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### **Two-Way Molecular Switches with Large Nonlinear Optical Contrast**

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**Abstract:** To optimize the nonlinear optical (NLO) contrast, a series of indolinooxazolidine derivatives with electron-withdrawing substituents in the *para* position on the indolinic residue have been synthesized. Their linear and nonlinear optical properties have been characterized by UV-visible absorption and hyper-Rayleigh scattering measurements, as well as by ab initio calculations. The two-way photo- or pH-triggered switching mechanism has been demonstrated by comparing the absorption spectra of the zwitterionic

#### Introduction

In recent years, the development of optoelectronic devices for optical information transport and storage has motivated the design of molecular systems with commutable nonlinear optical (NLO) properties.<sup>[1]</sup> Among them, organic photochromic compounds are targeted as potential candidates for integration into functionalized materials that combine the unique electronic and optical properties of conjugated mole-

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and protonated open forms (POF). Hyper-Rayleigh measurements have revealed that the second-order NLO contrast between the closed indolinooxazolidine and the open  $\pi$ -conjugated colored forms remain very large upon substitution. Theory and meas-

**Keywords:** ab initio calculations • hyper-Rayleigh measurements • indolinooxazolidine derivatives • molecular switches • nonlinear optics urements show that for the POFs the amplitude of the first hyperpolarizability follows the Hammett parameters of the withdrawing groups. However, because the measurements are performed in resonance, to recover this behavior, elaborate procedures including homogeneous and inhomogeneous broadenings, as well as single-mode vibronic structures are necessary to extrapolate to the static limit.

cules with the typical advantages of organic materials, such as tailored synthesis, easy processing, and low cost. The efficiency of such NLO switches results from a subtle compromise between several aspects, which are sometimes contradictory. First, the hyperpolarizability ( $\beta$ ) of the ON state must be as large as possible, whereas it should ideally be zero for the OFF state, in order to maximize the contrast of the property. Second, the two forms must be stable, energetically equiprobable, and have a significant activation barrier to avoid thermally activated reverse reactions. Third, the geometry changes in the molecule during the transformation should be limited to obtain a commutation as quickly as possible, as well as the possibility of switching in the solid state.

Within this framework, the NLO properties of keto/enol systems have been extensively studied by experimental and theoretical means, owing to, in particular, their ability to commute in the crystalline state, by using either light or temperature.<sup>[2]</sup> Hence, Sliwa and co-workers have recently highlighted that the small difference between the N-(3,5-di-*tert*-butylsalicylidene)-2-aminopyridine and N-(3,5-di-tert-butylsalicylidene)-4-aminopyridine isomers lead to very different switching mechanisms. In the latter, the switching mechanism is triggered by light, whereas in the former the trigger





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is thermochromic. This difference has been related to the relative position of the pyridine ring, which, for the former but not for the latter, is in the same plane as the benzene ring with the enol function. However, the relatively small NLO responses of the two forms ( $\chi^{(2)}$ , the second-order non-

linear susceptibility, which is the macroscopic equivalent of  $\beta$ , is only a few times that of urea crystals) and their weak NLO contrast upon switching limit their potential applica-Nitrobenzylpyridines tions. represent another class of compounds that display phototautomerization and thermoswitchable behavior, which leads to substantial variations of the quadratic NLO response.<sup>[3]</sup> Dithiazolylethenebased derivatives incorporating

based derivatives incorporating a push–pull structural motif<sup>[4]</sup> have been investigated for their photoswitchable NLO properties. Spiropyran/merocyanine systems have also been investigated and ab initio calculations predict large hyperpolarizability contrasts when appropriate substitutions by donor and acceptor groups are realized.<sup>[5]</sup> In fact, spiropyran- and spirooxazine-derivatives have already been incorporated in poly(methyl methacrylate) (PMMA) films to obtain materials that exhibit both photochromism and photoswitchable NLO responses.<sup>[6]</sup> Zinc(II) complexes that contain a pair of dithienylethene moieties have also demonstrated photoswitchable activity associated with a variation of the  $\mu\beta$  contrast by up to a factor of 20.<sup>[7]</sup>

A large contrast of the first hyperpolarizability has also been combined with other mechanisms of commutation, in particular, those based on redox or protonation/deprotonation reactions. Reversible redox-switching NLO behaviors have been investigated in detail in Ru<sup>II</sup>- and Fe<sup>II</sup>-based chromophores,<sup>[8]</sup> as well as in substituted helicenes<sup>[9]</sup> and in stacks of tetrathiafulvalene.<sup>[10]</sup> In the case of commutations triggered by the pH, 6s-cis-retinal and its 13-cis isomer,<sup>[11]</sup> as well as pyridine-based octupolar systems<sup>[12]</sup> have shown large  $\beta$  contrasts. Moreover, other studies have shown that large NLO variations can be triggered by an electric field, as in the case of a push-pull bisboronate chromophore,<sup>[13]</sup> or simply by doping with different alkaline atoms (which is a kind of redox reaction) as in the case of polyacetylene.<sup>[14]</sup> In this last case, the switching property is the second hyperpolarizability  $(\gamma)$ ; the third-order NLO response.

Substituted diarylethenes have been found to exhibit photoswitching-based contrasts of both  $\beta$  and  $\gamma$ .<sup>[15]</sup> Applying a magnetic field to induce spin transition is another means of changing the NLO responses, but, to date, this has been mostly used in the case of  $\gamma$  compounds.<sup>[16]</sup>

As systems of interest in this context, several years ago we presented a new family of organic molecular switches based on the association of an indolinooxazolidine core with various styrylic residues.<sup>[17]</sup> The switching mechanism, which consists of light-induced cleavage of the  $\sigma$ -C–O bond on the oxazolidine moiety of the closed form (CF) that leads to a zwitterionic open form (OF; Scheme 1), is associated with a large variation in the NLO response. In particular, a con-



Scheme 1. Photo/acidochromic equilibrium for the dimethylaminophenylethylenylindolino[2,1-b]oxazolidine derivatives. The Cartesian frame used in the calculations is also displayed.

trast of about 10 is observed in the first hyperpolarizability associated with the second harmonic generation (SHG) process, making these compounds highly efficient switchable frequency doublers. Another interesting property of these systems lies in the fact that the reversible transformation may be triggered either by light or pH variations. Indeed, acid addition generates a protonated open form (POF), the absorption spectrum of which is perfectly superimposable on that of the zwitterionic form.

The efficiency of these compounds in terms of NLO contrast between the closed and open forms is currently under optimization within an iterative approach that combines molecular synthesis, hyper-Rayleigh scattering (HRS) measurements, and theoretical simulations. Structure-property relationships deduced from the latter constitute a guide for the synthesis of new compounds, and optical characterizations, in turn, highlight the qualities and deficiencies of the computational methods. Optimal systems could then be computationally designed by performing structural modifications, which aimed to improve the electron conjugation within the open forms, and these systems could be used to plan further syntheses. After investigating the impact of the styrylic residue linked to the indolinic core, and selecting p-N,N-dimethylaminophenyl as the most efficient donor group, the effect of replacing the indolinic unit by a benzimidazolic or a benzothiazolic residue was addressed, with a view to increase the number of delocalizable electrons in the system.<sup>[18]</sup> Very high  $\beta$  values were indeed obtained in the POF with the benzothiazolic moiety, but they were accompanied by a loss of stability of the light-induced OF. Preliminary theoretical investigations also predicted that a significant enhancement of the NLO response in the POF should also be achieved by grafting electron-attracting substituents onto the indolinic residue.<sup>[19]</sup> These two ways (substituents and linkers) for designing more efficient switchable NLO materials follow the general strategy that was established several years ago to maximize the NLO responses of organic molecules and leads to rationalizing  $\beta$  in terms of geometrical parameters, charge distribution, excited-state properties, donor/acceptor strengths, electronic versus vibrational contributions, and effects of the surroundings. Note, however, that the situation is more complex for switches because, as discussed above, in addition to the NLO responses and contrasts, the switching characteristics need to be optimized. This paper focuses on the substituent aspect and reports on 1) the synthesis of a series of compounds with an aldehyde, bromine, or nitro as electron-attracting groups on the indolinic moiety, 2) the measurement of their linear and nonlinear optical properties, and 3) the interpretation of these results in light of quantum chemical calculations.

