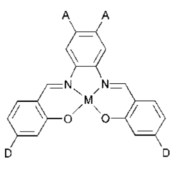
Second-order nonlinear optical properties of transition metal complexes



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This contribution presents an overview of the principal classes of second-order nonlinear optical (NLO) transition metal (organometallic and coordination) complexes and illustrates how organometallic and coordination chemistry can offer a very large variety of NLO structures in relation to the metal *n*d configuration, oxidation state, spin state, *etc*. Moreover, metal complexes can satisfy the very different demands of second-order NLO materials such as switchable, tuneable, and multidimensional NLO properties, depending on the subtle interplay of structure–property relationships. Recent advances and perspectives in metal complexes as NLO materials are also presented.

1 Introduction

The current intense research activity in second-order nonlinear optical (NLO) molecule-based materials has produced a wide variety of new chromophores.[1–3] Among them, metal (organometallic and coordination) complexes represent an emerging and growing class of materials.[4–7] Compared to organic molecules, they offer a larger variety of molecular structures, the possibility of high environmental stability, and a diversity of electronic properties by virtue of the coordinated metal center.[8–10]

Since the report in 1987 by Green *et al.*, in which good second-harmonic generation (SHG) efficiency was revealed for a ferrocenyl derivative,[11] attention has been paid to metal complexes as potential second-order NLO materials. Thus, various classes of metal complexes have systematically been explored in terms of new and optimised NLO materials. Early[4,5] and more recent[6,7] review articles on NLO metal complexes indicate the breadth of the active research in this field. Moreover, reviews on some specific NLO topics involving coordination complexes have also appeared.[12,13] These review contributions, however, have essentially been involved in the context of NLO materials, while less attention has been paid to organometallic and coordination chemistry and to the unique possibilities offered by metal complexes.

This contribution surveys the principal classes of second-order NLO transition metal complexes and illustrates how organometallic and coordination chemistry can offer a very large variety of molecular and bulk NLO structures in relation to the metal *n*d configuration, oxidation state, spin state, *etc*. It will show that NLO metal complexes, as organic NLO chromophores, can be classified within a simple molecular scheme constituted by a donor–(π-conjugate bridge)–acceptor (D–π–A) structure, in which the donor and/or the acceptor, or the bridge moieties are selectively replaced by a organometallic group. A brief introduction to NLO phenomena and related materials will precede the following overview of NLO transition metal complexes within the above molecular scheme, with the aim of understanding structure–property relationships and of developing new NLO materials. We emphasize that, beyond any real application in NLO devices, the goal of such a contribution is to show the general and unique characteristics of NLO metal complexes.

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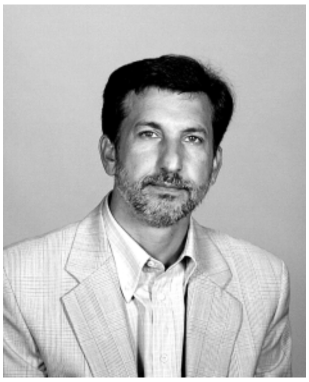

2 Principles of nonlinear optics

This section is dedicated to a brief introductory description of the nature and origin of second-order NLO effects, related materials and methods, to give readers a starting point, from a chemical point of view, for understanding structure–property relationships. A detailed description of basics, materials and methods for nonlinear optics can be found in refs. 14, and 1–3.

Nonlinear optics deals with the interaction of applied electromagnetic fields in various materials to generate new electromagnetic fields, altered in frequency, phase, or other physical properties. When a molecule is subjected to an oscillating external electric field (light), the induced change in molecular dipole moment (polarisation) can be expressed by a power series in the field strength E_j as in eqn. (1), where p_i is the electronic polarisation induced along the *i*th molecular axis, α is the linear polarisability, β the quadratic hyperpolarisability, and γ the cubic hyperpolarisability. α in eqn. (1) is a second-rank tensor because it relates all of the components of the polarisation vector to all of the components of the electric field vector, and is responsible for the linear optical behaviour.

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Analogously, β and γ in eqn. (1), which relate the polarisation to the square and the cube of the field strength, are respectively, third-rank and fourth-rank tensors, responsible for second-order and third-order NLO effects. The even-order tensor, β, vanishes in a centrosymmetric environment.

For small fields the quadratic and cubic terms in eqn. (1) can be neglected, so that the induced polarisation is proportional to the strength of the applied field (linear optical behaviour). However, when a molecule is subjected to an intense electric field such as that due to an intense laser pulse, the second and third terms in eqn. (1) become important, such that nonlinear optical behaviour can be observed. Note that, the 'nonlinear' term originates from the nonlinear dependence (quadratic or cubic) of the induced polarisation of the applied field.

$$p_i = \sum_j \alpha_{ij} E_j + \sum_{j \le k} \beta_{ijk} E_j E_k + \sum_{j \le k \le l} \gamma_{ijkl} E_j E_k E_l + \dots \quad (1)$$

The macroscopic polarisation for an array of molecules is given by eqn. (2), where the χ values are the macroscopic susceptibilities. The macroscopic susceptibilities are related to the corresponding molecular terms α, β, γ, *etc*., by local field factors, F (which take into account intermolecular interactions), molecular packing density, N_s, and appropriate coordinate transformation, $\langle T_{IJK} \rangle$ (*e.g*., eqn. (3) for $\chi^{(2)}_{IJK}$). Note that the noncentrosymmetry requirement for second-order NLO processes needs to be fulfilled also on a macroscopic level.

$$P_I = \sum_J \chi^{(1)}_{IJ} E_J + \sum_{J \le K} \chi^{(2)}_{IJK} E_J EK + \sum_{J \le K \le L} \chi^{(3)}_{IJKL} E_J E_K E_L + \dots \quad (2)$$

$$\chi^{(2)}_{IJK} = N_s F \beta_{ijk} \langle T_{IJK} \rangle \quad (3)$$

A variety of nonlinear optical effects can occur through $\chi^{(2)}$ and $\chi^{(3)}$. In the following discussion, however, we will refer only to second-order NLO interactions. Among them, frequency doubling (SHG), frequency mixing, and the electro-optic Pockels effect (linear change in the index of refraction), represent the most important NLO processes. While the frequency conversion (SHG and frequency mixing) originates from the second-order polarisation created in a medium by an optical field of a given frequency, $E_j(\omega)$, the Pockels effect requires the presence of an external dc electric field, $E(0)$ in addition to the optical $E(\omega)$ field. Therefore, the tensor $\chi^{(2)}_{IJK}$ is often written as: $\chi^{(2)}_{IJK}$ $(-\omega_3;\ \omega_2,\ \omega_1)$, where the frequency arguments, ω, indicate the frequency of the resultant field ω_3, for input frequencies ω_2, ω_1. Thus, for the SHG it is written: $\chi^{(2)}_{IJK}$ $(-2\omega;\ \omega,\ \omega)$, and for the linear electro-optic effect: $\chi^{(2)}_{IJK}$ $(-\omega;\ \omega,\ 0)$.

2.1 The molecular quadratic (hyper)polarisability

From the above discussion it is clear that second-order NLO effects of molecular materials are ultimately related to the microscopic quadratic or first hyperpolarisability, β. The polarisation is the instantaneous displacement of the electron density of a molecule by the applied electric field. It can be viewed in terms of the electric field of the light wave modifying the ground electronic state of the molecule. The original molecular ground state is no longer a quantum state for the molecule when it is perturbed by the electric field. The new quantum state can be described as a linear combination of the ground and excited states of the unperturbed system. The latter have different electron distributions from the ground state, so that mixing the excited states into the ground state leads to a net charge redistribution (polarisation). Note that although the mixing introduces excited-state character in the ground state, it does not result in a long-lifetime population of any excited state. The instantaneous formation of these polarised states has been sometimes referred to as 'virtual transitions'. These concepts are the basis of the quantum-mechanical 'sum over states' (SOS) perturbation theory for the description of the molecular polarisation. Thus, the electronic states created by the perturbing field are treated as an infinite expansion over a complete set of unperturbed excited states and the individual tensor components of the molecular first hyperpolarisability can be related exactly to *all* the excited states of the molecule. A simplification of this approach can be made by restricting the 'summation' to one excited state, eqn. (4), and assuming that one tensor component (β_{iii}) dominates the NLO response [in the case of a unidirectional charge-transfer (CT) transition]. For instance, for SHG we have eqn. (4) where $\hbar\omega_{\mathrm{ge}}$ is the frequency of the lowest CT transition ($\omega_{\mathrm{ge}} = E_{\mathrm{ge}}/\hbar$, $2\pi c/\lambda_{\mathrm{ge}}$), r_{ge}, and $\Delta\mu_{\mathrm{ge}}$ are, respectively, the transition dipole moment, and the dipole moment variation, between the ground (g) and the involved excited (e) state. This so called 'two-state' model is a very good approximation for estimating the frequency dependent (dynamic) first hyperpolarisability for mostly NLO chromophores, when a single CT state dominates the NLO response. It implies that frequency doubling will be enhanced near resonance, that is, when the input (laser) frequency or the second harmonic approach the frequency of the lowest optical CT transition. The two-state model is of great value to chemists because it allows a simple, direct analysis of β-determining parameters and, hence, a chemical interpretation of molecular NLO properties. On the other hand, on the basis of the knowledge of linear optical spectroscopic parameters, it allows the prediction and estimation of the molecular second-order NLO response. Extrapolation to zero frequency ($\hbar\omega = 0.0$ eV; $\lambda = \infty$) allows estimation of the static first hyperpolarisability, β_0 (eqn. (5)). The first hyperpolarisability, β, can be expressed in either the cgs (cm^4 statvolt^{-1} = esu) or the SI (C m^3 V^{-2}) unit systems. The conversion from the SI to the cgs system is given by the relation: 10^{-50} C m^3 V^{-2} = 2.694×10^{-30} esu.

