-zero time-averaged cube of the total field ($\langle E^3 \rangle_t \neq 0$) [13]. Such a situation is met by interfering single photon and two-photon absorption processes in side-chain polymers with dipolar nonlinear side-groups and has led to the demonstration of second-harmonic generation in polymer films with efficiencies comparable to that of electrically poled films [14]. Although inspired by the initial breakthrough of the experimental evidence, in the mid-1980s, of second harmonic generation in silica fibers [15], the implementation of optical poling in photosensitive polymers has opened-up a distinctive avenue in molecular engineering which took its full measure when optically-induced acentric macroscopic organization of octupolar molecules was demonstrated for the first time [16,17]. Tensorial control via the polarization states of the write beams [18] (see the article by Brasselet et al. [19] in the present issue) has brought an increased dimension to a domain which can be viewed as a particularly illustrative implementation of the broader domain by coherent control.

2. Molecular engineering schemes

We review in the following some major trends which have been proposed in recent years so as to steer synthetic studies towards useful molecular targets. This domain stands at a crucial interface between chemistry and physics, where the boundaries between disciplines are being somewhat blurred. Core specificities of both activities, namely organic synthesis for chemistry on the one hand, and definitions of targeted functional properties and related characterization for physics on the other hand, remain the basic and equally important ingredients of activities in this domain. The approach followed here stands, however, more at the physical side of the barrier as it is based on the elaboration of basic guidelines depicted in terms of simple and purposely very general templates which are then proposed to chemists towards subsequent implementation in various synthetic avenues. A central example of great current interest to illustrate this approach is the multipolar cube [4,5], which has inspired throughout recent years a variety of molecular and supramolecular synthetic implementation. Also downstream to chemistry, physics has developed a number of experimental tools, mainly in solution and films, which are now capable, thanks to advances in computerized laser instrumentation, of providing now an almost routine experimental feedback towards subsequent refinement of organic synthetic schemes.

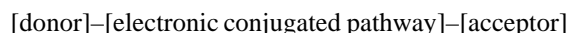
2.1. Optimization steps – a multifunctional approach

The engineering of molecular materials for quadratic nonlinear optics (NLO) can be decomposed into two distinct, although strongly interconnected steps. As the internal cohesion energy of individual molecular units surpasses by far that of intermolecular interactions energies (Van der Waals, dipole–dipole, hydrogen bonding) the first step consists in optimizing the quadratic hyperpolarizability tensor β of microscopic entities, whereas the subsequent one aims at the macroscopic organization of molecular units in a noncentrosymmetric material that sustains a sizeable macroscopic nonlinear susceptibility $\chi^{(2)}$ (the coefficient $d = \chi^{(2)}/2$ being more frequently cited in the literature). It is clear that a successful outcome for this second step is crucially conditioned by adequate functionalization at the molecular level, which must tend to favor an acentric packing (e.g. in single crystals) or improve the stability of the NLO

response at the material level (as in electrically poled electro-optic (EO) polymers). Such a ‘multifunctional’ character for NLO molecules is now becoming an essential requirement in order to find out the best trade-off between various, and sometimes contradictory demands. For example, even for EO applications in optical telecommunication systems, where the operating wavelength (1.55 μm) would seem to lie at a safely remote spectral distance from the absorption bands of the molecular electronic spectra, significant losses in this domain may arise either from the absorption tails of long wavelength ($\lambda_{\text{max}} > 800 \text{ nm}$) transitions (frequently associated with huge β values) or, more generally, from overtones of the infrared (IR) vibrational frequencies of typical chemical bonds (C–H, C–O or O–H). Another compromise has to be found between high β values, as typically met in polyene-like structures, and a good thermal stability at the poling temperature corresponding to the host matrix glass transition temperature T_g , an acceptable orientational stability of d values being usually ensured for T_g of the order of 200 °C. Therefore, more sophisticated synthetic strategies must be elaborated in order to design NLO molecules simultaneously fulfilling various requirements such as a high NLO response, excellent transparency in the near IR spectral range (typically $< 1 \text{ dB/cm}$ in guest–host polymer waveguide format), as well as satisfactory thermal and orientational stability.

2.2. NLO optimization: a first generation dipolar strategy

The rapid development of poled polymers for EO-related applications has widely stimulated the search for highly efficient molecular systems displaying a large molecular factor of merit $\mu \cdot \beta$, where μ , the ground-state dipole moment of the NLO molecule, ensures a strong orientation factor via dipolar coupling with the external poling field E_p . The vector part of the hyperpolarizability tensor at zero frequency $\beta(0)$ is directly related to the macroscopic EO coefficients of the poled polymer r_{33} and r_{13} . Starting from the classical scheme for a one-dimensional internal charge transfer molecule:



various optimization methods have been proposed: increase of the donor or acceptor strength, modification of the electronic structure of the conjugated path, or adequate combinations of the end donor or acceptor groups with the conjugated bridge (see Fig. 1). Special attention has been paid to the nature and length of the conjugated path. Polyene-like ‘push–pull’ molecules have been widely synthesized and characterized as model systems towards the maximization of quadratic [20–22] and cubic [23] hyperpolarizabilities and the investigation of possible ‘saturation’ of hyperpolarizabilities for large values of the number N of carbon–carbon double bonds [24]. Such a saturation effect is related, according to various theoretical models, to the bond length alternation (BLA) δ corresponding to the difference between the lengths of two adjacent carbon–carbon bonds in the polyenic path [25]. A saturation of the cubic hyperpolarizability γ has been demonstrated experimentally [24] for $N > 50$ in centrosymmetric polyene derivatives, but no push–pull equivalents could be synthesized and properly characterized to-date to show a similar behavior for the quadratic hyperpolarizability β . The nonresonant $\mu \cdot \beta(0)$ value of the ‘reference’ Disperse Red One (DR1) molecule is $500 \cdot 10^{-48} \text{ esu}$, a value that has been successfully challenged in the late 1990s, the currently highest NLO molecular factors of merit reaching $10\,000 \cdot 10^{-48}$ in the most favorable cases [26,27]. Some examples of some highly efficient molecules are provided in Fig. 1. The relevance of this almost exclusively dipolar, one-dimensional molecular engineering strategy has been confirmed by the demonstration of low-operating voltage polymer-based electro-optic devices, some of which being currently under way for industrial development [28].

2.3. NLO optimization: a second generation octupolar strategy

The hyperpolarizability β being a third-rank tensor, this limitation to 1D bipolar structures failed, until the early 1990s, to comprehend systematic engineering of the two- and three-dimensional architectures

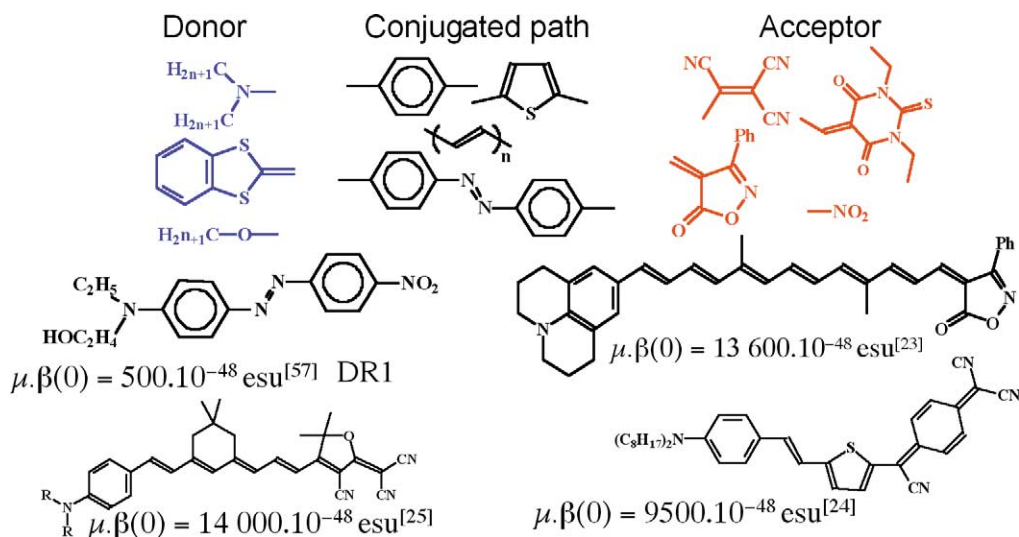


Figure 1. (Top) Various examples of donor or acceptor groups, together with currently used conjugations paths, for β optimization of dipolar intramolecular charge transfer molecules. (Bottom) Molecular factors of merit $\mu \cdot \beta(0)$ for some of the most efficient molecules reported to-date, as compared to the reference compound DR1.

