FULL PAPER

Dipolar Donor–Acceptor-Substituted Schiff Base Complexes with Large Off-Diagonal Second-Order Nonlinear Optical Tensor Components

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Abstract: The synthesis, characterization, and two-dimensional second-order nonlinear optical (NLO) response of a dipolar Ni^{II} donor–acceptor Schiff base complex and the related ligand are reported. Electric-field-induced second-harmonic generation and harmonic light (hyper-Rayleigh) scattering techniques, in combination with INDO/SCI-SOS theoretical calculations, were used to investigate the vector part of the hyperpolarizability tensor and the two-dimensional character of the molecular nonlinearity, respectively. Off-diagonal hyperpolarizability tensors can be related to charge-transfer transitions that are polarized perpendicular to the molecular di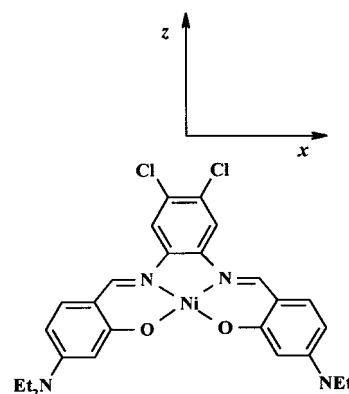polar axis, while parallel transitions account for the diagonal hyperpolarizability tensor. The role of the metal center in enhancing the two-dimensional NLO response of such molecules is twofold since it acts both as the donor and the bridging moiety of the planar donor–(π-conjugate-bridge)–acceptor system. These dipolar two-dimensional molecules are interesting candidates from the perspective of polarization-independent NLO materials.

Keywords: nickel · nonlinear optics · Schiff bases · second-order hyperpolarizability · semiempirical calculations

Introduction

In recent years much attention has been paid to the synthesis and development of multi-dimensional second-order nonlinear optical (NLO) molecule-based materials,[1] ranging from strongly dipolar molecules[2] to purely octupolar structures.[3] Compared with classical one-dimensional dipolar chromophores,[4, 1d] octupoles may offer advantages of better nonlinearity/transparency tradeoff[1–3] and, in the case of nonpolar species, may favor the formation of noncentrosymmetric architectures,[5] owing to the lack of a permanent dipole moment. Multidimensional dipolar chromophores are attractive candidates for poled polymer thin-film applications, as they can be easily poled as classical dipolar chromophores,[4, 6] by the application of a strong electric field to the polymer film above the glass transition temperature. If the octupolar contribution to the β value is much higher than the dipolar one, it has been theoretically[7] and experimentally[8] demonstrated that the NLO film anisotropy significantly decreases, opening new possibilities for the development of polarization-independent materials that would be suitable for optical telecommunications.[9] However, few examples of dipolar second-order multidimensional NLO chromophores have been reported in the literature, most of them based on benzene derivatives.[1, 10]

We present here a comparative experimental and theoretical investigation of the molecular second-order two-dimensional (2D) NLO properties, $\beta_{ijk}(-2\omega;\omega,\omega)$, of a donor–acceptor bis(salicylaldiminato)Ni^{II} Schiff base complex (NiL) and the related ligand (H_2L),[11] which is the first example of a

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two-dimensional dipolar NLO metallo-organic material.[12] This study focuses on the synthesis, linear optical spectroscopic, and second-order NLO response (sampled by the electric-field-induced second-harmonic generation

(EFISH)[13] and harmonic light-scattering (HLS)[14] techniques), in combination with a quantum chemical analysis within the proven INDO/SCI-SOS (ZINDO) formalism,[15] to describe the electronic structure and structure/NLO-property relationships of this new class of inorganic 2D dipolar NLO-chromophores.

Results and Discussion

Synthesis, characterization, and molecular structure: The H_2L Schiff base ligand was prepared in high-yield by condensation of the 4-(diethylamino)salicylaldehyde with the 4,5-dichloro-1,2-phenylenediamine. The yellow imine was readily purified by recrystallization from a mixture of absolute ethanol/chloroform. The crystal structure of the unsubstituted H_2(salophen)[16] indicates an enolimine tautomeric (nonplanar) structure, also evident in solution.[17] Thus, an analogous, predominantly enol–iminic, structure can be assumed for the related donor–acceptor substituted H_2L imine. In support of this formulation, a broad resonance in the $\delta = 13.25$ region is evident in the ^1H NMR spectrum. It disappears upon exchange with D_2O and can be associated with the $-OH$ protons presumably involved in intramolecular hydrogen bonding with iminic nitrogen atoms.

The optimized geometrical structure of H_2L, obtained without any symmetry constraint, is in agreement with the above description (Figure 1). It predicts a nonplanar C_2 structure, with two *trans*-imine linkages, in which the plane of each 4-(diethylamino)salicylidene fragment and that containing the phenylene bridge make an angle of 46.5°.

Figure 1. Optimized geometry of the H_2L ligand.

