Top Organomet Chem (2010) 28: 1–55
DOI: 10.1007/978-3-642-01866-4_1

Coordination and Organometallic Complexes as Second-Order Nonlinear Optical Molecular Materials

Santo Di Bella, Claudia Dragonetti, Maddalena Pizzotti, Dominique Roberto, Francesca Tessore, and Renato Ugo

Abstract Coordination and organometallic complexes with second-order nonlinear optical (NLO) properties have attracted increasing attention as potential molecular building block materials for optical communications, optical data processing and storage, or electrooptical devices. In particular, they can offer additional flexibility, when compared to organic chromophores, due to the presence of metal–ligand charge-transfer transitions, usually at relatively low-energy and of high intensity, tunable by virtue of the nature, oxidation state, and coordination sphere of the metal center. This chapter presents an overview of the main classes of second-order NLO coordination and organometallic complexes with various ligands such as substituted amines, pyridines, stilbazoles, chelating ligands (bipyridines, phenanthrolines, terpyridines, Schiff bases), alkynyl, vinylidene, and cyclometallated ligands, macrocyclic ligands (porphyrins and phthalocyanines), metallocene derivatives, and chromophores with two metal centers. The coverage, mainly from 2000 up to now, is focused on NLO properties measured at molecular level from solution studies, as well as on NLO properties of bulk materials.

Keywords Coordination and organometallic complexes, Second-order nonlinear optics

---

S. Di Bella (✉)
Dipartimento di Scienze Chimiche, Università di Catania, Viale A. Doria 8, 95125, Catania, Italy
e-mail: sdibella@unict.it

C. Dragonetti, M. Pizzotti, D. Roberto (✉), F. Tessore and R. Ugo
Dipartimento di Chimica Inorganica, Metallorganica e Analitica “Lamberto Malatesta” dell’Università degli Studi di Milano, UdR-INSTM di Milano and ISTM-CNR, Via Venezian 21, 20133 Milano, Italy
e-mail: dominique.roberto@unimi.it

Contents

1 Introduction

Compounds with second-order nonlinear optical (NLO) properties are of great interest as molecular building block materials for optical communications, optical data processing and storage, or electrooptical devices [1–3]. Among them, organometallic and coordination metal complexes represent an emerging and growing class of second-order NLO chromophores that can offer additional flexibility, when compared to organic chromophores, due to the presence of metal–ligand charge-transfer (MLCT) transitions usually at relatively low energy and of high intensity, tunable by virtue of the nature, oxidation state, and coordination sphere of the metal center. Since the discovery of the second harmonic generation (SHG) for a ferrocenyl compound [4], increasing attention has been paid to organometallic and coordination complexes as potential second-order NLO chromophores. Extensive investigations have thus been carried out in this area. Early [5–9] and more recent [10–19] review articles on coordination and organometallic complexes with second-order NLO activity indicate the breadth of the active research in this field.

The goal of this overview is to report on the recent advances in order to analyze the main characteristics of second-order NLO organometallic and coordination complexes, and their potential as new NLO active molecular materials. After a brief introduction about the principles of nonlinear optics, this chapter illustrates the main classes of second-order NLO organometallic and coordination chromophores, producing examples of chromophores with monodentate nitrogen donor ligands (amines, pyridines, stilbazoles), chelating ligands (bipyridines, phenanthrolines, terpyridines, Schiff bases), alkynyl, vinylidene, and cyclometallated ligands, macrocyclic ligands (porphyrins and phthalocyanines), metallocene derivatives, and chromophores with two metal centers. The coverage, mainly from 2000 up to now, is not exhaustive, but allows the nonspecialist to get into this specific field and to understand its potentiality. Relevant older data of prototypical compounds are also reported. The focus is on both NLO properties measured at molecular level from solution studies and NLO properties of bulk materials.

2 Principles of Second-Order Nonlinear Optics

The principles of nonlinear optics, including the techniques to evaluate the second-order NLO properties, are briefly presented here. Major details can be found in excellent books [1–3] and various reviews [5–19].

2.1 Basic Concepts and Methods

Nonlinear optics deals with optical phenomena, caused by the interaction of applied electromagnetic fields to molecules or materials with emission of new electromagnetic fields which differ in frequency, phase, or other physical properties from the incident ones [1–3]. This kind of optical phenomena are related to the polarizability of a molecule or of a bulk material.

When a bulk material is subjected to an oscillating external electric field produced by an incident radiation, there is a polarization effect, expressed by

$$\vec{P} = \overrightarrow{P_0} + \overrightarrow{P_{\text{ind}}} = \overrightarrow{P_0} + \chi^{(1)}\vec{E}, \tag{1}$$

where $\overrightarrow{P_0}$ is the intrinsic polarity, $\overrightarrow{P_{\text{ind}}}$ the induced polarization, and $\chi^{(1)}$ the electrical susceptibility or linear polarizability tensor. If the electric field strength $\vec{E}$ of the incident radiation is very high, as is the case with laser pulses, the perturbation is not linear and the induced polarization is better expressed by a power series according to

$$\vec{P} = \overrightarrow{P_0} + \chi^{(1)}\vec{E} + \chi^{(2)}\overrightarrow{E^2} + \cdots + \chi^{(n)}\overrightarrow{E^n}, \tag{2}$$

where $\chi^{(2)}$, $\chi^{(3)}$, and $\chi^{(n)}$ tensors are, respectively, the second-, third-, and n-order electrical susceptibilities, controlling the nonlinear response of the material.

If, instead of a bulk material, the applied electromagnetic field is interacting with a molecule, the induced polarization is expressed by

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

where μ_0 is the molecular ground state electric dipole moment, α the linear polarizability tensor, β and γ the non linear quadratic and cubic hyperpolarizability tensors, respectively, responsible for second- and third-order NLO effects. It is important to underline that both β and $\chi^{(2)}$ vanish in a centrosymmetric environment. Therefore, to have a second-order NLO effect, the acentricity requirement must be fulfilled. This is not true for γ and $\chi^{(3)}$.

The second-order NLO properties are of interest for a variety of NLO processes [1–3]. One of the most relevant is the SHG, originated by the mixing of three waves; two incident waves with frequency ω interact with the molecule or the bulk material with NLO properties, defined by a given value of the quadratic hyperpolarizability, β, or of the second-order electrical susceptibility, $\chi^{(2)}$, respectively, to produce a new electrical wave, named SH, of frequency 2ω. Another important second-order NLO process is the electrooptic Pockels effect which requires the presence of an external d.c. electric field, $E(0)$, in addition to the optical $\vec{E}(\omega)$ electrical field. This effect produces a change in the refractive index of a material proportional to the applied electric field, and can be exploited in devices such as optical switches and modulators [1–3].

To obtain molecular or bulk materials displaying significant second-order NLO effects, high values of β or of $\chi^{(2)}$, respectively, are required. In the case of molecules, in 1977 Oudar gave a theoretical interpretation of the electronic factors controlling β [20, 21]. The quadratic hyperpolarizability of a molecule is originated by the mobility of polarizable electrons under the effect of a strong electric field $\vec{E}$ associated with an incident radiation. It follows that it is dependent on electronic transitions which, being associated with a significant electronic mobility, are of high CT character. Oudar assumed that, when the second-order NLO response is dominated by one major CT process, β_{zzz} can be defined according to

$$\beta_{zzz} = \frac{3}{2h^2c^2} \frac{\nu_{\mathrm{eg}}^2 r_{\mathrm{eg}}^2 \Delta\mu_{\mathrm{eg}}}{\left(\nu_{\mathrm{eg}}^2 - \nu_{\mathrm{L}}^2\right)\left(\nu_{\mathrm{eg}}^2 - 4\nu_{\mathrm{L}}^2\right)}, \tag{4}$$

where z is the axis of the direction of the CT, ν_{eg} (cm^{-1}) the frequency of the CT transition, r_{eg} the transition dipole moment, $\Delta\mu_{\mathrm{eg}}$ the difference between excited state μ_{e} and ground state μ_{g} molecular dipole moments, and ν_{L} the frequency of the incident radiation. Equation (4) is the so-called "two level" model, a way to estimate the frequency dependent quadratic hyperpolarizability for specific types of second-order NLO chromophores, characterized by a single dominant CT transition. Extrapolation to zero frequency ($\nu_{\mathrm{L}} = 0.0$ eV; $\lambda = \infty$) allows estimation, according to Eq. (5), of the static quadratic hyperpolarizability β_0, a useful figure of merit to evaluate the basic second-order NLO properties of a molecule:

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

where β_λ is the quadratic hyperpolarizability value at λ incident wavelength and $\lambda_{\max}$ is the absorption wavelength of the controlling major CT. The molecular quadratic hyperpolarizability β can be expressed both in the cgs (cm^4 statvolt^{-1} = esu) or in 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).

From the "two level" model it is possible to extrapolate the dipolar electronic requirements that a molecule must fulfill in order to show a significant second-order NLO response. It must be noncentrosymmetric, with CT transitions with large $\Delta\mu_{\mathrm{eg}}$ and r_{eg} and at relatively low energy. This can be achieved, for instance, by separation of an electron-donor and an electron-acceptor group with a π-conjugated polarizable spacer, as occurs in classical 1D dipolar push–pull organic systems. Recently, multipolar systems, such as octupolar molecules, have been increasingly investigated, because it was shown that it is not only dipolar structures that may be the origin of significant SHG [1–3, 10–19].

From a theoretical point of view, various quantum mechanical methods allow the calculation of the molecular quadratic hyperpolarizability, β. Among them, the "sum over states" (SOS) approach also gives a useful way to define the electronic origin of the NLO response. Density functional theory (DFT) and time-dependent DFT (TD-DFT) or time-dependent HF (TD-HF) calculations [22, 23] are the most advanced theoretical methods. In particular, referring to the SOS method, it describes the tensor β_{ijk} in terms of all the electronic states interacting with the perturbing electric field, as an infinite expansion over a complete set of unperturbed excited states. Obviously, a simplification of this approach is the two-state model (Eq. 4) described above. These theoretical methods are a useful way of understanding hyperpolarizability–structure relationships, thus helping chemists to the design of new efficient molecular NLO chromophores.

Experimentally, mainly two techniques – the electric field induced second harmonic generation (EFISH) and hyper-Rayleigh scattering (HRS, also termed harmonic light scattering method) – are used in order to determine in solution the experimental value of the quadratic hyperpolarizability of molecular NLO chromophores.

The EFISH technique [24], suitable for dipolar neutral molecules, provides information on the molecular NLO properties through

$$\gamma_{\mathrm{EFISH}} = (\mu\beta_{\lambda}/5kT) + \gamma(-2\omega;\omega,\omega,0), \tag{6}$$

where $\mu\beta_{\lambda}/5kT$ represents the dipolar orientational contribution, and γ $(-2\omega;\ \omega,\ \omega,\ 0)$, β_{λ} a third-order term at frequency ω of the incident wavelength, is the electronic contribution which is negligible for many molecules with a limited electronic polarizability. β_{λ} is the projection along the dipole moment axis of β_{VEC}, the vectorial component of the β_{ijk} tensor of the quadratic hyperpolarizability, working with an incident wavelength λ of a pulsed laser. To obtain the value of β_{λ}, it is thus necessary to know the value of the ground state dipole moment μ of the molecule. Moreover, in order to avoid overestimation of the quadratic hyperpolarizabilty due to resonance enhancements, it is necessary to choose an incident wavelength whose second harmonic is far from any electronic absorption of the molecule.

The HRS technique [25–27] involves the detection of the incoherently scattered second harmonic generated by the molecule in solution under irradiation with a laser of wavelength λ, leading to the mean value of the $\beta \times \beta$ tensor product. By analysis of the polarization dependence of the second harmonic signal, which can be evaluated selecting the polarization of the incident and scattered radiation, it is possible to obtain information about the single components of the quadratic hyperpolarizability tensor β. Unlike EFISH, HRS can also be used for ionic molecular species and for nondipolar molecules such as octupolar molecules. In this chapter, the quadratic hyperpolarizability measured with an incident wavelength λ by the EFISH and HRS techniques will be indicated as β_λ(EFISH) and β_λ(HRS), respectively.

Since the “two level” model (Eq. 4) applies well to NLO chromophores characterized by a major CT transition, the solvatochromic method may afford a way to evaluate the quadratic hyperpolarizability, but only the component along the major CT direction, β_λ(CT), by recording electronic absorption spectra of this absorption band in a series of solvents covering a wide range of dielectric constants and of refraction indexes [28]. This method, which does not require sophisticated instrumentation, can give a fair to good estimate of the quadratic hyperpolarizability, for instance in the case of 1D dipolar push–pull molecules, and at the same time it may allow the evaluation of the contribution of a given absorption band to the β value. This method may be more accurate in the case of fluorescent compounds, by combining the solvatochromic study of both absorption and emission spectra [28]. It should be emphasized that β_λ(EFISH) and β_λ(CT) values can be compared only when the dipole moment axis and the direction of the CT are roughly the same.

The static hyperpolarizability β_0 can also be evaluated by means of Stark (electroabsorption) spectroscopy, which affords the value of $\Delta\mu_{eg}$ by analyzing the effects of an applied electric field on the shapes of the major absorption bands of CT character [29–31]. The contribution of each transition to the quadratic hyperpolarizability value is thus obtained according to the “two level” model (Eq. 4). However, the estimated β_0 are generally approximate, especially when dynamic β data are resonantly enhanced, or when many excited states contribute to the NLO response [32].

In the case of bulk materials or films the second-order susceptibility values, $\chi^{(2)}$, can be obtained by means of the investigation of the SHG [1–3]. The Kurtz–Perry technique [33] is often used to compare the intensity of the SHG of a powder sample with that of a reference sample of known $\chi^{(2)}$, such as quartz or urea. Although this technique is limited (the magnitude of the response is also dependent on particle size), it is a simple and rapid method for screening a large number of powder materials.

2.2 *Organic Molecular Materials*

Although this chapter deals with molecular second-order NLO chromophores based on organometallic and coordination complexes, for the sake of clarity we report here a brief summary of the structural features of molecular organic second-order NLO chromophores, which have been extensively investigated [1–3]. In this way, we can give a description of the actual approach to the design of second-order NLO active chromophores.

As stated in the previous paragraph, the noncentrosymmetry is generally a prerequisite for second-order NLO activity of a molecule. However, in order to obtain efficient second-order molecular responses, intense, low-energy electronic transitions having CT character are required. With these concepts in mind, various synthetic strategies, through an appropriate molecular design, also recently based on sophisticated theoretical approaches, such as TD-DFT or TD-HF, have been developed in order to produce efficient second-order molecular NLO chromophores. Actually, for material chemists involved in the investigation of NLO properties, this is one of the most important topics of the latest two decades.

Two main families of organic molecular NLO chromophores can be identified: dipolar and octupolar species. The former, which are not centrosymmetric, follow a general scheme involving a polarizable molecular structure (e.g., a π-conjugated pathway) having an asymmetrical charge distribution (e.g., with donor and/or acceptor group substituents) to form a donor–π–conjugated bridge-acceptor (D–π–A) network. The prototypical example of a dipolar molecule is represented by *p*-nitroaniline. The second-order optical nonlinearity originates from the existence of D→A electronic CT transitions mediated by the π-conjugated-bridge, which in many cases are referred to the lowest-energy transition, so that the "two level" model applies quite well. To this category of molecular materials belong most conjugated organic species.

Octupolar molecules, instead, may be centrosymmetric but they imply the existence of twofold (D_2) or threefold (D_3) rotational axes. They are characterized by multidirectional CT excitations. The theoretical description of nonlinearity of such systems implies, even in the simplest case, a three-level approach. The prototypical example of an octupolar molecule is represented by 1,3,5-triamino-2,4,6-trinitrobenzene.

2.3 Coordination and Organometallic Complexes

Second-order NLO active coordination and organometallic complexes have progressively occupied in the last decade a relevant role in the panorama of molecular NLO chromophores because of the unique, structural and electronic characteristics associated with a metal center interacting with organic ligands [5–19]. Actually, compared to organic molecules, coordination and organometallic complexes can offer a larger variety of electronic structures, controlled by the metal electronic configuration, oxidation state, coordination sphere, etc. In particular, in the case of dipolar NLO chromophores, the metal center may act as the donor, or as the acceptor, or even as the bridge of a donor–acceptor network.

In fact, as coordination and organometallic complexes may possess intense, low-energy MLCT, ligand-to-metal CT (LMCT), or intraligand CT (ILCT) excitations, the metal can effectively act as the donor, the acceptor, or the polarizable bridge of a donor–acceptor network. Finally, metal ions are well suited to build molecular structures based on octupolar coordination of organic ligands with D_2 or D_3 symmetry.

In the following paragraphs is reported an overview, mainly limited to the last 8–10 years, on coordination and organometallic second-order NLO active chromophores, focusing the attention only on specific and relevant aspects associated with each class of NLO chromophores; therefore the overview is not exhaustive.

3 Coordination and Organometallic Complexes for Second-Order Nonlinear Optics

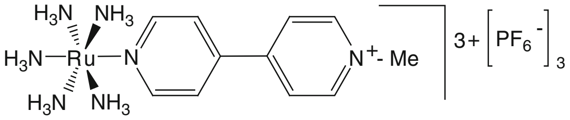
3.1 Complexes with Amine, Pyridine, and Stilbazole Ligands

3.1.1 Amines

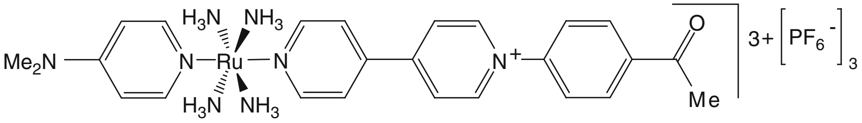
Coe et al. investigated deeply the second-order NLO properties of various ruthenium amine complexes with pyridine ligands [18, 34–51]. In particular, they systematically investigated, in acetonitrile solution by the HRS technique working at 1.064 μm incident wavelength, Ru^{II} NLO chromophores such as *trans*-$[Ru(NH_3)_4(L^D)(L^A)][PF_6]_n$ ($n = 2$ or 3) where L^D (e.g., 4-(dimethylamino) pyridine) and L^A (e.g., 4-acetylpyridine or *N*-methyl-4,4′-bipyridinium, MeQ^+) are electron-rich and electron-deficient ligands, respectively [35]. In such chromophores, intense $Ru^{II} \rightarrow L^A$ MLCT transitions dominate the β(HRS) value. A rather high β_0(HRS) value was reported for the chromophores $[Ru(NH_3)_5(MeQ^+)][PF_6]_3$ (**1**, 123×10^{-30} esu) and *trans*-$[Ru(NH_3)_4(4\text{-}Me_2N\text{–}C_5H_4N)(MeQ^+)][PF_6]_3$ (130×10^{-30} esu). Complexes with the charged MeQ^+ ligand show larger β_0 values, when compared with their analogs with neutral pyridine L^A ligands, due to a more extended π-conjugation and to the presence of a ligand carrying a positive charge [35].

N-Arylation of the 4,4′-bipyridinium cation leads to an even higher β_0(HRS) value (**2**, 410×10^{-30} esu) [37], and, by placing a *trans*-ethylene bridge between the pyridine and pyridinium rings of L^A, β_0 increases up to 50% [41].

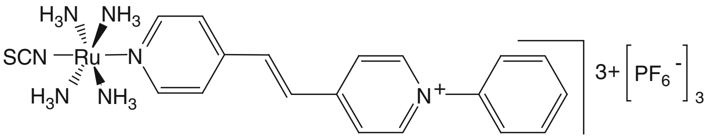
Besides, replacement of a neutral L^D ligand such as $4\text{-}Me_2N\text{–}C_5H_4N$ with a presumably N-coordinated thiocyanate anion (see **3**) increases the electron-donating strength of the Ru^{II} center and consequently the β_0(HRS) value to 513×10^{-30} esu [42]. The β_0 values obtained by the HRS technique for these Ru^{II} chromophores were confirmed by means of the method based on Stark spectroscopy [41, 42]. Also, calculations based on TD-DFT gave values of β_0 reasonably in agreement with the experimental β_0(HRS) values [46]. Interestingly, an $[Ru(NH_3)_5NC_5H_4\text{-}]^{2+}$ moiety is more effective than a 4-NMe_2–C_6H_4- moiety as a π-electron-donor, in terms of enhancing β_0(HRS) [47].



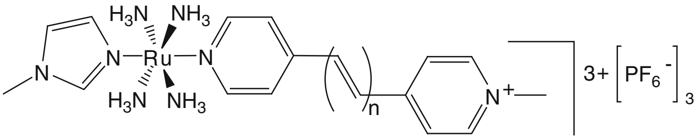
1



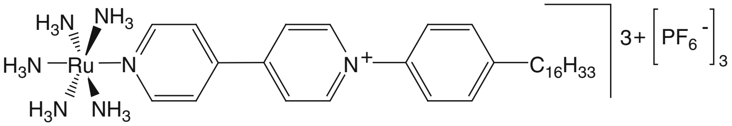
2



3



4



5

Within three series of pyridyl polyene chromophores **4**, the β_0 values obtained by the HRS technique or Stark spectroscopy (about 100–600 × 10^{-30} esu) maximize when $n = 2$. This is in contrast with the behavior of known organic chromophores based on an electron-donor–acceptor system linked by a polyene bridge, in which β_0(HRS) increases steadily with the increase of the π delocalization of the polyene bridge [48, 49]. TD-DFT calculations show that the HOMO level of these

Ru^{II} complexes gains in π character as n increases; consequently, the lowest energy transition usually considered as purely MLCT in character has some opposite ILCT contribution which becomes significant when $n > 2$ and which increases with the conjugated pathlength, causing the value of β_0(HRS) to decrease [49]. Electrochemical studies, ^{1}H NMR, and an investigation based on Stark spectroscopy all confirm that the role of an extended conjugated π-system is more effective in the purely organic chromophores than in their Ru^{II} analogs [50, 51].

