molecules

MDPI

Article

Luminescent 1,10-Phenanthroline β-Diketonate Europium Complexes with Large Second-Order Nonlinear Optical Properties

Francesco Fagnani [1], Alessia Colombo [1], Graziella Malandrino [2], Claudia Dragonetti [1] and Anna Lucia Pellegrino [2,*]

[1] Dipartimento di Chimica, Università di Milano and INSTM UdR Milano, 20126 Milan, Italy
[2] Dipartimento di Scienze Chimiche, Università di Catania and INSTM UdR Catania, 95125 Catania, Italy
* Correspondence: annalucia.pellegrino@unict.it; Tel.: +39-095-7385011

Abstract: Substitution of the diglyme ligand of [Eu(hfa)$_3$(diglyme)] (where hfa is hexafluoroacetylacetonate) with a simple 1,10-phenanthroline leads to a six-fold increase of the product $\mu\beta_{EFISH}$, as measured by the Electric-Field-Induced Second Harmonic generation (EFISH) technique. Similarly, [Eu(tta)$_3$(1,10-phenanthroline)] (where Htta is 2-thenoyltrifluoroacetone) is characterized by a large second-order NLO response. Both 1,10-phenanthroline europium complexes have great potential as multifunctional materials for photonics.

Keywords: europium complexes; antenna-ligand; second-order nonlinear optics

Citation: Fagnani, F.; Colombo, A.; Malandrino, G.; Dragonetti, C.; Pellegrino, A.L. Luminescent 1,10-Phenanthroline β-Diketonate Europium Complexes with Large Second-Order Nonlinear Optical Properties. *Molecules* **2022**, *27*, 6990. https://doi.org/10.3390/molecules27206990

Academic Editors: Paola Deplano, Flavia Artizzu and Luca Pilia

Received: 23 September 2022
Accepted: 14 October 2022
Published: 18 October 2022

1. Introduction

The design and characterization of molecules with a second-order nonlinear optical (NLO) response have received considerable attention due to their application in a range of fields such as optical communications, electrooptical devices, and optical data processing [1,2]. To present good second-order NLO properties, a molecule has to be non-centrosymmetric, with a great difference between the excited state and the ground state dipole moment; in addition, it has to be characterized by charge-transfer transitions at relatively low energy. Thus, organic molecules containing electron-acceptor and electron-donor groups connected by a polarizable π-conjugated bridge can reach a good NLO response [1–6]. In the last twenty years, coordination compounds, characterized by low-energy ligand-to-metal, metal-to-ligand, ligand-to-ligand and intraligand charge-transfer (LMCT, MLCT, LLCT, and ILCT, respectively) excited states, have shown their great potential for second-order nonlinear optics [7–22]. In the design of NLO-active complexes, a useful aspect is that the energy of the charge-transfer states is easily controlled by the nature and oxidation state of the metal and by the choice of the ligands. In particular, it appeared that the second-order NLO response of various π-delocalized nitrogen donor ligands such as pyridines, stilbazoles, phenanthrolines, bipyridines, and terpyridines can be greatly enhanced upon coordination to a metal center [8–15,20,22–26]. Coordination complexes with various metals have been studied. However, surprisingly, although lanthanide (Ln) complexes have been intensively investigated for their luminescent and magnetic properties [27,28], as well as for biological applications [29–33], there are only a few reports on their peculiar NLO properties [34–43].

It was reported that dipolar lanthanide complexes such as [LLn(NO$_3$)$_3$] (where L is a dibutylaminophenyl-functionalized annelated terpyridine) are characterized by a good second-order NLO response, measured by the Harmonic Light Scattering (HLS) technique in solution [44–47], which increases as the number of f electrons increases [34,36]. Similarly, the increase in the quadratic hyperpolarizability, β_{HLS}, of Na$_3$[Ln(pyridyl-2,6-dicarboxylate)$_3$] along the Ln series can be explained by the increased number of f electrons [35]. The