#### **Experimental and Computational Details**

**Synthesis**: Indolino[2,1-b]oxazolidines are usually obtained by using 2,3,3-trialkylindolenines as starting materials. These compounds are then quaternarized with 2-iodoethanol to afford 1-(2-hydroxyethyl)-2,3,3-trialkylindoleninium iodides, which are subsequently treated with aromatic aldehydes in ethanol, and the process is completed by a basic treatment with sodium hydroxide or *N*-methylmorpholine. This three-step synthetic route to form the desired two-way targets has been previously described for compound  $\mathbf{1}$ .<sup>[17]</sup>

**5-Bromo-2,3,3-trimethylindolenine (2a)**: A mixture of 4-bromophenylhydrazine hydrochloride (1.0 g, 4.47 mmol) and 3-methyl-2-butanone (0.6 mL, 5.61 mmol) was dissolved in glacial acetic acid (15 mL), and then heated under reflux for 8 h under nitrogen. The solvent was evaporated in vacuo. The residue was dissolved in  $CH_2Cl_2$  (30 mL) and washed with 10% aqueous Na<sub>2</sub>CO<sub>3</sub> (2×30 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, and the solvent was evaporated to afford **2a** as a brown oil (0.96 g, 90%). The product was used in the next reaction without further purification. <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>):  $\delta$ =7.38 (m, 3H; ArH), 2.25 (s, 3H; -CH<sub>3</sub>), 1.28 ppm (s, 6H; -CH<sub>3</sub>).



1-(2-Hydroxyethyl)-5-bromo-2,3,3-trimethylindoleninium iodide (2b): A mixture of 2a (1.5 g, 6.3 mmol) and 2-iodoethathol (0.74 mL, 9.5 mmol) was dissolved in toluene (10 mL) and heated under reflux for 8 h under nitrogen before the medium was allowed to cool and washed with Et<sub>2</sub>O( $3 \times 10$  mL). The precipitate was filtered and washed with Et<sub>2</sub>O/EtOH (10:0.1 mL) to afford 2b as a brown solid (4.7 g, 91%). <sup>1</sup>H NMR (250 MHz, [D<sub>6</sub>]DMSO):  $\delta$ =8.19 (s, 1H; ArH), 7.93 (d, J=8.5 Hz, 1H; ArH), 7.84 (d, J=8.6 Hz, 1H; ArH), 4.87 (s, 1H; -OH), 4.58 (t, J=4.6 Hz, 2H; -NCH<sub>2</sub>-), 3.84 (t, J=4.6 Hz, 2H; -OCH<sub>2</sub>-), 2.81 (s, 3H; -CH<sub>3</sub>), 1.56 ppm (s, 6H; -CH<sub>3</sub>).



1-(2-Hydroxyethyl)-5-bromo-2-[2-(4-dimethylaminophenyl)ethenyl]-3,3trimethylindoleninium iodide (2 c): A mixture of 2b (2.56 g, 6.24 mmol) and 4-dimethylaminobenzaldehyde (0.93 g, 6.24 mmol) was dissolved in absolute EtOH (10 mL) under nitrogen. *N*-Methylmorpholine (0.7 mL, 6.24 mmol) was added to the solution under reflux over 60 min. After the addition was complete, the reaction was maintained at reflux for 8 h before the medium was allowed to cool, concentrated in vacuo, and the residue was purified by column chromatography (SiO<sub>2</sub>; CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>OH, 9:1) to afford 2c as a purple solid (2.1 g, 62 %).



10-[2-(4-Dimethylaminophenyl)ethenyl]-9,9-trimethyl-7-bromoindolino

[2,1-b]oxazolidine (2): A mixture of 2c (1.5 g, 2.8 mmol) and NaOH (0.4 g, 10.0 mmol) was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (40 mL) and stirred at ambient temperature overnight. The solution was then concentrated in vacuo, and the residue was washed with water (2×25 mL) and hexane (20 mL) to afford 2 as a purple solid (0.9 g, 70%). <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>):  $\delta$ =7.33–7.16 (m, 4H; ArH), 6.79–6.64 (m, 4H; ArH, =CH-), 6.38 (d, *J*= 15.9 Hz, 1 H; =CH-) 3.77–3.46 (m, 4H; -CH<sub>2</sub>-), 2.97 (s, 6H; -NCH<sub>3</sub>), 1.40 (s, 3H; -CH<sub>3</sub>), 1.15 ppm (s, 3H; -CH<sub>3</sub>); MS (EI) *m/z* (%): 413 (48), 411 (51), 383 (26), 381 (27), 254 (97), 252 (100); elemental analysis calcd (%) for C<sub>22</sub>H<sub>25</sub>N<sub>2</sub>OBr: C 63.93, H 6.10; found: C 64.26, H 5.87.



10-[2-(4-Dimethylaminophenyl)ethenyl]-9,9-trimethylindolino[2,1-b]oxazolidine-7-carboxaldehyde (3): nBuLi (2.5 M) in hexane (0.60 mL, 1.50 mmol) was added dropwise to a stirred solution of 2 (0.50 g, 1.21 mmol) in THF (15 mL) at -78 °C over 10 min. After a further 10 min dry DMF (0.12 mL, 1.55 mmol) was added swiftly, and the reaction mixture was allowed to reach room temperature over 1 h. The reaction continued for 30 min before water (1 mL) was added. Most of the solvent was removed in vacuo and CH<sub>2</sub>Cl<sub>2</sub> (15 mL) and water (10 mL) were added. The aqueous phase was extracted by using CH<sub>2</sub>Cl<sub>2</sub> (2× 10 mL) before the organic phase was collected, dried and concentrated to afford compound 3 as brown solid (0.37 g, 83 %). <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>):  $\delta = 9.84$  (s, 1H; -CHO), 7.69 (d, J = 8.25 Hz, 1H; ArH), 7.63 (s, 1H; ArH), 7.35 (d, J=8.25 Hz, 1H; ArH), 6.87-6.68 (m, 4H, ArH; = CH-), 6.00 (d, J=15.9 Hz, 1H; =CH-), 3.82-3.55 (m, 4H; -CH<sub>2</sub>-), 2.97 (s, 6H; -NCH<sub>3</sub>), 1.46 (s, 3H; -CH<sub>3</sub>), 1.17 ppm (s, 3H; -CH<sub>3</sub>); MS (EI) m/z (%): 362 (31), 332 (26), 202 (100); elemental analysis calcd (%) for C<sub>23</sub>H<sub>26</sub>N<sub>2</sub>O<sub>2</sub>: C 76.21, H 7.23; found: C 75.96, H 7.07.