Remarkably, the β_0(HRS) values of certain complexes (e.g., **1**) can be reversibly and very effectively (10- to 20-fold) attenuated by a Ru^{III}/Ru^{II} redox process involving chemical reagents such as H_2O_2 [39, 40, 43–45].

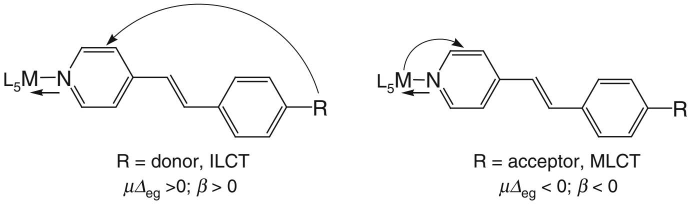
The redox-switching of the linear optical absorption of self-assembled monolayers and Langmuir–Schäfer films of $[Ru(NH_3)_5(4,4'\text{-bipyridinium})]^{3+}$ complexes [52–54] and a redox-switching of the NLO response of Langmuir–Blodgett thin films based on **5** were recently reported. Oxidation to Ru^{III} causes ca. 50% decrease of the intensity of the SHG, which is almost completely restored by reduction to Ru^{II} [55].

3.1.2 Pyridines and Stilbazoles

The effect of coordination to a metal center on the second-order NLO response of pyridine and stilbazole ligands has been deeply studied mainly by Marks, Ratner et al., and by Ugo et al. [10–16]. The quadratic hyperpolarizability β, measured in solution by the EFISH technique, of *para*-substituted pyridines and stilbazoles, such as 4-R-C_5H_4N and 4,4′-*trans or trans,trans*-R-$C_6H_4(CH{=}CH)_n{-}C_5H_4N$ (R = donor or acceptor substituent; $n = 1, 2$), increases upon coordination to various metal centers, the enhancement factor (EF) being modulated by the nature of the metal (electronic configuration, oxidation state, coordination sphere) which can act as an electron-acceptor or an electron-donor. For example, the quadratic hyperpolarizability, measured by the EFISH technique of 4,4′-*trans*-$Me_2N{-}C_6H_4CH{=}CHC_5H_4N$ increases by a factor of 2 ($\beta_{1.06}$(EFISH) goes from 28.2×10^{-30} to 61×10^{-30} esu) upon coordination to a zerovalent "$W(CO)_5$" moiety which acts mainly as electron-acceptor [56]. Similarly, coordination of a pyridine or stilbazole ligand bearing an electron-withdrawing group to a low oxidation state organometallic fragment such as "$M(CO)_5$" (M=Cr, W), that may also act as electron-donor, could produce a relevant increase of the absolute value of the second-order NLO response. Thus, the $\beta_{1.91}$(EFISH) value of 4-COH–pyridine (-0.10×10^{-30} esu) increases its absolute value (-12×10^{-30} esu) upon coordination to a zerovalent "$W(CO)_5$" [56–58].

This ambivalent donor or acceptor role of a zerovalent metal has suggested two different mechanisms controlling the second-order NLO response of this kind of NLO organometallic chromophores [56] (Scheme 1).

When the R substituent is a strong electron-donating group, the increase of the value of the quadratic hyperpolarizability β is dominated by an intraligand CT (ILCT) transition, with the metal center, which behaves as an electron-acceptor,



Scheme 1 Two mechanisms controlling the second order NLO response

producing a red-shift of this transition and therefore an increase of the value of β according to the "two level" model [20, 21]. In contrast, when R is a strong electron-accepting group, the quadratic hyperpolarizability β is dominated mainly by an MLCT transition. In this latter case the negative sign of β is due to a reduction of the dipole moment in the excited state of the MLCT transition ($\Delta\mu_{eg} < 0$), according to the "two level" model [20, 21].

An extended EFISH investigation of the second-order NLO response of *cis*-[M(CO)$_2$Cl(4-R-C$_5$H$_4$N)] (M = Rh, Ir) and *fac*-[Os(CO)$_3$Cl$_2$(4-R-C$_5$H$_4$N)] (R = electron-donor or -acceptor substituent) has confirmed such interpretation of the ambivalent role of the metal center. In fact, the ambivalent acceptor or donor role is controlled by the intrinsic softness of the metal center and by the presence in the pyridine ligand of an electron-donor or -acceptor group R [59]. For instance, the values of $\beta_{1.06}$(EFISH) of *cis*-[M(CO)$_2$Cl(4-R-C$_5$H$_4$N)] (M = Ir^I (5d^8), Rh^I (4d^8)) are dependent upon the nature of R: (1) $\beta > 0$ with strong electron-donating groups (e.g., R = NMe$_2$ and M = Ir, $\beta_{1.06}$(EFISH) = 9×10^{-30} esu); (2) β is positive but very small with weak electron-donating groups (e.g., R = CMe$_3$ and M = Ir, $\beta_{1.06}$(EFISH) = ca. 0.1×10^{-30} esu); (3) $\beta < 0$ with strong electron-withdrawing groups (e.g., R = CN and M = Ir, $\beta_{1.06}$(EFISH) = -9×10^{-30} esu). Independently from the strong electron-donating or withdrawing properties of the R group, a very strong enhancement of one or two orders of magnitude of the absolute value of $\beta_{1.06}$(EFISH) of the pyridine ligands occurs upon coordination [16].

Remarkably, it is possible to modulate the NLO response of a pyridine ligand by an increased acceptor or donor strength of the metal centers, which is controlled by their oxidation state and ancillary ligands [16]. Thus, coordination of 4-Me$_2$N–C$_5$H$_4$N to "*cis*-M(CO)$_2$Cl" (M = Rh^I, 4d^8 or Ir^I, 5d^8) or "*fac*-Os(CO)$_3$Cl$_2$" (Os^{II}, 5d^6) produces an increase of the $\beta_{1.06}$(EFISH) value about tenfold higher than coordination to the less accepting zerovalent "Cr(CO)$_5$" moiety (Cr^0, 3d^6). Besides, the quadratic hyperpolarizability $\beta_{1.91}$(EFISH) of [W(CO)$_5$(4-MeCO–C$_5$H$_4$N] (-9.3×10^{-30} esu) is larger than that of the complex of this substituted pyridine with the "Os^{II}(CO)$_3$Cl$_2$" moiety, due to the better donor properties of the "W(CO)$_5$" fragment [56, 57, 59]. Moreover, the value of $\beta_{1.34}$(EFISH) decreases upon substitution of the carbonyl ligands of "*cis*-M(CO)$_2$Cl" (M = Rh^I or Ir^I) with cyclooctadiene or with two cyclooctene ligands, according to a decrease of the acceptor properties of the metal center [59].

In push–pull 1D organic chromophores, an increase of the delocalized π-electron bridge between the donor and the acceptor groups leads to a significant increase of the second-order NLO response [60, 61]. In contrast, there is a buffering of the second-order NLO response upon coordination, because the effect due to coordination becomes less relevant by increasing the length of the π-delocalized bridge of the nitrogen donor ligand. For example, on going from 4-$Me_2N–C_5H_4N$ to 4,4′-*trans*-$Me_2N–C_6H_4CH{=}CHC_5H_4N$ the EF of $\beta_{1.34}$(EFISH) is of the order of 10^3 while on going from *cis*-[$M(CO)_2Cl$(4-$Me_2N–C_5H_4N$)] to *cis*-[$M(CO)_2Cl$(4,4′-*trans*-$Me_2N–C_6H_4CH{=}CHC_5H_4N$)] the EF is only ten times [59]. Coordination to "*cis*-$Ir(CO)_2Cl$" of 4,4′-*trans*-$Me_2N–C_6H_4CH{=}CHC_5H_4N$ causes an EF of $\beta_{1.34}$(EFISH) of only 2.3, quite small when compared to the large EF produced when 4-$Me_2N–C_5H_4N$ is coordinated to the same metal moiety [59].

Also, a zerovalent trimeric cluster core such as "$Os_3(CO)_{11}$" shows this ambivalent acceptor-donor effect on the second-order NLO response of *para*-substituted stilbazole ligands. However, strangely enough, its acceptor and donor strengths are comparable to those of "*fac*-$Os(CO)_3Cl_2$" and "*cis*-$Ir(CO)_2Cl$" [62]. While one expects a significant MLCT electron transfer from the "$Os_3(CO)_{11}$" core to the π* orbital system of a stilbazole ligand carrying in *para* position an electron-withdrawing substituent such as CF_3, in consideration of a significant polarizability of the *d* electron density of a trimeric cluster core with metals in the zero oxidation state, the significant σ acceptor properties of the zerovalent "$Os_3(CO)_{11}$" core when the stilbazole carries an electron-donor group such as NMe_2, comparable to that of an Os^{II} metal carbonyl center, is unexpected [62].

In contrast to the effect of coordination to a low oxidation state metal carbonyl moiety, the $\beta_{1.34}$(EFISH) value of 4,4′-*trans*-$Me_2N–C_6H_4CH{=}CHC_5H_4N$ is almost unaffected by coordination to the relatively soft "*cis*-$PtCl_2$" moiety and, strangely enough, also to the less soft "$Zn(CH_3CO_2)_2$" Lewis acid moiety, in agreement with an irrelevant red-shift upon coordination of the ILCT transition of the stilbazole [63]. However, a more significant red-shift occurs upon coordination to harder "ZnY_2" (Y = Cl^- [63], $CF_3CO_2^-$ [63], $CF_3SO_3^-$ [64, 65]) Lewis acid moieties. It appears that the β EF is function of the ancillary ligands Y which tune the acceptor properties of the Zn^{II} center ($CH_3CO_2^- < Cl^- < CF_3CO_2^- < CF_3SO_3^-$), as confirmed by both EFISH measurements and solvatochromic investigations [63–65].

For instance, at concentrations higher than 1×10^{-4} M, the value of $\beta_{1.91}$(EFISH) of [$Zn(CF_3SO_3)_2$(4,4′-*trans*-$Me_2N–C_6H_4(CH{=}CH)_nC_5H_4N)_2$] ($n$ = 1,2) is increased by a factor of about 4–6 times, when compared to that of the related complexes with the $CH_3CO_2^-$ ancillary ligand, in agreement with a higher Lewis acidity of the Zn^{II} center, as confirmed by the much higher red-shift of the ILCT transition upon coordination (for $n = 1$, $\Delta\lambda_{max} = 2$ and 116 nm when Y = $CH_3CO_2^-$ and $CF_3SO_3^-$, respectively). Of interest is the unexpected evidence that, in $CHCl_3$ solution at concentrations lower than about 10^{-4} M, the $\beta_{1.91}$(EFISH) value of these triflate complexes increases abruptly by decreasing concentration, up to very large values, while this effect is not observed for the related acetate or trifluoroacetate complexes. Such behavior was attributed to an increased concentration of the cation [$Zn(CF_3SO_3)$(4,4′-*trans*-$Me_2N–C_6H_4(CH{=}CH)_nC_5H_4N)_2]^+$ (n = 1,2), characterized by a stronger second-order

NLO response due to the positive charge, produced by the facile solvolysis of the triflate ligand, as confirmed by electrical conductivity measurements which evidenced a sharp conductivity increase at concentrations below 10^{-4} M for the triflate complexes [64, 65]. A similar behavior of the quadratic hyperpolarizability in $CHCl_3$ solution by dilution was observed for Zn^{II} complexes with the same stilbazoles and with ancillary ligands such as the methansulfonate or *para*-toluensulfonate anions [66].

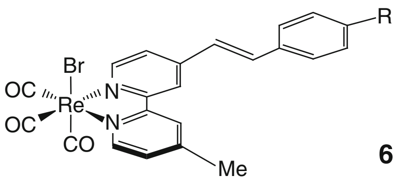
3.2 Complexes with Chelating Ligands

3.2.1 Bipyridines and Phenanthrolines

The second-order NLO response of various bipyridine and phenanthroline ligands increases upon coordination to a metal center, as in the case of pyridines and stilbazoles (see Sect. 3.1.2), the EF of the quadratic hyperpolarizability still depending on the electronic configuration of the metal, its oxidation state, and its sphere of ancillary ligands [10, 16].

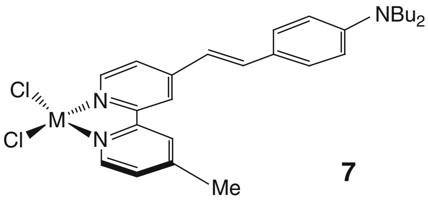
An investigation was carried out on powders of Re, Pd, and Pt complexes with 2,2′-bipyridine, which exhibit modest second-order NLO activities as evidenced by the Kurtz technique [67]. A more extended investigation on the second-order NLO response of various Re^{I}, Zn^{II}, and Hg^{II} complexes with donor-substituted vinyl bipyridines (for examples, **6** and **7**) was done by the EFISH technique, working at 1.34 μm incident wavelength [10, 68, 69].

$\beta_{1.34}$(EFISH) increases with the strength of the electron-donor substituent group (NBu_2 is more efficient than Ooctyl) and with the Lewis acidity of the metal center (the relative increase of the acceptor strength, which parallels the increase of the red-shift of the ILCT transition upon coordination, follows the order: "$Hg(OAc)_2$" < "$HgCl_2$" < "$Zn(OAc)_2$" < "$ZnCl_2$" < "$Re(CO)_3Br$"), the best value being obtained for a complex with "$ZnCl_2$" (for **7** with M = Zn, $\beta_{1.34}(\text{EFISH}) = 152 \times 10^{-30}$ esu; $\mu\beta_0 = 831 \times 10^{-48}$ esu). The complexes with "$Re(CO)_3Br$" were less efficient than the corresponding Zn complexes due to the presence of two vectorially opposed CT transitions (MLCT and ILCT) [68, 69].



6

R = NBu_2, O = Ooctyl

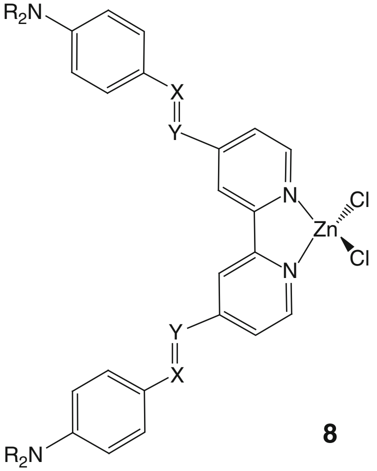


7

M = Zn, Hg

In the related complexes **8**, for a given donor group, a slight increase of the value of $\mu\beta_{1.34}$(EFISH) occurs by replacing CH with N. However, the significant increase of the NLO response seems to be mainly controlled by resonant enhancement [70].

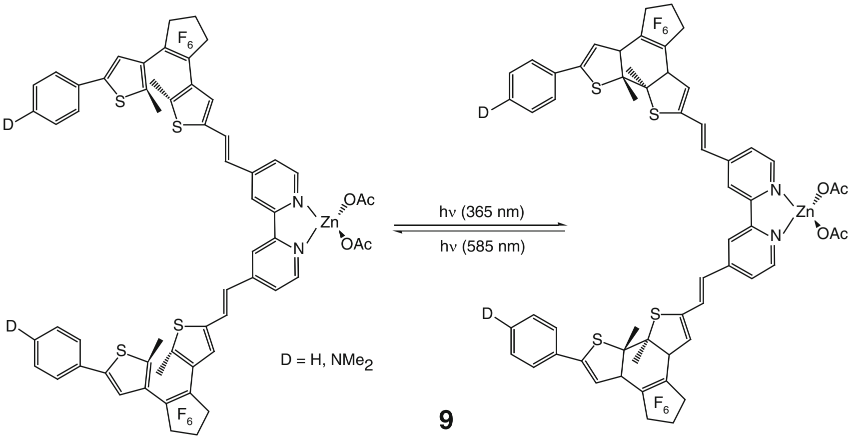
Interestingly, the $\mu\beta_{1.34}$(EFISH) value of **8a** [70] is twice that of the structurally related nonchelated complex [$ZnCl_2(4,4'$-*trans*-$Me_2N–C_6H_4CH{=}CHC_5H_4N)_2$] [63], due to the rather planar arrangement of the chelated ligand upon coordination and consequently to a shift of the ILCT transition at lower energy [16].



a X = Y = CH, R = Bu
b X = Y = CH, R = Et
c X = Y = N, R = Bu
d X = N, Y = CH, R = Et

8

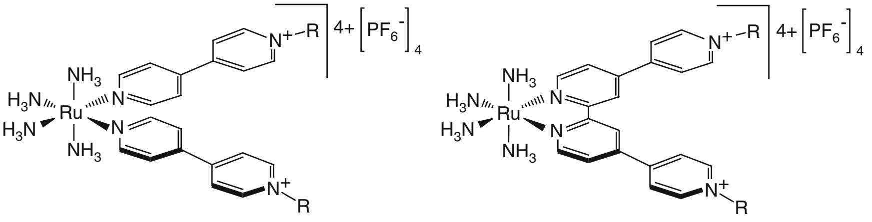
Very recently, the efficient photoswitching of the second-order NLO responses of some dipolar photochromic Zn^{II} complexes (**9**) was reported [71]. The NLO activity for the open forms is very small, as expected for the absence of π-conjugation between the two thiophene rings. Upon conversion to the closed form in the photo-stationary state, the NLO activity increases dramatically ($\mu\beta_0$(EFISH) from 75–160 × 10^{-48} to 1,020–1,800 × 10^{-48} esu). This substantial enhancement reflects a more efficient delocalization of the π-electron system in the closed forms favoring an efficient on/off switching of the NLO responses [71].



D = H, NMe_2

9

Two-dimensional second-order NLO, positively charged, chromophores incorporating the “$Ru(NH_3)_4^{2+}$” moiety linked to two structurally related electron-accepting *N*-methyl/aryl-pyridinium systems (either two monodentate pyridine ligands or one bipyridine chelated ligand) were studied (**10**) [72]. The $\beta_{0.80}$(HRS) for the chelated complexes (32–48 × 10^{-30} esu) are smaller than those of the nonchelated counterparts (135–160 × 10^{-30} esu). The possibilities for redox-switching of the NLO properties, by exploiting reversible $Ru^{III/II}$ oxidation processes and ligand-based reductions, were investigated [72].

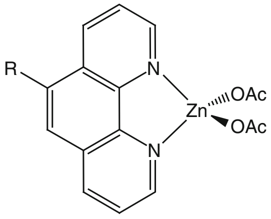


R = Me, Ph, 4-Acetyphenyl

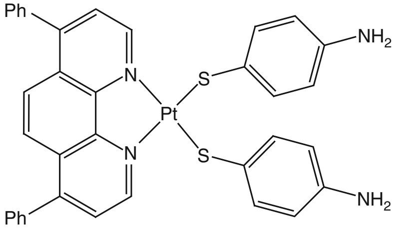
R = Me, Ph, 4-Acetyphenyl

10

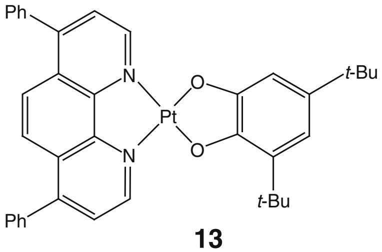
The quadratic hyperpolarizability of 5-R-1,10-phenanthroline (R = donor group such as OMe, NMe_2, *trans*-CH=CHC$_6$H$_4$-4′-NMe$_2$ and *trans,trans*-(CH=CH)$_2$C$_6$H$_4$-4′-NMe$_2$) increases upon coordination to a Zn^{II} center but not to the softer Cd^{II} center [63]. The EF of $\beta_{1.34}$(EFISH) upon coordination to “$Zn(CH_3CO_2)_2$” is, as expected, higher for the donor group NMe_2 (EF = 4.6) than for the donor group OMe (EF = 3.2). Such enhancement becomes less and less relevant by increasing the length of the π-delocalized bridge between the donor group NMe_2 and the phenanthroline chelated ligand, as already observed in the case of 4-R-pyridines (Sect. 3.1.2) [63]. Notably, the second-order NLO chromophore **11** (R = *trans,trans*-(CH=CH)$_2$C$_6$H$_4$-4′-NMe$_2$) is characterized by a good value of $\beta_{1.34}$(EFISHG) (112 × 10^{-30} esu) [63].



