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Nonlinear optical switches

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1. Introduction

A molecular switch is a molecule that adjusts its structural and electronic properties when it is triggered by external stimuli. These stimuli can be of different natures (light irradiation, pH change, application of a redox potential, pressure, etc.) and molecular switches can adopt at least two states. Generally, all states are stable or metastable under the proper stimulus, while the system returns to its initial state when the stimulus is turned off, but those are not general requirements [1]. Conceptually speaking, in a molecular logic context, while the applying a stimulus corresponds to the writing operation, the measurement of the system consists of the "reading" counterparts. To be recognized upon "reading", it is important that the different states should be well differentiable when measuring this property, and the larger the difference, the better.

Even though there are many examples of biological molecular switches (e.g., *cis-trans* isomerization of retinal, which is the basic process in animal vision), the pH indicators are among the most recognized ones (including for the *general public*). In fact, pH indicators feature what is probably the first synthetic molecular switch, phenolphthalein (Figure 1) [2]. Since then, this field has been (and is still) highly active, with, for instance, the recent (2016) Nobel prize in Chemistry of Savage, Stoddart and Feringa for "the design and synthesis of molecular machines".

While in the pH indicators mentioned above the states differ by their absorption spectra (in the visible), the interactions between light and matter can give rise to a wider range of phenomena. These light-matter interactions also constitute the basis of many spectroscopies, which differs by the range of incident wavelengths and by the intensity of the beam that probe the matter. Since the advent



Figure 1: Forms of the phenolphthalein molecule at acidic (left, colorless) and basic (right, pink) pH. It is often used as indicator in pH titrations.

of the laser, it was discovered that some properties of matter may not depend linearly on the intensity of the incident beam, hence characterized by the terminology "nonlinear optics". One example is the discovery, in 1961 by Franken *et al.* [3] of the second harmonic generation (SHG) phenomenon, in which pairs of photons of frequency ω are transformed into photons of twice the frequency (2 ω) upon interaction with a nonlinear optical (NLO) material.

1.1. Molecular nonlinear optics and description of the SHG phenomenon

At the molecular level, the interaction between an electric field, E, and a molecule induces a reorganization of the charges (electrons and nuclei), which is described by a modification of its dipole moment and an induced contribution, $\Delta\mu(E)$. Note that for simplicity, the equations of this section have been simplified, since electric fields are vectors with three components, and thus $\Delta\mu(E)$ is in practice a vector quantity. A phenomenological description of this phenomenon is given by a Taylor series expansion [4],

$$\mu(E) = \Delta \mu_0 + \Delta \mu(E)$$
, with $\Delta \mu(E) = \alpha E + \frac{1}{2} \beta E^2 + \frac{1}{6} \gamma E^3 + \dots$

where μ_0 is the intrinsic dipole moment of the molecule, α , the polarizability, β , the first hyperpolarizability, and γ , the second hyperpolarizability (in practice, these are tensors). From this expression, it is clear that β is the first nonlinear term, which needs to be considered if *E* gets large, like when applying an intense (both in term of the flux of photon and in energy) laser light. In the case of time-dependent electric field, oscillating at angular frequency ω , $E(\omega) = E_0$ $cos(\omega t)$, up to second order, Eq. (1) becomes:

$$\Delta\mu(E) = \alpha(-\omega; \omega) E_0 \cos(\omega t) + \frac{1}{2}\beta(0; \omega, -\omega) E_0^2$$
(2)
+ $\frac{1}{2}\beta(-2\omega; \omega, -\omega) E_0^2 \cos(2\omega t) + ...$

in which two NLO phenomena appear: i) SHG, associated with the last term and $\beta(-2\omega;\omega,\omega)$ as well as ii) optical rectification (OR), governed by $\beta(0;\omega,-\omega)$, where two photons of frequency ω generate an induced static dipole. Other combinations of static and dynamic electric fields