The reaction of the ligand with the Ni^{II} ion leads to the formation of the stable noncentrosymmetric NiL complex. This was characterized by FAB mass spectrometry, ^1H NMR spectroscopy, and satisfactory microanalysis. The FAB mass spectrum indicates the existence of a monomeric species in the gas phase. Furthermore, available X-ray structures of the unsubstituted Ni(salophen)[18] and of a closely related donor–acceptor-substituted Ni^{II} complex[19] indicate monomeric, planar species in the solid state. Thus, an analogous planar, monomeric molecular structure can be safely assumed for the present donor–acceptor-substituted NiL complex. Such a structure is also obtained from the geometric optimization.

Linear optical spectra: UV-visible absorption spectra of H_2L and NiL are reported in Figures 2 and 3, respectively. The spectrum of the free ligand H_2L (Figure 2) exhibits two intense absorption bands in the visible near-UV region at 410 ($\varepsilon = 5.9 \times 10^4$) and 374 nm ($\varepsilon = 9.4 \times 10^4$), which presumably involve $\pi \rightarrow \pi^*$ transitions. Compared with the absorption spectrum of the unsubstituted H_2(salophen) ligand,[11c] these bands are more intense and red-shifted. This is consistent with an increased π-charge delocalization due to the donor and acceptor substituents.
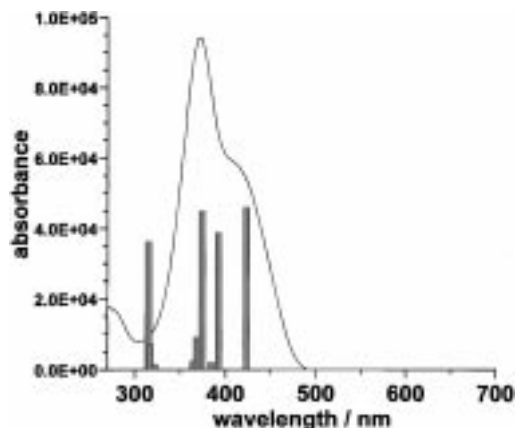

Figure 2. Optical absorption spectra and INDO/SCI-derived electronic transitions of H_2L. The bars represent the oscillator strength of the various transitions in arbitrary units, adjusted to the strongest transition in the experimental optical spectrum in chloroform solution (solid line). Computed electronic transitions are shifted by $+80$ nm.

The optical spectrum of the NiL complex (Figure 3), compared with that of the ligand, has an additional overlapping feature at longer wavelength, and is generally red-shifted. Complexation involves a larger charge delocalization, mediated by the metal center, over the whole planar molecule.
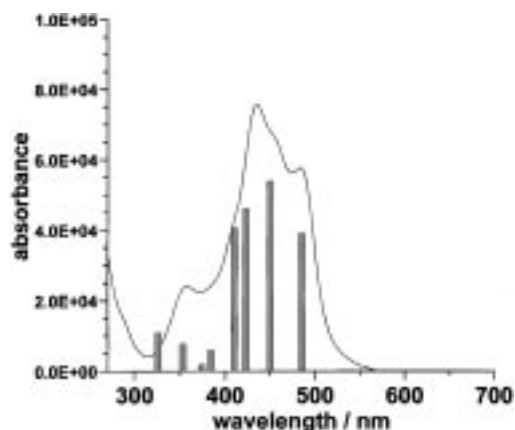

Figure 3. Optical absorption spectra and INDO/SCI-derived electronic transitions of NiL. The bars represent the oscillator strength of the various transitions in arbitrary units, adjusted to the strongest transition in the experimental optical spectrum in chloroform solution (solid line). Computed electronic transitions are shifted by $+65$ nm.

This is responsible for the red shift of the optical spectrum and for the existence of additional bands, absent in the absorption spectrum of the free ligand, which presumably involve both the ligand and the metal center. Unfortunately, the overlapping nature of these bands precluded any accurate evaluation of solvatochromism.

Theoretical calculations on H_2L and NiL are consistent with the above description. Actually, the calculated optical spectrum of H_2L in the visible near-UV region (Figure 2) indicates the existence of various $\pi \rightarrow \pi^*$ transitions involving frontier molecular orbitals. In particular, they essentially involve orbitals of 4-(diethylamino)salicylidene fragments and those of the C=N$^-$ groups mediated by the phenylene bridge. These transitions have some charge-transfer (CT) character and are, to some extent, responsible for the second-order NLO response of the molecule.

On switching to the optical spectrum of the NiL complex, the calculated low-energy transitions (Figure 3) may be characterized as $\pi \rightarrow \pi^*$, involving both the ligand and the metal center. Under C_{2v} symmetry, both the "in-plane" z-polarized and x-polarized transitions are allowed. They involve absorption of radiation with its electric vector vibrating parallel and perpendicular with respect to the molecular dipolar z axis, respectively. Actually, the lowest energy electronic transitions for NiL consist of three intense x-polarized (perpendicular), z-polarized (parallel), and x-polarized (perpendicular) transitions, that have CT character. These transitions are mainly responsible for the two-dimensional second-order NLO response of this molecule (vide infra).