Figure 1. (Haut) Exemples de substituants donneurs et accepteurs d'électrons, et de quelques chemins de conjugaison d'usage courant pour l'optimisation de l'hyperpolarisabilité β de molécules dipolaires à transfert de charge intramoléculaire. (Bas) Facteurs de mérite $\mu \cdot \beta(0)$ de quelques molécules choisies parmi les plus efficaces, comparés à celui de la molécule de référence, le DR1.

that are made available by organic and metallo–organic synthesis. In fact, molecular characterization techniques, as well as macroscopic organization schemes, were essentially focusing on one-dimensional orientation techniques based on the coupling between the ground state dipole moment μ of the molecule and an externally applied DC electric field E_P with $W = -\mu \cdot E_P$ as the coupling energy term. Such methods precluded any exploration of non-dipolar, albeit noncentrosymmetric molecules, and reduced in practice the exploitation of an otherwise potentially rich β -tensor to a single Cartesian component. Such exclusive focusing of molecular engineering research on dipolar systems was clearly biased by the symmetry bottleneck imposed by electric-field poling techniques, such as in solution (EFISH) towards molecular property screening as well as electrooptic polymers for devices.

A first detrimental confusion which might account for the relatively late recognition of multipolar, eventually non-dipolar systems, may have resulted from a widespread and abusive identification of noncentrosymmetry with polarity. Indeed, whereas all polar systems are by nature noncentrosymmetric, the reverse is not true because acentric generic systems like planar threefold symmetry systems or cubic-tetrahedra abiding to the $\bar{4}3m$ zinc-blende-type point group symmetry are deprived of dipoles. A subtler, although no less pervading, misleading confusion, as will be shown later, has to do with an identification between dipolar and rod-like systems (the latter defined by the existence of a single coefficient along the rod axis for tensorial properties).

In the early 1990s, the experimental evidence of frequency doubling in the 1,3,5-trinitro-2,4,6-triaminobenzene (TATB) crystal [29] based on the simplest octupolar extension of paranitroaniline, has triggered the opening of a broader molecular engineering avenue, whereby symmetry-ensured cancellation of the molecular dipole moment is shown to be compatible with non-zero and sometimes significantly larger β -tensor coefficients than for purely dipolar systems. In this perspective, the multipole concept has been introduced for the design of more isotropic NLO chromophores where the tensorial nature of β can be fully deployed. Indeed, the investigation of 2D and 3D hyperpolarizabilities cannot be understood when limiting

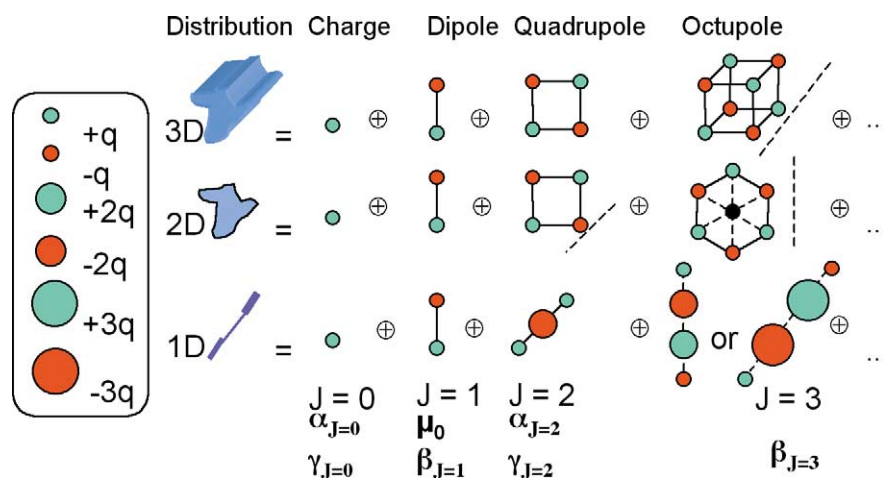


Figure 2. One-, two- and three-dimensional charge distributions for dipolar, quadrupolar and octupolar systems.

Figure 2. Distributions uni-, bi- et tridimensionnelles de systèmes dipolaires, quadrupolaires et octupolaires.

the β tensor to its purely dipolar part. In the absence of resonances, the hyperpolarizability tensor can be decomposed into dipolar ($\beta_{J=1}$) and octupolar ($\beta_{J=3}$) spherical components:

$$\beta = \beta_{J=1} \oplus \beta_{J=3}. \quad (1)$$

A more general expression for Eq. (1) would entail the more exotic $J = 0$ and $J = 2$ axial contributions, which come into play in the case of resonant configurations when Kleinman relations are no more valid [30]. For the sake of basic molecular engineering consideration in off-resonant configurations, it suffices to consider here odd terms.

In this generalized molecular engineering scheme, earlier 1D systems can thus be embedded in the broader realm of multipolar systems whereby the quadratic nonlinearity of any molecule can be decomposed in rotationally invariant dipolar and octupolar components. Full exploitation of the tensorial character of β has thus permitted to the enlargement of the pool of candidate molecular structures to more isotropic 2D and 3D multipolar systems [4,5], whereas a n -level model (with $n > 2$) has been shown to adequately describe the frequency dispersion of multipolar β tensors [31–33]. At a structural level, it can be shown that the most generic template for 3D octupolar molecules is amenable to a cube with alternating charges at the edges [4,5] such as accounting for donor and acceptor substituents. 2D octupolar and 1D dipolar distributions can be inferred from this general scheme by projection along the 3-fold axis of the cube on a plane perpendicular to such axis, as well as on this 3-fold axis parallel to its orthogonal plane, as illustrated on Fig. 2. It is noteworthy that this apparently ‘cubic’ template is robust with respect to regular deformations such as would lead to a parallelogram abiding to the 222 point group symmetry [34].

The implementation in real structures of the basic cubic point charge template has followed so far two main avenues in the realm of 2D structures:

- a central π -electron reservoir mediating intramolecular charge transfer (ICT) interactions between peripheral electro-active side groups (Fig. 3a). Examples are 1,3,5 benzene [35,36] or triazine derivatives [37,38];
- a donor (acceptor) atom occupying a central position at the cornerstone of the molecular structure mediating a multipolar ICT interaction with three accepting (donating) groups through a conjugated system (Fig. 3b). Typical systems are Crystal Violet [39], oligothiophenyl analogues [40], or ruthenium^{II} (2,2′bipyridine)₃ complexes [41], or subphthalocyanines [42]. The propeller shape of such systems as the

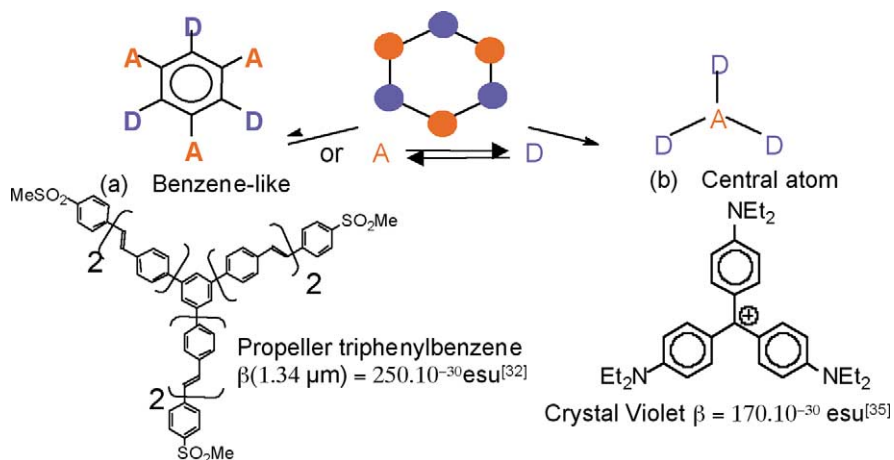


Figure 3. Benzene-like (left) and central atom (right) strategy for 2D octupolar engineering.

Figure 3. Deux stratégies d'ingénierie octupolaire 2D : dérivés du benzène (à gauche) et atome central (à droite).