$$\beta_{iii}(-2\omega;\omega,\omega) = \frac{3e^2}{2} \frac{\left(\hbar\omega_{ge}\right)^2 \left(r_{ge}\right)^2 \Delta\mu_{ge}}{\left[\left(\hbar\omega_{ge}\right)^2 - (2\hbar\omega)^2\right]\left[\left(\hbar\omega_{ge}\right)^2 - (\hbar\omega)^2\right]} \quad (4)$$

$$\beta_0 = \frac{3e^2}{2} \frac{\left(r_{ge}\right)^2 \Delta\mu_{ge}}{\left(E_{ge}\right)^2} \quad (5)$$

2.2 Methods for second-order nonlinear optics

A variety of experimental techniques have been used for investigating the second-order NLO activity of molecular materials. The molecular first hyperpolarisability, $\beta(-2\omega;\ \omega,\ \omega)$, can be obtained by the *electric field induced second harmonic generation* (EFISH) technique and is useful for neutral, dipolar molecules. 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, *i.e*., the vector component of the β_{ijk} tensor along the dipole moment direction, can be thus extracted if the ground-state dipole moment, μ_{g}, is known. Alternatively, the *hyper-Rayleigh scattering* (HRS) technique involves detecting the incoherently scattered second harmonic generated from an isotropic solution and allows the determination of the 'whole' β tensor, or more exactly, the mean value of the $\beta \times \beta$ tensor product. Analysis of the polarisation dependence of the second harmonic signal can provide information about single tensor β_{ijk} components. This method has the advantage that it can be used even for non-dipolar or charged molecules. Frequency dependent β(EFISH) or β(HRS) values are eventually extrapolated to static β_0 ones by means of the two-level model discussed above [eqns. (4) and (5)]. In fact, the static hyperpolarisability represents the most important feature when comparing the molecular second-order

NLO response of different chromophores. However, these estimated β_0 data are generally approximate, especially when dynamic β data are resonantly enhanced or when the two-level model breaks down, that is, when many states, instead of one, contribute to NLO response.

In the *Kurtz powder* technique a powdered sample is irradiated with a laser and scattered emitted light at the second harmonic frequency is collected and compared to that of a reference sample, such as quartz or urea, to obtain a measure of the SHG efficiency. Although this technique is crude (the magnitude of the response depends on particle size), it is an excellent method for screening large numbers of powdered materials. Second-order susceptibility values, $\chi^{(2)}_{IJK}$, can be obtained by means of SHG or electro-optical measurements on noncentrosymmetric single crystals or thin films of engineered acentric molecular assemblies.

Various theoretical approaches have been developed for the calculation of the molecular hyperpolarisability.[15] The above SOS method and the related two-state simplification represent, however, the most useful approaches for chemists to understand structure–hyperpolarisability relationships, and for designing new, highly efficient second-order NLO molecular materials.

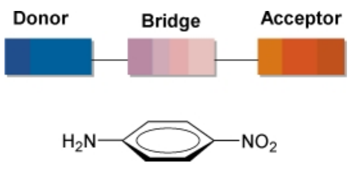
2.3 Materials for second-order nonlinear optics

The SOS approach and the related two-level simplification [eqns. (4) and (5)] provide a simple prescription for second-order NLO molecular materials: the existence of strong intramolecular CT excitations in a noncentrosymmetric molecular environment. This can be satisfied by considering a polarisable molecular system (*e.g.*, a π-conjugated pathway) having an asymmetric charge distribution (*e.g.*, with donor and/or acceptor group substituents), such as the prototypical *p*-nitroaniline molecule (Scheme 1).

In this respect, almost all successful strategies for obtaining second-order NLO dipolar organic molecules and metal complexes have been developed within a simple molecular scheme formed by a D–π–A structure, and the design of new second-order NLO chromophores has focused primarily on engineering the electronic nature of the donor and the acceptor, and the conjugation length of the bridge.

In addition to dipolar molecules, recently there has been increasing interest for octupolar molecules. These are non-dipolar species whose second-order NLO response is related to multidirectional charge transfer excitations, rather than to dipolar unidirectional excitations. Therefore, the first hyperpolarisability for such molecules cannot be described by the two-level model ($\Delta\mu_{ge} = 0$). In this case the two-level model should be extended to a three-level model. A prototypical example of a trigonal octupolar (D_3 or D_{3h}) chromophore and the related octupolar charge distribution are shown in Scheme 2.

An enormous variety of second-order NLO dipolar and octupolar molecular materials have been developed. Moreover, the requirement for engineering acentric bulk architectures has stimulated the development of various techniques such as the Langmuir–Blodgett, the self-assembly, or the electric-field poling of chromophore-functionalised polymers, to get thin films of acentric molecular assemblies. Very large second-order nonlinearities, both at microscopic and macroscopic levels, orders of magnitude larger than those of classical inorganic NLO crystals such as lithium niobate ($LiNbO_3$) or potassium dihydrogen phosphate (KDP), have been achieved. Excellent reviews of recent advances in second-order NLO molecular materials can be founds in refs. 3, 16 and 17.



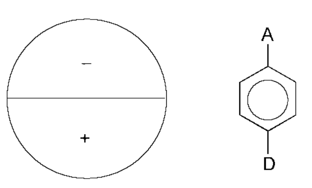
Scheme 1 The prototypical dipolar D–π–A *p*-nitroaniline molecule.

3 Metal complexes for second-order nonlinear optics

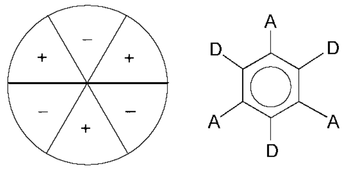
As illustrated in the previous section, most second-order NLO metal complexes, as organic NLO chromophores, can be envisaged within a simple molecular scheme constituted by a D–π–A system, in which the donor and/or the acceptor, or the bridge moieties are selectively replaced by an organometallic group. This is because metal complexes possess intense, low-energy metal-to-ligand charge transfer (MLCT), ligand-to-metal charge transfer (LMCT), or intraligand charge transfer (ILCT) excitations. Therefore, they can effectively behave as donor and/or acceptor groups of the D–π–A system, or as constituents of the polarisable bridge. With this scheme in mind, several classes of second-order NLO transition metal complexes can be identified. Some representative examples of dipolar molecules are reported in Fig. 1. Octupolar species will be treated as a separate class. Note that, although many transition metal complexes are known to possess LMCT transitions (essentially in complexes of metals with high oxidation numbers), no documented examples have been reported of second-order materials whose NLO response is governed by such excitations.

