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Cyclometalated Ir(III) Complexes with Curcuminoid Ligands as Active Second-Order NLO Chromophores and Building Blocks for SHG Polymeric Films [†]

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[†] This paper is dedicated to Prof. Maddalena Pizzotti for her 70th birthday and for her important contribution to the field of coordination compounds for optical and energy-related applications.

Received: 1 April 2020; Accepted: 13 May 2020; Published: 14 May 2020

Abstract: The second-order nonlinear optical (NLO) properties of iridium(III) complexes having two cyclometalated 2-phenylpyridines and curcumin or tetrahydrocurcumin as ancillary ligand have been investigated both in solution and as guest in a polymeric organic matrix. In solution, these complexes are characterized by a significant second-order NLO response, as determined by the Electric Field Induced Second Harmonic (EFISH) technique, like the related complex with acetylacetonate. Whereas the low second-harmonic generation response of a composite film of [Ir(2-phenylpyridine)₂(acetylacetonate)] in polymethyl methacrylate was not stable and fell down to zero upon turning off the electric field. A good and stable response was obtained with a film based on the iridium(III) complex bearing two cyclometalated 2-phenylpyridines and curcumin.

Keywords: cyclometalated iridium(III) complexes; second-order nonlinear optics; EFISH; second-harmonic generation

1. Introduction

In the last thirty years, a lot of work has been devoted to molecular compounds with second-order nonlinear optical (NLO) properties, due to their potential in optoelectronic devices [1–3]. To have a high second-order NLO response, a molecule should not be centrosymmetric; it should have charge-transfer transitions of low energy, and there must be a big difference between the excited state dipole moment and the ground state dipole moment. Organic molecules with electron-donor (D) and electron-acceptor (A) fragments coupled via a π -conjugated polarizable moiety can have a respectable NLO response [4–9]. Coordination compounds also showed promise because they were characterized by low-energy ligand-to-metal (LM), metal-to-ligand (ML), ligand-to-ligand (LL), and intraligand (IL) charge transfer (CT) excited states. The intensity and energy of these transitions can be easily regulated by a judicious choice of the nature, oxidation state, and ligands of the metal center [10–27].

As determined by the Electric Field Induced Second Harmonic generation (EFISH) technique in solution [28–30], coordination complexes often reach a second-order NLO response larger than that of the prototypal Disperse Red One, *trans*-4,4'-O₂NC₆H₄N=NC₆H₄NEt(CH₂CH₂OH)], which has been used in electrooptic polymeric poled films [31]. Indeed, they can reach $\mu\beta$ values (β is the projection

along the ground state dipole moment (μ) axis of the vectorial component of the tensor of the quadratic hyperpolarizability) superior to 500×10^{-48} esu, making them competitive with respect to organic compounds and of interest for optoelectronic applications [10–27]. Among them, photoactive iridium complexes are very appealing not only for their attractive second-order NLO properties [27,32–37], but also because they find application in various fields, including in electroluminescent devices [38–41], in dye-sensitized solar cells [41–45], in sensing [41], as two-photon absorption reagents for high image resolution [46–50], as bioimaging probes [41,51–53], and in photodynamic therapy [54–57].

