Second-Order Optical Nonlinearities in Coordination Chemistry: The Case of Bis(salicylaldiminato)metal Schiff Base Complexes

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In memory of my greatly respected mentor Professor Olivier Kahn

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Since the mid-1980s, there has been a growth of interest in the search and development of molecular second-order nonlinear optical (NLO) materials that possess various device applications. Beside the most traditional donor-acceptor ("push-pull") organic chromophores (e.g. the stilbene family), chemists have increasingly extended their field of investigations to newer generations of organic molecules of greater complexity. In recent years, coordination complexes through their unique characteristics such as various redox and magnetic properties, in addition to their great diversity of geometries, have introduced a new dimension to the area. This review attempts to summarize the NLO capabilities of bis(salicylaldiminato)metal Schiff base complexes: (*i*) chromophores with enhanced hyperpolarizabilities (β) can be obtained by virtue of the coordinated metal center; (*ii*) the use of chiral substituents allows the engineering of the chromophores into various non-centrosymmetric environments and efficiencies of about 10 times that of urea in second-harmonic generation; (*iii*) the general trend observed for the high temperature stability in this family of chromophores, while combined with the large β×μ products, makes these systems interesting candidates for their incorporation into poled polymers with high glass transition temperatures (*Tg*); (*iv*) the possibility for β modulation induced by magnetic transition is also seen with respect to the concept of molecular switching.

1. Introduction

Materials which exhibit highly nonlinear optical (NLO) responses are currently of great scientific and technological interest.[1] While inorganic solids such as $LiNbO_3$ and KH_2PO_4 have traditionally attracted the widest attention,[2] it is now recognized that molecular-based materials possess many superior NLO characteristics: ultrafast response times, lower dielectric constants, better processability as thin-film devices, and enhanced non-resonant NLO responses relative to the traditional inorganic solids.[3] When a molecule is subjected to laser light [i.e. very high intensity electric field (*E*)], the polarization of the molecule is expressed by Equation (1).[4]

$$\mu(E) = \mu_0 + \alpha E + \beta E^2 + \ldots \qquad (1)$$

In this expression, μ_0 is the permanent dipole moment, α the linear polarizability, and β the quadratic hyperpolarizability (origin of the NLO response). According to the widely used two-level model,[5] β can be described in terms of a ground and first excited state, having a charge-transfer character, and is related to the energy of the optical transition (ΔE), its oscillator strength (*f*), and the difference between the ground and excited state dipole moments ($\Delta\mu$) through Equation 2).

$$\beta = \frac{3e^2\hbar f\Delta\mu}{2m(\Delta E)^3} \times \frac{(\Delta E)^4}{\left((\Delta E)^2 - (2\hbar\omega)^2\right)\left((\Delta E)^2 - (\hbar\omega)^2\right)} \qquad (2)$$

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The author was born in Dole, France. He received his PhD under the supervision of Prof. Olivier Kahn, at the university of Orsay (France) in 1989. He entered the field of nonlinear optics as a postdoctoral fellow, with Prof. Tobin J. Marks, at Northwestern University (Evanston, USA) from 1989 to 1991. He then returned to Orsay, where he pursued in the field of hybrid magnetic-NLO materials designed by intercalation chemistry. He moved to the Laboratoire de Chimie de Coordination (Toulouse, France) in 1994. His current research interest concerns multi-property materials with nonlinear optical, magnetic, and conducting properties.

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The largest β values are obtained when the molecules contain π-electronic systems with charge asymmetry arising from contributions from the substituents-induced asymmetry. This situation is optimized with "push-pull" molecules, in which the magnitude of β can be correlated with the electron-donating and -accepting strength of the substituent,[6] but can also be enhanced by increasing the path of conjugation between the substituents.[7] The most traditional experimental determination of β is the Electric-Field-Induced-Second-Harmonic (EFISH) method,[8] which requires the molecules to be aligned by a strong electric field by means of their static dipole moments (μ). Therefore, the EFISH signal is proportional to β×μ. Measurements of β can also be carried out with the Hyper-Raleigh Scattering (HRS) method,[9] which does not require electric fields, and therefore is suitable for nonpolar and ionic chromophores.

The polarization of a macroscopic material is again given by an expression analogous to Equation (1), where the macroscopic polarization (P) is expressed by Equation (3).

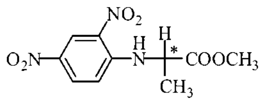
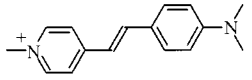
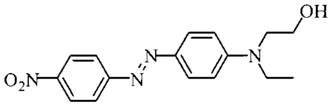
$$P = \chi^{(1)}E + \chi^{(2)}E^2 + ... \qquad (3)$$

$\chi^{(2)}$ is the quadratic susceptibility and is related to the underlying β. An important point to note is that for $\chi^{(2)}$ to be non-zero, the material needs to be non-centrosymmetric. This can be explained by the fact that $P(-E) = -P(E)$ in a centrosymmetric material. Therefore, $\chi^{(2)}(-E)(-E) = -(\chi^{(2)}E^2)$, and $\chi^{(2)} = 0$. Consequently, the search for materials with efficient quadratic nonlinearities has to be conducted in two steps which include: (*i*) the designing of molecular structures with a large β value, and (*ii*) the engineering of the chromophores into non-centrosymmetric environments.

