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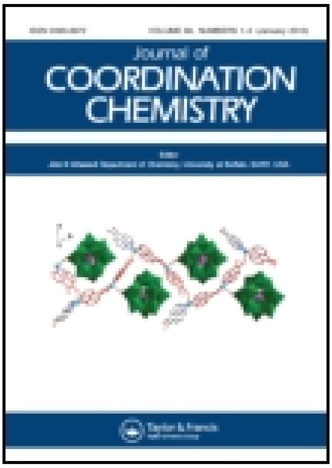

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Review: Second order nonlinearities of Schiff bases derived from salicylaldehyde and their metal complexes

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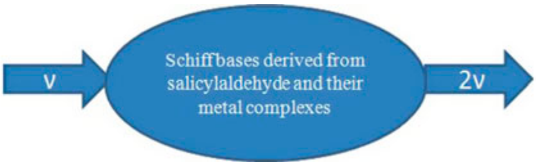

Current trends suggest that light, rather than electricity, will increasingly be used in the area of information technology, with potential in optical communications, data storage and computer systems. Therefore there has been a growth of interest in development of molecular second order non-linear materials. In the last few years, organometallic and coordination complexes have emerged as interesting chromophores for producing NLO materials due to the large variety of structures and diversity of electronic properties tunable by metal centre. N_2O_2 Schiff base complexes are a promising class of efficient chromophores exhibiting large NLO responses. This review summarizes second order NLO ligands and metal complexes of Schiff bases derived from salicylaldehyde.

Keywords: Nonlinear optics; Metal complexes; Schiff bases; Second Harmonic Generation; Salicylaldehyde

1. Introduction

The world in which we live is naturally nonlinear because reactions of real physical systems are never exactly proportional to the stimulus. The extent of nonlinearity varies with the nature of the stimulus. In life, one seeks to minimize the effect of nonlinearity but in some conditions, nonlinearity can be put to excellent use. In this review, we compile and show the unique effects of the nonlinearity of chemical compounds in optical physics. Optical physics is the study of the production and properties of electromagnetic radiation and the detection of linear and non-linear responses when it interacts with matter.

2. Theoretical explanation of nonlinear optics

Before the invention of the laser, the answer would have been an absolute NO to the question ‘Are the optical properties of a medium dependent upon the radiation intensity?’

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The reason for this is that the field strength of conventional light sources is much weaker (below 10^3 V/cm) than the atomic and inter-atomic fields (10^7 to 10^{10} V/cm). Therefore, the resultant perturbations are too small to cause any change in the optical parameters. However, a laser has high field strength, within the range of atomic fields, and hence, shows some interesting non-linear optical effects when it interacts with matter [1–3].

The explanation of nonlinear effects lies in the way in which a beam of light propagates through a solid. The nuclei and associated electrons of the atom in the solid form an electric dipole. The electromagnetic radiation interacts with these dipoles, causing them to oscillate, which results in the dipoles themselves acting as a source of electromagnetic radiation. The optical response of a material is expressed in terms of the induced polarization, *i.e.*, the dipole moment per unit volume P. The orienting effect of an external field on the molecular dipoles depends on the properties of the medium and the field strength.

$$P = \varepsilon_0 \chi E \tag{1}$$

Here χ is the polarizability or dielectric susceptibility of the medium. This relation is valid only for conventional sources whose field strength will not affect the optical properties of the medium. Hence, it is known as linear optics.

With sufficiently intense laser radiation, the relation does not hold and must be generalized as shown below.

$$P = \varepsilon_0(\chi^1 E + \chi^2 E^2 + \chi^3 E^3 + \cdots\cdots\cdots\cdots) \tag{2}$$

Here χ^1 is the same as χ in equation 1, and χ^2, χ^3 ..... define the degree of nonlinearity and are known as the second order, third order .... susceptibilities. When we use high-intensity laser radiation, the optical properties of the medium depend on the field strength, and the higher order terms become more significant. This is known as nonlinear optics (NLO). When we consider the case where the radiation is passed through a molecule and not the bulk material, the polarization can be expressed as follows:

$$P = \mu_0 + \alpha E + \beta E^2 + \gamma E^3 + \cdots\cdots\cdots\cdots \tag{3}$$

where $\mu_0$is the permanent dipole moment, α is the linear polarizability tensor, and β and γ are the quadratic and cubic hyperpolarisability tensors, respectively [4–6].

The terms χ^1 and α are linear terms responsible for linear optical properties such as refractive index, absorption, permittivity, *etc*. χ^2 and β are quadratic terms, which are responsible for nonlinear optical properties such as second harmonic generation, electro-optic effect, *etc*. The cubic nonlinear effects arising from χ^3 and γ are responsible for the third harmonic generation, optical phase conjugation and the Kerr effect. This shows that the induced polarization can convert the fundamental frequency to the second, third and higher order frequencies.

3. Second harmonic generation

One of the extensively used applications of nonlinear optics is the generation of second harmonic radiation. Second harmonic generation (SHG), or frequency mixing, is the process where the energy or frequency of a radiation becomes twice the incident value when passed through a certain medium. When two radiations of frequency v are passed through a material having characteristic χ^2 and β, the emitted radiation will have a frequency of 2ν. The produced wave has the same direction as the incident wave. To create a new material showing the NLO effect, the first step is to prepare molecules with a high β value and skillfully craft them into a macroscopic material with a high χ^2 value.

