# Second-Order Nonlinear Optical Properties of Tetraaza-Coordinated Nickel(II) Complexes

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**Keywords:** Nickel / Nonlinear optics / Semiempirical calculations

In this contribution, we report the design and theoretical analysis, using the INDO/SCI-SOS quantum chemical formalism, of novel molecular architectures based on planar $[N_4]$-, (2-aminobenzylideneiminato)- and tetraazamacrocycle-coordinated nickel(II) complexes, having second-order nonlinear optical (NLO) properties. Calculations indicate that these molecules possess comparable, or even larger, second-order nonlinearity to the bis(salicylaldiminato)$Ni^{II}$ Schiff-base analogues. The nonlinearity of substituted complexes is dominated by the nature and position of substituents on the tribenzo[*b*,*f*,*l*] and/or cyclotetradecine rings, and is determined by the relative directions of the ground- and excited-state dipole moments. Moreover, substitution with acceptor groups in the dibenzo[*b*,*l*] rings involves a significant octupolar contribution to optical nonlinearity.

## Introduction

An intense research activity is currently associated with the synthesis and development of molecule-based second-order nonlinear optical (NLO) materials,[1] involving organic chromophores[2] and metal complexes.[3] The latter represent an emerging and growing class of materials by virtue of unique properties associated with the metal center. Various classes of transition metal complexes have been explored systematically, including organometallic and coordination complexes.[3]

Most second-order NLO metal complexes, as organic NLO chromophores, can be envisaged within a simple molecular scheme constituted by a donor$-\pi$-conjugate-bridge$-$acceptor ($D-\pi-A$) structure, in which an organometallic group selectively replaces the donor and/or the acceptor, or the bridge moieties.[3a] This requirement is because metal complexes possess intense, low-energy metal-to-ligand charge transfer (MLCT), ligand-to-metal charge transfer (LMCT), or intraligand charge transfer (ILCT) excitations. Therefore, they can behave effectively as donor and/or acceptor groups of the $D-\pi-A$ system, or to be a constituent of the polarizable bridge.

Bis(salicylaldiminato)$M^{II}$ (M = Co, Ni, Cu, Zn) Schiff-base complexes are prototypical examples of the latter case.[4,5] Complexation is accompanied by formation of geometrically constrained acentric, generally planar, structures. It always involves an enhancement of optical nonlinearity, compared to that of related free ligands and, in some cases, a "switching on" of the NLO response with resulting tunable hyperpolarizabilities, ranging from negative to positive $\beta$ values.[6] Moreover, the nature of the metal deeply influences the nonlinearity.[7] The role of the metal centre in determining the NLO response in such structures is twofold, since it can act both as the donor and as the bridging moiety of the $D-\pi-A$ system. Finally, the appropriate donor/acceptor substitution pattern results in an "in-plane" two-dimensional second-order nonlinearity.[8] Thus, bis(salicylaldiminato)$M^{II}$ Schiff-base complexes represent suitable templates for second-order NLO molecular materials. Actually, starting from unsubstituted bis(salicylaldiminato)$M^{II}$ Schiff-base complexes it is possible to design other molecular structures in which, instead of changing the donor or the acceptor substituents on the benzene rings, the donor atoms are changed.

In this paper, we report the design and a theoretical analysis, using the INDO/S-SOS quantum chemical formalism,[7a,9] of novel molecular architectures based on planar $[N_4]Ni^{II}$ complexes, having second-order NLO properties (Scheme 1). We demonstrate that these (2-aminobenzylideneiminato)- and tetraazamacrocycle-coordinated nickel(II) complexes represent suitable candidates for second-order NLO molecular materials.

## Results and Discussion

### Theoretical Method

Within the framework of the Sum-Over-excited-particle-hole-States (SOS) perturbation theory, the molecular quadratic hyperpolarizability, for instance the second harmonic