Several examples of chromophores are shown in Table 1. They all have been successfully embodied into non-centrosymmetric environments in the solid state following various methodologies. The oldest strategy in crystal engineering for $\chi^{(2)}$ NLO materials is chirality, which ensures the crystallization of a pure enantiomer in a non-centrosymmetric space group. Methyl 2-[(2,4-dinitrophenyl)amino]propanoate (MAP, **1**) was the first $\chi^{(2)}$ NLO material studied in depth, which exploited this strategy.[10] Among several alternative attempts, we have previously reported on the intercalation of cationic chromophores such as 4′-dimethylamino-1-methylstilbazolium (DAMS, **2**) into lamellar matrices as a possible route towards highly efficient $\chi^{(2)}$ NLO materials.[11] However, the method which has been widely adopted since the late 1980s requires poling the chromophores at high temperatures in polymers with high glass transition temperatures (Tg).[12] Disperse Red One (DR1, **3**) is an example of an organic chromophore which has widely been investigated in poled polymers for fifteen years.[13] High Tg NLO polymers have recently been reviewed.[14]

The macroscopic NLO properties are usually measured by Second-Harmonic Generation (SHG), and the results are expressed as the d_{33} tensor component of $\chi^{(2)}$ in poled polymer materials,[14] or as the SHG efficiency versus that of urea in the Kurtz−Perry powder test[15] for microcrystalline solids. However, it has to be emphasized that this test, which has a modest reliability, is not sufficient to fully understand the origin and extent of the NLO response.

Table 1. Examples of chromophores for which non-centrosymmetric solid-state environments have been obtained by crystal growth (**1**), intercalation into layered host matrices (**2**) or as functionalized poled polymers (**3**)

Compounds	[ref.]
 **1**	[10]
 **2**	[11]
 **3**	[13]

2. Organometallic and Inorganic Chromophores

2.1. "Push-pull" Organometallic Chromophores

Besides organic molecules, which up to now have been the most widely investigated systems, organometallic structures should be intriguing candidates as second-order NLO chromophores by virtue of their low-energy electronic charge-transfer excitations. The report in 1987 that *cis*-1-ferrocenyl-2-(4-nitrophenyl)ethylene[16] exhibited an SHG efficiency 62 times that of urea has motivated many organometallic chemists to enter the field. As a result, a number of reports of organotransition metal systems with NLO properties have appeared in the literature.[17] Nevertheless, in the late 1980s, despite many synthetic efforts, the measured NLO responses of organometallic chromophores were almost invariably lower than those of π-organic chromophores of comparable molecular dimensions. Understanding the reasons for such modest NLO responses became possible when the Zerner Intermediate Neglect of Differential Overlap (ZINDO) method in conjunction with the Sum Over States (SOS) formalism made the NLO response−electronic structure relationships available.[18] It was pointed out that many organometallics possess pseudo-centrosymmetric electronic environments and, therefore, lack the extreme electronic asymmetry required for large second-order NLO responses.[19] This tendency is illustrated in Table 2 where the calculated hyperpolarizabilities of organometallics are compared with a stilbene analogue.[18]

Table 2. Comparison of calculated molecular hyperpolarizabilities for organometallic chromophores and a prototypical organic structures (ref.[18])

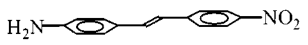
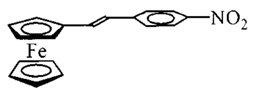
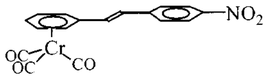
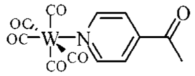
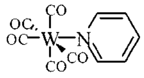
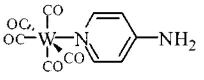
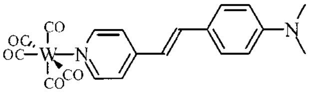
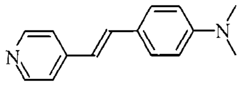
Compound	β ($\times 10^{-30}$ cm^5 esu^{-1})
 **4**	65.9
 **5**	30.8
 **6**	23.5

Table 3. Comparison of experimental (EFISH) molecular hyperpolarizabilities for a series of $(CO)_5W-$pyridine derivatives and for stilbazole-based chromophores at 1.907 μm (**7−9**) and 1.064 μm (**10−11**)

