ACCOUNTS
of chemical research

Design and Characterization of Molecular Nonlinear Optical Switches

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RECEIVED ON APRIL 3, 2013

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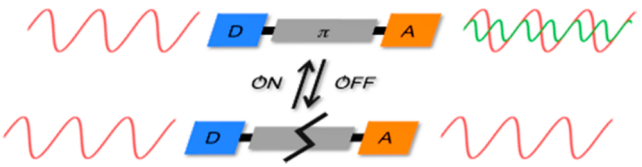


Nanoscale structures, including molecules, supramolecules, polymers, functionalized surfaces, and crystalline/amorphous solids, can commute between two or more forms, displaying contrasts in their nonlinear optical (NLO) properties. Because of this property, they have high potential for applications in data storage, signal processing, and sensing. As potential candidates for integration into responsive materials, scientists have been intensely studying organic and organometallic molecules with switchable first hyperpolarizability over the past two decades. As a result of this, researchers have been able to synthesize and characterize several families of molecular NLO switches that differ by the stimulus used to trigger the commutation. These stimuli can include light irradiation, pH variation, redox reaction, and ion recognition, among others. The design of multistate (including several switchable units) and multifunctional (triggered with different stimuli) systems has also motivated a large amount of work, aiming at the improvement of the storage capacity of optical memories or the diversification of the addressability of the devices.

In complement to the synthesis of the compounds and the characterization of their NLO responses by means of hyper-Rayleigh scattering, quantum chemical calculations play a key role in the design of molecular switches with high first hyperpolarizability contrasts. Through the latter, we can gain a fundamental understanding of the various factors governing the efficiency of the switches. These are not easily accessible experimentally, and include donor/acceptor contributions, frequency dispersion, and solvent effects.

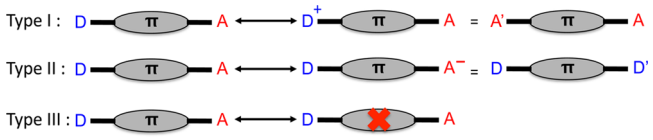
In this Account, we illustrate the similarities of the experimental and theoretical tools to design and characterize highly efficient NLO switches but also the difficulties in comparing them. After providing a critical overview of the different theoretical approaches used for evaluating the first hyperpolarizabilities, we report two case studies in which theoretical simulations have provided guidelines to design NLO switches with improved efficiencies. The first example presents the joint theoretical/experimental characterization of a new family of multi-addressable NLO switches based on benzazolo-oxazolidine derivatives. The second focuses on the photoinduced commutation in merocyanine–spiropyran systems, where the significant NLO contrast could be exploited for metal cation identification in a new generation of multiusage sensing devices. Finally, we illustrate the impact of environment on the NLO switching properties, with examples based on the keto–enol equilibrium in anil derivatives. Through these representative examples, we demonstrate that the rational design of molecular NLO switches, which combines experimental and theoretical approaches, has reached maturity. Future challenges consist in extending the investigated objects to supramolecular architectures involving several NLO-responsive units, in order to exploit their cooperative effects for enhancing the NLO responses and contrasts.

1. Introduction

Nonlinear optics is the branch of optics that describes the behavior of light in media where the dielectric polarization responds nonlinearly to (the electric field component of) light. The doubling of the frequency of the incident beam, through the second harmonic generation (SHG) process, constitutes one example of nonlinear optical (NLO) phenomena that is currently exploited in laser components as

Published on the Web 07/19/2013 www.pubs.acs.org/accounts
10.1021/ar4000955

SCHEME 1. Different Types of NLO Switching in Dipolar D–π–A Molecules Where the Push-Pull Character Is Tuned upon Switching[a]



[a]Type I = redox/proton transfer on D; type II = redox/proton transfer on A; type III = alteration of the bridge π-conjugation. Adapted from ref **2a**.

well as in optical information processing and data storage devices.[1] In particular, organic materials with commutable NLO responses are sought for optoelectronic applications such as molecular-scale memory devices with multiple storage and nondestructive reading capacity. In this context, the design of NLO switches, that is, molecules (but also supramolecules and polymers) characterized by their ability to alternate between two or more chemical forms displaying contrasts in one of their NLO properties (generally the second harmonic intensity), has motivated much experimental and theoretical works since the end of the 1990s.[2] A large variety of NLO switches exhibiting large changes in the first hyperpolarizability, β, the molecular second-order NLO response, have been designed, synthesized, and characterized during the last 20 years.

