





Communication

# A Chiral Bis(salicylaldiminato)zinc(II) Complex with Second-Order Nonlinear Optical and Luminescent Properties in Solution

Paola Matozzo <sup>1</sup>, Alessia Colombo <sup>1</sup> , Claudia Dragonetti <sup>1</sup>, Stefania Righetto <sup>1</sup>,  
Dominique Roberto <sup>1,\*</sup> , Paolo Biagini <sup>2</sup>, Simona Fantacci <sup>3</sup> and Daniele Marinotto <sup>4</sup>

<sup>1</sup> Dipartimento di Chimica dell'Università degli Studi di Milano, UDR-INSTM, Via C. Golgi 19, I-20133 Milano, Italy; paola.matozzo@studenti.unimi.it (P.M.); alessia.colombo@unimi.it (A.C.); claudia.dragonetti@unimi.it (C.D.); stefania.righetto@unimi.it (S.R.)

<sup>2</sup> Research Center for Renewable Energy & Environmental Istituto Donegani, Eni S.p.A., via Fauser 4, I-28100 Novara, Italy; paolo.biagini@eni.com

<sup>3</sup> Computational Laboratory for Hybrid/Organic Photovoltaics (CLHYO), CNR-SCITEC, via Elce di Sotto 8, I-06213 Perugia, Italy; simona.fantacci@gmail.com

<sup>4</sup> CNR-SCITEC, Via C. Golgi 19, I-20133 Milano, Italy; daniele.marinotto@scitec.cnr.it

\* Correspondence: dominique.roberto@unimi.it; Tel.: +39-02-5031-4399

Received: 4 March 2020; Accepted: 31 March 2020; Published: 1 April 2020



**Abstract:** Whereas there is an increasing amount of reports on the second-order nonlinear optical (NLO) and luminescence properties of tetradentate [N<sub>2</sub>O<sub>2</sub>] Schiff base–zinc complexes, the study of zinc complexes having two bidentate [NO] Schiff-base ligands is relatively unexplored from an NLO point of view. This work puts in evidence that the known chiral bis{2-[(R)-(+)-1-phenylethyliminomethyl]phenolato-*N,O*}zinc(II) complex is a fascinating multifunctional molecular inorganic–organic hybrid material characterized by interesting second-order NLO and luminescent properties in solution. The emissive properties of the organic 2-(R)-(+)-1-phenylethyliminomethyl]phenol proligand are greatly enhanced upon coordination to the inorganic Zn(II) center.

**Keywords:** zinc(II) complexes; second-order nonlinear optics; EFISH; luminescence

## 1. Introduction

Coordination compounds with second-order nonlinear optical (NLO) properties represent a topic of growing interest as molecular inorganic–organic hybrid materials for emerging optoelectronic and optical signal processing [1–15]. Compared to purely organic compounds [16–18], they have the advantage of possessing both inorganic and organic elements with a lot of different electronic structures related to the metal oxidation state and coordination sphere, which can give rise to fascinating tunable electronic and photophysical properties [1–15]. Also, metals serve as perfect templates to construct three-dimensional structures, affording dipolar and octupolar molecules [10,19]. In this panorama, coordination compounds showing both luminescent and NLO properties are particularly appealing as new multifunctional molecular materials [20–36].

An increasing amount of work has been devoted to low-cost zinc(II) complexes for their interesting third-order [37–40] and second-order NLO [41] and luminescent [42] properties. Due to its *d*<sup>10</sup> configuration, the zinc(II) center does not have a favorite stereochemistry caused by ligand field stabilization effects. Therefore, depending on the nature of the ligands, Zn(II) complexes can have various geometries (tetrahedral, square pyramidal, octahedral) and number of coordination (4, 5, and 6), affording NLO-active dipolar and octupolar compounds. Besides, they are particularly

attractive as concerns transparency considerations due to the lack of both  $d-d$  electronic transitions of the metal and metal-to-ligand transitions at low energy. In fact, an important requirement for second-harmonic generation (SHG) applications is transparency in a large spectral range in order to avoid absorption of the second harmonic [43]. Many zinc compounds having nitrogen-donor ligands such as monodentate stilbazole [44–46], bidentate bipyridine [26,47–52] or phenanthroline [44,53], tridentate terpyridine [54–56] or tetradentate porphyrin [57–59], characterized by a good second-order NLO response, have been reported, whereas the great potential of bis(salicylaldiminato)zinc Schiff base complexes [60–63] has recently been the subject of a deep exploration.

Lacroix and co-workers [64] studied the second-order NLO response of a tetradentate  $[N_2O_2]$  bis [4-(diethylamino)salicylaldiminato] zinc compound, observing an increase of the quadratic hyperpolarizability of the ligand upon coordination to Zn(II). This increase was higher than that observed upon coordination to Ni(II) and Cu(II), due to the presence of significant intraligand charge transfer transitions; contrarily to the other investigated metals, the zinc atom had a square-pyramidal geometry, with a molecule of ethanol acting as an additional donor in the apical position. It was shown by Di Bella et al. [65] that this kind of tetradentate  $[N_2O_2]$  Schiff-base complexes behave as Lewis acids due to the incapability of the Zn(II) ion to reach a tetrahedral coordination, as a result of the ring strain produced by the diamine moiety. Consequently, in the absence of Lewis bases, there is aggregation, with Zn...O intermolecular interactions, while addition of a Lewis base causes deaggregation, with formation of monomeric adducts having a penta-coordinated distorted square-pyramidal structure [66,67]. This deaggregation can switch on the quadratic hyperpolarizability [68], a phenomenon that was the springboard of an unprecedented mode of NLO switching in molecular materials. In order to increase the second-order NLO properties of bis(salicylaldiminato) Zn(II) complexes, the use of unsymmetrical tetradentate  $[N_2O_2]$  Schiff-base ligands was also investigated [69,70]. Remarkably, some of these tetradentate  $[N_2O_2]$  Schiff-base zinc complexes also show interesting luminescent properties [70]. Thanks to their Lewis acidic character, this kind of complexes are characterized by fascinating aggregation/deaggregation properties in relation to the absence or presence of a Lewis base, accompanied by significant changes of their spectroscopic properties that can find a lot of applications [71–77].

Surprisingly, whereas there is an increasing amount of reports on the second-order NLO properties of tetradentate  $[N_2O_2]$  Schiff-base zinc complexes, to our knowledge, only one paper was published, almost 20 years ago, on those of zinc complexes having two bidentate [NO] Schiff-base ligands [78]. Thus, a bis(salicylaldiminato)zinc(II) complex, synthesized from a Schiff base obtained by the condensation of chiral (*R*)-(+)-1-phenylethylamine with salicylaldehyde (Figure 1), crystallizes in the non-centrosymmetric space group  $P2_12_12_1$ , and powder samples exhibit SHG of intensity between that of 3-methyl-4-nitropyridine-1-oxide and that of *N*-(4-nitrophenyl)-(*S*)-prolinol, as determined by the Kurtz and Perry powder test [79], when illuminated with a Nd:YAG laser ( $\lambda = 1.064 \mu\text{m}$ ) [78]. In this complex, the geometry of the zinc(II) center is nearly tetrahedral, with two oxygen and two nitrogen donor atoms from the bidentate ligands, and has the  $\Lambda$  (*R,R*) absolute configuration [80] with  $\pi-\pi^*$  intraligand charge transfer along the O(phenolato)  $\rightarrow$  CN(imino) direction [78]. Surprisingly, the second-order NLO response of this complex was reported in the solid state but not in solution. This observation prompted us to prepare this appealing chiral bis(salicylaldiminato)zinc(II) complex and to study both its NLO activity at a molecular level, by means of the Electric-Field-Induced Second-Harmonic generation (EFISH) technique [81–83] in solution, and its luminescence properties.