lead to other NLO processes, such as dc-Pockels, $\beta(-\omega;\omega,0)$, at second order, or dc-Kerr, $\gamma(-\omega;\omega,0,0)$, electric-field induced SHG, $\gamma(-2\omega;\omega,\omega,0)$, and third-harmonic generation, $\gamma(-3\omega;\omega,\omega,\omega)$, at third order [5]. β is a rank-3 tensor with 27 components but, as a function of the symmetry of the molecule, some of these components might be exactly zero while others might be identical (non-independent). In any case, centrosymmetric structures have zero first hyperpolarizabilities. This makes the first hyperpolarizability a suitable candidate to create molecular NLO switches, as this property is extremely sensitive to symmetry, geometry, and environment. Thus, to create a NLO switch, the two states should present much different β values: one with a large β (the "on" state) and a second with a small (or ideally null) β (the "off" state). It is therefore critical to develop a detailed understanding of the parameters that influence this quantity. Along these lines, one could rely on the two-state approximation, which has been derived using perturbation theory [6], and which relates the β response to quantities determined by the (electronic) ground state (q)and the excited state (e) that dominates the lowenergy absorption spectrum. Within that model, the first hyperpolarizability reads [7]:

$$\beta \alpha \frac{\Delta \mu_{ge} (\mu_{ge})^2}{\Delta E_{ge}^2}$$
(3)

where ΔE_{qe} is the (vertical) excitation energy, μ_{qe} is the transition dipole, and $\Delta \mu_{qe} = \mu_e - \mu_q$, with μ_q and μ_{e} the ground and excited state dipole moments. From this equation, a molecule presents a large β if i) the excitation energy is small, ii) the transition dipole is large (or the related oscillator strength, which is proportional to the area under the curve of a UV/VIS absorption band), and iii) the change of dipole moment upon excitation is large. Pushpull molecules (composed of a donor and an acceptor group linked together by a π -conjugated segment) generally check all those requirements. Yet, the donor/acceptor strengths should be tuned carefully, as predicted by a valence bond (VB) – charge transfer (CT) model, which describes the ground (and excited state) of a molecule as a certain percentage of pure VB and CT states [8]. Thus, β can be expressed as a function of $m_{CT} \in [-1,1]$ (Figure 2):

$$\beta \alpha m_{CT} (1 - m_{CT})^2 \tag{4}$$

which is the charge transfer character of the electronic ground state, ranging from -1 (valence bond state) to +1 (zwitterionic state). So, from simple mathematical analysis of Eq. 4, when m_{CT} is equal to ± 1 , β vanishes whereas it is maximum for $m_{CT} = \pm \sqrt{5/5}$.



Figure 2: Intermediate $(m_{CT} = 0)$ and limiting $(m_{CT} = -1, 1)$ forms of the VB-CT model.

However, while many one-dimensional NLO compounds have been studied in the past, octupolar architectures (see Section 4C) can also achieve large β , as originally demonstrated by Zyss [9]. Figure 3 corroborates this statement by describing the evolution of the hyper-Rayleigh scattering (HRS) β (β_{HRS}) as a function of m_{CT} The curve for the octupolar systems, which has been obtained after generalizing the VB-CT model to octupolar architectures, highlight the monotonic increase of β with m_{CT} whereas in the linear case it presents two maxima.



Figure 3: Evolution of β_{HRS} (arbitrary units) as a function of the charge transfer character of the ground state (m_{CT}) for linear (red) or octupolar (blue) model compounds [10].

1.2. From NLO molecules to NLO switches

While the above rules enable designing structures with large β ("on" state), their alteration is required to get the "off" state. Starting from a push-pull architecture, Coe proposed in 1995 to categorize the NLO switches depending on the part of the molecule that is modified by the stimulus (Figure 4) [11]. Type I and II consist of modifying the D or A moiety. They generally rely on redox or acido-basic processes, while type III encompasses a wider range of processes (e.g., thermal, photochemical, acido-basic, ...). The figure of merit of a NLO switch is the contrast of NLO responses (here, the first hyperpolarizability) between the different forms.



Figure 4: Strategies for switching the first hyperpolarizability response of a dipolar D- π -A molecule (adapted from Ref. 11). While the first two correspond to modifications of the nature of the donor or the acceptor (generally through a redox process), the last one consists of altering the π -conjugated linker.