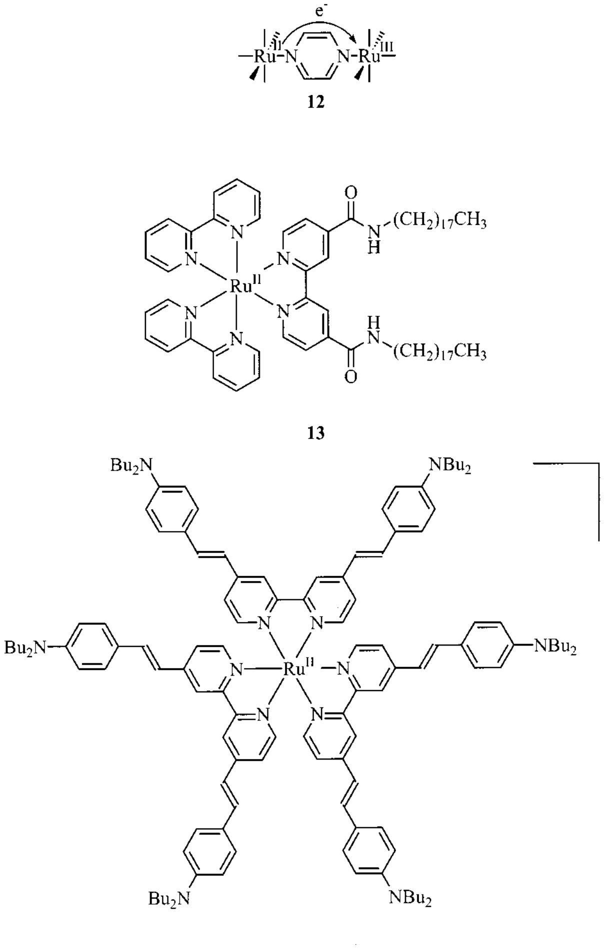
Compounds	β ($\times 10^{-30}$ cm^5 esu^{-1})	[ref.]
 **7**	-9.3	[17a]
 **8**	-4.4	[17a]
 **9**	-2.1	[17a]
 **10**	61	[20]
 **11**	28	[20]

Our interest in the field of coordination complexes based NLO chromophores started at this point, by examination of $(CO)_5W-L$ (where L represents an extended π-organic system).[20] The reason for this choice is related to the topological similarity to the conventional push-pull organic chromophores which could offer attracting alternatives to the aforementioned η^5-ferrocenyl complexes and (η^6-arene)chromium structures. Our study pointed out the versatility of the pyridine$-W(CO)_5$ based chromophores (Table 3) in which $-W(CO)_5$ usually acts as a donor,[21] in compounds **7−9**, and by contrast with the withdrawing effect of the pyridine$-W(CO)_5$ moiety evidenced in **10**. The molecular orbital analysis indicates that the carbonylmetal fragment acts as σ-acceptor, forcing the adjacent pyridine ring to become the molecular LUMO. As a consequence, the seemingly innocent pyridine becomes a strong acceptor.[20] Since the early 1990s, the interest in using a metal center for converting a pyridine into a strong acceptor for NLO purposes has grown with respect to the concept of octupolar chromophores,[22] which are non-centrosymmetric and nonpolar molecules (e.g. point groups T_d, and D_{3d}). NLO (pyridine)metal complexes, including intriguing new octupolar architectures, have recently been reviewed by Le Bozec.[23]

2.2. A New Approach in the Search of Inorganic NLO Candidates

Until the early 1990s, the main strategy in the design of metal-organic NLO chromophores was to simply mimic organic molecules by using metal centers instead of organic donors[16,17a,17b]. The ferrocene derivative **5** is probably the best example that illustrates this methodology. However, the fact that the NLO response of such chromophores was almost invariably lower than that of π-organics gave rise to the idea that copying organic NLO structures by means of organometallic substituents might not have been the best guideline towards coordination compounds with enhanced optical nonlinearities. This idea becomes more relevant in the case of inorganic complexes, where the d-electrons are more strongly held by the metal atom than in the case of organometallic compounds. This difference can raise difficulties in the designing of classical push-pull chromophores, within the framework of a two-level model built up in the realm of organic chemistry with extended π-conjugated electronic structures.

Our interest in inorganic chromophores started in 1990 by a short theoretical investigation of (pentammine)ruthenium derivatives. A lot of work had been devoted to mixed-valence Ru^{II}/Ru^{III} complexes[24] since the initial report on the mixed-valence $[Ru(NH_3)_5]_2pz^{5+}$ (**12**, Figure 1) by Creutz and Taube.[25] In this compound an electron is almost fully delocalized with $(Ru^{II})^{1/2}/(Ru^{III})^{1/2}$ centers (class III in the Robin−Day classification of mixed-valence systems[26]). Consequently, the $(NH_3)_5Ru^{II}$ fragment can formally be seen as a very strong electron donor. However, although ruthenium-based complexes have exhibited sizeable NLO responses as push-pull chromophores in some cases (e.g. $\beta = 70 \times 10^{-30}$ cm^3 esu^{-1} for compound **13**[27]), the largest NLO responses were reported in compounds in which the pyridine−Ru^{II} fragments act as electron acceptors and not donors (e.g. $\beta = 2200 \times 10^{-30}$ cm^3 esu^{-1} for the octupolar systems **14**[28]). This versatility prompted us to greatly modify our approach to inorganic chromophores in the early 1990s. It became increasingly clear that the traditional donor/acceptor chemical guidelines would probably no longer be fully sufficient in finding the best candidates in chromophore design.