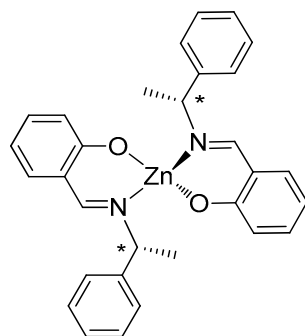
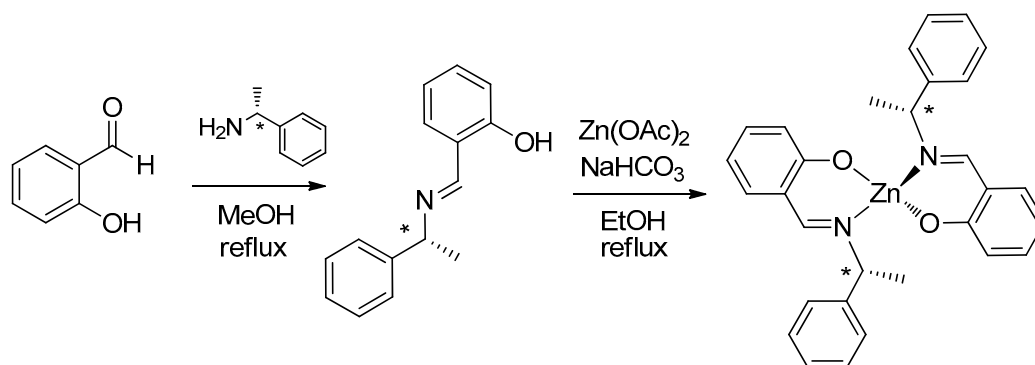


Figure 1. Investigated zinc complex.

## 2. Results and Discussion

The known 2-(*R*)-(+)-1-phenylethyliminomethyl]phenol was prepared as previously reported by reaction of (*R*)-1-phenylethylamine with salicylaldehyde in refluxing methanol, as shown in Scheme 1 [84]. Deprotonation with NaHCO<sub>3</sub> and reaction with zinc(acetate)<sub>2</sub> in refluxing ethanol afforded the related bis[2-[(*R*)-(+)-1-phenylethyliminomethyl]phenolato-*N,O*]zinc(II) complex [78,80].



Scheme 1. Synthesis of bis[2-[(*R*)-(+)-1-phenylethyliminomethyl]phenolato-*N,O*]zinc(II).

The second-order NLO properties of 2-(*R*)-(+)-1-phenylethyliminomethyl]phenol and of the related zinc(II) complex were studied by means of the EFISH method. This technique [81–83] affords information on the molecular second-order NLO properties, through the following Equation (1):

$$\gamma_{\text{EFISH}} = (\mu\beta_{\lambda}/5kT) + \gamma(-2\omega; \omega, \omega, 0) \quad (1)$$

in which  $\mu\beta_{\lambda}/5kT$  represents the dipolar orientational contribution to the molecular nonlinearity, whereas  $\gamma(-2\omega; \omega, \omega, 0)$  is the third-order polarizability, an electronic cubic contribution to  $\gamma_{\text{EFISH}}$  which is usually neglected when investigating the second-order NLO properties of dipolar molecules.  $\beta_{\lambda}$  represents the projection along the ground-state dipole moment ( $\mu$ ) axis of the vectorial component of the tensor of the quadratic hyperpolarizability ( $\beta_{\text{VEC}}$ ), when the incident wavelength of the pulsed laser is  $\lambda$ . In order to have a compound of interest for second-order NLO applications, one needs a high  $\mu\beta_{\text{EFISH}}$  value. Extrapolation to zero frequency ( $\nu_{\Lambda} = 0.0$  eV;  $\lambda = \infty$ ) allows the determination of  $\mu\beta_0$ , the product of the ground-state dipole moment by the static quadratic hyperpolarizability  $\beta_0$ , a useful figure of merit to evaluate the basic second-order NLO properties of a molecular material. The  $\mu\beta_0$  value can be obtained by using the following Equation (2):

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

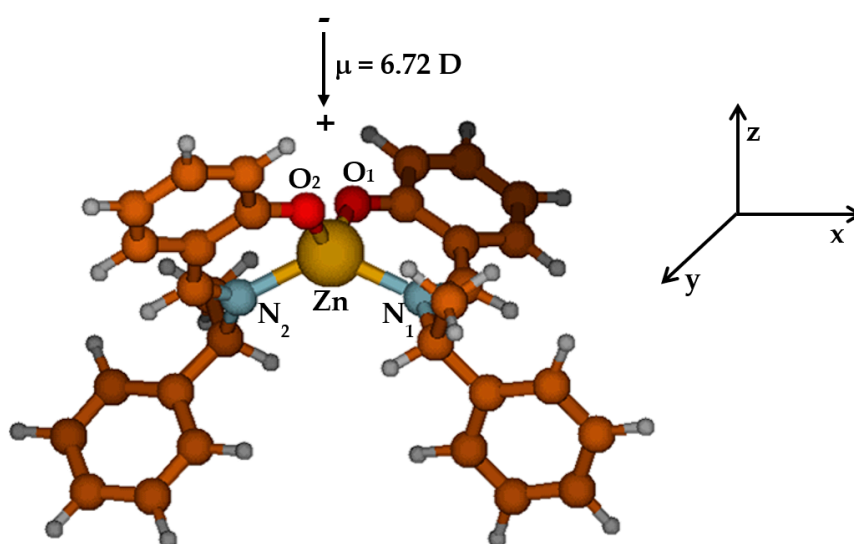
where  $\beta_{\lambda}$  is the quadratic hyperpolarizability value at the incident wavelength  $\lambda$ , and  $\lambda_{\text{max}}$  is the absorption wavelength of the major charge-transfer transition considered.

Besides, it is essential to avoid overestimation of the quadratic hyperpolarizability value due to resonance enhancements. For this reason, one has to use an incident wavelength whose second harmonic is remote from any absorption of the molecule investigated. In the present study, we chose an incident wavelength of 1.907  $\mu\text{m}$ , obtained by Raman-shifting the fundamental 1.064  $\mu\text{m}$  wavelength produced by a Q-switched, mode-locked Nd:YAG laser.

We found that both 2-(*R*)-(+)-1-phenylethyliminomethyl]phenol and the related zinc(II) complex are characterized by a positive value of  $\mu\beta_{\lambda}$ , in agreement with a positive value of  $\Delta\mu_{\text{eg}}$  (difference of the dipole moment in the excited and ground states) upon excitation, according to the “two-level” model [85,86].