Second-order molecular nonlinearity, EFISH results: The dipolar molecular hyperpolarizability of the H_2L and NiL compounds was measured by the EFISH technique.[13] This technique allows the determination of the $\mu \cdot \beta$ dot product when an electric field is applied to a solution of an NLO-active species. The β_μ value, that is, the vector component of the β_{ijk} tensor along the dipole moment direction,[20] can be extracted if the ground state dipole moment is known. Experimental results for H_2L and NiL are reported in Table 1 and are compared with calculated data. A good agreement between theoretical and experimental $\mu \cdot \beta$ values is found for EFISH data of NiL. In contrast, the calculated $\mu \cdot \beta$ value is significantly underestimated for the free ligand H_2L.

Table 1. Experimental and calculated second-order NLO response[a, b, c] for NiL and H_2L.

	$\langle \beta^2 \rangle^{1/2}$	u	β_{zzz}	β_{zxx}	$\mu \cdot \beta_{EFISH}$ measured	$\mu \cdot \beta_{EFISH}$ from HLS
NiL						
experiment	24	0.47	43	20	157	208
calculation	18	0.54	29.3	15.7	146	–
H_2L						
experiment	14	0.46	24	11	240	190
calculation	8	0.55	13.3	7.33	107	

[a] In 10^{-30} cm^5 esu^{-1}; $\hbar\omega = 0.92$ eV. Hyperpolarizability values are given in the phenomenological convention, where β_{ijk} are by a factor of 1/4 smaller than in the Taylor series convention.[30] [b] For definition of parameters, see text. [c] Estimated uncertainties are $\pm 8\%$ on EFISH and $\pm 15\%$ on HLS data.

It is interesting to compare these experimental EFISH results for H_2L with values that can be inferred from a simple additive vectorial model, in which the μ and β vectors of the 4-dimethylamino-4′-chlorostilbene (DMCS) parent molecule[13] are added, assuming an ideal planar geometry of the H_2L ligand. Of course, from a chemical point of view, a stilbene-conjugated derivative significantly differs from that of a Schiff base. However, in terms of dipolar hyperpolarizabilities, it has been experimentally demonstrated[21] that differences found between analogous stilbene and Schiff base derivatives are not very large ($\pm 15\%$) in view of experimental errors. Thus, in a preliminary stage of analysis, we may propose a "naive" additive model of the two arms of the ligand to account for the EFISH response of H_2L. As the angle (θ) between the two Schiff base arms of H_2L approaches $\theta = 96°$,[22] the $\mu \cdot \beta$ value resulting from this simple additive vector model is ($\mu \cdot \beta_{H_2L}) = 2\mu \cdot \beta_{DMCS}(1 - \cos\theta)$ (in which $\mu \cdot \beta$ (1.34 μm) = 120×10^{-48} esu, as deduced from data given in ref. [13] at 1.06 μm, using a two-level dispersion model valid for the one-dimensional DMCS molecule). We find $\mu \cdot \beta_{H_2L} = 215 \times 10^{-48}$ esu, a value comparable with the experimental EFISH value for H_2L, taking into consideration the experimental error, the structural differences between DMCS and the Schiff base arms of H_2L, and the possibility of a nonzero twist angle between these two arms (as results from the optimized structure).

The higher $\mu \cdot \beta$ value for the free ligand, as compared with that of the complex, confirms the tendency indicated by the calculated dipole moments: $\mu(NiL) = 3.3$ D and $\mu(H_2L) = 5.4$ D. Clearly, the relative dipolar contribution to the whole β tensor decreases upon complexation.

Second-order molecular nonlinearity, HLS results: We have used both EFISH and HLS techniques (at 1.34 μm) in order to experimentally determine the purely dipolar contribution to the β tensor (EFISH), and to investigate the two dimensional character of the microscopic nonlinearity of these molecules, which involves a significant octupolar contribution to the β tensor (HLS). Moreover, since only the two Cartesian components β_{zzz} and β_{zxx} should display significant values in the case of C_2 molecules,[23] the HLS technique provides experimental determination of these two β_{zzz} and β_{zxx} values from the analysis of the depolarization ratio $D = \langle \beta^2_{zxx} \rangle / \langle \beta^2_{zzz} \rangle$.[10, 24] This, in turn, depends on the ratio $u = \beta_{zxx}/\beta_{zzz}$, which defines the "Cartesian nonlinear anisotropy",[1] and is a relevant parameter for describing the 2D character of the molecular β_{ijk} tensor. The parameter $\langle \beta^2 \rangle^{1/2}$ represents the orientational average value of the $\beta \otimes \beta$ tensor product, resulting in a sixth-rank tensor, that is, an even-order tensor, which is nonzero even in centrosymmetric media, such as standard solutions of NLO molecules. In the case of C_{2v} molecules Equation (1) is valid. HLS data indicate a sizable 2D character for H_2L and NiL dipolar molecules, with a significant in-plane anisotropy ($u = \beta_{zxx}/\beta_{zzz}$) ~ 0.5 (Table 1).

$$\langle \beta^2 \rangle^{1/2} = \frac{6}{35}\beta^2_{zzz} + \frac{38}{105}\beta^2_{zxx} + \frac{16}{105}\beta_{zzz}\beta_{zxx} \tag{1}$$

For both molecules, a very good agreement is found between the experimental and calculated in-plane anisotropy.