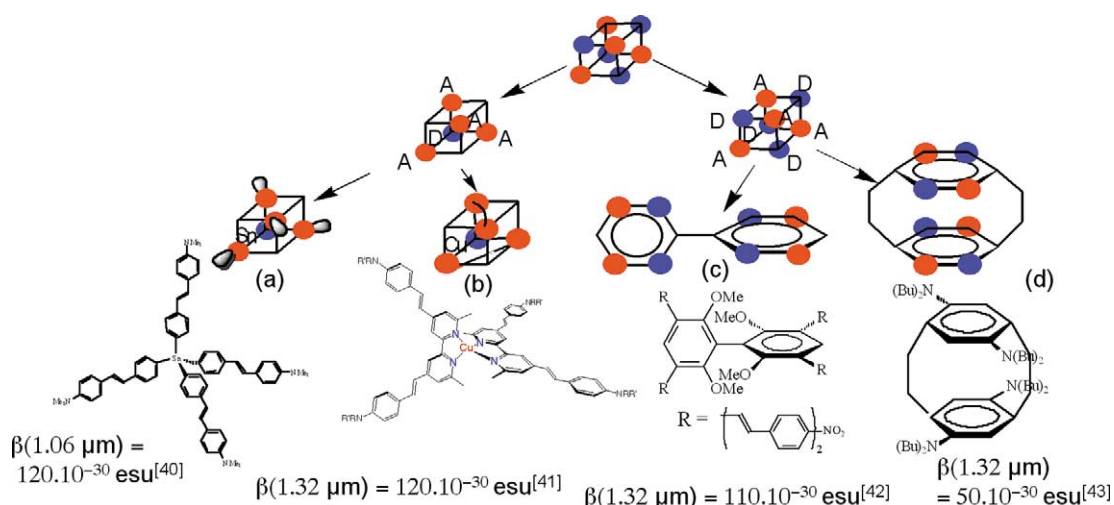


Figure 4. 3D octupolar engineering schemes as derived from the cubic octupolar template. (a) Covalent tetrahedral Sn derivative. (b) Tetrahedral metal complex. (c) Substituted biphenyl derivative. (d) Paracyclophane derivative.

Figure 4. Schémas d'ingénierie moléculaire octupolaire 3D dérivés du modèle du cube : (a) dérivé tétraédrique covalent ; (b) complexe métallique tétraédrique ; (c) dérivés du biphenyle ; (d) paracyclophanes.

bipyridine complexes provide room for chirality which starts to be revealed by sophisticated nonlinear dichroism experiments [43].

Design of efficient 3D structures is mainly illustrated by metal complexes. The structures allow for rich 3D hybridization schemes, and provide appealing possibilities for the octupolar engineering of 3D molecules, in view of their potentially available symmetry features, metal core oxidation potential, open-shell electronic structures, as well the existence of built-in chirality features. Tetrahedral covalent bonding or complexation, as derived from the very general 3D cubic octupolar scheme made of two intricate donor or acceptor tetrahedral substructures mirroring each other results in efficient T_d octupolar systems such as tetrasubstituted tin derivatives [44] (Fig. 4(a)), or tetrahedral copper bipyridine complexes (Fig. 4(b)) [45].

Purely organic alternatives such as based on functionalized biphenyls [46] (Fig. 4(c)) or paracyclophane derivatives (Fig. 4(d)) [47] also exhibit large octupolar β values, with the clear evidence, in the case of paracyclophane derivatives, of a strong ‘through-space’ multidimensional charge transfer between the upper and lower ring of the pCP moiety.

3. Modelization of molecular NLO properties

Modeling the nonlinear polarization properties of multipolar systems based on quantum mechanical approaches provides interesting insights into the underlying excited states, transparency, polarized charge redistribution and β magnitudes. Regardless of the actual approximation level of quantum mechanical descriptions of octupolar systems, the two-level quantum model proposed for 1D intramolecular charge transfer molecules is clearly grossly inadequate to depict octupoles, owing to the cancellation of all vectorial quantities including in particular $\Delta\mu$, the difference between excited- and ground-state dipole moments.

3.1. The valence bond charge transfer model

In order to provide simple pictures for the structure-NLO-property relationships of various multipolar molecules, the valence-bond (VB) charge-transfer (CT) models have been extensively studied. The VB and CT states corresponding to 1D dipoles [48], 1D linear quadrupoles [49], 2D planar octupoles [50], and 3D tetrahedral octupoles are depicted in Fig. 5. The four-state model (Fig. 5(c)) consisting of a single valence-bond (VB) configuration and three charge-transfer (CT) configurations describes two-dimensional octupolar molecules [51,52], whereas a five-state model is needed to tetrahedral, three-dimensional species [33].

As can be seen in Fig. 5, a single valence-bond (neutral) configuration and four charge-transfer (zwitterionic) configurations are considered to be the minimal set of basis functions required for the description of the electronic structure of a given tetrahedral donor–acceptor molecule. Referring to the

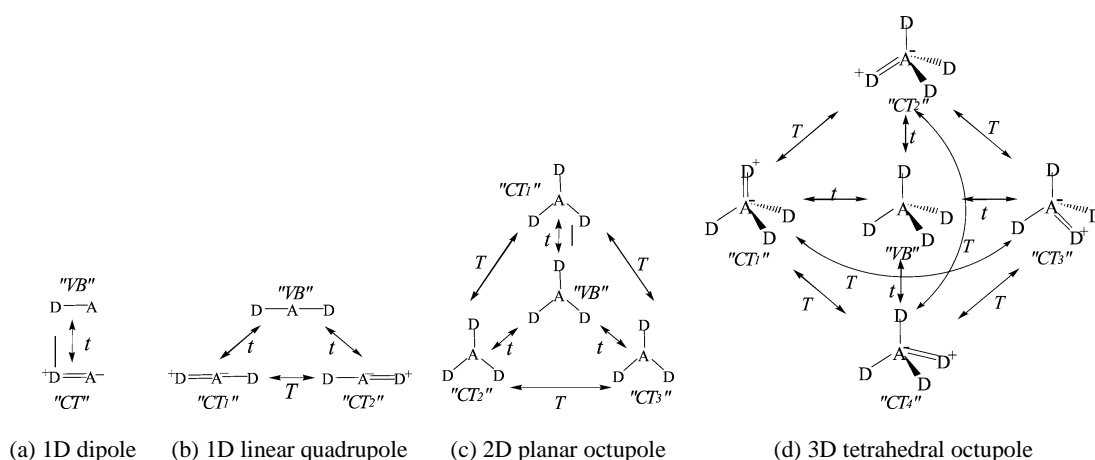


Figure 5. The coupling schemes for various VB-CT models. (a) The two-state model for the 1D dipole molecules such as push–pull polyenes. (b) The three-state model for the linear quadrupole molecules with centrosymmetry. (c) The four-state model for the planar octupolar molecules, e.g., Crystal Violet. (d) The five-state model for the tetrahedral octupolar molecules considered in this paper.

Figure 5. Schémas de couplage pour divers modèles VB-CT. (a) Modèle à 2 niveaux pour les molécules dipolaires 1D telles que des polyènes donneur-accepteur. (b) Modèle à 3 niveaux pour les molécules quadrupolaires centrosymétriques. (c) Modèle à 4 niveaux pour les molécules octupolaires planes telles que le cristal violet. (d) Modèle à 5 niveaux pour les molécules octupolaires tétraédriques 3D.

corresponding wave functions as $|VB\rangle$ and $|CT_j\rangle$ (with $j = 1-4$), respectively, one can construct an electronic Hamiltonian with the following matrix form:

$$H = \begin{pmatrix} E_{VB} & -t & -t & -t & -t \\ -t & E_{CT} & -T & -T & -T \\ -t & -T & E_{CT} & -T & -T \\ -t & -T & -T & E_{CT} & -T \\ -t & -T & -T & -T & E_{CT} \end{pmatrix}, \quad (2)$$

where the electronic energies of VB and CT configurations are denoted as E_{VB} and E_{CT} , respectively. There exist two transfer integrals, t and T , where the former represents a charge-transfer coupling between the VB configuration and one of the CT configurations and the latter couples any pair of CT configurations. From the inspection of eigenvalues of this Hamiltonian, the excited-state spectrum appears to be spanned by a 3-fold degenerate excited and a non-degenerate excited state. The existence of the 3-fold degenerate excited state can be easily inferred by group theoretical considerations, and it is a straightforward exercise to generalize this result by introducing the four bond-length-alternation coordinates of each branch (see [51,52] for detailed discussion on the extension of the VB-4CT model by including four BLA coordinates).

In the case of the linear push-pull polyene, the BLA varies from -0.12 to 0.12 Å. In contrast, for the tetrahedral donor-acceptor molecules with polyene bridges it is found here that the allowed range of BLA is from -0.12 to -0.06 Å. The range of BLA values allowed for the tetrahedral donor-acceptor molecules is rather small in comparison to that of the *linear* (dipolar) donor-acceptor molecules. Perhaps, this is why the NLO properties of the tetrahedral donor-acceptor molecules show monotonic behavior contrary to those of the linear push-pull polyenes.