The  $\mu\beta_{1.907}$  value of bis{2-[(*R*)-(+)-1-phenylethyliminomethyl]phenolato-*N,O*}zinc(II) is  $420 \times 10^{-48}$  esu, a value somewhat larger than the double of that of the pro-ligand ( $195 \times 10^{-48}$  esu). This behavior is in agreement with that previously observed in the case of tetradentate [ $\text{N}_2\text{O}_2$ ] Schiff bases and related zinc complexes [64]. The  $\mu\beta$  value of the investigated zinc(II) complex, calculated by using Equation (2) and its low energy  $\pi-\pi^*$  intraligand charge-transfer absorption band (374 nm) [78], is  $342 \times 10^{-48}$  esu, a value not too far from that ( $450 \times 10^{-48}$  esu) of the prototypical organic 1D push-pull NLO chromophore Disperse Red One (*trans*-4,4'- $\text{O}_2\text{NC}_6\text{H}_4\text{N}=\text{NC}_6\text{H}_4\text{NEt}-(\text{CH}_2\text{CH}_2\text{OH})$ ), which finds application in electrooptic polymeric poled films [87].

In order to determine the  $\beta_{1.907}$  and  $\beta_0$  values, it is necessary to know  $\mu$ . Therefore, the geometry of the zinc complex was optimized, and its dipole moment was calculated by means of the Density Functional Theory. We used the B3LYP exchange correlation functional, the 6-311g\*\* basis set for all atoms except for Zn, which has been described with the LANL2DZ basis set, along with the corresponding pseudopotentials. The  $\text{CHCl}_3$  solution effects were included by means of the conductor-like polarizable continuum model. Geometry optimization, performed with Gaussian09 [88] without any symmetry constraints, showed a pseudo- $\text{C}_2$  symmetry (Figure 2). In agreement with the structure determined by X-ray crystallography, the dihedral angle between plane  $\text{O}_1\text{ZnN}_1$  and plane  $\text{O}_2\text{ZnN}_2$  is  $84.4^\circ$ , so that the geometry around the zinc atom is almost tetrahedral, with a small distortion on the way to a *cis*-planar geometry [78]. The computed dipole moment, 6.72 D, is aligned on the bisector of  $\text{O}_1\text{ZnO}_2$  angle from the oxygen atoms to the metal center.



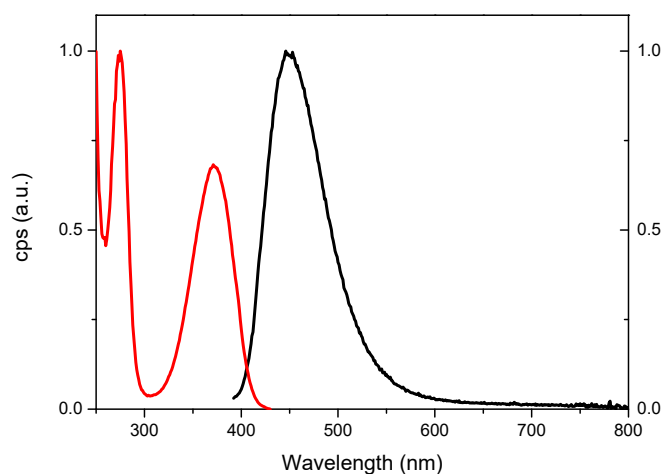
**Figure 2.** Optimized geometry of the investigated zinc complex.

The  $\beta_{1.907}$  and  $\beta_0$  values, obtained by using the calculated dipole moment (6.72 D), are 62.5 and  $50.9 \times 10^{-30}$  esu, respectively. These values are higher than those previously reported for [(4,4'-*trans*- $\text{NMe}_2-\text{C}_6\text{H}_4\text{CH}=\text{CHC}_5\text{H}_4\text{N}$ ) $_2\text{Zn}(\text{CF}_3\text{CO}_2)_2$ ] [44], a remarkable result for such a simple

complex. This opens a new avenue for the design of NLO-active zinc complexes, by using two bidentate [NO] Schiff-base ligands.

As a further step, we were curious to investigate the luminescence properties of the complex. Indeed, there is interest in the study of organic–inorganic hybrid materials consisting of Schiff base–Zn(II) complexes in polymethyl methacrylate (PMMA) to impart new features such as luminescence properties [89]. Akitsu et al. prepared various organic–inorganic materials containing an organic photochromic dye and a chiral Schiff base–zinc(II) complex in PMMA in order to obtain multi-input and multi-output digital logic circuits [90]. They proposed that a chiral Schiff base–zinc(II) complex could be used in logic circuits in combination with a photochromic dye by using intermolecular quenching of emission [91]. Of interest for this application was bis[2-[(R)-(+)-1-phenylethyliminomethyl]phenolato-*N,O*]zinc(II), which emits at 451 nm, in combination with spiropyran (or its photoisomerized form merocyanine) [91], but the quantum yield of this complex was not reported. These observations prompted us to reinvestigate its photophysical properties.

Whereas 2-[(R)-(+)-1-phenylethyliminomethyl]phenol is not luminescent, the related zinc(II) complex is intensely luminescent in dichloromethane solution, displaying a band at 451 nm upon excitation at 372 nm (Figure 3), a behavior that puts in evidence the strong luminescent effect of complexation to a Zn(II) center. The luminescent quantum yield ( $\varphi_{\text{lum}} = 0.17$ ) was very good, being similar to that of the most luminescent Schiff base–zinc(II) complexes [70].



**Figure 3.** Excitation and emission spectra of the Zn(II) complex in dichloromethane ( $2 \times 10^{-5}$  M) at room temperature. Red line: Excitation spectrum,  $\lambda_{\text{em}} = 451$  nm. Black line: Emission spectrum,  $\lambda_{\text{exc}} = 372$  nm.

### 3. Materials and Methods

#### 3.1. Synthesis of 2-[(R)-(+)-1-phenylethyliminomethyl]phenol and Bis[2-[(R)-(+)-1-phenylethyliminomethyl]phenolato-*N,O*]zinc(II)

The compound 2-[(R)-(+)-1-phenylethyliminomethyl]phenol was prepared following a reported procedure [84]. A solution of (*R*)-1-phenylethylamine (0.75 mL, 5.8 mmol) and salicylaldehyde (0.30 mL, 3.1 mmol) was refluxed in methanol (10 mL) for 4 h. The solution was cooled at room temperature, and the solvent was removed under reduced pressure, affording a solid which was recrystallized from ethanol, affording the product as a bright yellow powder (0.550 g, 2.44 mmol; 79% yield).

Then, in a Schlenk tube, 2-[(R)-(+)-1-phenylethyliminomethyl]phenol (0.400 g; 1.77 mmol) was dissolved in ethanol (12 mL) under reflux. Powdered  $\text{NaHCO}_3$  (0.151 g, 1.79 mmol) was added to deprotonate the phenol group, and after 15 min, zinc(acetate) $_2$  (0.198 g, 0.902 mmol) was added. The mixture was refluxed for 2 h and then filtered, and the filtrate was concentrated under reduced

pressure until crystals precipitated. The known complex [78,80] was obtained by filtration as pale yellow crystals (0.420 g; 0.817 mmol; 91% yield; see elemental analysis and  $^1\text{H}$  NMR in Supplementary Materials).

