

An unprecedented switching of the second-order nonlinear optical response in aggregate bis(salicylaldiminato)zinc(II) Schiff-base complexes†

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A luminescent bis(salicylaldiminato)zinc(II) Schiff-base complex, **1**, is characterized by a concentration dependent second-order nonlinear optical response, related to the degree of aggregation of the complex in a dichloromethane solution. The formation of the monomeric adduct, by addition of a Lewis base, such as pyridine, to concentrated solutions of **1**, leads to a switch-on of the quadratic hyperpolarizability. This represents an unprecedented mode of NLO switching in molecular materials.

Introduction

Currently, there is great interest in the study of second-order nonlinear optical (NLO) properties of molecular materials.¹ Among them, metal complexes have been investigated for their unique properties, since they offer additional flexibility, when compared to organic chromophores, by the presence of NLO active electronic charge-transfer transitions between the metal and the ligands, which is tunable by virtue of the nature, oxidation state and coordination sphere of the metal centre.² From an application point of view, another interesting aspect of metal complexes is the possibility to switch their NLO response, either by a redox process or photochemically.^{2,3}

M(II) (M = Fe, Co, Ni, Cu, Zn) bis(salicylaldiminato) Schiff-base complexes have been extensively investigated for their variegated second-order NLO properties, in relation to the metal-d configuration and the donor–acceptor substitution on the salicylidene rings.⁴ Tunable values of the quadratic hyperpolarizability, ranging from negative to positive values, have been obtained.⁵ The symmetric donor–acceptor substitution in dipolar planar Schiff-base complexes also allowed the investigation of their in-plane two-dimensional NLO properties.⁶ More recently, a variety of noncentrosymmetric Schiff-base complexes, either by an unsymmetrical donor–acceptor substitution on the bis(salicylidene) ligand or by an unsymmetrical [N₂O₂] tetradentate coordination, have been investigated.⁷

An interesting characteristic of tetracoordinated Zn^{II} metal complexes is the possibility to form molecular aggregates to

saturate the coordination sphere of the metal. Actually, bis(salicylaldiminato)Zn^{II} Schiff-base complexes are Lewis acidic species, which saturate their coordination sphere by coordinating a large variety of neutral and anionic Lewis bases^{8,9} or, in their absence, can be stabilized through an intermolecular Zn...O axial coordination involving the phenolic oxygen atoms of the ligand framework.¹⁰ Alternatively, the axial coordination to the Zn^{II} ion can be saturated by the side chains in the salicylidene rings appropriately derivatized with Lewis bases.¹¹ These complexes have recently been investigated for their fluorescent features also, which are related to the structure of the salicylidene template and the axial coordination.^{8–12} Thus, the amphiphilic Zn^{II} Schiff-base complex, **1** (Chart 1), has been investigated as a new highly sensitive fluorescent probe for the detection of some important classes of alkaloids¹³ and has been used to rank the relative Lewis basicities of relevant amines and nonprotogenic solvents.¹⁴

The objective of the present study is to investigate the second-order NLO response of the amphiphilic aggregate Zn^{II} Schiff-base complex, **1**, and the switching of the quadratic hyperpolarizability upon deaggregation.

Results and discussion

Schiff-base Zn^{II} complex **1** was prepared as previously reported.⁸ It was demonstrated that this complex, when dissolved in

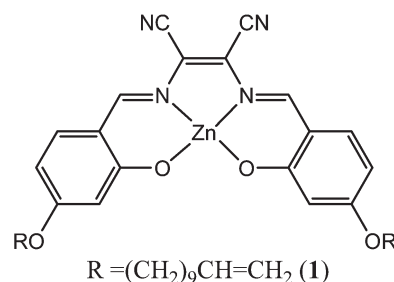


Chart 1 The structure of the investigated complex, **1**.