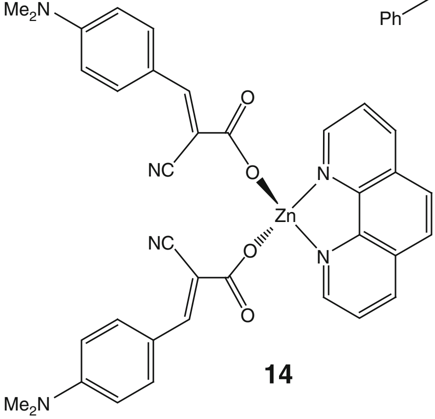
11



12



13



14

The $\beta_{1.91}$(EFISH) value of a large series of square planar M(substituted 1,10-phenanthroline)(dithiolate) complexes (M = Pt^{II}, Pd^{II}, Ni^{II}) was measured [73]. In these second-order NLO chromophores, the HOMOs are a mixture of metal and thiolate orbitals whilst the LUMOs are phenanthroline π* orbitals. Therefore, the presence of an electron-donor group on the dithiolate ligand, acting on the HOMOs level, increases the value of the quadratic hyperpolarizability by acting on the energy of the CT involving the HOMO–LUMO transition. The best NLO response is obtained when M = Pt^{II} (**12**, $\beta_{1.91}$(EFISH) = -39×10^{-30} esu; $\mu\beta_0 = -260 \times 10^{-48}$ esu) since this latter Pt^{II} complex shows an increased oscillator strength of the HOMO–LUMO transition when compared to that of the related Pd^{II} or Ni^{II} NLO complexes. The structurally related complex **13**, which shows a $\mu\beta_0$ value between -523 and -669×10^{-48} esu, dependent on the nature of the solvent, was also investigated [74].

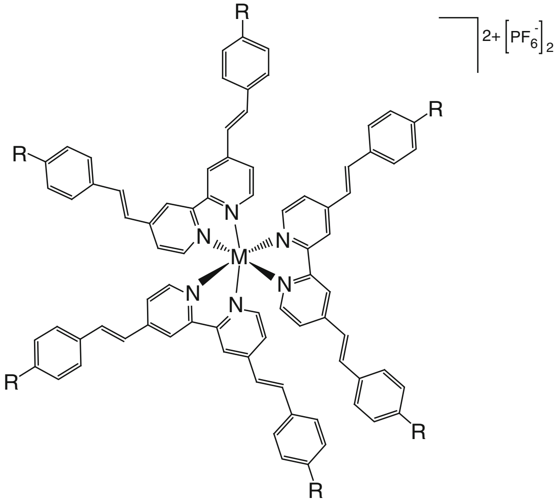
The quadratic hyperpolarizability of various one-dimensional push–pull carboxylate ligands increases upon coordination to a "(1,10-phenanthroline)Zn^{II}" center. For example, **14** has a β_0(HRS) value of 39×10^{-30} esu, much higher than that of the related carboxylate ligand (6.6×10^{-30} esu) [75].

Metal ions are excellent templates to build D_{2d} and D_3 octupolar second-order NLO chromophores; therefore their associations with functionalized bipyridyl ligands give rise to octahedral and tetrahedral metal complexes with large quadratic hyperpolarizabilities [76]. The adequate functionalization of these octupoles allows their incorporation into macromolecular architectures such as polymers and metallodendrimers [76]. Various D_3 octupolar tris chelated Ru^{II} complexes are characterized by a significant second-order NLO response as evidenced by HRS [18].

For example, the β_0(HRS) value of **15**, when M = Ru^{II} and R = NBu_2, is 380 × 10^{-30} esu [77, 78]. Similar values are obtained upon substitution of $PF_6{}^-$ with other anions such as $TRISPHAT^-$ (tris(tetrachlorobenzendiolato)phosphate anion) [79]. Polarized HRS investigations and Stark spectroscopic measurements support a second-order NLO response of **15** controlled by multiple degenerate dipolar CT transitions, rather than by an octupolar transition. In accordance the transitions dominant on the NLO response are ILCT excitations red-shifted by coordination to Ru^{II} and MLCT transitions with a CT process opposite as direction [78, 80].

Holding fixed the bipyridine carrying R = NBu_2, but changing the metal, substitution of Ru^{II} with Fe^{II} causes a decrease of β_0(HRS) due to both a blue-shift of the ILCT and a red-shift of the MLCT [78, 81]. The analogs Zn^{II} or Hg^{II} complexes, which have only the ILCT transition, show β_0(HRS) values of 380 and 256 × 10^{-30} esu, respectively, in accordance with the different Lewis acidity of the metal center [78]. By introducing the less donor R = Ooctyl group in the Ru^{II} NLO chromophore, the β_0(HLS) value decreases due to a ILCT absorption band at higher energy [78]. The NLO chromophore **15**, with M = Zn^{II} and R = *trans*-$CH{=}CHC_6H_4NBu_2$, exhibits the highest value of the quadratic hyperpolarizability reported for an octupolar NLO chromophore (β_0(HRS) = 657 × 10^{-30} esu; $\beta_{1.91}$(HRS) = 870 × 10^{-30} esu) [82].

Tetrahedral D_{2d} octupolar metal NLO chromophores (where the metal center M is Cu^I, Ag^I, Zn^{II}) with the same functionalized bipyridyl ligands were studied. Their quadratic hyperpolarizabilities, measured by HRS at 1.907 μm incident wavelength, are much lower when compared to those of the related octahedral D_3 NLO chromophores (β_0(HRS) = 70–157 × 10^{-30} esu and 200–657 × 10^{-30} esu for D_{2d} and D_3 complexes, respectively) [82].



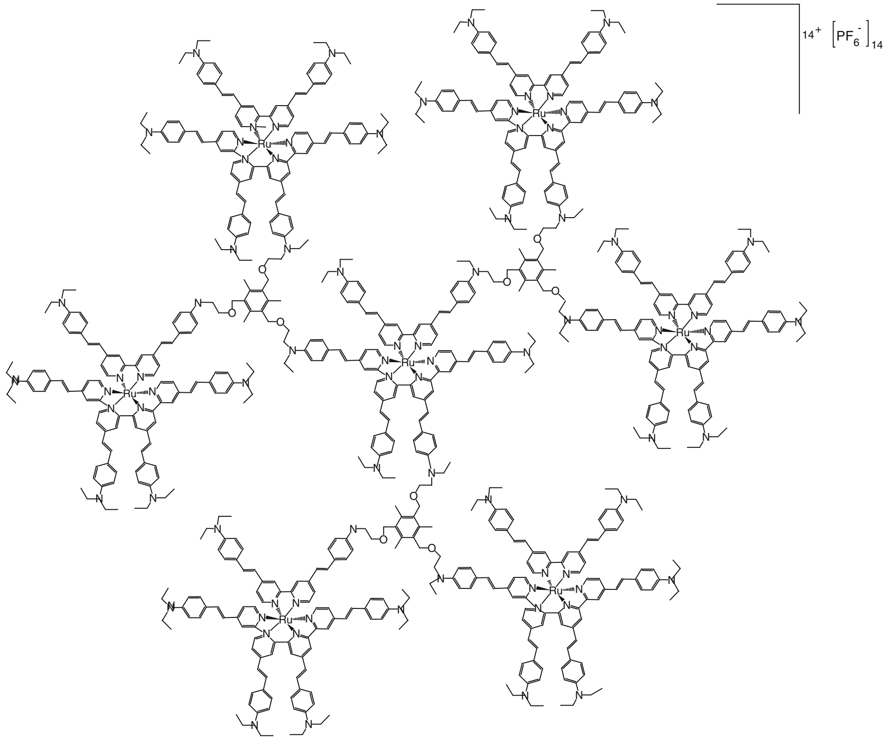
15

M = Ru^{II}, Zn^{II}, Hg^{II}, Fe^{II}

R = NBu_2, Ooctyl, trans-$CH{=}CHC_6H_4NBu_2$

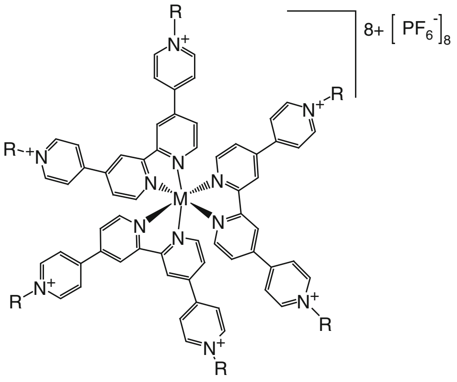
Le Bozec and coworkers have incorporated the Ru^{II} NLO chromophore **15**, adequately functionalized with an appropriate R = amino group, into macromolecular systems of interest as building blocks for the preparation of second-order NLO active bulk materials [83–86]. A thermally stable polyimide derivative of **15** shows, in CH_2Cl_2 solution, a $\beta_{1.91}$(HRS) value of $1{,}300 \times 10^{-30}$ esu, larger than that of the monomeric counterpart [83], whereas a dendrimeric species **16** with seven units shows a $\beta_{1.91}$(HRS) value of $1{,}900 \times 10^{-30}$ esu (in CH_2Cl_2) [84, 85]. The quasi-optimized octupolar ordering of the dendrimeric structure is responsible for the greater second-order NLO response compared to that of a linear arrangement of 14 basic units of the polyimide derivative [84, 85].

A star-shaped arrangement based on an octupolar Zn^{II} second-order NLO chromophore containing three photoisomerizable ligands (in two geometries) such as 4,4′-bis-(styryl)-2,2′-bipyridine functionalized with a dialkylamino-azobenzene shows a $\beta_{1.91}$(HRS) value of 863×10^{-30} esu in CH_2Cl_2 solution [87]. By using both photophysical and second-order NLO properties of this chromophore, all-optical poling, an interference process between one- and two-photon excitations that locally induces macroscopic second-order effects in polymeric films, was investigated. Grafting these chromophores onto the polymer network improves the stability of the macroscopic photoinduced nonlinearity [88].



16

Coe et al. investigated some related tris-chelate complexes of Ru^{II} and Fe^{II}, with bipyridines substituted with electron-withdrawing pyridinium groups (**17**) [89]. In these particular octupolar chromophores the second-order NLO response is dominated by two MLCT transitions; HRS measurements working with a 0.800 μm incident wavelength have produced larger quadratic hyperpolarizabilities for the Ru^{II} chromophores (170–290 $\times 10^{-30}$ esu) than for the Fe^{II} analogs (78–110 $\times 10^{-30}$ esu). However, this is probably due to the presence of a resonant enhancement in the case of the Ru^{II} chromophores. A Stark spectroscopic investigation and computations based on TD-DFT theory and the finite field method have shown in fact that the second-order NLO response of these chromophores is controlled by two substantial components producing slightly larger β_0 values for the Fe^{II} chromophore (86–151 $\times 10^{-30}$ esu) than for the Ru^{II} chromophore (68–114 $\times 10^{-30}$ esu) [89]. Since MLCT transitions determine the second-order NLO response of these chromophores, NLO redox switching based on these Fe^{II}/Fe^{III} or Ru^{II}/Ru^{III} species is possible.



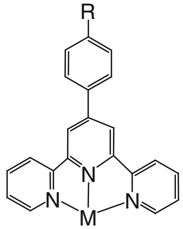
M = Fe, Ru
R = Me, Ph, 4-Acetyphenyl

17

3.2.2 Terpyridines

The second-order NLO properties of metal complexes with terpyridine ligands were recently studied for the first time [90, 91]. Coordination of a terpyridine such as 4′-(1-C_6H_4-*p*-NBu_2)-2, 2′: 6′, 2″-terpyridine to Zn^{II}, Ru^{III}, and Ir^{III} metal centers (**18**) induces a significant enhancement of its second-order NLO response measured by the EFISH technique working with an incident wavelength of 1.34 μm [90, 92]. In all these chromophores the ILCT transition of the terpyridine at about 416–465 nm is red-shifted by coordination, due to an increased π delocalization of the ligand upon chelation. The enhanced value upon coordination of the terpyridine to the Lewis center "ZnY_2" ($\beta_{1.34}$(EFISH) = 67 and 88 $\times 10^{-30}$ esu for Y = Cl^-, $CF_3CO_2^-$, respectively) remains positive, as expected for an ILCT transition dominating the second-order NLO response [16], the EF being higher for the more electron-withdrawing ancillary ligand $CF_3CO_2^-$. However, coordination of these terpyridine metal centers with different d^n configurations such as

Ir^{III} ($5d^6$ in "$Ir(4\text{-}EtPhCO_2)_3$") or Ru^{III} ($4d^5$ in "$Ru(CF_3CO_2)_3$"), produces an NLO response no longer influenced just by the ILCT transition, but also by MLCT and/or LMCT transitions, in such a way that these latter transitions can even change the sign of the quadratic hyperpolarizability. This relevant role of MLCT and LMCT transitions was confirmed by solvatochromic [92] and TD-DFT investigations [93]. As expected, the relevance of the MLCT transition increases when the terpyridine is carrying an electron-withdrawing substituent ($\beta_{1.34}$(EFISH) from -70 to -230×10^{-30} esu for R = NBu_2 and NO_2, respectively, when the terpyridine is coordinated to "$Ir(4\text{-}EtPhCO_2)_3$") [92].



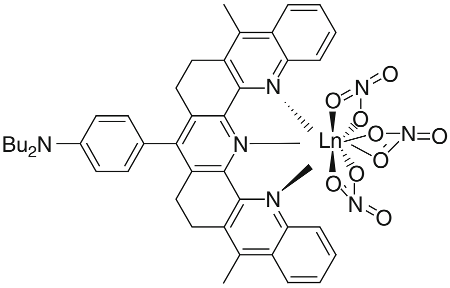
18

R = NBu_2, NO_2, (*E*)-CH=CH-C_6H_4-*p*-NBu_2,
(*E*),(*E*)-$(CH=CH)_2$-C_6H_4-*p*-NMe_2,

M = $ZnCl_2$, $Zn(CF_3CO_2)_2$, $RuCl_3$,
$Ru(CF_3CO_2)_3$, $IrCl_3$, $Ir(4\text{-}EtPhCO_2)_3$

Langmuir–Blodgett films of Zn^{II} and Ir^{III} complexes of 4′-(1-C_6H_4-*p*-NMe($C_{16}H_{33}$))-2, 2′: 6′, 2″-terpyridine have been investigated, measuring their SHG at 1.064 μm incident wavelength. Rather low $\chi^{(2)}$ values were unexpectedly obtained, probably due to a scarce noncentrosymmetric ordering of these rather bulk chromophores [94].

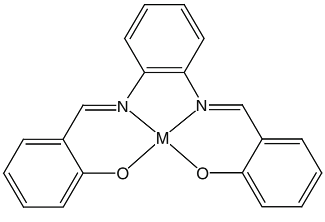
Recently, the second-order NLO properties of new lanthanide complexes of the type [$Ln(NO_3)_3$–L] (Ln = La, Gd, Dy, Yb, Y; **19**), where L is a rather rigid terpyridine-like ligand, have been determined by HRS, working with a nonresonant incident wavelength of 1.907 μm. The value of the quadratic hyperpolarizability $\beta_{1.91}$(HRS) increases by increasing the number of *f*-electrons, from 186 to 288 × 10^{-30} esu [95]. The dependence of the second-order NLO response on the nature of the lanthanide metal center suggests that *f*-electrons may contribute to the second-order NLO response [95].



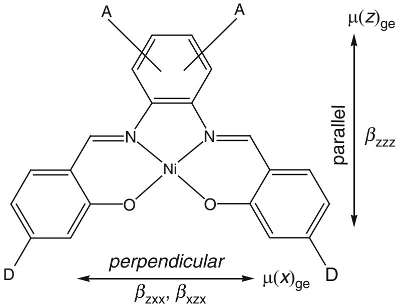
19

3.2.3 Schiff-Bases

Schiff-bases, arising from condensation of substituted salicylaldehydes with various bridging diamines, represent suitable templates to generate noncentrosymmetric molecular architectures. Various bis(salicylaldiminato)M^{II} (M = Fe, Co, Ni, Cu, Zn) complexes have been investigated as second-order NLO molecular chromophores [96, 97], exploring various aspects of their second-order nonlinear optics. In these NLO chromophores the metal ion templates noncentrosymmetric structures and acts as donor counterpart of a donor (D)–acceptor (A) system involving MLCT transitions. Starting from the more simple unsubstituted species (**20**), for the first time the role of the metal-*d* configuration was demonstrated in controlling the second-order NLO response, when MLCT transitions are dominating such a response. In particular, on passing from the closed-shell Ni^{II} (d^8) ($\beta_{1.34}$(EFISH) = -20×10^{-30} esu) to the open-shell Cu^{II} (d^9) ($\beta_{1.34}$(EFISH) = -50×10^{-30} esu) and Co^{II} (d^7) ($\beta_{1.34}$(EFISH) = -170×10^{-30} esu) homologues, the substantial increase of the absolute values of the quadratic hyperpolarizability is clearly related to the increased accessibility of lower-lying CT states [98, 99]. However, in the presence of strong donor/acceptor substituents on the Schiff-base structure, the metal ion mostly acts as a bridge, and its role in controlling the second-order NLO response becomes less defined. Tunable values of the quadratic hyperpolarizability, ranging from negative to positive values [97], were obtained for these molecular NLO chromophores, depending upon the strength of the donor/acceptor substituents. The symmetric donor–acceptor substitution in dipolar planar Schiff-base complexes also allowed investigation of the in-plane two-dimensional (2D) NLO properties (**21**), of interest for the development of polarization-independent materials.



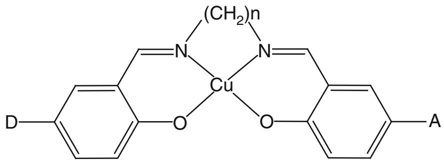
20



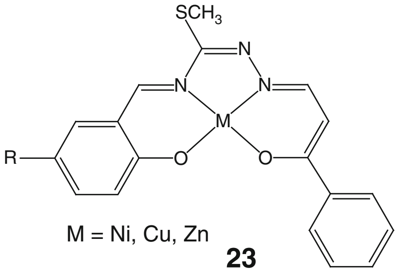
21

Dipolar 1D donor/acceptor systems are generally characterized by a prevalent single hyperpolarizability tensor, namely β_{zzz}, parallel to the dipolar *z* axis of the molecule. However, an appropriate donor/acceptor substitution pattern on the bis(salicylaldiminato) framework, resulting in a C_{2v} molecular symmetry, leads to large off-diagonal β_{ijk} tensors components (e.g., **21**, D = NEt_2; A = Cl, $\beta_{zzz(1.34)}$(HRS) = 43×10^{-30} esu; $\beta_{zxx(1.34)}$(HRS) = 20×10^{-30} esu) [100], due to the existence of CT transitions (**21**), perpendicular to the two axes, $\mu(x)_{ge}$ [100, 101].

A further variety of noncentrosymmetric Schiff-base structures can be envisaged, either by an unsymmetrical donor/acceptor substitution on the bis(salicylidene) ligand of a series of Cu^{II} complexes (**22**) [102], or by an unsymmetrical $[N_2O_2]$ tetradentate coordination in M^{II} (M = Ni, Cu, Zn, VO) complexes (**23**) [103], or finally in a series of Ni^{II} complexes with ligands derived by a monocondensation of the bridging diamine [104]. Appreciably optical nonlinearity has been achieved (e.g., **23**, M = Zn; R = N_2Ph, $\beta_{1.91}$(EFISH) = -280×10^{-30} esu) [103]. Therefore a large diversity of structures can produce second-order nonlinearity in this class of NLO chromophores. Further examples of second-order NLO chromophores based on Schiff bases are represented by a series of octahedral M^{II} (M = Fe, Co, Ni, Zn) metal complexes of *N*-2′-pyridylmethylene-4-aminopoly (phenyl) ligands, in which the molecular quadratic hyperpolarizability is strongly influenced by the metal electronic configuration and parallels the number of unpaired electrons. The largest values of the quadratic hyperpolarizability are those of the Mn^{II} complexes with a $3d^5$ electronic configuration [105]. Moreover, the switching of the second-order NLO response can be envisaged in the case of spin-crossover of Fe^{II} complexes. Bimetallic NLO chromophores involving dicopper(II) [106] or Cu^{II}-Gd^{III} [107] complexes have been investigated with the aim of finding possible interplay between magnetism and second-order NLO response. These "multifunctional" molecular chromophores, even possessing a rather modest optical nonlinearity, represent interesting models for further investigations of this field of research.



22



23

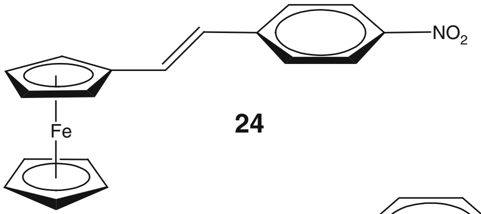
The use of chiral diamines in Schiff bases complexes allowed exploration of the powder SHG efficiency of crystalline materials based on this class of NLO chromophores, otherwise inactive because of the almost always crystal centrosymmetry. Relatively high powder SHG efficiency (up to 13 times that of urea) has been achieved in the case of the (1*R*,2*R*)-(+)-1,2-diphenylethylenediamine Ni^{II} derivative [108]. Analogous Zn^{II} complexes using the chiral (*R*)-(+)-1-phenylethylamine have given appreciable powder SHG efficiencies [109]. This strategy has been extended using a series of chiral amino alcohols [110] and amino acids [111] to obtain noncentrosymmetric crystals based on Sn^{IV} derivatives, with an attempt to correlate their SHG efficiencies with the molecular chirality.

In spite of the above studies on molecular NLO chromophores, investigations as NLO materials based on these chromophores remain almost unexplored. Monolayers of Ni^{II} complexes on glassy [112] or Si(100) [113] substrates have been obtained, but their second-order NLO activity has not yet been investigated.