The quadratic hyperpolarizability of a molecule originates from the mobility of polarizable electrons under the effect of a strong electric field associated with an incident radiation. The molecular polarization can be described by quantum mechanical 'sum over states' (SOS) perturbation theory. According to this theory, the electronic states are created by the perturbing field and are treated as an infinite expansion over a complete set of unperturbed excited states. Hence, the individual tensor component of the molecular hyperpolarizability is related to all the excited states of the molecule. A simplification of this approach can be made by restricting the summation to one excited state and assuming that one tensor component dominates the NLO response.

In 1977, Oudar [7–9] predicted that the following equation could be used to calculate the hyperpolarizability β for an asymmetric 1D organic NLO molecule whose second-order nonlinearity is associated with a single charge-transfer (CT) process.

$$\beta = \frac{3}{2h^2c^2}\,\frac{\vartheta_{eg}^2 r_{eg}^2 \Delta\mu_{eg}}{(\vartheta_{eg}^2 - \vartheta_L^2)(\vartheta_{eg}^2 - 4\vartheta_L^2)} \tag{4}$$

Here ϑ_{eg} is the frequency of the charge-transfer transition, r_{eg} is the dipole moment of the transition, $\Delta\mu_{eg}$ is the difference between the molecular dipole moment of the excited and ground states $(\mu_e - \mu_g)$ and ϑ_L is the frequency of the incident radiation. Equation (4) is known as the 'two state' model and is a very good approximation for calculating β when a single CT state dominates the NLO response. It implies that the frequency doubling will be enhanced when the input frequency approaches the frequency of the lowest optical CT transition.

Extrapolation to the zero frequency allows an estimation of the static or zero frequency first hyperpolarizability, which provides an estimate of the intrinsic molecular hyperpolarizability in the absence of any resonance effects. It can be evaluated by the following equation:

$$\beta_0 = \beta_\lambda \left[1 - \left(\frac{2\lambda_{max}}{\lambda}\right)^2\right]\left[1 - \left(1 - \left(\frac{\lambda_{max}}{\lambda}\right)^2\right)\right] \tag{5}$$

where β_λ is the quadratic hyperpolarizability at an incident radiation with wavelength λ and λ_{max} is the wavelength of the charge-transfer transition.

When we consider the case of a macromolecule, the polarization is given by equation (2), where χ^2 is a quadratic polarizability related to the underlying β value. In most crystalline materials, the nonlinear polarizability χ^2, which is a tensor, depends on the direction of propagation, the polarization of the electric field and the orientation of the optic axis of the crystal. The second-order polarization can be written as follows:

$$P_1^2 = \varepsilon_0 \sum_{j,k} \chi_{i,j,k}^2 E_j E_k \ldots \tag{6}$$

where i, j and k represent the coordinates x, y and z, respectively. However, most of the coefficients $\chi_{i,j,k}$ are zero.

Second harmonic generation, represented by equation (6), can occur only in certain types of crystals that are structurally different in one direction from the opposite direction. This type of crystal is said to be non-centrosymmetric, that is, it lacks a centre of symmetry. In other words, when it is important to get a nonzero χ^2 value, the material should be non-centrosymmetric.

This can be shown by considering the case of an isotropic crystal where $\chi_{i,j,k}$ is not dependent on a direction and is constant [1]. Let us assume that the direction of a field and the polarizability remains the same but the direction of an axis is reversed ($x \rightarrow -x$, $y \rightarrow -y$ and $z \rightarrow -z$); then the equation becomes

$$-P_i^2 = \varepsilon_0 \sum_{j,k} \chi_{i,j,k}^2 (-E_j)(-E_k) \ldots\ldots.. \tag{7}$$

$$-P_i^2 = +P_i^2 \tag{8}$$

$$\chi_{i,j,k}^2 = 0 \tag{9}$$

This shows that the isotropic crystal has a zero χ^2 and therefore cannot generate second harmonic radiation. Therefore, the initial criterion to show second harmonic generation is that the molecule should be non-centrosymmetric.

4. Measurement of nonlinearities

It is clear that the second harmonic generation depends on two characteristics of the material, *i.e.*, the χ^2 and β values. There are various methods to measure these values. The second-order polarizability χ^2 is often determined in the solid state by the Kurtz powder method [10]. This technique involves irradiation with light from a Nd^{3+}:YAG laser of 1064 nm and collecting radiation of half the wavelength. The SHG efficiencies are compared with respect to quartz, ADP, KDP, urea, *etc*. Molecular β values are normally determined in solution by different methods such as the electric field-induced second harmonic generation technique (EFISHG), hyper Rayleigh scattering (HRS) and the solvatochromic method. In the traditional EFISHG [11, 12], a strong electric field is used to induce the alignment of molecules to produce SHG. Therefore, it is necessary to know the ground state dipole moment (μ). The HRS [13, 14] technique analyzes the incoherently scattered second harmonic generations produced by a NLO material when it is irradiated with laser light. The advantage of this method over the other is that it is not necessary to know the ground state dipole moment and can be used for ionic and non-polar molecules, as it does not require electric fields. The solvatochromic process involves recording the electronic spectra of the compound in a series of solvents with different dielectric constants and refractive indices to calculate ($\Delta\mu_{eg}$)[15–18].