In contrast, a larger difference is observed between experimental and calculated $\langle\beta^2\rangle^{1/2}$, β_{zzz}, and β_{zxx} values, especially for H_2L.

As $\mu \cdot \beta_{EFISH} = \mu \cdot [\beta_{zzz} + 1/3(\beta_{zxx} + \beta_{xzx} + \beta_{xxz})]$, it can also be calculated from HLS results. We have calculated this value and compared it with the experimental value obtained by the EFISH technique. The agreement is reasonable, when considering the relative experimental uncertainties associated with the EFISH ($\pm 8\%$) and HLS ($\pm 15\%$) experimental data.

Second-order molecular nonlinearity, theoretical calculations: In view of the reasonable agreement between experimental and theoretical data for NiL, especially for $\mu \cdot \beta$ and the in-plane anisotropy, it is interesting to analyze the contribution of each excited state to the β_{ijk} components (Table 2). The nonlinearity of NiL can be mainly attributed to the three lowest-energy CT excited states mentioned above (S1–S3, Figure 4). Transition dipole moment elements, r_{gn}^i, associated with these states are perpendicular, parallel, and perpendicular, respectively. Moreover, since this molecule possesses C_{2v} symmetry, only perpendicular transition dipole moment matrix elements (r_n^j; $j \neq i$, where i is the dipolar axis) will contribute to off-diagonal tensors.[25] In fact, while the S2 state mainly contributes ($\approx 65\%$) to the β_{zzz} tensor, S1 and S3 states account for off-diagonal tensor components. Moreover, theoretical analysis indicates that the off-diagonal nonlinearity of NiL is dominated by the two-level contributions, with the three-level terms being almost negligible.[26] This is in contrast with off-diagonal nonlinearities of nondipolar multi-dimensional NLO chromophores, the NLO response of which is necessarily related to three-level terms.[1, 3]

The difference in electronic populations between the ground state and the three lowest (S1–S3) excited states (Figure 4), clearly indicates that the metal and the 4-(diethylamino)salicylidene rings act as the electron donor, while the imine groups essentially are the acceptor counterparts.

The calculated and observed enhancement of the NLO response on passing from the free H_2L ligand to the NiL complex is clearly a consequence of a larger charge delocalization over the whole planar molecule, as well as of the increasing CT character of the involved excited states.

Conclusion

This paper presents the synthesis and characterization of a novel class of 2D dipolar NLO complexes. It represents the first example of a 2D dipolar NLO metallo-organic material
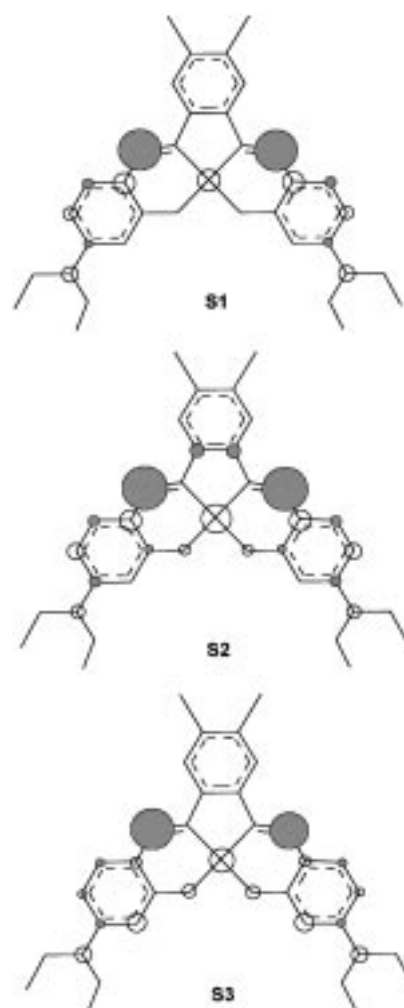

Figure 4. Difference in electronic populations between the ground state and the three (S1–S3) excited states involved in the NLO response for NiL. Solid circles are indicative of an increases of the electron density in the charge transfer process.

involving a 2D charge transfer between a metal center and a 2D ligand with complexing sites located inside the conjugation path. The few examples of 2D multipolar (nondipolar) complexes for quadratic NLO reported in the literature to date,[12] all involve complexation sites located at the extremities of the ligand. The role of the metal center in enhancing the 2D NLO response of such complexes is manifold; it involves a larger charge delocalization (than in the free ligand) between the arms of the 2D chromophore ligand on the whole planar molecule. This is turn favors the 2D character of the charge transfer. Moreover, it acts both as

Table 2. Computed linear optical spectroscopic and state-by-state analysis[a] of the second-order NLO response (10^{-30} cm^5 esu^{-1}; $\hbar\omega = 0.92$ eV) for NiL.