It turns out that for tetrahedral 3D molecules as well as for planar C_3 octupolar compounds, β is a monotonically increasing function with respect to the extent of the charge-transfer character in the ground electronic state, as confirmed by ab-initio calculations. The bond-length-alternation coordinate can be used to represent the extent of the CT character. This investigation provides guidelines towards a design strategy for tetrahedral donor-acceptor molecules with large NLO properties; in particular, the ‘spreading’ of the electron delocalization over 3 or 4 conjugated branches for 2D or 3D molecules may offer specific advantages as it probably shifts away towards large values of conjugated double bonds, the saturation phenomena predicted for quadratic and cubic hyperpolarizabilities in the case of 1D polyene-like molecules.

3.2. Equivalent internal potential modeling of multipolar nonlinearities in conjugated molecules

One important earlier traditional model for second-order polarizabilities β is being referred to as the ‘Equivalent Internal Field’, and is able to account for the emergence of a dominant β_{xxx} coefficient for singly substituted aromatic rings. The core of the approximation consists in replacing the action of the substituent on the ring by an internal field which is responsible for polarizing the π -electron system in conjunction with the externally applied field [53]. Identification of the two equivalent systems, namely the actual substituted species and the benzene ring embedded in the equivalent internal field provides the following linear relationship:

$$\beta_{xxx} = 3(\gamma_{xxx}^\circ/\alpha_{xx}^\circ)\Delta\mu_x^\circ \quad (3)$$

where γ_{xxx}° and α_{xx}° stand for the cubic and linear polarizability tensor coefficients of the unsubstituted backbone, with $\Delta\mu_x^\circ$ as the π -electron dipole of the substituted molecule.

An obvious shortcoming of this model is its limitation to dipolar systems, as it is impossible to account for an octupolar molecule by a vector-like perturbation in the form of an equivalent internal field. This has led to the generalization of the equivalent internal field into an equivalent internal potential entailed with full-fledged tensorial features capable of adjusting to any substitution pattern including an octupolar one. This model has been applied to two-dimensional octupolar chromophores [54], the equivalent effective

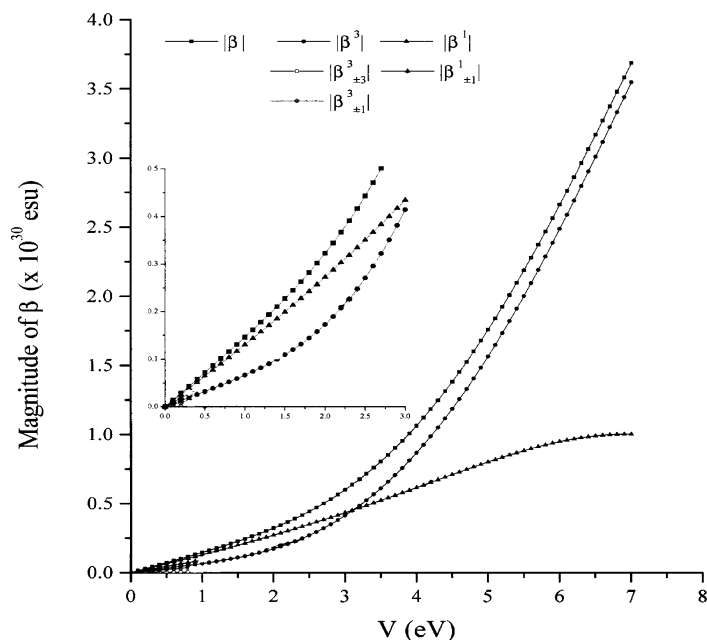


Figure 6. Dependence of dipolar (triangles), octupolar (circles) and total (squares) β values as a function of the internal potential. Insert: internal field dependence of β for weak V values.

Figure 6. Variation des valeurs de β dipolaires (triangles), octupolaires (cercles) et totales (carrés) avec le potentiel interne V . Les courbes insérées indiquent le comportement de β pour de faibles valeurs de V .

electrostatic potential function, associated to a given arbitrary substitution pattern and its subsequent expansion in terms of spherical harmonics, entailing the well-known advantages of rotational invariance based on tensorial group representation.

The internal potential for the benzene skeleton can be represented by its value at each of the six carbon atoms arranged in the following vector form:

$$\mathbf{V} = (V_1^{\text{int}}, V_2^{\text{int}}, V_3^{\text{int}}, V_4^{\text{int}}, V_5^{\text{nt}}, V_6^{\text{nt}})$$

where V_i^{nt} is the value of the potential at the i th site. The β tensor can then be expressed in the following condensed form:

$$\bar{\beta} = \beta + \mathbf{L}\mathbf{V} \quad \text{where } [\mathbf{L}] = \left. \frac{\partial \beta}{\partial V} \right|_{V=0}. \quad (4)$$

Eq. (4) provides a linear relationship between the susceptibility of the system and the internal potential. The linear response matrix \mathbf{L} is a function only of the skeleton and completely specifies the linear response of the molecule. Quantum chemistry (at Hückel, PPP and INDO levels of approximation) was used to calculate \mathbf{L} .

By applying internal potentials of increasing magnitude to the benzene skeleton, it is possible to determine the point at which NLO effects become important beyond the linear expression (4), as illustrated in Fig. 6. The hyperpolarizability β is found to be linearly related to the internal potential provided the potential difference between carbon atoms is below 2 eV. The linear regime is found for donor or moderate electron acceptor substituents; for strong acceptors such as NO_2 and CN , strong effects from nonlinear coupling are predicted.

4. Instrumentation techniques for molecular engineering

We describe now, downstream to synthesis, the various experiments capable of providing evidence for nonlinear optical activity, a crucial step in the molecular optimization process.

4.1. Electric field induced second harmonic generation

Most β measurements reported in the literature are performed in a few organic solvents (chloroform, acetone, methanol, less usually DMF or DMSO) combining good solubility of the nonlinear chromophores with low dipole moments and dielectric constants. As far as dipolar molecules are concerned, the Electric-Field-Induced Second Harmonic Generation (EFISH) experiment [55] has been considered as the most suitable technique since the early 1970s. NLO dipolar molecules are oriented in solution using a DC electric field E° (or, more precisely, a pulsed field with adjustable μ s to ms time-plateau in synchronism with the fundamental laser pulse). The resulting quadratic susceptibility takes the following form $\chi^{(2)} = NF\gamma E^\circ$ where

$$\gamma = \gamma_e + \mu \cdot \beta / 5kT \quad (5)$$

where N is the number of molecules per volume unit, F is a local field factor, μ the ground state dipole moment of the molecule, γ is the global EFISH hyperpolarizability, i.e. the sum of a purely electronic cubic contribution γ_e and a quadratic, orientational one $\mu \cdot \beta / 5kT$. If the direction of the μ vector coincides with the z axis of the molecule, then $\beta = \beta_{\text{EFISH}} = \beta_{zzz} + \beta_{zxx} + \beta_{zyy}$, where (x, y, z) are the Cartesian axes of the molecule. In most chromophores investigated in this field, the cubic term can be reasonably neglected with respect to the quadratic one. The coherently emitted second harmonic signal from the oriented solution is proportional to $N^2 \langle \beta \rangle^2 \sin^2 l / l_c$ where l is the optical pathway through the solution and l_c the coherence length of the second harmonic generation process. The $\mu\beta$ value of the investigated chromophore can then be inferred from the amplitude and period of the resulting so-called ‘Maker Fringes’. In Fig. 7 the EFISH measurement cell is sketched, together with an example of a SHG signal plotted as a function of the sample thickness.

As the EFISH experiment is based on *coherent* second harmonic generation, the resulting SHG signals are usually easily detectable; fundamental wavelengths as long as 1.91 μm (as generated from an Hydrogen Raman shifting cell pumped at 1.06 μm) can be used, then allowing for reliable results even for molecules that display a wide and red-shifted electronic absorption spectrum in the visible range. However, the $C_{\infty v}$ symmetry of the cylindrically poled fluid medium gives access to the $\mu \cdot \beta_{J=1}$ scalar quantity only, the octupolar tensor component being geometrically ruled-out from such a vectorial configuration.

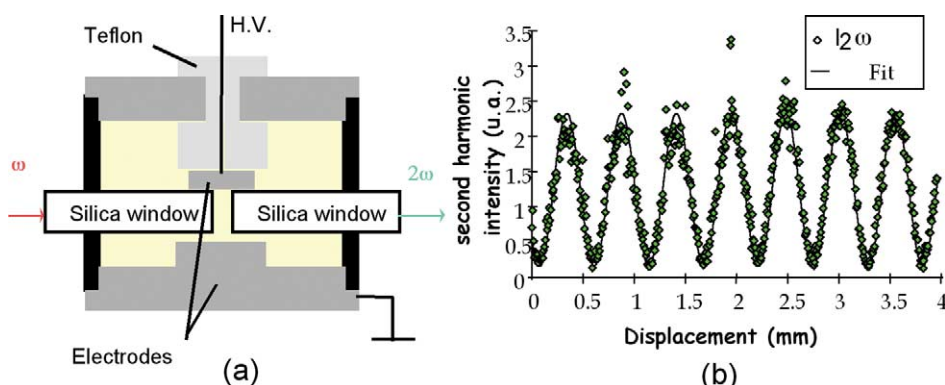


Figure 7. (a) Design of the EFISH measurement cell; (b) plot of the SHG signal from the EFISH cell as a function of the cell displacement.