5. Compounds showing second harmonic generations

Crucial prerequisites for achieving a large second order NLO response are that the constituents should show a large molecular response β value and be arranged in a non-centric environment to contribute to the bulk effect. Such a non-centrosymmetric environment has generally been obtained through the use of inorganic crystals such as potassium dihydrogen phosphate, lithium niobate, *etc*. These are then incorporated into optical applications. They exhibit high χ^2 values, on the order of 1–100 × 10^{-9} esu. However, the material design is difficult due to complications in crystal growth, poor environmental stability, *etc.* [19].

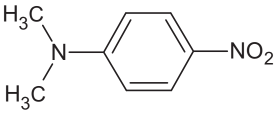
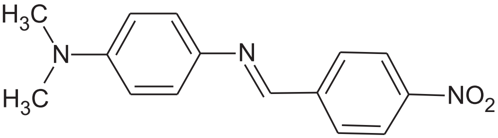
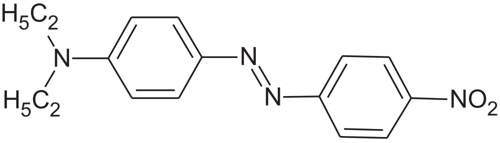
As an alternative to inorganic crystals, organic molecules have been of considerable interest for use in nonlinear optics due to their large optical nonlinearities. Conjugated organic molecules show high polarizability due to their delocalized pi electrons. These electrons are easily affected by the electric field. Asymmetry is achieved by attaching an electron donor (D) and an electron acceptor (A) group at either end of the molecule [20]. The permanent dipole moment provided by these groups creates an asymmetry-induced moment. The resulting molecule will have relatively low energy charge-transfer transitions and large $\Delta\mu_{eg}$ and r_{eg}. This is called a push-pull system.

Here, charge transfer occurs between the donor and the acceptor through the polarizable π system. The polarizability can be increased by either increasing the electron donor and acceptor group strength or the conjugation length between them. Some examples are shown in table 1 [2].

Like inorganic crystals, organic NLO materials also encounter some disadvantages such as difficulties in growing single crystals to large sizes, poor environmental stability, poor mechanical stability, *etc*.

In the last few years, organometallic and coordination complexes have emerged as chromophores for producing NLO materials, due to the large variety of structures and diversity of electronic properties that are possible by virtue of the tunable metal centre [21–25]. These compounds have the combined properties of both organic and inorganic compounds. The metal centers usually form π bonds with ligands and with each other, resulting in charge-transfer transitions, *i.e.*, ligand to metal, metal to ligand, *etc*. Initial studies concentrated on organometallic compounds. Later it was found that their NLO responses were

Table 1. Hyperpolarizabilities and structures of some organic chromophores.

Chromophore	Structure	β_0 (10^{-30} esu)
DMNA		12
NB-DMAA		37
Disperse red 1		47

lower than those of organic chromophores [26–29]. The reason for this was that many such compounds possess a pseudocentrosymmetry. This caused researchers to change their interest to coordination complexes. In this regard, N_2O_2 Schiff base complexes have appeared to be a promising class of efficient chromophores exhibiting large NLO responses [4]. These bases are derived from the condensation of a salicylaldehyde or its derivatives with amines. The amines can be either monoamines or diamines. They are similar to porphyrins and can be easily prepared. They are generally described as salen or salophen or salmalen-type ligands (figure 1).

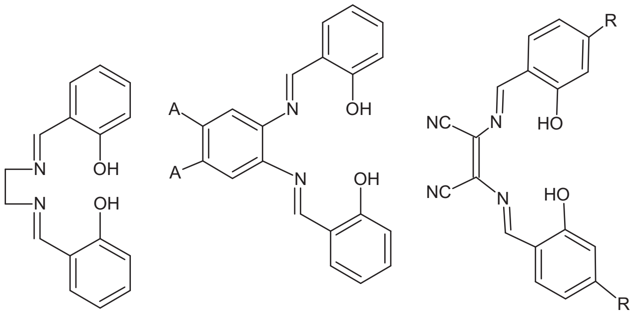
These bases are particularly interesting because of

(i) their preparative convenience
(ii) their thermal stability
(iii) their active role, strategic position, and nature (closed vs. open shell) of the metal ion, which is a constituent of the polarizable bridge in the D-π-A structure
(iv) their low energy charge-transfer transitions.

In such compounds, metal complexation leads to the formation of geometrically constrained acentric, generally planar structures, which leads to an enhancement of the optical nonlinearity compared to the ligand alone. They can be used to modify the structural and electronic properties of donor-acceptor frameworks [30–33].