5-Nitro-2,3,3-trimethylindolenine (4a): A mixture of 4-nitrophenylhydrazine (containing 30% H<sub>2</sub>O, 3.0 g, 13.7 mmol), 3-methyl-2-butanone (1.91 mL, 17.8 mmol), and H<sub>2</sub>SO<sub>4</sub> (2 mL) was dissolved in glacial acetic acid (20 mL) and then heated under reflux for 8 h under nitrogen. After it was cooled to room temperature, the solvent was evaporated in vacuo before the residue was dissolved in  $CH_2Cl_2$  (30 mL), washed with 10%

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aqueous Na<sub>2</sub>CO<sub>3</sub> (2×30 mL), dried with Na<sub>2</sub>SO<sub>4</sub>, and the solvent was removed in vacuo. The crude product was obtained as a black solid, which was purified by column chromatography (SiO<sub>2</sub>; CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>OH, 60:1) to afford **4a** as a yellow solid (2.05 g, 73%). <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>):  $\delta$ =8.24 (d, *J*=8.3 Hz, 1H; ArH), 8.15 (s, 1H; ArH), 7.60 (d, *J*=8.3 Hz, 1H; ArH), 2.35 (s, 3H; -CH<sub>3</sub>), 1.37 ppm (s, 6H; -CH<sub>3</sub>).



**1-(2-Hydroxyethyl)-5-nitro-2,3,3-trimethylindoleninium iodide (4b)**: A mixture of **4a** (0.9 g, 4.41 mmol) and 2-iodoethanol (0.52 mL, 6.62 mmol) was dissolved in toluene (8 mL) and heated under reflux for 8 h under nitrogen, before the medium was allowed to cool and was washed with Et<sub>2</sub>O ( $3 \times 10$  mL). The precipitate was filtered and washed with Et<sub>2</sub>O/EtOH (10:0.1 mL) to afford **4b** as a black solid (0.98 g, 59%). <sup>1</sup>H NMR (250 MHz, CD<sub>3</sub>CN):  $\delta$ =8.60 (s, 1H; ArH), 8.49 (d, *J*=8.2 Hz, 1H; ArH), 8.00 (d, *J*=8.5 Hz, 1H; ArH), 4.59 (s, 2H; -NCH<sub>2</sub>-), 4.03 (s, 2H; -OCH<sub>2</sub>-), 2.88 (s, 3H; -CH<sub>3</sub>), 1.67 ppm (s, 6H; -CH<sub>3</sub>).



#### 10-[2-(4-Dimethylaminophenyl)ethenyl]-9,9-trimethyl-7-nitroindolino-

[2,1-b]oxazolidine (4): A mixture of 4b (0.50 g, 1.33 mmol) and 4-dimethylaminobenzaldehyde (0.24 g, 1.61 mmol) was dissolved in absolute EtOH (10 mL) under nitrogen. N-Methylmorpholine (0.16 mL, 1.46 mmol) was added over 60 min into the solution under reflux. After the end of the addition, the solution was maintained at reflux for 8 h. The medium was then allowed to cool and was concentrated in vacuo before the residue was purified by column chromatography (SiO2;  $CH_2Cl_2/CH_3OH,\ 25{:}1)$  to afford 4 as a yellow solid (0.34 g, 68%). <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>):  $\delta = 8.13$  (d, J = 7.6 Hz, 1H; ArH), 7.96 (s, 1H; ArH), 7.35 (d, J=8.3 Hz, 2H; ArH), 6.80-6.69 (m, 4H, ArH; =CH-), 5.98 (d, J=15.9 Hz, 1H; =CH-), 3.83-3.55 (m, 4H; -CH<sub>2</sub>-), 2.98 (s, 6H; -NCH<sub>3</sub>), 1.47 (s, 3H; -CH<sub>3</sub>), 1.19 ppm (s, 3H; -CH<sub>3</sub>);  $^{13}C$  NMR  $(300 \text{ MHz}, \text{ CDCl}_3): \delta = 157.3, 150.6, 142.6, 141.1, 133.0, 127.8, 125.1,$ 124.2, 119.1, 118.9, 112.3, 111.1, 110.3, 63.5, 49.4, 47.4, 40.4, 28.1, 20.2 ppm; MS (EI) m/z (%): 379 (22), 349 (16), 219 (100); elemental analysis calcd (%) for C<sub>22</sub>H<sub>25</sub>N<sub>3</sub>O<sub>3</sub>: C 69.64, H 6.64; found: C 69.98, H 6.27.

**HRS experiments**: HRS experiments were performed on dilute solutions (between  $10^{-4}$  and  $10^{-6}$  M) in acetonitrile or chlorobenzene, which correspond to typical concentrations used to check the linear dependency of absorbance and to determine the extinction coefficient  $\varepsilon$ . In this NLO scattering technique, the intensity of the incoherent scattered light at the second harmonic frequency of an IR Nd:YAG pulsed laser (nanosecond regime) is used to determine the first hyperpolarizability  $\beta$ . The scattered harmonic light is related to quadratic products between components of the molecular  $\beta$  tensor that correspond to isotropic averaging over the molecular motions (noninteracting molecules). Assuming pseudo- $C_{2\nu}$  mo-





bining measurements in HV (horizontally polarized incident light and vertically polarized scattered light) and VV (vertically polarized incident and scattered lights) configurations. More details about the procedure can be found in reference [17].

Calculations: The molecular structures were optimized in vacuo at the density functional theory (DFT) level by using the B3LYP hybrid exchange-correlation functional and the 6-31G(d) basis set. Time-dependent DFT (TDDFT) calculations were carried out at the same level of theory to determine the vertical excitation energies  $(\Delta E_{ge} = \hbar \omega_{ge} = \hbar (\omega_e - \omega_g))$  and the excited-state properties of the compounds. This approach provides UV/Vis spectra in good qualitative agreement with respect to experimental data for both excitation energies and oscillator strength.<sup>[20]</sup> The time-dependent Hartree-Fock (TDHF)<sup>[21]</sup> and the coupled-perturbed Hartree-Fock (CPHF) schemes, respectively, were applied to obtain dynamic and static first hyperpolarizabilities by using an incident wavelength of 1064 nm. Solvent effects were included by using the polarizable continuum model within the integral equation formalism (IEFPCM)<sup>[22]</sup> by taking  $\varepsilon_0$ =36.640 ( $\varepsilon_{\infty}$ =1.806) for acetonitrile, and  $\varepsilon_0 = 5.621$  ( $\varepsilon_{\infty} = 2.320$ ) for chlorobenzene. The cavity of the solute is built up by using atomic radii from the universal force field (UFF) force field by placing individual spheres around each heavy and hydrogen atom. To account for correlation effects, the second-order Møller-Plesset (MP2) method was employed in combination with a finite field (FF) procedure,<sup>[23]</sup> implying a Romberg scheme to improve the accuracy of the numerical derivatives.<sup>[24]</sup> FF/MP2 calculations have already provided reli-able first hyperpolarizabilities for organic chromophores.<sup>[17-18]</sup> Moreover, in many cases the MP2 method recovers the largest part of the electron correlation effects, as estimated from higher-order methods.<sup>[25]</sup> To account for frequency dispersion at the MP2 level, the multiplicative correction scheme was applied.<sup>[26]</sup> It consists of multiplying the static MP2 value by the TDHF/CPHF ratio:

$$\beta_{\rm MP2}(-2\omega;\omega,\omega) \approx \beta_{\rm MP2}(0;0,0) \times \frac{\beta_{\rm TDHF}(-2\omega;\omega,\omega)}{\beta_{\rm CPHF}(0;0,0)} \tag{1}$$

DFT methods were not used to compute  $\beta$  because conventional DFT methods have demonstrated serious drawbacks.<sup>[27]</sup> Improved approaches, such as optimized effective potential for exact exchange (OEP-EXX) and long range (LR)-DFT have recently appeared, but still need to be optimized.<sup>[28]</sup> For example, we have recently compared the NLO responses of anil derivatives calculated by using DFT (employing the B3LYP exchange-correlation functional) to those determined by using the CPHF and FF/MP2 methods.<sup>[2e]</sup> It appears that FF Kohn–Sham calculations provide  $\beta$  values that are sometimes in good agreement with the MP2 results, sometimes close to the CPHF values, and also sometimes far away from both CPHF and MP2 results. Moreover, the solvent effects on the first hyperpolarizabilities are determined by inserting  $\beta_{\text{TDHF}}(-2\omega; \omega, \omega)$  or  $\beta_{\text{MP2}}(0;0,0)$  quantities, which are evaluated within the IEFPCM method, into Equation (1).