These simple (two-state) building blocks may eventually be combined with: i) polymers, through, e.g., post-functionalization, ii) surfaces, in the form of self-assembled monolayers (so that if the stimulus is applied locally, the β is spatially dependent), or iii) other switching units, to create multi-state switches. This paper features examples of the latter. Applications for such molecules range from digital processors based on molecular gates [12] to molecular storage devices and sensors [13].

2. Objectives

Our research aims at designing efficient NLO switches by employing a multi-disciplinary approach that combines quantum chemistry (QC) calculations with synthesis and experimental characterizations. In particular, QC calculations are used to explain experimental data, to unravel structure-property relationships, and therefore to help in the design step. The rest of this article is organized as follows: the next Section briefly reviews the main calculation and experimental techniques to evaluate the first hyperpolarizability, followed by an overview of different NLO switches investigated in the Laboratoire de Chimie Théorique of the University of Namur. Emphasis is put on multistate molecular switches with three-dimensional architectures. Finally, in the last Section, conclusions and perspectives are drawn.

3. Experimental and theoretical methods

3.1. Calculations

Evaluating the first hyperpolarizability tensor elements requires: i) computing the wavefunction of the system, generally evaluated at the Density Functional Theory (DFT) levels while accounting for solvent effects (needed to compare to experimental results), and then ii) adopting the time-dependent DFT (TD-DFT) scheme [14] to evaluate the first hyperpolarizability, which is evaluated from the response of the wavefunction/ density to the perturbations created by external electric fields. All calculations reported here have been performed with the Gaussian 16 quantum chemistry package [15].

3.2. Measurement

In this article, QC results are compared to measurements obtained from the Hyper-Rayleigh Scattering (HRS) experiments (Figure 5). In this technique, the intensity of the scattered light (at this stage, without any information on the light polarization) is given by:

$$I^{2\omega}\alpha \langle \beta^2 \rangle (I^{\omega})^2 \tag{5}$$

where I^{ω} and $I^{2\omega}$ are the intensities of the incident and scattered lights, respectively, while $\langle \beta^2 \rangle$ (incoherent scattering) is an orientationalaverage of the β tensor components [4].



Figure 5: Sketch of the experimental HRS setup (from Ref. 4). X, Y and Z stand for the coordinate axes in the laboratory frame. The measurement (blue) is performed at 90° with respect to the incident beam direction. The incident light (red, ω) might be polarized horizontally or vertically ($\Psi = 0^{\circ}$ or 90°) while the vertically polarized component of the scattered light (blue, 2ω) is generally analyzed. Other combinations exist, which therefore probe different quantities (see, e.g., Ref. 16).

One generally distinguishes between two polarization combinations: VV (both lights are polarized vertically, along Z) and HV (the incident light is polarized horizontally, along X, while the scattered one, vertically). The intensity in the first combination is proportional to $\langle \beta^2_{ZZZ} \rangle$, while to $\langle \beta^2_{Zxx} \rangle$ in the second (uppercase letters indicate laboratory frame coordinates). This allows defining the two quantities extracted from the HRS measurements [17]:

$$\beta_{HRS} = \sqrt{\langle \beta_{zzz}^2 \rangle + \langle \beta_{zxx}^2 \rangle}, \text{ and } DR = \frac{\langle \beta_{zzz}^2 \rangle}{\langle \beta_{zxx}^2 \rangle}$$
 (6)

While β_{HRS} is the molecular first hyperpolarizability measured by HRS, the depolarization ratio, *DR*, gives information on the geometry and symmetry of the NLOphore. Indeed, its value is bound between 1.5 for octupolar compounds and 9 for dipolar ones.