6. Second order nonlinearities of Schiff bases derived from salicylaldehyde and their metal complexes

A number of second-order nonlinearity studies involving Schiff bases derived from salicylaldehyde and their metal complexes have been carried out by Pascal G. Lacroix. In 2001, he reviewed these types of metal complexes and their second order nonlinearities [4]. The first report on the NLO properties of these types of compounds was performed by Thompson *et al*. [33] in 1991 on the tetradentate salen [*N*,*N*′-bis(salicyleneaminato)ethylene] ligand and its metal complexes. According to this study, the metal salen core was not directly involved in the charge-transfer transition responsible for the NLO behavior. The metal salen core was used to enhance the NLO response of an apically substituted pyridine ligand. Lacroix noted that it was a report from Di Bella *et al.* on various Ni salen complexes that



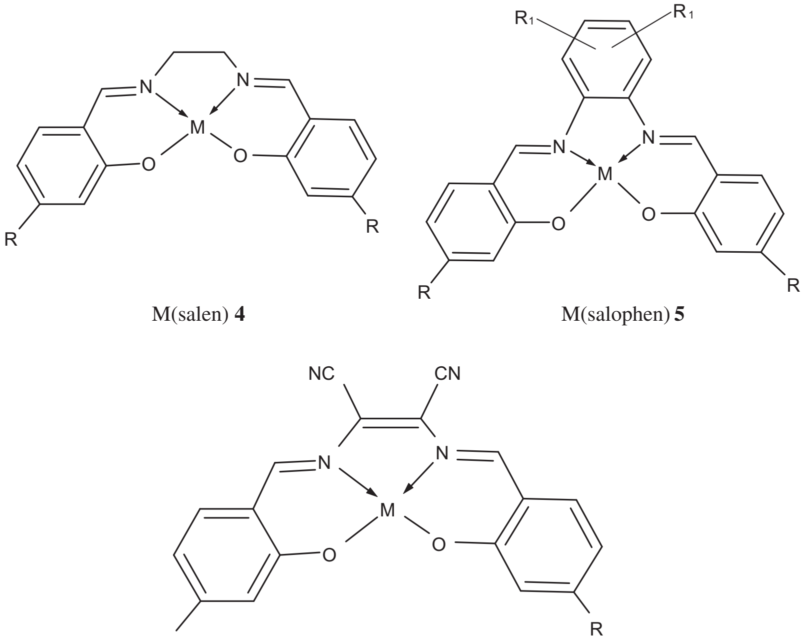
1 **2** **3**

Figure 1. The structure of salen **1**, salophen **2** and salmalen **3**.

showed the role of the metal electronic configuration in determining the second-order nonlinearities [34]. This discovery opened interesting possibilities for metal complexes to produce NLO responses. His review recapitulates how they modified salen-type ligands to obtain better β values with the same metal centre and also with different metal centers. It was also reported that this family of derivatives shows excellent thermal stability [36]. This is important when this compound is poled in polymers with very high glass transition temperatures while converting to any optical device. For stable and efficient poling, it has been realized that polymers with a T_g greater than 250 °C are necessary. Thus, good thermal stability has become an important prerequisite for NLO materials and is satisfied by salen metal derivatives. Lacroix also states the importance of using chiral complexes, which guarantee the formation of non-centrosymmetric bulk materials [37]. He concludes the review with the possibility of developing versatile synthetic methodologies to produce molecular switches.

Di Bella *et al.* developed a new synthetic strategy for obtaining thermally stable non-centrosymmetric coordination complexes with sizeable NLO responses that are tunable based on the metal center [38–40]. A series of donor-acceptor bis(salicylaldiminato) M(II) complexes were synthesized with general formulae from simple unsubstituted ligands to substituted ligands (figure 2).

In all cases, metal complexation resulted in a thermally stable, constrained acentric planar structure. The UV-Visible spectra of the ligands (except compound **4**) showed a relatively intense band at 350 nm in addition to a less intense band at longer wavelengths. The complexes showed red shifts corresponding to the charge-transfer transitions. The experimental hyperpolarizabilities of the ligands and complexes were calculated using the EFISHG



M(salen) **4**

M(salophen) **5**

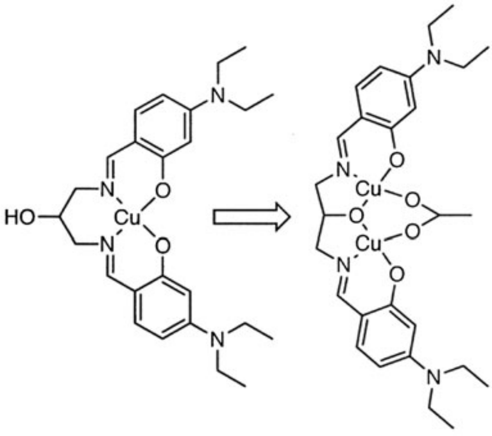
M(salmalen) **6**

Figure 2. The structure of M(salen) **4**, M(salophen) **5** and M(salmalen) **6** [M = Ni(II), Co(II) and Cu(II)].

technique. The unsubstituted ligands possess vanishing or small NLO, whereas the substituted ligand and its metal complexes show positive β values. This observation illustrated the efficacy of metal complexation in 'switching on' and tuning the NLO responses. The β values for coordination complexes increased from Ni (salen) to Ni (salmalen). Similarly, for a homologous series of unsubstituted M (salophen), the nonlinearity increased on substituting Cu(II) and Co(II) for Ni(II), indicating the role of the metal's electronic configuration in determining the second-order nonlinearity. The role of the metal centre in determining the NLO response in such structures is two-fold, as it can act as either the donor or the bridging moiety of the donor (π conjugate-bridge)-acceptor system. It was also suggested that appropriate substitution in the salicylidene rings of the above complexes would allow their incorporation into main chain copolymers. These peculiar characteristics and their facile processability into main chain copolymers make these new materials intriguing candidates for applications.

