



Review

Zinc(II) as a Versatile Template for Efficient Dipolar and Octupolar Second-Order Nonlinear Optical Molecular Materials §

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§ This review is dedicated to Prof. Renato Ugo, on the occasion of his 80th birthday, for his essential contribution to the field of metal complexes with second-order nonlinear optical properties.

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Abstract: This short review outlines the main results obtained in the field of molecular materials based on zinc coordination compounds for second-order nonlinear optics. It presents an overview of the main classes of second-order nonlinear optical (NLO) active complexes bearing monodentate, bidentate, tridentate, or tetradentate π -delocalized ligands such as substituted stilbazoles, bipyridines, phenanthrolines, terpyridines, and Schiff bases. Macrocyclic ligands such as porphyrins and phthalocyanines are not covered. This paper shows how coordination to the Zn(II) center of π -delocalized nitrogen donor ligands produces a significant enhancement of their quadratic hyperpolarizability. Dipolar complexes are mainly presented, but octupolar zinc complexes are also presented. The coverage is mainly focused on NLO properties that are measured at the molecular level, working in solution, by means of the electric field-induced second harmonic generation (EFISH) or the hyper-Rayleigh scattering (HRS) techniques.

Keywords: Zinc(II) complexes; second-order nonlinear optics; EFISH; HRS

1. Introduction

Second-order nonlinear optical (NLO) coordination complexes are of great interest for nonlinear optics [1–3], mostly due to the unique characteristics associated with the metal center [4–20]. Compared to organic compounds, metal complexes offer a greater variety of electronic structures, in relation to the coordination sphere, electronic configuration, and oxidation state of the metal. They possess intense, low-energy metal-to-ligand charge-transfer (MLCT), ligand-to-metal charge-transfer (LMCT), or intraligand charge-transfer (ILCT) transitions, and therefore, the metal can act as a donor, acceptor, or polarizable bridge of a dipolar donor– π –bridge–acceptor system. Besides, some metal centers are ideal templates to build compounds based on octupolar coordination with D_2 or D_3 symmetry [21].

In the panorama of NLO active coordination compounds, low-cost zinc complexes have progressively occupied a role of primary interest for their third-order [22–25] and second-order [19–21] NLO properties. Due to the d^{10} configuration of the metal center, zinc(II) complexes do not exhibit stereochemistry preference arising from ligand field stabilization effects. Therefore, they can adopt a variety of geometries and coordination numbers, depending on the nature and structure of the ligand

framework. Coordination numbers 4, 5, and 6, which are associated to tetrahedral, square pyramidal, and octahedral geometry, respectively, are often encountered. The unique characteristics of zinc allow the preparation not only of NLO-active dipolar compounds, thanks to intense ILCT transitions at low energy, but also of NLO-active octupolar compounds, owing to the capacity of the zinc center to act as a versatile template, allowing a suitable coordination sphere. Moreover, the absence of low-energy metal-to-ligand or metal $d-d$ electronic transitions makes these zinc complexes generally more optically transparent than the metal d^n congeners.

In the following sections, we report an overview on the dipolar and octupolar second-order NLO active zinc complexes bearing stilbazole, bipyridine, phenanthroline, terpyridine, or Schiff bases as ligands, focusing on the relevant aspects associated to each class of complexes. Macrocyclic ligands such as porphyrins and phthalocyanines are not presented, being already covered in excellent papers and reviews [15,19,26–28].

2. Principles of Second-Order Nonlinear Optics

In this section, we briefly present the principles of second-order nonlinear optics. More details can be found in various books [1–3] and reviews [4–20].

NLO is due to the interaction of an applied electromagnetic field with a molecule or material leading to the emission of a new electromagnetic field which differs in frequency, phase, or other physical properties from the incident one [1–3]. One important nonlinear optical process is the second harmonic generation (SHG), which is due to the interaction of two incident waves, having ω frequency, with the molecule characterized by a quadratic hyperpolarizability value β to produce a new wave with the frequency of 2ω .

In order to obtain molecular materials characterized by high second-order NLO effects, it is necessary to have high values of β . Oudar gave an interpretation of the electronic origin of β [29–31]. The hyperpolarizability of a compound depends on the mobility of electrons under the effect of an electric field \vec{E} related to light; therefore, it requires electronic transitions with high charge-transfer character. Oudar assumed that, in suitable organic chromophores, the second-order NLO response is dominated by one charge-transfer process, so that:

$$\beta_{zzz} = \frac{3}{2h^2c^2} \frac{\nu_{eg}^2 r_{eg}^2 \Delta\mu_{eg}}{(\nu_{eg}^2 - \nu_L^2)(\nu_{eg}^2 - 4\nu_L^2)} \quad (1)$$

where z is the direction of the charge transfer, ν_{eg} is the frequency of the charge-transfer transition, r_{eg} is the transition dipole moment, $\Delta\mu_{eg}$ is the difference between the excited state and ground state molecular dipole moment ($\mu_e - \mu_g$) and ν_L is the frequency of the incident radiation. This equation represents the so-called “two-level” model. Extrapolation to zero frequency ($\nu_L = 0.0$ eV; $\lambda = \infty$) gives the static quadratic hyperpolarizability β_0 [32], which is the figure of merit to determine the second-order NLO properties of a molecule, and can be calculated by using the following equation:

$$\beta_0 = \beta_\lambda [1 - (2\lambda_{\max}/\lambda)^2][1 - (\lambda_{\max}/\lambda)^2] \quad (2)$$

where β_λ is the quadratic hyperpolarizability value at λ incident wavelength, and λ_{\max} is the absorption wavelength of the major charge-transfer transition that is considered [33].

This “two-level” model helps to prepare new efficient molecule-based NLO materials. In fact, one can extrapolate the requirements that a molecule must have to show a large second-order NLO response: it should be non-centrosymmetric, with charge-transfer transitions with high $\Delta\mu_{eg}$ and r_{eg} values. This can be accomplished by the separation of an electron donor and an electron acceptor moiety with a π -conjugated polarizable bridge, for example, in D- π -A systems. It appeared that not only dipolar structures but also multipolar systems, such as octupoles, may be of interest for SHG. The octupolar molecules, which are characterized by the presence of multidirectional CT excitations,

should have a twofold (D_2) or threefold (D_3) rotational axis. The description of the nonlinearity of such systems implies a three-level approach.