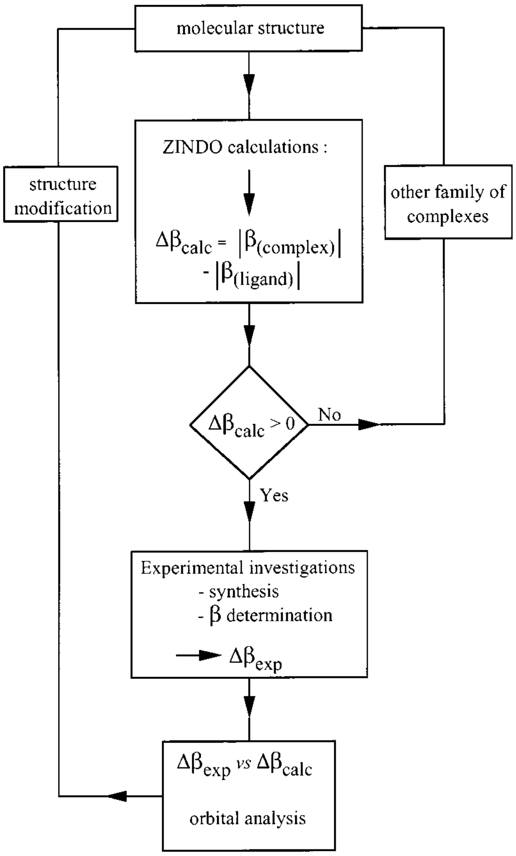
12

13

14

Figure 1. Ruthenium-based charge-transfers in mixed valence complexes **12** and NLO chromophores **13**, and **14**; the five NH_3 of $Ru(NH_3)_5$ are omitted for clarity in **12**

To avoid tedious synthetic programs, with the outcome of uncertain NLO properties, theoretical quantum procedures have been very helpful in the last decade.[18] We became convinced that the search for new families of inorganic chromophores should require preliminary calculations conducted on idealized molecular structures for selecting new inorganic candidates with sizeable nonlinearities. The criteria for the selection is as follows: $\beta_{complex} > \beta_{ligand}$, the comparison between experimental and calculated data being the test to prove the relevance of the quantum description of the properties. Our methodology is summarized in Scheme 1. Besides the gain in synthesis time, this approach is an attempt to fully understand what orbitals are actually involved in the NLO response, and finally to provide chemical guidelines for designing molecules with enhanced capabilities. In conclusion to this section, it is worth noting the tetrahedral cobalt(II) complex with two 1-(*p*-dimethylaminophenylhydrazono)-2-(*p*-nitrophenylimino)ethane ligands reported in 1992 by Simon et al.[29] Although the complex did not follow the traditional push-pull structures, the authors provided evidence for enhanced nonlinearities after metal complexation. The reasons for such behavior are probably related to a better conjugation within the donor−acceptor chromophore by virtue of the metal center. This example also illustrates the fact that pure chemical intuition may no longer be fully appropriate in predicting the extent of the NLO response, and emphasizes the need for efficient screening methods for selecting inorganic NLO materials. This approach has been successfully used in the design of bis(salicylaldiminato)metal Schiff base complexes with NLO capabilities.



Scheme 1

3. Bis(salicylaldiminato)metal Schiff Base Complexes

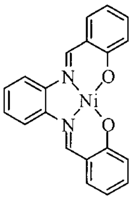
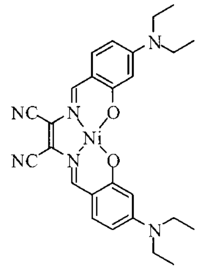
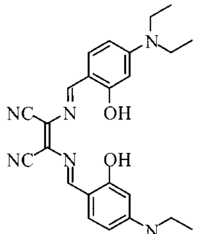
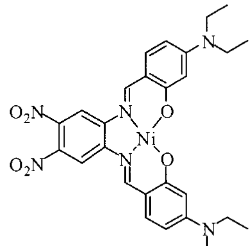
3.1. Complexes with NLO Responses Larger than that of the Related Ligands

The first report of an NLO metal complex of the tetradentate salen [*N*,*N*′-bis(salicyleneaminato)ethylene] ligand was that of Thompson et al. in 1991.[30] The authors observed second-harmonic generation in M^{III}-(salen)Py−NHCH$_2$X derivatives. However, in these systems, the metal−salen core was probably not directly involved in the charge-transfer process responsible for the NLO response, but was rather used to enhance the NLO response of an apical substituted pyridine ligand, in a way similar to that observed in **10** or **14**. The report by Di Bella et al.[31] on various Ni(salen) (**15**, Table 4) derivatives with experimental sizeable NLO responses opened interesting perspectives for metal complexes. In contrast with the widely investigated push-pull organic chromophores, such complexes offer a large variety of structures that allows to locate the metal atom in a more strategic position at the center of the charge-transfer system, making better use of the metal d-orbital hybridization schemes in an organic environment. Importantly, it was proven by a ZINDO theoretical analysis that the NLO response of Ni(salen) complexes is dominated by the HOMO → LUMO transition, in which the nickel atom acts as a donor. This result indicates that this family of derivatives can offer suitable candidates for the strategy introduced in the preceding section.