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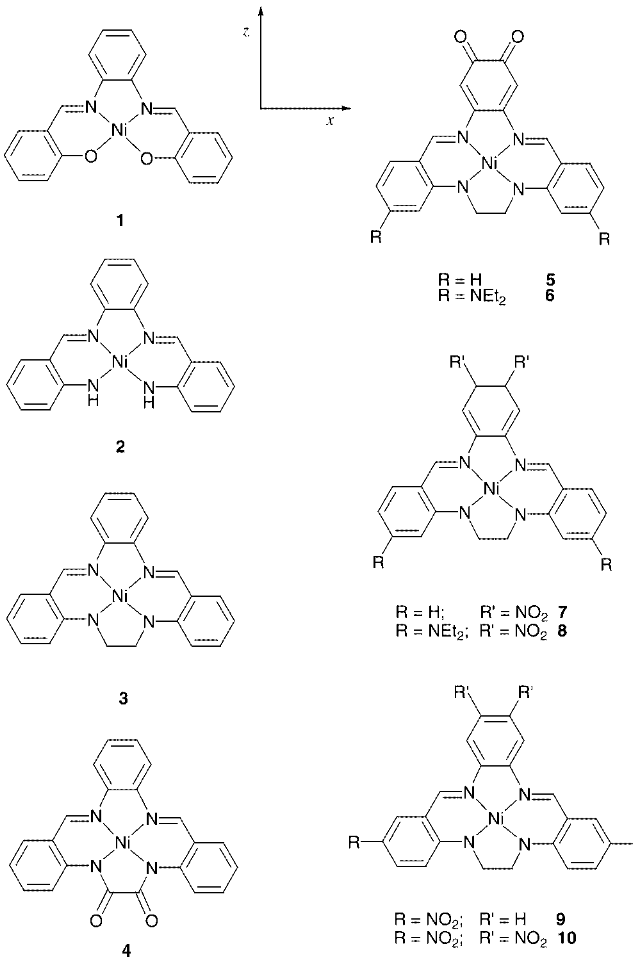
Supporting information for this article is available on the WWW under http://www.eurjoc.org or from the author.

DOI: 10.1002/ejic.200300023



Scheme 1

generation, $\beta_{ijk}(2\omega; \omega, \omega)$, can be related exactly to all the excited states of the molecule in terms of energy, $\hbar\omega_{ge}$, transition dipole moment, $r^{i}_{ge}$, and dipole moment variation, $\Delta\mu^{i}_{ge} = r^{i}_{ee} - r^{i}_{gg}$, between ground ($g$) and excited ($n$) states.[10] The hyperpolarizability determined by a sum-over-states expression can be partitioned into two contributions,[9] the so-called two-level ($\beta_{ijk,2}$) terms and three-level ($\beta_{ijk,3}$) terms, such that: $\beta_{ijk}(2\omega; \omega, \omega) = \beta_{ijk,2} + \beta_{ijk,3}$. Each two-level component in the sum for $\beta_{ijk,2}$ contains only two states, the ground and one excited state, and is related to the product $r^{j}_{ge}r^{k}_{ge}\Delta\mu^{i}_{ge}$ (generic two-level term); the three-level contributions involve the ground state and two excited states, $e$, $e'$, and are related to the product $r^{j}_{ge'}r^{i}_{e'e}r^{k}_{ge}$ (generic three-level term). For dipolar molecules, the molecular hyperpolarizability is generally related to the $\beta_\mu$ value, i.e., the vector component of the $\beta_{ijk}$ tensor along the dipole moment direction, given by

$$\beta_\mu = \sum_{i=1}^{3} \frac{\mu_i \beta_i}{|\mu|}$$

where $\mu$ is the ground state dipole moment and $\beta_i = \beta_{iii} + 1/3\Sigma_{j\neq i}(\beta_{ijj} + \beta_{jij} + \beta_{jji})$. For most dipolar molecules, in which $\Delta\mu^{i}_{ge}$ and $r^{i}_{ge}$ matrix elements are parallel to the dipolar $i$ axis, the $\beta_{ijk,2}$ sum generally dominates the NLO response, resulting in 1D dipolar species with a single hyperpolarizability diagonal tensor component $\beta_{iii}$, so that $\beta_\mu \approx \beta_{iii}$. A further simplification of this approach can be made by restricting the "summation" to one excited state, the so-called "two-state" model,[11] in which: $\beta_{iii} \propto (r_{ge})^2\Delta\mu_{ge}/\hbar\omega_{ge}$. On the other hand, only nonzero, off-the-$i$-diagonal, dipole moment ($\Delta\mu^{j}_{ge}$, $j \neq i$) or transition dipole moment ($r^{j}_{ge}$, $j \neq i$) matrix elements, contribute to off-diagonal $\beta_{ijk}$ hyperpolarizability tensor components. For dipolar molecules of $C_{2v}$ symmetry, $\beta$ has seven nonvanishing tensor components, five of which are independent. The nonzero components are $\beta_{zzz}$, $\beta_{xzx} = \beta_{xxz}$, $\beta_{zxx}$, $\beta_{yzy} = \beta_{yyz}$, $\beta_{zyy}$, where $z$ is the $C_2$ axis. Since transition dipole moments perpendicular to the $zx$ molecular plane are generally small, the components $\beta_{yzy} = \beta_{yyz}$, $\beta_{zyy}$ are usually negligible. Thus, the parameter $u = \beta_{\text{off-diagonal}}/\beta_{zzz}$, where $\beta_{\text{off-diagonal}} = 1/3(\beta_{xzx} + \beta_{xxz} + \beta_{zxx})$, reflects the anisotropy of the in-plane optical nonlinearity.[12]