unexpected fact that the quadratic hyperpolarizability depends on the number of f electrons was attributed to the polarization of the 4f electrons [41]. Additionally, it has been reported that the quadratic hyperpolarizibilities of Ln complexes bearing nonadentate ligands based on triazacyclononane, functionalized with pyridyl-2-phosphinate groups, reach a maximum around the center of the lanthanide series, with a bell-shaped trend [42]. A similar trend of the quadratic hyperpolarizibilities was observed in the case of Ln complexes of *trans*-cinnamic acid [44]. In parallel, some of us studied the second-order nonlinear optical response of [Ln(hfa)$_3$(diglyme)] (hfa = hexafluoroacetylacetonate; diglyme = bis (2-methoxyethyl) ether) by a combination of Electric-Field Induced Second Harmonic generation (EFISH) and HLS techniques in solution, confirming the role of f electrons in controlling the second-order NLO properties [38]. In these systems, the molecular quadratic hyperpolarizabilities measured by the EFISH method [48], β_{EFISH}, initially increase rapidly with the number of f electrons, whereas the increase is much lower for the last seven f electrons; additionally, the β_{HLS} values increase, but much less rapidly, along the Ln series [38]. Similarly, the β_{EFISH} values of trinuclear lanthanide adducts [Ln(NO$_3$)$_3$(CuL)$_2$] (Ln = La, Ce, Sm, Eu, and Er; L = N,N′-1,3-propylen-bis (salicylideniminato)) are significantly influenced by the number of f electrons: the values initially increase rapidly with the number of f electrons, starting from lanthanum to europium; then the increase is less marked upon addition of the other f electrons, with the β_{EFISH} value of the Er complex (11 f electrons) being only 1.1 times higher than that of the Eu complex (6 f electrons) [39]. This study confirmed that the surprising polarizable character of f electrons is the origin of the fascinating NLO properties. As general trend, the increase of the second-order NLO response is significant up to fulfilment of half f shell, while it becomes much less relevant with the addition of further f electrons up to the total fulfilment of the f shell [39].

This latter observation and the fact that lighter lanthanides (Ce-Eu) are more abundant than the heavier ones (Gd-Lu), and therefore are generally less expensive [49], render europium complexes of particular interest for NLO studies.

In the present work, we found that two known luminescent β-diketonate europium complexes [Eu(hfa)$_3$(1,10-phenanthroline)] and [Eu(tta)$_3$(1,10-phenanthroline)], from now on [Eu(hfa)$_3$(phen)] and [Eu(tta)$_3$(phen)], show an unexpected large NLO response, much higher than that previously reported for the related [Eu(hfa)$_3$(diglyme)] [38], as evidenced by the Electric-Field Induced Second Harmonic generation (EFISH) technique in solution [41], opening a promising route for easily prepared multifunctional NLO-active lanthanide complexes.

The Eu complexes under investigation are schematized in Figure 1. The structures present the Eu as central metal in the most stable oxidation state 3+ and stabilized by six oxygens coming from the β-diketonate ligands and by two nitrogens of the phenanthroline for [Eu(hfa)$_3$(phen)] and [Eu(tta)$_3$(phen)] (complexes **1** and **2** in Figure 1), while the Eu coordination sphere is completed with three additional oxygens of the polyether for [Eu(hfa)$_3$(diglyme)], complex **3**.

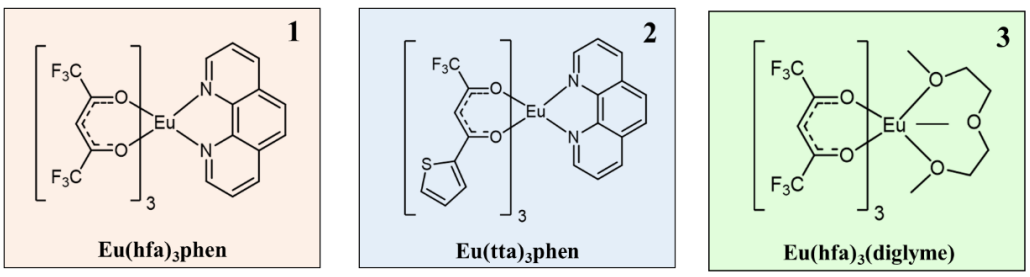


Figure 1. Molecular structures of (**1**) [Eu(hfa)$_3$(phen)], (**2**) [Eu(tta)$_3$(phen)] and (**3**) [Eu(hfa)$_3$ (diglyme)] complexes.

2. Results and Discussion

The europium fluorinated β-diketonate complexes have been obtained through a facile synthesis starting from the europium acetate and the ligands. The present approach finds counterparts in the route previously reported for the analogous [Eu(hfa)$_3$(diglyme)] complex [28,38] and offers several advantages, such as high yield, synthesis in a single step, low-cost route from commercially available chemicals. Additionally, all the complexes can be handled in air, are non-hygroscopic, soluble in common organic solvents and present high thermal and chemical stability.