Although NLO switching has been demonstrated for octupolar molecules,[3] most of the systems synthesized to date are π-conjugated donor–acceptor molecules, which consist of strong electron-donor (D) and electron-acceptor (A) groups anchored onto a π-conjugated linker. In the first review dedicated to NLO switches,[2a] Coe proposed to categorize the various systems on the basis of the part of the molecule that is altered during the commutation reaction, that is, the donor part (type I), the acceptor part (type II), or the conjugated bridge (type III), as depicted in Scheme 1.

NLO switches of types I and II rely on redox switching, where the electron-donating (withdrawing) capability of the donor (acceptor) group is reduced by oxidation (reduction), or on acido-switching, in which the electron-donating capability of the donor group is reduced by protonation. While NLO switching based on redox interconversion has been demonstrated in a wide range of organometallic complexes,[4] reversible acido-switching of type I has been achieved, for instance, in azafulleroid[5] and dicyanoimidazole[6] derivatives. Most NLO switches of type III are photochromic compounds characterized by different commutation processes, including intramolecular proton transfer as in anil derivatives,[7] *cis–trans* photoisomerization in azobenzenes,[8] and opening/closure of a conjugated ring in diarylethenes[9] or spiropyrans.[10]

Recent studies also revealed the ability of photoswitchable fluorescent proteins (FPs) such as DRONPA to display second-order NLO responses.[11] Note that NLO switching was also demonstrated for the third-order NLO response, described at the molecular level by the second hyperpolarizability, γ.[12] Design, preparation, and use of these switches is however at a less mature stage owing to the smaller amplitude of the third-order NLO effects and the larger difficulty to get high contrasts with γ (even order tensor), in contrast with β (odd order tensor), which can drastically be impacted by centrosymmetry.

This Account illustrates key aspects in the design of NLO switches. This research field is interdisciplinary and combines (i) the synthesis of new compounds, (ii) the characterization of their second-order NLO properties, for which hyper-Rayleigh scattering (HRS) is the most appropriate method since it can be used for both neutral and charged species,[13] and (iii) quantum chemical calculations. By providing relationships between the structure of the compounds and their NLO responses, these calculations provide a fundamental understanding of the structural and electronic features driving the efficiency of the switches and allow drawing of guidelines for targeted syntheses. Thus, after introducing the principle of HRS measurements, we briefly review the pros and cons of the different theoretical approaches used for evaluating β. From the characterization of a new family of multiaddressable NLO switches, the first example highlights the complementarity of experimental and theoretical characterizations but also the difficulties to compare them. The second example focuses on the contribution of theoretical simulations through the *in silico* design of NLO switches based on merocyanine–spiropyran systems. This leads subsequently to the description of a new concept for detecting cations, based on the β contrast. Finally, the last section addresses the effects of the environment on the NLO switching properties, with illustrations based on the keto–enol equilibrium of anil derivatives in various solvents as well as in the solid state.

2. Experimental and Theoretical Methods

2.1. Hyper-Rayleigh Scattering. Two major experimental techniques exist to probe the molecular first hyperpolarizability of solutions: the electric field induced second harmonic generation (EFISHG)[14] and the hyper-Rayleigh scattering (HRS).[15] The EFISHG technique consists in measuring the light intensity at a frequency twice the fundamental frequency of an incident laser pulse generated by a solution submitted to a static electric field. This method gives information on the projection of the vector part of β on the dipole

moment vector, so that only a combination of tensorial components of β can be obtained. On the other hand, the HRS method allows measurements of nonpolar and ionic molecules, which are out of reach for the EFISHG technique. The first hyperpolarizability is extracted from the intensity of the incoherent scattered light at optical frequency 2ω on incidence of an intense laser pulse at ω. For plane-polarized incident light and observation made perpendicular to the propagation plane, the full HRS intensity reads

$$\beta_{HRS} = \sqrt{\langle {\beta_{HRS}}^2 \rangle} = \sqrt{\langle {\beta_{ZZZ}}^2 \rangle + \langle {\beta_{ZXX}}^2 \rangle} \quad (1)$$

where $\langle {\beta_{ZZZ}}^2 \rangle$ and $\langle {\beta_{ZXX}}^2 \rangle$ correspond to orientational averages of the β tensor components in the molecular frame. The associated depolarization ratio,

$$DR = \frac{\langle {\beta_{ZZZ}}^2 \rangle}{\langle {\beta_{ZXX}}^2 \rangle} \quad (2)$$

gives information on the symmetry of the molecular scatterers. For instance, DR = 5 in the case of ideal 1D systems, while DR = 1.5 for octupolar molecules. The dominant β tensor components of push–pull π-conjugated organic molecules are usually extracted from β_{HRS} and DR by assuming a pseudoplanar C_{2v} symmetry as well as Kleinman's permutation rules on all indices. Note that a more accurate description of molecules/clusters in isotropic media is possible when the irreducible spherical representation of the hyperpolarizability β tensor without symmetry assumption is evoked (e.g., see ref 16).