In the field of nonlinear optics, iridium complexes characterized by luminescent and NLO properties are fascinating as multifunctional molecular materials [58,59], as some of them have a versatile NLO redox-switching response [60,61]. In particular, those with two cyclometalated 2-phenylpyridine ligands (ppy) and a β -diketonate ancillary ligand, known for their luminescence and two-photon absorption properties [62], are of particular interest because they are characterized by a large second-order NLO response in solution [63]. The complex with acetylacetonate as an ancillary ligand is characterized by a $\mu\beta_{1.907}$ value, determined by the EFISH technique working with a $1.907 \mu\text{m}$ incident wavelength of -910×10^{-48} esu. A similar value was obtained when the acetylacetonate is functionalized with the electron acceptor 2,4-dinitrophenyl group, whereas a slightly higher absolute value was obtained with 1,3-diphenyl-1,3-propanedione (-1340×10^{-48} esu), which is in agreement with the higher polarizability of the phenyl compared to the methyl substituent [63]. A Sum-Over-States Time-Dependent Density Functional Theory (SOS-TDDFT) investigation showed that the large NLO response of these complexes is principally caused by π – π^* intraligand charge transfer transitions involving the cyclometalated 2-phenylpyridines, while transitions involving the β -diketonate ligand do not contribute meaningfully [63]. Remarkably, the second-order NLO response of the free 2-phenylpyridine is very low, putting in evidence the important role of cyclometalation, and therefore of iridium, in increasing the quadratic hyperpolarizability. In order to understand if an appropriate functionalization of the 2-phenylpyridine ligands could improve the second-order NLO activity, a series of iridium(III) acetylacetonate compounds with various cyclometalated 4-styryl-2-phenylpyridines substituted with donor (NEt_2 , OMe) or acceptor (NO_2) substituents was investigated [64]. The best $\mu\beta_{1.907}$ value, obtained with the 4-styryl-2-phenylpyridine bearing the nitro group, was slightly lower than that of the complex with the simple 2-phenylpyridine [64]. Thus, the simple luminescent iridium(III) complex with two cyclometalated 2-phenylpyridine ligands and acetylacetonate as an ancillary ligand appeared as a particularly appealing tool for NLO applications. However, various attempts to prepare stable NLO-active hybrid polymeric films based on this complex failed.

These observations prompted us to investigate the second-order NLO properties of two iridium(III) complexes with two cyclometalated 2-phenylpyridines and curcumin (complex **Ir1**) or tetrahydrocurcumin (complex **Ir2**) as an ancillary ligand (Figure 1), recently studied for their luminescence and photoactivated anticancer activity [54]. Both show large $\mu\beta_{1.907}$ absolute values, and, remarkably, complex **Ir1** can be used to prepare hybrid polymeric films with a good second harmonic generation response. The results of this investigation are presented in this report.