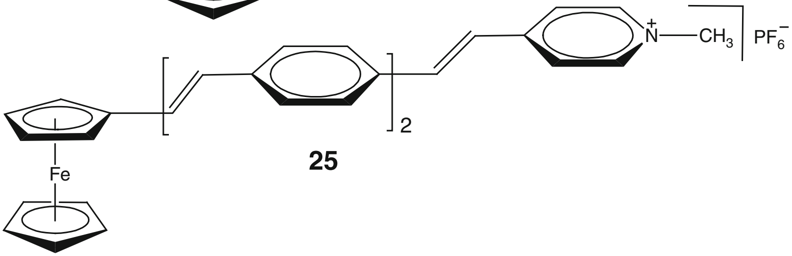
3.3 *Complexes with Metallocene Ligands*

Since the first report in 1987 by Green et al. [4], metallocene derivatives represent one of the most widely investigated classes of second-order NLO metal-based chromophores [114–116]. Starting from the prototypical stilbene (*trans*)-1-ferrocenyl-2-(4-nitrophenyl)ethylene derivative (**24**, $\beta_{1.91}$(EFISH) = 31 × 10^{-30} esu) [117] and related phenylethenyl oligomers [118], a very large variety of ferrocenyl species have been investigated. They range from various polyenes having a terminal acceptor group [119], such as *N*-alkylpyridinium salts (e.g., **25**, $\beta_{1.06}$(HRS) = 458 × 10^{-30} esu) [120], fullerene [121], sesquifulvalene (e.g., **26**, $\beta_{1.06}$(HRS) = 1,539 × 10^{-30} esu; β_0(HRS) = 821 × 10^{-30} esu) [122], fluorene (e.g., **27**, R = CO_2Me, $\mu\beta_{1.54}$(EFISH) = 5,000 ± 1,500 × 10^{-48} esu) [123], indanone [124], thiazole [125], dicyanomethylene (e.g., **28**, $\mu\beta_{1.00}$(EFISH) = 1,120 × 10^{-48} esu), [126] and related derivatives [127–129], including some (dicyanomethylene)indane species (e.g., **29**, $\mu\beta_{1.91}$(EFISH) = 5,200 (8,720) × 10^{-48} esu) [130], and various bimetallic (see Sect. 3.7) [131–133] and trimetallic [134] compounds, connected to the ferrocenyl unit through a conjugated π-linker. The values of the quadratic hyperpolarizability of these species parallel the strength of the acceptor group and, generally, increase with the length of conjugated π-network, as usually observed for related organic chromophores [60, 61]. In all cases, the metallocene unit represents the donor group of the donor-acceptor system connected by a π linker. Actually, the ferrocene unit possesses ionization energy and redox potential features comparable to those of the best organic donors. However, the values of the quadratic hyperpolarizability of the NLO chromophores based on ferrocene as donor group indicate a donor capability of the ferrocenyl group comparable to that of the poorly donor organic methoxyphenyl group. These relatively poor donor properties are due to a weak electronic coupling between the metal-*d* orbitals of the metallocenyl donor group and the π-network of the linker connecting the donor-acceptor push-pull systems. Thus, the very large hyperpolarizability values observed for some of the NLO chromophores reported above are in some cases due to resonant enhancement effects. On the other hand, even extrapolated β_0 values [117–134] cannot be considered reliable [32], since it has been assessed that, for ferrocenyl derivatives, many electronic states contribute to optical nonlinearity [115, 116].

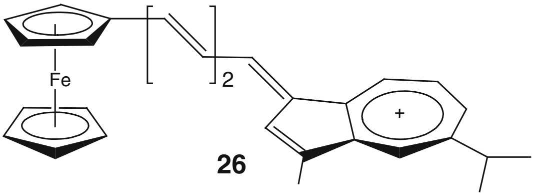
Some related ruthenocene species have also been investigated [117], almost always showing lower quadratic hyperpolarizabilities, in accordance with the higher ionization energy of the ruthenocene vs ferrocene moiety [115].



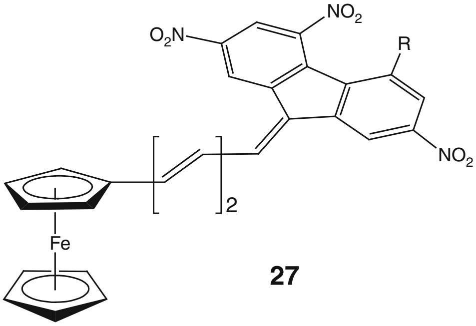
24



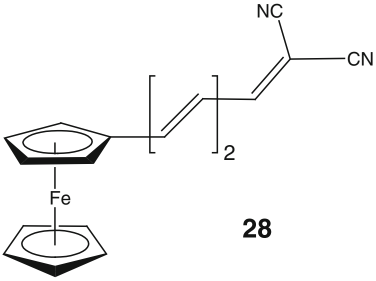
25



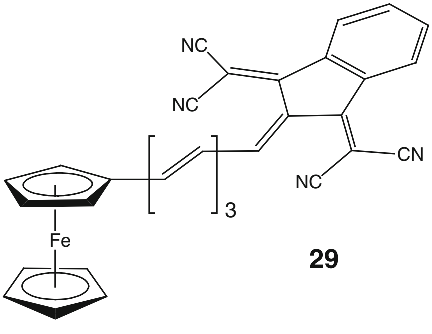
26



27

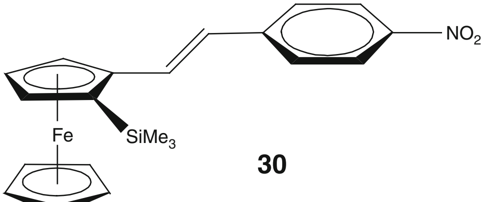


28

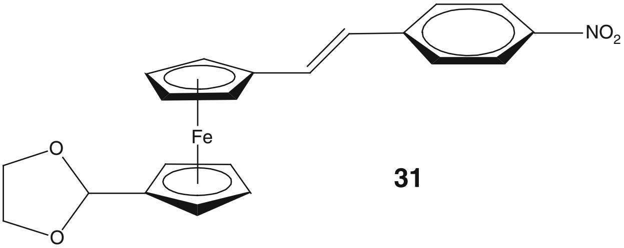


29

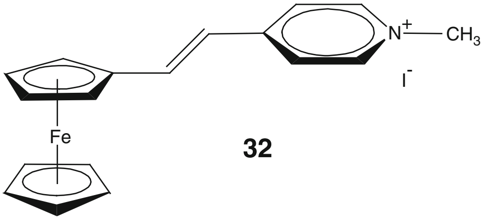
The interest in this class of NLO chromophores is also due to their capability to crystallize in noncentrosymmetric structures characterized by a high SHG, because the acceptor substituents are usually bulky species [135] or pyridinium salts [4, 136] which favor noncentrosymmetric packing. Also relevant is the possibility of engineering crystalline structures through chirality of the ferrocenyl group (e.g., **30**, powder efficiency 100 times that of urea) [137], or by an appropriate substituent on the second cyclopentadienyl ring (e.g., **31**, powder efficiency 140 times that of urea) [138]. Actually, the crystalline species based on ferrocene NLO chromophores are among the most SHG efficient organometallic materials, e.g., the pyridinium derivative **32** possesses powder efficiency 220 times that of urea [136].



30



31

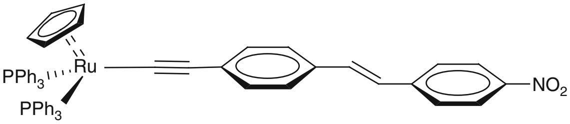


32

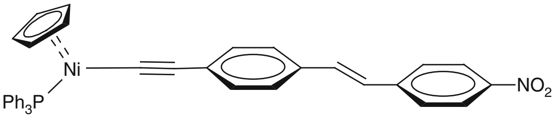
The large variety of molecular NLO chromophores based on metallocenes rends them suitable for the investigation of various bulk second-order NLO materials. Thus, some studies devoted to electrically poled polymers including a metallocene NLO molecular chromophore as guest [126, 139], or to self-assembled nanostructures of these metallocene NLO chromophores [140, 141], appeared quite recently in the literature. Moreover, the facile and reversible accessibility to the ferrocenium oxidized species [142], allowed the redox switching of the SHG signal in self-assembled monolayers [140] or the molecular multifunctional (linear optical, NLO, and magnetic properties) redox switching [143] to be obtained.

3.4 Complexes with Alkynyl and Vinylidene Ligands

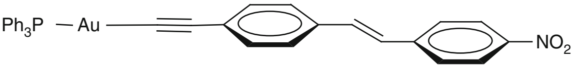
(Cyclopentadienyl) (alkylphosphine) metal σ-acetylides of group 8, group 10, and group 11 metals represent a widely investigated class of second-order NLO chromophores, mainly developed by Humphrey et al., whose relevant results are summarized in recent review articles [11, 19, 144].



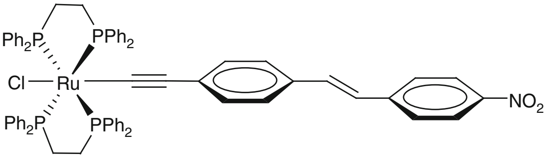
33



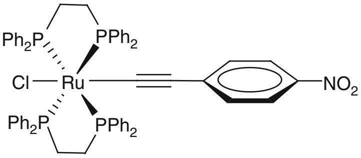
34



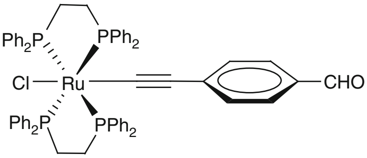
35



36



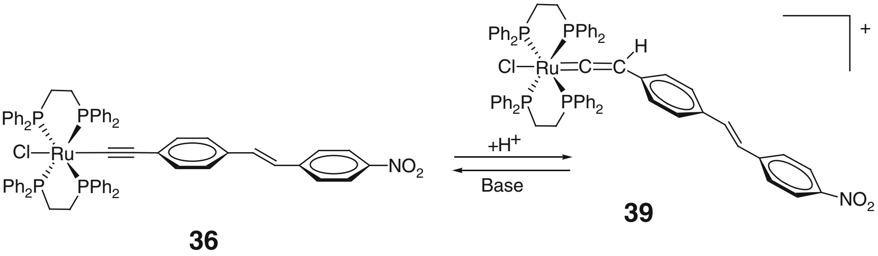
37



38

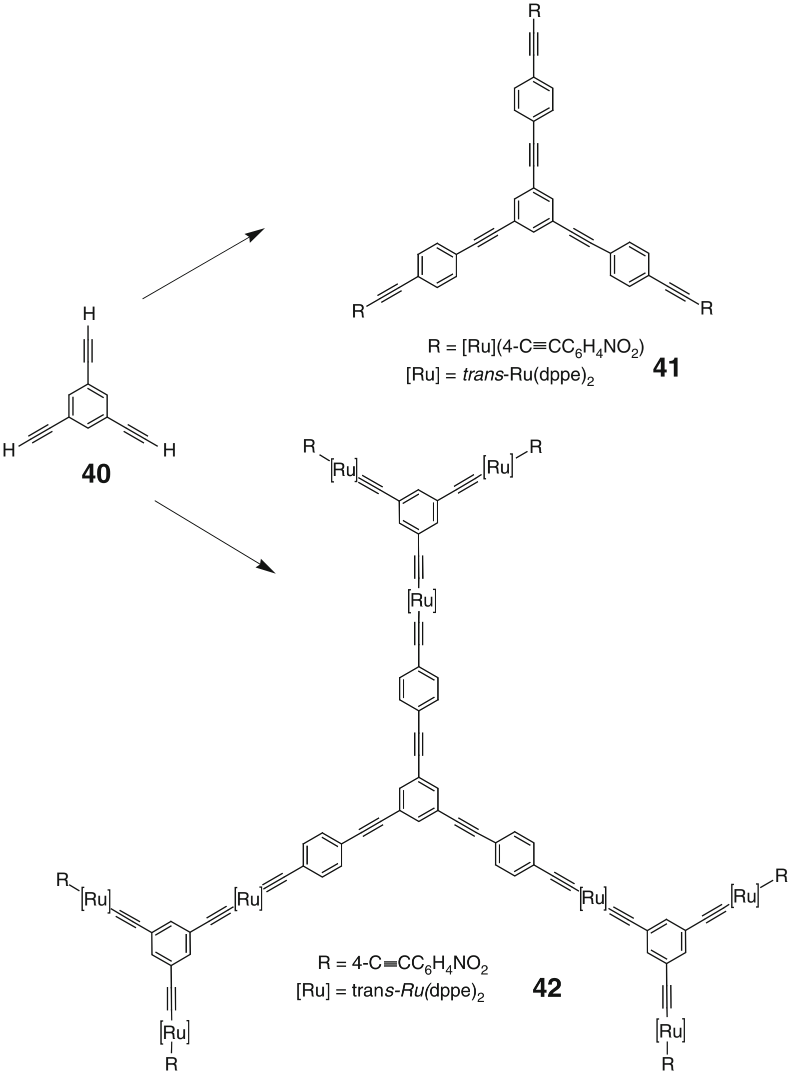
Analogous to metallocenes, in these complexes the metal acts as the donor group of a donor-acceptor system connected by a π-linker. The second-order nonlinearity is controlled by low-energy MLCT excitations. Large values of the quadratic hyperpolarizability, even if resonantly enhanced, have been achieved [11, 19, 144]. Accordingly, with the relative oxidizability ($Ru^{II} > Ni^{II} > Au^{I}$) [11, 19] the largest values of the quadratic hyperpolarizability have been obtained for the readily oxidizable Ru^{II} centers (e.g., **33**, $\beta_{1.06}$(HRS) = 1,455 × 10^{-30} esu), followed by the Ni^{II} complexes (e.g., **34**, $\beta_{1.06}$(HRS) = 445 × 10^{-30} esu), and by the 14-valence-electron, less readily oxidizable, Au^{I} species (e.g., **35**, $\beta_{1.06}$(HRS) = 120 × 10^{-30} esu) [11]. Group 8 complexes, in particular Ru^{II} compounds, consist of the largest group of acetylides studied [11, 19, 144–147], possessing the highest values of the quadratic hyperpolarizability (e.g., **36**, $\beta_{1.06}$(HRS) = 2,676 × 10^{-30} esu; β_0(HRS) = 342 × 10^{-30} esu) [145], thus resulting in very efficient donors. As expected, the quadratic hyperpolarizability [11, 19, 144–147] increases upon increasing the chain length of the acetylide bridge (e.g., **36** vs **37**, $\beta_{1.06}$(HRS) = 351 × 10^{-30} esu; β_0(HRS) = 55 × 10^{-30} esu, for the latter) [145], and increasing the strength of the acceptor (e.g., **37** vs **38**, $\beta_{1.06}$(HRS) = 120 × 10^{-30} esu, for the latter) [145]. Moreover, replacement of the cyclopentadienyl ligand by a tertiary-phosphine, always produces a substantial increase of the quadratic hyperpolarizability (e.g., **33** vs **36**). Compared to metallocene based second-order NLO chromophore, σ-acetylide based second-order NLO chromophores, which possess an almost linear M–C≡C–R structure, give rise to a better coupling between the d metal orbitals and the π* system of the σ-acetylide bridge and, hence, to larger second-order nonlinearity (e.g., **24,** $\beta_{1.91}$(EFISH) = 31 × 10^{-30} esu vs **37**). Bimetallic complexes involving σ-acetylide Ru^{II} complexes as donor and the "$W(CO)_5$" fragment as acceptor have also been investigated [19] (see Sect. 3.7).

Vinylidene [11, 145], aryldiazovinylidene [148], and alkenyl [149] species represent parallel families closely related to σ-acetylides. However, their second-order optical nonlinearity is generally lower [11]. Their interest is mostly related to the possibility of switching the NLO properties by virtue of the facile interconvertibility of acetylide and protonated vinylidene pairs via protonation/deprotonation sequences (e.g., **36** vs **39,** $\beta_{1.06}$(HRS) = 441 × 10^{-30} esu; β_0(HRS) = 74 × 10^{-30} esu, for the latter) [145] (Scheme 2).



Scheme 2 Swtiching of second-order NLO response in the acetylide/vinylidene pairs upon protonation/deprotonation sequences

σ-Acetylide Ru^{II} complexes have also been investigated as octupolar and dendrimeric species [144, 150]. Actually, starting from the 1,3,5-substituted aromatic species, e.g., **40**, a variety of octupolar (e.g., **41**, $\sqrt{\langle \beta^2{}_{1.06} \rangle} = 1{,}220 \times 10^{-30}$ esu; $\sqrt{\langle \beta^2{}_{0} \rangle} = 254 \times 10^{-30}$ esu measured by HRS) or dendrimeric (e.g., **42**, $\sqrt{\langle \beta^2{}_{1.06} \rangle} = 1{,}880 \times 10^{-30}$ esu; $\sqrt{\langle \beta^2{}_{0} \rangle} = 350 \times 10^{-30}$ esu measured by HRS) structures have been synthesized and investigated [150]. They involve very large static and dynamic hyperpolarizabilities with an improved efficiency/transparency trade-off for SHG applications (e.g., **37**, $\lambda_{max} = 477$ nm vs **41**, $\lambda_{max} = 459$ nm).



40

R = [Ru](4-C≡C$C_6H_4NO_2$)
[Ru] = *trans*-Ru(dppe)$_2$

41

R = 4-C≡C$C_6H_4NO_2$
[Ru] = tran*s-Ru(*dppe)$_2$

42

Applications of these molecular NLO chromophores, to produce second-order bulk NLO materials or structured films, are very limited. Actually, in spite of their very large molecular hyperpolarizabilities, they exhibit crystalline materials with modest bulk SHG efficiency [11], e.g., the most efficient crystalline material shows a powder efficiency of only eight times that of urea [11], in consequence of the reluctance of acetylide complexes to crystallize in noncentrosymmetric structures.

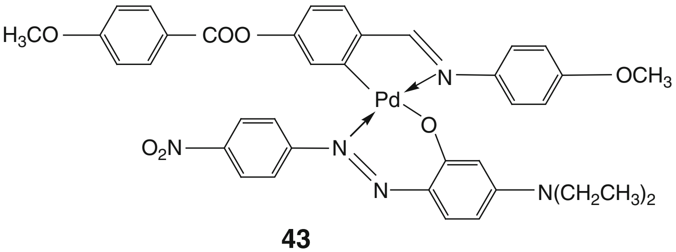
Recently, poled polymer films involving, as guest, a dipolar Fe^{II} σ-acetylide NLO chromophore have shown the traditional temperature-dependent SHG properties [151], while a film of an Ru^{II} oligothienylacetylide NLO chromophore incorporated into a PMMA matrix revealed an acoustically induced SHG signal, reaching values ($\chi^{(2)} = 0.80$ pm V^{-1}) among the highest reported so far for this kind of unusual way to induce SHG [152].

In the last few years, this class of molecular materials has attracted renewed interest by virtue of their remarkable third-order NLO properties [11, 19, 150].

3.5 Cyclometallated Complexes

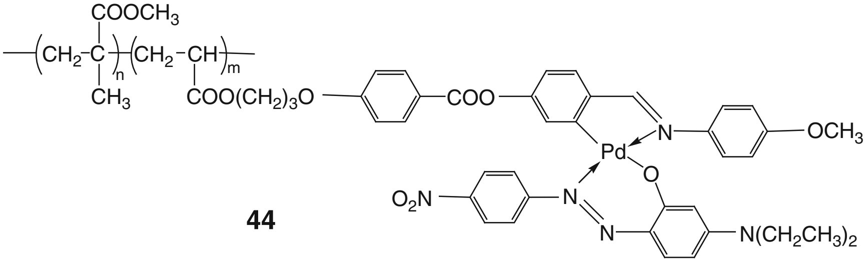
Recently, three classes of cyclometallated complexes have been reported to show interesting second-order NLO properties, therefore opening a novel route for the design of new efficient second-order NLO chromophores.

New orthopalladated NLO chromophores based on a parallel alignment of two different push-pull ligands have been synthesized by Centore et al. [153] and their second-order NLO activity has been measured by the EFISH technique working in $CHCl_3$ with an incident wavelength of 1.907 μm. The maximum value of $\mu\beta_{1.91}$(EFISH) (610×10^{-48} esu) was obtained for the NLO chromophore **43**.



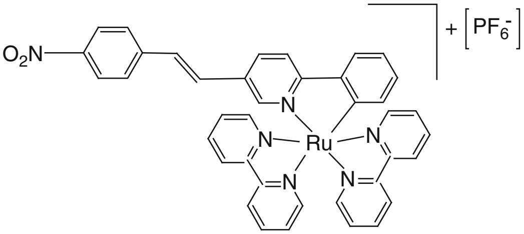
43

Corona-poled thin polymeric films of **44** containing as guests this kind of NLO chromophores are characterized by large macroscopic NLO coefficients d_{33} (25 pm V^{-1}), as determined by means of SHG measurements working with an incident wavelength of 1.064 μm [154].



44

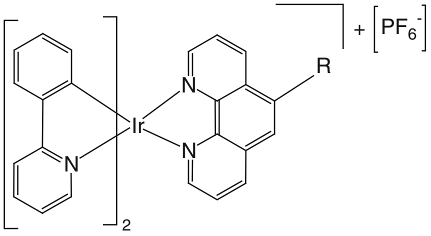
Recently, Labat et al. [155] studied the second-order NLO properties of a new cyclometallated Ru^{II} complex (**45**) for which the HRS technique, working in acetonitrile, gives a β_0(HRS) value of 230 × 10^{-30} esu. In this particular NLO chromophore the Ru^{II} moiety seems to act as the donor group of a push–pull system.