Figure 7. (a) Schéma de la cellule de mesure EFISH. (b) Variation du signal de second harmonique d’une solution sous champ électrique avec l’épaisseur traversée l .

4.2. Harmonic light scattering

Harmonic Light Scattering (HLS) (or sometimes also called ‘Hyper-Rayleigh Scattering’) experiment had been demonstrated at the very beginning of nonlinear optics [56], but had been somehow superseded by EFISH in view of the dominance of the bipolar scheme. It has been revived in the current context to provide adequate and relatively easy measurements techniques of octupolar β 's. Noncoherent HLS experiments performed in centrosymmetric solutions indeed allow one to retrieve some basic tensorial features of the β tensor for multipolar molecules of interest. The nonlinear effect in HLS originates from orientational fluctuations of the scattering centers, leading to a NLO response proportional to the orientationally averaged $\langle \beta \otimes \beta \rangle$ quantity. Different polarization configurations of the fundamental and harmonic waves are used to evaluate the $\langle \beta \otimes \beta \rangle_{IJKLMNOP}$ macroscopic components which subsequently permit to retrieve the norms of the dipolar and octupolar parts of the β tensor in non-resonant conditions. The experimental set-up, derived from that initially proposed by Terhune and Maker, is sketched on Fig. 8, and has been adapted for polarization dependent measurements. In this configuration, complete determination of $\|\beta_{J=1}\|$ and $\|\beta_{J=3}\|$ requires two steps [7,18]: at first, the global $\langle \beta \otimes \beta \rangle = \langle \beta_{ZZX}^2 \rangle + \langle \beta_{XXZ}^2 \rangle$ is inferred from the slope of the scattered second harmonic light plotted as a function of a ‘reference’ SHG signal (emitted by a frequency doubling powder like NPP, for example). In a second step, performed at a fixed incident intensity, the SHG scattered signal is plotted as a function of the incident polarization angle φ . The collected SHG intensity $I^{2\omega}$ is then related to φ according to

$$I^{2\omega} = \{ \langle \beta_{ZZX}^2 \rangle + \langle \beta_{XXZ}^2 \rangle \} \cos^2 \varphi + 2 \langle \beta_{ZZX}^2 \rangle \sin^2 \varphi, \quad (6)$$

the depolarization ration $D = \langle \beta_{ZZX}^2 \rangle / \langle \beta_{XXZ}^2 \rangle$ can be easily inferred from experimental data collected in both steps. As

$$\langle \beta^2 \rangle = \frac{2}{9} \|\beta_{J=1}\|^2 + \frac{2}{21} \|\beta_{J=3}\|^2 \quad \text{and} \quad (7)$$

$$D = \frac{1}{9} \frac{7 + 12\rho^2}{7 + 2\rho^2} \quad (8)$$

where $\rho = \|\beta_{J=3}\| / \|\beta_{J=1}\|$ is being defined as the nonlinear anisotropy ratio.

Determination of $\|\beta_{J=1}\|$ and $\|\beta_{J=3}\|$ can then be completed on the basis of the above expressions.

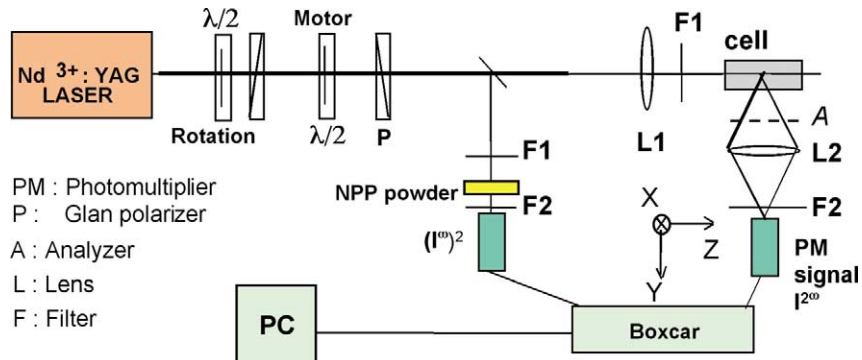


Figure 8. Experimental set-up for HLS measurements. NPP (N-4-nitrophenyl-L-prolinol) is used as a frequency doubling crystalline powder material for the SHG reference path.

Figure 8. Montage expérimental de l'expérience de diffusion harmonique de la lumière. Une poudre de NPP (N-4-nitrophényle-(L)-prolinol) est utilisée comme matériau doubleur de fréquence sur la voie de référence.

5. Molecular materials: from electric to all-optical poling

The next step on the way to usable materials for device applications addresses the target of adequate organization of molecular species so as to promote their nonlinear response from the molecular to the macroscopic material level. Whereas linear and cubic nonlinear properties, expressed respectively by such optical properties as birefringence and intensity-dependent refractive index, are not constrained by any special symmetry requirement, three-wave mixing tensors, being of odd-rank, require the breaking of centrosymmetry, at least under reasonably well-behaved situations such as coherent interactions and field amplitude variations adhering to the slowly varying envelope approximation. Such a constraint can be met by a crystalline engineering approach which was implemented in the 1980s [57,58] and bears fruit to this day with record high nonlinearities in such crystals as DAST [59] and applications ranging from optical parametric amplification [60] to electrooptic modulation [61] and THz generation [62].

Another approach, of statistical nature, as opposed to the deterministic periodic pattern of crystals, relies on externally assisted schemes to imprint some degree of order onto the initially isotropic orientational distribution function of guest–host polymers. This approach entails the bonus of a predictable symmetry for the engineered material which is bound to express the symmetry of the perturbation as a result of the Curie symmetry principle. There again, poling methods can be broken down in two major avenues. The first one, following Langevin and Benoit [63], relies on the electric field coupling and is thus well fit to the linear and nonlinear dipolar features of molecular bipolar diodes while its principle basically derives from that of EFISH measurements in solution [64]. However, its basically vectorial nature fails to meet the octupolar symmetry requirement which is a prerequisite to promote an octupolar order from molecule to material. As we shall see, this is obtained precisely by applying an external optical perturbation with built-in and adjustable octupolar (partial or total) symmetry features. The latter domain, known as optical poling, belongs to the more general class of Coherent Control [65] of which it is a particularly original and efficient illustration.

5.1. Acentric ordering of dipolar molecules

5.1.1. Crystalline engineering of dipolar species: outcomes and limitations

The search for ‘optimized’ dipolar-like crystalline materials has stimulated a number of crystalline engineering schemes. As dipolar molecules tend to pack in an antiparallel crystalline geometry, corresponding to the interaction energy minimum of an ensemble of polar species, various strategies have been proposed, especially in the early 1980s, involving additional intermolecular interactions so as to be able to eventually counteract such dipole-induced ‘head-to-tail’ ordering. Early attempts to ensure acentric crystalline packing were based on the introduction of chiral units made of σ -type asymmetric carbons attached to the NLO molecular backbone through a single bond; in spite of some successful attempts as illustrated, for example, with methyl[2,4-dinitrophenylamino]propanoate (MAP) [66], such configurations cannot generally avoid antiparallel coupling of NLO π moieties of neighbouring molecules, whereas the chiral σ group may form a noncentrosymmetric sublattice, however of no relevance towards the promotion of nonlinear optical properties. Another strategy, based on the cancellation of the ground state dipole, has led to the elaboration of 3-methyl-4-nitropyridine-1-oxide (POM) single crystals [8]. Introduction of hydrogen bonds may also favor acentric packing as the corresponding interaction energy usually dominates over dipole–dipole interaction; the huge NLO response of the N-4-nitrophenyl(L)prolinol (NPP) crystal [67] (up to 80 pm/V in the near IR) and its ability to exhibit low-threshold Optical Parametric Oscillation (OPO) in a pulsed nanosecond regime [60] (the first near-IR OPO set-up working with a purely organic crystal) confirms the relevance of this crystalline engineering approach for dipolar structures.