Two techniques, the electric field-induced second harmonic generation (EFISH) and hyper-Rayleigh scattering (HRS), which is also called harmonic light scattering (HLS), allow the determination of β in solution. The EFISH method [34] is suitable for dipolar molecules only, and gives the quadratic hyperpolarizability through the following equation:

$$\gamma_{\text{EFISH}} = (\mu\beta_{\lambda}/5kT) + \gamma(-2\omega;\omega,\omega,0) \quad (3)$$

where $\mu\beta_{\lambda}/5kT$ is the dipolar orientational contribution and $\gamma(-2\omega;\omega,\omega,0)$, a third-order term at frequency ω of the incident light, is the electronic contribution, which is negligible for molecules with a low electronic polarizability. β_{λ} is the projection along the dipole moment axis of β_{VEC} , which is the vectorial component of the tensor of the quadratic hyperpolarizability, working with an incident wavelength λ of a pulsed laser. To obtain the value of β_{λ} , the ground state dipole moment μ of the molecule should be known.

In the HRS technique [35–37], the detection of the incoherently scattered second harmonic, generated by the molecule in solution under irradiation with a laser of wavelength λ , leads to the mean value of the $\beta \times \beta$ tensor product. From the polarization dependence of the second harmonic signal, which was evaluated by selecting the polarization of the incident and scattered radiation, one has information on the components of the quadratic hyperpolarizability tensor β . Contrarily to EFISH, HRS is used also for octupolar molecules. In this review, the quadratic hyperpolarizability determined with an incident wavelength λ by the EFISH and HRS techniques will be indicated as β_{λ} (EFISH) and β_{λ} (HRS), respectively.

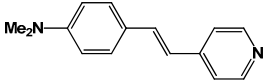
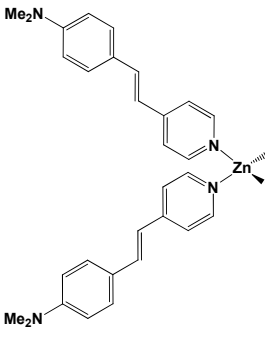
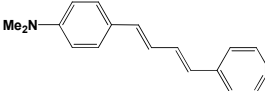
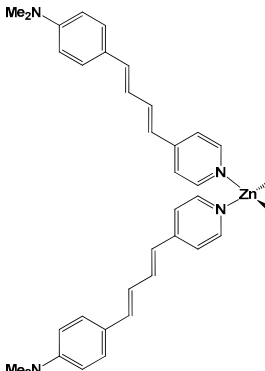
3. Dipolar Complexes

3.1. Monodentate Nitrogen Ligands: Stilbazoles

The effect of coordination to a zinc center on the second-order NLO response of stilbazole ligands bearing a strong electron-donating group such as NMe_2 has been deeply studied by Ugo et al. by means of the EFISH technique in solution [38–40]. In these systems, the quadratic hyperpolarizability is dominated by the stilbazole ILCT transition. The metal center behaves as an inductive electron acceptor, which can increase the acceptor strength of the π^* orbitals of the pyridine, and therefore produce a red-shift of the ILCT transition with an increase of the quadratic hyperpolarizability. The relevant data for this family of complexes are collected in Table 1.

The $\mu\beta_{1.91}$ (EFISH) value of 4,4'-*trans*- $\text{NMe}_2\text{-C}_6\text{H}_4\text{CH=CHC}_5\text{H}_4\text{N}$ (CHCl_3 , 5×10^{-4} M) [41] increases by a factor of 2.3 upon coordination to the " $\text{Zn}(\text{CH}_3\text{CO}_2)_2$ " moiety [38], which is mainly due to the large increase of the dipole moment (complex 1, Table 1). In fact, the quadratic hyperpolarizability is quite similar, which is in agreement with the irrelevant red-shift upon coordination of the stilbazole ILCT ($\Delta\lambda_{\text{max}} = 2$ nm) [38]. However, an increase of the acceptor properties of the Zn(II) ancillary ligands ($\text{CH}_3\text{CO}_2 < \text{CF}_3\text{CO}_2 < \text{CF}_3\text{SO}_3$) tunes the acceptor properties of the Zn(II) center, leading to an increase of the ILCT red-shift observed upon coordination (with " $\text{Zn}(\text{CF}_3\text{CO}_2)_2$ " (2), $\Delta\lambda_{\text{max}} = 46$ nm [38]; with " $\text{Zn}(\text{CF}_3\text{SO}_3)_2$ " (3), $\Delta\lambda_{\text{max}} = 116$ nm) [39]. Such a behavior is reflected by an enhancement of the quadratic hyperpolarizability. Thus, on passing from (1) to (2) and (3), the $\beta_{1.91}$ (EFISH) value increases by factors of 1.3 and 4.2, respectively [39]. It turned out that with other less electron-withdrawing non-fluorinated sulfonate ligands, such as CH_3SO_3^- (4) or *p*- $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_3^-$ (5), the second-order NLO response is much lower than with CF_3SO_3^- (3), despite the significantly high red-shift of the ILCT transition of the stilbazole ligand ($\Delta\lambda_{\text{max}} = 101\text{--}102$ nm), showing the unique property of the triflate ancillary ligand, which increases the second-order NLO response due to its extremely low nucleophilic character [40].

Table 1. Electronic spectra, dipole moments, and $\beta_{1,91}$ (EFISH) of Zn(II) stilbazole complexes in CHCl_3 solution [38–40]. EFISH: electric field-induced second harmonic generation.

Molecule	Y (Complex)	λ_{max} (nm)	$\mu\beta_{1,91}$ (EFISH) (10^{-48} esu) ^a	μ (10^{-18} esu)	$\beta_{1,91}$ (EFISH) (10^{-30} esu)
		374	136	3.9	35
	CH_3CO_2 (1)	376	316	8.0	39
	CF_3CO_2 (2)	420	512	10.5	49
	CF_3SO_3 (3)	490	2715	16.7	163
	CH_3SO_3 (4)	475	450	15.5	29
	<i>p</i> - $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_3$ (5)	476	428	16.0	27
		396	310	4.5	69
	CH_3CO_2 (6)	406	680	6.7	101
	CF_3SO_3 (7)	519	3840	14.7	261

^a Working at a concentration 5×10^{-4} M.

Similarly, the quadratic hyperpolarizability of 4,4'-*trans,trans*-NMe₂-C₆H₄(CH=CH)₂C₅H₄N is increased upon coordination to a Zn(II) center, in which the enhancement is much larger with “Zn(CF₃SO₃)₂” (7) than with “Zn(CH₃CO₂)₂” (6). This is in agreement with a higher Lewis acidity of the Zn(II) center, as confirmed by the much larger red-shift of the ILCT transition upon coordination ($\Delta\lambda_{\text{max}} = 123$ and 10 nm, for CF₃SO₃ and CH₃CO₂, respectively; Table 1) [39].