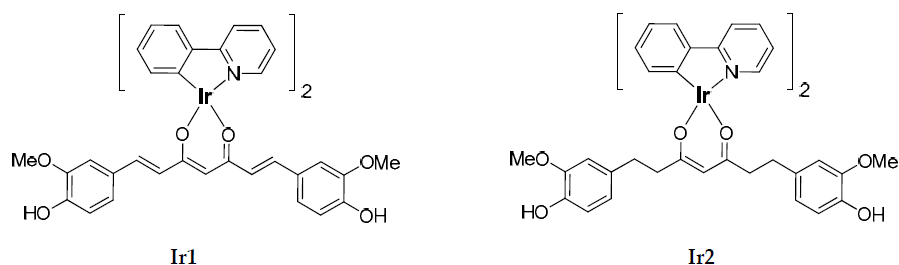


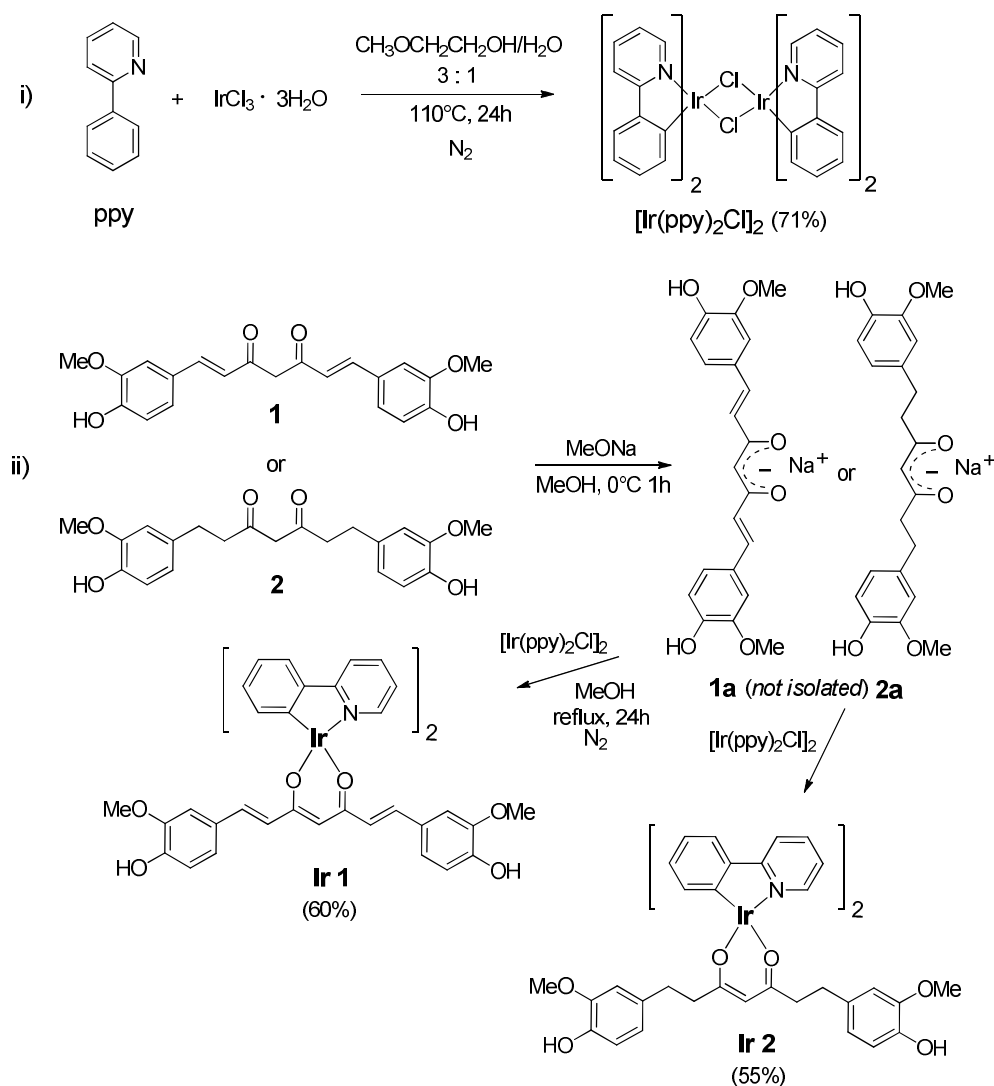
Figure 1. Investigated iridium (III) complexes.

2. Results and Discussion

The cyclometalated curcuminoid iridium(III) complexes are easily prepared in two steps, as shown in Scheme 1:

- Preparation of the chloro-bridge dimer $[\text{Ir}(\text{ppy})_2\text{Cl}]_2$ (ppy = cyclometalated 2-phenylpyridine) from $\text{IrCl}_3 \cdot 3\text{H}_2\text{O}$ [65];
- Bridge splitting reaction with the deprotonated curcumin or tetrahydrocurcumin [53].

The pure complexes, obtained by recrystallization, were well characterized (see Materials and Methods).



Scheme 1. Preparation of cyclometalated curcuminoid iridium(III) complexes.

The Electric Field Induced Second Harmonic generation (EFISH) method was used to determine the second-order nonlinear optical (NLO) properties in chloroform solution (10^{-3} M) of complexes **Ir1** and **Ir2**. It is known that this method [28–30] allows the study of the molecular second-order NLO response, by using Equation (1):

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

where $\beta_\lambda/5kT$ characterizes the dipolar orientational impact on the molecular nonlinearity, while $\gamma(-2\omega; \omega, \omega, 0)$ describes the third order polarizability, which is an electronic cubic contribution to

γ_{EFISH} . The latter is commonly ignored when studying the second-order NLO properties of dipolar compounds. μ is the ground state dipole moment. β_{λ} describes the projection along the μ axis of β_{VEC} , which is the vectorial element of the quadratic hyperpolarizability tensor when working with an incident wavelength, λ . Extrapolation to zero frequency ($\nu_A = 0.0$ eV; $\lambda = \infty$) permits the determination of $\mu\beta_0$ where β_0 is the static quadratic hyperpolarizability, a useful figure of merit to compare the second-order NLO properties of molecules. This value can be obtained by using Equation (2):

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

where β_{λ} is the quadratic hyperpolarizability value at the incident wavelength, λ , and λ_{max} is the absorption wavelength of the major charge transfer transition considered. A molecule having a $\mu\beta_0$ higher than that of Disperse Red One (450×10^{-48} esu), which was used in electrooptic polymeric poled films [31], is commonly considered of interest for second-order NLO applications.