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lecular symmetry, in which the mole-

cule lies in a mean (xz) plane (with z as the two-fold symmetry axis), and assuming Kleinman symmetry, two in-

Comparisons between experimental measurements and theoretical estimates are made by considering the square root of the HRS intensity for plane-polarized incident light observed perpendicularly to the propagation direction, as well as the associated depolarization ratios, as shown in Equation (2):

$$\beta_{\rm HRS}(-2\omega;\omega,\omega) = \sqrt{\left\{ \left< \beta_{ZZZ}^2 \right> + \left< \beta_{ZXX}^2 \right> \right\}} \quad DR = \frac{I_{\rm VV}^{2\omega}}{I_{\rm HV}^{2\omega}} = \frac{\left< \beta_{ZZZ}^2 \right>}{\left< \beta_{ZXX}^2 \right>} \tag{2}$$

in which  $\langle \beta_{ZZZ}^2 \rangle$  and  $\langle \beta_{XZZ}^2 \rangle$  correspond to orientational averages of the  $\beta$  tensor and are calculated without assuming Kleinman's conditions (full expressions of these terms can be found in reference [29]). All calculations were performed by using Gaussian 03,<sup>[30]</sup> as well as homemade codes to carry out the FF–Romberg differentiation scheme.

### **Results and Discussion**

**Linear optical properties**: The linear optical properties of the compounds are given by UV-visible absorption spectroscopy. As already mentioned, the switching mechanism is two-way for all compounds: the absorption spectra arising from UV irradiation and acidic addition are totally superimposable, indicating that photo-induced and acido-generated colored forms adopt similar structures. Total back photobleaching could be achieved by irradiating the zwitterionic OFs with an appropriate visible light, or upon base addition to the POFs. The experimental data discussed in this section were obtained by considering the pH-induced switching process. The absorption properties of the POF molecules were obtained by addition of a large excess of acetic acid to CF molecules. Experimental and theoretical results for compounds **1–4** are gathered in Tables 1 and 2, respectively. For

Table 1. Absorption maxima ( $\lambda_{max}$ , nm), transition energies ( $\Delta E_{ge}$ ) and molar extinction coefficient ( $\varepsilon$ , Lmol<sup>-1</sup>cm<sup>-1</sup>) of substituted indolinooxazolidine derivatives in their CFs and POFs measured in acetonitrile and chlorobenzene.

	$\lambda_{\rm max}$	$\Delta E_{\rm ge}  [{\rm eV}]$	$\varepsilon (\lambda_{\max})$	$\lambda_{\max}$	$\Delta E_{\rm ge}  [{\rm eV}]$	$\varepsilon (\lambda_{\max})$
	CF in acetonitrile		CF in chlorobenzene			
1(R = H)	298	4.16	27000	302	4.10	18000
2(R = Br)	300	4.13	30 000	306	4.05	23 000
3(R = CHO)	310	4.00	30 000	312	3.97	32 000
$4(R = NO_2)$	302	4.10	23 000	306	4.05	12500
	332	3.73	20 000	336	3.69	11000
	POF	in acetonitril	e	POF in chlorobenzene		
1(R = H)	544	2.28	93 000	554	2.24	56500
2(R = Br)	546	2.27	13 0000	564	2.20	74000
3(R = CHO)	548	2.26	96 000	562	2.21	80 000
$4(R = NO_2)$	582	2.13	106000	592	2.09	42 500

all compounds, a good agreement between the experimental and simulated excitation spectra is obtained, as illustrated in Figure 1 for compounds 1 and 4 in acetonitrile. Indeed, despite the systematic blueshift observed in the simulated spectra of the POF, the relative position of the low-energy charge-transfer bands is well reproduced within the sets of substituted CFs and POFs, as well as their relative intensities in the POF and closed forms.

Table 2. Absorption maxima ( $\lambda_{ge}$ , nm), transition energies ( $\Delta E_{ge}$ ), oscillator strength ( $f_{ge}$ ), and electronic transitions implied in the dominant lowenergy charge-transfer states calculated at the PCM/B3LYP/6-31G(d) level.

	$\lambda_{\mathrm{ge}}$	$\Delta E_{\rm ge}  [{\rm eV}]$	$f_{\rm ge}$	$\lambda_{\rm ge}$	$\Delta E_{\rm ge}  [{\rm eV}]$	$f_{\rm ge}$
	CF in	acetonitrile		CF in	chlorobenzei	ne
1(R = H)	304	4.08	0.923	304	4.07	0.970
	280	4.43	0.203	280	4.43	0.206
2(R = Br)	305	4.06	0.988	306	4.05	1.035
	280	4.42	0.194	280	4.42	0.152
3(R = CHO)	308	4.02	1.337	309	4.01	1.384
	294	4.22	0.152	294	4.22	0.169
	280	4.44	0.119	279	4.44	0.099
$4 (R = NO_2)$	354	3.50	0.583	351	3.53	0.617
	306	4.05	0.747	307	4.03	0.776
	280	4.43	0.159	280	4.43	0.152
	POF	POF in acetonitrile		POF in chlorobenzene		
1(R = H)	474	2.62	1.523	483	2.57	1.568
2(R = Br)	481	2.58	1.625	489	2.54	1.670
3(R = CHO)	486	2.55	1.675	492	2.52	1.723
$4(R = NO_2)$	503	2.46	1.500	505	2.46	1.643



Figure 1. Absorption spectra of compounds 1 (top, R = H) and 4 (bottom,  $R = NO_2$ ) in their CFs (—) and POFs (—) measured in acetonitrile. The simulated spectra (dotted lines) have been calculated at the IEFPCM/B3LYP/6-31G(d) level and each transition has been enlarged by using a Gaussian function that has a full width at half maximum (FWHM) value of 0.3 eV for the POF and 0.5 eV for the CF. The intensities at the absorption maxima in the experimental and simulated spectra were adjusted to coincide in the POF.

# **FULL PAPER**

In all POFs, the most absorbing charge-transfer excited state is dominated by a  $\pi \to \pi^*$  transition between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), with these two MOs being delocalized over the whole molecule (Figure 2). The



Figure 2. Molecular orbitals of compound 4  $(R=NO_2)$  in its closed and protonated open forms involved in the main UV-visible electronic transitions, as calculated at the PCM/B3LYP/6-31G(d) level in acetonitrile.

maximum absorption wavelengths are significantly impacted by the nature of the substituent, and range in acetonitrile from 544 nm for the nonsubstituted compound **1** to 582 nm for compound **4**, which includes the most electron-withdrawing group. When changing the solvent to chlorobenzene, the maximum absorption band is redshifted by 10–18 nm for all compounds. Although slightly underestimated, this redshift is well reproduced by the TDDFT calculations.