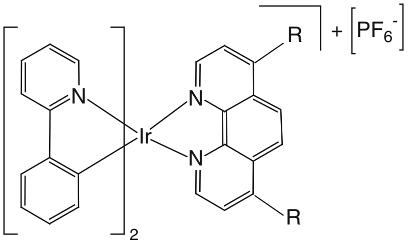
45

Finally, in the last 3 years, ionic cyclometallated Ir^{III} complexes with chelated π-delocalized ligands, such as bipyridines [156, 157] or phenanthrolines [158–160], have shown interesting photoemissive properties with potential applications in electroluminescent devices. Ugo et al. have extended their investigations on the second-order NLO response of these chromophores, such as for instance [Ir(cyclometallated-2-phenylpyridine)$_2$(5-R-1,10-phenanthroline)][PF_6] (R = H, Me, NMe_2, NO_2; **46**) and [Ir(cyclometallated-2-phenylpyridine)$_2$(4-R′,7-R′-1,10-phenanthroline)][PF_6] (R′ = Me, Ph; **47**) [160]. The quadratic hyperpolarizability was measured by the EFISH technique working with a nonresonant 1.907 μm incident λ in a low polarity solvent, like CH_2Cl_2, which allows by ion-pairing the extension of the use of this technique to ionic compounds. These Ir^{III} complexes show a large negative second-order response ($\mu\beta_{1.91}$(EFISH) ranging from −1,270 to −2,230 × 10^{-48} esu). Most notably, they do not show strong absorptions above 450 nm so that a significant SHG may be obtained without a significant cost in transparency. The highest absolute $\mu\beta_{1.91}$(EFISH) value is that of the complex carrying the phenanthroline with the strong electron-withdrawing group NO_2 [161]. A SOS-TDDFT theoretical investigation confirmed that the second-order NLO response of these Ir^{III} NLO chromophores is mainly controlled by the MLCT transition from the HOMOs phenylpyridine-Ir based orbital of the cyclometallated moiety to the

LUMOs π* orbitals of the phenanthroline [161]. Therefore, the second-order NLO response is strongly controlled by the donor or acceptor properties of the substituent on the phenanthroline ligand.



46



47

Substitution of cyclometallated 2-phenylpyridine with the more π-delocalized cyclometallated 2-phenylquinoline does not affect significantly the NLO responses, while a lower NLO response is obtained for the Ir^{III} NLO chromophore with a cyclometallated 3′-(2-pyridyl)-2,2′:5′,2″-terthiophene (ttpy), since the structure of ttpy induces a significant downshift of the HOMO's energy, compared to that of cyclometallated 2-phenylpyridine and 2-phenylquinoline [162].

3.6 Compounds with Macrocyclic Ligands

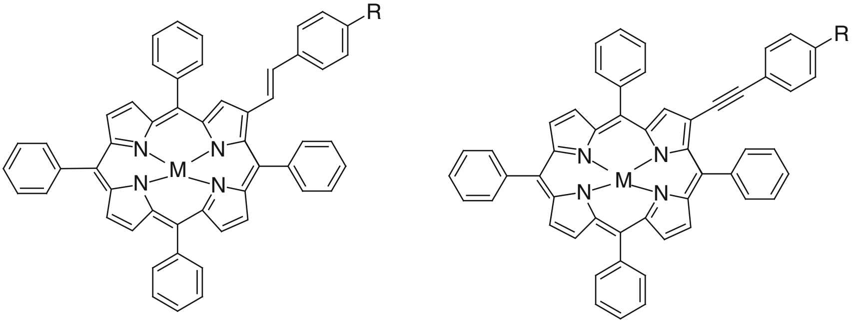
3.6.1 Metalloporphyrins

The macrocyclic structure of porphyrins, consisting of an extended π system formed by four pyrrolic rings connected by methine bridges, is a typical example of a very polarizable architecture with a variety of low lying excited states. Therefore the presence of various substituents in the *meso* or pyrrolic position of the porphyrin ring could produce significant perturbations. These structural features, together with the high chemical and thermal stability, can explain the widespread interest in these chromophores during the last few decades in the area of new optical materials.

Due to the high polarizability of the electronic cloud of the porphyrin ring, a large amount of work has been devoted to third-order NLO responses. For instance, we can refer to some comprehensive reviews [13, 163, 164] for applications based on third-order responses such as optical limiting (OL), for which metalloporphyrins are of great interest, given their tendency to show reverse saturable absorption (RSA) behavior because of their strong absorbing, long-lived triplet excited states and their transparency gap between the intense Soret (B) and Q π−π* absorption bands (in the range 400–500 nm and 600–700 nm, respectively). A certain amount of work has been devoted to two-photon absorption (TPA) responses of asymmetric porphyrinic structures [165]. The aim is not only that of possible applications in OL devices, requiring a high TPA absorption cross section, but also of exploiting their application in the field of photodynamic therapy [166]. In the last two decades a significant amount of work has also been devoted to the investigation of the second-order NLO properties of porphyrin architectures of increasing complexity; a recent review has been partially devoted to this specific area [164].

Taking into account the significant third-order NLO response of the porphyrin ring, when the asymmetric substitution of such a ring is too weak, the determination of the quadratic hyperpolarizability by the EFISH technique can be affected by significant errors because the third-order electronic contribution $\gamma\ (-2\omega; \omega, \omega, 0)$ to γ_{EFISH} cannot be neglected [167].

Pizzotti et al. reported [168] an EFISH investigation, working in $CHCl_3$ solution with a nonresonant incident wavelength of 1.907 μm, on the second-order NLO response of various push–pull tetraphenylporphyrins and their Zn^{II} complexes substituted at the β pyrrolic position by a π-delocalized organic substituent carrying either an electron-withdrawing or electron-donating group (**48**).

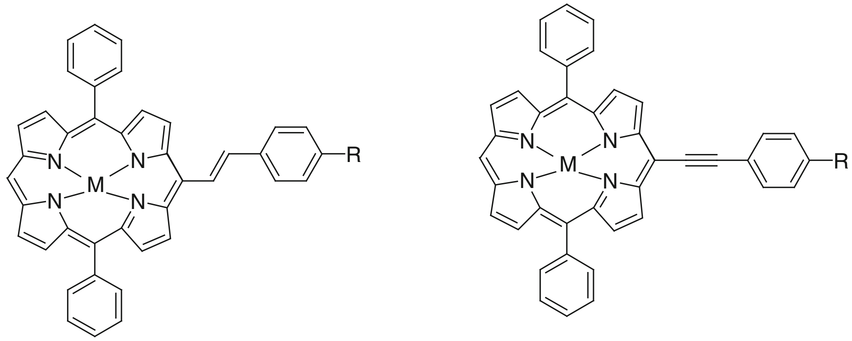


M = H_2, Zn; R = NBu_2, NMe_2, NO_2

48

Interestingly, the porphyrin ring shows in these push-pull NLO chromophores an ambivalent character as donor (due to the high polarizability of its electronic cloud) or as acceptor (due to the presence of various low-lying excited-states). When the substituent is an electron-acceptor group, the porphyrin ring behaves as a significant donor group, comparable to a ferrocenyl group. The value of $\beta_{1.91}$(EFISH) decreases only slightly on going from the free porphyrin to its Zn^{II} complex, in agreement with the assumption that the second-order NLO response is controlled by a CT process, favored by π conjugation, from the occupied π levels of the pyrrolic ring, acting as a push system, to the π* antibonding orbitals of the linker. This latter process should be scarcely affected by coordination of the porphyrin ring to Zn^{II}. In contrast, when the substituent is a strong electron-donor π-system, the $\beta_{1.91}$(EFISH) is not only higher but it increases by complexation to Zn^{II}, as expected for an increased acceptor property.

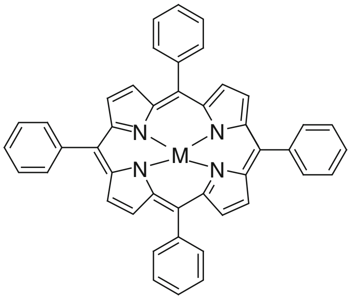
Diphenyl porphyrins and their Zn^{II} complexes substituted in the *meso* position by a π-delocalized substituent carrying an electron-donor or an electron-withdrawing group (**49**) were also investigated by the EFISH technique [169]. These second-order NLO chromophores have confirmed the ambivalent role of the polarizable porphyrin ring, which, in the ground state, already acts as a donor or acceptor, depending on the nature (acceptor or donor) of the substituent in the *meso* position. There is a significant increase of $\beta_{1.91}$(EFISH) for the same π-delocalized substituent carrying an electron-acceptor group, going from the substitution in the *meso* position to that in the β pyrrolic position. When the π-delocalized substituent is carrying an electron-donor group, the position of the substitution (*meso* or β pyrrolic) is influential on the value of $\beta_{1.91}$(EFISH). Interestingly, when the electron-acceptor substituent is in position *meso*, the donor property of the porphyrin ring becomes quite similar to that of the organic strong donor system *trans*-4-$NMe_2C_6H_4CH{=}CH_2$.



M = H_2, Zn; R = NBu_2, NMe_2, NO_2 **49**

A combined electrochemical, HRS and theoretical DFT investigation has also been carried out on *meso*-tetraphenylporphyrin (H_2TPP) and its first transition series metal complexes (MTPP) (**50**) [170].

While neutral MTPP, due to their centrosymmetric structure, have a zero second-order NLO response, the one and two-electron oxidized products of CuTPP and ZnTPP show significant β(HRS) values ($\beta_{1.06}$(HRS) $= 351$ and 371×10^{-30} esu, for $CuTPP^{+}$ and $CuTPP^{++}$; $\beta_{1.06}$(HRS) $= 407$ and 606×10^{-30} esu, for $ZnTPP^{+}$ and $ZnTPP^{++}$), confirmed by TD-DFT calculations. Electrochemical switching of their optical nonlinearity between the neutral and the oxidized forms has been achieved, but its repetition was demonstrated only for the first oxidation step.

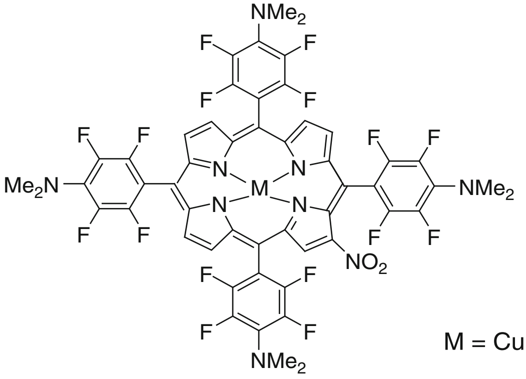


50

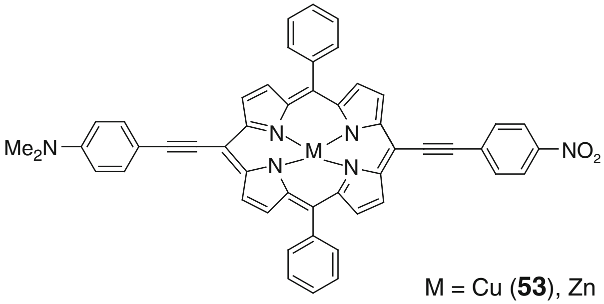
M = H_2, Cr, Mn, Fe, Co, Ni, Cu, Zn

Axial coordination of stilbazoles like 4,4′-*trans* or *trans,trans*-$Me_2N–C_6H_4(CH{=}CH)_nC_5H_4N$ ($n = 1, 2$) to tetraphenylporphyrinates of Zn^{II}, Ru^{II}, and Os^{II} [171] does not produce the increase of the quadratic hyperpolarizability which usually occurs when this kind of stilbazoles coordinates to hard or soft Lewis acid metallic centers (see Sect. 3.1.2). This lack of increase of the second-order NLO response upon axial coordination can be interpreted as being due to a significant axial π backdonation from the d_π orbitals of the metal into the π* antibonding orbitals of the stilbazoles. This effect produces a contribution, opposite to that of σ donation, to the quadratic hyperpolarizability of the stilbazole, thereby giving rise to a balance of the positive (σ−donation) and negative (π-backdonation) effect on the quadratic hyperpolarizability. When 4,4′-*trans*-$F_3C–C_6H_4(CH{=}CH)C_5H_4N$ is axially coordinated, the axial π backdonation becomes very relevant and prevails, thus resulting in a threefold increase of the EFISH quadratic hyperpolarizability. Therefore, the role of the axial π backbonding, when π-delocalized ligands, like stilbazoles, are axially coordinated to metal porphyrinates, causes the metal atoms of porphyrinates to act not only as σ acceptors, but also as π donors according to the nature of the stilbazoles.

From HRS measurements, working in $CHCl_3$ solution with a resonant incident wavelength of 1.064 μm, asymmetric *meso*-tetraaryl-metallo porphyrins such as **51** (Cu^{II}) and **52** (Zn^{II}) [172] have shown a relatively low second-order NLO response ($\beta_{1.06}$(HRS) = 118 and 92 × 10^{-30} esu, respectively) when compared to asymmetric arylethynyl push–pull porphyniric NLO chromophores like **53** (Cu^{II}) and **54** (Zn^{II}) [173] ($\beta_{1.06}$(HRS) = 1,501 and 4,933 × 10^{-30} esu, respectively), for which a very strong coupling between the donor and the acceptor substituents occurs [173]. In this latter case, the porphyrin ring acts mainly as a very polarizable and long π linker. The value of $\beta_{1.06}$ of **54**, deduced from both an absorption and electroabsorption investigation (Stark effect), has been subsequently reported to be lower ($\beta_{1.06}$ = 1,710 × 10^{-30} esu), although still very high [174]. For **55**, carrying a Ni^{II} instead of a Zn^{II} or Cu^{II} metal center, much lower values have been measured by the EFISH technique working in $CHCl_3$ with a nonresonant incident wavelength of 1.907 μm [175]. Similar low values ($\beta_{1.91}$(EFISH) = 66–124 × 10^{-30} esu) of the quadratic hyperpolarizability have been reported for structurally related porphyrin arylethynyl push–pull NLO chromophores measured by EFISH under the same experimental conditions [176]. Such striking differences have suggested that the metal could strongly influence the second-order NLO response of this kind of push-pull NLO chromophores. However, recent theoretical DFT or HF and coupled-perturbed (CP) DFT or HF investigations on the linear and second-order nonlinear properties of **53**, **54** and **55** [177] have shown that their second-order NLO response is barely affected by changing the metal. Moreover, the values of β_0 of **54–55** calculated by CP-HF and CP-DFT level of theory are similar and in the range 61–66 × 10^{-30} esu and 301–327 × 10^{-30} esu, respectively, with $\beta_{1.91}$(CP-HF) values in the range 76–79 × 10^{-30} esu. These are much lower values than those reported for **54**, when measured by HRS working at a resonant incident wavelength of 1.064 μm. The discrepancy of the experimental measurements is probably due to the different incident wavelengths, as confirmed by the comparison of the calculated $\beta_{1.06}$ and $\beta_{1.91}$ values of **54** at HF level of theory, with the former showing a much higher value, as a result of a resonance between the second harmonic (532 nm) and the strong Q band at about 600 nm.

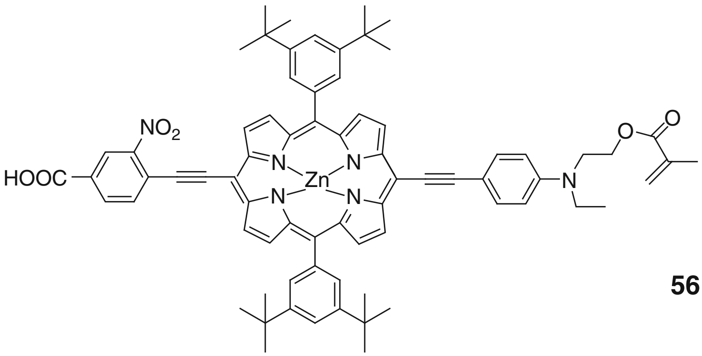


M = Cu (**51**), Zn (**52**)



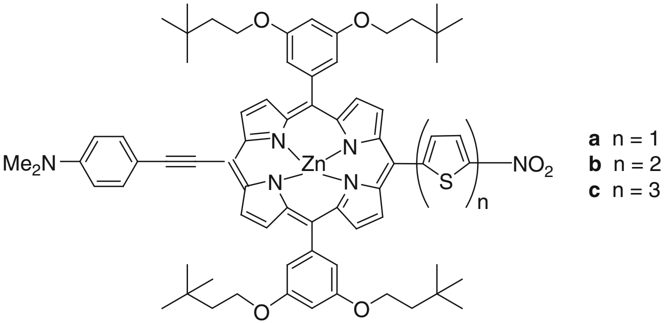
M = Cu (**53**), Zn (**54**), Ni (**55**)

An attempt to link covalently an NLO chromophore structurally related to **54** to a polymeric network has been made by introducing a methacrylate group on the donor part of the molecule and a carboxylic acid function on the acceptor one (**56**) [178]. Copolymerization with glycidyl methacrylate has been successfully carried out, affording a composite polymeric film whose electrooptical properties are under investigation.



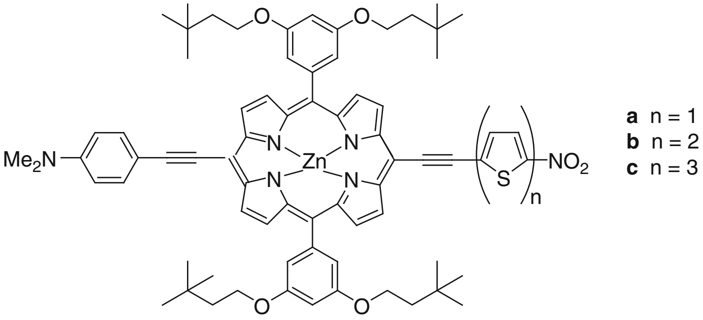
56

In order to improve the second-order NLO response, working at 1.30 μm incident wavelength, new push-pull NLO chromophores based on the porphyrin ring have been synthesized, coupling to the porphyrin ring thiophene or thiazole rings.

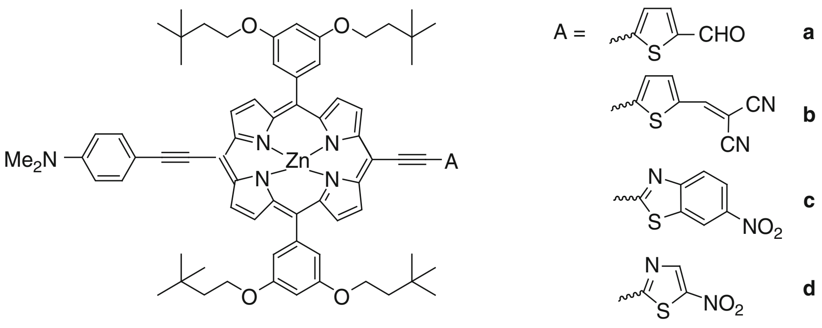


57

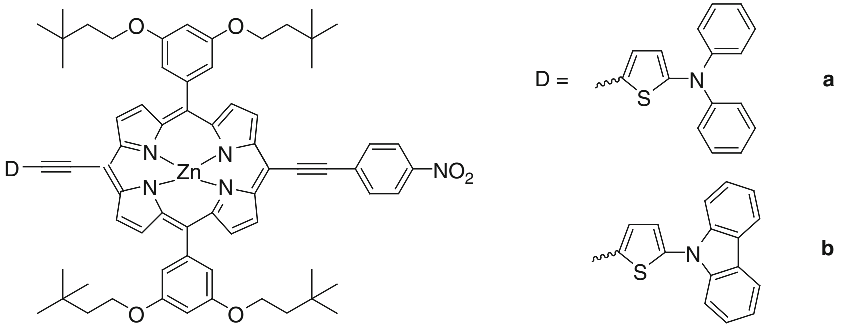
The second-order NLO response of molecular architectures such as **57** and **58** [179] or **59** and **60** [180] (structurally related to **58a**) has been determined by the HRS technique in THF solution. $\beta_{1.30}$(HRS) values from 650 to 4,350 × 10^{-30} esu have been measured for **57** and **58** (the highest value was obtained for **57c**). The lower values of the quadratic hyperpolarizability have been measured when thiophene or oligothiophene units are linked to the porphyrinic core through a C≡C triple bond (**58**). For the NLO chromophores **59** and **60**, $\beta_{1.30}$(HRS) values of about 785–1,400 × 10^{-30} esu have been measured, with **60b** showing the highest value. It must be pointed out, however, that the second harmonic at 0.65 μm (650 nm) is in the region of intense Q absorption bands. Therefore, it is possible that the values of the quadratic hyperpolarizabilities could be affected by a significant enhancement due to resonance effects. A detailed theoretical analysis of the origin of the quadratic hyperpolarizability of these NLO chromophores, which is beyond the scope of this review, can be found in [179] and [180]. In conclusion, chromophores such as **57**–**60** may be interesting for long-wavelength optoelectronic applications.