3.1 Metal complexes as donor or acceptor groups in D–π–A second-order NLO dipolar structures

The first case we consider is that of metallocene derivatives, which represent one of the most widely investigated classes of NLO metal complexes.[4–7,18,19] Among them, several main families such as (*E*)-1-metallocenyl-2-(4-nitrophenyl)ethylene derivatives (**2**, Fig. 2), including (*Z*)-analogues, chiral species, (*N*-alkylpyridinium) salts and bimetallic species (*vide infra*) can be mentioned. In all cases, the metallocene unit, generally a ferrocenyl, represents the donor group of the D–π–A structure. Although controversial,[15,19] the molecular second-order nonlinearity of such complexes can been rationalised in terms of two-level contributions involving CT excitations between low-lying, filled metallocene orbitals and empty π* orbitals of the conjugated π–A system. Moreover, relatively large first



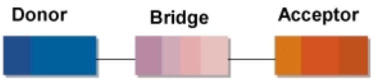
Dipole

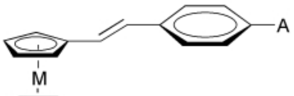


Octupole

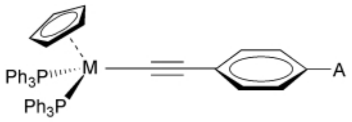
Scheme 2 Dipolar *vs*. octupolar charge distribution in prototypical dipolar and trigonal octupolar systems.

hyperpolarisability values have been found (Fig. 2). Actually, both experimental and theoretical data indicate that the donor strength of the ferrocenyl group is comparable to that of the organic methoxyphenyl donor, although electron-rich, 18-valence-electron ferrocenes are expected to be stronger donors on the basis of the binding energies and redox potentials of their low-energy, metal-based electrons. This has been explained in terms of a relatively poor coupling between the metal of the ferrocenyl donor group and the π-network of the organic π–A system, which reduces the donor properties of the former.

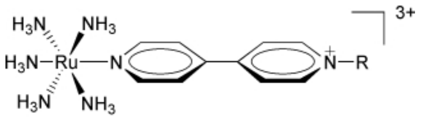




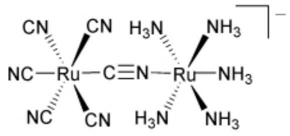
Metallocenes



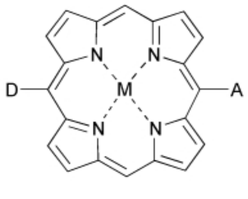
σ-acetylides



Ruthenium(II) amines

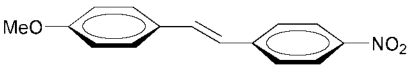


Bimetallics

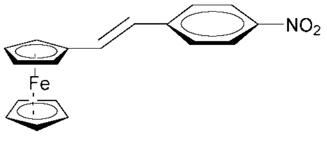


Metalloporphyrins

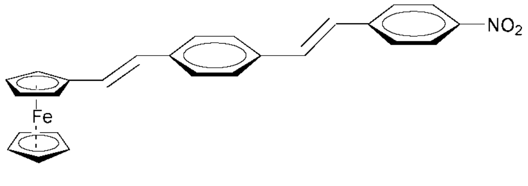
Fig. 1 Representative examples of second-order NLO dipolar metal complexes.



1, λ_{max} = 364 nm; $\beta_{(1.91)}$ = 28 x 10^{-30} esu



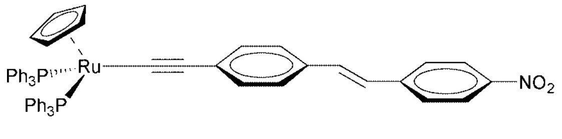
2, λ_{max} = 356 nm; $\beta_{(1.91)}$ = 31 x 10^{-30} esu



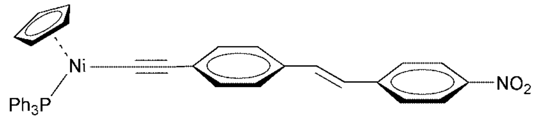
3, λ_{max} = 387 nm; $\beta_{(1.06)}$ = 403 x 10^{-30} esu

Fig. 2 Selected examples of second-order NLO ferrocenyl complexes. The 4,4′-substituted stilbene derivative (**1**) is reported for comparison. Experimental data from refs. 18 and 19.

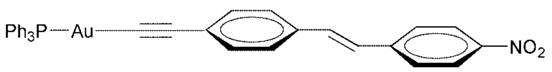
Another important class of NLO metal complexes is represented by (cyclopentadienyl)(alkylphosphine)metal σ-acetylide complexes, developed by Humphrey and co-workers.[7,20] In fact, systematic experimental/theoretical studies on Ru^{II}, Ni^{II} and Au^{I} σ-acetylides provided interesting results and trends for the second-order NLO properties of this class of materials. Analogously to metallocenes, the metal acts as the donor group of the D–π–A structure and the second-order nonlinearity can be related to low-energy MLCT excitations. Very large second-order nonlinearities, even if resonantly enhanced, have been achieved (Fig. 3). Electrochemical studies indicated a relative oxidisability: $Ru^{II} > Ni^{II} > Au^{I}$.[7] Accordingly, the largest β values were obtained for the Ru^{II} complexes that are electron-rich, have 18 valence electrons, and are more easily oxidisable (*e.g.*, **4**); these values can be compared with the smaller observed nonlinearity for 14-valence-electron, less readily oxidisable Au^{I} species (**6**), with intermediate values for the 18-valence-electron Ni^{II} complexes (**5**). The trends observed in chromophore variation



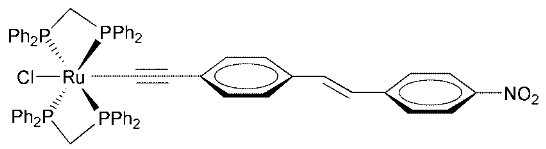
4, λ_{max} = 476 nm; $\beta_{(1.06)}$ = 1455; $\beta_{(0)}$ = 232 x 10^{-30} esu



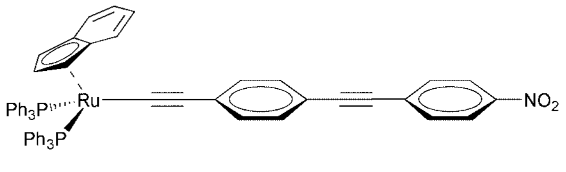
5, λ_{max} = 437 nm; $\beta_{(1.06)}$ = 445; $\beta_{(0)}$ = 120 x 10^{-30} esu



6, λ_{max} = 386 nm; $\beta_{(1.06)}$ = 120; $\beta_{(0)}$ = 49 x 10^{-30} esu



7, λ_{max} = 490 nm; $\beta_{(1.06)}$ = 1946; $\beta_{(0)}$ = 235 x 10^{-30} esu

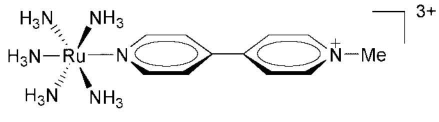


8, λ_{max} = 463 nm; $\beta_{(1.06)}$ = 1027; $\beta_{(0)}$ = 202 x 10^{-30} esu

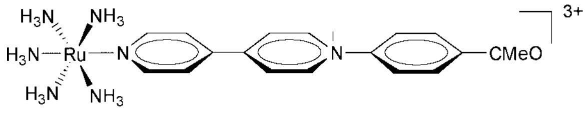
Fig. 3 Selected examples of second-order NLO σ-acetylide complexes. Experimental data from refs. 7, 20 and 21.

are consistent across the Ru^{II}, Au^{I} and Ni^{II} complexes, as found from plots obtained from correlation of experimentally determined quadratic nonlinearities of metal acetylides with their precursor acetylenes.[7] The $Ph_3PAu(C{\equiv}C)$– unit has comparable efficiency to the strongest organic donors, suggesting that the more efficient oxidisable 18-valence-electron Ru^{II} and Ni^{II} complexes can provide access to stronger donors than are possible in organic systems. Studies on analogous σ-acetylide Ru^{II} complexes, in which the more electron-rich donor indenylruthenium(II), $[Ru(\eta^5\text{-}C_9H_7)(PPh_3)_2]$[21] (**8**) or the (*E*)-$[RuCl(Ph_2PCH_2PPh_2)_2]$[20] (**7**) moieties replace the $[Ru(\eta^5\text{-}C_5H_5)(PPh_3)_2]$ group, indicated a further enhancement of the molecular hyperpolarisability (Fig. 3), thus confirming the role of the donor group in determining the optical nonlinearity of such systems. Compared to 18-valence-electron metallocenes, σ-acetylides, which possess an almost linear $M\text{–}C{\equiv}C\text{–}R$ (R = Ph, CH=CH–Ph) structure, give rise to a better coupling between the metal and the σ-acetylide and, hence, to larger second-order nonlinearities (*e.g.*, **3** *vs.* **4**). In this regard, it is instructive to compare in-plane MLCT transitions in σ-acetylides (MLCT lies in the plane formed by the conjugated π–A system) with out-of-plane MLCT transitions in metallocenes (the MLCT axis is perpendicular to the plane formed by the conjugated π–A system).