2.2. Theoretical Methods. Response theory and perturbation theory approaches are the two classes of methods to compute the hyperpolarizabilities. Within each class, several levels of approximation have been worked out, providing more and more accurate estimates going in parallel with increasing computer needs. In most cases, theoretical predictions concentrate uniquely on the electronic response because for the SHG process the pure vibrational contribution is negligible whereas the zero-point vibrational averaging is small.[17] Within response theory approaches, the time-dependent Hartree–Fock (TDHF) scheme[18] and its static analog, the coupled-perturbed Hartree–Fock (CPHF) scheme, are the most common procedures to evaluate the static and frequency-dependent electronic first hyperpolarizabilities of molecules. However, these methods are limited by the fact that they do not include electron correlation effects, which are highly recommended for quantitative predictions of β. These latter can be accounted for by employing the numerical finite field (FF) procedure in combination with post-HF levels of calculation, along with expressing β as the third-order derivative of the total electronic energy. An advantage of the FF procedure is its general application to a broad range of levels of approximation, provided field-dependent energies can be evaluated, therefore enabling easy assessment of electron correlation effects. For typical π-conjugated organic molecules, the second-order Møller–Plesset (MP2) level was shown to be the best compromise between accuracy and computational cost[19] and is now used routinely. Correlated FF schemes are however restricted to the evaluation of the static NLO responses. Still, to include both electron correlation and frequency dispersion effects, a common approximation consists in correcting the static responses by a multiplicative factor accounting for frequency dispersion, defined as the ratio between the TDHF and CPHF hyperpolarizabilities:

$$\beta_{CORR}(-2\omega;\omega,\omega) \approx \beta_{CORR}(0;0,0) \times \frac{\beta_{TDHF}(-2\omega;\omega,\omega)}{\beta_{CPHF}(0;0,0)} \quad (4)$$

This approximation is based on the assumption that frequency dispersion and electron correlation effects can be treated independently, which has been shown to be suitable for a variety of compounds in off-resonant conditions.[20] Response calculations can also be performed at correlated levels to provide frequency-dependent quantities.[21] These are however mostly applied to small compounds.

Correlated dynamic NLO responses can also be computed using the time-dependent density functional theory (TDDFT) method, whose basic equations are similar to those of TDHF. However, although DFT approaches have often been proposed as efficient solutions to account for electron correlation at low computational cost, conventional exchange–correlation (XC) functionals suffer from severe drawbacks when computing the NLO properties of extended conjugated systems.[22] Besides limitations for calculating β, these XC functionals are also subject to criticism when estimating the β contrasts. This is illustrated in Figure 1, which compares the β_{HRS} contrast calculated using standard XC functionals for various merocyanine (M)/spiropyran (S) systems to values issued from CPHF and MP2 calculations. When going from CPHF to MP2, β_{HRS} increases similarly for both the M and S forms, showing the limited impact of electron correlation on the β contrast, which slightly increases for compounds **1a** and **1c** but decreases for **1b**.

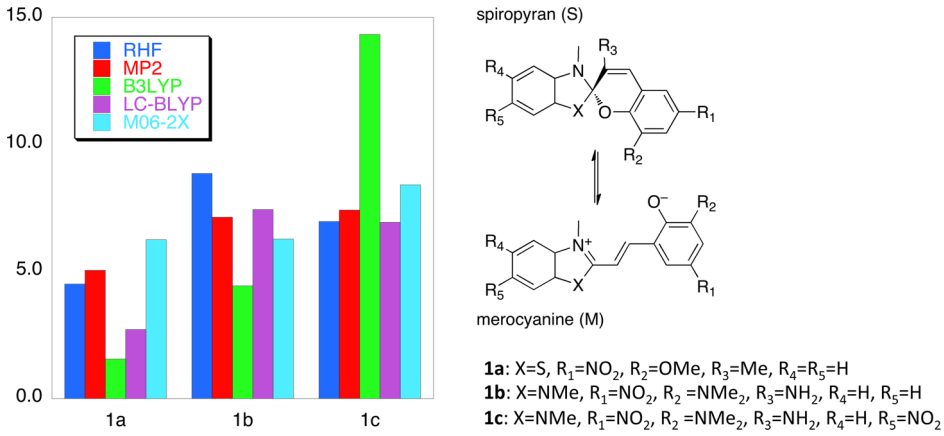


FIGURE 1. Static β_{HRS} contrasts for selected merocyanine/spiropyran systems calculated at various levels of approximation with the 6-311+G* basis set.