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Table 1 The values of $\mu\beta_{1,907}$ for complex **1** in CH_2Cl_2 with and without the addition of pyridine or 1,2-bis-(4-pyridyl)ethane (dpe)

Concentration of complex 1 ($\times 10^{-3}$ M)	$\mu\beta_{1,907}$ ($\times 10^{-48}$ esu)	$\mu\beta_{1,907}$ ($\times 10^{-48}$ esu) with pyridine ^a	$\mu\beta_{1,907}$ ($\times 10^{-48}$ esu) with dpe ^b
1.0	≈ 0	−2070	−420
0.7	−526		
0.5	−1010		
0.3 ^c	−1120	−1950	−347

^a Molar ratio of pyridine : **1** = 1.2 : 1. ^b Molar ratio of dpe : **1** = 0.6 : 1.^c At this concentration a dimeric species is formed.⁸

dichloromethane, yields concentration-dependent aggregates. Dilute solutions ($\leq 4 \times 10^{-4}$ M) are characterized by the presence of defined dimers, whereas larger oligomeric aggregates are likely formed at higher concentrations.⁸ Therefore, we have investigated the second-order NLO properties of this complex by means of the electric field induced second harmonic generation (EFISH) method,¹⁵ working in dichloromethane at various concentrations.

The EFISH technique can provide direct information about the intrinsic molecular NLO properties through eqn (1):

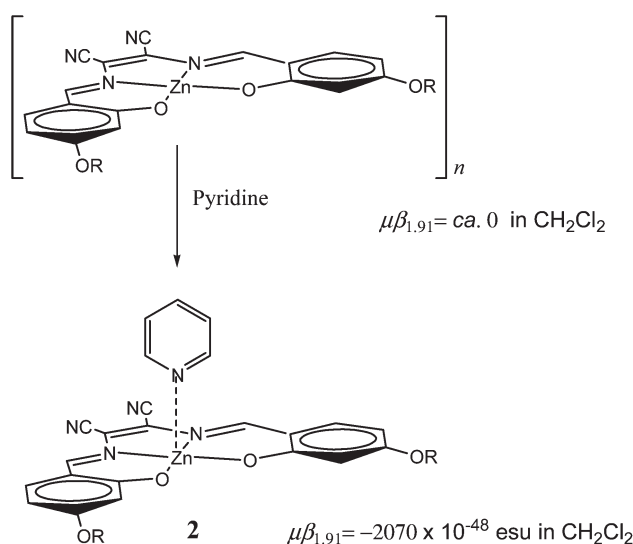
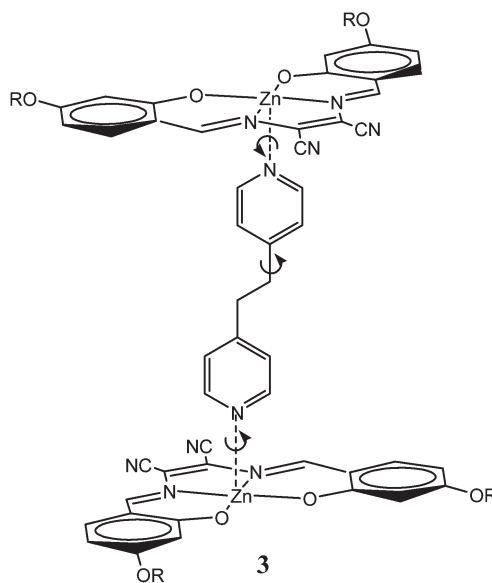
$$\gamma_{\text{EFISH}} = (\mu\beta_{\lambda}/5kT) + \gamma(-2\omega; \omega, \omega, 0) \quad (1)$$

where $\mu\beta_{\lambda}/5kT$ is the dipolar orientational contribution and $\gamma(-2\omega; \omega, \omega, 0)$, a third order term corresponding to the mixing of two optical fields at ω and the DC poling field at $\omega = 0$, is the electronic cubic contribution to γ_{EFISH} . This latter term is usually negligible in this kind of metal complex. β_{λ} is the projection along the dipole moment axis of the vector component of the quadratic hyperpolarizability β tensor, at a specific incident wavelength, λ .²

Table 1 reports the $\mu\beta_{1,907}$ values for complex **1** measured in a dichloromethane solution at different concentrations, with an incident wavelength of 1.907 μm .