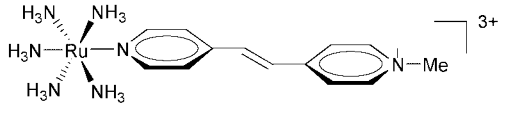
Ruthenium(II) amine complexes, *trans*-$[Ru^{II}(NH_3)_4L]^{2+}$ (L = axial ligand) of 4,4′-bipyridinium (L′) ligands, represent another interesting class of second-order NLO metal complexes, developed by Coe and co-workers.[12,22] These complexes exhibit very large β values, even if resonantly enhanced, which are associated with intense, low-energy $[d\pi(Ru^{II}) \rightarrow \pi^*(L')]$ MLCT excitations (Fig. 4). The electron-rich, d^6 Ru^{II} centre behaves as a powerful π-donor, strongly coupled with the 4,4′-bipyridinium acceptor. In the case of $[Ru^{II}(NH_3)_5]^{2+}$ bipyridinium-derived complexes (*e.g.*, **9**) they are reversibly readily oxidised to their electron-deficient Ru^{III} analogues, either chemically or electrochemically ($\mathbf{9^{ox}}$, Scheme 3). The d^5 $[Ru^{III}(NH_3)_5]^{3+}$ moiety is a powerful electron-withdrawing group and does not possess low-energy MLCT excitations. Consequently, a dramatic decrease of the second-order NLO response of such oxidised Ru^{III} species (*e.g.*, $\mathbf{9^{ox}}$), containing two opposing electron acceptors attached to a pyridyl ring, has been observed.[23] Therefore, the NLO responses of such ruthenium(II) amine complexes can be reversibly and very effectively switched *via* the $Ru^{III/II}$ redox couple. This represents the first case in which β switching has been achieved through the redox reaction of a donor group. Recently, reversible switching of the first hyperpolarisability has been achieved by redox interconversion of an octamethylferrocene complex.[24]



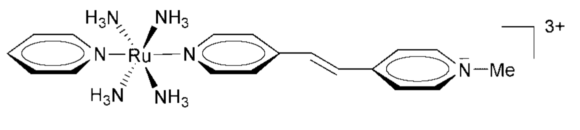
9, λ_{max} = 590 nm; $\beta_{(1.06)} = 750$; $\beta_{(0)} = 123 \times 10^{-30}$ esu



10, λ_{max} = 654 nm; $\beta_{(1.06)} = 1112$; $\beta_{(0)} = 354 \times 10^{-30}$ esu



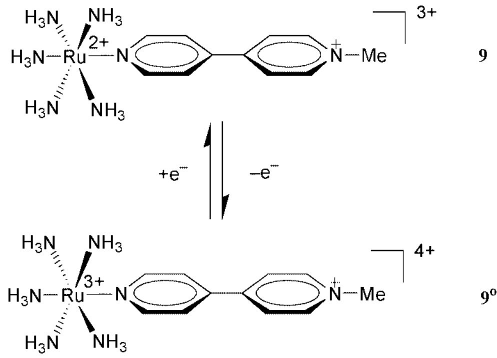
11, λ_{max} = 595 nm; $\beta_{(1.06)} = 828$; $\beta_{(0)} = 142 \times 10^{-30}$ esu



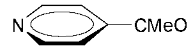
12, λ_{max} = 563 nm; $\beta_{(1.06)} = 904$; $\beta_{(0)} = 78 \times 10^{-30}$ esu

Fig. 4 Selected examples of second-order NLO ruthenium(II) amine complexes. Experimental data from ref. 22.

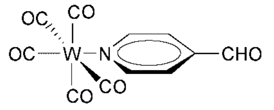
Low-valent (M^0) group 6 metal carbonyls, containing pyridine or styrylpyridine σ-bonded ligands, can be identified as another class of second-order NLO metal complexes.[25] Their NLO response is dominated by MLCT excitations involving low-lying, filled metal-carbonyl-based orbitals and empty π* orbitals of pyridine or styrylpyridine ligands. However, their second-order NLO response is rather modest, even if strongly enhanced with respect to the pyridine or styrylpyridine uncomplexed ligands (*e.g.*, **13** *vs.* **14**, Fig. 5). They do not display the dramatic increases in β with conjugation length observed for traditional organic chromophores (*e.g.*, **14** *vs.* **15**). It was suggested that these metal complexes involve a relatively poor π-coupling between the metal carbonyl fragment and the π-network of pyridine ligands.[26] This minimises the effect of the conjugation length upon the second-order nonlinearity. Moreover, in the case of complexes of *para*-donor substituted



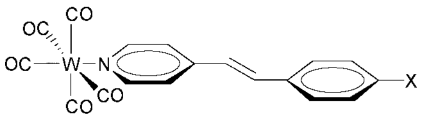
Scheme 3 Redox reaction of complex **9**.



13, $\beta_{(1.91)} < 0.2 \times 10^{-30}$ esu



14, $\beta_{(1.91)} = -12 \times 10^{-30}$ esu



15, X = NO_2; $\beta_{(1.91)} = -20 \times 10^{-30}$ esu

16, X = NMe_2; $\beta_{(1.06)} = 61 \times 10^{-30}$ esu

Fig. 5 Selected examples of second-order NLO tungsten carbonyl pyridine complexes. The 4-acetylpyridine ligand (**13**) is reported for comparison. Experimental data from ref. 26.

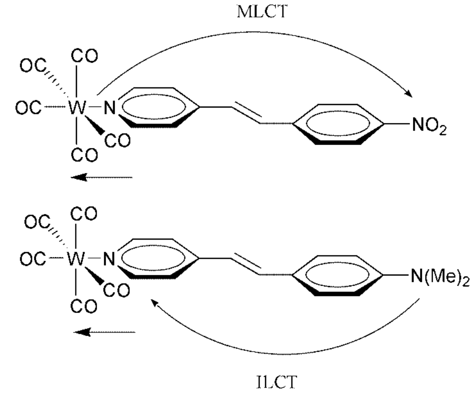
stilbazole ligands (**16**), the NLO response is dominated by ILCT excitations (involving the π-network of pyridine ligands) and the role of the metal carbonyl fragment is mostly as an inductive σ-acceptor (Scheme 4).[26] This ambivalent donor or acceptor role of the carbonyl moiety in complexes of *para*-substituted pyridines has been further probed by studying various Rh^I ($4d^8$), Ir^I ($5d^8$) and Os^{II} ($5d^6$) carbonyls.[27] In fact, on going from M^0 group 6 (d^6) metal carbonyls (NLO response dominated by MLCT excitations) to complexes with a higher oxidation state Rh^I ($4d^8$), Ir^I ($5d^8$), and Os^{II} ($5d^6$) (and a lower number of d electrons for the latter) a progressive lowering of donor properties of the organometallic moiety is expected along with a parallel increase in its electron acceptor character (NLO response dominated by ILCT excitations). Thus, tuneable β (ranging from negative to positive values) values have been obtained on changing the metal centre and/or the *para-* (donor or acceptor) substituent on the pyridine ligands.

On the basis of the above discussion, metal carbonyl fragments can be primarily regarded as electron-withdrawing groups, since CO ligands are strong π-acceptors. Therefore, they can act as the inductive σ-acceptor part in a D–A structure, for example as in chromium tricarbonyl arene complexes (**17**, **18**, Fig. 6).[15] However, these complexes are characterised by small, negative β values. In fact, even if the tricarbonyl fragment acts as the electron acceptor in the ground state, it is the donor in the β-determining excited state, because of an MLCT excitation involving filled metal-carbonyl-based and empty arene π* orbitals. The net result is a reduction of the dipole moment in the excited state and, hence, negative β values (Fig. 6). Extension of the conjugation by alkenylated (**19**) and alkynylated (**20**, **21**) substituted arenes, first suggested on theoretical grounds,[15] was recently proved experimentally[28] as a possible strategy for the optimisation of optical nonlinearity in chromium carbonyl complexes. The introduction of an extended π-electron system into the arene moiety involves a ground state dipole component and the existence of new, stronger ILCT excitations both perpendicular to the MLCT direction (*e.g.*, in **20**, **21**, Fig. 6). These new ILCT excitations are mainly responsible for the NLO response in these complexes, which remain essentially unchanged within the series of both alkenylated and alkynylated arenes having comparable donor or acceptor substituents (*e.g.*, **20** *vs.* **21**).[28] Thus, the chromium carbonyl arene fragment behaves in an electronically amphoteric manner, *i.e.*, as an ambivalent donor or acceptor, depending on the substituent on the conjugated side chain.