State	Symmetry (polarization)	$\hbar\omega_{eg}$ [eV]	r_{ge}^z [D]	r_{ge}^x [D]	Δr_n^z [D]	β_{zzz}	$\beta_{xzx} = \beta_{xxz}$	β_{zxx}	β_μ
S1	$B_1(x)$	2.93	0.00	-6.75	1.99	0.0	4.5	3.0	3.7
S2	$A_1(z)$	3.21	-7.55	0.00	3.63	19.1	0.0		17.9
S3	$B_1(x)$	3.45	0.00	-6.71	6.27	0.0	15.5	10.0	16.0
$\sum_n S_n$						29.3	17.8	11.5	44.3

[a] For definition of parameters, see text.

the donor and the bridging moiety of the planar donor – (π-conjugate-bridge) – acceptor system.

Thus, the in-plane 2D optical nonlinearity of the NiL complex may be related to various low-energy CT states. While z-polarized electronic transitions, parallel with respect to the molecular dipolar (z) axis, contribute to the diagonal β_{zzz} tensor, perpendicular x-polarized transitions contribute to off-diagonal β_{ijk} hyperpolarizability tensors. The good agreement between experimental and theoretical results for the in-plane anisotropy factor is quite encouraging, as calculations appear to be able to predict the nonlinear anisotropy of these molecules, a crucial parameter for the selection of novel and efficient molecules for designing polarization-independent materials and devices.

Experimental Section

General: Nickel(II) acetate tetrahydrate (reagent grade, Aldrich) was used without purification. 4,5-Dichloro-1,2-phenylenediamine and 4-(diethyl-amino)salicylaldehyde (Aldrich) were purified by sublimation in vacuo. Elemental analyses were performed on a Carlo Erba 1106 elemental analyzer. FAB mass spectra were recorded on a Kratos MS50 double-focusing mass spectrometer equipped with a standard FAB source. FAB MS spectra were obtained by using 3-nitrobenzyl alcohol (3NBA) as the matrix. ^{1}H NMR spectra were recorded on a VARIAN INOVA 500 spectrometer, using TMS as internal standard. UV/Vis spectra were recorded with a Beckman DU 650 spectrophotometer, and λ_{max} values are considered accurate to ± 1 nm.

Synthesis of H$_2$L: A solution of 4,5-dichloro-1,2-phenylenediamine (0.595 g, 3.36 mmol) in absolute ethanol (20 mL) was added to a solution of 4-(diethylamino)salicylaldehyde (1.30 g, 6.72 mmol) in absolute ethanol (20 mL) under stirring at room temperature. One drop of sulfuric acid was added to the stirring solution as a catalyst, and an immediate orange precipitate was obtained. The mixture was stirred overnight at room temperature. The precipitated Schiff base ligand was collected by filtration, and recrystallized from a mixture of 10:1 absolute ethanol/chloroform (1.24 g, 70%). The compound was soluble in most common organic polar solvents and moderately soluble in nonpolar solvents. M.p. 188–190 °C; ^{1}H NMR (500 MHz, CDCl$_3$, 25 °C, TMS): $\delta = 1.19$ (t, $J = 7.0$ Hz, 12 H; CH$_3$), 3.38 (q, $J = 7.0$ Hz, 8 H; CH$_2$), 6.23 (m, 4 H; Ph), 7.14 (d, $J = 9.5$ Hz, 2 H; Ph), 7.26 (s, 2 H; Ph), 8.38 (s, 2 H; CH=N), 13.25 (s, 2 H; OH); UV/Vis (CHCl$_3$): ($\varepsilon \times 10^4$) = 374 (9.41), 410 nm (5.86); FAB-MS (3NBA): m/z: 528 $[M+H]^+$; elemental analysis calcd (%) for C$_{28}$H$_{32}$Cl$_2$N$_4$O$_2$: C 63.76, H 6.11, N 10.62; found: C 63.45, H 6.25, N 10.57.

Synthesis of NiL: The complex was prepared by reaction of an aqueous solution (50 mL) of nickel(II) acetate (0.321 g, 1.29 mmol) with a warm 4:1 alcoholic/chloroform solution (170 mL) of the Schiff base acetate (0.679 g, 1.29×10^{-3} mol). A red-brown precipitate was obtained. The mixture was stirred at room temperature for 24 h. The precipitated complex was collected by filtration, washed with an H$_2$O/ethanol mixture, and then recrystallized from a mixture of 3:1 absolute ethanol/chloroform (0.57 g, 75%). ^{1}H NMR (500 MHz, CDCl$_3$, 25 °C, TMS): $\delta = 1.20$ (t, $J = 7.0$ Hz, 12 H; CH$_3$), 3.37 (q, $J = 7.0$ Hz, 8 H; CH$_2$), 6.20 (dd, $J = 9.0$, 2.2 Hz, 2 H; Ph), 6.27 (d, $J = 2.2$ Hz, 2 H; Ph), 7.07 (d, $J = 9.0$ Hz, 2 H; Ph), 7.57 (s, 2 H; Ph), 7.68 (s, 2 H; CH=N); UV/Vis (CHCl$_3$): λ_{max} ($\varepsilon \times 10^4$) = 357 (2.42), 435 (7.57), 455 (shoulder) (6.62), 484 nm (5.75); FAB-MS (3NBA): m/z: 585 $[M+H]^+$; elemental analysis calcd (%) for C$_{28}$H$_{30}$Cl$_2$N$_4$O$_2$Ni: C 57.57, H 5.17, N 9.59; found: C 57.35, H 5.25, N 9.37.