When determining the quadratic hyperpolarizability, it is important to avoid resonance enhancements that would lead to an overestimation of the value. Therefore, it is essential to choose an incident wavelength with a second harmonic far from the absorption wavelengths of the investigated compound. In order to study complexes **Ir1** and **Ir2**, we worked with a $1.907 \mu\text{m}$ incident wavelength achieved by Raman-shifting the $1.064 \mu\text{m}$ wavelength obtained from a Q-switched, mode-locked Nd:YAG laser.

We found that both cyclometalated curcuminoid iridium(III) complexes have a negative value of $\mu\beta_{1.907}$, like other β -diketonate cyclometalated iridium(III) complexes [63,64], showing that there is a negative value of $\Delta\mu_{\text{eg}}$ (difference of the dipole moment in the excited state and in the ground state) upon excitation, following the “two-level” model [66,67].

The $\mu\beta_{1.907}$ value of complex **Ir1** is -1050×10^{-48} esu, corresponding to a $\mu\beta_0$ value of -747×10^{-48} esu calculated by using Equation (2). The low energy charge transfer absorption band (470 nm [54]) much higher than that of Disperse Red One [31] and slightly larger than that of the related complex with acetylacetonate instead of the curcumin ligand. The use of tetrahydrocurcumin as an ancillary ligand (complex **Ir2**) affords a similar second-order NLO response ($\mu\beta_{1.907} = -930 \times 10^{-48}$ esu; $\mu\beta_0 = -661 \times 10^{-48}$ esu by using Equation (2) and $\lambda_{\text{max}} = 470$ nm [54]). This is a significant result, because compounds showing both luminescent and nonlinear optical properties are of growing interest as multifunctional molecular materials for optoelectronics [68–77].

As a further step, we were curious to study the second-order NLO properties of a composite polymethyl methacrylate (PMMA) polymeric film based on complex **Ir1**. The composite film was prepared by spin coating a dichloromethane solution of complex **Ir1** and PMMA (5% wt complex **Ir1**/PMMA) on ordinary glass substrate. The corona wire poling dynamic of the second harmonic generation (SHG) is shown in Figure 2a.

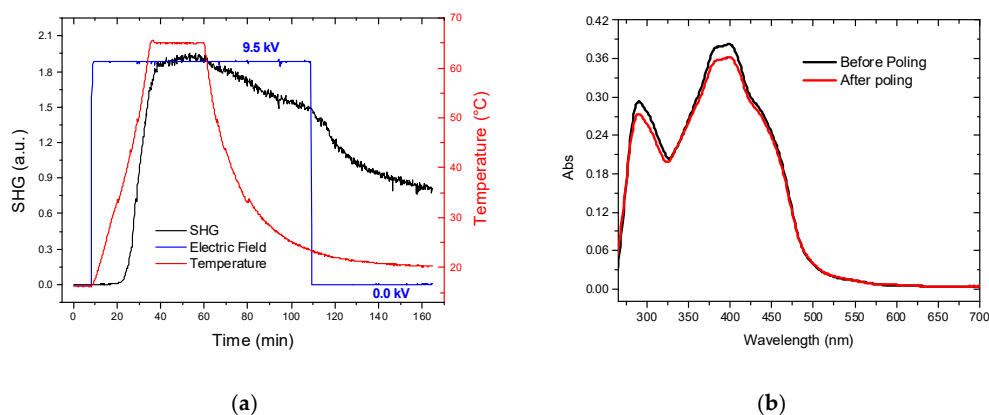


Figure 2. (a) Second harmonic generation (SHG) plot of composite films containing 5% (wt) of complex **Ir1** in a PMMA matrix. (b) Absorbance spectrum before (black line) and after (red line) poling.

The SHG signal is insignificant at room temperature, but it rapidly intensifies upon heating in the presence of the electric field (9.5 kV) under nitrogen, due to the diminution of the polymeric film viscosity which permits an easier orientation of the dipolar molecules of complex **Ir1**. The signal reaches a plateau at 65 °C. It was halved after cooling to room temperature and switching off the electric field. Remarkably, contrarily to what happened with the composite PMMA film containing [Ir(ppy)₂(acetylacetonate)] [64], the SHG signal does not fall to zero, showing that the curcumin ligand is able to stabilize the orientation of the NLO-active Ir(III) complex in the polymeric PMMA matrix.