### 3.2. Instrumentation

Steady-state fluorescence data and absolute luminescence quantum yields measurements were obtained using an FLS980 spectrofluorimeter (Edinburg Instrument Ltd., Livingston, United Kingdom) and a C11347 Quantaaurus Hamamatsu Photonics K.K spectrometer (Hamamatsu Photonics, Shizuoka, Japan), respectively.

EFISH measurements were carried out in  $\text{CHCl}_3$  solutions at a concentration of  $10^{-3}$  M, with a non-resonant incident wavelength of 1.907  $\mu\text{m}$ , obtained by Raman-shifting the fundamental 1.064  $\mu\text{m}$  wavelength produced by a Q-switched, mode-locked Nd:YAG laser manufactured by Atalaser (see Supplementary Materials). The reported  $\mu\beta_{\text{EFISH}}$  values are the mean values of 16 measurements performed on the same sample, the error is ca. 10%.

## 4. Conclusions

In conclusion, this work unveils the interesting properties in solution of the chiral bis(2-[(*R*)-(+)-1-phenylethyliminomethyl]phenolato-*N,O*)zinc(II) complex. It was previously reported that powder samples of this complex exhibit second-harmonic generation [78]. The present study shows that this hybrid inorganic–organic compound is also characterized by good second-order NLO properties at the molecular level in solution. This is an interesting aspect, from an applicative point of view, because it suggests that dispersion of this complex in organic matrices is a promising route for the preparation of NLO-active polymeric films. This fascinating zinc complex is characterized by multifunctional properties. As a matter of fact, it is also intensely luminescent at 451 nm in dichloromethane, with a quantum yield ( $\varphi_{\text{lum}} = 0.17$ ) similar to that of the most luminescent tetradentate  $[\text{N}_2\text{O}_2]$  Schiff base–zinc(II) complexes. It is worth noting that the free ligand 2-[(*R*)-(+)-1-phenylethyliminomethyl]phenol is not luminescent, a behavior that puts in evidence the strong effect of complexation of the organic ligand to the inorganic Zn(II) center on the luminescent properties. This work opens the door to the exploration of related bidentate  $[\text{NO}]$ –zinc(II) complexes with various substituents on the phenolato moiety to understand their effects on the second-order NLO and luminescence properties.

**Supplementary Materials:** The following are available online at <http://www.mdpi.com/2304-6740/8/4/25/s1>. Elemental analysis and  $^1\text{H}$  NMR spectrum of the investigated zinc complex; details on the EFISH measurements.

**Author Contributions:** A.C., C.D., D.R., and P.B. conceived the study and designed the experiments; P.M. prepared the zinc complex; S.R. carried out the EFISH measurements; D.M. and S.R. studied the luminescence of the compounds; S.F. calculated the optimized geometry of the complex and the dipole moment. D.R. wrote the first draft of the manuscript; A.C., S.F., and D.M. did the figures and graphical abstract. All authors have read and agreed to the published version of the manuscript.

**Funding:** We thank Università degli Studi di Milano (PSR 2019-Linea 2 Azione A – PSR2019\_DIP\_005\_PI\_CDRA “Coordination complexes and organic–inorganic hybrid materials for photonics and optoelectronics” for financial support. Fondazione Cariplo and Regione Lombardia are acknowledged for the instrumentation bought during the *SmartMatLab Centre* project (2014). Part of this work was performed under research contract No. 4310316177 between National Interuniversity Consortium of Materials Science and Technology (INSTM) and Eni S.p.A, Rome, Italy.

**Conflicts of Interest:** The authors declare no conflict of interest.

## References

1. Long, N.J. Organometallic Compounds for Nonlinear Optics—The Search for En-light-enment! *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 21–38. [[CrossRef](#)]
2. Whittal, I.R.; McDonagh, A.M.; Humphrey, M.G. Organometallic complexes in nonlinear optics I: Second-order nonlinearities. *Adv. Organomet. Chem.* **1998**, *42*, 291–362.