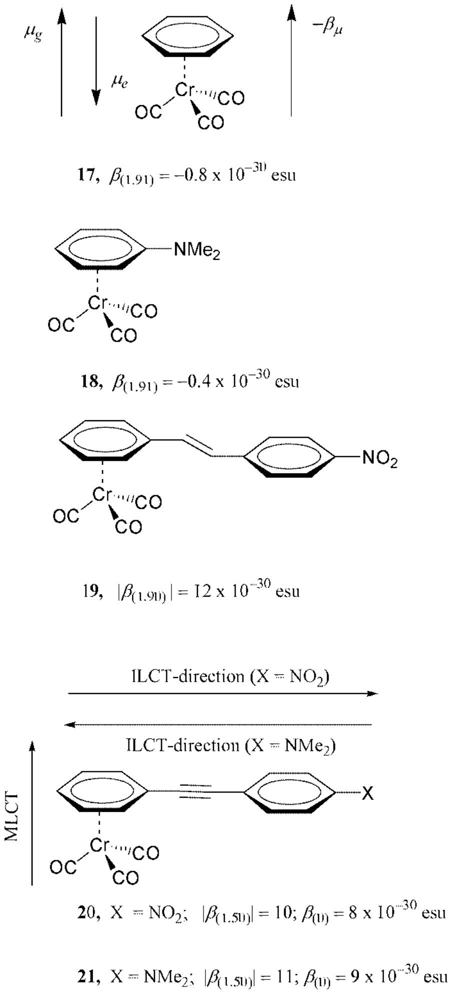
3.2 Metal complexes in bimetallic D–π–A second-order NLO dipolar structures

The combination of a donor with an acceptor organometallic moiety in a D–π–A structure identifies a new class of second-order NLO materials, so called bimetallic compounds (Figs. 7 and 8). Prototypical examples are represented by mixed-valence bimetallic ruthenium complexes (**22**, **23**), which consist of two Ru^{II} (d^6), donor, and Ru^{III} (d^5), acceptor, moieties linked by a simple C≡N group.[29] Charge asymmetry is established by stabilising the Ru^{II} with π-acid ligands and Ru^{III} with ammines. The relatively large nonlinearity in such compounds has been related to intervalence charge transfer (IVCT) states involving Ru^{II}–Ru^{III} (d^6d^5) → Ru^{III}–Ru^{II} (d^5d^6) excitations.

Various other examples of NLO bimetallic systems can be mentioned. The first investigated example was related to a series of ferrocenyl bimetallic complexes with group 10 metals (*e.g.*, **24**).[7] In this case, however, the effect of the second metal ion has a weak influence on the β values of related ferrocenyls. Recently, various heterobimetallic systems have been investigated by coupling the donor ferrocenyl or indenylruthenium(II) (σ-enynyl or cyano-bridged) with an acceptor such as the $[Ru^{III}(NH_3)_5]^{3+}$ (**26**) or a group 6 pentacarbonyl (**27**, **28**),[21] including Fischer carbene (**29**, **30**)[30] groups (Fig. 8). Very large β values, the largest for bimetallic systems, were obtained. It is interesting to compare the NLO response in the case of bimetallic $M(CO)_5$ derivatives (M = Cr, W), including Fischer carbenes, having the same D–π moiety (*e.g.*, **27** *vs.* **28**; **29** *vs.* **30**). They always involve larger β values for tungsten than chromium derivatives, in accordance with the more efficient back-donation to the carbonyl groups from the heavier metal, which reduces its electron density and, hence, produces better σ-acceptor character of the $M(CO)_5$ moiety. Moreover, in the case of Fischer carbene derivatives a strong dependence of β on changes in solvent relative permittivity was observed (*e.g.*, **29**, **30**). Surprisingly, even by combining two donor groups as in **31**,



Scheme 4 Ambivalent donor or acceptor role of metal carbonyl complexes.



17, $\beta_{(1.91)} = -0.8 \times 10^{-30}$ esu

18, $\beta_{(1.91)} = -0.4 \times 10^{-30}$ esu

19, $|\beta_{(1.90)}| = 12 \times 10^{-30}$ esu

20, X = NO_2; $|\beta_{(1.50)}| = 10$; $\beta_{(0)} = 8 \times 10^{-30}$ esu

21, X = NMe_2; $|\beta_{(1.50)}| = 11$; $\beta_{(0)} = 9 \times 10^{-30}$ esu

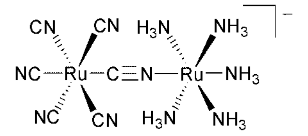
Fig. 6 Selected examples of second-order NLO chromium tricarbonyl arene complexes. Experimental data from refs. 15 and 28.

large β values could be obtained. It was suggested that the difference in the donor strengths of both groups was sufficiently large to induce molecular asymmetry.[21]

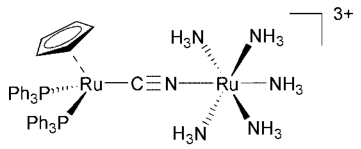
Finally, another class of bimetallic systems is represented by μ-η^5:η^7-cyclopentadienylcycloheptatrienyl (sesquifulvalene) complexes developed by Heck and co-workers,[31] in which cyclopentadienyl and cycloheptatrienyl fragments of two organometallic moieties are directly linked or linked by a conjugated bridge, leading to strongly coupled, almost coplanar rings of sesquifulvalene ligands (*e.g.*, **25**, Fig. 7). Various sesquifulvalene complexes have been investigated, and large β values have been achieved. They involve the ferrocenyl or the $Mn^{I}(CO)_3$-cyclopentadienyl/indenyl group as donor and the $[(\eta^7\text{-}C_7H_6)Cr(CO)_3]^+$ as acceptor. In all cases, the effect of the $Cr(CO)_3$ group is likely to stabilise the positive charge on the $[(\eta^7\text{-}C_7H_6)Cr(CO)_3]$ moiety, more than in the naked tropylium system.

3.3 Metal complexes as the polarisable bridge in D–π–A second-order NLO dipolar structures

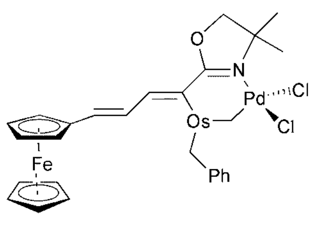
When a metal complex is a constituent of the polarisable bridge in a D–π–A structure, two limiting cases can be identified: (i) the related uncomplexed D/A-substituted bridge already possesses second-order nonlinearity; (ii) complexation generates new NLO structures, from those originally with vanishing or small nonlinearity. In these two cases the metal ion can play two different functions: (i) it enhances the bridge conjugation and, hence, the nonlinearity; (ii) it 'switches on' or enhances the NLO response.



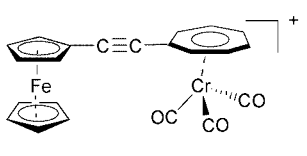
22, $\beta_{(0)} = 81 \times 10^{-30}$ esu



23, $\beta_{(1.06)} = 157$; $\beta_{(0)} = 69 \times 10^{-30}$ esu



24, $\beta_{(1.34)} = 123$; $\beta_{(0)} = 19 \times 10^{-30}$ esu

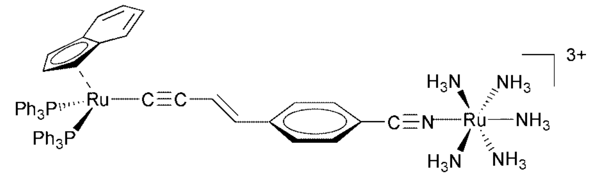


25, $\beta_{(1.06)} = 570$; $\beta_{(0)} = 105 \times 10^{-30}$ esu

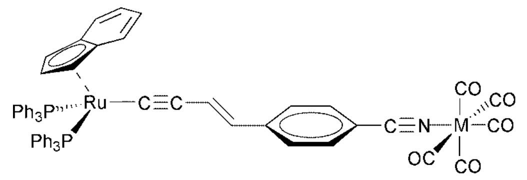
Fig. 7 Selected examples of second-order NLO bimetallic complexes. Experimental data from refs. 7, 29 and 31.