The best result, which successfully applied this methodology was obtained in the investigation of the NLO properties of ligand **16**, compared with that of the corresponding nickel(II) complex **17** (Table 4).[32] It was shown that the complex exhibits an enlarged NLO response relative to that of the free ligand, with experimental β values of 109 and 235×10^{-30} cm^5 esu^{-1} for **16** and **17**, respectively. In this family, a slight red shift of about 15 nm upon metal complexation provides a modest β enhancement. Moreover, the intrinsic role of the metal center can be understood from a comparative analysis of the calculated data for **16** and **17**. In contrast to the two-level description of the NLO properties of push-pull organic chromophores, the data indicate that two transitions (1→2 and 1→3) are involved in the NLO response for both ligand and metal complex. The differences in electronic populations between the ground state and the two excited states are shown in Figure 2 for **16** and **17**. The picture clearly reveals the enhancement of the intramolecular charge transfer, once the metal atom has been introduced in the molecular structure. This suggests that the metal center, which acts as a donor, favors the conjugation of the chromophore, and hence allows a larger charge transfer in the excited states. One may expect various NLO responses by simply changing the nature of the metal center in this family of inorganic chromophores, a situation that would provide a possibility for optimizing β, once a suitable ligand has been selected. This has been achieved for the Zn^{II} derivative, with a β value of 400×10^{-30} cm^5 esu^{-1}, roughly twice that of the Ni^{II} complex. However, the orbital origin of this difference was not clarified, because of the different geometries between Zn^{II} and Ni^{II} complexes. The search for bis(salicylaldiminato)metal Schiff base complexes with NLO capabilities has been further optimized with the design of compound **18**.[33] However, the β enhancement upon complexation is modest and the metal center itself behaves as a weak donor, in contrast to the situation encountered in **17**, and depicted in Figure 2.

Besides the large β value, it has to be emphasized here that this family of derivatives exhibits excellent thermal stabilities (e.g. 360, 400, and 300 °C for **15**, **17**, and **18**, respectively). It is now generally believed that molecular second-order NLO materials will enter the marketplace, depending on the ability of the chromophores to be poled in

Table 4. Experimental (EFISH) NLO responses of various bis(salicylaldiminato)metal Schiff base complexes (ref.[31,32])

Compounds		β ($\times10^{-30}$ cm^5 esu)		Compounds		β ($\times10^{-30}$ cm^5 esu)	
		1.34 μm	1.9 μm			1.34 μm	1.9 μm
	**15**	-20.5			**17**	235	800 (β×μ)
	**16**	109			**18**		1530 (β×μ)

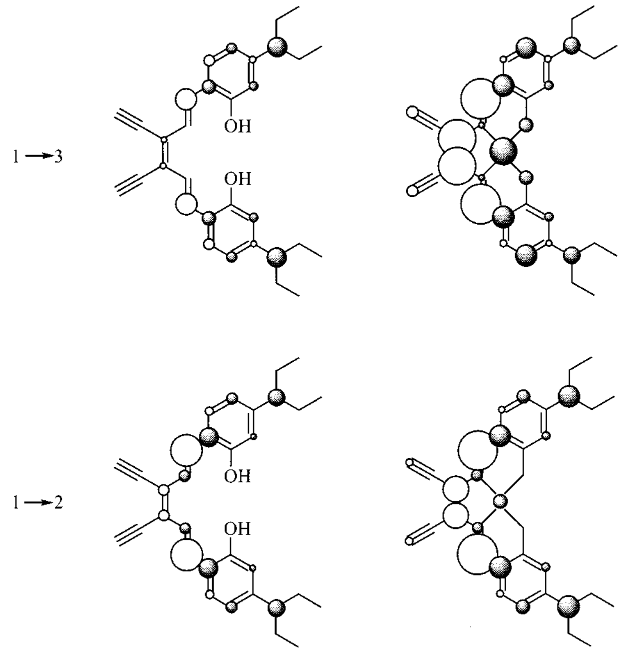


Figure 2. Difference in electronic populations between the ground state and the two excited states for **16** (left) and **17** (right); the black (white) contributions indicate a decrease (increase) in electron density in the charge-transfer process