The electronic absorption spectra of the composite PMMA film containing complex **Ir1**, recorded before and after the poling process, are shown in Figure 2b. There was a small decrease of the intensity of the main absorption peaks after poling, probably due to a dichroism effect caused by the reorientation of dipolar molecules [78], whereas no significant Stark shift was observed.

The second order NLO response, $\chi^{(2)}_{33}$, was determined by using the Maker fringes method [79–83]. A value of 2.82 pm/V was obtained, a remarkable response for such a simple complex. These results put in evidence that substitution of acetylacetonate by a curcuminoid ligand is a simple avenue to stabilize the orientation of the NLO-active Ir(III) complex in the polymeric PMMA matrix, allowing a good SHG response.

3. Materials and Methods

3.1. Synthesis of [Ir(ppy)₂(μ-Cl)]₂

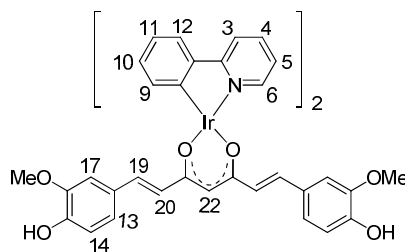
2-Phenylpyridine (506 μL, 3.03 mmol) was added to a solution of IrCl₃·3H₂O (360 mg, 1.01 mmol) in 2-methoxyethanol/water (60 mL/20 mL) under nitrogen. After stirring under reflux for 24 h, the reaction mixture was cooled to room temperature. The precipitated yellow powder was filtered, washed first with methanol, and then with diethyl ether. The pure product (576 mg) was obtained as a yellow solid by recrystallization from dichloromethane and pentane. Yield = 71%.

¹H NMR (400 MHz, DMSO): δ (ppm) 9.81 (d, *J* = 8.1 Hz, 2H), 9.55 (d, *J* = 8.1 Hz, 2H), 8.26 (d, *J* = 8.1 Hz, 2H), 8.18 (d, *J* = 8.0 Hz, 2H), 8.12 (t, *J* = 8.0 Hz, 2H), 8.01 (t, *J* = 8.1 Hz, 2H), 7.79 (d, *J* = 8.0 Hz, 2H), 7.73 (d, *J* = 8.0 Hz, 2H), 7.57 (t, *J* = 8.0 Hz, 2H), 7.45 (t, *J* = 8.0 Hz, 2H), 6.90 (t, *J* = 8.0 Hz, 2H), 6.86 (t, *J* = 8.0 Hz, 2H), 6.77 (t, *J* = 8.0 Hz, 2H), 6.69 (t, *J* = 8.0 Hz, 2H), 6.27 (d, *J* = 8.1 Hz, 2H), and 5.67 (d, *J* = 8.1 Hz, 2H).

3.2. Synthesis of Complex **Ir1**

NaOMe (40 mg, 0.74 mmol) was added to a solution of curcumin (274 mg, 0.74 mmol) in methanol (15 mL) at 0 °C. After stirring for 1 h, [Ir(ppy)₂(μ-Cl)]₂ (398 mg, 0.37 mmol) was added, affording an orange solution. After stirring for 24 h under reflux, the precipitate was filtered and then crystallized from dichloromethane and diethylether affording 392 mg of pure product as an orange powder; Yield = 60% (Scheme 2).