3. Heck, J.; Dabek, S.; Meyer-Friedrichsen, T.; Wong, H. Mono- and dinuclear sesquifulvalene complexes, organometallic materials with large nonlinear optical properties. *Coord. Chem. Rev.* **1999**, *190–192*, 1217–1254. [[CrossRef](#)]
4. Le Bozec, H.; Renouard, T. Dipolar and Non-Dipolar Pyridine and Bipyridine Metal Complexes for Nonlinear Optics. *Eur. J. Inorg. Chem.* **2000**, *2*, 229–239. [[CrossRef](#)]
5. Di Bella, S. Second-order nonlinear optical properties of transition metal complexes. *Chem. Soc. Rev.* **2001**, *30*, 355–366. [[CrossRef](#)]
6. Pizzotti, M.; Ugo, R.; Roberto, D.; Bruni, S.; Fantucci, P.C.; Rovizzi, C. Organometallic Counterparts of Push–Pull Aromatic Chromophores for Nonlinear Optics: Push–Pull Heteronuclear Bimetallic Complexes with Pyrazine and *trans*-1,2-Bis(4-pyridyl)ethylene as Linkers. *Organometallics* **2002**, *21*, 5830–5840. [[CrossRef](#)]
7. Powell, C.E.; Humphrey, M.G. Nonlinear optical properties of transition metal acetylides and their derivatives. *Coord. Chem. Rev.* **2004**, *248*, 725–756. [[CrossRef](#)]
8. Coe, B.J. Nonlinear Optical Properties of Metal Complexes. In *Comprehensive Coordination Chemistry II*; McCleverty, J.A., Meyer, T.J., Eds.; Elsevier Pergamon: Oxford, UK, 2004; Volume 9, pp. 621–687.
9. Coe, B.J.; Curati, N.R.M. Metal complexes for molecular electronics and photonics. *Comments Inorg. Chem.* **2004**, *25*, 147–184. [[CrossRef](#)]
10. Maury, O.; Le Bozec, H. Molecular Engineering of Octupolar NLO Molecules and Materials Based on Bipyridyl Metal Complexes. *Acc. Chem. Res.* **2005**, *38*, 691–704. [[CrossRef](#)]
11. Cariati, E.; Pizzotti, M.; Roberto, D.; Tessore, F.; Ugo, R. Coordination and organometallic compounds and inorganic–organic hybrid crystalline materials for second-order non-linear optics. *Coord. Chem. Rev.* **2006**, *250*, 1210–1233. [[CrossRef](#)]
12. Coe, B.J. Switchable Nonlinear Optical Metallochromophores with Pyridinium Electron Acceptor Groups. *Acc. Chem. Res.* **2006**, *39*, 383–393. [[CrossRef](#)] [[PubMed](#)]
13. Coe, B.J. Ruthenium Complexes as Versatile Chromophores with Large, Switchable Hyperpolarizabilities. In *Non-Linear Optical Properties of Matter*; Papadopoulos, G.M., Sadlej, A.J., Leszczynski, J., Eds.; Springer: Dordrecht, The Netherlands, 2006; pp. 571–608.
14. Morrall, J.P.; Dalton, G.T.; Humphrey, M.G.; Samoc, M. Organotransition Metal Complexes for Nonlinear Optics. *Adv. Organomet. Chem.* **2007**, *55*, 61–136.
15. Di Bella, S.; Dragonetti, C.; Pizzotti, M.; Roberto, D.; Tessore, F.; Ugo, R. Coordination and organometallic complexes as second-order nonlinear optical materials. In *Molecular Organometallic Material for Optics*; Bozec, H., Guerschais, V., Eds.; Springer: Heidelberg, Germany, 2010; pp. 1–55.
16. Beverina, L.; Ruffo, R.; Patriarca, G.; De Angelis, F.; Roberto, D.; Righetto, S.; Ugo, R.; Pagani, G.A. Second harmonic generation in nonsymmetrical squaraines: Tuning of the directional charge transfer character in highly delocalized dyes. *J. Mater. Chem.* **2009**, *19*, 8190–8197. [[CrossRef](#)]
17. Dalton, L.R.; Sullivan, P.A.; Bale, D.H. Electric Field Poled Organic Electro-optic Materials: State of the Art and Future Prospects. *Chem. Rev.* **2010**, *110*, 25–55. [[CrossRef](#)]
18. Dalton, L.R.; Günter, P.; Jazbinsek, M.; Kwon, O.P.; Sullivan, P.A. *Organic Electro-Optics and Photonics: Molecules, Polymers and Crystals*; Cambridge University Press: Cambridge, UK, 2015.
19. Maury, O.; Viau, L.; Sénéchal, K.; Corre, B.; Guégan, J.P.; Renouard, T.; Ledoux, I.; Zyss, J.; Le Bozec, H. Synthesis, Linear, and Quadratic-Nonlinear Optical Properties of Octupolar  $D_3$  and  $D_{2d}$  Bipyridyl Metal Complexes. *Chem. Eur. J.* **2004**, *10*, 4454–4466. [[CrossRef](#)]
20. Guloy, A.M.; Tang, Z.; Miranda, P.B.; Srdanov, V.I. A New Luminescent Organic–Inorganic Hybrid Compound with Large Optical Nonlinearity. *Adv. Mater.* **2001**, *13*, 833–837. [[CrossRef](#)]
21. Cariati, E.; Roberto, D.; Ugo, R.; Ford, P.C.; Galli, S.; Sironi, A. X-ray Structures and Emissive and Second-Order Nonlinear Optical Properties of Two Inorganic–Organic Polymeric Adducts of CuI with 4-Acetylpyridine. The Role of Both “Intrastrand” Charge Transfers and Structural Motifs on the Nonlinear Optical Response of Cu(I) Polymeric Adducts with Pseudoaromatic  $\eta^1$ -Nitrogen Donor Ligands. *Chem. Mater.* **2002**, *14*, 5116–5123.
22. Barsu, C.; Fortrie, R.; Nowika, K.; Baldeck, P.L.; Vial, J.C.; Barsella, A.; Fort, A.; Hissler, M.; Bretonnière, Y.; Maury, O.; et al. Synthesis of chromophores combining second harmonic generation and two photon induced fluorescence properties. *Chem. Commun.* **2006**, 4744–4746. [[CrossRef](#)]

23. Feuvrie, C.; Maury, O.; Le Bozec, H.; Ledoux, I.; Morrall, J.P.; Dalton, G.T.; Samoc, M.; Humphrey, M.G. Nonlinear Optical and Two-Photon Absorption Properties of Octupolar Tris(bipyridyl)metal Complexes. *J. Phys. Chem. A* **2007**, *111*, 8980–8985. [[CrossRef](#)]
24. Dragonetti, C.; Righetto, S.; Roberto, D.; Ugo, R.; Valore, A.; Demartin, F.; De Angelis, F.; Sgamellotti, A.; Fantacci, S. The role of 5-R-1,10-phenanthroline (R = CH<sub>3</sub>, NO<sub>2</sub>) on the emission properties and second-order NLO response of cationic Ir(III) organometallic chromophores. *Inorg. Chim. Acta* **2008**, *361*, 4070–4076. [[CrossRef](#)]
25. Valore, A.; Colombo, A.; Dragonetti, C.; Righetto, S.; Roberto, D.; Ugo, R.; De Angelis, F.; Fantacci, S. Luminescent cyclometallated Ir(III) and Pt(II) complexes with  $\beta$ -diketonate ligands as highly active second-order NLO chromophores. *Chem. Commun.* **2010**, *46*, 2414–2416. [[CrossRef](#)] [[PubMed](#)]
26. Todescato, F.; Fortunati, I.; Carlotta, S.; Ferrante, C.; Grisanti, L.; Sissa, C.; Painelli, A.; Colombo, A.; Dragonetti, C.; Roberto, D. Dimers of polar chromophores in solution: Role of excitonic interactions in one- and two-photon absorption properties. *Phys. Chem. Chem. Phys.* **2011**, *13*, 11099–11109. [[CrossRef](#)] [[PubMed](#)]
27. Ka Man Chan, C.; Tao, C.-H.; Li, K.-F.; Wong, K.M.-C.; Zhu, N.; Cheah, K.-W.; Yam, V.W.-W. Synthesis, characterization, luminescence and nonlinear optical (NLO) properties of truxene-containing platinum(II) alkynyl complexes. *J. Organomet. Chem.* **2011**, *696*, 1163–1173. [[CrossRef](#)]
28. Rossi, E.; Colombo, A.; Dragonetti, C.; Righetto, S.; Roberto, D.; Ugo, R.; Valore, A.; Williams, J.A.G.; Lobello, M.G.; De Angelis, F.; et al. Tuning the dipolar second-order non-linear optical properties of cyclometallated platinum(II) complexes with tridentate N<sup>C</sup>N-binding ligands. *Chem. Eur. J.* **2013**, *19*, 9875–9883. [[CrossRef](#)] [[PubMed](#)]
29. Zaarour, M.; Singh, A.; Latouche, C.; Williams, J.A.G.; Ledoux-Rak, I.; Zyss, J.; Boucekkine, A.; Le Bozec, H.; Guerchais, V.; Dragonetti, C.; et al. Linear and nonlinear optical properties of tris-cyclometalated phenylpyridine Ir(III) complexes incorporating  $\pi$ -conjugated substituents. *Inorg. Chem.* **2013**, *52*, 7987–7994. [[CrossRef](#)]
30. Cariati, E.; Dragonetti, C.; Lucenti, E.; Nisic, F.; Righetto, S.; Roberto, D.; Tordin, E. An acido-triggered reversible luminescent and nonlinear optical switch based on a substituted styrylpyridine: EFISH measurements as an unusual method to reveal a protonation–deprotonation NLO contrast. *Chem. Commun.* **2014**, *50*, 1608–1610. [[CrossRef](#)]
31. Boixel, J.; Guerchais, V.; Le Bozec, H.; Chantzis, A.; Jacquemin, D.; Colombo, A.; Dragonetti, C.; Marinotto, D.; Roberto, D. Sequential double second-order nonlinear optical switch by an acido-triggered photochromic cyclometallated platinum(II) complex. *Chem. Commun.* **2015**, *51*, 7805–7808. [[CrossRef](#)]
32. Chavan, S.S.; Pawal, S.B.; Lolage, S.R.; Garadkar, K.M. Synthesis, spectroscopic characterization, luminescence and NLO properties of heterometallic M(II)–Ru(II) (M = Ni and Zn) hybrid complexes composed of coordination and organometallic sites. *J. Organomet. Chem.* **2017**, *853*, 18–26. [[CrossRef](#)]
33. Guerchais, V.; Boixel, J.; Le Bozec, H. Linear and Nonlinear Optical Molecular Switches Based on Photochromic Metal Complexes. In *Photon-Working Switches*; Yokoyama, Y., Nakatani, K., Eds.; Springer: Tokyo, Japan, 2017; pp. 363–384.
34. Zhao, H.; Garoni, E.; Roisnel, T.; Colombo, A.; Dragonetti, C.; Marinotto, D.; Righetto, S.; Roberto, D.; Jacquemin, D.; Boixel, J.; et al. Photochromic DTE-Substituted-1,3-di(2-pyridyl)benzene Platinum(II) Complexes: Photomodulation of Luminescence and Second-Order Nonlinear Optical Properties. *Inorg. Chem.* **2018**, *57*, 7051–7063. [[CrossRef](#)]
35. Chakrabarty, R.; Dutta, A.; Roy, S.; Das, G.; Ledoux-Rak, I.; Mondal, P.; Prasad, S.K.; Rao, D.S.S.; Bhattacharjee, C.R. Multifunctional Lanthanide Complexes: Mesomorphism, Photoluminescence and Second Order NLO Property. *Chemistry Select* **2018**, *3*, 8245–8251. [[CrossRef](#)]
36. Lucenti, E.; Forni, A.; Marinotto, D.; Previtali, A.; Righetto, S.; Cariati, E. Tuning the Linear and Nonlinear Optical Properties of Pyrene-Pyridine Chromophores by Protonation and Complexation to  $d_{10}$  Metal Centers. *Inorganics* **2019**, *7*, 38. [[CrossRef](#)]
37. Righetto, S.; Rondena, S.; Locatelli, D.; Roberto, D.; Tessore, F.; Ugo, R.; Quici, S.; Roma, S.; Korystov, D.; Srdanov, V. An investigation on the two-photon absorption activity of various terpyridines and related homoleptic and heteroleptic cationic Zn(II) complexes. *J. Mater. Chem.* **2006**, *16*, 1439–1444. [[CrossRef](#)]
38. Mazzucato, S.; Fortunati, I.; Scolaro, S.; Zerbetto, M.; Ferrante, C.; Signorini, R.; Pedron, D.; Bozio, R.; Locatelli, D.; Righetto, S.; et al. Two-photon absorption of Zn(II) octupolar molecules. *Phys. Chem. Chem. Phys.* **2007**, *9*, 2999–3005. [[CrossRef](#)] [[PubMed](#)]