4. Results and discussions

4.1. Oxazines as prototypical NLO switches

As a prototypical example of building blocks for multi-state switches, the performances of [1,3]-benzoxazine (simply referred to as oxazine in the rest of this text) derivatives (Figure 6) were studied in a joint theoretical and experimental investigation [18]. Those systems have been synthesized by F.M. Raymo and collaborators [19] (University of Miami), characterized by V. Rodriguez (University of Bordeaux), while quantum chemistry calculations have been

performed in UNamur, in collaboration with F. Castet at the University of Bordeaux. For this system, the switching mechanism consists in modifying the π -conjugation (Type III in Figure 4). In particular, the opening extends the conjugation between the R_1 unit and the (acceptor) indolenium unit. Therefore, large contrasts were expected. However, the nitrophenol moiety that is revealed in this process is also a prototypical NLOphore: quantum chemistry investigation was required to have a better understanding of the impact of this part on the overall response. Another interesting feature is that this opening could be triggered by two types of stimuli: light irradiation $(\mathbf{a} \rightarrow \mathbf{b})$ and change of pH ($\mathbf{a} \rightarrow \mathbf{b}^{+}$). This is therefore an example of a multi-addressable switch [20].

During this investigation, the impact of the R_1 on the β_{HRS} response of the different forms has been rationalized: owing to the acceptor character of the indolinium, a donor should be preferred to match the push-pull architecture. Thanks to that, contrasts between the closed and open forms $\beta_{HRS}(\mathbf{b}^+) / \beta_{HRS}(\mathbf{a})$, up to 15 were predicted. The quantum chemistry calculations also supplied useful insights into the impact of the nitrophenol moiety on nonlinear optical properties. In particular, the relative orientation of this moiety and R_1 might lead to an enhancement (generally observed for donor R_1) of a decrease (generally observed for acceptor R_1) of the β_{HRS} . Finally, a good agreement between QC calculations and experiment has been observed for both linear and nonlinear optical properties (Figure 7). The large



Figure 6: Derivatives of the oxazines in their closed (a), open (b) and protonated open (b^+) forms studied in Ref. 18. Different substituents were considered with an electron donor or acceptor character.



Figure 7: Experimental (extrapolated from 1064 nm results, red) versus calculated [computed at the MP2/6-311+G(d) level in chloroform (IEF-PCM), blue] β_{IRS} results for the closed (left) and open (right) forms of 4 different oxazines (here, with donor substituents), at λ =1907 nm. Results from Ref. 18.

differences for compounds 3a and $3b^+$ might be due to specific solute-solvent interactions that are not well reproduced by implicit solvation models.

4.2. Multi-state NLO switches

Following the previous investigation, a family of similar compounds were considered, within a collaboration with L. Sanguinet and coworkers (University of Angers). These are benzozalooxazolidines (simply referred to as BOXs in the rest of the text) derivatives (Figure 8), which are also multi-addressable [21]. Their NLO properties have already been addressed both experimentally and theoretically in the past, together with structure-activity relationship studied by QC investigations, in line with what has been presented above [22]. Furthermore, they can be easily combined to form multi-state switches. Indeed, to achieve systems with multiple states, one way is to covalently link the units, here thanks to different π -conjugated segments. This results in 2^n distinct states if the units are different, or n + 1 states if they are identical. One of the goals of our investigation targets a better understanding of the interplay between the states of the different units upon switching, and the linear and nonlinear optical properties.

First, the properties of diBOXs (with two identical BOX units) were assessed with three different linkers (Figure 9): a bithiophene (Bt), two 3,4-ethylenedioxythiopene (EDOT) unit (BtO) and an EDOT-thiophene-EDOT sequence (TtO). The systems can be sequentially opened with both pH change and redox reaction [24]. It should be noted that such structures can adopt different conformations (minima on the potential energy hypersurface), some with a (non-negligible or different) contributions to β_{HRS} . Therefore, in order to provide reliable β_{HRS} responses (within a statistical thermodynamics frame) using QC methods, explorations of potential energy hypersurface (mostly varying key torsion angles) were first performed to select the main



Figure 8: Top) BOX multi-addressable NLO switch family. R_1 is "ideally" an acceptor group, while R_2 a donor [22]. Bottom) example of a BOX, with its β_{HRS} at $\lambda = 1907$ nm [computed at the M06-2X/6-311+G(d) level in acetonitrile (IEF-PCM)] as a function of its closed (**C**) or open (**O**) state. Results from Ref. 23.

conformers, *i.e.*, those with the lowest energies (up to 10 for certain forms/states). Then, the first hyperpolarizabilities of these conformers were calculated at the TD-DFT level (M06-2X) and finally averaged by using the Maxwell-Boltzmann weights evaluated at the previous step.