¹H NMR (600 MHz, CD₃CN, δ) ppm: 8.58 (d, *J* = 5.6 Hz, 2H, H₆), 8.02 (d, *J* = 8.2 Hz, 2H, H₃), 7.86 (t, *J* = 7.5 Hz, 2H, H₄), 7.68 (d, *J* = 7.7 Hz, 2H, H₁₂), 7.27 (d, *J* = 6.1 Hz, 2H, H₅), 7.17 (d, *J* = 15.7 Hz, 2H, H₁₉), 7.12 (d, *J* = 1.6 Hz, 2H, H₁₇), 6.99 (dd, *J*₁ = 8.2 Hz, *J*₂ = 1.6 Hz, 2H, H₁₄), 6.86 (t, *J* = 7.3 Hz, 2H, H₁₁), 6.78 (d, *J* = 8.2 Hz, 2H, H₁₃), 6.72 (t, *J* = 7.3 Hz, 2H, H₁₀), 6.61 (d, *J* = 15.7 Hz, 2H, H₂₀), 6.25 (d, *J* = 7.5 Hz, 2H, H₉), 5.75 (s, 1H, H₂₂), and 3.87 (s, 6H, OCH₃). ¹³C NMR (150 MHz, CD₃CN, δ) ppm: 176.8 (C²¹), 168.2 (C²), 148.1 (C⁶), 147.8, 147.6, 147.6 (C₁₆, C₈, C₁₅), 145.4 (C⁷), 137.8 (C⁴), 136.1 (C²⁰), 133.0 (C⁹), 128.7 (C¹⁰), 128.4 (C¹⁸), 128.0 (C¹⁹), 123.9 (C¹²), 122.2 (C⁵), 121.7 (C¹⁴), 120.8 (C¹¹), 118.7 (C³), 115.0 (C¹³), 110.0 (C¹⁷), 103.1 (C²²), and 55.7 (OCH₃). Anal. Calcd. (%) for C₄₄H₃₉IrN₂O₆: C, 59.78; H, 4.45; and N, 3.17. Found: C 59.85, H 4.46, and N 3.16.

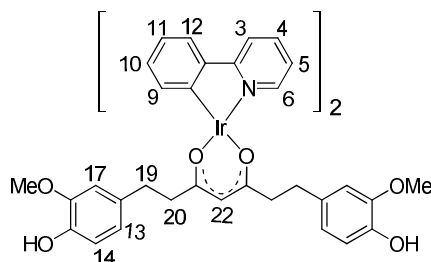


Scheme 2. Numeration for NMR of Ir1.

3.3. Synthesis of Complex Ir2

NaOMe (45 mg, 0.83 mmol) was added to a solution of tetrahydrocurcumin (310 mg, 0.83 mmol) in methanol (21 mL) at 0 °C. After stirring for 1 h, $[\text{Ir}(\text{ppy})_2(\mu\text{-Cl})]_2$ (420 mg, 0.4 mmol) was added, affording a yellow solution. After stirring for 24 h under reflux, the precipitate was filtered and then crystallized from dichloromethane and diethylether, affording 405 mg of pure product as a dark yellow powder; Yield = 55% (Scheme 3).

^1H NMR (600 MHz, CD_3CN , δ) ppm: 8.24 (d, $J = 4.98$ Hz, 2H, H_6), 8.00 (d, $J = 8.1$ Hz, 2H, H_3), 7.86 (t, $J = 8.1$ Hz, 2H, H_4), 7.64 (d, $J = 5.2$ Hz, 2H, H_{12}), 7.16 (t, $J = 6.54$ Hz, 2H, H_5), 6.83 (t, $J = 7.4$ Hz, 2H, H_{11}), 6.70 (s, 2H, H_{17}), 6.67 (t, $J = 7.4$ Hz, 2H, H_{10}), 6.61 (d, $J = 8.0$ Hz, 2H, H_{14}), 6.39 (t, $J = 8.0$ Hz, 2H, H_{13}), 6.17 (d, $J = 7.4$ Hz, 2H, H_9), 5.34 (s, 1H, H_{22}), 3.77 (s, 6H, OCH_3), 2.63–2.55 (m, 4H, H_{19}), 2.37–2.32 (m, 2H, H_{20}), and 2.27–2.21 (m, 2H, H_{20}). ^{13}C NMR (150 MHz, CD_3CN , δ) ppm: 186.8 (C^{21}), 168.0 (C^2), 148.2 (C^6), 147.8, 147.6, 147.6 (C^{16} , C^8 , C^{15}), 144.1 (C^{18}), 145.4 (C^7), 137.6 (C^4), 133.1 (C^9), 128.6 (C^{10}), 123.8 (C^{12}), 122.1 (C^5), 120.7 (C^{13}), 120.7 (C^{11}), 118.6 (C^3), 114.4 (C^{14}), 111.9 (C^{17}), 99.8 (C^{22}), 55.6 (OCH_3), 42.8 (C^{20}), and 31.9 (C^{19}). Anal. Calcd. (%) for $\text{C}_{44}\text{H}_{43}\text{IrN}_2\text{O}_6$: C, 59.50; H, 4.88; and N, 3.15. Found: C 59.68, H 4.91, and N 3.16.