EFISH measurements: Second-order molecular hyperpolarizability analyses were performed by using a Q-switched mode-locked Nd:YAG laser operating at 1.34 μm ($\hbar\omega = 0.92$ eV) by the electric-field-induced second-harmonic generation method. The laser delivers pulse trains with a total duration envelope around 90 ns, each pulse duration being 160 ps. The molecules to be measured were dissolved in chloroform (used a reference) at various concentrations, x, between $5 \times 10^{-3} - 10^{-4}$ M. The sign of $\vec{\beta}_\mu \vec{\beta}_\mu = \beta_{zzz} + 1/3(\beta_{zxx} + \beta_{xzx} + \beta_{xxz})$ was determined by studying the variation of

the macroscopic susceptibility, $\Gamma(x)$, as a function of x. Further details of the experimental methodology and data analysis are reported elsewhere.[13]

Harmonic light-scattering measurements: HLS experiments were performed at 1.34 μm, by using a Nd^{III}:YAG laser emitting nanosecond pulse trains at a 10 Hz repetition rate. The typical pulse energy was 1 mJ. Solutions at various concentrations of the molecule to be measured were placed in a 4 cm long fluorescence cell, at the focus of the incoming fundamental beam. Harmonic incoherent emission was collected in a 90° configuration by using two convergent lenses, detected by a Hamamatsu R2228 Photomultiplier, and sampled and averaged by using a Stanford Boxcar Integrator. The incident fundamental intensity was continuously varied by rotating a half-wave plate between two crossed polarizers. A small part of the incoming beam was collected by using a glass plate and sent onto a reference nonlinear crystalline powder for frequency doubling. The second harmonic signal was used as the reference signal. The slope of the line describing the Harmonic light scattering from the studied sample as a function of this reference signal provided a value of the "whole" β tensor, or more exactly the mean value of the $\beta \otimes \beta$ tensor product. β values were calibrated with respect to the value of the pure solvent (chloroform).

In a second step, the incident intensity was kept constant, and the incident polarization was continuously varied by rotating a half-wave plate located behind a Glan polarizer. The dependence of the harmonic light scattering on the angle between the incident polarization and a given axis of the polarization plane (here a vertical axis) provides information about the two Cartesian components β_{zzz} and β_{zxx} of the β tensor of the C_2 molecules, in which the z axis is parallel to the ground state dipole moment and the x axis, perpendicular to z, is located in the molecular plane. Details concerning this procedure are given in ref. [10].

Special attention was paid to the elimination of the two-photon fluorescence contribution. A factor of four between the whole signal as detected at 0.67 μm and the purely harmonic one was evaluated, leading to a large error (by a factor of two) in the measurement of $\langle\beta\rangle^{1/2}$ and in the Cartesian components of the hyperpolarizability tensor. The fluorescence background spectrum was recorded between 0.58 and 0.70 μm by using a spectrometer in front of the photomultiplier tube. This background was subtracted from the whole signal at 0.67 μm, yielding a reasonable estimate of the pure harmonic scattering emission from the solution.

Computational methods: The all-valence INDO/S (intermediate neglect of differential overlap) formalism,[27] in connection with the sum over excited particle-hole-states (SOS) formalism,[28] was employed. Details of the computationally-efficient ZINDO–SOS-based method for describing second-order molecular optical nonlinearities have been reported elsewhere.[15] Standard parameters and basis functions were used.[27] 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 150 energy transitions between SCF and CIS electronic configurations were chosen to undergo CI 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. All calculations were performed with the ZINDO program[15a] implemented on an IBM SP system. Metrical parameters used for INDO/S calculations were taken from fully optimized structures, without any symmetry constraint, at AM1 and ZINDO/1 levels, for H$_2$L and NiL, respectively, by using the HyperChem package.[29] For NiL a C_{2v} planar structure was found, while a conformation with two *trans*-imine linkages (C_2 symmetry) was found to be the most stable for H$_2$L.

Acknowledgements

[1] For some leading references on multipolar NLO materials see: a) S. Brasselet, J. Zyss, *J. Opt. Soc. Am. B* **1998**, *15*, 257; b) J. Zyss, I. Ledoux, *Chem. Rev.* **1994**, *94*, 77; c) J. Zyss, *J. Chem. Phys.* **1993**, *98*, 6583. d) J. J. Wolf, R. Wortmann, *Adv. Phys. Org. Chem.* **1999**, *32*, 121.

[2] a) J. J. Wolff, D. Längle, D. Hillenbrand, R. Wortmann, R. Matschiner, C. Glania, P. Krämer, *Adv. Mater.* **1997**, *9*, 138; b) H. S. Nalwa, T.