Each of the three diBOX systems can adopt three different states, and the (non-centrosymmetric) **CO** state is the one with the largest β_{HRS} because it bears the prototypical D- π -A unit. The **CC** state presents the smallest β_{HRS} because there are no D- π -A moieties. On the other hand, the fully-open form bears two D- π -A moieties but they are completely or to a large extend organized in a centrosymmetric way so that β_{HRS} vanishes or is small. Consequently, for **diBOX-Bt**, while the (experimental, at $\lambda = 1300$ nm) contrast β_{HRS} (**CO**) / β_{HRS} (**CC**) amounts to at least 20. Moreover, the β_{HRS} (**CO**) / β_{HRS} (**CO**) ratio is of the order of 0.5 which is sufficient to distinguish the three different forms. Similar trends were predicted by quantum chemistry calculations

(Figure 9). Furthermore, if the centrosymmetry of CC and OO is enforced, as it is the case with the **BtO** linker, the contrasts between the forms get exceptionally large, but the CC and OO forms become merely indistinguishable based on their β_{HRS} responses (though their UV/visible absorption spectra are clearly different). Finally, owing its larger π -conjugated path, diBOX-TtO is the compound with the largest β_{HRS} , leading to contrasts that were predicted to be 53.1 (CC \rightarrow CO) and 5.3 (OO \rightarrow CO). It should also be noted that for all systems, the most stable conformation of **OO** adopts a A-shape, characterized by an octupolar-like DR (close to 3) in comparison to the two other forms, where DR is close to 5, characteristic of a linear NLOphore.

In a following step, more complex structures were proposed. These are two triBOXs systems, elaborated from triarylamine. They differ by the nature of the linker (Figure 10), either three identical phenylthiophene (**triBOX-s**), or three different linkers (**triBOX-u**).



Figure 9: Compounds investigated in Ref. 24, linking two identical BOXs units. They present 3 states: fully closed (CC), partially open (CO) and totally open (OO). For each state, their β_{HRS} at $\lambda = 1907$ nm, computed at the M06-2X/6-311+G(d) level in acetonitrile (IEF-PCM), are given (results from Ref. 23).



Figure 10: Structure of the symmetric (triBOX-s) and unsymmetric (triBOX-u) systems with their identical (PhTh) or different π -conjugated linkers, i.e., phenyl (Ph), biphenyl (PhPh), and phenylthiophene (PhTh), respectively [23].



Figure 11: Each arrow indicates the change in Gibbs free energy (ΔG^{θ} , in kJ/mol) of the corresponding opening reaction of **triBOX-u**, as computed at the ω B97X-D/6-311G* level in acetonitrile (IEF-PCM). The percentage of each form at a given level of opening is given in blue. Red arrows indicate the most spontaneous sequence of opening. Adapted from Ref. 25.

It should be noted that for triBOX-u, while sequential opening is possible (with both redox and pH change), the first (and second) opening leads to a statistical mixture of structures with one (and two) BOXs open, depending on the linker. For the unsymmetric compound, in collaboration with UAngers and UBordeaux, it has been demonstrated both theoretically (by the calculation of Gibbs free energies of reaction) and experimentally (by titration) [25], that the most favorable sequence of opening is $Ph \rightarrow PhTh \rightarrow PhPh$ (Figure 11). After the first opening, a mixture composed of 61% of Ph(O)-PhPh(C)-PhTh(C), 37% of Ph(C)-PhPh(C)-PhTh(O), and 2% of Ph(O)-PhPh(C)-PhTh(C) is predicted (this notation indicates that the BOX bearing the corresponding linker is closed or open). After the second opening, the percentage of each form is 87% for Ph(O)-PhPh(C)-PhTh(O), 11% for Ph(O)-PhPh(O)-PhTh(C), and 2% of Ph(C)-PhPh(O)-PhTh(O).