Remarkably, the quadratic hyperpolarizability of both Zn(II) triflate complexes (3, 7) increases abruptly by decreasing the concentration, up to very large values. For example, the $\beta_{1,91}$ (EFISH) value of 3 is 163×10^{-30} , 220×10^{-30} and 404×10^{-30} esu working in CHCl_3 solution at 5×10^{-4} , 1×10^{-4} and 0.5×10^{-4} M, respectively. This behavior, which is not observed for the related acetate or trifluoroacetate complexes, can be attributed to an increased concentration of the [Zn(CF₃SO₃)₂(4,4'-*trans*-Me₂N-C₆H₄(CH=CH)_{*n*}C₅H₄N)₂]⁺ (*n* = 1, 2) cation produced by solvolysis of the triflate ligand. This explanation was confirmed by electrical conductivity measurements, which showed a sharp conductivity increase at concentrations below 10^{-4} M for triflate complexes [39]. A similar behavior of the quadratic hyperpolarizability in CHCl_3 solution upon dilution was observed in the case of Zn(II) complexes with the methanesulfonate or *para*-toluene sulfonate anions instead of

the triflate anion as ancillary ligands [40]. Therefore, ionic dissociation by working in diluted CHCl_3 solution is a behavior that is typical of all $\text{Zn}(\text{II})$ complexes bearing an ancillary sulfonate ligand.

3.2. Bidentate Nitrogen Ligands: Bipyridines, Phenanthrolines, and Diazafluorens

The second-order NLO response of various bidentate chelating nitrogen ligands such as bipyridine, phenanthroline, and diazafluorene increases upon coordination to a zinc center, as observed in the case of stilbazoles (see Section 3.1). The enhancement factor of the quadratic hyperpolarizability depends on both chelating ligands and ancillary ones [19].

Le Bozec et al. studied by means of the EFISH technique (1.34 μm incident wavelength) the second-order NLO response of various $\text{Zn}(\text{II})$ complexes with 4-(*p*-R-styryl)-4'-methyl-2,2'-bipyridine where R is a donor substituent [42,43]. They found that the quadratic hyperpolarizability increases with the Lewis acidity of the metal center (" ZnCl_2 " > " $\text{Zn}(\text{OAc})_2$ ") and with the strength of the electron donor group R on the bipyridine (Octyl is less efficient than NBu_2). The best value ($\beta_{1,34}(\text{EFISH}) = 152 \times 10^{-30}$ esu; $\mu\beta_{1,34}(\text{EFISH}) = 1780 \times 10^{-48}$ esu) was obtained for the ZnCl_2 complex with 4-(*p*-(dibutylamino)styryl)-4'-methyl-2,2'-bipyridine (complex 8; Figure 1) [43]. The quadratic hyperpolarizability and the dipole moment were 11 and 2.3 times higher, respectively, than those determined for the related free bipyridine [42].

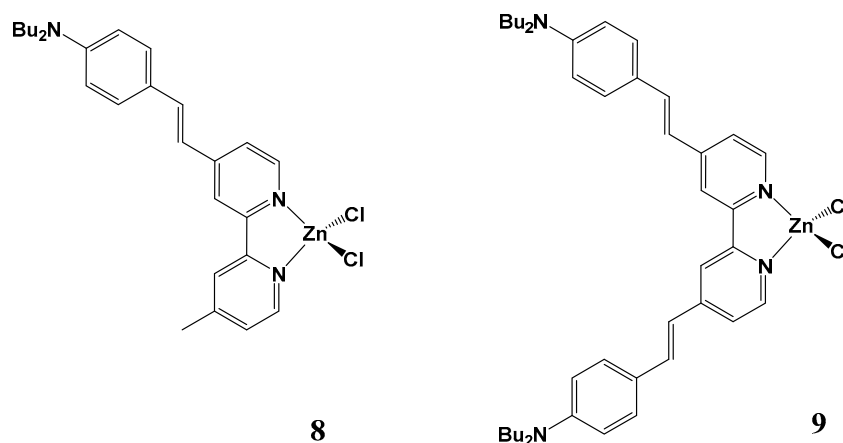


Figure 1. Second-order nonlinear optical (NLO)-active $\text{Zn}(\text{II})$ bipyridine complexes.

Besides, Le Bozec et al. reported that the ZnCl_2 complex bearing a 4,4'-bis(*p*-(dibutylamino)styryl)-2,2'-bipyridine (complex 9, Figure 1) is characterized by a $\mu\beta_{1,34}(\text{EFISH})$ of 1420×10^{-48} esu [44]. Remarkably, this value is much higher than that of the related nonchelated complex $[\text{ZnCl}_2(4,4'\text{-trans-NMe}_2\text{-C}_6\text{H}_4\text{CH=CHC}_5\text{H}_4\text{N})_2]$ [38], due to the planar arrangement of the bidentate ligand upon coordination, and a shift of the ILCT transition at lower energy [19,45]. Substitution of the two HC=CH groups of the bipyridine ligand by azo moieties leads to an increase of the NLO response, but this effect is due to resonant enhancement [44]. Upon coordination of these bipyridines to the ZnCl_2 moiety, a red-shift of the intense ILCT (intraligand charge transfer) band is observed ($\Delta\lambda_{\text{max}} = 45\text{--}60$ nm), as expected from the inductive acceptor strength of the Lewis acid [44].

The development of switchable nonlinear optical (NLO) materials is of recent interest. An elegant approach to the reversible switching of NLO properties is the use of photochromic moieties such as dithienylethene (DTE) [20]. In fact, DTE derivatives undergo reversible interconversion between an unconjugated open form and a π -conjugated closed form when irradiated in the UV and visible spectral ranges, respectively. Therefore, with the aim of photoswitching the NLO properties, Le Bozec et al. prepared novel dipolar $\text{Zn}(\text{II})$ complexes bearing a 4,4'-bis(ethenyl)-2,2'-bipyridine ligand functionalized by phenyl and dimethylaminophenyl DTE groups [46] (Figure 2). The NLO response for the open forms is low ($\mu\beta_{1,91}(\text{EFISH}) = 90$ and 200×10^{-48} esu, for $\text{D} = \text{H}$ and NMe_2 ,

respectively; **10**) due to the lack of π -conjugation between the thiophene moieties. As expected, upon conversion to the closed form by irradiation with a suitable wavelength, the NLO response increases ($\mu\beta_{1,91}(\text{EFISH}) = 2020$ and 4220×10^{-48} esu for $D = \text{H}$ and NMe_2 , respectively; **11**) due to the more efficient delocalization of the π -electron system. As expected, the complex featuring the strongly electron-donating dimethylamino substituent shows the largest NLO response. These novel photochromic zinc complexes are fascinating, allowing an excellent on/off switching of the NLO responses [46].