The situation is different when considering the TDDFT results. The B3LYP functional behaves poorly, leading to underestimations (**1a** and **1b**) or overestimations (**1c**) of the β contrasts. The performance of the LC-BLYP (which includes long-range corrections in the exchange potential) and M06-2X functional is better, though the improvement over HF is not systematic. Besides the XC functionals, the basis set effects were also addressed for number of push−pull π-conjugated systems or NLO switches.[19,23] Split-valence double- or triple-ζ basis sets including one set of diffuse and polarization functions, or even less, were shown to be generally sufficient to describe the dominant β tensor components and the depolarization ratios.

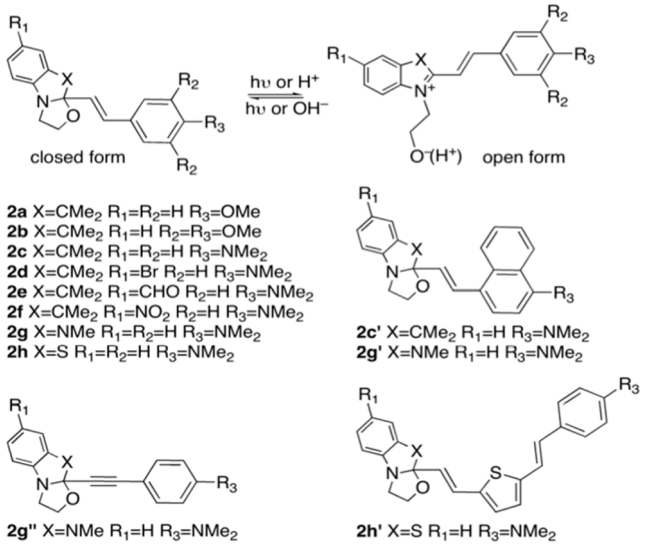
Another way to calculate β with different levels of electron correlation consists in using the sum-over-states (SOS) approach,[24] derived from the time-dependent perturbation theory. The main advantage of the SOS scheme is that it allows the interpretation of the NLO responses in terms of spectroscopic quantities. Its accuracy is dictated by the method used for determining the ground and excited state wave functions, as well as the corresponding excitation energies and transition dipole moments. The SOS scheme has been widely employed in the last 20 years in combination with the CIS (configuration interaction singles) method and semiempirical Hamiltonians for establishing structure−NLO properties relationships in a large range of conjugated molecules.[25] Besides, the SOS expression is frequently employed to extrapolate the static NLO responses of donor−acceptor systems from the dynamic quantities measured experimentally, assuming that only one electronic excited state contributes to β. Within this two-state approximation,[26] the frequency dispersion factor, $F(\Delta E_{0e},\omega,\Gamma)$, reads:

$$F(\Delta E_{0e},\omega,\Gamma) = \frac{\beta_{zzz}(-2\omega;\omega,\omega)}{\beta_{zzz}(0;0,0)} = \frac{\Delta E_{0e}{}^2(\Delta E_{0e} - i\Gamma)^2}{([\Delta E_{0e} - i\Gamma]^2 - \omega^2)([\Delta E_{0e} - i\Gamma]^2 - 4\omega^2)} \quad (5)$$

A $F(\Delta E_{0e},\omega,0)$ correction factor is however applicable but only in the off-resonance region, where $2\omega \ll \Delta E_{0e}$. Then, a homogeneous broadening parameter Γ can extend the validity of the two-state approximation to near-resonant regimes. More sophisticated expressions, including inhomogeneous broadening based on the shape of the absorption spectrum or accounting for the vibronic structure of the excited states, have also been established.[27] These phenomenological models are however difficult to use since the parameters are *a priori* not known.

Finally, one of the key aspects for an accurate evaluation of the NLO responses is to account for solute/solvent interactions. Among the available approaches, the most popular ones are the polarizable continuum models (PCM), in which the molecular surrounding is replaced by a structureless medium characterized by its dielectric permittivity.[28] However, these approaches are limited by the fact that they cannot fully catch the impact of specific local interactions between the molecule and its environment, such as van der Waals interactions, London dispersion, hydrogen bonds, or nonisotropic induction and polarization phenomena. Mixed models, in which few solvent molecules (e.g., the first solvation shell) are explicitly considered within a PCM embedding,

SCHEME 2. Benzazolo-oxazolidines Derivatives[a]