## Computational Details and Results

Table 1. Computed ground-state dipole moment and second-order NLO response for (2-aminobenzylideneiminato)- and tetraazamacrocycle-coordinated nickel(II) complexes **1**–**10**, and for representative free ligands **3a**, **6a**, **8a** and **10a**

| Compd.[a][b] | $\mu_g$ [D] | $\hbar\omega$ [eV] | $\beta_{zzz}$ | $\beta_{xzx} = \beta_{xxz}$ | $\beta_{zxx}$ | $u$ | $\beta_\mu$ |
|---|---|---|---|---|---|---|---|
| **1**[c] | 7.4 | 0.0 | −8.4 | 0.4 | 0.4 | −0.05 | −8.1 |
| | | 0.92 | −13.3 | 1.2 | 2.7 | −0.13 | −12.0 |
| **2** | 2.7 | 0.0 | −10.4 | 2.1 | 2.1 | −0.20 | −8.2 |
| | | 0.92 | −20.5 | 4.1 | 5.4 | −0.23 | −15.7 |
| **3** | 2.4 | 0.0 | −12.9 | 1.9 | 1.9 | −0.15 | −11.0 |
| | | 0.92 | −26.2 | 4.1 | 5.5 | −0.17 | −21.7 |
| **3a** | 2.2 | 0.0 | −5.2 | 0.8 | 0.8 | −0.15 | −4.3 |
| | | 0.92 | −7.8 | 1.7 | 2.5 | −0.25 | −5.8 |
| **4** | 13.6 | 0.0 | −7.4 | 1.1 | 1.1 | −0.15 | −6.4 |
| | | 0.92 | −14.1 | 0.0 | 3.9 | −0.09 | −12.2 |
| **5** | 10.2 | 0.0 | 39.0 | −0.4 | −0.4 | −0.01 | 38.7 |
| | | 0.92 | 75.0 | −0.7 | −4.1 | −0.02 | 74.3 |
| **6** | 14.6 | 0.0 | 49.7 | 11.8 | 11.8 | 0.24 | 61.5 |
| | | 0.92 | 89.6 | 24.9 | 15.6 | 0.24 | 111.4 |
| **6a** | 14.0 | 0.0 | 38.2 | 13.2 | 13.3 | 0.35 | 50.1 |
| | | 0.92 | 67.1 | 24.2 | 21.7 | 0.35 | 88.4 |
| **7** | 7.8 | 0.0 | 43.0 | −9.4 | −9.4 | −0.22 | 33.3 |
| | | 0.92 | 94.4 | −20.7 | −24.5 | −0.23 | 72.3 |
| **8** | 12.3 | 0.0 | 57.7 | −0.3 | −0.3 | −0.01 | 57.2 |
| | | 0.92 | 126.2 | −9.2 | −13.5 | −0.08 | 115.1 |
| **8a** | 13.0 | 0.0 | 49.2 | −2.5 | −2.5 | −0.05 | 45.9 |
| | | 0.92 | 99.8 | −9.9 | −12.3 | −0.11 | 87.7 |
| **9** | 3.7 | 0.0 | −10.9 | 5.2 | 5.2 | −0.48 | −5.7 |
| | | 0.92 | −21.5 | 10.2 | 17.5 | −0.59 | −8.8 |
| **10** | 5.5 | 0.0 | 28.1 | −12.3 | −12.3 | −0.44 | 15.5 |
| | | 0.92 | 54.9 | −24.4 | −35.5 | −0.51 | 26.4 |
| **10a** | 6.2 | 0.0 | 14.9 | −6.5 | −6.5 | −0.44 | 6.1 |
| | | 0.92 | 25.2 | −12.1 | −15.1 | −0.52 | 7.6 |