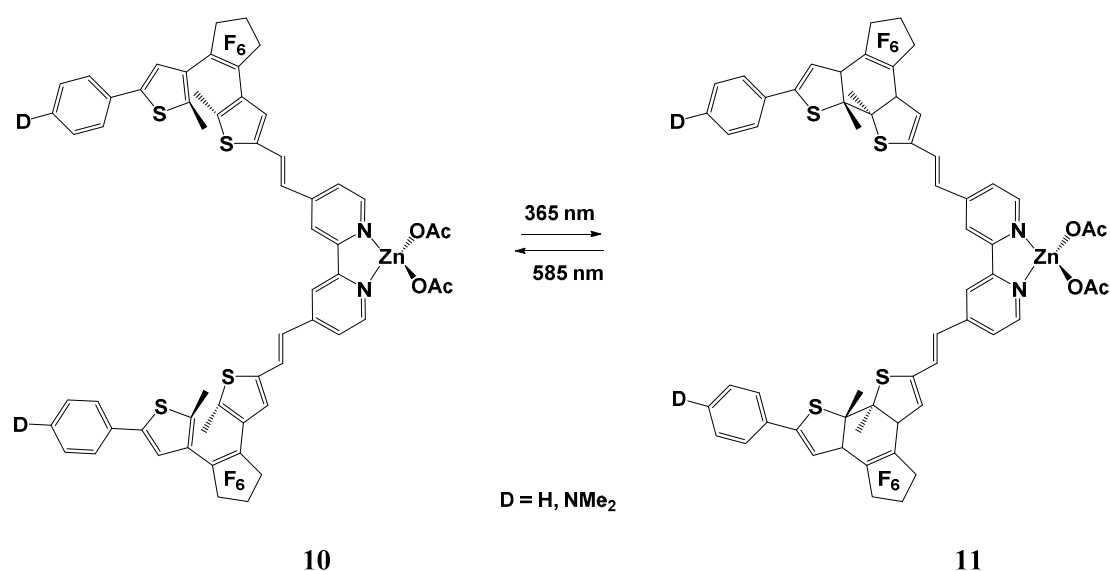
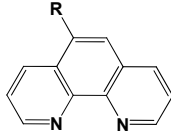
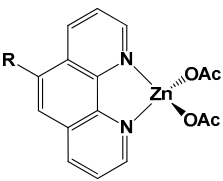


Figure 2. Zn(II) bipyridine complexes with a photoswitchable second-order NLO-response; Ac = acetyl.

Ugo et al. showed that the second-order NLO response of 5-R-1,10-phenanthroline (R = donor group such as OMe, NMe_2 , *trans*- $\text{CH}=\text{CHC}_6\text{H}_4\text{-4}'\text{-NMe}_2$, and *trans,trans*-($\text{CH}=\text{CH}$) $_2\text{C}_6\text{H}_4\text{-4}'\text{-NMe}_2$) increases upon coordination to the “ $\text{Zn}(\text{CH}_3\text{CO}_2)_2$ ” moiety, which is in agreement with the ILCT red-shift (Table 2) [38]. There is a twofold increase of the dipole moment upon coordination to the metal center. Interestingly, the enhancement factor (EF) of the $\beta_{1,34}(\text{EFISH})$ value of the phenanthroline upon coordination is higher for the better donor group NMe_2 ($\text{EF} = \beta_{1,34}(\text{EFISH})$ complex / $\beta_{1,34}(\text{EFISH})$ free phenanthroline = 4.6; **13**) than for OMe ($\text{EF} = 3.2$; **12**). It becomes less and less relevant by increasing the length of the π -delocalized bridge between the donor group NMe_2 and the phenanthroline moiety, ($\text{EF} = 1.9$ and 1.5 for *trans*- $\text{CH}=\text{CHC}_6\text{H}_4\text{-4}'\text{-NMe}_2$ (**14**) and *trans,trans*-($\text{CH}=\text{CH}$) $_2\text{C}_6\text{H}_4\text{-4}'\text{-NMe}_2$ (**15**), respectively). It should be pointed out that the increase of the quadratic hyperpolarizability of planar 5-X-1,10-phenanthrolines upon coordination to a Zn(II) center is lower than that of the nonplanar and flexible ligand 4-(*p*(dibutylamino)styryl)-4'-methyl-2,2'-bipyridine, which is probably because this latter ligand becomes planar and rigid upon coordination [38,42].

Table 2. Electronic spectra, dipole moments, and $\beta_{1,34}$ (EFISH) of Zn(II) phenanthroline complexes in CHCl_3 solution [38].

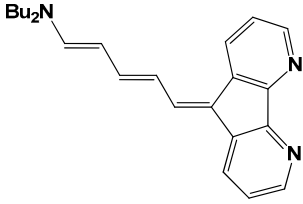
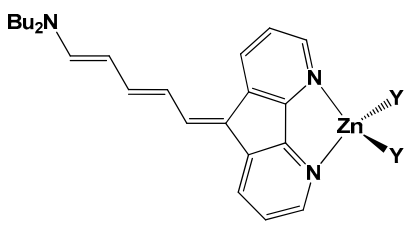
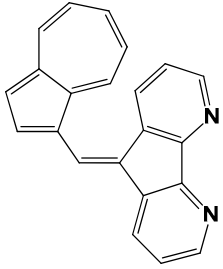
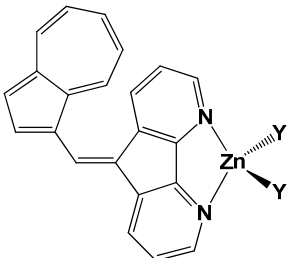
Molecule	R (Complex)	λ_{max} (nm)	$\mu\beta_{1,34}$ (EFISH) (10^{-48} esu) ^a	μ (10^{-18} esu)	$\beta_{1,34}$ (EFISH) (10^{-30} esu)
	OMe	272	16	4.0	4
	NMe ₂	328	27	3.8	7.2
	<i>trans</i> - CH=CHC ₆ H ₄ -4'-NMe ₂	371	201	4.9	41
	<i>trans,trans</i> - (CH=CH) ₂ C ₆ H ₄ -4'-NMe ₂	399	368	4.9	75
	OMe (12)	284	99	7.6	13
	NMe ₂ (13)	344	254	7.7	33
	<i>trans</i> - CH=CHC ₆ H ₄ -4'-NMe ₂ (14)	419	616	8.0	77
	<i>trans,trans</i> - (CH=CH) ₂ C ₆ H ₄ -4'-NMe ₂ (15)	432	862	7.7	112