It turns out that the $\mu\beta_{1,907}$ value of complex **1** is strongly concentration dependent. Working at a concentration of 1.0×10^{-3} M, it is nearly 0; however, it becomes negative with an absolute value that increases rapidly upon dilution down to 3×10^{-4} M. The very low NLO response with the most concentrated solution can be reasonably explained by the presence of oligomeric aggregates,⁸ which have an expected almost centric arrangement. Upon dilution to $3\text{--}5 \times 10^{-4}$ M, there is the formation of defined dimers,⁸ characterized by a negative but quite high $\mu\beta_{1,907}$ value. Remarkably, the addition of a stoichiometric amount of pyridine to the concentrated solution of **1** (1.0×10^{-3} M) switches on the NLO response and $\mu\beta_{1,907}$ becomes -2070×10^{-48} esu (Table 1 and Fig. 1) due to the deaggregation of the Zn^{II} complex and the formation of a 1 : 1 pyridine adduct, **2** (see ESI†).⁸ As expected, the addition of pyridine to the dimeric Zn^{II} species (3×10^{-4} M) also affords adduct **2** with a similar $\mu\beta_{1,907}$ value (Table 1).¹⁶

It was established that the addition of a ditopic ligand as a coordinating species, such as 1,2-bis-(4-pyridyl)ethane (dpe), leads to the formation of the supramolecular 2 : 1 adduct, **3** (Chart 2, see ESI†).⁸ We found that this designed adduct is also characterized by a good absolute $\mu\beta_{1,907}$ value, although it is

**Fig. 1** Switching on the second-order NLO response for complex **1** by the addition of pyridine.**Chart 2** The structure of the supramolecular adduct, **3**.

found to be lower than that of adduct **2** (Table 1). This is likely to be due to the presence of some centric conformers.

It is worth pointing out that the negative sign of the $\mu\beta_{1,907}$ value observed for adducts **2** and **3** and for the dimer of complex **1** suggests that the dipole moment is lower in the excited state than in the ground state,^{5d,17} and this is common for $\text{M}(\text{II})$ Schiff-base complexes.^{4–7} Actually, a negative quadratic hyperpolarizability has recently been reported for a Zn^{II} complex with an unsymmetrical Schiff-base of *S*-methylisothiosemicarbazide.^{7c}

In the case of adducts **2** and **3** it was possible to determine the dipole moment using the Guggenheim technique¹⁸ and, therefore, to evaluate the $\beta_{1,907}$ value, which was found to be -518 and -105×10^{-30} esu, respectively (Table 2).

Table 2 Absorption maximum and NLO properties for adducts **2** and **3** in CH₂Cl₂

	Adduct 2	Adduct 3
λ_{\max}^a (nm)	555	554
$\mu\beta_{1.907}^b$ ($\times 10^{-48}$ esu)	−2070	−420
μ^c ($\times 10^{-18}$ esu)	4	4
$\beta_{1.907}$ ($\times 10^{-30}$ esu)	−518	−105
β_0 ($\times 10^{-30}$ esu)	−313	−64
$\mu\beta_0$ ($\times 10^{-48}$ esu)	−1250	−254

^a ESI.† ^b By working with a concentration of 10^{-3} M; the error on the EFISH measurements is $\pm 10\%$. ^c Determined in CHCl₃; the error on the dipole moment is $\pm 1 \times 10^{-18}$ esu.