polymers with very high glass transition temperatures.[12a] The rationale is that if *Tg* is far above the device's operating temperature, the alignment will not decay significantly over the life-time of the device. For stable and efficient poling, it has been realized that polymers with *Tg* higher than 250 °C have to be used and consequently, a good thermal stability has become an important prerequisite for $\chi^{(2)}$ NLO materials. This is undoubtedly one of the major characteristics of metal−salen derivatives. An important point to note is that the poling process requires the use of external electric fields. Therefore although β is the origin of the NLO effect, $\beta\times\mu$ is the molecular figure of merit for poled polymer films. The NLO response of **18** ($\beta\times\mu = 1530\times10^{-48}$ cm^5 D esu^{-1} at 1.907 μm, which corresponds to a static $\beta_0\times\mu = 968\times10^{-48}$ cm^5 D esu^{-1} at zero frequency) can be compared with that of the best organic candidates of similar molecular size.[3a] Although μ enhancement rather than β enhancement is mostly responsible for the large $\beta\times\mu$ value, this large NLO response definitely establishes the potential of these derivatives in the poled polymer approach.

Several metal−salen-based polymers have already been reported,[34] one of them using NLO monomers (polymer **19**, Figure 3).[35] On the other hand, the compounds were found to be rather insoluble, and no NLO effects have been reported. The crystal structure of a chain made of Mn^{III}(salen)(4-pyridylglycinate) blocks (**20**) has also been reported.[36] The structure reveals head-to-tail alignment of adjacent dipoles, but adjacent polymer chains are antiparallel, so no NLO effects are observed. To the best of our knowledge, the only report of NLO properties for an amorphous polymer containing metal Schiff base complexes has been that of poled polyhydroxystyrene doped with chromophore **18** (5% w/w). It exhibits a d_{33} value of 0.65 pm V^{-1} at 1.907 μm, and retains 85% of its NLO response after one week.[33] Although this value is a sizable NLO response for host-guest systems, larger d_{33} values (ca. 10 pm V^{-1}) would require functionalized polymers with chromophores covalently bonded. This has not been achieved yet.

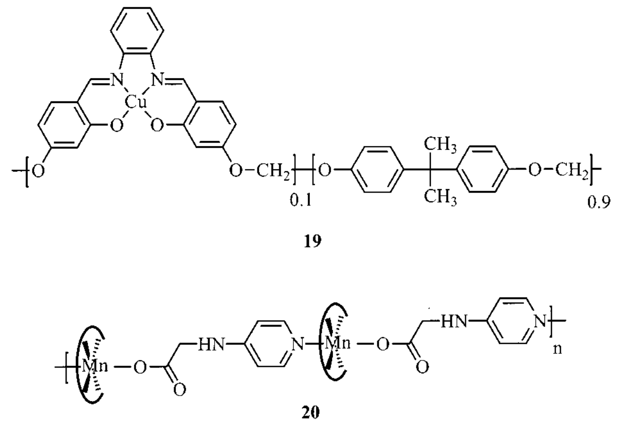
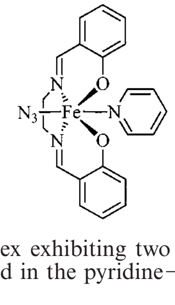


Figure 3. Chains containing bis(salicylaldiminato)metal Schiff base, with NLO capabilities; the ellipse represents a salen ligand in **20**

3.2. Chiral Complexes Efficient in Second-Harmonic Generation

In 1996, Chiang reported on an Fe^{III} derivative **21** (Figure 4), which was found to crystallize in the non-centrosymmetric $P6_5$ space group, with a powder efficiency twice that of urea.[37] The origin of the quadratic NLO response was attributed to both the pyridine−Fe π-system and the salen ligand, the first component most likely being dominant. In contrast to **21**, the Cambridge data base reveals that most of the crystal structures of bis(salicylaldiminato)metal complexes reported to date exhibit centrosymmetric space groups. In particular, bis(salicylaldiminato)nickel(II) complexes all possess centrosymmetric crystal structures, except those made with a chiral diamine (pure enantiomer). This observation strongly supports the idea that derivatives such as **15−18** will most likely exhibit vanishing NLO properties due to crystal centrosymmetry.

As is well known, chirality provides the chemist with a means of guaranteeing that crystallization of a pure enantiomer will occur in a non-centrosymmetric space group. In order to promote SHG efficiencies in the solid state, careful examination of Figure 2 provides interesting chemical

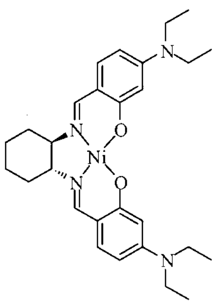
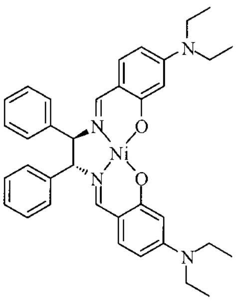
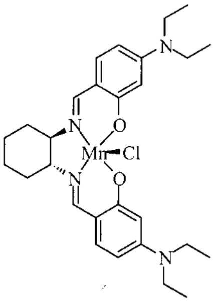


21

Figure 4. Fe^{III} complex exhibiting two charge-transfer transitions in the salen ligand and in the pyridine−Fe^{III} π-system

guidelines. It appears that the "C=N−C" linkage plays an important role as the withdrawing counterpart of the chromophore, in terms of charge transfer, whereas the contribution of the nitrile substituent is weak. Thus, complexes such as **22−24** (Table 5) are preferred in which the "C=N−C" linkage is present, with the addition of two asymmetric carbon atoms to force the crystallization into a non-centrosymmetric space group for the pure (1*R*−2*R* or 1*S*−2*S*) enantiomers. Complex **22** is the first bis(salicylaldiminato)-based metal complex on which this methodology was successfully applied for NLO purposes.[38] However, an unexpectedly low SHG efficiency, < 0.25 times that of urea was observed, arising from a pseudo-centrosymmetric crystal structure.