Watanabe, S. Miyata, *Adv. Mater.* **1995**, *7*, 754; c) H. S. Nalwa, T. Watanabe, S. Miyata, *Opt. Mater.* **1993**, *2*, 73; d) R. Wörtmann, P. Krämer, C. Glania, S. Lebus, N. Detzer, *Chem. Phys.* **1993**, *173*, 99.

[3] For some recent experimental studies on nondipolar two-dimensional NLO chromophores see: a) J. J. Wolff, F. Segler, R. Matschiner, R. Wortmann, *Angew. Chem.* **2000**, *112*, 1494; *Angew. Chem. Int. Ed.* **2000**, *39*, 1436; b) S. Brasselet, F. Cherioux, P. Audebert, J. Zyss, *Chem. Mater.* **1999**, *11*, 1915; c) C. Lambert, G. Nöll, E. Schmälzlin, K. Meerholz, C. Bräuchle, *Chem. Eur. J.* **1998**, *4*, 2129; d) R. Wortmann, C. Glania, P. Krämer, R. Matschiner, J. J. Wolff, S. Kraft, B. Treptow, E. Barbu, G. Längle, G. Görlitz, *Chem. Eur. J.* **1997**, *3*, 1765; e) C. Dhenaut, I. Ledoux, I. D. F. Samuel, J. Zyss, M. Bourgault, H. Le Bozec, *Nature* **1995**, *374*, 339.

[4] For recent reviews on one-dimensional NLO materials see: a) L. R. Dalton, W. H. Steier, B. H. Robinson, C. Zhang, A. Ren, S. Garner, A. Chen, T. Londergan, L. Irwin, B. Carlson, L. Fifield, G. Phelan, C. Kincaid, J. Amend, A. Jen, *J. Mater. Chem.* **1999**, *9*, 1905; b) T. Verbiest, S. Houbrechts, M. Kauranen, K. Clays, A. Persoons, *J. Mater. Chem.* **1997**, *7*, 2175; c) I. Ledoux, J. Zyss, in *Novel Optical Materials and Applications* (Eds.: I. C. Khoo, F. Simoni, C. Umeton), Wiley, New York, **1997**; d) L. R. Dalton, A. W. Harper, R. Ghosn, W. H. Steir, M. Ziari, H. Fetterman, Y. Shi, R. V. Mustacich, A. K.-Y. Jen, K. J. Shea, *Chem. Mater.* **1995**, *7*, 1060; e) R. G. Benning, *J. Mater. Chem.* **1995**, *5*, 365; f) "Optical Nonlinearities in Chemistry": *Chem. Rev.* **1994**, *94*, 1.

[5] For some recent studies on multipolar NLO bulk materials see: a) C. Bourgogne, Y. Le Fur, P. Juen, P. Masson, J.-F. Nicoud, R. Masse, *Chem. Mater.* **2000**, *12*, 1025; b) C. C. Evans, R. Masse, J.-F. Nicoud, M. Bagieu-Beucher, *J. Mater. Chem.* **2000**, *10*, 1419; c) W. Lin, Z. Wang, L. Ma, *J. Am. Chem. Soc.* **1999**, *121*, 11249; d) V. R. Thalladi, S. Brasselet, H.-C. Weiss, D. Bläser, A. K. Katz, H. L. Carrell, R. Boese, J. Zyss, A. Nangia, G. R. Desiraju, *J. Am. Chem. Soc.* **1998**, *120*, 2563; e) J. Zyss, S. Brasselet, V. R. Thalladi, G. R. Desiraju, *J. Chem. Phys.* **1998**, *109*, 658.

[6] For general reviews on poled polymer NLO materials, see: a) T. J. Marks, M. A. Ratner, *Angew. Chem.* **1995**, *107*, 167; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 155; b) D. M. Burland, R. D. Miller, C. A. Walsh, *Chem. Rev.* **1994**, *94*, 31.

[7] S. Brasselet, E. Toussaere, J. Zyss, unpublished results.

[8] I. Cazenobe, I. Ledoux, S. Brasselet, E. Toussaere, J. Zyss, unpublished results.

[9] A. Donval, E. Toussaere, R. Hierle, J. Zyss, *J. Appl. Phys.* **2000**, *87*, 3258.

[10] S. Brasselet, J. Zyss, *J. Nonlinear Opt. Phys. Mater.* **1996**, *5*, 671.

[11] Bis(salicylaldiminato)M^{II} Schiff base complexes have recently been developed as a new class of efficient second-order NLO materials; see, for example: a) S. Di Bella, I. Fragalà, *Synth. Met.* **2000**, *115*, 191; b) G. Lenoble, P. G. Lacroix, J. C. Daran, S. Di Bella, K. Nakatani, *Inorg. Chem.* **1998**, *37*, 2158; c) S. Di Bella, I. Fragalà, I. Ledoux, M. A. Diaz-Garcia, T. J. Marks, *J. Am. Chem. Soc.* **1997**, *119*, 9550; d) P. G. Lacroix, S. Di Bella, I. Ledoux, *Chem. Mater.* **1996**, *8*, 541; e) S. Di Bella, I. Fragalà, I. Ledoux, T. J. Marks, *J. Am. Chem. Soc.* **1995**, *117*, 9481.