[a] In units of $10^{-30}$ cm$^5$ esu$^{-1}$. Values of nonresonant hyperpolarizability are given in the phenomenological convention, where $\beta_{ijk}$ is by a factor of $^1/_4$ smaller than in the Taylor series convention (see ref.[14]). [b] For definition of parameters, see text. [c] Computed $\mu g$ and $\beta_\mu$ data for compound **1** differ slightly from those previously reported,[6a] because of the presently adopted optimized geometrical parameters and the different number of CIS configurations.

The all-valence INDO/S (Intermediate Neglect of Differential Overlap) model,[13] in connection with the SOS formalism,[10] was employed. Details of the computationally efficient ZINDO-SOS-based method for describing second-order molecular optical nonlinearities have been reported elsewhere.[7a,9] Standard parameters and basis functions were used.[13] In particular, the resonance integrals for the nickel atom were chosen to be $\beta_{sp} = -1$ eV and $\beta_d = -45$ eV.[13b] In the present approach, the closed-shell-restricted Hartree−Fock (RHF) formalism was adopted. The monoexcited configuration interaction (CIS) approximation was employed to describe the excited states. In all calculations, the lowest 250 energy transitions between SCF and CIS electronic configurations were chosen to undergo CI

Table 2. Computed linear optical spectroscopic data of relevant, low-energy CT transitions and relative contributions of the two-level and three-level terms to the static second-order NLO response ($10^{-30}$ cm$^5$ esu$^{-1}$) for complexes **1**−**10** and representative free ligands **3a**, **6a**, **8a** and **10a**[a]