Lacroix and co-workers [41] reported a new ligand synthesized by the condensation of 4-diethylaminosalicylaldehyde and 1,3-diamino-2-propanal and its mono and dicopper(II) complexes (figure 3). The results of the EFISHG measurements and ZINDO/SCI-SOS of the two copper complexes are in good agreement and showed an 83% enhancement of the hyperpolarizability β on passing from the mono to the dinuclear species. They showed good transparencies in the visible frequency range, with absorptions at 353 and 372 nm. Another salicylaldimine ligand derived from 4-dimethyl aminosalicylaldehyde and 4-nitroaniline showed an enhancement in quadratic NLO properties and thermal stability upon complexation to cobalt ion (table 2). The β enhancement is due to a combination of both geometric and electronic effects. The cobalt complex exhibits a pseudo-tetrahedral molecular structure [42].

Lacroix *et al.* [43] theoretically investigated the effect of a spin transition on the second-order molecular hyperpolarizability of a bis(salicylaldiminato) Fe(II) Schiff base complex and noted for the first time that β depends on temperature. The intermediate neglect of differential overlap-based (INDO-based) sum over states perturbation theory and density functional theory (DFT) were used to explore the spin crossover phenomenon on the quadratic molecular NLO responses of an Fe(II) complex, in which the ligand was



7 **8**

Figure 3. The structure of mono copper(II) **7** and dicopper(II) **8** complexes.

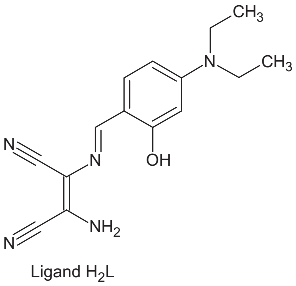
Table 2. Experimental (EFISH) values of first hyperpolarizabilities (esu) and temperature.

Compound	β (10^{-30} cm^5 esu)	Tc°
Ligand	66	260
Cobalt complex	110	320

obtained from the Schiff base condensation of 5-nitrosalicylaldehyde with 1,4,7,10-tetraazadecane. The calculations show an increase of 25% due to the geometric modifications occurring upon the spin transitions.

Later in 2005, Lacroix and co-workers reported another series of nickel complexes as molecular switches [31] using the ligands synthesized from the condensation of diaminomaleonitrile and 4-diethylaminosalicylaldehyde (figure 4). Crystal structures of the ligand and its complexes have been solved. Compound **10** crystallizes in a non-centrosymmetric *p2₁2₁2₁* space group and compound **11** in a monoclinic *p2₁/n* space group. It is evident from the calculated and crystal data that the molecules exhibit a planar salicyleneaminato ethylene (L^{2-}) structure, which suggests the possibility of long-range electron delocalization and hence sizeable NLO responses. The UV absorption of the complexes exhibits red shifting and a reduction in intensity. Although there is a slight difference in the calculated and experimental λ_{max} values, the red shift and reduction in intensity are observed in both. The spectra, with an absorption maximum located at 486 nm and an additional but less intense band at approximately 450 nm, agree fully with an NLO response [44, 45]. In contrast to previous reports [44], the nickel complex **10** shows lower NLO responses at both the experimental and theoretical levels (table 3).

Within the framework of sum over state perturbation theory, β is related to all the excited states of the molecule and can be expressed as the sum of two contributions, the so-called two level (β_{2L}) and three level (β_{3L}) terms. In most cases, β is dominated by β_{2L}, as in the ligand. However, in the case of nickel complex **8**, β_{3L} dominates. The suggested reason for this is that complexation leads to the formation of an unusual nickel amido (-NH-Ni^{II}) bond by deprotonation of the primary amine of the ligand; thus, the amide maleonitrile fragment, which was the acceptor in the ligand, turned into an efficient donor. Qualitative ZINDO/SCI quantum chemical calculations suggested that the β orientation in compound **10** is surprisingly strongly dependent on the laser frequency, which is in contrast to observations of $[Ni(HL)(MePhCHNH_2)]^+$. In particular, a β rotation strictly equal to 90° could be



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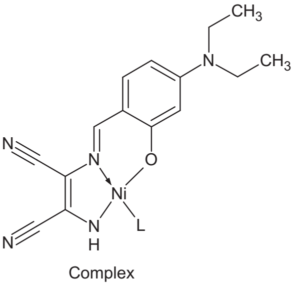


10-13

Figure 4. The structure of the ligand **9** and complexes where **10**. L = $MePhCHNH_2$, **11**. L = $PrNH_2$, **12**. L = Py and **13**. L = PPH_3.

Table 3. Experimental (EFISH) and calculated (ZINDO) values of first hyperpolarizabilities (esu) and dipole moment (Debye).