Compound	Reference	$\beta_{HRS}^{POF}(\omega)$	$\beta_{HRS}^{POF}(\omega)/\beta_{HRS}^{CF}(\omega)$
2a	[30]	75	/
2b	[30]	87	/
2c	[30]	470	20
2c'	[30]	370	/
2d	[31]	698	34
2e	[31]	332	5
2f	[31]	436	9
2g	[32a]	117	33
2g'	[32a]	55	5
2g''	[32a]	394	6
2h	[32b]	755	/
2h'	[32b]	865	/

[a]Inset, dynamic (λ=1064 nm) β_{HRS} (in 100 au) of the POFs and β_{HRS} contrasts, as measured in acetonitrile.

are the best compromise to improve the simulation of solvent effects.[29]

3. Case Studies

3.1. Multiaddressable NLO Switches. One of the actual challenging tasks in miniaturizing the components of electronics down to the molecular level embodies the integration of several switchable functions and the integration of multiaddressable functions into a single molecule. Developments in molecular switching technology thus imply the design of molecular systems with tunable properties revealed using more than one stimulus. Benzazolo-oxazolidine derivatives (Scheme 2) are good examples of such systems, owing to their ability to commute indifferently upon light irradiation or pH variations. The photochromic process implies the breaking of a σ-bond on the oxazolidine moiety, leading to the formation of a colored zwitterionic form. The geometrical relaxation induced by the oxazolinic ring-opening leads to an improved electron conjugation/delocalization

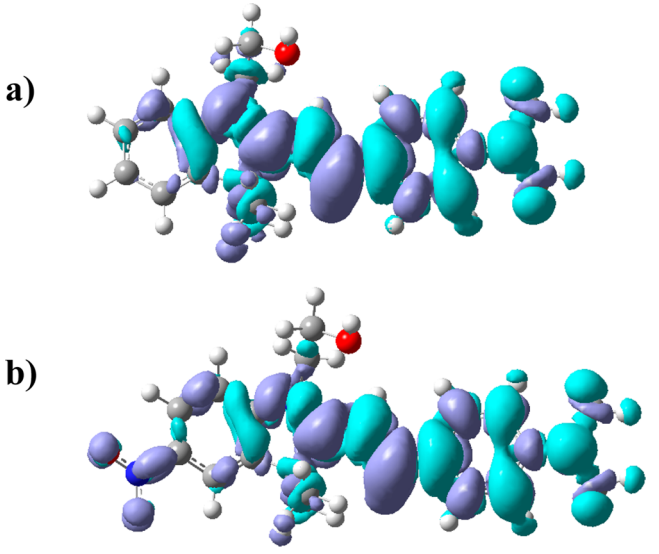


FIGURE 2. Electron density difference between the ground and lowest-energy charge-transfer excited state for compounds **2c** (a) and **2f** (b), as calculated at the TDDFT/M06-2X/6-31G(d) level. Blue (violet) lobes are associated with negative (positive) values.

along the molecule, responsible for the change in optical signatures. Upon acidic addition, a protonated open form (POF) is generated, whose absorption spectrum is identical to that of the zwitterionic form, indicating that these two species adopt similar structures. Total back photobleaching is achieved either by irradiation of the zwitterionic forms with an appropriate visible light or by base addition on the POF.

The first series of oxazolidine derivatives was synthesized by combining the 10-(2-arylethenyl)indolino[2,1-*b*]oxazolidine unit with various styrylic residues (**2a**−**c**, **2c'**).[30] HRS measurements revealed that the structures involving the strong electron-donating *N*,*N*-dimethylamino group on the aryl moiety (**2c**,**c'**) exhibit the largest β in their protonated open forms, 1 order of magnitude larger than that of the associated closed form (CF). However, theoretical calculations evidenced that the light-induced charge transfer does not spread over the whole length of the open molecules, which limits the magnitude of their second harmonic responses. This is illustrated in Figure 2a, where no significant changes upon photon absorption are observed in the total electron density on the terminal phenyl group of the oxazolidine. Two strategies were then adopted to extend the conjugation path and hence to enhance the NLO response of the open form. A first way consisted in increasing the strength of the acceptor moiety by grafting electron-withdrawing substituents in the para position of the indolinic residue (**2d**−**f**),[31] while a second consisted in increasing the number