| Compd.[a] | State | Polarization | $\hbar\omega_{ge}$ [eV] | $r_{ge}^{z}$ [D] | $r_{ge}^{x}$ [D] | $\Delta\mu_{ge}^{z}$ [D] | $\beta_{zzz,2}$ | $\beta_{zzz,3}$ | $\beta_{zxx,2}$ | $\beta_{zxx,3}$ | $\lvert\beta_\mu\rvert$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **1** | S1 | $x$ | 2.85 | 0.00 | 1.86 | −1.8 | | | | | |
| | S2 | $z$ | 3.14 | 5.99 | 0.00 | −4.64 | | | | | |
| | $\sum_n S_n$ | | | | | | −11.7 | 3.3 | −3.7 | 3.3 | 8.1 |
| **2** | S1 | $x$ | 2.70 | 0.00 | 2.11 | −2.74 | | | | | |
| | S2 | $z$ | 2.78 | 5.97 | 0.00 | −4.40 | | | | | |
| | $\sum_n S_n$ | | | | | | −14.3 | 3.9 | −3.8 | 5.9 | 8.2 |
| **3** | S1 | $x$ | 2.62 | 0.00 | −1.77 | −3.12 | | | | | |
| | S2 | $z$ | 2.71 | 6.07 | 0.00 | −4.79 | | | | | |
| | $\sum_n S_n$ | | | | | | −20.1 | 7.2 | −4.2 | 6.1 | 11.0 |
| **3a** | S1 | $x$ | 3.08 | 0.00 | 2.41 | −1.68 | | | | | |
| | S2 | $z$ | 3.31 | −4.12 | 0.00 | −1.68 | | | | | |
| | $\sum_n S_n$ | | | | | | −6.6 | 1.4 | −0.9 | 1.7 | 4.3 |
| **4** | S3 | $x$ | 2.76 | 0.00 | −1.19 | −2.14 | | | | | |
| | S4 | $z$ | 3.05 | 6.41 | 0.00 | −6.00 | | | | | |
| | $\sum_n S_n$ | | | | | | −16.5 | 9.1 | 0.6 | 0.5 | 6.4 |
| **5** | S2 | $x$ | 2.03 | 0.00 | −0.21 | 12.72 | | | | | |
| | S4 | $z$ | 2.73 | −8.04 | 0.00 | 4.65 | | | | | |
| | $\sum_n S_n$ | | | | | | 53.0 | −14.0 | 6.7 | −7.1 | 38.7 |
| **6** | S1 | $x$ | 2.06 | 0.00 | −0.80 | 12.14 | | | | | |
| | S2 | $z$ | 2.80 | 8.27 | 0.00 | 4.08 | | | | | |
| | $\sum_n S_n$ | | | | | | 88.0 | −38.3 | 14.5 | −2.7 | 61.5 |
| **6a** | S1 | $x$ | 2.57 | 0.00 | −1.42 | 6.99 | | | | | |
| | S2 | $z$ | 3.11 | 9.59 | 0.00 | 10.66 | | | | | |
| | $\sum_n S_n$ | | | | | | 74.8 | −36.6 | 12.2 | 1.1 | 50.1 |
| **7** | S1 | $x$ | 2.12 | 0.00 | −1.74 | 14.69 | | | | | |
| | S2 | $x$ | 2.58 | 0.00 | −5.10 | 1.83 | | | | | |
| | S3 | $z$ | 2.66 | −9.43 | 0.00 | 4.59 | | | | | |
| | $\sum_n S_n$ | | | | | | 40.0 | 3.0 | 13.7 | −23.1 | 33.3 |
| **8** | S1 | $x$ | 2.12 | 0.00 | −1.54 | 14.22 | | | | | |
| | S2 | $x$ | 2.60 | 0.00 | 5.23 | 3.00 | | | | | |
| | S3 | $z$ | 2.72 | 11.07 | 0.00 | 6.27 | | | | | |
| | $\sum_n S_n$ | | | | | | 86.4 | −28.7 | 23.0 | −23.3 | 57.2 |
| **8a** | S1 | $x$ | 2.41 | 0.00 | 4.57 | 3.92 | | | | | |
| | S2 | $z$ | 2.86 | 9.03 | 0.00 | 13.26 | | | | | |
| | S4 | $x$ | 2.98 | 0.00 | −5.07 | 6.17 | | | | | |
| | $\sum_n S_n$ | | | | | | 102.8 | −53.6 | 18.7 | −21.2 | 45.9 |
| **9** | S3 | $x$ | 2.72 | 0.00 | 4.14 | −3.35 | | | | | |
| | S4 | $z$ | 2.80 | −5.73 | 0.00 | −5.33 | | | | | |
| | S5 | $x$ | 3.20 | 0.00 | −9.53 | 0.75 | | | | | |
| | $\sum_n S_n$ | | | | | | −12.6 | 1.7 | −3.7 | 8.9 | 5.7 |
| **10** | S1 | $x$ | 2.33 | 0.00 | −2.30 | 7.71 | | | | | |
| | S2 | $x$ | 2.64 | 0.00 | 5.54 | 2.88 | | | | | |
| | S3 | $z$ | 2.70 | 8.80 | 0.00 | 2.84 | | | | | |
| | $\sum_n S_n$ | | | | | | 6.0 | 22.1 | 8.4 | −20.7 | 15.5 |
| **10a** | S1 | $x$ | 2.49 | 0.00 | −4.35 | 0.67 | | | | | |
| | S6 | $z$ | 3.12 | −4.88 | 0.00 | 5.90 | | | | | |
| | S7 | $z$ | 3.18 | 7.86 | 0.00 | −5.31 | | | | | |
| | $\sum_n S_n$ | | | | | | −6.9 | 21.8 | −0.3 | −6.1 | 6.1 |

[a] For definition of parameters, see text.