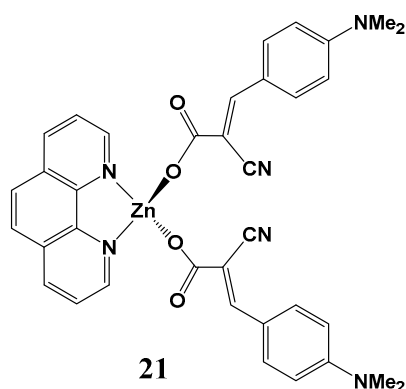
^a working at a concentration 5×10^{-4} M. Ac = Acetyl.

More recently it was observed that, with respect to 5-*trans*-CH=CHC₆H₄-4'-NMe₂-1,10-phenanthroline (Table 2), *N,N*-dibutyl-(4,5-diazafluorenyl-9-ylidene-penta-1,3-dienyl)-amine (Table 3) is characterized by a much lower value of the λ_{max} of the ILCT transition ($\Delta\lambda_{\text{max}} = 114$ nm), reflecting the large π -delocalization of its structure, and suggesting a large NLO response [47]. This was confirmed by EFISH measurements (Table 3) [47]. In fact, the $\mu\beta_{1,91}$ value for this novel free ligand is rather large (998×10^{-48} esu), and it increases upon coordination to a “Zn(CH₃CO₂)₂” moiety (**16**), due to an increase of the dipole moment and to the red-shift of the ILCT transition. This increase is easily controlled by the Lewis acceptor properties of the metal moiety, and therefore by the ancillary ligands that tune its acceptor properties. Thus, the $\mu\beta_{1,91}$ value increases upon the substitution of CH₃CO₂[−] (**16**) by CF₃CO₂[−] (**17**) or CF₃SO₃[−] (**18**), as expected from the λ_{max} value dominating the NLO response of the related Zn(II) complexes (Table 3). As previously observed for the stilbazole Zn(II) complexes (Section 3.1) [39], the second-order NLO response of the triflate complex **18** increases exponentially with decreasing concentration (Table 3), which is an effect that is not observed for the related complexes with the acetate or trifluoroacetate ligand, and can be attributed to the formation of cationic Zn(II) species, given the low nucleophilicity of the triflate anion [47]. Similarly, the coordination of 9-[(1-azulenyl)methylene]-4,5-diazafluorene to “Zn(CF₃CO₂)₂” (**19**) leads to an enhancement of the second-order NLO response and the red-shift of the ILCT transition (Table 3). As expected, the $\mu\beta_{1,91}$ value increases upon the substitution of CF₃CO₂[−] (**19**) with CF₃SO₃[−] (**20**). The $\mu\beta_{1,91}$ value of the triflate complex **20** is also dependent on concentration, but in a minor way with respect to the zinc complex with *N,N*-dibutyl-(4,5-diazafluorenyl-9-ylidene-penta-1,3-dienyl)-amine (**18**) [47].

Interestingly, it was also reported that the β_0 (HRS) of *push-pull* carboxylate ligands increases upon coordination to the “(1,10-phenanthroline)Zn(II)” moiety. Thus, complex **21** (Figure 3) has a β_0 (HRS) of 39×10^{-30} esu, which is a value that is six times higher than that of the free carboxylate ligand [48].

Table 3. Electronic spectra and $\mu\beta_{1.91}$ (EFISH) of Zn(II) diazafluoren complexes in CHCl₃ solution [47].

Molecule	Y (Complex)	λ_{\max} (nm)	Concentration (10 ⁻⁴ M)	$\mu\beta_{1.91}$ (EFISH) (10 ⁻⁴⁸ esu)
		485	10	998
	CH ₃ CO ₂ (16)	490	10	1230
	CF ₃ CO ₂ (17)	548	10	1900
	CF ₃ SO ₃ (18)	10	2230	
		5	3170	
		1	5750	
0.5	12,000			
		439	10	760
	CF ₃ CO ₂ (19)	447	10	1320
	CF ₃ SO ₃ (20)	486	10 0.5	1640 3570

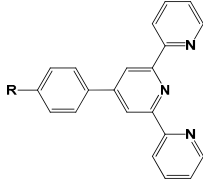
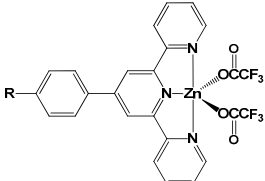
**Figure 3.** Zn(II) phenanthroline complex bearing a push-pull carboxylate ligand.

3.3. Tridentate Nitrogen Ligands: Terpyridines

The second-order NLO properties of zinc complexes with 4'-(1-C₆H₄-*p*-R)-2,2':6',2''-terpyridines (R = NBU₂, *trans*-CH=CHC₆H₄-*p*-NBU₂, *trans,trans*-(CH=CH)₂C₆H₄-*p*-NMe₂) ligands have also been studied by Ugo et al. [49,50]. By looking at the free terpyridines, and increasing the length of the

π -conjugated spacer between the amino group and the chelated system of the terpyridine, a significant increase of $\beta_{1,34}$ (EFISH) occurs (from 22 to 95×10^{-30} esu, Table 4). Coordination to a “ZnY₂” moiety (Y = Cl, CF₃CO₂) leads to an enhancement of both the dipole moment and the $\beta_{1,34}$ (EFISH) value, in which the enhancement is higher for the more electron-withdrawing ligand CF₃CO₂ (22–24) [49]. This behavior is in agreement with the red-shift of the ILCT transition of the terpyridine due to an increase of the acceptor properties of the π^* orbitals upon chelation (Table 4).

Table 4. Electronic spectra, dipole moments, and $\beta_{1,34}$ (EFISH) of Zn(II) terpyridine complexes in CHCl₃ solution [49,50].