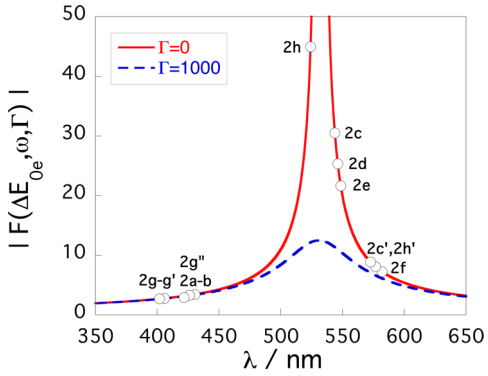


FIGURE 3. Frequency dispersion factor as a function of the maximum absorption wavelength of the benzazolo-oxazolidine derivatives, calculated using the two-state approximation (eq 5) with a homogeneous damping of (a) $\Gamma = 0$ cm^{-1} [red] and (b) $\Gamma = 1000$ cm^{-1} [blue]. The circles indicate the maximum absorption wavelength positions for the compounds in acetonitrile.

of delocalizable electrons along the conjugated backbone by replacing the indolinic unit by a benzimidazolic (**2g**, **2g′**) or benzothiazolic (**2h**) unit or by changing the ethylenic linker by an acetylenic (**2g″**) or a divinylthiophene (**2h′**) bridge.[32] As predicted by theoretical calculations, the addition of electron-withdrawing substituents on the oxazolidine (**2d**–**f**) unit increases the efficiency of the light-induced charge transfer (Figure 2b), which was subsequently evidenced experimentally by the red shift of the maximum absorption band. Optimized compounds were shown to exhibit very high HRS responses in the open forms along with large β contrasts (inset of Scheme 2).

Oxazolidine derivatives are prototypical of compounds in which structure–properties relationships are difficult to extract without the help of theoretical calculations, because of resonance between the scattered wave and the main absorption transition of the open forms. Figure 3 illustrates the dispersion of the HRS response for a scattering frequency at 532 nm, as calculated using the two-state approximation with or without including a typical homogeneous damping Γ of 1000 cm^{-1} (eq 5). As reported in ref 31 for compounds **2c**–**f**, the static $\beta_{HRS}(0)$ values could also be evaluated by using damping factors proportional to the half-width at half-maximum of the main absorption band or by incorporating an inhomogeneous broadening that implicitly contains information on the distribution of the transition frequencies. These more elaborated models were in better agreement with the $\beta_{HRS}(0)$ values calculated using *ab initio* methods.

3.2. NLO Sensors. TDHF and FF/MP2 calculations were used to unravel the relationships between molecular structures and β in a large set of spiropyran/merocyanine

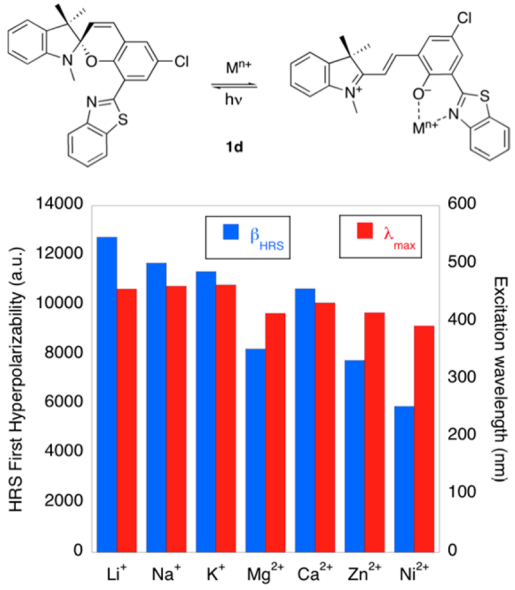


FIGURE 4. (top) Equilibrium between the spiropyran form and its merocyanine *alter ego* complexing a cation; (bottom) calculated HRS first hyperpolarizabilities and excitation wavelengths of the metal–merocyanine complex as a function of the cation.

couples.[23] They highlighted in particular the cooperative effects of the chemical substituents on the HRS responses and allowed us to draw general strategy rules for designing new commutable compounds with NLO enhancements of 1 order of magnitude. Optimal switches were thus obtained when (i) substituents at R_1 and R_2 positions on the phenolate ring of the merocyanine form (see Figure 1) are, respectively, strong acceptor and donor substituents, (ii) the ethylenic bridge is substituted by donor groups, (iii) the benzimidazole unit is used rather than the indole or benzothiazole units, and (iv) strong donor substituents are placed on the benzimidazolo moiety. Moreover, for most of these systems, the β_{HRS} amplitude of the merocyanine form was shown to correlate with the bond length alternation (i.e., the average difference in length between the single and double bonds) along the ethylenic bridge. This structural parameter, associated with the aromatic/quinoid character of the conjugated linker, is therefore a reliable criterion to predict β contrasts in these systems, as it was previously evidenced for β of push–pull molecules.[33]