Besides, as EFISH measurements are performed in a non-resonant regime ($\lambda_{\text{harm}} \gg \lambda_{\text{max}}$), we applied the simple two-level approximation^{15,19} to extrapolate the zero-frequency static quadratic hyperpolarizability, β_0 , from the experimental $\beta_{1.907}$ EFISH using the following expression:

$$\beta_0 = \beta_{1.907}(1 - (2\lambda_{\text{max}}/\lambda)^2)(1 - (\lambda_{\text{max}}/\lambda)^2) \quad (2)$$

where λ is the fundamental wavelength of the incident photon (1907 nm) and λ_{max} is the maximum absorption value (Table 2). Thus, a β_0 value of −313 and -64×10^{-30} esu, for adducts **2** and **3**, respectively, may be calculated. As the static hyperpolarizability is not frequency dependent, it represents the most important figure of merit when comparing the molecular second-order NLO response of different chromophores. Remarkably, the absolute value of $\mu\beta_0$ (-1250×10^{-48} esu) for adduct **2** is among the highest reported for metal complexes.² For comparison, the azo dye Disperse Red 1 (4-[N-ethyl-N-(2-hydroxyethyl)amino-4'-nitroazobenzene]), which is currently used as a dopant molecule in polymeric matrices for electro-optic applications, has a $\mu\beta_0 = 500 \times 10^{-48}$ esu.²⁰

Conclusions

Organometallic and coordination complexes with both luminescent and second-order nonlinear optical (NLO) properties are of growing interest for us as new molecular multifunctional materials.²¹ Complex **1** is characterized by a concentration dependent second-order nonlinear optical response, which is related to the degree of aggregation of the complex in a dichloromethane solution. An appealing aspect of this work is the easy switch-on of its second-order NLO response, which is achieved by the addition of a Lewis base, such a pyridine, with formation of a 1 : 1 adduct, **2**. The high NLO response of this adduct, already known for its luminescence properties,^{8,13} is of relevance for the development of new electro-optics materials. Moreover, the use of 1,2-bis-(4-pyridyl)ethane allowed the production of supramolecular adduct **3**, which is also characterized by a significant $\mu\beta_{1.907}$ value. Thus, Zn^{II} Schiff-base complexes represent suitable synthons for the design and development of supramolecular architectures with large second-order NLO responses.

Experimental

General information

Reagents were purchased from Sigma–Aldrich. Zn^{II} complex **1** was prepared as previously reported,⁸ and characterized by ¹H NMR (Bruker DRX-300 spectrometer), UV/vis (Jasco V-530 spectrophotometer) spectroscopy and elemental analysis. The formation of adducts **2** and **3** was assessed by ¹H NMR and UV/vis spectroscopy (see ESI†). Dichloromethane stabilized with amylene was used to prepare solutions of **1**. Fresh prepared dichloromethane solutions of **1**, obtained from stock solutions at a concentration of 1.0×10^{-3} M, were used for all the measurements. Dipole moments, μ , were determined using a WTW-DM01 dipolemeter coupled with a RX-5000 ATAGO digital refractometer in order to measure, respectively, the dielectric constant and the refractive index of the solutions in CHCl₃. From these experimental data the dipole moment can be calculated according to the Guggenheim method.¹⁸

EFISH measurements

All EFISH measurements were carried out at the Dipartimento di Chimica Inorganica Metallorganica e Analitica “Lamberto Malatesta” at the Università degli Studi di Milano, in CH₂Cl₂ solutions in concentration ranges of 10^{-4} – 10^{-3} M. The measurements were performed working with a non-resonant incident wavelength of 1.907 μm , which was obtained by Raman-shifting the fundamental 1.064 μm wavelength that was produced by a Q-switched, mode-locked Nd³⁺–YAG laser manufactured by Atalaser. The apparatus for the EFISH measurements was a prototype made by SOPRA (France). The $\mu\beta_{\text{EFISH}}$ values reported are the mean values of 16 successive measurements performed on the same sample. The sign of $\mu\beta$ was determined by comparison with the reference solvent (CH₂Cl₂).

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