Table 5. SHG powder efficiencies (vs. urea) of chiral bis(salicylaldiminato)metal Schiff base complexes at 1.907 μm

Compounds		Efficiencies	[ref.]
	**22**	< 0.25	[38]
	**23**	13	[39]
	**24**	8	[38]

This strategy was further optimized in complex **23**, which crystallizes in the non-centrosymmetric $P2_1$ space group, and to date exhibits the highest SHG efficiency (13 × that of urea) in this class of materials.[39] The structure−NLO property relationships established by Zyss lead to the *d* component of $\chi^{(2)}$ given in Equation (4) where θ is defined as the angle between β and the 2_1 two-fold axis of the crystal, and *N*, the concentration of chromophores per volume unit.[40]

$$d_{ZXX} = N\beta\cos\theta\sin^2\theta \qquad (4)$$

θ is equal to 57.8° for **23** and corresponds to an angular factor of 0.381. This value must be compared with the $2/\sqrt{3} = 0.385$ theoretical value which maximizes the angular factor for the most favorable crystal structure.[40] Consequently, the molecular orientation of **23** is optimized in the solid, and an efficiency 13 times that of urea is probably close to the upper limit for bis(salicylaldiminato)nickel(II) Schiff base complexes based on this π-electronic structure.

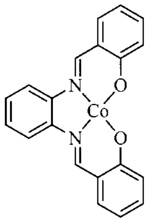
The deleterious effect of pseudo-centrosymmetry on the bulk SHG efficiency of molecules such as **22** can tentatively be related to the fact that the chiral substituent lies near the mean plane of the chromophore. Therefore, two isomers made from (1*R*,2*R*)-cyclohexanediyl or (1*S*,2*S*)-cyclohexanediyl, placed on top of each other almost coincide. Indeed, a calculation indicates that an average distance between the carbon atoms of the cyclohexanediyl and the NiO_2N_2 plane of **22** is to 0.31 Å. In other words, the molecule is "weakly chiral" in the sense of the quantification of chirality developed by Mislow.[41] By contrast, the out-of-plane displacement of the chiral substituents is large in **23**, in which the centroids of the phenyl substituents are located about 3.2 Å apart from the NiO_2N_2 plane. This difference can account for an enhanced "degree of chirality" for **23** relative to that of **22**.

To encourage out-of-plane displacements, alternative chromophores were envisioned such as **24**. Beside an SHG efficiency 8 times that of urea, **24** exhibits a different optical spectrum with a red shift, strongly indicative of reduced transition energy [Δ*E* in Equation (2)], and hence an enhanced β value.[38] It is worth mentioning that **24** brings about NLO chromophores with additional magnetic ($S = 2$) capabilities. The possibilities for interplay between magnetic and NLO behaviors will be discussed in the next section.

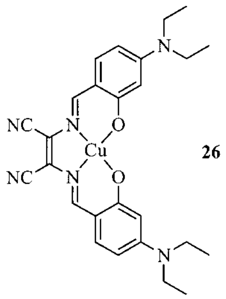
3.3. A Possibility for NLO Switching in Metal Schiff Base Complexes

Coordination complexes offer a large variety of magnetic properties by virtue of the coordination metal center,[42] that could bring about NLO chromophores with unique characteristics as multi-property building blocks. However, the possibility for direct interplay between both properties remains a challenging question. Di Bella et al. have shown that, on passing from close-shell Ni^{II}(salophen) to open-shell Cu^{II} or Co^{II} analogues **25** (Figure 5), experimental β values could increase from −20 to −50, and -170×10^{-30} $cm^5\ esu^{-1}$, respectively.[43] This effect has been ascribed to the different natures of the electronic excited states. By contrast, we have investigated the paramagnetic complex **26**, which is the Cu^{II} analogue of **17**.[32] EFISH measurements revealed a β value of 200×10^{-30} $cm^5\ esu^{-1}$, which is comparable with the 235×10^{-30} $cm^5\ esu^{-1}$ value measured for **17** within the range of uncertainty of the EFISH method.

However, various recent investigations have pointed out the possibility of β enhancement in organic radicals.[44,45] Such observations open interesting perspectives towards a possible interplay between magnetic and NLO behaviors.