mixing and were included in the SOS. This SOS truncation was found to be sufficient for complete convergence of the second-order response in all cases considered. Non-resonant hyperpolarizabilities were calculated within a perturbation series expansion employing the Ward definition,[10] the so-called phenomenological convention.[14] All calculations were performed using the ZINDO Version 3.5 program of the Cerius$^2$ package from Accelrys Inc.[15] on an SGI Origin3800 system. Metrical parameters of **1−10** used for INDO/S calculations were taken from fully optimized structures (at ZINDO/1 level) using the HyperChem package.[16] A $C_{2v}$ planar structure of the bis(2-aminobenzylideneiminato) or the tetraazamacrocycle frameworks was always found in all cases presently considered.[17] Present optimised planar structures are consistent with available crystallographically derived planar structures of related complexes (vide infra). Moreover, optimized geometrical parameters (Supporting Information, see also the footnote on the first page of this article) are in favorable agreement with available experimental data (vide infra). In addition, INDO/S calculations were performed for representative free ligands **3a**, **6a**, **8a**, and **10a**, on the basis of their optimized structures (at ZINDO/1 level). Optimized structures of ligands **3a−10a** indicate a nonplanar structure of the tetraazamacrocycle framework, with $C_2$ symmetry. The computed ground state dipole moment and second-order NLO response for **1−10** and representative free ligands are collected in Table 1, while calculated low-energy CT transitions and analysis of relative two-level and three-level contributions to the static hyperpolarizability[18] are reported in Table 2.

## Discussion

Bis(salicylaldiminato)M$^{II}$ Schiff-base complexes have recently been developed as a new and versatile class of efficient second-order NLO materials.[4−8] The optical nonlinearity of the unsubstituted [Ni(salophen)] (**1**), has been related to a low-energy charge transfer (CT) transition, characterized as being principally $\pi \rightarrow \pi^*$ (HOMO → LUMO) in character, essentially involving the metal $3d_{xz}$,oxygen $2p_z$ and C=N orbitals.[6a] Therefore, the optical nonlinearity of M(salophen) complexes strongly depends on the nature of the ($MN_2O_2$) chelate and is tuned by the D/A substitution on the benzo rings.[6a,7,8] On this basis, it is expected that alternative chelate NLO structures could be envisaged on changing the donor atoms of the (salophen) template.

Substitution of the oxygen donor atoms of [M(salophen)] by NH groups results in the isoelectronic $MN_4$, bis(2-aminobenzylideneiminato) [M(abphen)] planar chelate. Some physicochemical properties of [M$^{II}$(abphen)] (M = Co, Ni, Cu) complexes have been previously reported.[19] These complexes presumably possess a planar structure,[19a] according to the present optimized planar structure of [Ni(abphen)] (**2**). On switching from **1** to **2**, theoretical data indicate a decrease of the ground state dipole moment, $\mu_g$, which, analogously to **1**, is directed between the imino groups. Thus, the calculated smaller value of $\mu_g$ of **2** can be related to the less electron-withdrawing effect of NH groups compared to oxygen donor atoms. The calculated nonlinearity of **2** is similar to that of **1**, and can be related essentially to a single low-energy excited state, having a polarization parallel with respect to the molecular dipolar ($z$) axis. In fact, although the lowest state consists of an $x$-polarized transition, the associated low intensity ($r^x_{ge}$ = 2.11 D) and CT character ($\Delta\mu_{ge}$ = −2.74 D) imply a negligible contribution to off-diagonal $\beta_{ijk}$ tensors and, hence, to optical nonlinearity (Table 2). Thus, analogously to **1**, a single diagonal hyperpolarizability tensor component, $\beta_{zzz}$, parallel to the dipolar $z$ axis of the molecule, mainly contributes to the NLO response (Table 1). Moreover, the slightly larger $\beta_\mu$ value of **2** can be related essentially to the calculated red-shift of the low-energy, $z$-polarized CT transition. A red-shift of the lowest electronic transitions also can be observed experimentally on comparing optical absorption spectra of **1**[6a] and **2**.[19a] Finally, calculated negative $\beta$ values are a consequence of the negative dipole moment change between the ground and excited states, $\Delta\mu_{ge}$, associated with the $\beta$-determining CT transition (Table 2). While in the ground state the dipole moment is directed between the imine groups, in the excited state it has an opposite orientation, i.e., between the nitrogen donor atoms. Thus, [M(abphen)] complexes represent a new family of second-order NLO chromophores having an analogous nonlinearity to that of [M(salophen)] complexes.

