

Communication

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

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**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

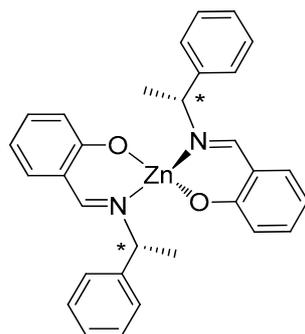
Coordination compounds with second-order nonlinear optical (NLO) properties represent a topic of growing interest as molecular inorganic–organic hybrid materials for emerging optoelectronic and optical signal processing [1–15]. Compared to purely organic compounds [16–18], they have the advantage of 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].

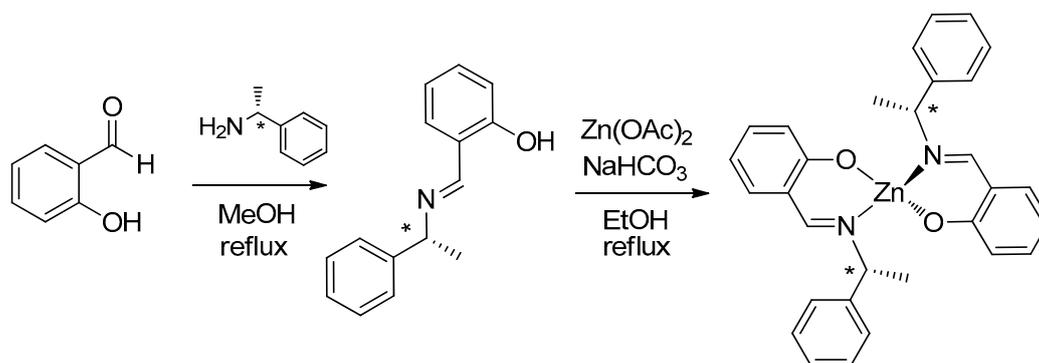
Surprisingly, whereas there is an increasing amount of reports on the second-order NLO properties of tetradentate  $[N_2O_2]$  Schiff-base zinc complexes, to our knowledge, only one paper was published, almost 20 years ago, on those of zinc complexes having two bidentate [NO] Schiff-base ligands [78]. 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):

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

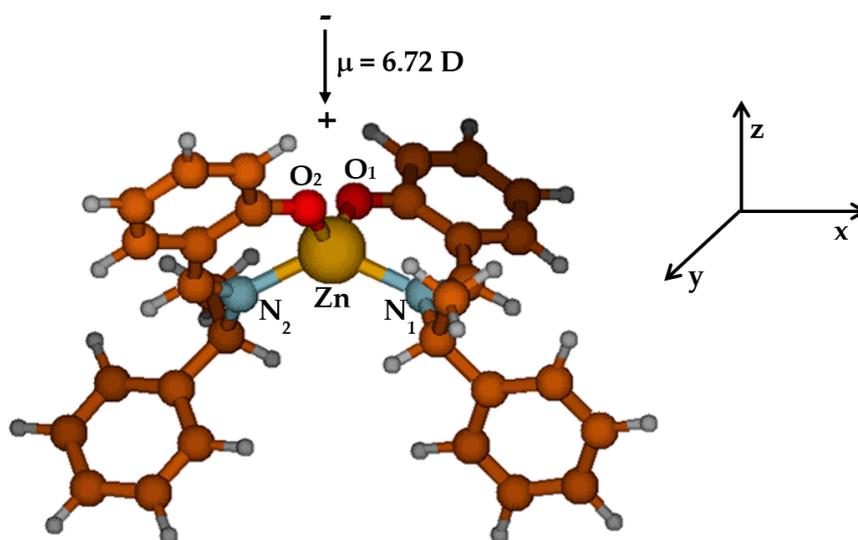
where  $\beta_{\lambda}$  is the quadratic hyperpolarizability value at the incident wavelength  $\lambda$ , and  $\lambda_{\text{max}}$  is the absorption wavelength of the major charge-transfer transition considered.

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.



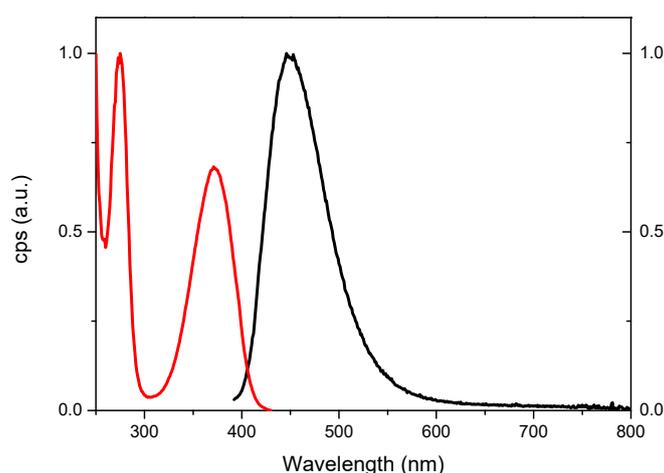
**Figure 2.** Optimized geometry of the investigated zinc complex.

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.

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

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