As recently demonstrated, the large NLO contrasts associated with the photoinduced commutation in merocyanine/spyropyran systems could be exploited for sensing applications thanks to the ability of the merocyanine form to complex metal cations. The proof of concept was given by considering the derivative in Figure 4, already known for its metallochromic properties.[34] Ab initio calculations

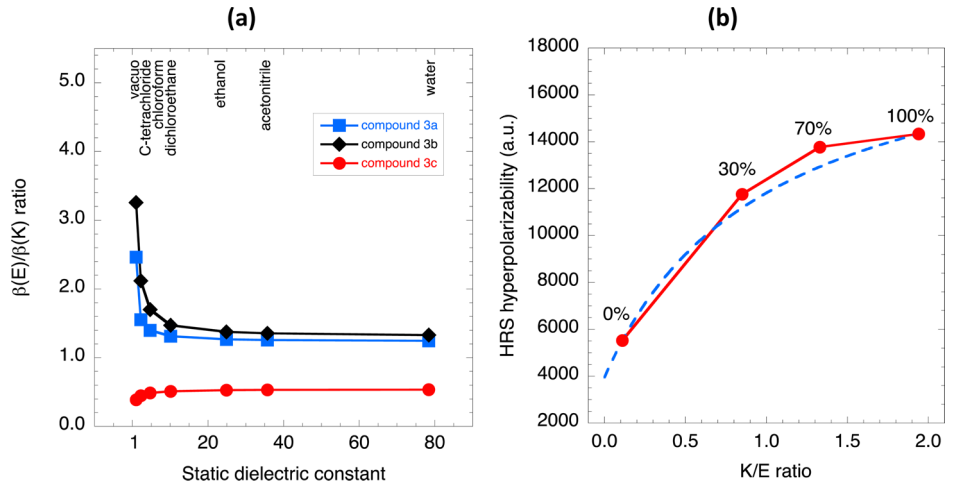
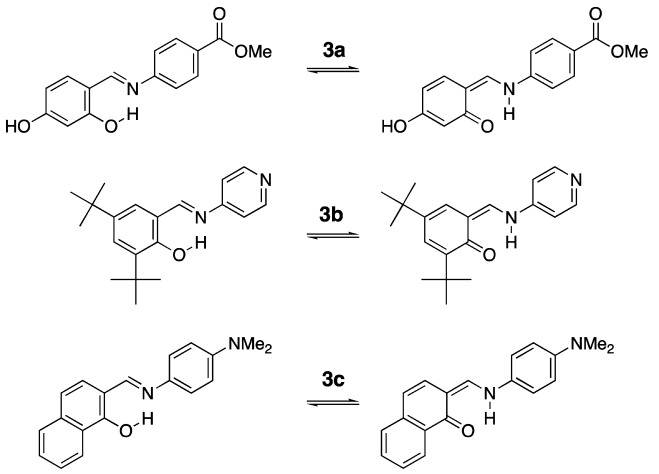


FIGURE 5. (a) HRS first hyperpolarizability contrasts for compounds **3a**–**c** as a function of the solvent polarity, as calculated at the PCM:MP2/6-31G(d) level; (b) HRS first hyperpolarizability (red plain line) of solutions of **3c** with various K/E ratios controlled by varying the percentage (indicated) of ethanol in the solvent mixture. Dotted line is obtained assuming that HRS responses are additive and solvent-independent (see text).

SCHEME 3. Enol (E) and Keto (K) Tautomeric Forms of Anil Derivatives



combined with mixed implicit/explicit solvent models, revealed that the β response of the metal–merocyanine complex and thus the β contrasts strongly depend on the nature of the cations, opening a promising way for a new selective detection technique. Moreover, the possibility to photocommute from the complexed merocyanine back to the spiropyran species could make these systems a new class of reusable probes for environment monitoring.

3.3. Effect of the Environment on the NLO Switching Properties. This last section illustrates the impact of the environment (solute/solvent or solid state interactions) on the NLO responses of molecular switches, with the example of anil derivatives (Scheme 3). These compounds have the ability to switch between an enol (E) and a keto (K) form, through an intramolecular hydrogen transfer that can occur both in the liquid and in the crystalline state.[7] As reviewed by Bishop,[35] the solvent, and by extension any medium including the surrounding molecules in the solid state, has a double effect on the NLO properties, because it modulates the field amplitudes that are experienced by the solute and modifies its geometry and electronic structure from what it is in the gas phase. In the case of molecular switches, the solvent has an additional role since it can shift the equilibrium between the different forms. Direct solvent effects are illustrated in Figure 5a, which reports the static β_{HRS} contrasts of compounds **3a**–**c** computed at the PCM:MP2 level as a function of the dielectric constant used in the solvation model. Compared with gas phase, solvent effects induce a significant enhancement of β_{HRS} of both the E and K forms, whose magnitude increases with the solvent polarity. For compounds **3a** and **3b**, the solvent-induced enhancement is larger for the K forms, leading to a decrease of the β_{HRS}(E)/β_{HRS}(K) contrast when increasing the solvent polarity. A reverse effect is observed for compound **3c**. These behaviors have been rationalized as resulting from the donor or acceptor character of the substituents on the phenyl ring.[7b]