Molecule	R (Complex)	λ_{\max} (nm)	$\mu\beta_{1,34}$ (EFISH) (10 ⁻⁴⁸ esu) ^a	μ (10 ⁻¹⁸ esu)	$\beta_{1,34}$ (EFISH) (10 ⁻³⁰ esu)
	NBu ₂	360	46	2.1	22
	<i>trans</i> - CH=CHC ₆ H ₄ - <i>p</i> -NBu ₂	395	187	3.6	52
	<i>trans,trans</i> - (CH=CH) ₂ C ₆ H ₄ - <i>p</i> -NMe ₂	399	370	3.9	95
	NBu ₂ (22)	427	880	10	88
	<i>trans</i> - CH=CHC ₆ H ₄ - <i>p</i> -NBu ₂ (23)	454	1502	8.3	181
	<i>trans,trans</i> - (CH=CH) ₂ C ₆ H ₄ - <i>p</i> -NMe ₂ (24)	444	1219	8.9	137

As previously observed for other metal complexes [15,19], the quadratic hyperpolarizability enhancement factor upon coordination to a “Zn(CF₃CO₂)₂” moiety (EF given by $\beta_{1,34}$ (EFISH) complex/ $\beta_{1,34}$ (EFISH) free terpyridine) decreases when the length of the π -conjugated system of the linker connecting the donor group increases (EF = 4.0, 3.5, and 1.4 for R = NBu₂ (22), *trans*-CH=CHC₆H₄-*p*-NBu₂ (23), and *trans,trans*-(CH=CH)₂C₆H₄-*p*-NMe₂ (24), respectively; Table 4). Such enhancement factors can be attributed to the red-shift of the ligand ILCT transition and the stabilization of the *cisoid* conformation of the terpyridine due to chelation [50].

Interestingly, the second-harmonic generation (1064-nm incident wavelength) of Langmuir Blodgett films of a Zn(II) complex bearing a 4'-(1-C₆H₄-*p*-NMe(C₁₆H₃₃))-2, 2': 6', 2''-terpyridine has been measured. A fair $\chi^{(2)}$ value of 8.1 pm/V was obtained [51].

3.4. Schiff-Bases

Although Schiff-base metal complexes—mainly involving Ni(II) [52–55] and Cu(II) [56,57] ions—have been widely investigated and reviewed as second-order NLO materials [58–61], the great potential of their Zn(II) analogues has not been fully explored.

Lacroix et al. [62] first investigated the second-order NLO properties of a Zn(II) bis[4-(diethylamino)salicylaldiminato] complex—a derivative of the 2,3-diaminomaleonitrile as a diamine bridge—in comparison with the free ligand and the related Ni(II) and Cu(II) complexes. As expected, Zn(II) complexation involves an increased nonlinearity and, surprisingly, larger hyperpolarizability values ($\beta_{1,34}$ (EFISH) up to 400×10^{-30} esu), compared to Ni(II) and Cu(II) analogues, despite the *d*¹⁰ metal configuration of the Zn(II) ion. This was related to the existence of strong ILCT transitions in which the zinc(II) center acts as a bridge in a square-pyramidal arrangement with an apical molecule of solvent.

The NLO properties of analogous 4-alkoxy substituted—instead of 4-diethylamino—Zn(II) complexes were recently studied in relation to their interesting aggregation/deaggregation properties [63]. Actually, tetradentate [N₂O₂] Schiff-base complexes are coordinatively unsaturated

Lewis acidic species because of the inability of the Zn(II) ion to reach a tetrahedral coordination, which is a consequence of the ring strain generated by the diamine bridge [64]. Therefore, in the absence of Lewis bases, these complexes are aggregated by intermolecular Zn...O interactions, while, in the presence of Lewis bases, they deaggregate with the formation of monomeric adducts [65,66]. This phenomenon was appropriately exploited to explore NLO changes upon deaggregation. It was found that starting from concentrated dichloromethane solutions of complex **25**, deaggregation with a strong Lewis base, such as pyridine, leads to a switch-on of the quadratic hyperpolarizability ($\beta_{1,91}(\text{EFISH}) = -518 \times 10^{-30}$ esu; Figure 4). This represents an unprecedented mode of NLO switching in molecular materials.

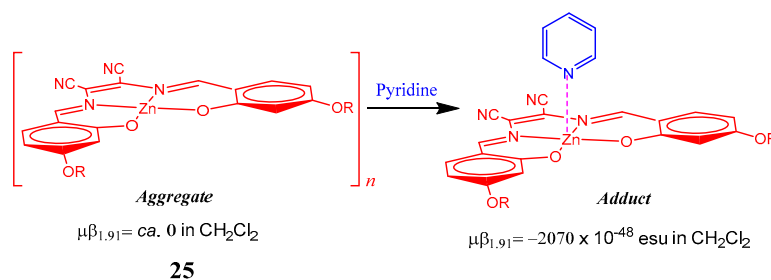


Figure 4. Switching on the second-order NLO response for complex **25** by the addition of pyridine. Reproduced from Ref. [63] with permission from The Royal Society of Chemistry.

In order to increase the NLO properties of bis(salicylaldiminato) M(II) complexes, Gradinaru et al. [67] performed a detailed study on a series of Ni(II), Cu(II), and Zn(II) complexes with two unsymmetrical tetradentate $[\text{N}_2\text{O}_2]$ Schiff-base ligand derivatives from *S*-methylisothiosemicarbazone (Figure 5). These complexes were structurally characterized, revealing in the case of Zn(II) complexes a distorted square pyramid geometry around the Zn(II) center, in which the oxygen atom of a methanol molecule occupies the apical position. Again, the Zn complex shows the largest hyperpolarizability values along the series ($\mu\beta_{1,91}(\text{EFISH}) = -1650 \times 10^{-48}$ esu; $\beta_{1,91}(\text{EFISH}) = -280 \times 10^{-30}$ esu), even though the metal ion is not involved in the charge transfer transitions that are responsible for the NLO response of these complexes.

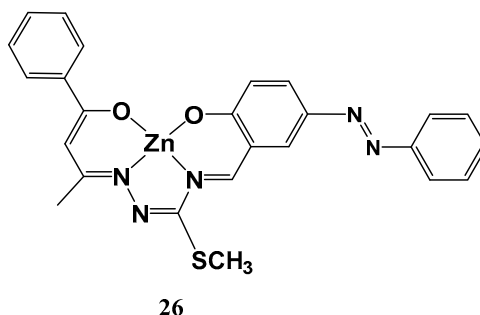
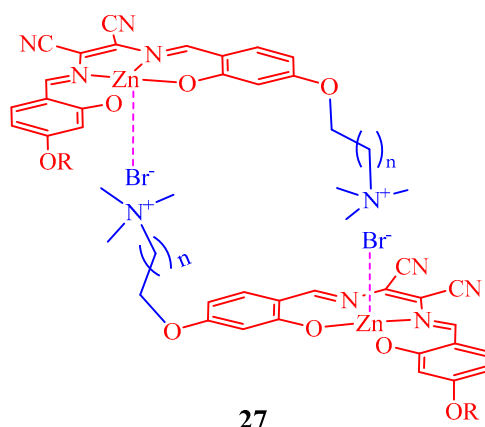


Figure 5. Structure of unsymmetrical Schiff bases of the *S*-methylisothiosemicarbazide derivative.