25



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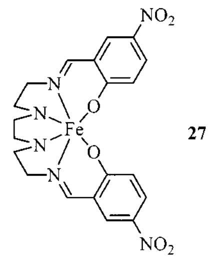

27

Figure 5. Paramagnetic bis(salicylaldiminato)metal Schiff base complexes with NLO capabilities

The possibility of bulk NLO modulation occurring upon ferromagnetic phase transition in a material containing NLO chromophores can be theoretically envisioned. It has long been known that a rotation of the axis of linearly polarized light occurs on passage through a magnetized material. This is commonly called the Faraday rotation.[46] This effect, which modifies the angle between *E* (the electric field component of the light) and β, should therefore modulate the NLO behavior of the solid. Nevertheless, the β value of the chromophores would not be affected by such a magnetic transition. By contrast, in bis(salicylaldiminato) Schiff base complexes, the spin carrier is the NLO chromophore itself. Therefore, one might wonder if this unique characteristic could encourage a relationship between both properties at the molecular level.

The first evidence for β modulation occurring upon magnetic phase transition has recently been reported in compound **27** (Figure 5).[47] Compound **27** is an iron(II) derivative, which reveals metal-to-ligand charge-transfer capabilities. The frontier orbitals of **27** are shown in Figure 6. By virtue of the two nitro substituents, the compound exhibits the push-pull character required for a sizable β value. At high temperatures, the two chromophores present in the crystal unit cell are equivalent (spin state, $S = 2$), and therefore possess the same β. Interestingly, the compound undergoes a spin transition ($S = 2 \rightarrow S = 0$) in two steps upon cooling down. A phase at intermediate temperature (around 150 K) has been observed in which one half of the chromophores are $S = 0$, and one half are $S = 2$.[48] This unique characteristic allows us to calculate the hyperpolarizability for both spin states in nearly identical solid-state environments. It is found that an enhancement of the static hyperpolarizability (β_0) of about 25% (36.9 to 45.9 $\times 10^{-30}$ cm^5 esu^{-1}) occurs on passing from $S = 0$ to $S = 2$. The main origin of this effect is likely to be related to geometry modifications occurring in the coordination sphere of the metal center.

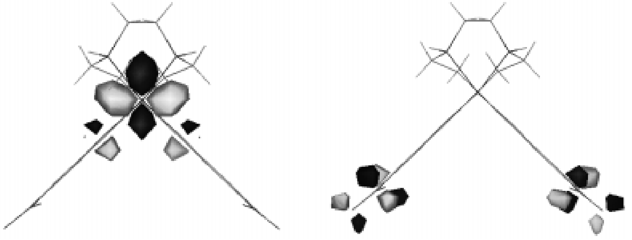

Figure 6. HOMO (left) and LUMO (right) for **27**

In these last few years, the intriguing concept of molecular switches has attracted great interest from a variety of perspectives.[49,50] These molecular NLO materials have recently been reviewed.[51] The switch is usually achieved by isomerization or redox/proton transfer. For example, Coe et al. have reported on an efficient redox switching in ruthenium(II) complexes.[52] By contrast, **27** is the first example of a new class of molecules in which a β switch could be envisioned from a magnetic phenomenon. However, in order to be fully convincing, a switch should be attached to an "on and off" behavior, which has not yet been observed.

4. Concluding Remarks

Until the late 1980s the push-pull one-dimensional electronic model has been the basis of almost every NLO chromophore such as the typical benchmark *p*-nitroaniline molecule. We have reported on various examples of ferrocene-, W(CO)$_5$-, or Ru(NH$_3$)$_5$-based organometallic and inorganic molecules for which an unexpectedly low NLO response has suggested, in the early 1990s, that the design of chromophores could be reconsidered aside from the traditional push-pull framework in coordination chemistry. Owing to the ability of computational models to provide efficient screening methods of selection, a new family of bis(salicylaldiminato) Schiff base complexes has finally emerged. It is worth noting that, in most reports on these materials, a large part of the work was invariably devoted to theoretical investigations of the properties.

Various Schiff-base complexes have now been reported to exhibit significant β enhancement upon metal complexation. For instance, Espinet et al. have recently obtained Pd^{II} and Pt^{II} complexes in which β_0 enhancements as high as 80% of those of the corresponding ligands were measured.[53] In the present paper, we have presented a class of bis(salicylaldiminato) Schiff base complexes, which appear to be thermally robust NLO materials possessing large $\beta \times \mu$ products. Therefore, they provide interesting candidates for incorporation into high *Tg* polymer matrices. The next challenging goal for this research program would be to be able to covalently link the best of the bis(salicylaldiminato) Schiff base complexes (e.g. **17** and **18**) into polymers, such as polyimides. Beside the poled polymers approach, versatile synthetic methodologies allow for the design of chiral derivatives, with solid-state SHG efficiencies or paramagnetic multifunctional building blocks, in which the properties are expected to be related in some way to the concept of molecular switches. As the NLO field matures, it can be anticipated that materials with switchable NLO responses will find various novel applications.

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