In their CFs, the four compounds have absorption maxima at about 4 eV and the associated oscillator strengths depend on the substituent R, especially in chlorobenzene. The spectrum of compound 4 displays a characteristic second band of similar intensity at 3.7 eV, which is well reproduced by the calculations. The lowest-energy absorption band is dominated by a [HOMO-1-LUMO] transition (localized on the oxazolidine moiety), whereas the peak at 4 eV is mainly associated with [HOMO $\rightarrow$ LUMO+1] (localized on the dimethylaminophenyl part, as shown in Figure 2). In compound 3 (R = CHO), the absorption maximum at 4 eV is also associated with a [HOMO $\rightarrow$ LUMO+ 1] transition, whereas this band is dominated by the [HOMO $\rightarrow$ LUMO] transition in compounds 1 (R=H) and 2 (R = Br). For compounds 1–3, the MOs involved in the transition at 4 eV are fully localized on the dimethylaminophenyl moiety. Besides, the impact of the solvent is smaller than for the OFs, with the redshift of the main band being observed between 2-6 nm.

As shown in Table 1, the magnitude of the experimental absorption intensity of the CF compounds is weakened when going from acetonitrile to chlorobenzene, except for compound **3**, which has the aldehyde group, for which the molar extinction coefficients are similar in the two solvents. This effect seems to be generalized for all POFs because in chlorobenzene the magnitude of the absorption is always smaller than in acetonitrile. This result is not reproduced by the calculations, which predict oscillator strengths in chlorobenzene in the same range as, or slightly higher than, those in acetonitrile. Interactions between chromophore molecules that lead to the formation of J aggregates, or between the chromophore and chlorobenzene, can explain such differences between theory and experiment.

#### Nonlinear optical properties

*Experimental results*: Table 3 reports the longitudinal ( $\beta_{zzz}$ ), transverse ( $\beta_{zxx}$ ), and hyper-Rayleigh ( $\beta_{HRS}$ ) hyperpolarizabilities, as well as the depolarization ratios (DR) for com-

Table 3. Longitudinal ( $\beta_{zzz}^{1064}$ ), transverse ( $\beta_{zxx}^{1064}$ ), and HRS ( $\beta_{HRS}$ ) hyperpolarizabilities, depolarization ratios (DRs); and normalized efficiencies ( $\tau$ , in parentheses), obtained from HRS measurements at  $\lambda = 1064$  nm. All  $\beta$  values are given in atomic units ( $1 \text{ au} = 3.62 \ 10^{-42} \text{ m}^4 \text{ V}^{-1} = 3.2063 \times 10^{-53} \text{ C}^3 \text{ m}^3 \text{ J}^{-2} = 8.641 \times 10^{-33} \text{ esu}$ ).

	DR	$ eta_{zzz}^{1064} $	$\beta_{zzz}^{1064}/\beta_{zxx}^{1064}$	$\beta_{ m HRS}$		
		CF in acetonitrile				
1 (R = H)	4.1	6000	-0.096	2200		
2(R=Br)	4.0	4700	+0.109	2300		
3(R = CHO)	3.8	16800	-0.136	5600		
$4 (R = NO_2)$	4.4	12700	-0.069	5100		
		POF	in acetonitrile			
1 (R = H)	4.0	117800	-0.110	41 600 (94.8)		
2(R=Br)	4.0	175000	-0.110	60500 (96.2)		
3(R = CHO)	3.6	84000	-0.155	26600 (79.1)		
$4 (R = NO_2)$	3.7	110000	-0.142	35700 (85.7)		
		POF in	n chlorobenzen	e		
1 (R = H)	4.5	-50000	-0.056	19100		
2(R=Br)	4.2	-114600	-0.085	41 600		
3 (R = CHO)	4.1	-49000	-0.093	17700		
$4 (R = NO_2)$	3.8	-67000	-0.132	26 500		

pounds 1–4 issued from HRS measurements at 1064 nm. The normalized efficiency of the HRS hyperpolarizability, defined as  $\tau = [\beta_{\text{HRS}}(\text{POF}) - \beta_{\text{HRS}}(\text{CF})]/\beta_{\text{HRS}}(\text{POF}) \times 100$ , differentiates between the POF and the CF, and is also reported for measurements performed in acetonitrile.

Measurements performed in acetonitrile reveal that the first hyperpolarizabilities of the POFs are one order of magnitude larger than those of the CFs, giving rise to very high contrasts of the NLO responses under the switching reaction. Indeed, the normalized efficiency of the HRS hyperpolarizability varies from 79.1 to 96.2%, demonstrating that these compounds act as highly powerful two-way NLO switches. Although it was not possible to measure the responses for the CFs in chlorobenzene, owing to signals

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lower than the detection limit of our experimental setup, the very high values obtained for the POF demonstrate that the commutation mechanism is also accompanied by a large contrast of the second-order NLO property in this solvent. The HRS responses of the CF in acetonitrile of compounds 1 and 2 are two to three times smaller than those of compounds 3 and 4, in agreement with the relative magnitude of their maximum absorption wavelengths. Besides, it has been noticed that solvent effects induce changes in the relative ordering of the  $\beta_{\text{HRS}}$  values of the POF, which is CHO $\rightarrow$ H $\rightarrow$  $NO_2{\rightarrow}Br$  in chlorobenzene and  $CHO{\rightarrow}NO_2{\rightarrow}H{\rightarrow}Br$  in acetonitrile. Also note that the  $\beta_{\rm HRS}$  values obtained in acetonitrile for the POF of compounds 1-3 (and to a lesser extent of compound 4) were measured under resonant conditions. Hence, the NLO responses for the first three compounds are likely to be enhanced because the two-photon scattering frequency lies within their main absorption band. On the contrary, the measurements for compound 4 were also made out of resonance, so that its large hyperpolarizability should result mainly from the presence of the nitro substituent, ensuring a better charge transfer along the molecule. The DR values are all close to four and do not exhibit a specific dependency on the nature of the solvent or on the open/closed form of the chromophore. It can, however, be observed that the DR of the NO2-substituted compound is slightly smaller (larger) in its POF (CF).

Theoretical results: In the first paper of this series,<sup>[17]</sup> quantum chemical calculations were carried out on the nonsubstituted compound 1 both in its CF and POFs. The changes in terms of geometrical and electronic structures, as well as in terms of (non) linear optical properties during the switching reaction, were extensively discussed and the reader is referred to this previous article for further details. In the present work, we focused our computational efforts on the POF rather than on the CF, with the aim of rationalizing the significant impact of the substituent R, as well as solvent and frequency dispersion effects on the NLO responses of the optically active state. Static and dynamic hyperpolarizabilities were first calculated at the CPHF and TDHF levels of calculation. Tables 4 and 5 report the results obtained for molecules in the gas phase, as well as when including the solvent effects through the PCM scheme. At the CPHF/6-31G\* level in the gas phase, the static  $\beta_{\rm HRS}$  values increase with the acceptor strength of R in the order  $H{\rightarrow}Br{\rightarrow}$ CHO $\rightarrow$ NO<sub>2</sub>, whereas the DR values are similar for all compounds and amount to  $4.35\pm0.10$ , accounting for the predominance of one component in the  $\beta$  tensor (i.e., chargetransfer character). Adding diffuse Gaussian functions in the basis set increases  $\beta_{\rm HRS}$  by less than 10% and does not change the relative ordering of the values. The enhancement of  $\beta_{\text{HRS}}$  due to frequency dispersion effects, calculated in the gas phase by comparing the CPHF and TDHF values, is similar for all compounds and ranges between 95 and 110%. However, for molecules in the gas phase,  $\beta_{HRS}(R=CHO)$  is slightly larger than  $\beta_{\text{HRS}}(R=NO_2)$  at the TDHF level with both basis sets. The DR values increase by approximately

Table 4. Static longitudinal first hyperpolarizability ( $\beta_{zzz}$ ), HRS first hyperpolarizability ( $\beta_{HRS}$ ), and DRs of POFs evaluated by using the CPHF scheme. All values are given in atomic units. Values relative to the non-substituted compound are given in parentheses.