In spite of these highly successful outcomes, the crystalline engineering strategy is far from being fully predictable and the investigation of novel, highly efficient materials largely depends on serendipity-based findings. Moreover, the integration of single crystalline structures, even in a thin film configuration, into an optoelectronic chip is highly problematic. An interesting compromise which combines the technological

assets of polymer films with the order and density of crystals has been proposed by Ibanez et al. [68]. It consists in growing nanosized single crystals of controlled dimension (this can be nicely ensured, as shown in the work by Ibanez, by adjustment of the solvent evaporation rate by way of the rotation speed in spin coating deposition) in a polymer thin film. The nonlinear nanocrystallites are then oriented by application of an electric or magnetic field (see article by Ibanez et al. [69] in this issue).

It has also been proposed to benefit from the superior robustness of mineral crystals by anchoring highly nonlinear chromophores to polyanionic lattices such as phosphates or arseniates. This has led to an interesting still ongoing avenue with the demonstration of near IR low threshold parametric emission [70] and oscillation [71] in 2-amino-5-nitropyridine-dihydrogenophosphate (2A5NPDP) crystals. At the present stage, molecular NLO devices for optical signal processing are made of polymers containing nonlinear dipolar chromophores.

5.1.2. Electric-field poled dipolar-like polymers: optimization steps towards EO polymer-based devices

5.1.2.1. From hyperpolarizability to macroscopic NLO properties

As already pointed-out, any bulk material composed of NLO molecules must lack an inversion center in order to display a macroscopic susceptibility $\chi^{(2)}$. Organic compounds offer a wide choice of macroscopic organization modes, ranging from perfectly ordered crystals to fully disordered amorphous polymers, with various intermediate states such as liquid crystals or self-oriented multilayers. In the following, we will concentrate on amorphous structures, as the use of polymer matrices containing highly NLO molecules present specific advantages, such as the availability of low-cost, large surface deposition technologies, possibility of hybrid integration with other optical and electronic devices and low dielectric constants towards high speed operation. Polymers can be spin-coated on various types of substrates: just after deposition, the material is still centrosymmetric and deprived of any odd-rank tensorial property such as a second order nonlinearity. Therefore, in order to induce noncentrosymmetry and endow the polymer with EO or second harmonic generation activity, an adequate poling procedure needs to be further carried-out. The most widely used poling technique consists in heating the polymer close to its glass-transition temperature T_g , in order to increase molecular mobility of the guest nonlinear chromophores, while a DC electric field is applied so as to orient the molecular dipoles along the field direction. Cooling down to room temperature while maintaining the field will then allow the freezing-in of the polar orientation. Further chemical efforts, to be described in the following, are of course needed to maintain such freezing of the dipoles in the longer term (up to years) to satisfy application requirements. The induced quadratic susceptibility is given by

$$\chi_{333}^{(2)} = NF \frac{\mu \cdot \beta_{\text{EFISH}}}{5kT} \quad (9)$$

where N is the number of molecules per volume unit, and F is a local field factor. This expression is valid only in the case of ‘weak’ poling fields, i.e. when the coupling energy $\mu \cdot E$ remains small with respect to the thermal energy kT . Note that, owing to $C_{\infty v}$ cylindrical symmetry, $\chi_{333}^{(2)}$ is related to the other component of the $\chi^{(2)}$ tensor $\chi_{311}^{(2)}$ by the relation $\chi_{333}^{(2)} = 3\chi_{311}^{(2)}$. A strong anisotropy results from this ratio in the quadratic NLO response of the electric-field oriented polymers, thus precluding, as such, polarization-independent response of an electro-optic polymeric material in the case of a ‘weak’ DC poling field. We shall see in Part III how to adapt this technique precisely to ensure polarization independence (this is discussed also in more details in this issue in the article by P. Labbé et al. [72]).

A simple calculation of $\chi^{(2)}$ as derived from Eq. (9), using highly nonlinear dipolar chromophores like those exemplified in Fig. 1, should yield to very high values (more than 100 pm/V for both $\chi_{333}^{(2)}$ and the corresponding electro-optic coefficient r_{333} in the near IR) for reasonable dye concentrations in polymeric matrices (typically $4 \cdot 10^{20}$ molecules per cm^3) and realistic poling field values of the order of a few hundreds of volts per μm . However, even for low N values (e.g. less than 10^{20} molecules per cm^3) experimental $\chi^{(2)}$ and r values clearly and unfavorably depart from the oversimplified description, whereby NLO molecules

are assumed to behave as purely independent particles during and after the poling process. In fact, plots of electro-optic coefficient *versus* chromophore number density frequently exhibit maxima that usually shift to lower concentrations as the dipole moment and the polarizability of the NLO molecule increase. Models based on electrostatic interactions have pointed-out the possible influence of the molecular shape on the $\chi^{(2)}$ value of electric-field poled polymers [73]; in practice, functionalization of NLO chromophores with bulky, electronically inactive sidegroups has led to the elaboration of highly electro-optic polymers, with r_{333} values reaching more than 120 pm/V at 1.06 μm [74].

5.1.2.2. Optical propagation losses

Reducing optical losses around 1.55 μm is also a crucial challenge to qualify polymer-based devices as competitors to lithium niobate modulators. Losses may originate either from absorption of light or from light scattering due to refractive index inhomogeneities or to defects at the core-cladding interface of the waveguide. Absorption losses may arise either from the absorption tail of the electronic absorption if the corresponding maximum absorption wavelength is strongly red-shifted, or from absorption associated with overtones of C–H vibrations. The latter can be in principle reduced by fluorination, at the heavy cost of additional or exotic synthetic strategies and possible changes of the NLO response of the chromophores dyes due to the electron-attracting character of the fluorine atom. A partial replacement of C–H by C–F bonds, at least on the polymeric backbone itself, yields to an improved IR transparency, losses being then reduced to 1 dB/cm or less. Losses originating from the electronic absorption tail can be more easily avoided by maintaining a large spectral offset between λ_{max} and the operating wavelength. Typically, λ_{max} should not exceed 700 nm for operation wavelength around 1.55 μm .

5.1.2.3. Orientational stability

Device operation demands both long-term (mainly orientational) stability of the electro-optic response at the operating temperatures (up to 85 °C) as well as short term (thermal) stability at poling temperatures (above 200 °C). The latter requirement is now currently met using some specific stabilizing groups such as thiophene units, diphenyl amino donor groups or planarized conjugated paths, as exemplified in Fig. 1. The former can be met by following two strategies.

The first one is based on the simple preparation of doped polymers with a host matrix, such as polyimide, exhibiting a high glass transition temperature T_g . The thermal stability of the NLO response may be then correlated with the difference between the operating temperature and the T_g of the doped polymer. Although this strategy is the most convenient one, as it does not require any further synthetic modification of the NLO chromophore, it presents several drawbacks such as a lower value of maximum achievable dye loading, possible sublimation of chromophores during the electric field poling step, poor solubility of polyimides in traditional spin casting solvents, and a significant short-term relaxation of some of the chromophores after electric-field poling.

The second strategy consists in grafting chromophores to the polymer backbone, either after or before polymerization (in the latter case monomers functionalized with the NLO dye have to be synthesized first, the final material being prepared by copolymerization with normal monomer units). The orientational stability of the material can be further improved by using thermally-induced polymer cross-linking where additional anchoring sites of the chromophore onto the matrix are induced upon heating during the poling process itself. An optimized poling procedure must be found, as the increase in temperature may further activate the cross-linking process which then becomes progressively detrimental to chromophore orientation [75]. Various examples of cross-linked materials, based either on organic polymer synthesis or on hybrid sol-gel materials have been reported in the literature. Highly stable cross-linked EO materials derived from polyurethanes display remarkably constant drive voltage in EO modulators over a few years of operation at room temperature. Upon heating, the NLO response remains constant up to disorientation temperatures close to 200 °C in some cross-linked DR1-polyimide materials. More recently, a high orientational stability has been demonstrated in cross-linkable NLO dendrimers, combining high EO coefficients (up to 60 pm/V at 1.55 μm), perfect stability of the NLO response at 85 °C, high T_g (380 °C)

and low propagation losses (0.25 dB/cm at 1.55 μm) due to the partial replacement of the C–H bonds of the matrix by C–F links [76].

5.2. Acentric organization of octupolar molecules

Very much as in the earlier case of dipolar systems, the challenge standing now at the forefront of research in octupolar material design is to engineer adequate macroscopic organization of octupolar units. A major bottleneck which severely constrains advances precisely originates from the lack of dipole moment, which precludes, in particular, the use of electric-field poling techniques in guest-host polymer systems. Therefore, the concepts and methods developed so far in the context of dipolar material engineering must be revisited for crystals and for NLO polymers as well.