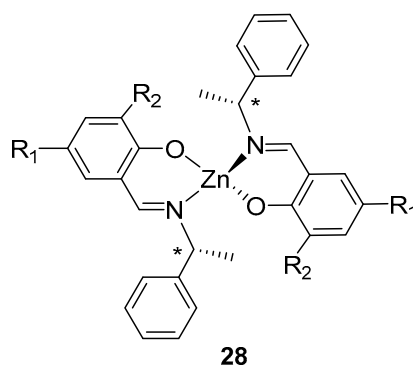
Unsymmetrical, alkoxy-derivatized Schiff-base Zn(II) complexes, having on one side an alkyl ammonium bromide as a Lewis base, were recently investigated to probe their aggregation and NLO properties [68]. These complexes are characterized by a significant nonlinearity ($\mu\beta_{1,91}(\text{EFISH}) = 400 \times 10^{-48}$ esu), even if the values are lower when compared to that of the **25** analogue. This can be related to the substitution of pyridine by a bromide ion and the relative cation–anion ion pair configuration [69], which are expected to involve major changes in the ground state dipole and in $\Delta\mu_{eg}$ values, and hence in the second-order nonlinearity. Experimental results and NLO data suggest the existence of acentric dimeric species such as **27** (Figure 6), in which each molecular unit mutually interacts with another unit through intermolecular Zn...Br[−] interactions.



27

Figure 6. Proposed structure for the acentric dimeric species 27. Reproduced from Ref. [68] with permission from The Royal Society of Chemistry.

ZnL₂ complexes of bidentate Schiff-base ligands derived from a chiral amine offered the opportunity to investigate their bulk nonlinearity [70]. These complexes, in fact, crystallize in noncentrosymmetric space groups, with a pseudo-tetrahedral geometry around the zinc(II) ion (28, Figure 7). It was found that these compounds give an intense powder SHG signal at 1.064 μm, which is between that of 3-methyl-4-nitropyridine-1-oxide and *N*-(4-nitrophenyl)-(*S*)-prolinol.



28

Figure 7. Structure of chiral ZnL₂ complexes.

4. Octupolar Complexes

As previously stated, the Zn(II) center has a strong propensity to expand its coordination sphere with ligands having an appropriate structure. This is especially true in the case of 2,2'-bipyridine ligands, for which the Zn(II) ion is an excellent template to build octupolar structures. Thus, a variety of octupolar, tetrahedral, and octahedral coordinated Zn(II) complexes have been synthesized and investigated for their second-order NLO properties. Most of this work has been developed and reviewed in an excellent paper [14] by Le Bozec et al.

The first work on this family of compounds was communicated in 2002 by these authors [71] on a series of 4,4'-bis(dibutylaminostyryl)-[2,2']-bipyridine Zn(II) derivatives (Figure 8). It was found that the switching from the dipolar complex 29 to the pseudo-tetrahedral octupolar complex 30 and the octahedral octupolar complex 31 is accompanied by an increased nonlinearity (Figure 8) and optical transparency, thus demonstrating the effective role of the octupolar strategy in improving the NLO properties of these molecular materials.

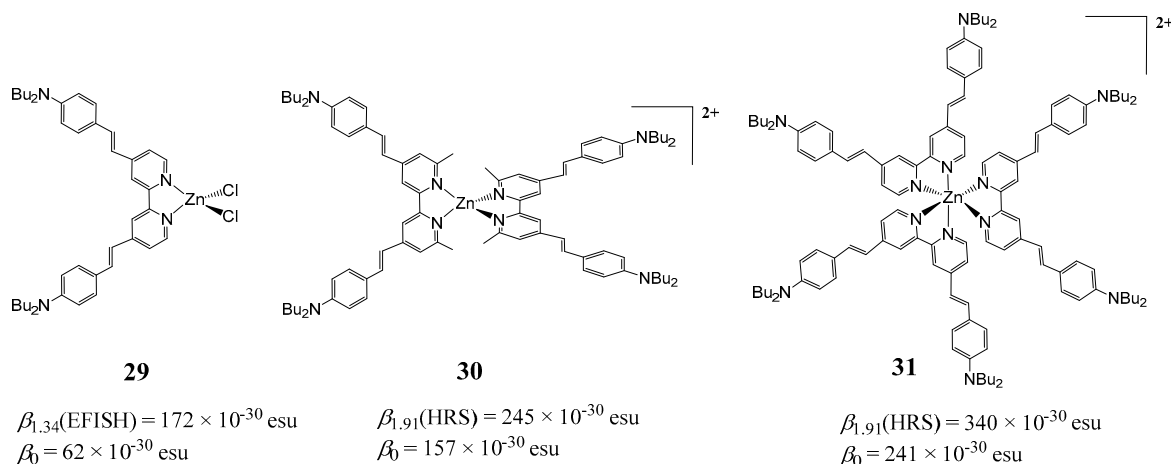


Figure 8. Dipolar and octupolar architectures based on zinc(II) complexes.

This approach was further developed through investigating octupolar D_3 and D_{2d} Zn(II) complexes with different functionalized bipyridyl ligands, in comparison with other D_3 (Fe(II), Ru(II), Hg(II)) [21], and D_{2d} (Cu(I), Ag(I)) metal complexes [21,72]. The pseudo-tetrahedral D_{2d} geometry in these complexes is stabilized by either alkyl or aryl substituents at the 6,6'-positions in the bipyridyl ligand. Very large hyperpolarizability values are achieved, especially for octahedral D_3 complexes, in relation to the nature of the ligands (donor end-groups and π -linkers) and the nature of the metal center. Interestingly, Zn(II) complexes always involve at least comparable or even larger $\beta(\text{HRS})$ values in comparison with the other metal complexes, despite the absence of MLCT transitions in the former species. Thus, the nonlinearity of these complexes seems governed by ILCT transitions, which, in turn, are correlated to the Lewis acidity of the metal ion. The length of the π -conjugated backbone of the ligand is a key parameter to maximize the NLO activity, more than the strength of the donor group. The tris(bipyridyl) Zn(II) derivative having the π -conjugated 4,4'-oligophenylenevinylene-functionalized 2,2'-bipyridine (**32**, Figure 9) exhibits the highest NLO activity, with a $\beta_{1,91}(\text{HRS})$ value of 870×10^{-30} esu and $\beta_0 = 657 \times 10^{-30}$ esu.