58



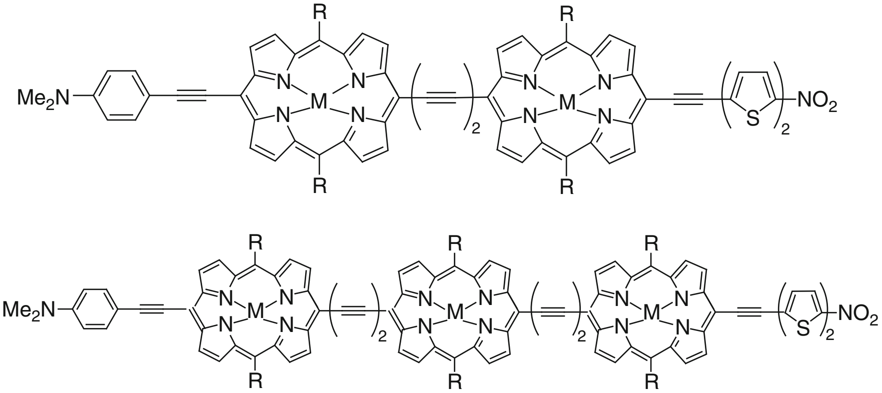
59



60

The effect of the central metal ion on the value of the quadratic hyperpolarizability has been studied for chromophores similar to **58b**, but carrying in the phenyl ring in 5,15 positions a CH_3 instead of a 3,5-bis(3,3-dimethyl-1-butyloxy)phenyl substituent. Metals such as Mg, Co, Ni, Cu, and Zn have been considered [181]. Their quadratic hyperpolarizabilty was theoretically evaluated by semiempirical ZINDO/CV calculations, which have shown that metalloporphyrins, due to significant CT transitions, may display values of the quadratic hyperpolarizability about one order of magnitude higher than that of the free porphyrins. Moreover, by varying the metal atom, an increase of the quadratic hyperpolarizability could be achieved, the highest value being computed for the NLO chromophore with Mg as metal center ($\beta_{1.91} = 1{,}120 \times 10^{-30}$ esu).

In order to investigate how the second-order NLO properties of this kind of NLO chromophores are affected by aggregation of many porphyrin rings, push-pull metalloporphyrins carrying two or three porphyrin rings, such as those reported below (**61**) [182] where the single porphyrin rings are connected by two C≡C triple bonds, have been theoretically investigated.

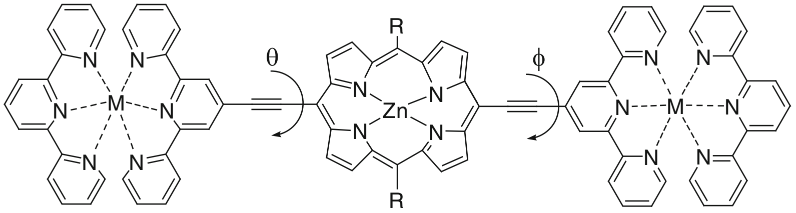


M = Mg, Co, Ni, Cu, Zn
R = CH_3

61

Semiempirical ZINDO/CV calculations have suggested that the quadratic hyperpolarizability of dimers and trimers are about one order of magnitude higher than that of the monomer [182]. A DFT/TDDFT investigation on the NLO chromophores **57b** and **58b** [183] has confirmed an almost planar architecture, which enhances the π-conjugation of the push–pull system and, as a consequence, the quadratic hyperpolarizability.

Structures with a Zn^{II} porphyrin cycle and a $metal^{II}$polypyridyl connected through the 10,20 *meso* position of the porphyrin by a C≡C linker have been studied by HRS working in CH_3CN solution with a 0.80 μm incident wavelength (**62**) [184]. HRS depolarization experiments have shown that the second-order NLO response of these architectures is mainly due to conformers in which the torsional angles between the polypyridyl unit and the porphyrin core are opposite in sign but equivalent in magnitude ($\theta \approx -\phi$). These species can thus be considered as interesting building blocks for nonpolar chiral electrooptic materials.



62

R = C_3F_7, M = Ru, Os

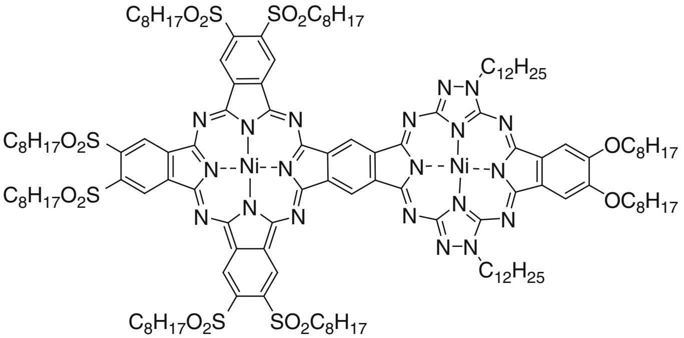
R = 2,6-bis(3,3-dimethylbutyloxy)phenyl, M = Os

3.6.2 Metallophthalocyanines

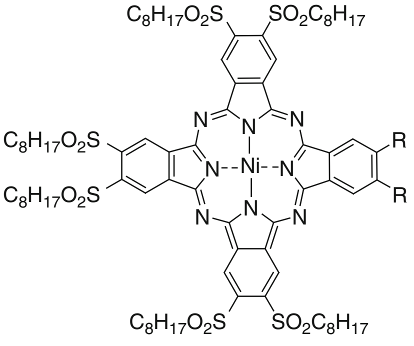
Phthalocyanines are macrocycles characterized by an extensive 2D planar and centrosymmetric 18 π-electron system. For this reason they have been widely investigated as third-order NLO materials and in particular as potential materials for OL; some recent reviews have appeared in this specific field [163, 185, 186]. Only in the last decade have the second-order NLO properties been investigated and some of the reviews reported above describe the first significant results [164, 185]. Hereafter, we will highlight the must relevant results achieved since 2003 in the field of phthalocyanines showing second-order NLO properties.

By means of the EFISH technique, working in $CHCl_3$ with a nonresonant incident wavelength of 1.907 μm, the second-order NLO response of the asymmetric phthalocyanine **63** has been measured and compared to that of phthalocyanines **64** and **65** [187].

The dipole moments of push-pull NLO chromophores **63** and **64a** are exceptionally high (38.8 D and 33.6 D, respectively), while the measured γ(EFISH) values are negative for all of them (γ(EFISH) $= -41.3 \times 10^{-34}$ esu for **64a**;

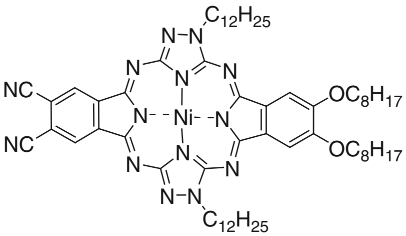


63



R = OC_8H_{17} **a**
R = $SO_2C_8H_{17}$ **b**

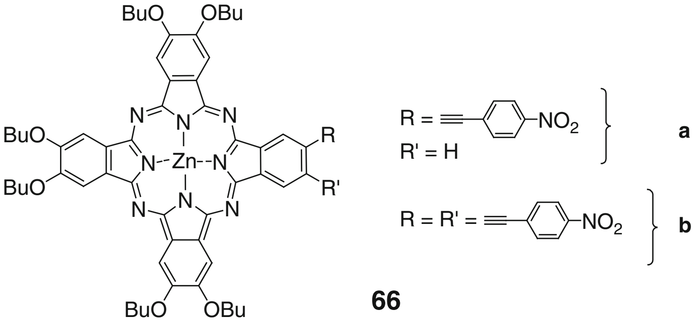
64



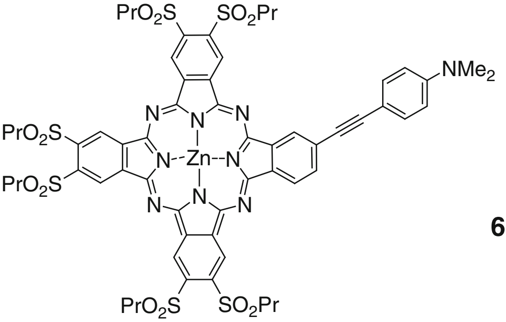
65

γ(EFISH) = −57.4 × 10^{-34} esu for **64b**; γ(EFISH) = −16.8 × 10^{-34} esu for **65**) except for **63** (γ(EFISH) = 5.25 × 10^{-34} esu). The high value found for the centrosymmetric phthalocyanine **64b** clearly shows that, for this kind of second-order NLO chromophores, the electronic contribution γ (−2ω; ω, ω, 0) to the EFISH measurement is significant and cannot be neglected. The comparison between the positive value obtained for **63** and the negative value measured for **64a**, which bears a similar substitution pattern but without a triazolehemiporphyrazine bridge between the donor and the acceptor part of the molecule, suggests a change in the sign of $\Delta\mu_{eg}$.

In a further investigation [188], a new family of substituted push-pull phthalocyanines (**66** and **67**), carrying triple bonds as linkers between the donor and the acceptor groups, has been investigated.



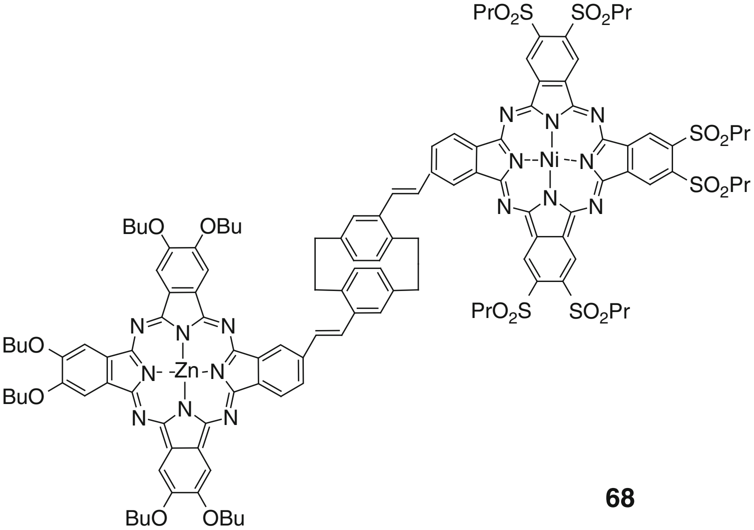
66



67

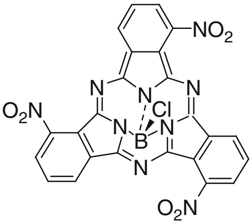
The second-order NLO response of these push–pull NLO chromophores has been measured by means of both EFISH (in $CHCl_3$, working at 1.064 and 1.907 μm incident wavelength) and HRS (working at 1.064 μm incident wavelength) techniques. The largest $\beta_{1.91}$(EFISH) and $\beta_{1.91}$(HRS) values (522 × 10^{-30} esu and 530 × 10^{-30} esu, respectively) were obtained for **66b**, which exhibits the highest degree of dipolar asymmetry. The ethynyl based linker seems, therefore, to be an excellent spacer for enhancing the second-order NLO response of this kind of asymmetric push-pull phthalocyanines.

In order to overcome the nonlinearity transparence trade-off (the lengthening of the π conjugation increases the second-order NLO response of this kind of second-order NLO chromophores, but at the same time decreases their transparency), a bisphthalocyanine, with the CT between the donor and the acceptor guaranteed through space by a [2,2] paracyclophane unit (**68**), has been synthesized [189] and its second-order NLO response measured in $CHCl_3$ by both EFISH and HRS, working at 1.064 μm incident wavelength; a significant value of $\beta_{1.06}$(HRS) (180×10^{-30} esu) was measured.

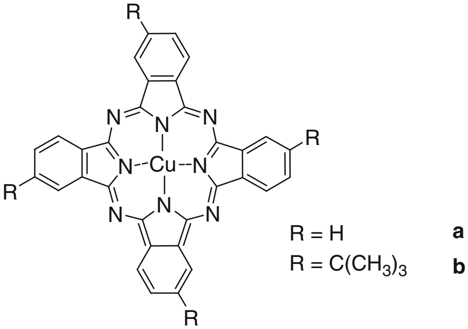


68

Of particular interest for their high second-order NLO response are the intrinsically noncentrosymmetric phthalocyanines analogs called subphthalocyanines. These cone-shaped macrocycles, consisting of three isoindole moieties with a central boron atom coordinated to an axial halogen ligand, have been studied for both their dipolar and their octupolar characters, given that they possess not only a dipole moment along the B-halogen bond, but also an octupolar charge distribution



69



70

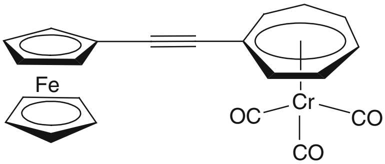
within their three-dimensional aromatic architecture [185]. For instance, the NLO chromophore **69** is characterized by a significant $\beta_{1.34}$(HRS) value (104 × 10^{-30} esu), due to the strong octupolar character of the subphthalocyanine core and to a fair $\gamma_{1.34}$(EFISH) value (17.9 × 10^{-34} esu) corresponding mainly to the dipolar orientational contribution to $\gamma_{1.34}$(EFISH). A fine-tuning of the dipolar and octupolar contributions was reached by varying the substituents of the subphthalocyanine core [190].

The effect of a static electric field on the SHG of the centrosymmetric copper phthalocyanines **70** has been investigated, applying an external d.c. voltage to an Au-phthalocyanine film-Au system that induces a second-order polarization [191]. A SHG signal has also been obtained at the interface of a Langmuir-Blodgett film of **70b**, deposited on a metal-coated glass slide [192] and from a film obtained by vacuum-evaporation of **70a** at a metal electrode interface [193].

3.7 Bimetallic Complexes

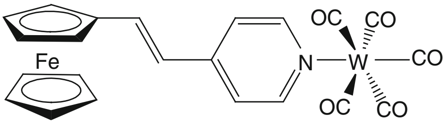
The investigation of the second-order NLO response of asymmetric bimetallic complexes in which the electron-accepting and donating properties of two metal-based fragments are combined has been an area of interest in the past few years [13, 19].

The ferrocenyl moiety has a donor strength comparable to that of a methoxyphenyl group [194]; therefore many bimetallic complexes containing a ferrocenyl moiety linked via a π-delocalized bridge to another organometallic fragment, acting as acceptor group, have been investigated [13, 19]. For example, when η^7-cycloheptatrienyltricarbonylchromium is used as acceptor group, a high quadratic hyperpolarizability has been measured by HRS (**71**, $\beta_{1.06}$(HRS) = 570 × 10^{-30} esu) [195].

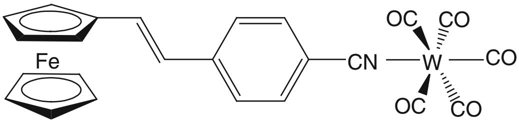


71

The "$W(CO)_5$" fragment, which can behave as donor or acceptor in monometallic NLO chromophores (see Sect. 3.1), appeared as an efficient acceptor group in these NLO chromophores with ferrocene as donor. For example, the $\beta_{1.06}$(HRS) value of *trans*-(1-ferrocenyl-2-(4-pyridyl)ethylene] increases by a factor of about 5 upon coordination to "$W(CO)_5$" (**72**, $\beta_{1.06}$(HRS) = 101 × 10^{-30} esu). The EF is less significant when changing the metal and it decreases in the order "$W(CO)_5$" > "$Mo(CO)_5$" >"$Cr(CO)_5$," probably due to the higher π-backdonation of the electron *d* density in the case of W, if compared to Cr and Mo [196]. Interestingly, no significant EF is observed upon coordination of the pyridyl ligand to "$Re(CO)_3Br$" [197]. As expected, an increase in the conjugation length of the linker, for instance by insertion of a vinylenephenylene between the ethylene and the ferrocenyl, results in higher $\beta_{1.06}$(HRS) values (for *trans,trans*-(η^5-C_5H_5)Fe {η^5-$C_5H_4CH{=}CHC_6H_4CH{=}CH$–$C_5H_4N$–$W(CO)_5$, 535 × 10^{-30} esu [120]). Coordination of *trans*-[1-ferrocenyl-2-(4-cyanophenyl)ethylene] to "$W(CO)_5$" (**73**) also leads to an enhancement of the $\beta_{1.06}$(HRS) value (by a factor of 3.6; $\beta_{1.06}$(HRS) = 375 × 10^{-30} esu), less significant than that of the related ferrocenyl system based on the donor pyridine ligand (**72**) [196].



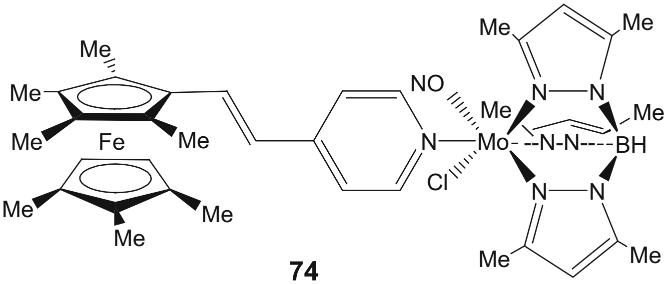
72



73

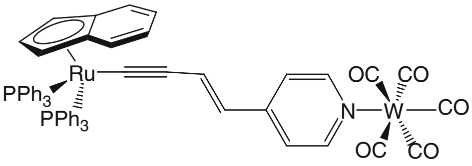
Various bimetallic complexes with ferrocenyl as electron-donor group linked via a π-delocalized system and pyridine coordination to electron-deficient "Mo^{II}(NO) Tp*X" (Tp* = tris(3,5-dimethylpyrazolyl)borate; X = Cl, Br, I) or "$W(CO)_5$" centers have been studied by McCleverty et al. [132]. For example, the complex **74** is characterized by a $\beta_{1.06}$(HRS) value of 205 × 10^{-30} esu. Although the measured HRS data are resonance enhanced, the $\beta_{1.06}$(HRS) trends imply the following conclusions: (1) the quadratic hyperpolarizability increases when the ligand Cl^- or Br^- is replaced by I^-, which is reasonable in the light of the more substantial polarizability of I^- when compared with Cl^- and Br^-; (2) methylation of ferrocene increases its electron-donor ability; and (3) the electron-accepting abilities of the "Mo^{II}(NO)Tp*Cl" and "$W(CO)_5$" moieties are similar. Furthermore, chemical oxidation of the ferrocenyl donor group or chemical reduction of the molybdenum nitrosyl acceptor fragment in selected NLO chromophores caused a reduction of between 25% and 100% of the NLO response, therefore allowing redox-induced switching of the NLO responses [132].

Jayaprakash et al. [198] reported the series of push–pull bimetallic polyene complexes $[(CO)_5M{=}C(OCH_3)(–CH{=}CH–)_n(\eta^5C_5H_4)Fe(\eta^5C_5H_5)]$ (M = W, Cr; n = 1–4) with ferrocene as donor and a carbene complex of Cr or W as acceptor. The $\beta_{1.06}$(HRS) values increase with increasing the conjugation of the π linker; for the same π linker, the chromophore based on W exhibits higher second-order NLO responses than that based on Cr, as expected for a more efficient π backdonation from the W atom. The quadratic hyperpolarizability of these bimetallic push-pull polyene NLO chromophores exhibits significant solvent polarity dependence, suggesting a CT from the ferrocene donor to the carbene acceptor along the polyene backbone with significant $\Delta\mu_{eg}$. The highest $\beta_{1.06}$(HRS) value (780 and 2,420 × 10^{-30} esu, in hexane and acetonitrile, respectively) was reached for the NLO chromophore with $M = W$ and $n = 4$.

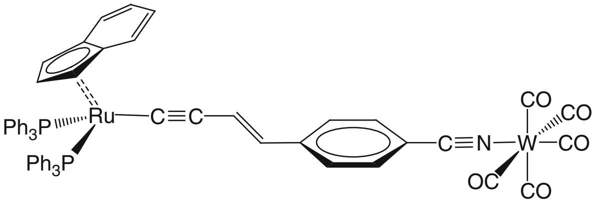


74

In this kind of bimetallic chromophores, another efficient electron-donor group is a ruthenium σ-acetylide complex [13, 19] which can lead to large $\beta_{1.06}$(HRS) values (535 and 700 × 10^{-30} esu for **75** and **76**, respectively [199]). Comparison with complexes **72** and **73** confirms that a ruthenium σ-acetylide complex is a better donor than the 1-ferrocenyl-ethylene moiety. In all these NLO chromophores, "$W(CO)_5$" is an efficient acceptor group, better than "$Cr(CO)_5$" [199].

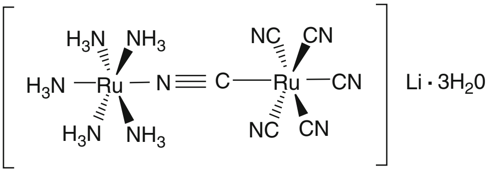


75



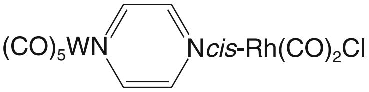
76

Significant quadratic hyperpolarizabilities for two mixed-valence bimetallic complexes have also been reported [13, 19]; for example complex **77** is characterized by a $\beta_{1.06}$(Stark) of 37 × 10^{-30} esu [200]. In such NLO chromophores, the electron-accepting d^5 Ru^{III} center is stabilized by strongly basic amine ligands, whilst the electron-donating d^6 Ru^{II} is stabilized by π-accepting cyanides.