39. Dragonetti, C.; Balordi, M.; Colombo, A.; Roberto, D.; Ugo, R.; Fortunati, I.; Garbin, E.; Ferrante, C.; Bozio, R.; Abbotto, A.; et al. Two-photon absorption properties of Zn(II) complexes: Unexpected large TPA cross section of dipolar [ZnY<sub>2</sub>(4,4'-bis(*para*-di-*n*-butylaminostyryl)-2,2'-bipyridine)] (Y = Cl, CF<sub>3</sub>CO<sub>2</sub>). *Chem. Phys. Lett.* **2009**, *475*, 245–249. [[CrossRef](#)]
40. Grisanti, L.; Sissa, C.; Terenziani, F.; Painelli, A.; Roberto, D.; Tessore, F.; Ugo, R.; Quici, S.; Fortunati, I.; Garbin, E.; et al. Enhancing the efficiency of two-photon absorption by metal coordination. *Phys. Chem. Chem. Phys.* **2009**, *11*, 9450–9457. [[CrossRef](#)] [[PubMed](#)]
41. Di Bella, S.; Colombo, A.; Dragonetti, C.; Righetto, S.; Roberto, D. Zinc(II) as a versatile template for the preparation of fascinating dipolar and octupolar second-order nonlinear optical molecular materials. *Inorganics* **2018**, *6*, 133. [[CrossRef](#)]
42. Tian, X.; Hussain, S.; de Pace, C.; Ruiz-Prez, L.; Battaglia, G. Zn<sup>II</sup> Complexes for Bioimaging and Correlated Applications. *Chem. Asian J.* **2019**, *14*, 509–526.
43. *Zyss, in Conjugated Polymeric Matenals: Opportunities in Electronics, Optoelectronics and Molecular Electronics*; Brédas, J.-L.; Chance, R.R. (Eds.) Kluwer Academic Publishers: Dordrecht, The Netherlands, 1990.
44. Roberto, D.; Ugo, R.; Tessore, F.; Lucenti, E.; Quici, S.; Vezza, S.; Fantucci, P.C.; Invernizzi, I.; Bruni, S.; Ledoux-Rak, I.; et al. Effect of the Coordination to M(II) Metal Centers (M = Zn, Cd, Pt) on the Quadratic Hyperpolarizability of Various Substituted 5-X-1,10-phenanthrolines (X = Donor Group) and of *trans*-4-(Dimethylamino)-4'-stilbazole. *Organometallics* **2002**, *21*, 161–170. [[CrossRef](#)]
45. Tessore, F.; Roberto, D.; Ugo, R.; Mussini, P.; Quici, S.; Ledoux-Rak, I.; Zyss, J. Large, Concentration-Dependent Enhancement of the Quadratic Hyperpolarizability of [Zn(CH<sub>3</sub>CO<sub>2</sub>)<sub>2</sub>(L)<sub>2</sub>] in CHCl<sub>3</sub> on Substitution of Acetate by Triflate. *Angew. Chem. Int. Ed.* **2003**, *42*, 456–459. [[CrossRef](#)] [[PubMed](#)]
46. Tessore, F.; Locatelli, D.; Righetto, S.; Roberto, D.; Ugo, R.; Mussini, P. An Investigation on the Role of the Nature of Sulfonate Ancillary Ligands on the Strength and Concentration Dependence of the Second-Order NLO Responses in CHCl<sub>3</sub> of Zn(II) Complexes with 4,4'-*trans*-NC<sub>5</sub>H<sub>4</sub>CH=CHC<sub>6</sub>H<sub>4</sub>NMe<sub>2</sub> and 4,4'-*trans,trans*-NC<sub>5</sub>H<sub>4</sub>(CH=CH)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>NMe<sub>2</sub>. *Inorg. Chem.* **2005**, *44*, 2437–2442.
47. Bourgault, M.; Mountassir, C.; Le Bozec, H.; Ledoux, I.; Pucetti, G.; Zyss, J. Synthesis and second-order nonlinear optical properties of new bipyridyl metal complexes. *J Chem. Soc. Chem. Comm.* **1993**, *21*, 1623–1624. [[CrossRef](#)]
48. Bourgault, M.; Baum, K.; Le Bozec, H.; Pucetti, G.; Ledoux, I.; Zyss, J. Synthesis and molecular hyperpolarisabilities of donor–acceptor bipyridyl metal complexes (M = Re, Zn, Hg). *New J. Chem.* **1998**, *22*, 517–522. [[CrossRef](#)]
49. Hilton, A.; Renouard, T.; Maury, O.; Le Bozec, H.; Ledoux, I.; Zyss, J. New bipyridyl ligands bearing azo- and imino-linked chromophores. Synthesis and nonlinear optical studies of related dipolar zinc complexes. *Chem. Commun.* **1999**, 2521–2522. [[CrossRef](#)]
50. Sénéchal, K.; Maury, O.; Le Bozec, H.; Ledoux, I.; Zyss, J. Zinc(II) as a Versatile Template for the Design of Dipolar and Octupolar NLO-phores. *J. Am. Chem. Soc.* **2002**, *124*, 4560–4561. [[CrossRef](#)]
51. Viau, L.; Bidault, S.; Maury, O.; Brasselet, S.; Ledoux, I.; Zyss, J.; Ishow, E.; Nakatani, K.; Le Bozec, H. All-Optical Orientation of Photoisomerizable Octupolar Zinc(II) Complexes in Polymer Films. *J. Am. Chem. Soc.* **2004**, *126*, 8386–8387. [[CrossRef](#)] [[PubMed](#)]
52. Aubert, V.; Guerchais, V.; Ishow, E.; Hoang-Thy, K.; Ledoux, I.; Nakatani, K.; Le Bozec, H. Efficient Photoswitching of the Nonlinear Optical Properties of Dipolar Photochromic Zinc(II) Complexes. *Angew. Chem. Int. Ed.* **2008**, *47*, 577–580. [[CrossRef](#)] [[PubMed](#)]
53. Das, S.; Jana, A.; Ramanathan, V.; Chakraborty, T.; Ghosh, S.; Das, P.K.; Bharadwaj, P.K. Design and synthesis of 1,10-phenanthroline based Zn(II) complexes bearing 1D push–pull NLO-phores for tunable quadratic nonlinear optical properties. *J. Organomet. Chem.* **2006**, *691*, 2512–2516. [[CrossRef](#)]
54. Roberto, D.; Tessore, F.; Ugo, R.; Bruni, S.; Manfredi, A.; Quici, S. Terpyridine Zn(II), Ru(III) and Ir(III) complexes as new asymmetric chromophores for nonlinear optics: First evidence for a shift from positive to negative value of the quadratic hyperpolarizability of a ligand carrying an electron donor substituent upon coordination to different metal centres. *Chem. Commun.* **2002**, 846–847.
55. Tessore, F.; Roberto, D.; Ugo, R.; Pizzotti, M.; Quici, S.; Cavazzini, M.; Bruni, S.; De Angelis, F. Terpyridine Zn(II), Ru(III), and Ir(III) Complexes: The Relevant Role of the Nature of the Metal Ion and of the Ancillary Ligands on the Second-Order Nonlinear Response of Terpyridines Carrying Electron Donor or Electron Acceptor Groups. *Inorg. Chem.* **2005**, *44*, 8967–8978. [[CrossRef](#)]