[12] a) Very few examples of 2D multipolar complexes for quadratic NLO are reported in the literature; all of them involve nondipolar species,[12b] except for a dipolar σ-acetylide Ni^{II} complex,[12c] whose two dimensional nonlinearity has not been explored; b) For a review, see: H. Le Bozec, T. Renouard, *Eur. J. Inorg. Chem.* **2000**, 229; c) I. R.

Whittall, M. G. Humphrey, S. Houbrechts, J. Maes, A. Persoons, S. Schmid, D. C. R. Hockless, *J. Organomet. Chem.* **1997**, *544*, 277.

[13] J.-L. Oudar, *J. Chem. Phys.* **1977**, *67*, 446.

[14] a) R. W. Terhune, P. D. Maker, C. M. Savage, *Phys. Rev. Lett.* **1965**, *61*, 681; b) K. Clays, A. Persoons, *Phys. Rev. Lett.* **1991**, *66*, 2980.

[15] a) S. Di Bella, I. Fragalà, T. J. Marks, M. A. Ratner, *J. Am. Chem. Soc.* **1996**, *118*, 12747; b) D. R. Kanis, M. A. Ratner, T. J. Marks, *Chem. Rev.* **1994**, *94*, 195.

[16] N. Bresciani Pahor, M. Calligaris, P. Delise, G. Dodic, G. Nardin, L. Randaccio, *J. Chem. Soc. Dalton Trans.* **1976**, 2478.

[17] *Comprehensive Coordination Chemistry*, *Vol 2* (Ed.: G. Wilkinson), Pergamon, Oxford, **1987**, p. 730.

[18] A. Gaetani Manfredotti, C. Guastini, *Acta Crystallogr. Sect. C* **1983**, *39*, 863.

[19] F. Averseng, P. G. Lacroix, I. Malfant, G. Lenoble, P. Cassoux, K. Nakatani, I. Maltey-Fanton, J. A. Delaire, A. Aukauloo, *Chem. Mater.* **1999**, *11*, 995.

[20] $\beta_\mu(-\omega;\omega\omega) = \sum_{i=1}^{3} \frac{\mu_i \beta_i}{|\mu|}$; where $\beta_i = \beta_{iii} + \frac{1}{3} \sum_{j \neq i} (\beta_{ijj} + \beta_{jij} + \beta_{jji})$.

[21] A. Hilton, T. Renouard, O. Maury, H. Le Bozec, I. Ledoux, J. Zyss, *Chem. Commun.* **1999**, 2521.

[22] Corresponding to an average angle between that found in the present optimized structure (102°) and that related to the X-ray structure of the unsubstituted H$_2$(salophen) (90°) ref. [16].

[23] J. Zyss, S. Brasselet, *J. Nonlinear Opt. Phys. Mater.* **1998**, *7*, 397.

[24] a) In the analysis of HLS data to determine the off-diagonal β_{zxx} tensor, we assumed the validity of the Kleinman's symmetry conditions (i.e., $\beta_{zxx} = \beta_{xzx} = \beta_{xxz}$).[24b] In reality, this approximation may be not fully valid, especially for NiL (because the harmonic frequencies are not far from resonance, see also Table 2). Therefore, the experimentally derived β_{zxx} tensor should be considered as an "averaged" off-diagonal value; b) D. A. Kleinman, *Phys. Rev.* **1962**, *126*, 1977.

[25] Actually, for a dipolar C_{2v} molecule the dipole moment variation between ground and excited states is: $\Delta r_n^j = 0$; $j \neq i$.

[26] The hyperpolarizability determined by a sum-over-states expression can be partitioned into two contributions, so-called two-level ($\beta_{ijk,2}$) 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 $r_{gn}^i r_{gn}^k \Delta r_n^i$ (generic two-level term); the three-level contributions involve the ground-state and two excited states, n, n', and are related to the product $r_{gn}^i r_{n'n}^i r_{gn}^k$ (generic three-level term). For a full account of this aspect related to 2D dipolar chromophores, see: S. Di Bella, I. Fragalà, *J. Phys. Chem. B*, submitted.

[27] a) M. Zerner, G. Loew, R. Kirchner, U. Mueller-Westerhoff, *J. Am. Chem. Soc.* **1980**, *102*, 589; b) W. P. Anderson, D. Edwards, M. C. Zerner, *Inorg. Chem.* **1986**, *25*, 2728; c) A. D. Bacon, M. C. Zerner, *Theor. Chim. Acta* **1979**, *53*, 21; d) J. Ridley, M. C. Zerner, *Theor. Chim. Acta* **1973**, *32*, 111.

[28] J. F. Ward, *Rev. Mod. Phys.* **1965**, *37*, 1.

[29] HyperCube HYPERCHEM, Release 4.5 for Windows, HyperCube, **1995**.

[30] A. Willetts, J. E. Rice, D. M. Burland, D. P. Shelton, *J. Chem. Phys.* **1992**, *97*, 7590.