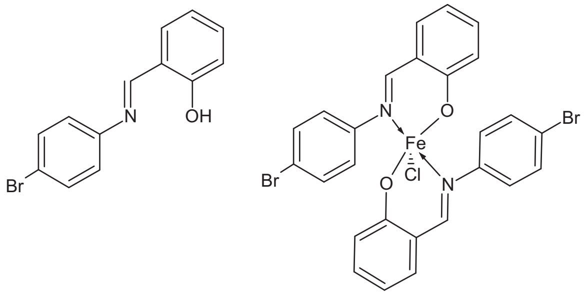
	Experimental		Calculated	
Compound	μ	β (10^{-30} cm^5 esu)	μ	β (10^{-30} cm^5 esu)
9	8.6	38	12	16.4
10	11	17.5	12	10.5

obtained with 1022 nm incident light on passing from [Ni(L)($MePhCHNH_2$)] to a hypothetical [Ni(HL)($MePhCHNH_2$)]$^+$ protonated complex, thus raising the possibility for a new type of molecular switch.

Lacroix and Farfan [46] were able to design a large family of chiral push-pull organotin derivatives using a one-step synthesis. The complexes exhibited sizeable SHG efficiencies, up to eight times that of urea in second harmonic generation, in addition to good transparencies (λ_{max} at approximately 395 nm). A correlation was observed between the degree of chirality and the solid-state efficiencies of the derivatives, which possess the same molecular and solid-state electronic and structural features.

Ayhan Elmali *et al*. reported the NLO properties of bis[(*p*-bromophenylsalicylaldiminato) chloro] Fe(III) and its ligand *N*-(4-bromo)-salicylaldimine [47]. They made an attempt to relate the second-order NLO response β and the electric dipole moments computed by the *ab initio* finite field second-order Møller-Plesset perturbation method with the electronic properties of the coordinated metal centre in the synthesized complex (figure 5).

The UV-Visible spectra recorded for both ligand **14** and metal complex **15** using various solvents such as DMSO, methanol, tetrahydrofuran and chloroform showed solvatochromic behavior, that is, the absorption maxima showed bathochromic shifts. These shifts indicate that they have high molecular hyperpolarizabilities. Complex **15** showed a broad band near 300-344 nm, which is absent in the spectrum of ligand **14**, and can therefore be attributed to the metal to ligand charge-transfer transition. The ligand and metal complex exhibited similar spectra in the 200-270 nm range. These maximum absorption wavelengths of the synthesized compounds found below 400 nm are indicative of a nonzero molecular first hyperpolarizability [48, 49]. The first hyperpolarizabilities were calculated theoretically by the *ab initio* FF MP2 method. The calculations showed that the iron complex had a distorted square pyramidal geometry with a *trans* conformation. The centrosymmetric nature



Free Ligand 14 Iron (III) complex 15

Figure 5. The structure of **14** and **15**.

of the crystal structure of the investigated complex suggested that there might not be macroscopic NLO behavior. However, this complex was polar, with nonzero dipole moment components, and thus it was predicted that it may display microscopic NLO behavior. This was confirmed by the low energy charge-transfer transition. The complex showed high β_{total} values due to the strong electronic communication between the metal and its ligand. The two electron-withdrawing groups (Br) might have enhanced the acceptor character of the ligand bound to the metal atom through two nitrogen and two oxygen atoms. The ligand provided extended conjugation and a strong electronic communication within the complex that led to high β values. It is observed that β_{total} for the free ligand with a closed-shell electronic state is much greater than the complex with an open-shell electronic state. This can be either due to the presence of the *para* acceptor Br, which enhances the donor character of the amine N, or due to the intra-ligand hydrogen bonding between the O and N of the free ligand. It was also reported that the investigated compounds had high dipole moments (table 4).

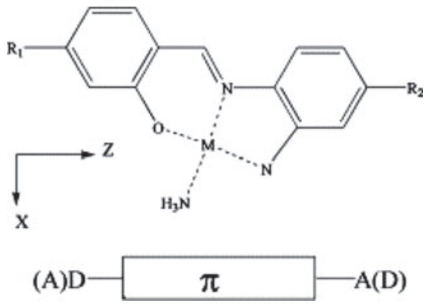
Yong-Quing Qiu *et al*. performed DFT studies on the second-order nonlinear properties of a series of mono Schiff base metal complexes through donor-acceptor exchange and metal substitution [50] (figure 6). **16a** and **16b**, **17a** and **17b** and **18a** and **18b** are isomeric compounds. The coordinated central metals selected were Ni, Pt and Pd, which have the same electronic configuration for their corresponding cations. The first hyperpolarizabilities were calculated at the FFB3LYP/Lanl2dz level. It was reported that the first hyperpolarizabilities of **16b**, **17b** and **18b** and the dipole moments of **16a**, **17a** and **18a** were enhanced due to the molecular structure (table 5).

The TD-DFT calculations clearly showed that the transition energy values of **16b**, **17b** and **18b** are small, which is in agreement with the two level model approximation. They also reported that the donors of **16b**, **17b** and **18b** contributed more to the HOMO and HOMO-1 than those of **16a**, **17a** and **18a**. The HOMO-1 → LUMO and HOMO → LUMO transitions of **16b**, **17b** and **18b** augment the β enhancement. Thus, the results of the study indicated that the mono Schiff base complexes were good candidates for second-order NLO materials.