Push–pull metalloporphyrins are prototypical examples of case (i). Coordination of a metal ion in porphyrins is always accompanied by an enhanced nonlinearity due to a more pronounced conjugation. In fact, the push–pull arylethynyl(porphinato)zinc^{II} derivative (**32**) exhibits the largest hyperpolarisability reported to date for a metal complex: $\beta_{(0)}$ up to 800×10^{-30} esu.[32] This substantially higher nonlinearity, compared to that of analogous push–pull porphyrins, is due to the strong electronic coupling between the coplanar donor/acceptor arylethynyl moieties and the polarisable porphinato bridge. Unsymmetrically substituted metallophthalocyanines can regarded in a similar way.[33] For example, related arylethynyl metallophthalocyanine structures such as **33** are expected to be promising candidates for large first hyperpolarisabilities. Their potentially large second-order molecular response remains, however, still unexplored.

A prototypical example of case ii) is represented by bis(salicylaldiminato)M^{II} (M = Co, Ni, Cu, Zn) Schiff base complexes whose second-order NLO properties have been recently reviewed by Di Bella and by Lacroix.[34,35] In this case complexation is accompanied by formation of geometrically constrained acentric, generally planar, structures. It always involves an enhancement of optical nonlinearity, compared to that of related free ligands, and, in some cases, a 'switching on' of the NLO response. Tuneable hyperpolarisabilities, ranging from negative to positive β values, were obtained (Fig. 9). Even

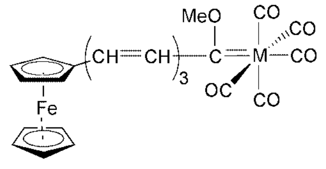


26, $\beta_{(1.06)} = 315$; $\beta_{(0)} = 80 \times 10^{-30}$ esu



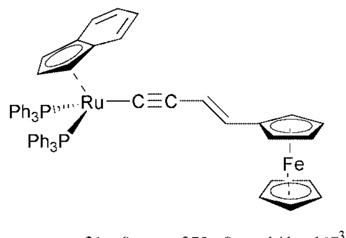
27, M = Cr; $\beta_{(1.06)} = 465$; $\beta_{(0)} = 119 \times 10^{-30}$ esu

28, M = W; $\beta_{(1.06)} = 700$; $\beta_{(0)} = 150 \times 10^{-30}$ esu



29, M = Cr; $\beta_{(1.06)} = 342 \times 10^{-30}$ esu (hexane);
$= 1030 \times 10^{-30}$ esu (acetonitrile)

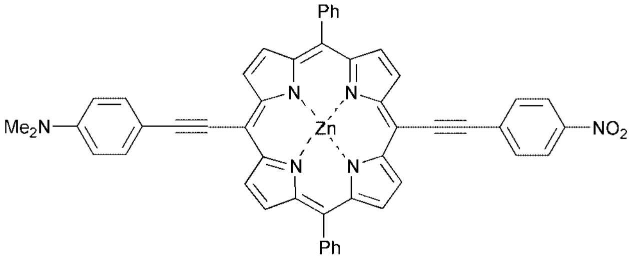
30, M = W; $\beta_{(1.06)} = 408 \times 10^{-30}$ esu (hexane);
$= 1140 \times 10^{-30}$ esu (acetonitrile)



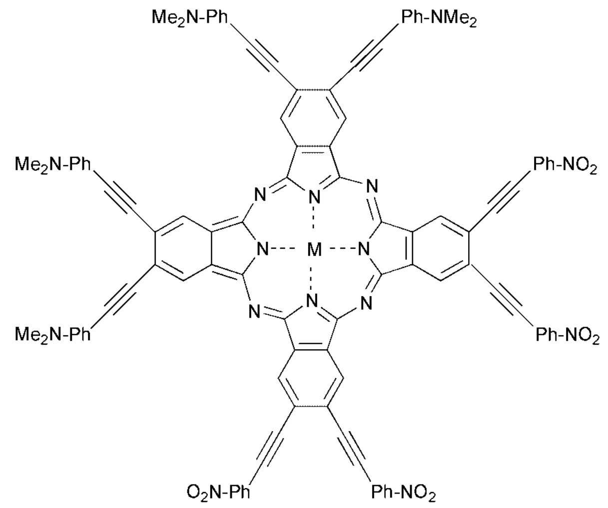
31, $\beta_{(1.06)} = 273$; $\beta_{(0)} = 141 \times 10^{-30}$ esu

Fig. 8 Selected examples of second-order NLO bimetallic complexes. Experimental data from refs. 21 and 30.

if the second-order nonlinearity of these materials is modest compared to that of other NLO metal complexes or organic chromophores, they present a number of interesting features. The observed negative β values along the unsubstituted M(salophen) series (**34–36**) are a consequence of a reduction of the dipole moment on passing from the ground to the excited states (Scheme 5). The role of the metal centre in determining the NLO response in such structures is twofold since it can act as either the donor or the bridging moiety of the D–π–A system (Scheme 6). In fact, their second-order nonlinearity is generally dominated by MLCT excitations. Moreover, the nonlinearity is deeply influenced by the nature of the metal. In the case of the homologous series of unsubstituted M^{II}(salophen) complexes (**34–36**), it was found that the nonlinearity increases ~3× and ~8× on substituting Cu^{II} (d^9) and Co^{II} (d^7) for Ni^{II} (d^8), respectively. This substantially larger nonlinearity observed for the Cu^{II} and Co^{II} systems having open-shell electronic states, compared to that of the closed-shell Ni^{II} homologue, is likely a consequence of the increased accessibility of lower-lying CT excited electronic states. However, in the presence of strong donor/acceptor substituents (**37–40**), the metal mostly acts as a bridge (Scheme 6), and the role of the metal electronic configuration in determining the NLO response is less defined (*e.g.*, **39** *vs.* **40**). Moreover, the corresponding donor/acceptor



32, $\beta_{(1.06)} = 4933; \beta_{(0)} = 800 \times 10^{-30}$ esu



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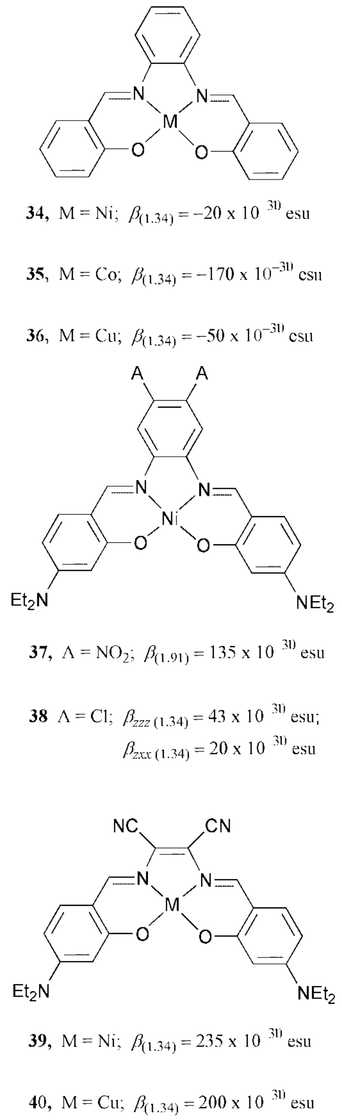


34, M = Ni; $\beta_{(1.34)} = -20 \times 10^{-30}$ esu

35, M = Co; $\beta_{(1.34)} = -170 \times 10^{-30}$ esu

36, M = Cu; $\beta_{(1.34)} = -50 \times 10^{-30}$ esu

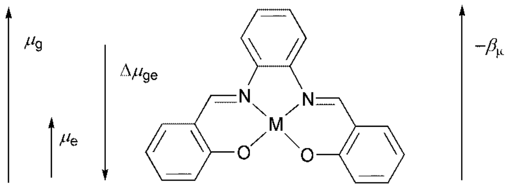
37, A = NO$_2$; $\beta_{(1.91)} = 135 \times 10^{-30}$ esu

38 A = Cl; $\beta_{zzz\,(1.34)} = 43 \times 10^{-30}$ esu; $\beta_{zxx\,(1.34)} = 20 \times 10^{-30}$ esu

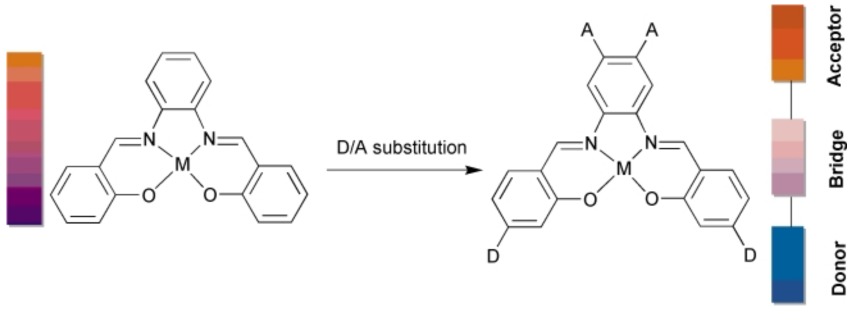
39, M = Ni; $\beta_{(1.34)} = 235 \times 10^{-30}$ esu

40, M = Cu; $\beta_{(1.34)} = 200 \times 10^{-30}$ esu

Fig. 9 Selected examples of second-order NLO Schiff base complexes. Experimental data from refs. 34–36.