56. Locatelli, D.; Quici, S.; Righetto, S.; Roberto, D.; Tessore, F.; Ashwell, G.J.; Amiri, M. Second-harmonic generation from monolayer Langmuir-Blodgett films of various push-pull pyridine and terpyridine metal complexes. *Prog. Solid State Chem.* **2005**, *33*, 223–232. [[CrossRef](#)]
57. Annoni, E.; Pizzotti, M.; Ugo, R.; Quici, S.; Morotti, T.; Bruschi, M.; Mussini, P. Synthesis, Electronic characterization and Significant Second Order Non Linear Optical Responses of meso Tetraphenylporphyrins and their Zn(II) Complexes Carrying a Push or Pull Group in  $\beta$  Pyrrolic Position. *Eur. J. Inorg. Chem.* **2005**, 3857–3874. [[CrossRef](#)]
58. Morotti, T.; Pizzotti, M.; Ugo, R.; Quici, S.; Bruschi, M.; Mussini, P.; Righetto, S. Electronic Characterisation and Significant Second Order NLO response of 10,20-Diphenylporphyrins and their Zn(II) complexes Substituted in the meso position with  $\pi$ -Delocalised Linkers Carrying Push or Pull Groups. *Eur. J. Inorg. Chem.* **2006**, 1743–1757. [[CrossRef](#)]
59. Tessore, F.; Orbelli Biroli, A.; Di Carlo, G.; Pizzotti, M. Porphyrins for Second Order Nonlinear Optics (NLO): An Intriguing History. *Inorganics* **2018**, *6*, 81. [[CrossRef](#)]
60. Di Bella, S.; Fragalà, I. Synthesis and second-order nonlinear optical properties of bis(salicylaldiminato)M(II) metalloorganic materials. *Synth. Met.* **2000**, *115*, 191–196. [[CrossRef](#)]
61. Lacroix, P.G. Second-Order Optical Nonlinearities in Coordination Chemistry: The Case of Bis(salicylaldiminato)metal Schiff Base Complexes. *Eur. J. Inorg. Chem.* **2001**, 339–348. [[CrossRef](#)]
62. Nayar, C.R.; Ravikumar, R. Second order nonlinearities of Schiff bases derived from salicylaldehyde and their metal complexes. *J. Coord. Chem.* **2014**, *67*, 1–16. [[CrossRef](#)]
63. Liu, X.; Manzur, C.; Novoa, N.; Celedón, S.; Carrillo, D.; Hamon, J.-R. Multidentate unsymmetrically-substituted Schiff bases and their metal complexes: Synthesis, functional materials properties, and applications to catalysis. *Coord. Chem. Rev.* **2018**, *357*, 144–172. [[CrossRef](#)]
64. Lacroix, P.G.; Di Bella, S.; Ledoux, I. Synthesis and Second-Order Nonlinear Optical Properties of New Copper(II), Nickel(II), and Zinc(II) Schiff-Base Complexes. Toward a Role of Inorganic Chromophores for Second Harmonic Generation. *Chem. Mater.* **1996**, *8*, 541–545. [[CrossRef](#)]
65. Forte, G.; Oliveri, I.P.; Consiglio, G.; Failla, S.; Di Bella, S. On the Lewis acidic character of bis(salicylaldiminato)zinc(II) Schiff-base complexes: A computational and experimental investigation on a series of compounds varying the bridging diamine. *Dalton Trans.* **2017**, *46*, 4571–4581. [[CrossRef](#)]
66. Consiglio, G.; Failla, S.; Finocchiaro, P.; Oliveri, I.P.; Purrello, R.; Di Bella, S. Supramolecular Aggregation/Deaggregation in Amphiphilic Dipolar Schiff-Base Zinc(II) Complexes. *Inorg. Chem.* **2010**, *49*, 5134–5142. [[CrossRef](#)]
67. Oliveri, I.P.; Di Bella, S. Lewis basicity of relevant monoanions in a non-protogenic organic solvent using a zinc(II) Schiff-base complex as reference Lewis acid. *Dalton Trans.* **2017**, *46*, 11608–11614. [[CrossRef](#)] [[PubMed](#)]
68. Di Bella, S.; Oliveri, I.P.; Colombo, A.; Dragonetti, C.; Righetto, S.; Roberto, D. An unprecedented switching of the second-order nonlinear optical response in aggregate bis(salicylaldiminato)zinc(II) Schiff-base complexes. *Dalton Trans.* **2012**, *41*, 7013–7016. [[CrossRef](#)] [[PubMed](#)]
69. Gradinaru, J.; Forni, A.; Druta, V.; Tessore, F.; Zecchin, S.; Quici, S.; Garbalau, N. Structural, Spectral, Electric-Field-Induced Second Harmonic, and Theoretical Study of Ni(II), Cu(II), Zn(II), and VO(II) Complexes with [N<sub>2</sub>O<sub>2</sub>] Unsymmetrical Schiff Bases of S-Methylisothiosemicarbazide Derivatives. *Inorg. Chem.* **2007**, *46*, 884–895. [[CrossRef](#)] [[PubMed](#)]
70. Oliveri, I.P.; Failla, S.; Colombo, A.; Dragonetti, C.; Righetto, S.; Di Bella, S. Synthesis, characterization, optical absorption/fluorescence spectroscopy, and second-order nonlinear optical properties of aggregate molecular architectures of unsymmetrical Schiff-base zinc(II) complexes. *Dalton Trans.* **2014**, *43*, 2168–2175. [[CrossRef](#)]
71. Consiglio, G.; Oliveri, I.P.; Failla, S.; Di Bella, S. On the Aggregation and Sensing Properties of Zinc(II) Schiff-Base Complexes of Salen-Type Ligands. *Molecules* **2019**, *24*, 2514. [[CrossRef](#)]
72. Consiglio, G.; Oliveri, I.P.; Failla, S.; Di Bella, S. Supramolecular Aggregation of a New Substituted Bis(salicylaldiminato)zinc(II) Schiff-Base Complex Derived from trans-1,2-Diaminocyclohexane. *Inorganics* **2018**, *6*, 8. [[CrossRef](#)]
73. Oliveri, I.P.; Malandrino, G.; Mirabella, S.; Di Bella, S. Vapochromic and chemiresistive characteristics of a nanostructured molecular material composed of a zinc(II)-salophen complex. *Dalton Trans.* **2018**, *47*, 15977–15982. [[CrossRef](#)]