A closely related structure to [M(abphen)] is offered by the macrocyclic M[14]$N_4$ complexes of the tribenzo[*b*,*f*,*l*][1,4,8,11]tetrazacyclotetradecine (TAD) ligand, which represents a versatile system readily accessible to a variety of substitutions, both in the tribenzo[*b*,*f*,*l*] as well as the cyclotetradecine rings.[20] First, we consider the prototypical unsubstituted planar Ni(TAD) complex **3**.[21] As expected, on passing from **2** to **3** we observe only minor changes as far as calculated linear and nonlinear optical features (Tables 1 and 2). In fact, analogously to **2**, $\mu_g$ is directed between the imino groups and negative values of $\Delta\mu_{ge}$ and $\beta$ are predicted. The larger $\beta$ values of **3** are a consequence of the red-shift of its lowest electronic transitions, as have also been observed experimentally.[20d] Again, these results indicate that M(TAD) complexes possess NLO characteristics like those of [M(salophen)] and [M(abphen)]. In view of their versatility to achieve substituted donor−acceptor derivatives, they represent attractive candidates for further theoretical investigations.

As the first example of an Ni(TAD)-substituted species, we consider the 12,13-dione complex **4**. Its 2,3,6,19-tetramethyl derivative,[22a] as well as a variety of substituted species,[22b,22c] has been synthesized and characterized previously. The calculated dipole moment of **4** is larger than the unsubstituted derivative **3**, because of the electron-withdrawing effect of the dioxo groups. However, its calculated nonlinearity is smaller than that of the unsubstituted complex **3** (Table 1). The presence of the 12,13-dioxo groups results in a blue-shift of the lowest electronic transitions, with a consequent lower two-level contribution to optical nonlinearity (Table 2). Note that the calculated blue-shift of the lowest CT transitions on passing from **3** to **4** is in favorable agreement with that observed experimentally.[20d,22a,22c]

These results suggest that enhancement of nonlinearity in **3** necessarily implies that the acceptor substituents be on the benzo[*b*,*f*,*l*] rings. For this purpose we consider the 16,17-dione derivative **5**, whose related planar semiquinone has been synthesized and characterized previously.[20b] On switching from **3** to **5**, we observed a dramatic increase of the ground state dipole moment, which now has an opposite orientation, i.e., it is directed between the [1,4] nitrogen donor atoms of the TAD ring, thus involving positive values of $\Delta\mu_{ge}$, $\beta_{ijk}$ and $\beta_{\mu}$ (Tables 1 and 2). Moreover, we predicted a significant larger optical nonlinearity, in terms of both static and dynamic hyperpolarizabilities. In a two-state picture, this situation is consistent with the calculated stronger (**3** vs. **5**) low-energy, *z*-polarized CT transition, strengthened by the larger charge delocalization over the benzo[*f*] ring in the excited state involved, because of the 16,17-dioxo substituents.

The optical nonlinearity of **5** is further enhanced by considering the donor 3,10-diethylamino substitution on the benzo[*b*,*l*] rings (**6**). This feature is due to the further strengthening of both the *z*- and *x*-polarized, lowest CT transitions. Moreover, the latter transition involves a very large $\Delta\mu_{ge}$ and is responsible for the appreciable calculated off-diagonal $\beta_{ijk}$ tensors, thus resulting in a sizeable two-dimensional (2D) NLO character of **6** ($u = 0.24$) (Tables 1 and 2). Clearly, the two-state model is inadequate to describe the optical nonlinearity of such a system, since at least two states mainly contribute to the molecular hyperpolarizability.

Replacement of dioxo groups in **5** by two strong electron acceptors, such as nitro groups (**7**), does not result in an appreciable improvement in $\beta_{\mu}$. Unlike **5**, however, the nitro derivative **7** possesses some 2D character, owing to the strengthening of the lowest-energy, *x*-polarized CT transition, as in **6**, and to the presence of an additional low-energy, *x*-polarized CT transition. Moreover, the off-diagonal $\beta_{ijk}$ tensors have an opposite sign with respect the diagonal $\beta_{zzz}$ one, with a resulting negative nonlinear anisotropy ($u = -0.22$). Negative off-diagonal $\beta_{ijk}$ values for **7** are consequence of the larger negative contribution of three-level terms compared with two-level terms (Table 2).

The further donor substitution in **7** with two 9,16-diethylamino groups (**8**), leads to a one-dimensional character of the calculated optical nonlinearity, in spite of the existence, analogously to **7**, of two lowest-energy *x*-polarized CT transitions. In this case, however, both two-level and three-level contributions cancel each other, thus resulting in a single diagonal hyperpolarizability tensor component, $\beta_{zzz}$, and $\beta_{\mu}$ values similar to those of **6** (Table 2).