	1(R = H)	<b>2</b> (R=Br)	3(R = CHO)	$4(R = NO_2)$
		in the g	as phase	
CPHF	/6-31G*	e e		
$\beta_{zzz}$	5384 (1.000)	5697 (1.058)	6308 (1.172)	6318 (1.173)
$\beta_{\rm HRS}$	2192 (1.000)	2339 (1.067)	2615 (1.193)	2614 (1.193)
DR	4.30	4.33	4.36	4.29
CPHF	/6-31 <b>+</b> G*			
$\beta_{777}$	5755 (1.000)	5922 (1.029)	6524 (1.134)	6827 (1.186)
$\beta_{\rm HRS}$	2401 (1.000)	2438 (1.015)	2707 (1.127)	2834 (1.180)
DR	4.45	4.40	4.40	4.37
		in acet	onitrile	
CPHF	/6-31G*			
$\beta_{777}$	12736 (1.000)	13673 (1.074)	15591 (1.224)	17305 (1.359)
$\beta_{\rm HRS}$	5173 (1.000)	5598 (1.082)	6453 (1.247)	7188 (1.390)
DR	4.25	4.29	4.34	4.36
CPHF	/6-31 <b>+</b> G*			
$\beta_{zzz}$	13522 (1.000)	14278 (1.056)	16478 (1.219)	18437 (1.363)
$\beta_{\rm HRS}$	5508 (1.000)	5854 (1.063)	6827 (1.239)	7670 (1.393)
DR	4.31	4.32	4.36	4.38
		in chloro	obenzene	
CPHF	/6-31G*			
$\beta_{777}$	10841 (1.000)	11601 (1.070)	13133 (1.211)	14336 (1.322)
$\beta_{\rm HRS}$	4493 (1.000)	4753 (1.058)	5436 (1.210)	5950 (1.324)
DR	4.32	4.33	4.37	4.38
CPHF	/6-31 <b>+</b> G*			
$\beta_{zzz}$	11426 (1.000)	12100 (1.059)	13812 (1.209)	15167 (1.327)
$\beta_{\rm HRS}$	4750 (1.000)	4965 (1.045)	5722 (1.205)	6304 (1.327)
DR	4.40	4.37	4.40	4.40

0.2–0.3 for all compounds up to  $4.68 \pm 0.07$ , which is even closer to the asymptotic limit of a purely 1D character than in the static limit. When accounting for solvent effects, strong increases (103–111% with 6-31G\* and 129–171% with 6-31+G\*) are observed for the static  $\beta_{\rm HRS}$  values, whereas the enhancement of the dynamic  $\beta_{\rm HRS}$  is less pronounced (about 50% less than for the static  $\beta$  values), owing to the reduction of the dielectric constant of acetonitrile at 1064 nm.

Summarizing these results, it can be observed that  $\beta_{\text{HRS}}$  increases with the acceptor strength of R, and follows a quasilinear relationship with respect to the Hammett constants of the substituents R. As shown in Figure 3, the solvent has a direct effect on the slope, revealing higher solute–solvent interactions for compounds with strong electron-withdrawing substituents. On the contrary, frequency dispersion effects induce a global shift towards higher values but have a negligible impact on the slope.

To evaluate the impact of electron correlation on the static hyperpolarizabilities, FF MP2/6-31G\* calculations were carried out, both in the gas phase and in solution (Table 6). The latter results were obtained by calculating the third-order derivatives of the IEFPCM/MP2/6-31G\* energies with respect to the applied field. For molecules in the gas phase, electron correlation effects lead to an increase of the HRS first hyperpolarizabilities by 81–88%, except for

Table 5. Dynamic (SHG,  $\lambda = 1064$  nm) longitudinal first hyperpolarizability ( $\beta_{zzz}$ ), HRS first hyperpolarizability ( $\beta_{HRS}$ ), and DRs of POFs evaluated by using the TDHF scheme. All values are given in atomic units. Values relative to the nonsubstituted compound are given in parentheses.

	1(R = H)	2(R = Br)	3(R = CHO)	$4 (R = NO_2)$		
		in the g	as phase			
TDHF	/6-31G*					
$\beta_{zzz}$	10926 (1.000)	11 986 (1.097)	13289 (1.216)	13186 (1.207)		
$\beta_{\rm HRS}$	4437 (1.000)	4909 (1.106)	5477 (1.234)	5420 (1.222)		
DR	4.61	4.64	4.66	4.61		
TDHF	7/6-31 <b>+</b> G*					
$\beta_{zzz}$	11489 (1.000)	12539 (1.091)	13910 (1.211)	13837 (1.204)		
$\beta_{\rm HRS}$	4678 (1.000)	5144 (1.100)	5737 (1.226)	5688 (1.216)		
DR	4.66	4.69	4.69	4.63		
		in acet	onitrile			
TDHF	/6-31G*					
$\beta_{zzz}$	16027 (1.000)	18032 (1.125)	20719 (1.293)	22215 (1.386)		
$\beta_{\rm HRS}$	6507 (1.000)	7380 (1.134)	8539 (1.312)	9162 (1.408)		
DR	4.64	4.68	4.70	4.70		
TDHF	/6-31+G*					
$\beta_{zzz}$	17120 (1.000)	18991 (1.109)	22128 (1.293)	24057 (1.405)		
$\beta_{\rm HRS}$	6967 (1.000)	7783 (1.117)	9125 (1.310)	9931 (1.425)		
DR	4.69	4.71	4.73	4.72		
		in chloro	benzene			
TDHF	/6-31G*					
β	19604 (1.000)	21459 (1.099)	24484 (1.249)	27227 (1.389)		
$\beta_{\rm HRS}$	8080 (1.000)	8781 (1.087)	10080 (1.248)	11236 (1.390)		
DR	4.68	4.69	4.71	4.73		
TDHF	TDHF/6-31+G*					
$\beta_{zzz}$	20591 (1.000)	22631 (1.099)	26145 (1.270)	29301 (1.423)		
$\beta_{\rm HRS}$	8633 (1.000)	9270 (1.074)	10770 (1.248)	12101 (1.402)		
DR	4.72	4.72	4.74	4.75		



Figure 3. Evolution of the HRS first hyperpolarizability as a function of the Hammett constant of the substituents.  $\oplus$ : CPHF/6-31+G\* in the gas phase,  $\blacksquare$ : CPHF/6-31+G\* in acetonitrile,  $\blacklozenge$ : TDHF/6-31+G\* in the gas phase, and  $\blacktriangle$ : TDHF/6-31+G\* in acetonitrile.

compound 4 (R=NO<sub>2</sub>) in which the increase is smaller (61%). This results in a change of the  $\beta_{HRS}$  value ordering with respect to the CPHF scheme: H $\rightarrow$ NO<sub>2</sub> $\rightarrow$ Br $\rightarrow$ CHO. The DR values also increase when including electron correlation, but again to a lesser extent for compound 4, so that

Table 6. Static longitudinal first hyperpolarizability ( $\beta_{zzz}$ ), HRS first hyperpolarizability ( $\beta_{HRS}$ ), and DRs of POFs evaluated at the MP2/6-31G\* level. All values are given in atomic units. Values relative to the nonsubstituted compound are given in parentheses.