74. Oliveri, I.P.; Forte, G.; Consiglio, G.; Failla, S.; Di Bella, S. Aggregates of Defined Stereochemical Scaffolds: A Study in Solution of a Zinc(II) Schiff Base Complex Derived from the Enantiopure trans-1,2-Cyclopentanediamine. *Inorg. Chem.* **2017**, *56*, 14206–14213. [[CrossRef](#)]
75. Clarke, R.M.; Storr, T. The chemistry and applications of multimetallic salen complexes. *Dalton Trans.* **2014**, *43*, 9380–9391. [[CrossRef](#)]
76. Dalla Cort, A.; De Bernardin, P.; Forte, G.; Yafteh Mihan, F. Metal–salophen-based receptors for anions. *Chem. Soc. Rev.* **2010**, *39*, 3863–3874. [[CrossRef](#)]
77. Yin, H.-Y.; Tang, J.; Zhang, J.-L. Introducing metallosalens to biological studies: The renaissance of traditional coordination complexes. *Eur. J. Inorg. Chem.* **2017**, 5085–5093. [[CrossRef](#)]
78. Evans, C.; Luneau, D. New Schiff base zinc(II) complexes exhibiting second harmonic generation. *J. Chem. Soc., Dalton Trans.* **2002**, 83–86. [[CrossRef](#)]
79. Kurtz, S.K.; Perry, T.T. A Powder Technique for the Evaluation of Nonlinear Optical Materials. *J. Appl. Phys.* **1968**, *39*, 3798. [[CrossRef](#)]
80. Sakiyama, H.; Okawa, H.; Matsumoto, N.; Kida, S. A tetrahedral zinc(II) complex of *N*-(*R*)-1-phenylethylsalicylideneimine. Structural and circular dichroism spectral investigations on stereoselectivity. *J. Chem. Soc., Dalton Trans.* **1990**, 2935. [[CrossRef](#)]
81. Ledoux, I.; Zyss, J. Influence of the molecular environment in solution measurements of the Second-order optical susceptibility for urea and derivatives. *J. Chem. Phys.* **1982**, *73*, 203–213. [[CrossRef](#)]
82. Levine, B.F.; Bethea, C.G. Molecular hyperpolarizabilities determined from conjugated and nonconjugated organic liquids. *Appl. Phys. Lett.* **1974**, *24*, 445–447. [[CrossRef](#)]
83. Levine, B.F.; Bethea, C.G. Second and third order hyperpolarizabilities of organic molecules. *J. Chem. Phys.* **1975**, *63*, 2666–2682. [[CrossRef](#)]
84. Vaz, P.A.A.M.; Rocha, J.; Silva, A.M.S.; Guieu, S. Aggregation-induced emission enhancement of chiral boranils. *New J. Chem.* **2018**, *42*, 18166–18171. [[CrossRef](#)]
85. Oudar, J.L.; Chemla, D.S. Hyperpolarizabilities of the nitroanilines and their relations to the excited state dipole moment. *J. Chem. Phys.* **1977**, *66*, 2664–2668. [[CrossRef](#)]
86. Oudar, J.L. Optical nonlinearities of conjugated molecules. Stilbene derivatives and highly polar aromatic compounds. *J. Chem. Phys.* **1977**, *67*, 446–457. [[CrossRef](#)]
87. Singer, K.D.; Sohn, J.E.; King, L.A.; Gordon, H.M.; Katz, H.E.; Dirk, C.W. Second-order nonlinear-optical properties of donor- and acceptor-substituted aromatic compounds. *J. Opt. Soc. Am. B* **1989**, *6*, 1339–1350. [[CrossRef](#)]
88. Frisch, M.J.; Trucks, G.W.; Schlegel, H.B.; Scuseria, G.E.; Robb, M.A.; Cheeseman, J.R.; Scalmani, G.; Barone, V.; Mennucci, B.; Nakatsuji, H.; et al. Gaussian 09, Revision D.01. Gaussian, Inc.: Wallingford CT, UK, 2009.
89. Zhang, Z.; Feng, W.; Su, P.; Lu, X.; Song, J.; Fan, D.; Wong, W.-K.; Jones, R.A.; Su, C. Near-Infrared Luminescent PMMA-Supported Metallopolymers Based on Zn–Nd Schiff-Base Complexes. *Inorg. Chem.* **2014**, *53*, 5950–5960. [[CrossRef](#)] [[PubMed](#)]
90. Akitsu, T.; Itoh, T. Polarized spectroscopy of hybrid materials of chiral Schiff base cobalt(II), nickel(II), copper(II), and zinc(II) complexes and photochromic azobenzenes in PMMA films. *Polyhedron* **2010**, *29*, 477–487. [[CrossRef](#)]
91. Onodera, T.; Akitsu, T. Tuning of the optical properties of chiral Schiff base Zn(II) complexes by substituents. *Polyhedron* **2013**, *59*, 107–114. [[CrossRef](#)]