The 8,17-nitro substitution on the benzo[*b*,*l*] rings (**9**) offers the possibility to obtain an enhanced in-plane 2D character of the optical nonlinearity (Table 1). Actually, the calculated in-plane anisotropy for the dipolar complex **9** ($u = -0.5$) involves a significant octupolar contribution[12] to the optical nonlinearity. The negative in-plane anisotropy of **9** depends on off-diagonal $\beta_{ijk}$ tensors, which have an opposite (positive) sign with respect to the diagonal (negative) $\beta_{zzz}$ tensor (Table 2). Again, as in **7** and **8**, the presence of two low-energy *x*-polarized CT transitions leads to off-diagonal tensors dominated by the contribution of the three-level terms. In this case, however, the presence of 8,17-dinitro substituents on the benzo[*b*,*l*] rings implies that values of $\Delta\mu_{ge}$ associated with the two mentioned *x*-polarized CT transitions have opposite signs, resulting in a low two-level sum contribution. Thus, the calculated positive off-diagonal $\beta_{ijk}$ values of **9** are a consequence of the larger positive contribution of three-level vs. two-level sums (Table 2). Note that, the 8,17-dinitrobenzo[*b*,*l*] ring substitution involves a blue-shift of the lowest calculated electronic transitions on passing from **3** to **9** (Table 2), according to observed changes in optical absorption maxima.[20c,20d]

The combination of **7** and **9** in the tetrasubstituted nitro derivative **10** is expected to involve an enhanced nonlinearity with negative in-plane anisotropy. Actually, compound **10** is characterized by the two lowest *x*-polarized CT transitions, in addition to the *z*-polarized CT transition, and results in an increased nonlinearity, relative to **9**, again with a significant octupolar contribution. Both diagonal and off-diagonal tensors are dominated by the three-level terms (Table 2).

The evaluation of NLO properties of related free ligands **3a**−**10a** allows a useful comparison to be made with complexes **3**−**10** (Tables 1 and 2). Their calculated optical nonlinearity is generally lower (ca. 60% for **3a**, **10a**; 20% for **6a**, **8a**) and parallels the two-dimensional character of related Ni$^{II}$ complexes. The enhancement of the hyperpolarizability on switching from free ligands to Ni$^{II}$ complexes, which is less evident for D/A-substituted species **6a** and **8a**, can be related to the involvement of metal 3d orbitals that leads to a larger charge delocalization over the planar macrocycle and, hence, to red-shifted, and sometimes stronger, CT transitions (Table 2). Therefore, the optical nonlinearity of the present donor−acceptor TAD derivatives is dominated by substituents on the tribenzo[*b*,*f*,*l*] rings. In these cases, the metal ion mostly acts as a bridge of the D−π−A system, as previously observed for donor−acceptor bis(salicylaldiminato)Ni$^{II}$ complexes.[3a,4]

## Conclusions

In this paper, we have demonstrated that starting from bis(salicylaldiminato)Ni$^{II}$ Schiff'-base complexes it is possible to design alternative molecular NLO structures by changing the donor atoms of the (salophen) template. Thus, calculations on a series of novel molecular architectures, based on planar [N$_4$]Ni$^{II}$ complexes, indicate that these molecules possess comparable, or even larger, second-order nonlinearity to those of bis(salicylaldiminato)Ni$^{II}$ Schiff-base analogues. The nonlinearity of substituted Ni(TAD) complexes is dominated by the nature and position of substituents on the tribenzo[*b*,*f*,*l*] and/or cyclotetradecine rings, and is dictated by the relative magnitude and direction of the ground- and excited-state dipole moments. In particular, analogously to [Ni(salophen)] complexes, the donor substituents on the dibenzo[*b*,*l*] rings and the acceptors on the benzo[*f*] ring, involve larger nonlinearity. However, substitution with acceptor groups in the dibenzo[*b*,*l*] rings of the [Ni(TAD)] complex involves an enhanced octupolar $\beta$ contribution with respect the dipolar one. This feature is a very interesting one with the perspective of designing polarization-independent materials for electro-optical applications.

## Acknowledgments

This research was supported by the MIUR (Cofinaziamento per programmi di ricerca di interesse nazionale 2001).

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Received January 14, 2003