	1(R = H)	<b>2</b> (R=Br)	3(R = CHO)	$4(R = NO_2)$
		in the g	as phase	
$\beta_{zzz}$	10070 (1.000)	10376 (1.030)	11467 (1.139)	10222 (1.015)
$\beta_{\rm HRS}$	4112 (1.000)	4257 (1.035)	4730 (1.150)	4208 (1.023)
DR	4.68	4.68	4.71	4.59
		in acet	onitrile	
$\beta_{777}$	30203 (1.000)	32557 (1.078)	36893 (1.221)	36535 (1.210)
$\beta_{\rm HRS}$	12335 (1.000)	13372 (1.084)	15207 (1.233)	15063 (1.221)
DR	4.69	4.71	4.73	4.65
		in chloro	obenzene	
β	24276 (1.000)	26065 (1.074)	29304 (1.207)	27 994 (1.153)
$\beta_{\rm HRS}$	9918 (1.000)	10710 (1.080)	12083 (1.218)	11 540 (1.163)
DR	4.70	4.73	4.74	4.65

the DR value for this compound is slightly smaller than for the three other compounds.

When accounting for solvent effects (acetonitrile), the  $\beta_{\text{HRS}}$  responses are enhanced by 200, 214, 222, and 258% for compounds **1** to **4**, respectively, again indicating that solvent effects are larger if **R** is a strong acceptor group. The same tendency is observed, although weaker, in chlorobenzene; therefore, the  $\beta_{\text{HRS}}$  ordering becomes  $H \rightarrow Br \rightarrow NO_2 \rightarrow CHO$  when accounting for both solvent and electron correlation effects.

For computational reasons, it is currently not possible to calculate  $\beta_{\text{HRS}}$  responses, which simultaneously account for frequency dispersion, solvent, and MP2 electron correlation effects. Nevertheless, approximate values were estimated by using adaptations of Equation (1) to properties in solutions [Eqs. (3) and (4)].

$$\beta_{\rm MP2}^{\rm Solv}(-2\omega;\omega,\omega) = \beta_{\rm MP2}(0;0,0) \times \frac{\beta_{\rm TDHF}^{\rm Solv}}{\beta_{\rm CPHF}^{\rm Vacuo}}$$
(3)

$$\beta_{\text{MP2}}^{\text{Solv}}(-2\omega;\omega,\omega) = \beta_{\text{MP2}}^{\text{Solv}}(0;0,0) \times \frac{\beta_{\text{TDHF}}^{\text{Solv}}}{\beta_{\text{Solv}}^{\text{Solv}}}$$
(4)

In Equation (3), the static  $\beta_{\rm HRS}$  response obtained at the MP2 level for the molecule in the gas phase is multiplied by a correction factor by taking into account the impact of the solvent and frequency dispersion. In Equation (4), the reference  $\beta_{\rm MP2}$  response includes both correlation and solvent effects, whereas the multiplicative ratio provides a correction accounting for frequency dispersion effects (evaluated from  $\beta$  values determined by taking into account the solvent effects). The  $\beta_{\rm HRS}$  values estimated within the two schemes are reported in Table 7. Using Equation (4) gives rise to larger values, but the two sets of results follow very similar trends. Within this best theoretical level of approximation, the  $\beta_{\rm HRS}$  values of compounds 1–4 follow the ordering  $H \rightarrow Br \rightarrow NO_2 \rightarrow CHO$  in both solvents.

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Table 7. Dynamic (SHG,  $\lambda = 1064$  nm) longitudinal first hyperpolarizability ( $\beta_{zzz}$ ) and HRS first hyperpolarizability ( $\beta_{HRS}$ ) of POFs evaluated from Equations (3) and (4). All values are given in atomic units. Values relative to the nonsubstituted compound are given in parentheses.

	1(R=H)	2(R = Br)	3(R = CHO)	$4(R = NO_2)$		
		in acet	tonitrile			
Equation (3)	11932 (1.00)	13590 (1.14)	15945 (1.34)	14746 (1.24)		
Equation (4)	15516 (1.00)	17439 (1.12)	20119 (1.30)	19797 (1.28)		
	in chlorobenzene					
Equation (3)	14785 (1.00)	16186 (1.09)	18819 (1.27)	17968 (1.22)		
Equation (4)	17510 (1.00)	19787 (1.13)	22410 (1.28)	21367 (1.22)		

Discussion: Despite accounting for frequency dispersion, solvent, and electron correlation effects, the  $\beta_{\text{HRS}}$  (or  $\beta_{777}$ ) values predicted for the POFs by ab initio calculations do not follow the same ordering as the measured ones. From the former (Table 7), one obtains  $H \rightarrow Br \rightarrow NO_2 \rightarrow CHO$  in both solvents, whereas the experimental  $\beta$  values follow different ordering depending on the solvent:  $CHO \rightarrow H \rightarrow$  $NO_2 \rightarrow Br$  in chlorobenzene, and  $CHO \rightarrow NO_2 \rightarrow H \rightarrow Br$  in acetonitrile (Table 5). In addition, none of these experimental results follow the ordering of the Hammett parameters. It is therefore important, within our aim of designing new NLO switchable compounds, to point out possible origins of this difference and to see how much this divergence is apparent and results only from the differences in probing techniques. First, as mentioned above, the experimental data are impacted by resonance conditions because the measurements are carried out at a frequency within the absorption band, slightly above the maximum. This is, however, not true in the case of the theoretical values because the poles of the TDHF responses are underestimated. However, evaluating the exact magnitude of this effect is not straightforward.<sup>[31]</sup> The simplest way to estimate the impact of frequency dispersion in pseudodipolar chromophores is to consider the two-states approximation,<sup>[32]</sup> which assumes that only one excited state contributes to the second-order NLO response. Considering a homogeneous damping  $\gamma$  and neglecting the nonresonant terms,<sup>[18b,33]</sup> the frequency dispersion factor for the longitudinal component of the first hyperpolarizability tensor  $F(\omega, \omega_{ge}, \gamma)$ , gives Equation (5):

$$F(\omega, \omega_{ge}, \gamma) = \frac{\beta_{zzz}(-2\omega; \omega, \omega)}{\beta_{zzz}(0; 0; 0, 0)}$$

$$= \frac{\omega_{ge}^{2>}(\omega_{ge} - i\gamma)^2}{([\omega_{ge} - i\gamma]^2 - 4\omega^2)([\omega_{ge} - i\gamma]^2 - \omega^2)}$$
(5)

in which g and e are the two electronic (ground and excited) states contributing to the first hyperpolarizability, and  $\hbar\omega_{ge}$  is the corresponding excitation energy. This dispersion factor, reported in Figure 4 as a function of the positions of the main absorption band, varies substantially with both  $\omega_{ge}$  and  $\gamma$ . In the absence of homogeneous damping ( $\gamma=0$ ) when the solvent is acetonitrile the value of the dispersion factor is about 7.4 for compound **4**, whereas it ranges from



Figure 4. Frequency dispersion factor as a function of the maximum absorption wavelength of the compounds within the two-state approximation and different homogeneous damping values. The squares indicate the wavelength positions for compounds **1–4** in acetonitrile.  $\gamma = 0$  (——), 1000 (–––), and 2000 cm<sup>-1</sup> (----).

approximately 21 to 30 for the three other compounds. The resulting static  $\beta_{zzz}$  responses (abbreviated as  $\beta_0$ ) are then 3900, 7100, 3900, and 14900 a.u. for compounds 1-4, respectively, and thus follow the ordering  $H \approx CHO \rightarrow Br \rightarrow NO_2$ . Owing to the global redshift of the absorption maximum (Tables 1 and 2), frequency dispersion effects are slightly reduced in chlorobenzene and, consequently, the calculated  $\beta_0$ values are quite different from the values obtained in acetonitrile (3100, 10200, 4000 and 10800 a.u. for compounds 1-4, respectively), but they follow the same hierarchy as in acetonitrile. Though extrapolating to the static limit improves the correspondence between theory and experiment, differences remain. Indeed, when accounting for both solvent (acetonitrile in this case) and electron correlation, theoretical calculations predict that the  $\beta_0$  values of the H-, Br-, CHO-, and NO<sub>2</sub>-substituted compounds are in the ratio of 1.00:1.08:1.22:1.21, whereas the corresponding experimental values extrapolated to infinite wavelength are in the ratio of 1.00:1.82:1.00:3.82.