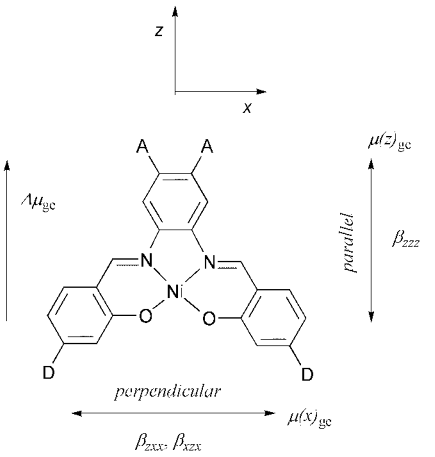


Scheme 5 Negative β values in unsubstituted M(salophen) complexes.



Scheme 6 Donor and/or bridge role of the metal centre in Schiff base complexes on passing from unsubstituted to D/A substituted species.

substitution pattern found in some Ni^{II} complexes (*e.g.*, **38**) results in an in-plane, two-dimensional second-order nonlinearity, due to the existence of various low-energy CT states.[36] While *z*-polarised electronic transitions, *parallel* to the molecular dipolar (*z*) axis, contribute to the diagonal β_{zzz} tensor, *perpendicular* *x*-polarised transitions contribute to the off-diagonal, β_{zxx}, β_{xzx}, hyperpolarisability tensors (Scheme 7). Finally, the effect of a spin-crossover phenomenon upon second-order molecular nonlinearity was theoretically investigated for the first time in an Fe^{II} Schiff base complex.[35] It was predicted that the spin transition ($S = 0 \rightarrow S = 1$) in this complex would involve an increase in β of about 25% of its initial value. This effect, however, was mainly attributed to the geometry modification occurring upon spin transition, rather than to the change in the spin state in the Fe^{II} ion.



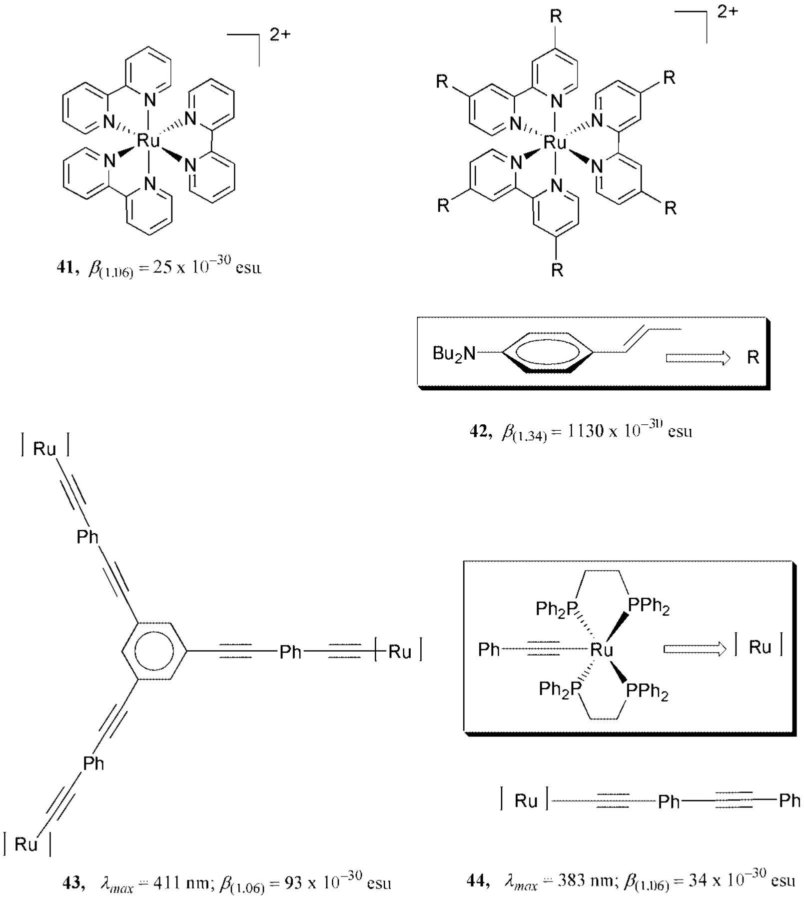
Scheme 7 Two-dimensional second-order NLO character in substituted Ni^{II} Schiff base complexes.

In a recent contribution, a series of octahedral M^{II} (M = Mn, Fe, Co, Ni, Zn) metal complexes of *N*-2′-pyridylmethylene-4-aminopoly(phenyl) and poly(phenylacetylene) ligands was investigated.[37] Again, the NLO response of coordinated complexes is higher than that of related free ligands, and is likely related to MLCT excitations. Interestingly, the optical nonlinearity of such complexes is strongly dependent upon the metal electronic configuration, and parallels the number of unpaired electrons of the metal ion. Accordingly, the largest β values were observed for Mn^{II} complexes possessing five unpaired electrons, while the lowest β values were observed for closed-shell Zn^{II} complexes. Since iron(II) complexes are high-spin at room temperature, this suggests that spin-crossover should switch their NLO response.

3.4 Metal complexes in octupolar second-order NLO structures

As octupolar molecules are non-dipolar species of two-dimensional (2D) or three-dimensional (3D) chromophores, metal ions are well suited to building coordination molecules with 2-fold (D_2) or 3-fold (D_3) rotational axes around the metal centre (*e.g.*, tetrahedral, octahedral, or trigonal bipyramidal geometries). Thus, a number of NLO octupolar metal complexes (Fig. 10), mainly based on bipyridine ligands, have been reported in the literature, and recently reviewed.[25]

Second-order NLO properties of octupolar metal complexes were first demonstrated by Zyss *et al.* for tris(bipyridine)- (**41**) and tris(phenanthroline)ruthenium(II) complexes. These complexes possess D_3 symmetry and exhibit intense multi-directional [$d_\pi(Ru^{II}) \rightarrow \pi^*$(bpy or phen)] MLCT excitations responsible for their relatively high second-order NLO response. An enhanced, very large NLO response was subsequently achieved with substitution of the bipyridine ligands by



41, $\beta_{(1.06)} = 25 \times 10^{-30}$ esu

42, $\beta_{(1.34)} = 1130 \times 10^{-30}$ esu

43, λ_{max} = 411 nm; $\beta_{(1.06)} = 93 \times 10^{-30}$ esu

44, λ_{max} = 383 nm; $\beta_{(1.06)} = 34 \times 10^{-30}$ esu

Fig. 10 Selected examples of second-order NLO octupolar complexes. Experimental data from refs. 25 and 40. Re-examined data for **41** and **42** are reported.

p-dibutylaminostyryl donor groups (**42**).[38] Clearly, in these cases the NLO response is related to very strong, multi-directional ILCT excitations, but the role of the Ru^{II} ion is fundamental in determining the octupolar molecular architecture. Recent studies on an octupolar Ru^{II} compound, nearly identical to **42**, have, however, indicated that its optical nonlinearity is likely a consequence of additive dipolar responses and not a direct result of the octupolar ground-state molecular geometry.[39]

Similarly to octupolar D_3 species, tetrahedral octupolar D_2 copper(I) bipyridyl complexes were recently obtained.[25] As in compound **42**, the NLO response is related to strong ILCT excitations. Again, the copper(I) ion allows such unique structures to be obtained. Compared to analogous Ru^{II} octupolar species, these Cu^{I} complexes possess a lower NLO response, as shown by the pronounced blue-shift of the ILCT absorption band. However, they have the advantage of being more optically transparent.

A second class of octupolar NLO materials, involving metal complexes, is represented by aromatic rings 1,3,5-substituted with Ru^{II} σ-acetylide complexes (*e.g.*, **43**, Fig. 10).[40] In this case the 3-fold symmetry axis is determined by the 1,3,5-substituted aromatic ring, while the organometallic moieties act as strong donor groups. In fact, passing from the one-dimensional complex (**44**) to the octupolar species (**43**) results in a 3-fold increase in oscillator strength for λ_{max} and in its quadratic hyperpolarisability, with little loss of optical transparency.