Scheme 3. Numeration for NMR of Ir2.

3.4. Measurement of the Second-Order NLO Properties in Solution

EFISH measurements were carried out by using a non-resonant incident wavelength of 1.907 μm , achieved by Raman-shifting the fundamental 1.064 μm wavelength given by a Q-switched, mode-locked Nd:YAG laser (from Atalaser). Complexes Ir1 and Ir2 were dissolved in chloroform at a concentration of 10^{-3} M. The reported $\mu\beta_{1.907}$ values are the mean values of 16 measurements performed on the same sample.

3.5. Preparation of Composite Films of Complex Ir1 in PMMA and Related SHG Measurements

Composite films were prepared by spin coating a dichloromethane solution (3.5 mL) of complex Ir1 (20 mg) and PMMA (400 mg) on ordinary glass substrates (thickness 1 mm), previously cleaned with water/acetone. Electronic absorption spectra of the composite films of complex Ir1 in PMMA were obtained with a UV-3600i Plus UV-VIS-NIR Spectrophotometer (Shimadzu Italia S.r.l., Milan, Italy). Second Harmonic Generation (SHG) measurements were carried out with a Quanta System Giant G790-20 laser with a 1.064 μm wavelength, a 7 ns pulse, and a 20 Hz repetition rate (Quanta System SpA, Samarate, Italy). The corona poling process was performed inside a dry box under N_2 ,

as previously reported [80–83]. The setup for Maker fringe measurements was similar to that previously described [80–83]. The SHG signal was normalized with a calibrated quartz crystal wafer (X-cut, 1 mm thick, $d_{11} = 0.46$ pm/V).

4. Conclusions

In conclusion, this work shows the significant second-order nonlinear optical properties in solutions of iridium(III) complexes with two cyclometalated 2-phenylpyridines, and curcumin or tetrahydrocurcumin as ancillary ligand. Notably, it unveiled the great potential of curcuminoid ligands for the preparation of NLO-active hybrid polymeric films based on metal complexes. As a matter of fact, a common drawback of NLO-active hybrid films, containing a metal complex with second-order NLO properties dispersed in a polymeric matrix and oriented by corona poling, is the progressive fading of the NLO signal with time due to the loss of orientation of the guest molecules in the host polymer once the electric field is removed. It turned out that, whereas the low second-harmonic generation response of a composite film of [Ir(2-phenylpyridine)₂(acetylacetonate)] in polymethyl methacrylate is not stable and fell down to zero upon turning off the electric field, a good and stable response was obtained with a film based on the iridium(III) complex with two cyclometalated 2-phenylpyridines and curcumin. This result is of particular relevance because it reveals the key role of the curcumin ligand in stabilizing the orientation of the NLO-active Ir(III) complex in the polymeric matrix. Clearly, the use of the curcumin ligand appears as an interesting way to design metal complexes for the preparation of hybrid films with a good and stable second-order nonlinear optical response.

Authors Contributions: Conceptualization, A.C., C.D., and D.R.; Data curation, A.C. and S.R.; Funding acquisition, C.D. and D.R.; Investigation, S.R. and D.M.; Methodology, M.F.; Software, A.C. and D.M.; Supervision, C.D.; Writing—original draft, D.R.; Writing—review & editing, M.F., A.C., C.D., S.R., D.R., and D.M. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by Università degli Studi di Milano, grant number PSR 2019-Linea 2 Azione A—PSR2019_DIP_005_PI_CDRAG “Coordination complexes and organic-inorganic hybrid materials for photonics and optoelectronics”, and by National Interuniversity Consortium of Materials Science and Technology, grant number INSTMMI012.

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

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