The impact of the solvent-induced equilibrium displacement on the NLO responses was investigated in the case of **3c**, by combining HRS measurements and *ab initio* calculations.[36] Different binary mixtures of ethanol and cyclohexane were used to control the ratio between the two tautomers. As shown, Figure 5b, a larger ethanol ratio shifts the tautomeric equilibrium toward the K form, giving rise to a bathochromic shift and a large β_{HRS} enhancement of the solute composition. Individual β_{HRS} values of both E and K

forms were extracted from the experiments performed in pure solvents assuming that they do not depend on the nature of the solvent. The evolution of β_{HRS} of the solution mixture estimated using this solvent-independent approximation and by assuming additivity of the HRS responses (i.e., that the measured HRS response of the solution is the sum of the individual responses of the two forms weighted by their populations) displays small deviations with respect to the measured values, substantiating that the β_{HRS} variations are in this case mainly driven by the equilibrium displacement.

Finally, the impact of intermolecular interactions in the solid state is addressed for crystals of **3a** and **3b** by combining molecular responses calculated using quantum chemistry methods and an electrostatic interaction scheme to account for the local field effects.[37] In the crystal **3a**, the surrounding effects on β are similar for the E and K forms, leading to optical contrasts very close to those of the isolated molecule. In contrast, a large enhancement of the second-order susceptibility, $[\chi^{(2)}]$, was observed in the K form of **3b**, leading to a very high contrast of the macroscopic second-order NLO response. These investigations rationalized the high NLO contrast of **3b** in the solid state, while they also predicted the larger $\chi^{(2)}$ value of **3a** (E form), in good agreement with experiment.[7a] Most importantly, they established a reliable computational methodology that opens the way to systematic analyses, which should prove useful to efficiently design new switching materials.

4. Conclusions

The physicochemical factors driving the efficiency of molecular NLO switches are now well established, due to theoretical investigations that addressed aspects not easily accessible to experiment, including frequency-dispersion and solvent effects and exploration of donor/acceptor contributions, while they make possible their interpretation in terms of simple concepts (molecular conformations, MOs topology, excitation energies, etc.). The potential interest of such systems for practical applications results however from compromises that overpass the molecular first hyperpolarizability. The gap with respect to preparing devices includes the incorporation of the switches into a solid phase, either under the form of small crystallites or anchored to polymer chains, like in the case of azobenzene derivatives functionalizing polymers.[38] In addition to molecule-based switches, polymers can display second-order NLO contrasts owing to backbone or side-chain transformations but mainly owing to conformational changes that can be triggered by light, solvent, temperature, or cation recognition.[39] Very recently, metal−organic frameworks (MOFs) have also demonstrated switchable ability with significant second-order susceptibility ($\chi^{(2)}$) contrasts.[40] Other systems for which modeling-based design could play a role to maximize the NLO contrasts are supramolecular assemblies that can be formed or tuned according to various mechanisms (H-bonds, van der Waals forces, ion−ligand interactions) and pattern recognitions. This illustrates the diversity of NLO switches, of which the dimensionality ranges from zero (molecules) to one (polymers), two (SAMs, supramolecular systems), and three (MOFs). Increasing the dimensionality of the investigated objects is one of the next challenges for theoretical modeling, in view to providing design rules to enhance the NLO responses and contrasts by exploiting the cooperative effects in complex supramolecular architectures.

The authors acknowledge fruitful collaborations with F. Adamietz, L. Antonov, I. Asselberghs, E. Bogdan, F. Bures, K. Clays, E. De Meulenaere, V. Enchev, M. Guillaume, V. Liégeois, N. Markova, F. Mançois, K. Nakatani, A. Ségerie, and T. Verbiest. This work has been supported by funds from the CNRS, the Région Aquitaine, the F.R.S.-FNRS, the AUL (ARC TinTin), and by the Belgian Government (IUAP No P7/5).

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FOOTNOTES

The authors declare no competing financial interest.

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