In a recent contribution were investigated analogous octupolar molecules constituted by aromatic rings 1,3,5-substituted with Fe^{II} σ-acetylide complexes, together with related oxidised Fe^{III} species.[41] Again, the lowest MLCT excitations are responsible for the NLO response. Interestingly, even if the oxidised Fe^{III} species possess new transitions to longer wavelength, which are related to LMCT excitations, their second-order NLO response seems still related to MLCT excitations, and has the same order of magnitude as that of the unoxidised Fe^{II} species. The role of the metal electronic configuration in determining the NLO response of such species remains thus undefined.

3.5 Second-order bulk nonlinearity of metal complexes

Although NLO metal complexes possess unique features, as compared to organic chromophores, investigations on their bulk second-order NLO response are largely limited to powder SHG efficiency tests. Most powder SHG data relate to organometallic compounds, and almost all of them (up to mid 1996) are collected in the review of Whittall *et al.*[7]

Some hundreds of metal complexes have been investigated for powder efficiency. So far, ferrocenyl-based complexes exhibit the largest powder SHG response, in spite of their relatively low molecular hyperpolarisabilities, especially if compared to those of other metal complexes. In other words, since the bulk nonlinearity is a function of both significant molecular optical nonlinearity and favourable crystal packing, the fact that ferrocenyl-based materials possess higher SHG efficiency than many other metal complexes implies that they have a greater propensity for optimal lattice alignment. Among the most SHG efficient ferrocenyl materials (Fig. 11), some of them are salts (*e.g.*, **45**, **46**), so that their large efficiency could not be predicted on the basis of their molecular structures. In addition, their bulk NLO response changes significantly upon variation of counteranions. It has been suggested that Coulombic interactions in salts may negate deleterious dipolar interactions, thus enhancing the possibility of favourable noncentrosymmetric packing.[7] On the other hand, in the case of heterobimetallic species (*e.g.*, **49**), the presence of bulky substituents at each end of the rod-shaped heterobimetallic complexes seems to be a requirement for producing packing arrangements favourable for SHG efficiency.[42] In fact, compounds having an organic (methoxy or dimethylamino) donor group, instead of ferrocenyl, were found to be SHG inactive.[42] Overall, differences in the bulk SHG response between these ferrocenyls and other derivatives seem to be attributable to structural rather than to electronic effects.

In spite of the very large structural variability of metal complexes, knowledge about correlation between molecular structure and solid state bulk NLO properties is very limited. In a recent review contribution Qin *et al.*[13] made an attempt to correlate SHG powder activity for some classes of coordination complexes in relation to their molecular configuration. The relationship, however, remains unclear, and the presence of hydrogen bonding or chirality, which favour molecular alignment, seems to dominate molecular configuration.

Hydrogen bonding and molecular chirality represent two useful approaches that can be used, even for metal complexes, to engineer noncentrosymmetric molecular alignment.[1–3] Even though these methods do not preclude the formation of pseudocentrosymmetric arrangements, in some cases there has been success in obtaining optimised crystal packing. An example of all these points is offered, again, by a chiral ferrocenyl compound.[43] The molecular engineering of **2**, by substitution of an $SiMe_3$ group in the 2-position of the cyclopentadienyl ring, yielded the chiral enantiomerically pure species (**48**) with an almost optimised molecular arrangement in the crystal frame. This compound possesses a powder SHG efficiency 100 times that of urea.

The use of NLO materials for frequency-doubling of a semiconductor laser requires optically transparent materials at both the fundamental and the second harmonic frequencies. Clearly, this prerequisite is not fulfilled for most organic chromophores and metal complexes possessing sizeable SHG efficiency. Colourless complexes of M^{II} (d^{10}) group 12 metals appear to be the best candidates to this end. Moreover, their tendency to adopt a tetrahedral coordination around the metal favours the formation of noncentrosymmetric crystal structures. Unfortunately, all these materials possess very small efficiency due to their inherently low molecular nonlinearity.[13] Recently, in an interesting study by Lin *et al.*[44] was reported the crystal engineering of Zn^{II} and Cd^{II} pyridinecarboxylate coordination compounds in an acentric diamondoid structure. Although the

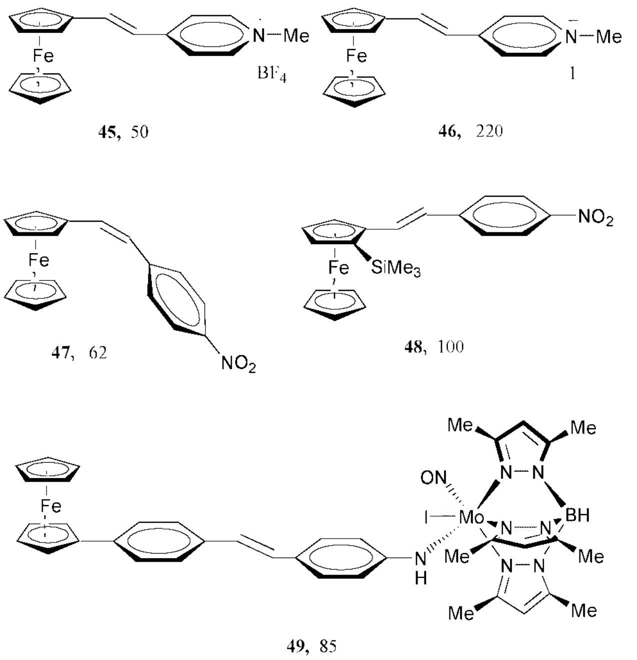


Fig. 11 Bulk second-order NLO response (powder efficiency related to urea) of selected ferrocenyl complexes. Experimental data from refs. 7, 42 and 43.

SHG activity of such materials is low (comparable to KDP), this represents a novel approach to the synthesis of acentric, optical transparent coordination networks.

Octupolar NLO materials have the advantage of improved transparency/optical nonlinearity trade-off and the lack of molecular dipole enhances the possibility of noncentrosymmetric crystal packing.[25,38–41] To date, however, only two contributions on octupolar transition metal complexes as bulk NLO materials have been reported in the literature,[45,46] both of them involving group 12 metals. Although the powder efficiency of these materials is relatively low, compared to that of more efficient dipolar species, they represent a good starting point for further studies.

Very few investigations on thin film materials containing NLO metal complexes have been performed. They include poled-polymer,[7] Langmuir–Blodgett (LB)[12,47] and self-assembled[48] applications. The last two examples present very interesting, peculiar features. It was demonstrated by Sakaguchi *et al.* that LB films of tris(bipyridine)ruthenium(II) complexes exhibit reversible photo-switching (on the ps timescale) of the SHG signal (decrease of 30%) upon UV-light irradiation.[12] Clearly, the reversible photochemical $Ru^{2+} \leftrightarrows Ru^{3+}$ interconversion upon MLCT excitations is responsible for the observed SHG photo-switching. Analogously, self-assembled monolayers (SAM) of the (*E*)-ferrocenyl (**2**) derivative were found to be reversibly electrochemically oxidised to ferrocenium cations.[48] This was accompanied by an increase of the SH intensity which returned to its original value when the ferrocenium cation was reduced to the neutral ferrocene. The changes in orientation of the SAM and in the second-order hyperpolarisabilities of the redox species are likely responsible for the observed SH intensity changes.

4 Conclusions and perspectives

Diverse and varied features emerge on examination of second-order NLO transition metal complexes. These characteristics certainly enrich the panorama of nonlinear optics. Metal complexes offer a very large variety of molecular and bulk structures and can satisfy very different aspects of second-order NLO materials. The concepts of NLO switching and tuning are for some aspects uniquely related to metal complexes. Thus, NLO switching can be achieved by (chemical, electrochemical, or photochemical) redox reactions, or by spin-crossover of the complexed metal atom, while tuneable first hyperpolarisabilities for a given class of metal complexes can be obtained by changing the metal centre or the substituent(s) on the ligand. Complexation is almost always accompanied by an increased second-order nonlinearity. Large first hyperpolarisabilities, rivalling those of efficient organic chromophores, have been achieved.

Various classes of transition metal complexes have been investigated and the structure–property relationships for mostly of them are well understood. The unique characteristics of metal complexes as bulk NLO materials remain, however, still largely unexplored. Moreover, multifunctional materials involving metal complexes, *e.g.*, combining optical nonlinearity with magnetic, optical, or electric properties, can be envisaged. These and other topics certainly deserve further investigations, in the perspective of new molecular materials.

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