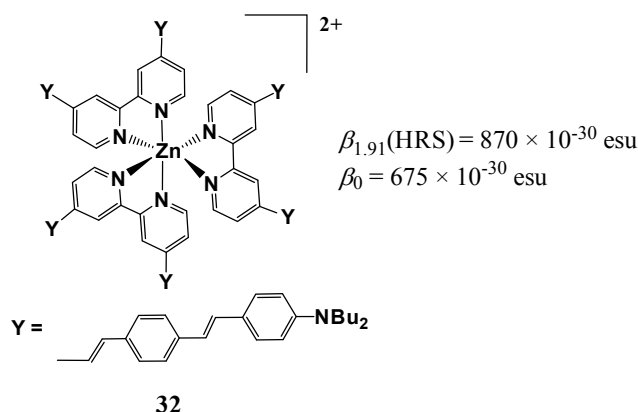


Figure 9. Structure of **32** displaying the highest NLO activity.

Analogous octupolar D_3 Zn(II) complexes, in which the six aminostyryl π -electron donor substituents are replaced by ferrocenyl groups, were developed by Coe et al. [73]. These complexes are almost unique in combining very large quadratic and cubic NLO effects in structures featuring multiple redox-switchable metal centers. Although a comparison of the experimental $\beta(\text{HRS})$ values for these complexes with those previously obtained for octupolar D_3 Zn(II) species cannot be done, because the former were obtained in resonant conditions, the Stark-derived β_0 values for these species are very large: as high as approximately 10^{-27} esu.

In order to achieve the macroscopic noncentrosymmetric orientation of these octupolar chromophores, the so-called “all-optical poling” technique [74], which is an interference process between one and two-photon excitations that locally induces macroscopic second-order effects in polymer films, has been employed. To this end, octupolar tris(bipyridyl)Zn(II) complexes containing three photoisomerizable ligands, such as 4,4'-bis-(styryl)-2,2'-bipyridine functionalized with a dialkylamino-azobenzene, **33**, were synthesized and studied [75,76]. These complexes allowed the synthesis of star-shaped polymers, in which the octupolar molecules are covalently linked to the organic backbone, **34**. It has been demonstrated that grafted polymers show an improved stability of the macroscopic photoinduced nonlinearity, in comparison with that of doped films (Figure 10).

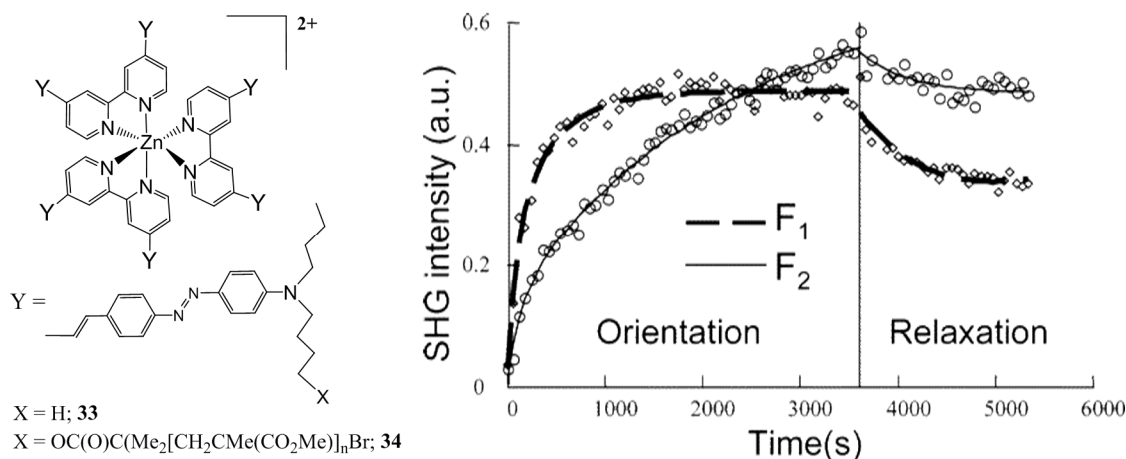


Figure 10. Optical orientation and relaxation of films **F1** and **F2** under resonant one-photon and two-photon excitations (open circles and diamonds) compared to a biexponential plot (lines). **F1** = doped film of **33**; **F2** = grafted polymer film of **34**. Adapted with permission from Ref. [75]. Copyright (2004) American Chemical Society.

More recently, Le Bozec and Jacquemin et al. communicated the first example of hexadithienylethene substituents on octahedral tris(bipyridine)M (M = Fe(II), Zn(II)) complexes [77]. The photostability of the isomeric forms of the Fe(II) complexes allowed to demonstrate the photoswitching of their second-order NLO responses.

To probe the effect of the metal center on the electronic density of π -extended ligands, a series of D_3 -symmetry octupolar Zn(II) complex derivatives of the phenanthroline were synthesized and studied [78]. Although their derived $\beta_{1.06}(\text{HRS})$ values are relatively low, especially in comparison with that of their 2,2'-bipyridine analogues, this work further demonstrated the active role of the Zn(II) center as a template for the octupolar coordination and as a tool for inducing polarization in the electronic density of the π -extended ligands.

5. Conclusions

An overview on the second-order NLO properties of the main families of Zn(II) complexes with π -delocalized ligands has been outlined. Thanks to their easy synthetic accessibility, a variety of dipolar and octupolar complexes have been explored as low-cost and efficient second-order NLO materials. Since the stereochemistry of Zn(II) complexes is not affected by ligand field stabilization, the Zn(II) ion can easily accommodate monodentate, bidentate, tridentate, or tetradentate π -delocalized ligands, in order to satisfy its coordination sphere. Thus, pyramidal, tetrahedral, and octahedral acentric structures have been achieved with relevant second-order NLO properties. Complexation almost always involves an enhancement of the nonlinearity, even in comparison with homologous metal complexes, due to intense ILCT transitions at low energy. Thus, large hyperpolarizability values have been reached within each investigated family of complexes. Moreover, for monodentate, bidentate,

and tridentate nitrogen donor ligands, a tunable NLO response, in relation to the nature of the ancillary ligands, has been found. In some cases, the switching of their NLO properties has been accomplished. In summary, zinc(II) complexes are resourceful and promising for the development of second-order NLO molecular materials.

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