This first set of extrapolated  $\beta_0$  values can be improved in several ways, including 1) by considering a finite value for the homogeneous damping associated with the optical transition [Eq. (5)],<sup>[34]</sup> 2) by incorporating an inhomogeneous broadening based on the absorption spectrum, which implicitly contains information on the distribution of the transition frequencies, 3) by taking into account the vibronic structure of the excited states, and 4) by including higher-energy excited states in the sum-over-state expression of  $\beta$ . In this work, to provide a better estimate of  $\beta_0$ , we have employed three additional approximations, which should also guide us in assessing their accuracy.

The first approach makes use of Equation (5). However, the difficulty arises from the fact that the value of  $\gamma$  is a priori not known and it depends on the compound, the excited states, and on the solvent. In line with previous studies,<sup>[33a,35]</sup> the  $\gamma$  value was chosen to correspond to approximately 1.2 times the half width at half maximum (HWHM) of the corresponding main absorption band, that is, it corresponds to the HWHM of the  $e^{-[(\omega-\omega_{gc})/\gamma]^2}$  Gaussian function. The  $\gamma$  values estimated from the absorption spectra of compounds **1–4** in acetonitrile amount to 0.193, 0.178, 0.208, and 0.149 eV, respectively. Using these results, the extrapolated  $\beta_0$  values are now in the ratio of 1.00:1.41:0.79:1.23. By keeping the same  $\gamma$  values for results measured in chlorobenzene, the extrapolated  $\beta_0$  values are in the ratio of 1.00:2.39:1.11:1.85.

An inhomogeneous broadening is employed in the second approach. According to Campo et al,<sup>[31]</sup> for an incoherent process like HRS, the dispersion factor is given by Equation (6):

$$\left|\frac{\beta^{\text{HRS}}(-2\omega;\omega,\omega)}{\beta^{\text{HRS}}(0;0,0)}\right| = \left\{\int N(\omega_{\text{ge}}') \left|F(\omega,\omega_{\text{ge}}',\gamma)\right|^2 d\omega_{\text{ge}}'\right\}^{1/2}$$
(6)

Here, a value of  $\gamma = 100 \text{ cm}^{-1}$  was chosen for the homogeneous damping, whereas  $N(\omega'_{ge})$ , the normalized distribution of the transition frequencies, is approximated by a Gaussian function that reproduces the experimental HWHM of the corresponding main absorption band. By applying Equation (6), the extrapolated  $\beta_0$  values of compounds **1–4** in acetonitrile are in the ratio of 1.00:1.44:0.75:1.94.

In the last approach employed in this study, the distribution of the transition frequencies is improved by considering the single-mode vibronic model so that  $N(\omega'_{ge})$  of Equation (6) is replaced by Equation (7):

$$N\left(\omega_{\rm ge}'\right) = \sum_{n}^{\rm vib.\ levels} \left[\frac{S^n e^{-S}}{n!}\right] e^{-\left[\left(\omega_{\rm ge}' - \omega_n\right)/\gamma_{\rm vib}\right]^2} \tag{7}$$

in which  $\omega_n = \omega_{ge} + n\omega_{vib}$  corresponds to the transition from the ground state to the nth vibrational level of the excited state. A Huang-Rhys factor (S) of 0.4 was adopted because it reproduces the shape of the absorption band. Values of  $\omega_{\rm vib}$  and  $\gamma_{\rm vib}$  were also chosen to best reproduce the absorption spectra.<sup>[36]</sup> Because the number of parameters is already large, no attempts were made to include additional vibrational normal modes or excited states. The corresponding extrapolated  $\beta_0$  values of compounds 1–4 in acetonitrile then become in the ratio of 1.00:1.50:0.80:1.63. These last two models are the most elaborate and, with the exception of R = CHO, reproduce the theoretical ordering for the  $\beta_0$  amplitudes. In addition, as shown in Figure 5 for  $R = NO_2$ , they provide similar dispersion factors as a function of  $\omega$ , whereas in the model including only homogeneous broadening, the resonance enhancement of  $\beta$  is about a factor of five smaller.

As mentioned in the Linear Optical Properties Section, specific interactions between the chromophore and the solvent might explain the remaining discrepancies. These include favorable electrostatic interactions between acetonitrile molecules and the positively charged nitrogen atom of



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Figure 5. Evolution of the dispersion factor with the second harmonic energy relative to the absorption spectrum. These were obtained for compound  $\mathbf{4}$  by using the three approaches and parameters described in the text.

the chromophore in its POF, whereas  $\pi$ - $\pi$  or dipole-dipole interactions between chlorobenzene and the chromophore could favor J-aggregates. Such solute/solvent interactions should affect the electron density and symmetry of the chromophores and consequently their NLO responses. The impact of such effects is underestimated when using a continuum solvation model. Including explicit solvent molecules in the calculation by combining, for example, molecular dynamics and quantum chemistry tools, would possibly be a good starting point to further improve the quality of the theoretical investigations. Additionally, we should not forget that the experiments are performed in the nanosecond regime, which affects the medium quite a lot. In particular, the input laser beam induces collisions between molecules that reduce the lifetime of the excited states. The use of a ps or fs laser source should reduce these collective effects and make the comparison between theory and experiments easier.

#### Conclusion

This paper is the last in a series aiming to optimize the NLO contrast of multiple-way indolinooxazolidine-based molecular switches. Following a theoretical study that predicted a significant NLO enhancement upon addition of electron-withdrawing substituents in the *para* position on the indolinic residue, we have reported herein on the synthesis and NLO characterization of three new indolinooxazolidine derivatives. In addition, the experimental results have been rationalized by means of ab initio calculations, including frequency dispersion, solvent, and electron correlation effects.

Like the nonsubstituted compound (R=H), these three new systems (R=Br, CHO, NO<sub>2</sub>) can commute reversibly, upon pH variation or UV-light irradiation, between the closed indolinooxazolidine form and the open  $\pi$ -conjugated

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colored form. This two-way switching mechanism has been substantiated by the similarity of the photo- and acido-triggered absorption spectra of the zwitterionic and POFs. In both measurements and calculations, the maximum of absorption is redshifted upon adding electron-withdrawing substituents and the effect is stronger for the POFs than for the CFs.

HRS measurements performed at 1064 nm have revealed that 1) the second-order NLO contrasts between the two forms remains very large upon substitution and 2) the dependence of  $\beta_{\rm HRS}$  of the open form with the substituent is difficult to explain owing to the fact that the measurements are performed in resonance conditions. On the other hand, calculations accounting for solvent effects predict a global increase of  $\beta_{\text{HRS}}$  of the POF with the Hammett parameter of the substituent:  $\beta_{\rm HRS}$  (R=H)  $< \beta_{\rm HRS}$  (R=Br)  $< \beta_{\rm HRS}$  (R= CHO)  $< \beta_{\text{HRS}}$  (R = NO<sub>2</sub>). When electron correlation effects are included at the Møller-Plesset second-order level of approximation, the  $\beta_{\rm HRS}$  values for R=CHO and R=NO<sub>2</sub> become very similar, but their relative  $\beta$  ordering is reverted. Extrapolations of the measured  $\beta_{\text{HRS}}$  values to the static limit has also been carried out by using models including homogeneous and inhomogeneous broadenings as well as single-mode vibronic structures. With the exception of the R=CHO compound, the extrapolated  $\beta_{\text{HRS}}$  values are consistent with the calculations and their linear optical properties.

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