5.2.1. Octupolar crystalline engineering

As far as two-dimensional molecules are concerned, the engineering challenge at the supramolecular level amounts to steering the structure of a trigonal molecule appropriately substituted by alternate donor (D) and acceptor (A) groups towards a trigonal, noncentrosymmetric network. Such an organization results from the directionality of specific dominant intermolecular interactions taking place either between ‘unlike’ groups (D–A interactions) in the molecular skeleton, or between ‘like’ groups (D–D or A–A interactions) (see Fig. 9(a)). The ‘like’ interactions in Fig. 9(a) will favor a detrimental centrosymmetric structure whereas the ‘unlike’ ones will lead to the desired 2D planar octupolar pattern. As recognized in the earlier proposition of octupolar crystals [29], the final structure then results from the balance between these two kinds of interactions which can be tuned by adjusting structural parameters related to the onset of an hydrogen-bonding network (for example, by replacing hydrogen-bonding subunits such as protonated groups by their aliphatic equivalent). The main task in crystal engineering lies in identifying the complementary elements and, therefore, in designing a molecule that exhibits these elements at appropriate sites. This strategy has been widely developed using triazine derivatives where ‘in-plane’ cohesion is

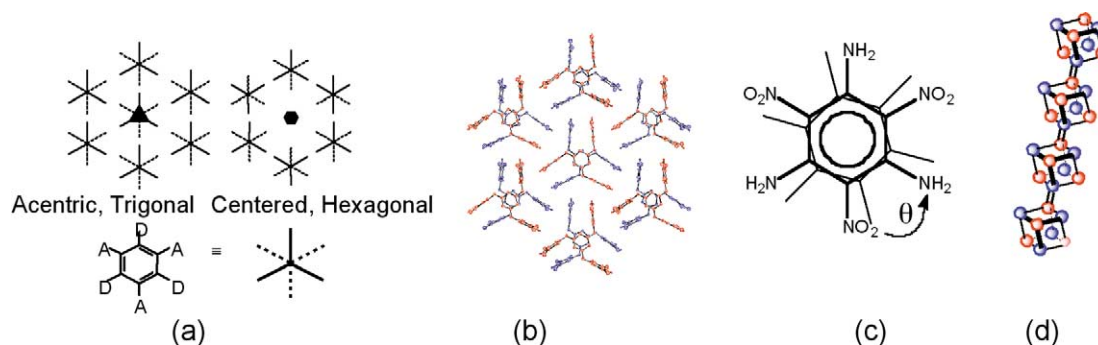


Figure 9. (a) Noncentrosymmetric trigonal lattice (left) induced by in-plane preferential interactions between donor and acceptor groups, as compared to a centrosymmetric hexagonal pattern resulting from attraction between identical substituents. (b) Trigonal structure induced by steric constraints in triaryloxy substituted 1,3,5 triazine dimers.

(c) Simplified top view of a pair of TATB molecules, evidencing an optimal acentric packing when $\theta = 0, 2\pi/3$ or $4\pi/3$; (d) 3D generalization of the TATB scheme by way of an helicoidal hypercubic arrangement of 3D octupoles.

Figure 9. (a) Réseau trigonal non centrosymétrique (à gauche) induit par des interaction préférentielles dans le plan entre groupements donneurs et accepteurs d'électrons, comparé à une architecture hexagonale centrosymétrique résultant de l'attraction entre substituants identiques. (b) Structure trigonale induite par des contraintes stériques dans des dimères de 1,3,5-triazine substitués en 2,4,6 par des groupements triaryloxy. (c) Vue de dessus simplifiée d'un ensemble de deux molécules de TATB, mettant en évidence une organisation non centrée optimale pour $\theta = 0, 2\pi/3$ ou $4\pi/3$. (d) Généralisation tridimensionnelle du schéma du TATB via un arrangement hélicoïdal « hypercubique » d'octupôles 3D.

ensured either by involving H-bonding between unlike groups, as illustrated by trinitro-triaminobenzene TATB [29], or by space filling processes using triaryloxy substituted 1,3,5-triazine dimers, as exemplified in Fig. 9(b) [77]. The resulting octupolar self-assembly is based on shape recognition for in-plane stacking and specific interactions between phenyl rings for intermolecular interactions in the direction perpendicular to the mean molecular planes. The 3-fold symmetry of the dimer is faithfully transmitted to the supramolecular organization. Optimizing the macroscopic nonlinearity requires additional adequate ordering between the trigonal crystallographic planes, as illustrated in Fig. 9(c): the ideal stacking corresponding then to an ‘eclipsed’ geometry. Attempts towards crystalline organization of octupolar systems has also been proposed [78], leading to quasi-optimal organization of phosphate-like 3D tetrahedral octupoles. Another templating model for the optimal organization of 3D octupoles in a crystalline lattice has been proposed in the form of an helical ‘hypercubic’ arrangement which generalizes the in-plane TATB scheme [79] (see Fig. 9(d)).

5.2.2. Nanoscale supramolecular organization: organometallic dendrimers

The three-dimensional character of octupolar nonlinear molecules derived from cubic or propeller-like geometries is particularly adequate for the formation of nanoscale supramolecules. Following demonstration of the large octupolar hyperpolarizability of ruthenium-tris-bipyridine building blocks [40,80], subsequent investigation of the quadratic nonlinear response of their dendritic extension is of crucial interest. The major stake is to eventually evidence spontaneous octupolar supramolecular order, by way of generalizing earlier observations for dipolar dendrimers.

Various oligomers containing N ruthenium-tris-bipyridine monomers have been synthesized and characterized. The quadratic NLO properties of supramolecular dendritic or predendritic structures has

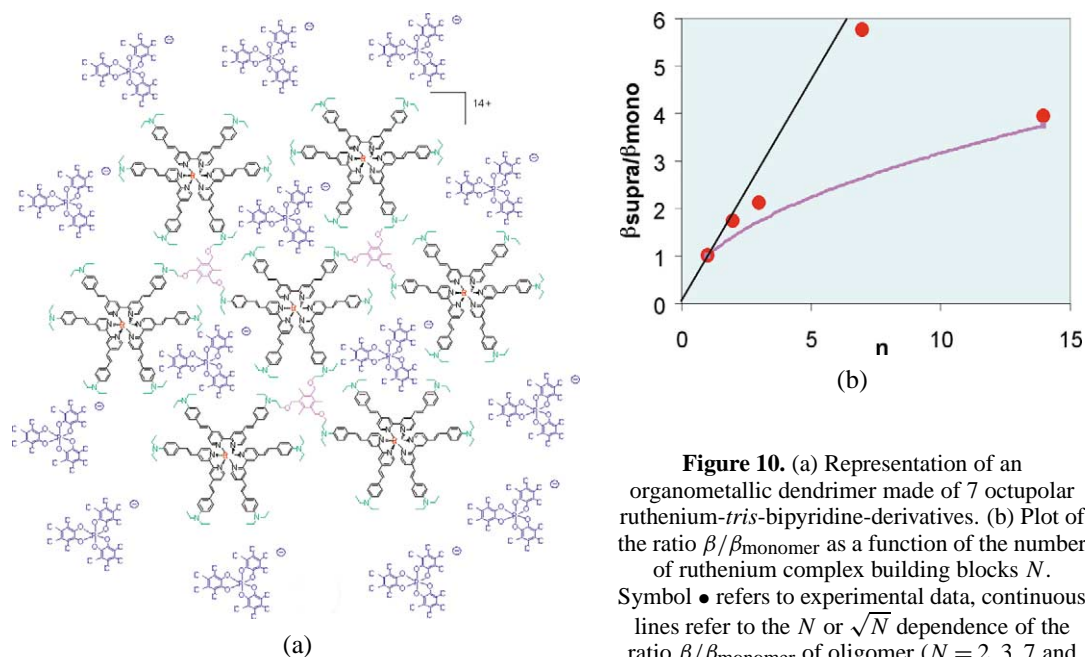


Figure 10. (a) Representation of an organometallic dendrimer made of 7 octupolar ruthenium-tris-bipyridine-derivatives. (b) Plot of the ratio $\beta/\beta_{\text{monomère}}$ as a function of the number of ruthenium complex building blocks N . Symbol \bullet refers to experimental data, continuous lines refer to the N or \sqrt{N} dependence of the ratio $\beta/\beta_{\text{monomère}}$ of oligomer ($N = 2, 3, 7$ and 14) of the overall β hyperpolarizability over that of the monomer $\beta_{\text{monomère}}$.