Rigamonti *et al*. reported a series of copper complexes of salen analogues with two different substituted salicylaldehyde moieties producing a push-pull charge asymmetry [35]. They made an attempt to study the effect of charge symmetry along the x-axis (figure 7). The combined experimental and DFT theoretical studies showed that the most relevant effects on the properties of the complexes were determined by the introduction of the NO_2 group in one sal moiety. Such an unsymmetrical substitution significantly increased the magnitudes of μ and β_{total}. On the other hand, the donor groups they investigated (Me, OMe and NMe_2) had a smaller effect in modulating μ but were able to enhance β_{total}. While studying the electronic spectra, they recognized that the NLO responses were controlled by the LMCT absorption. The nature of such a transition has been fully confirmed by TDDFT calculations, which evidenced the presence and relative importance of the two competing directions of CT within the complexes: one from the donor O to the Cu atoms, and the other from the donor to the acceptor groups. The sign of β_{CT} is determined by the predomi-

Table 4. The first hyperpolarizabilities (esu) and dipole moment (Debye) of the complexes.

Compound	β_{total} (10^{-30} cm^5 esu)	μ
15	35.307	5.7018
14	1104.342	15.8558



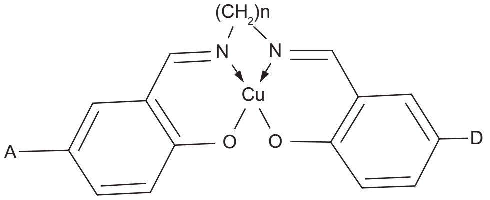
16a: R_1 = -N(C_2H_5)2, R_2 = -$CH_2C(CN)_2$, M = Ni
16b: R_1 = -$CH_2(CN)_2$, R_2 = -N$(C_2H_5)_2$, M = Ni
17a: R_1 = -N(C_2H_5)2, R_2 = -$CH_2C(CN)_2$, M = Pd
17b: R_1 = -$CH_2(CN)_2$, R_2 = -N$(C_2H_5)_2$, M = Pd
18a: R_1 = -N(C_2H_5)2, R_2 = -$CH_2C(CN)_2$, M = Pt
18b: R_1 = -$CH_2(CN)_2$, R_2 = -N$(C_2H_5)_2$, M = Pt

Figure 6. The structure of mono Schiff base M(II) complexes.

Table 5. The first hyperpolarizabilities (a.u) and dipole moment (Debye) of the complexes.

Compounds	β_{total}	μ
16a	27888.922	15.584
16b	57963.232	13.584
17a	29529.605	15.257
17b	56040.695	13.834
18a	29560.109	15.211
18b	53990.156	13.866

1 a.u = 8.6 × 10^{-33} esu.



19

Figure 7. The structure of compound **19**.

nant charge-transfer transition. This is the first computational analysis of second-order NLO responses of open-shell transition metal complexes. Although the β values of compound **19** were in the range reported for similar compounds, the charge asymmetry generated by the unsymmetrical substitution allows great freedom in the design of metal complexes with tunable properties. A proper choice of substituent provides great potential to modulate parameters such as μ and β.

Iran Sheikhshoaie and Samira Saeednia [51] reported on the nonlinear properties of three Schiff base compounds **20**, **21** and **22** (figure 8). They used a simple donor-(π electron bridge)-acceptor model for the NLO compounds. The molecular first hyperpolarizabilities of these compounds were calculated using an AM1 semi-empirical method.

The electron-donating and accepting capabilities of organoligand-metal fragments have been successfully applied to design and develop new highly efficient dipolar chromophores to achieve high second-order NLO responses [21, 22, 25]. For example, the attractive NLO properties of ferrocene-based complexes are coupled with good thermal stability, excellent donor capability and redox switching abilities. The cationic electron-withdrawing isolobal counterparts, namely the robust mixed sandwich derivatives $[\mathrm{Cp'M}\ (\eta^6\text{-arene})]^+$ (M = Fe, Ru, Cp′ = Cp = η^5-C_5H_5, Cp′ = Cp* = η^5-C_5Me_5), have proven their efficiency as organometallic chromophores to achieve second-order NLO responses. David Carrillo *et al.* utilized [52] the advantages of both ferrocenyl and $[\mathrm{Cp'M}\ (\eta^6\text{-arene})]^+$ units and obtained hetero trinuclear π conjugated donor-acceptor unsymmetrical Schiff base complexes. They reported the synthesis, spectroscopic characterization and electrochemical and linear optical properties of a family of binuclear M[Fc-C(O)CH=C(CH_3) N-X-N=CH-(2-O,5-R-C_6H_3)], where M = Ni (23) or Cu (24), X = 0-C_6H_4, R = H, M = Ni, X = CH_2CH_2, R = OH, and their corresponding trinuclear compounds [M{Fc-C(O)CH=C(CH_3) N-X-N=CH-(η^6-2-O,5-R-C_6H_3)Ru Cp*}][PF_6], where M = Ni (25) or Cu (26), and a new metalloligand precursor {Fc-C(O)CH=C(CH_3)N(H)CH_2CH_2N=CH-(2,5-$(OH)_2C_6H_3$)] (27) (figure 9). All the organometallic inorganic D-π-A conjugated molecules investigated contain ferrocene and M [ONNO] units. In the trinuclear series, the salicylidene ring of the acyclic tetradentate Schiff base forms the π bridge to the 12-electron cationic arenophile Ru Cp*. The electronic structure and absorption spectra were investigated thoroughly by experimental and DFT studies. The DFT-calculated energy levels of the frontier orbitals and the large spin density of the iron centres are in agreement with the experimental results. ILCT and MLCT contributions