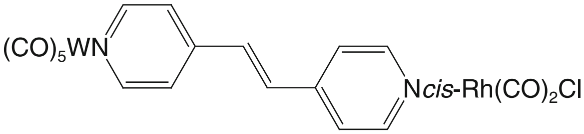


77

The second-order NLO response of a class of asymmetric push–pull bimetallic complexes, organometallic counterpart of classical push–pull aromatic chromophores, having pyrazine (pyz) and *trans*-1,2-bis(4-pyridyl)ethylene (bpe) as π-polarizable linkers between a metal carbonyl fragment acting as donor group (“$W(CO)_5$”) and a metal carbonyl fragment acting as acceptor group (e.g., “*cis*-$Rh(CO)_2Cl$”), was investigated [201]. Coordination of $(CO)_5W$(pyz, or bpe) to “*cis*-$Rh(CO)_2Cl$” leads to an increase of the absolute value of the quadratic hyperpolarizability ($\beta_{1.91}$(EFISH) = -33 and -41×10^{-30} esu, for **78** and **79**, respectively), dominated by a red-shift of the MLCT ($W^0 \rightarrow \pi^*$) transition of the $W(CO)_5$(pyz or bpe) moiety, due to the stabilization by interaction with the “*cis*-$Rh(CO)_2Cl$” acceptor group of the π* acceptor orbitals of the pyz or bpe bridge [201].



78

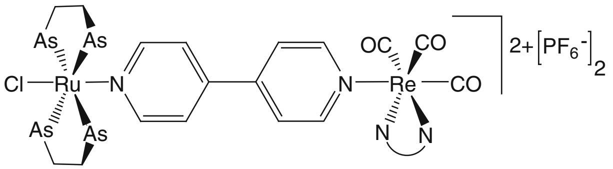


79

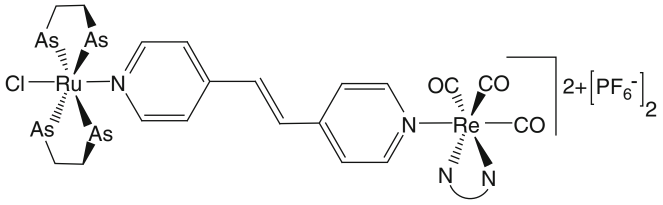
The CT is in the direction opposite to that of the ground state dipole moment, leading to a negative quadratic hyperpolarizability. In these NLO chromophores, the MLCT process ($W^0 \rightarrow \pi^*$), dominating the NLO response, remains localized on the part of the π bridge close to the push donor center (“$W(CO)_5$”) even after coordination at the other end of the bridge of a metallic center acting as pull acceptor center. Therefore, the electronic process controlling the second-order NLO response never assumes a MMCT (metal-to-metal CT) character, with the CT process involving both the donor and acceptor metal centers via the polarizable π bridge as it occurs between the donor and acceptor groups in structurally related classical push-pull aromatic 1D chromophores. In accordance, in these bimetallic NLO chromophores the quadratic hyperpolarizability is not strongly influenced by increasing the length of the π-delocalized bridge between the push and pull groups, while in structurally related organic π-delocalized push–pull 1D chromophores the second-order NLO response increases by increasing the length of the π-delocalized bridge [60, 61]. Consequently the value of $\beta_{1.91}$(EFISH) of **78** is, as absolute value, higher than that of *para*-nitro dimethyl aniline (12×10^{-30} esu), whereas that of **79** is lower than that of *trans*-4-dimethylamino, 4-nitro stilbene (73×10^{-30} esu) [201]. Theoretical TD-DFT and TD-HF calculations have confirmed such a view of the origin of the second-order NLO response in these push–pull NLO chromophores [202].

An interesting effect due to metal–metal bonding was studied in the case of bimetallic NLO chromophores such as [(CO)$_3$(1,10-phenanthroline)W-*fac*-MCO)$_3$Cl$_2$] (M = Ru^{II}, Os^{II}) and [(CO)$_3$(1,10-phenanthroline)W-*cis*-MCO)$_2$Cl] (M = Rh^{I}, Ir^{I}) which show an increased negative second-order NLO response ($\beta_{1.91}$(EFISH) from -25.8×10^{-30} up to -76×10^{-30} esu), the best value being measured for the Os^{II} derivative. The increase of the absolute value of the second-order NLO response when compared to that of the monometallic NLO chromophore [W(CO)$_4$(1,10-phenanthroline)] ($\beta_{1.91}$(EFISH) = -13×10^{-30} esu) is due, as shown by a solvatochromic investigation, to the additional negative contribution produced by a new absorption band involving the W(CO)$_3$(1,10-phenanthroline) moiety at around 385–450 nm, in addition to the contribution of the MLCT (W^{0}→π*phen) absorption band at around 499–526 nm, typical of [W(CO)$_3$(1,10-phenanthroline)L] (L = CO, CH$_3$CN) [203].

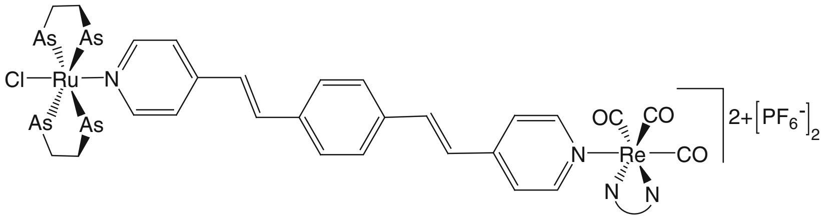
Recently Coe et al. synthesized some new push–pull bimetallic complexes with *trans*-[Ru^{II}Cl(pdma)$_2$]$^+$ (pdma = 1,2-phenylenebis(dimethylarsine)) as electron-donor group, linked via a π-conjugated bridging ligand to *fac*-[Re^{I}(biq)(CO)$_3$]$^+$ (biq = 2,2′-biquinolinyl) as electron-acceptor group [204]. The bridging units were 4,4′-bipyridyl (4,4′-bpy; **80**), *trans*-1,2-bis(4-pyridyl)ethylene (bpe; **81**), or 1,4-bis [*trans*-2-(4-pyridyl)ethenyl]benzene (bpvb; **82**). The electronic absorption spectra of these bimetallic species are dominated by intense and opposite Ru^{II}→π*(4,4′-bpy/bpe/bpvb) and Re^{I}→π*(biq) MLCT transitions. Cyclic voltammetric studies reveal both Ru$^{III/II}$ oxidation and ligand-based reduction processes and show no evidence for significant electronic communication between the two metal centers. Stark spectroscopic studies on the MLCT bands show that extending the π conjugation of the linker leads to an increase of the dipole moment change ($\Delta\mu_{eg}$) and of the transition dipole moment (r_{eg}). These effects combine to afford an increase of the static quadratic hyperpolarizabilities, β_0, estimated by applying the “two level” model (β_0(Stark) = 47, 114 and 122×10^{-30} esu, for **80**, **81**, and **82**, respectively). Comparisons with monometallic Ru^{II} complexes reveal that methylation of the free pyridyl nitrogen, to generate a pyridinium center, leads to larger β_0 responses (β_0(Stark) = 113, 123, and 131×10^{-30} esu, for the alkylated monometallic Ru^{II} complex with 4,4′-bpy, bpe, or bpvb, respectively) than does coordination to the *fac*-[Re^{I}(biq)(CO)$_3$]$^+$ center. The outcome can be attributed to the evidence that the Re^{I} moiety is a weaker net electron-acceptor. In fact, it is a Lewis acceptor but it also behaves as a π donor, and this offsets partially its electron-withdrawing effect. In contrast, an *N*-methylpyridinium group does not possess such an ambivalent electronic behavior [204].



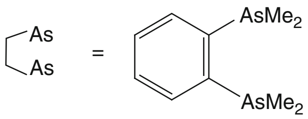
80

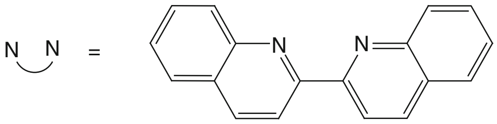


81



82





As evidenced from these examples, the introduction of two metal centers as donor and acceptor groups in a push–pull NLO chromophore can allow tuning of the electronic properties for a better second-order NLO response, affording relatively large quadratic hyperpolarizabilities.

4 Conclusions and Perspectives

This short and not exhaustive overview illustrates the actual level of the control of the structure – second-order NLO activity relationship in organometallic or coordination compounds and therefore their potentiality as second-order NLO chromophores.

Many coordination or organometallic compounds with various ligands such as substituted stilbazoles, bipyridines, phenanthrolines, terpyridines, Schiff bases, alkynyl and vinylidene ligands, metallocenes, or macrocycles such as metalloporphyrins, metallophthalocyanines, or the new emerging class of cationic cyclometalated or of bimetallic coordination complexes, have been investigated as second-order NLO chromophores in the last 10 years. They are characterized by rather large β_λ(HRS), $\mu\beta_\lambda$(EFISH), or $\mu\beta_0$(EFISH) values which can be favorably compared with that of the prototypical organic 1D push-pull NLO chromophore Disperse Red One (*trans*-4,4′-$O_2NC_6H_4N{=}NC_6H_4NEt{-}(CH_2CH_2OH)$, $\mu\beta_0$(EFISH) $= 450 \times 10^{-48}$ esu) currently proposed for electrooptic polymeric poled films [205, 206]. Moreover, a variety of push-pull Ru^{II} ammine salts and of octupolar metal (in particular of Ru^{II}) complexes, recently studied, are characterized by large static quadratic hyperpolarizabilities, as determined by HRS.

It appears from this overview that the interaction with a metal center represents a flexible way to tune the second-order NLO response of organic NLO chromophores acting as ligands. By the modulation of the electronic nature and the oxidation state of the metal and of its coordination sphere through ancillary ligands or chelation, such a response can not only be increased, sometimes in a very significant way, but its sign can also be changed. Besides, the metal may act as template for the stabilization of octupolar D_3 and D_{2d} structures, based on various chelated organic ligands, or of asymmetric Schiff-bases complexes, producing second-order NLO chromophores, either octupolar or dipolar, with significant and tunable second-order NLO response. Finally, it is possible to produce bimetallic push-pull NLO chromophores where metal based moieties, acting as donor or acceptor groups, are connected by a π organic linker. In these cases, there are significant differences with the corresponding traditional push–pull organic NLO chromophores about the general trends and the origin of the quadratic hyperpolarizability. The metal can also act as a bridge, thus permitting electron-transfer processes between various sites of its coordination sphere such as in some push–pull metal porphyrins or Schiff bases complexes and in the new cyclometallated chromophores. The great potentiality of TD-DFT, CP-DFT, and CP-HF theoretical approaches has recently given a way to understand better the electronic origin of the second-order NLO response of many NLO chromophores based on metal complexes or organometallic compounds. These useful theoretical tools may allow today the design of new and efficient coordination and organometallic second-order NLO chromophores.

Sufficiently large second-order NLO responses have already been achieved; therefore the research now hinges also on considerations such as thermal and chemical stability and multifunctionality (for example, combining second-order NLO response with emission or magnetic properties). Nanoorganization of second-order NLO chromophores based on metal complexes or organometallic compounds, for example in Langmuir–Blodgett films or in polymeric electrically poled films, has been investigated but is still under study in order to reach large and stable in time SHG. In the last few years, increasing effort has also been dedicated to achieve the switching of the second-order NLO response, for example by redox-induced switching or photo-switching controlled by the metal.

Therefore, metal complexes and organometallic compounds are attractive not only for their interesting second-order NLO properties but also for their potentiality as multifunctional materials. Up to now, however, no stable and efficient nanostructured materials or electro-optical devices based on coordination and organometallic compounds have reached the stage of real applications and commercialization. But this is normal for a relatively young field of research, of which almost all scientific contributions have appeared in the last two decades. In any case, given the rapid progress made over recent years, future prospects for applications seem possible.

Acknowledgements We sincerely thank Dr Lea Vaiana for assistance in drawing various figures, the Ministero dell'Istruzione, dell'Università e della Ricerca (Progetto FIRB 2003 RBNE03-3KMA Molecular compounds and hybrid nanostructured materials with resonant and non resonant optical properties for photonic devices) and the Centro Nazionale delle Ricerche (PROMO 2006 Nanostrutture organiche, organometalliche, polimeriche ed ibride: ingegnerizzazione supramolecolare delle proprietà fotoniche dispositivistiche innovative per optoelettronica) for financial support.

References

1. Prasad NP, Williams DJ (1991) Introduction to nonlinear optical effects in molecules and polymers. Wiley, New York
2. Zyss J (1994) Molecular nonlinear optics: materials, physics and devices. Academic, Boston
3. Roundhill DM, Fackler JP Jr (eds) (1999) Optoelectronic properties of inorganic compounds. Plenum, New York
4. Green MLH, Marder SR, Thompson ME, Bandy JA, Bloor D, Kolinsky PV, Jones RJ (1987) Nature 330:360–362
5. See for example Nalwa HS (1991) Appl Organomet Chem 5:349–377
6. Marder SR (1992) In: Bruce DW, O'Hare D (eds) Inorganic materials. Wiley, New York, pp 115–164
7. Long NJ (1995) Angew Chem Int Ed Engl 34:21–38
8. Whittall IR, McDonagh AM, Humphrey MG, Samoc M (1998) Adv Organomet Chem 42:291–362
9. Heck J, Dabek S, Meyer-Friedrichsen T, Wong H (1999) Coord Chem Rev 190/192:1217–1254
10. Le Bozec H, Renouard T (2000) Eur J Inorg Chem 229–239
11. Powell CE, Humphrey MG (2004) Coord Chem Rev 248:725–756
12. Di Bella S (2001) Chem Soc Rev 30:355–366
13. Coe BJ (2004) In: McCleverty JA, Meyer TJ (eds) Comprehensive coordination chemistry II. Elsevier, Oxford, pp 621–687
14. Coe BJ, Curati NRM (2004) Comments Inorg Chem 25:147–184
15. Maury O, Le Bozec H (2005) Acc Chem Res 38:691–704
16. Cariati E, Pizzotti M, Roberto D, Tessore F, Ugo R (2006) Coord Chem Rev 250:1210–1233
17. Coe BJ (2006) Acc Chem Res 39:383–393
18. Coe BJ (2006) In: Papadopoulos MG (eds) Non-linear optical properties of matter. Springer, Berlin Heidelberg New York, pp 571–608

19. Humphrey MG, Samoc M (2008) Adv Organomet Chem 55:61–136
20. Oudar JL, Chemla DS (1977) J Chem Phys 66:2664–2668
21. Oudar JL (1977) J Chem Phys 67:446–457
22. Kanis DR, Ratner MA, Marks TJ (1994) Chem Rev 94:195–242
23. Marques MAL, Gross EKU (2004) Annu Rev Phys Chem 55:427–455
24. Ledoux I, Zyss J (1982) Chem Phys 73:203–213
25. Maker PD (1970) Phys Rev A 1:923–951
26. Clays K, Persoons A (1991) Phys Rev Lett 66:2980–2983
27. Zyss J, Ledoux I (1994) Chem Rev 94:77–105
28. Bruni S, Cariati F, Cariati E, Porta FA, Quici S, Roberto D (2001) Spectrochim Acta A 57:1417–1426
29. Liptay W (1974) Dipole moments and polarizabilities of molecules in excited electronic states. In: Lim EC (ed) Excited states. Academic, New York, pp 129–229
30. Bublitz GU, Boxer SG (1997) Annu Rev Phys Chem 48:213–242
31. Willetts A, Rice JE, Burland DM, Shelton DP (1992) J Chem Phys 97:7590–7599
32. Di Bella S (2002) New J Chem 26:495–497
33. Kurtz SK, Perry TJ (1968) J Appl Phys 39:3798–3813
34. Coe BJ, Chadwick G, Houbrechts S, Persoons A (1997) J Chem Soc Dalton Trans 1705–1711
35. Coe BJ, Chamberlain MC, Essex-Lopresti JP, Gaines S, Jeffery JC, Houbrechts S, Persoons A (1997) Inorg Chem 36:3284–3292
36. Coe BJ, Essex-Lopresti JP, Harris JA, Houbrechts S, Persoons A (1997) Chem Commun 1645–1646
37. Coe BJ, Harris JA, Harrington LJ, Jeffery JC, Rees LH, Houbrechts S, Persoons A (1998) Inorg Chem 37:3391–3399
38. Coe BJ, Harris JA, Asselberghs I, Persoons A, Jeffery JC, Rees LH, Gelbrich T, Hursthouse MB (1999) J Chem Soc Dalton Trans 3617–3625
39. Houbrechts S, Asselberghs I, Persoons A, Coe BJ, Harris JA, Harrington LJ, Essex-Lopresti JP (1999) Mol Cryst Liq Cryst Sci Tech B Nonlinear Opt 22:161–164
40. Houbrechts S, Asselberghs I, Persoons A, Coe BJ, Harris JA, Harrington LJ, Chamberlain MC, Essex-Lopresti JP, Gaines S (1999) Proc SPIE Int Soc Opt Eng 3796:209–218
41. Coe BJ, Harris JA, Brunschwig BS (2002) J Phys Chem A 106:897–905
42. Coe BJ, Jones LA, Harris JA, Sanderson EE, Brunschwig BS, Asselberghs I, Clays K, Persoons A (2003) Dalton Trans 2335–2341
43. Asselberghs I, Houbrechts S, Persoons A, Coe BJ, Harris JA (2001) Synth Met 124:205–207
44. Coe BJ, Houbrechts S, Asselberghs I, Persoons A (1999) Angew Chem Int Ed 38:366–369
45. Coe BJ (1999) Chem Eur J 5:2464–2471
46. Lin C-S, Wu K-C, Snijders JG, Sa R-J, Chen X-H (2002) Acta Chim Sinica 60:664–668
47. Coe BJ, Harris JA, Clays K, Persoons A, Wostyn K, Brunschwig BS (2001) Chem Commun 1548–1549
48. Coe BJ, Jones LA, Harris JA, Brunschwig BS, Asselberghs I, Clays K, Persoons A (2003) J Am Chem Soc 125:862–863
49. Coe BJ, Jones LA, Harris JA, Brunschwig BS, Asselberghs I, Clays K, Persoons A, Garín J, Orduna J (2004) J Am Chem Soc 126:3880–3891
50. Coe BJ, Harris JA, Brunschwig BS, Garín J, Orduna J, Coles SJ, Hursthouse MB (2004) J Am Chem Soc 126:10418–10427
51. Coe BJ, Jones LA, Harris JA, Asselberghs I, Wostyn K, Clays K, Persoons A, Brunschwig BS, Garín J, Orduna J (2003) Proc SPIE Int Soc Opt Eng 5212:122–136
52. Sortino S, Petralia S, Conoci S, Di Bella S (2003) J Am Chem Soc 125:1122–1123
53. Sortino S, Di Bella S, Conoci S, Petralia S, Tomasulo M, Pacsial EJ, Raymo FM (2005) Adv Mater 17:1390–1393
54. Di Bella S, Sortino S, Conoci S, Petralia S, Casilli S, Valli L (2004) Inorg Chem 43:5368–5372

55. Boubekeur-Lecaque L, Coe BJ, Clays K, Foerier S, Verbiest T, Asselberghs I (2008) J Am Chem Soc 130:3286–3287
56. Kanis DR, Lacroix PG, Ratner MA, Marks TJ (1994) J Am Chem Soc 116:10089–10102
57. Cheng LT, Tam W, Meredith GR, Marder SR (1990) Mol Cryst Liq Cryst 189:137–153
58. Cheng LT, Tam W, Eaton DF (1990) Organometallics 9:2856–2857
59. Roberto D, Ugo R, Bruni S, Cariati E, Cariati F, Fantucci PC, Invernizzi I, Quici S, Ledoux I, Zyss J (2000) Organometallics 19:1775–1788
60. Cheng LT, Tam W, Stevenson SH, Meredith GR, Rikken G, Marder SR (1991) J Phys Chem 95:10631–10643
61. Cheng LT, Tam W, Marder SR, Stiegman AE, Rikken G, Spangler CW (1991) J Phys Chem 95:10643–10652
62. Lucenti E, Cariati E, Dragonetti C, Manassero L, Tessore F (2004) Organometallics 23:687–692
63. Roberto D, Ugo R, Tessore F, Lucenti E, Quici S, Vezza S, Fantucci PC, Invernizzi I, Bruni S, Ledoux-Rak I, Zyss J (2002) Organometallics 21:161–170
64. Tessore F, Roberto D, Ugo R, Mussini P, Quici S, Ledoux-Rak I, Zyss J (2003) Angew Chem 115:472–475
65. Tessore F, Roberto D, Ugo R, Mussini P, Quici S, Ledoux-Rak I, Zyss J (2003) Angew Chem Int Ed Engl 42:456–459
66. Tessore F, Locatelli D, Righetto S, Roberto D, Ugo R, Mussini P (2005) Inorg Chem 44:2437–2442
67. Calabrese JC, Tam W (1987) Chem Phys Lett 133:244–245
68. Bourgault M, Mountassir C, Le Bozec H, Ledoux I, Pucetti G, Zyss J (1993) J Chem Soc Chem Commun 1623–1624
69. Bourgault M, Baum K, Le Bozec H, Pucetti G, Ledoux I, Zyss J (1998) New J Chem 517–522
70. Hilton A, Renouard T, Maury O, Le Bozec H, Ledoux I, Zyss J (1999) Chem Commun 2521–2522
71. Aubert V, Guerchais V, Ishow E, Hoang-Thy K, Ledoux I, Nakatani K, Le Bozec H (2008) Angew Chem Int Ed 47:577–580
72. Coe BJ, Harris JA, Jones LA, Brunschwig BS, Song K, Clays K, Garin J, Orduna J, Coles SJ, Hursthouse MB (2005) J Am Chem Soc 127:4845–4859
73. Cummings SD, Cheng LT, Eisenberg R (1997) Chem Mater 9:440–450
74. Base K, Tierney MT, Fort A, Muller J, Grinstaff MW (1999) Inorg Chem 38:287–289
75. Das S, Jana A, Ramanathan V, Chakraborty T, Ghosh S, Das PK, Bharadwaj PK (2006) J Organomet Chem 691:2512–2516
76. Maury O, Le Bozec H (2005) Acc Chem Res 38:691–704
77. Dhenaut C, Ledoux I, Samuel IDW, Zyss J, Bourgault M, Le Bozec H (1995) Nature 374:339–342
78. Le Bozec H, Renouard T, Bourgault M, Dhenaut C, Brasselet S, Ledoux I, Zyss J (2001) Synth Met 124:185–189
79. Vance FW, Hupp JT (1999) J Am Chem Soc 121:4047–4053
80. Feuvrie C, Ledoux I, Zyss J, Le Bozec H, Maury O (2005) C R Chimie 8:1243–1248
81. Le Bozec H, Renouard T (2000) Eur J Inorg Chem 229–239
82. Maury O, Viau L, Senechal K, Corre B, Guegan JP, Renouard T, Ledoux I, Zyss J, Le Bozec H (2004) Chem Eur J 10:4454–4466
83. Le Bouder T, Maury O, Le Bozec H, Ledoux I, Zyss J (2001) Chem Commun 2430–2431
84. Le Bozec H, Le Bouder T, Maury O, Bondon A, Ledoux I, Deveau S, Zyss J (2001) Adv Mater 13:1677–1681
85. Le Bozec H, Le Bouder T, Maury O, Ledoux I, Zyss J (2002) J Opt A Pure Appl Opt 4: S189–S196
86. Le Bouder T, Maury O, Bondon A, Costuas K, Amouyal E, Ledoux I, Zyss J, Le Bozec H (2003) J Am Chem Soc 125:12284–12299