Figure 10. (a) Représentation de l’heptamère totalement octupolaire, constitué de 7 unités monomères elle-mêmes octupolaires sur la base d’un dérivé de ruthénium-tris-bipyridine. (b) Variation du rapport $\beta/\beta_{\text{monomère}}$ en fonction du nombre d’unités monomères N de complexes de ruthénium. Le symbole \bullet se rapporte aux données expérimentales, les lignes continues à la dépendance en N ou \sqrt{N} du rapport $\beta/\beta_{\text{monomère}}$ de l’oligomère ($N = 2, 3, 7$ et 14) entre leur hyperpolarisabilité β et celle du monomère $\beta_{\text{monomère}}$.

been investigated for $N = 2, 3$ and 7 . A linear polymer made of ruthenium-tris-bipyridine-functionalized oligoimide ($N = 14$) is also considered for comparison with the $N = 7$ dendrimer depicted in Fig. 10(a) [78].

In order to circumvent possible 2-photon-induced fluorescence that could overestimate the value of the HLS signal, β measurements of molecules **1–5** have been performed at $\lambda = 1.91 \mu\text{m}$ as the fundamental wavelength. As the harmonic wavelength at 955 nm is far from possible 2-photon resonances, any contribution from 2-photon fluorescence to HLS signal can be then safely discarded.

Size effects can be investigated for the different polymetallic species synthesized in this work, in view of the similarity in their absorption features. A large increase of β is clearly observed for the $N = 7$ dendrimer as compared to that of the monomer. The corresponding β value is significantly higher than that measured for the $N = 14$ linear polymer. It is interesting to plot β as a function of the number N of monomers, as displayed in Fig. 10(b). Comparison between the heptamer ($N = 7$) and polymer ($N = 14$) values points out strikingly different behaviors: values of β for $N = 14$ as well as for $N = 2$ and for $N = 3$ fit almost perfectly a $\beta(\text{polymer}) = \sqrt{N}\beta(\text{monomer})$ scaling law, whereas $\beta(N = 7)$ satisfactorily fits a linear relationship $\beta(\text{dendrimer}) = N\beta(\text{monomer})$. The latter quasi-linear dependence is the clear signature of a quasi-optimized octupolar ordering of individual building blocks in the dendritic heptamer, in contrast with the fully disordered structure expected for the linear polymer, as inferred from the \sqrt{N} dependence of the corresponding β value. NLO elementary units in the linear polymer do not display any acentric organization, and the corresponding HLS response of the polymer is similar to that from a set of 14 independent molecules in a solution. Conversely, a semi-rigid optimized acentric organization results in coherent second harmonic emission at the supramolecular level, the corresponding intensity from the dendrimer solution being almost proportional to $N_{\text{monomer}}^2(\beta_{\text{monomer}}^2)$. The N_{monomer}^2 dependence assumes a linear additive model whereby individual sub-units follow an interaction-free oriented gas behavior.

We have therefore clearly shown quasi-optimized octupolar ordering in a dendrimer made of highly nonlinear ruthenium complexes. This is, to the best of our knowledge, the most efficient type of self-assembled supramolecular octupolar order reported to date. The availability of nonlinear octupolar dendrimers opens attractive perspectives for nanoscale photonic applications eventually combined with other photonic functionalities such as pertain to luminescence.

5.2.3. Photoinduced multipolar ordering: from molecular to photonic engineering

Whereas the nonlinear octupole concept may be viewed as the ultimate answer to an almost two decades long quest for enhanced quadratic nonlinearity, together with the maximal level of anisotropy (both electronic polarizability and shape-wise) compatible with noncentrosymmetry, the very absence of dipole moment, characteristic of octupolar symmetry, had set a challenge to the classical electric field coupling scheme and triggered the search for alternative procedures. In this respect, ‘all-optical poling’ has emerged as a unique way to imprint refined tensorial anisotropy patterns with controllable spherical harmonic-like symmetry features. Based on group theory considerations, it can be shown that a prerequisite condition to promote octupolar molecular properties at the macroscopic level is to involve a coupling mechanism between the molecule and a rank-three field tensor comprehending a significant amount of octupolar contribution. All-optical poling provides a general answer to this requirement: it is based on dynamical resonant photoinduced processes whereby multipolar transition probabilities formally replace the steady-state coupling energy underlying the Langevin orientational mechanism. Extensive presentation of optical poling issues by Brasselet et al. is given in the present issue [19].

6. Conclusion

The demonstrated relevance of three-dimensional multipolar molecules and their subsequent arrangement in adequately organized multipolar materials has considerably widened the pool of candidate systems for molecular engineering while opening-up new application perspectives attached to a coherent control ap-

proach of material patterning. It appears indeed that the field is no more restricted to quasi one-dimensional bipolar molecules which do not permit one to fully deploy the tensorial properties of the quadratic susceptibility tensor. In fact, three-dimensional multipolar molecules are intrinsically in-keeping with the enhancement and exploitation of non-diagonal tensor coefficients which can be coupled to light polarization states of variable ellipticity with no loss of efficiency. Such adaptability to a range of light polarization configurations lends itself to the engineering of polarization-independent nonlinear devices which is a crucial prerequisite to key functional components in long haul optical telecommunication systems.

Retrospectively reviewing the field, it appears that each and every challenge it had to face turned out to have a solution opening new perspectives that were not even thought of in the previous context of bipolar molecular diodes. For example, the inadequacy of the EFISH method to provide a feedback in solution has generated a revival of interest in the Harmonic Light Scattering experiment pioneered by Maker and Terhune in the sixties and seventies, but somewhat left aside in the next decade before its relevance became clear again in the current context. Moreover, as a bonus in comparison with the more symmetry-constrained electric field poling technique, Harmonic Light Scattering offers a quantitative access to the determination of irreducible components of the β tensor which has allowed to introduce the notion of nonlinear anisotropy of interest to gauge the relative contributions of the various multipolar components. Such insight into the tensorial properties was new in this field and provides an avenue for synthetic chemists into the structural handling and optimization of tensorial properties, which was no part of chemical culture as such. Indeed, the introduction of a tensorial dimension into molecular engineering can be viewed as a major opening brought about by this work with possibly far reaching consequences beyond nonlinear optics.

While solving the issue of routine assessment in solution for the β tensor, the challenge of permanently organizing molecular units into noncentrosymmetric multipolar structures remained to be solved as the non-coherent nature of HLS had permitted one to ignore this constraint. This step really brought the field of multipolar nonlinear engineering to a mature status with the proposition of optical poling as an elegant and efficient way to get around the limitations of the permanent electric field coupling scheme. This issue is developed at length in the article of Brasselet et al. [19] in this issue. It is however worthwhile to note that here as well as in the search of an alternative to EFISH, the clue was found in earlier pioneering work, which can be traced back to R.J. Glauber in the 1960s to 1970s and the experimental breakthrough of Österberg and Margulis in the mid-1980s, pertaining to photoinduced second harmonic generation in silica fibers.

A crucial factor which helped cement and clarify the field from its very onset has been the persistent reference to tensorial group theory and its initially countermainstream implementation in the realm of molecular engineering and chemistry. Indeed, whereas algebraic foundations set-up by E. Wigner in the 1930s in the context of atomic physics had to be subsequently applied in the 1970s to nonlinear optics, this had remained at an abstract and purely phenomenological level providing no practical insight in terms of molecular and material engineering. Unambiguous connection between the occurrence and magnitude of irreducible tensor components and well-defined structural features of molecules and materials was developed in the last decade with more work ahead and gave rise to the multipolar engineering pathway reviewed in this article. Indeed, seeing an initially abstract theoretical formalism become an operational and practical engineering tool in the hands of synthetic chemists provided a rewarding experience, which took into account a decade to get fairly general acceptance. Moreover, the relevance of this formalism to tailor multiphoton fields (see contribution by Brasselet et al. [19] in this issue), consistent with the molecular structure, added considerable coherence to the field with a rather unique position at the interface of chemistry and physics. The recognition of the tensorial dimension of molecular polarization properties has also had an impact on their quantum mechanical modeling as reviewed in this work, leading to the reconsideration and generalization of the previously all-pervading two-level model.

From there on, it is difficult to predict where the field is heading to in view of the many possibilities opened-up in various areas of chemistry and towards new photonic functions in telecommunication and increasingly so towards bio-imaging and bio-labeling. Among such diversity, we propose to single-out two directions of particular interest for the future. Firstly, the three-dimensional nature of organometallic

multipoles and the specific assets of metallic systems permit to envision multifunctional molecules whereby nonlinear properties are combined with luminescent and magnetic features with new applications to be found. Secondly, the local nature of light-induced manipulation techniques such as permitted by optical poling allows to tailor spatial distributions of nonlinear properties leading to original nonlinear patterns hardly conceivable in the more rigid context of crystals. Such controllable flexibility of molecular media enlarges the scope of nonlinear optics from a set of functional properties and applications onto a technological tool of broad relevance.

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