Their β_{HRS} values were predicted in Ref. 23 using TD-DFT (ω B97X-D). For both symmetric and unsymmetric systems, the β_{HRS} are of the same order of magnitude for all states bearing at least one open BOX (CCO, COO, or OOO). However, their DRs follow a prototypical evolution: at the first opening (CCC \rightarrow CCO), both triBOXs go from octupolar to linear, since the response becomes dominated by one BOX unit. Then, the octupolar character increases with the second opening (CCO \rightarrow COO), owing to a Λ -shape (two active units). Finally, the third opening (COO \rightarrow **OOO**) restores the octupolar character. Thus, the DRs provide an additional way to differentiate between the forms, so that both systems result in a switch with 4 different states.

4.3. Octupolar NLO switches

Thanks to a suggestion by B. J. Coe, an octupolar switch containing 6 Ruthenium (II) amine centers has finally been studied (Figure 12). In pairs, these Ru centers are conjugated thanks to bipyridine moieties, forming 3 "arms" in a D_3 fashion, linked together by a zinc (II) core. Since the oxidation state of Ru can be II or III, this constitutes a (type I, Figure 4) redox-triggered NLO switch.



Figure 12: The octupolar NLO switch containing 6 Ruthenium centers, proposed by B. J. Coe and studied in Ref. 10. Here, only the fully reduced (all Ru^{III}) or fully oxidized (all Ru^{III}) systems are considered. The first (second) resulting charge (top right) is the one of the fully reduced (oxidized) system.

To attain a better understanding of the global response of this system, compounds containing one or two arms were also considered, forming one-dimensional and Λ -shape systems, respectively (Figure 13). Such systems, however, present β_{HRS} that are 3 times larger than their octupolar counterpart, as calculated at the TD-DFT level (B3P86). Furthermore, the charge transfers responsible for the β response (Eq. 2) has been studied. It originates mostly from metal(Ru)-to-ligand charge transfers. Furthermore, the oxidation $(Ru^{II} \rightarrow Ru^{III})$ leads to a strong decrease of β_{HRS} , which has been attributed to: i) reduction of the π -conjugation, ii) a loss of donor character of the ruthenium, together with iii) an inversion of the charge transfer direction, as revealed using a new scheme to describe variation of the electron density upon excitation for highly symmetrical compounds such as those studied here. Therefore, good contrasts [with $\beta_{HRS}(Ru^{II}) / \beta_{HRS}(Ru^{III}) > 3$ at 1064 nm] were predicted for all architectures. In addition, our QC calculations and models have shown that, to improve such octupolar contrasts, a specific balance between the donor/acceptor strength and the length of the π -conjugated path is required.



Figure 13: The corresponding Λ -shape (left) and one-dimensional (right) systems studied in Ref. 10. The first (second) resulting charge (top right) is the one of the fully reduced (oxidized) system.

5. Conclusions and perspectives

In my Ph.D. thesis, different NLO switches have been studied. Oxazines and BOXs are the basic building blocks, on which different structureproperty relationships have been derived. With the latter, multi-state switches containing two or three different BOX units have been build and fully characterized. It has been demonstrated, owing to sequential switching, that the different states can be differentiated thanks to their NLO properties ($\beta_{_{HRS}}$ or their DR). Furthermore, while the one-dimensional architecture is widely featured in the literature, other possibilities of design have been considered: A-shape and octupolar structures, which might also lead to large β_{HRS} and interesting contrasts (Figure 3). Altogether, these provide five examples where quantum chemistry helps rationalizing the results, providing insights and design rules. It also demonstrates the close interplay between theory and experiment in a multidisciplinary framework.

The challenges that remain to be faced are multiple. One is the quest for *accuracy*, with more complete description of the first hyperpolarizability response, either by considering additional effects (such as the inclusion of vibrational contributions [26]) or by using more accurate quantum chemistry methods. One of the most difficult areas is the inclusion of the *environment* effects in hyperpolarizability calculations since the implicit treatment is sometimes not enough to grasp specific effects such as hydrogen bonds. It is especially important if one wants to tackle complex environments, such as self-assembled monolayers [27], NLOphores embedded in cell membranes [28] or in a polymer matrix [29]. Another challenge is the *design* of new and improved NLO materials, such as biological [30] or solid-state [31] compounds and NLO switches, such as with octupolar architectures. This field would probably benefit from more data mining or machine learning insights [32].

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