87. Viau L, Bidault S, Maury O, Brasselet S, Ledoux I, Zyss J, Ishow E, Nakatany K, Le Bozec H (2004) J Am Chem Soc 126:8386–8387
88. Bidault S, Viau L, Maury O, Brasselet S, Zyss J, Ishow E, Nakatany K, Le Bozec H (2006) Adv Funct Mater 16:2252–2262
89. Coe BJ, Harris JA, Brunschwig BS, Asselberghs I, Clays K, Garn J, Orduna J (2005) J Am Chem Soc 127:13399–13410
90. Roberto D, Tessore F, Ugo R, Bruni S, Manfredi A, Quici S (2002) Chem Commun 846–847
91. Uyeda HT, Zhao Y, Wostyn K, Asselberghs I, Clays K, Persoons A, Therien MJ (2002) J Am Chem Soc 124:13806–13813
92. Tessore F, Roberto D, Ugo R, Pizzotti M, Quici S, Cavazzini M, Bruni S, De Angelis F (2005) Inorg Chem 44:8967–8978
93. De Angelis F, Fantacci S, Sgamellotti A, Cariati F, Roberto D, Tessore F, Ugo R (2006) Dalton Trans 852–859
94. Locatelli D, Quici S, Righetto S, Roberto D, Tessore F, Ashwell GJ, Amiri M (2005) Prog Solid State Chem 33:223–232
95. Sénéchal-David K, Hemeryck A, Tancrez N, Toupet L, Williams JAG, Ledoux I, Zyss J, Boucekkine A, Guégan JP, Le Bozec H, Maury O (2006) J Am Chem Soc 128:12243–12255
96. Di Bella S, Fragalà I, Ledoux I, Diaz-Garcia MA, Marks TJ (1997) J Am Chem Soc 119:9550–9557
97. Lacroix PG (2001) Eur J Inorg Chem 339–348
98. Di Bella S, Fragalà I, Ledoux I, Marks TJ (1995) J Am Chem Soc 117:9481–9485
99. Di Bella S, Fragalà I, Marks TJ, Ratner MA (1996) J Am Chem Soc 118:12747–12751
100. Di Bella S, Fragalà I, Ledoux I, Zyss J (2001) Chem Eur J 7:3738–3743
101. Di Bella S, Fragalà I (2002) New J Chem 26:285–290
102. Rigamonti L, Demartin F, Forni A, Righetto S, Pasini A (2006) Inorg Chem 45:10976–10989
103. Gradinaru J, Forni A, Druta V, Tessore F, Zecchin S, Quici S, Garbalau N (2007) Inorg Chem 46:884–895
104. Costes JP, Lamère JF, Lepetit C, Lacroix PG, Dahan F, Nakatani K (2005) Inorg Chem 44:1973–1982
105. Gaudry J-B, Capes L, Langot P, Marcén S, Kollmannsberger M, Lavastre O, Freysz E, Létard J-F, Kahn O (2000) Chem Phys Lett 324:321–329
106. Anverseng F, Lacroix PG, Malfant I, Périssé N, Lepetit C, Nakatani K (2001) Inorg Chem 40:3797–3804
107. Margeat O, Lacroix PG, Costes JP, Donnadieu B, Lepetit C, Nakatani K (2004) Inorg Chem 43:4743–4750
108. Anverseng F, Lacroix PG, Malfant I, Dahan F, Nakatani K (2000) J Mater Chem 10:1013–1018
109. Evans C, Luneau D (2002) J Chem Soc Dalton Trans 83–86
110. Rivera JM, Guzmán D, Rodriguez R, Lamère JF, Nakatani K, Santillan R, Lacroix PG, Farfán N (2006) J Organomet Chem 691:1722–1732
111. Rivera JM, Reyes H, Cortés A, Santillan R, Lacroix PG, Lepetit C, Nakatani K, Farfán N (2006) Chem Mater 18:1174–1183
112. Di Bella S, Fragalà I, Leonardi N, Sortino S (2004) Inorg Chim Acta 357:3865–3870
113. Di Bella S, Condorelli GG, Motta A, Ustione A, Cricenti A (2006) Langmuir 22:7952–7955
114. Kanis DR, Ratner MA, Marks TJ (1992) J Am Chem Soc 114:10338–10357
115. Barlow S, Bunting HE, Ringham C, Green JC, Bublitz GU, Boxer SG, Perry JW, Marder SR (1999) J Am Chem Soc 121:3715–3723
116. Barlow S, Marder SR (2000) Chem Commun 1555–1562
117. Calabrese JC, Cheng L-T, Green JC, Marder SR, Tam W (1991) J Am Chem Soc 113:7227–7232
118. Mata JA, Peris E, Asselberghs I, Van Boxel R, Persoons A (2001) New J Chem 25:299–304
119. Blanchard-Desce M, Runser C, Fort A, Barzoukas M, Lehn JM, Bloy V, Lanin V (1995) Chem Phys 199:253–261

120. Mata JA, Peris E, Asselberghs I, Van Boxel R, Persoons A (2001) New J Chem 25:1043–1046
121. Tsuboya N, Hamasaki R, Ito M, Mitsuishi M, Miyashita T, Yamamoto Y (2003) J Mater Chem 13:511–513
122. Farrell T, Meyer-Friedrichsen T, Malessa M, Haase D, Saak W, Asselberghs I, Wostyn K, Clays K, Persoons A, Heck J, Manning AR (2001) J Chem Soc Dalton Trans 29–36
123. Moore AJ, Chesney A, Bryce MR, Batsanov AS, Kelly, JF, Howard JAK, Perepichka IF, Perepichka DF, Meshulam G, Berkovic G, Kotler Z, Mazor R, Khodorkovsky V (2001) Eur J Org Chem 2671–2687
124. Janowska I, Zakrzewski J, Nakatani K, Delaire JA, Palusiak M, Walak M, Scholl H (2003) J Organomet Chem 675:35–41
125. Wrona A, Zakrzewski J, Jerzykiewicz L, Nakatani K (2008) J Organomet Chem 693:2982–2986
126. Liao Y, Eichinger BE, Firestone KA, Haller M, Luo J, Kaminsky W, Benedict JB, Reid PJ, Jen AKY, Dalton LR, Robinson BH (2005) J Am Chem Soc 127:2758–2766
127. Krishnan A, Pal SK, Nandakumar P, Samuelson AG, Das PK (2001) Chem Phys 265:313–322
128. Zhao X, Sharma HK, Cervantes-Lee F, Pannell KH, Long GJ, Shahin AM (2003) J Organomet Chem 686:235–241
129. Roy A-L, Chavarot M, Rose E, Rose-Munch F, Attias AJ, Kréher D, Fave JL, Kamierszky C (2005) C R Chimie 8:1256–1261
130. Janowska I, Zakrzewski J, Nakatani K, Palusiak M, Walak M, Sholl H (2006) J Organomet Chem 691:323–330
131. Sushanta KP, Krishnan A, Das PK, Samuelson AG (2000) J Organomet Chem 604:248–259
132. Malaun M, Kowallick R, McDonagh AM, Marcaccio M, Paul RL, Asselberghs I, Clays K, Persoons A, Bildstein B, Fiorini C, Nunzi J-M, Ward M D, McCleverty JA (2001) J Chem Soc Dalton Trans 3025–3038
133. Kumar R, Misra R, PrabhuRaja V, Chandrashekar TK (2005) Chem Eur J 11:5695–5707
134. Farrell T, Manning AR, Murphy TC, Meyer-Friedrichsen T, Heck J, Asselberghs I, Persoons A (2001) Eur J Inorg Chem 2365–2375
135. Coe BJ, Hamor TA, Jones CJ, McCleverthy JA, Bloor D, Cross GH, Axon TL (1995) J Chem Soc Dalton Trans 673–684
136. Marder SR, Perry JW, Tiemann BG, Schaefer WP (1991) Organometallics 10:1896–1901
137. Balavoine GGA, Daran J-C, Iftime G, Lacroix PG, Manoury E, Delaire JA, Maltey-Fanton I, Nakatani K, Di Bella S (1999) Organometallics 18:21–29
138. Chiffre J, Averseng F, Balavoive GGA, Daran J-C, Iftime G, Lacroix PG, Manoury E, Nakatani K (2001) Eur J Inorg Chem 2221–2226
139. Wright ME, Toplikar EG, Lackritz HS, Kerney JT (1994) Macromolecules 27:3016–3022
140. Kondo T, Horiuchi S, Yagi I, Ye S, Uosaki K (1999) J Am Chem Soc 121:391–398
141. Weidner T, Vor Der Brüggen J, Siemeling U, Träger F (2003) Appl Phys B 77:31–35
142. Malaun M, Reeves ZR, Paul RL, Jeffery JC, McCleverty JA, Ward MD, Asselberghs I, Clays K, Persoons A (2001) Chem Commun 49–50
143. Sporer C, Ratera I, Ruiz-Molina D, Zhao Y, Vidal-Gancedo J, Wurst K, Jaitner P, Clays K, Persoons A, Rovira C, Veciana J (2004) Angew Chem Int Ed 43:5266–5268
144. Cifuentes MP, Humphrey MG (2004) J Organomet Chem 689:3968–3981
145. Hurst SK, Cifuentes MP, Morrall JPL, Lucas NT, Whittall IR, Humphrey MG, Asselberghs I, Persoons A, Samoc M, Luther-Davies B, Willis AC (2001) Organometallics 20:4664–4675
146. Morrall JPL, Cifuentes MP, Humphrey MG, Kellens R, Robijns E, Asselberghs I, Clays K, Persoons A, Samoc M, Willis AC (2006) Inorg Chim Acta 359:998–1005
147. Fondum TN, Green KA, Randles MD, Cifuentes MP, Willis AC, Teshome A, Asselberghs I, Clays K, Humphrey MG (2008) J Organomet Chem 639:1605–1613
148. Cifuentes MP, Driver J, Humphrey MG, Asselberghs I, Persoons A, Samoc M, Luther-Davies B (2000) J Organomet Chem 607:72–77

149. Humphrey PA, Turner P, Masters AF, Field LD, Cifuentes MP, Humphrey MG, Asselberghs I, Persoons A, Samoc M (2005) Inorg Chim Acta 358:1663–1672
150. Cifuentes MP, Powell CE, Morral JP, McDonagh AM, Lucas NT, Humphrey MG, Samoc M, Houbrechts S, Asselberghs I, Clays K, Persoons A, Isoshima T (2006) J Am Chem Soc 128:10819–10832
151. Makowska-Janusik M, Kityk IV, Gauthier N, Frédéric P (2007) J Phy Chem C 111:12094–12099
152. Fillaut J-L, Perruchon J, Blanchard P, Roncali J, Golhen S, Allain M, Migalsaka-Zalas A, Kityk IV, Sahraoui B (2005) Organometallics 24:687–695
153. Centore R, Fort A, Panunzi B, Roviello A, Tuzi A (2004) Inorg Chim Acta 357:913–918
154. Aiello I, Caruso U, Ghedini M, Panunzi B, Quatela A, Roviello A, Sarcinelli F (2003) Polymer 44:7635–7643
155. Labat L, Lamere JF, Sasaki I, Lacroix PG, Vendier L, Asselberghs I, Perez-Moreno J, Clays K (2006) Eur J Inorg Chem 3105–3113
156. For example, see Lowry MS, Bernhard S (2006) Chem Eur J 12:7970–7977
157. De Angelis F, Fantacci S, Evans N, Klein C, Zakeeruddin SM, Moser JE, Kalyanasundaram K, Bolink HJ, Graetzel M, Nazeeruddin MK (2007) Inorg Chem 46:5989–6001
158. See for example Zhao Q, Liu S, Shi M, Wang C, Yu M, Li L, Li F, Yi T, Huang C (2006) Inorg Chem 45:6152–6160
159. Bolink HJ, Cappelli E, Coronado E, Graetzel M, Orti E, Costa RD, Viruela PM, Nazeeruddin MdK (2006) J Am Chem Soc 128:14786–14787
160. Dragonetti C, Falciola L, Mussini P, Righetto S, Roberto D, Ugo R, De Angelis F, Fantacci S, Sgamellotti A, Ramon M, Muccini M (2007) Inorg Chem 46:8533–8547
161. Dragonetti C, Righetto S, Roberto D, Ugo R, Valore A, Fantacci S, Sgamellotti A, De Angelis F (2007) Chem Commun 40:4116–4118
162. Dragonetti C, Righetto S, Roberto D, Valore A, Benincori T, Sannicolò F, De Angelis F, Fantacci S (2009) J Mater Sci Mater Electron 20:460–464
163. Calvete M, Yang GY, Hanack M (2004) Synth Met 141:231–243
164. Senge MO, Fazekas M, Notaras EGA, Blau WJ, Zawadzka M, Locos OB, Mhuircheartaigh EMN (2007) Adv Mater 19:2737–2774
165. Collini E, Mazzucato S, Zerbetto M, Ferrante C, Bozio R, Pizzotti M, Tessore F, Ugo R (2008) Chem Phys Lett 454:70–74 and references therein
166. Mc Donald IJ, Dougherty TJ (2001) J Porphyrins Phthalocyanines 5:105–129 and references therein
167. Pizzotti M, Ugo R, Annoni E, Quici S, Ledoux-Rak I, Zerbi G, Del Zoppo M, Fantucci PC, Invernizzi I (2002) Inorg Chim Acta 340:70–80
168. Annoni E, Pizzotti M, Ugo R, Quici S, Morotti T, Bruschi M, Mussini P (2005) Eur J Inorg Chem 3857–3874
169. Morotti T, Pizzotti M, Ugo R, Quici S, Bruschi M, Mussini P, Righetto S (2006) Eur J Inorg Chem 1743–1757
170. Wahab A, Bhattacharya M, Ghosh S, Samuelson AG, Das PK (2008) J Phys Chem B 112:2842–2847
171. Annoni E, Pizzotti M, Ugo R, Quici S, Morotti T, Casati N, Macchi P (2006) Inorg Chim Acta 359:3029–3041
172. Sen A, Ray PC, Das K, Krishnan V (1996) J Phys Chem 100:19611–19613
173. LeCours SM, Guan HW, DiMagno SG, Wang CH, Therien MJ (1996) J Am Chem Soc 118:1497–1503
174. Kim KS, Vance FW, Hupp JT, LeCours SM, Therien MJ (1998) J Am Chem Soc 120:2606–2611
175. Pizzotti M, Annoni E, Ugo R, Bruni S, Quici S, Fantucci PC, Bruschi M, Zerbi G, Del Zoppo M (2004) J Porphyrins Phthalocyanines 8:1311–1324
176. Yeung M, Ng ACH, Drew MGE, Vorpagel E, Breitung EM, Mc Mahon RJ, Ng DKP (1998) J Org Chem 63:7143–7150

177. De Angelis F, Fantacci S, Sgamellotti A, Pizzotti M, Tessore F, Orbelli Biroli A (2007) Chem Phys Lett 447:10–15
178. Monnereau C, Blart E, Montembault V, Fontaine L, Odobel F (2005) Tetrahedron 61:10113–10121
179. Zhang TG, Zhao Y, Asselberghs I, Persoons A, Clays K, Therien MJ (2005) J Am Chem Soc 127:9710–9720
180. Zhang TG, Zhao Y, Song K, Asselberghs I, Persoons A, Clays K, Therien MJ (2006) Inorg Chem 45:9703–9712
181. Bonifassi P, Ray PC, Leszczynski J (2006) Chem Phys Lett 431:321–325
182. Ray PC, Bonifassi P, Leszczynski J (2008) J Phys Chem A 112:2870–2879
183. Liao MS, Bonifassi P, Leszczynski J, Huang MJ (2008) Mol Phys 106:147–160
184. Duncan TV, Song K, Hung ST, Miloradovic I, Nayak A, Persoons A, Verbiest T, Therien MJ, Clays K (2008) Angew Chem Int Ed 47:2978–2981
185. De la Torre G, Vásquez P, Agulló-López F, Torres T (2004) Chem Rev 104:3723–3750
186. Chen Y, Hanack M, Blau WJ, Dini D, Liu Y, Lin Y, Bai J (2006) J Mater Sci 41:2169–2185
187. Martín G, Martínez-Díaz MV, De la Torre G, Ledoux I, Zyss J, Agulló-López F, Torres T (2003) Synth Met 139:95–98
188. Maya EM, García-Frutos EM, Vásquez P, Torres T, Martín G, Rojo G, Agulló-López F, González-Jonte RH, Ferro VR, García de la Vega JM, Ledoux I, Zyss J (2003) J Phys Chem A 107:2110–2117
189. De la Escosura A, Claessens CG, Ledoux-Rak I, Zyss J, Martínez-Díaz MV, Torres T (2005) J Porphyrins Phthalocyanines 9:788–793
190. Claessens CG, González-Rodríguez D, Torres T, Martín G, Agulló-López F, Ledoux I, Zyss J, Ferro VR, García de la Vega JM (2005) J Phys Chem B 109:3800–3806
191. Li CQ, Manaka T, Iwamoto M (2003) Thin Solid Films 438/439:162–166
192. Cheng X, Yao S, Li C, Manaka T, Iwamoto M (2003) Sci Chin 46:379–386
193. Li CQ, Manaka T, Iwamoto M (2004) Jpn J Appl Phys 43:2330–2334
194. Kanis DR, Ratner MA, Marks TJ (1992) J Am Chem Soc 114:10338–10357
195. Behrens U, Brussaard H, Hagenau U, Heck J, Hendrickx E, Kornich J, van der Linden JGM, Persoons A, Spek AL, Veldman N, Voss B, Wong H (1996) Chem Eur J 2:98–103
196. Mata J, Uriel S, Peris E, Llusar R, Houbrechts S, Persoons A (1998) J Organomet Chem 562:197–202
197. Briel O, Sünkel K, Krossing I, Nöth H, Schmälzlin E, Meerholz K, Brächle C, Beck W (1999) Eur J Inorg Chem 483–490
198. Jayaprakash KN, Ray PC, Matsuoka I, Bhadbhade MM, Puranik VG, Das PK, Nishihara H, Sarkar A (1999) Organometallics 18:3851–3858
199. Houbrechts S, Clays K, Persoons A, Cadierno V, Pilar Gamasa M, Gimeno J (1996) Organometallics 15:5266–5268
200. Vance FW, Karki L, Reigle JK, Hupp JT, Ratner MA (1998) J Phys Chem A 102:8320–8324
201. Pizzotti M, Ugo R, Roberto D, Bruni S, Fantucci PC, Rovizzi C (2002) Organometallics 21:5830–5840
202. Bruschi M, Fantucci PC, Pizzotti M (2005) J Phys Chem A 109:9637–9645
203. Pizzotti M, Ugo R, Dragonetti C, Annoni E, Demartin F, Mussini P (2003) Organometallics 22:4001–4011
204. Coe B J, Fitzgerald EC, Helliwell M, Brunschwig BS, Fitch AG, Harris JA, Coles SJ, Horton PN, Hursthouse MB (2008) Organometallics 27:2730–2742
205. Singer KD, Sohn JE, King LA, Gordon HM, Katz HE, Dirk CW (1989) J Opt Soc Am B 6:1339–1350
206. Dirk CW, Katz HE, Schilling ML, King LA (1990) Chem Mater 2:700–705