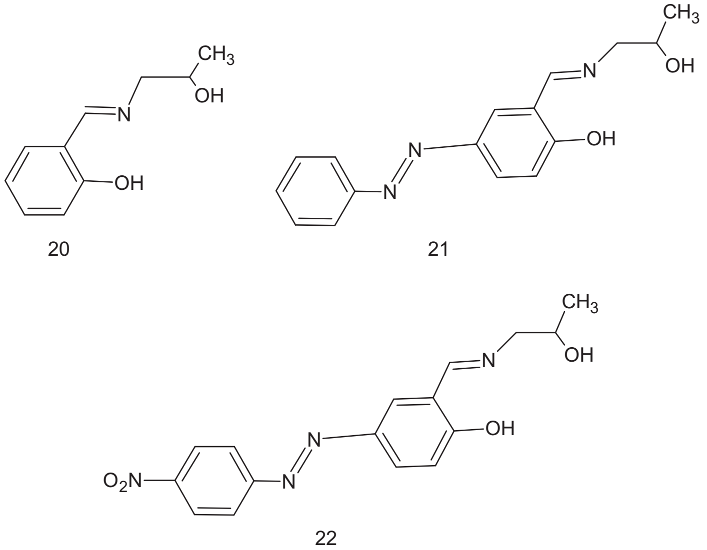
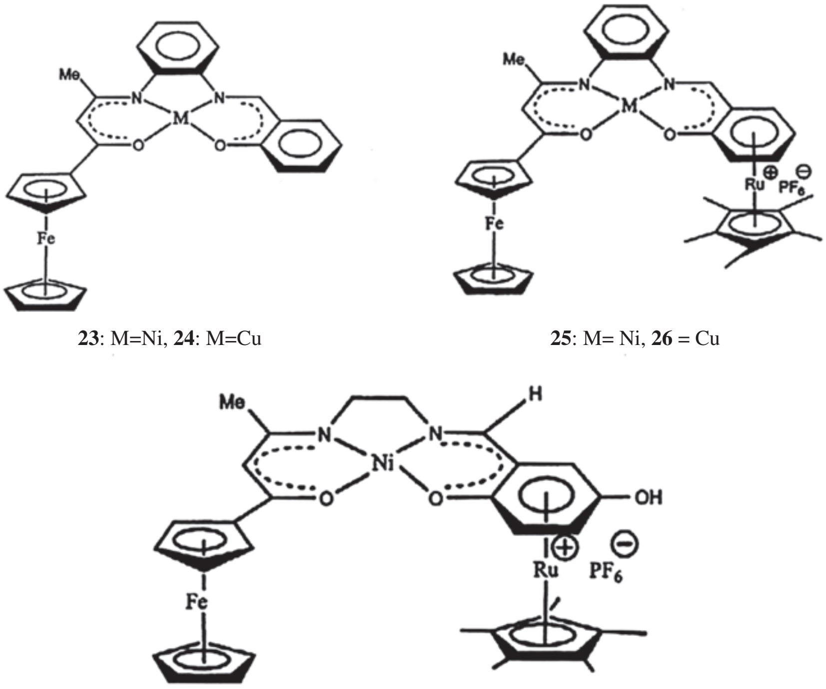


Figure 8. The structure of Schiff base compounds **20**, **21** and **22**.



23: M=Ni, **24**: M=Cu

25: M= Ni, **26** = Cu

27

Figure 9. The structure of compounds **23**-**27**.

in the overall spectra were also determined. The HLS measurements showed that all the compounds exhibited a second-order nonlinear response, and the hyperpolarizability value increased with the nuclearity of the compound.

Tang *et al.* [53] synthesized a series of Schiff bases with cyanide as an electron acceptor. The optimal geometries of these compounds were calculated using DFT and the electronic properties by TD-DFT methods. The results of the TD-DFT calculations indicate that the derivatives with electron-donating groups (CH_3, OCH_3 or $N(C_2H_5)_2$) showed a red shift compared to the derivatives with the electron-withdrawing groups (NO_2). The analysis of the MOS indicates that the CN contributes to the LUMO orbital while the OCH_3, $N(C_2H_5)_2$ and NO_2 groups contribute to the HOMO orbital. The compounds with the electron-rich groups OCH_3 and $N(C_2H_5)_2$ showed large hyperpolarisabilities. In contrast, the compound with a NO_2 substituent also showed a large hyperpolarizability. This is most likely because of the special transition model. The authors also calculated the energy gap between the HOMO and LUMO orbitals and showed that the smaller the energy gap, the larger the first hyperpolarizability. Shinya Hayami *et al.* [54] reported on the preparation of Langmuir-Blodgett films of long alkyl chains of some salen iron, nickel and manganese complexes. They showed second harmonic generation, whose intensity depends on the number of unpaired electrons. Their goal was to study the switching of the NLO response using SCO and LIESST effects.

7. Conclusion

Recently, many more metal salicylaldehyde-based Schiff bases have been prepared, and their NLO properties investigated. An attractive feature of these compounds as NLO materials is that their molecular architectures can be easily modulated to optimize both the microscopic parameters, such as hyperpolarizability, and the related macroscopic properties.

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