Furthermore, the second-order nonlinear optical properties in chloroform solution of complexes **1** and **2** have been deeply studied, working with an incident radiation of low energy (λ = 1.907 μm), by the EFISH method in solution [48].

This technique, suitable for dipolar molecules, provides information on the molecular NLO properties through the following equation:

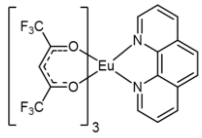
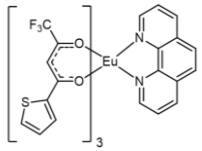
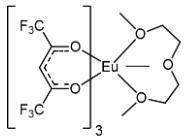
$$\gamma\text{EFISH} = (\mu\beta_\lambda/5kT) + \gamma\ (-2\omega;\ \omega,\ \omega,\ 0)$$

where $\mu\beta_\lambda/5kT$ is the dipolar orientational contribution and $\gamma\ (-2\omega;\ \omega,\ \omega,\ 0)$ is the electronic cubic contribution, which can usually be neglected when studying the second-order NLO properties of dipolar molecules. B_λ is the projection along the dipole moment axis of β_{VEC}, which is the vectorial component of the tensor of the quadratic hyperpolarizability, working with an incident wavelength λ of a pulsed laser. To avoid overestimation of the quadratic hyperpolarizability value, due to resonance enhancements, it is necessary to work with an incident wavelength λ whose second harmonic λ/2 is far from any absorption band of the compound investigated. For this reason, a wavelength of 1.907 μm was chosen to study complexes **1** and **2**. To obtain the value of β_{EFISH} it would be necessary to know the ground state dipole moment μ of the molecule. However, from an applicative point of view, it is the product $\mu\beta_{EFISH}$ that should be maximized. A compound with a $\mu\beta_{EFISH}$ value higher than that of Disperse Red One (500×10^{-48} esu), proposed for electrooptic polymeric poled films [50,51], can be considered of interest for photonic applications.

It turned out that [Eu(hfa)$_3$(phen)] (**1**; Figure 1) is characterized, in solution, by a $\mu\beta_{EFISH}$ of 1016×10^{-48} esu (Table 1), 6.3 times higher than that previously reported [38] for the related complex [Eu(hfa)$_3$(diglyme)] (**3**). Therefore, remarkably, replacement of diglyme with a simple 1,10-phenanthroline leads to a huge increase of the second-order NLO properties. Such a large NLO response is also observed for [Eu(tta)$_3$(phen)] (**2**; $\mu\beta_{EFISH} = 920 \times 10^{-48}$ esu) in which the hexafluoroacetylacetonate ligand has been replaced by the 2-thenoyltrifluoroacetonate. It is worth pointing out that these values are higher than that observed for the europium adduct [Eu(NO$_3$)$_3$(CuL)$_2$] in solution ($\mu\beta_{EFISH} = 720 \times 10^{-48}$ esu), which is much more difficult to prepare [39].

The large NLO response of **1** and **2** is thrilling also due to the simplicity of the 1,10-phenanthroline ligand. In fact, it is known that coordination of 5-X-1,10-phenanthrolines to a "Zn(CH$_3$CO$_2$)$_2$" moiety produces a significant enhancement of the product $\mu\beta_{EFISH}$, which becomes 99×10^{-48}, 254×10^{-48}, and 616×10^{-48} esu for X = OMe, NMe$_2$, and trans-CH=CHC$_6$H$_4$NMe$_2$, respectively) [52,53], but the best NLO response of these Zn(II) complexes is lower than that obtained for complexes **1** and **2**, although the 1,10-phenanthroline ligand is functionalized in the Zn systems.

Table 1. Main absorption bands in the UV-visible spectra and second-order NLO response.

Compound	Absorption [a] λ_{max}/nm (ε/M^{-1} cm^{-1})	$\mu\beta$ ($\times 10^{-48}$ esu) [b]
1 	233, 272 (11,851), 293	1016
2 	230, 272 (9347), 341 (10,000)	920
3 	306 (16,617)	161

[a] In CH_2Cl_2 10^{-4} M; [b] In $CHCl_3$ 10^{-3} M working at 1.907 μm; the experimental error is ±10%.

The absorption spectra of the complexes, reported in Figure 2, display various features as a function of the different ligands which compose the structures.

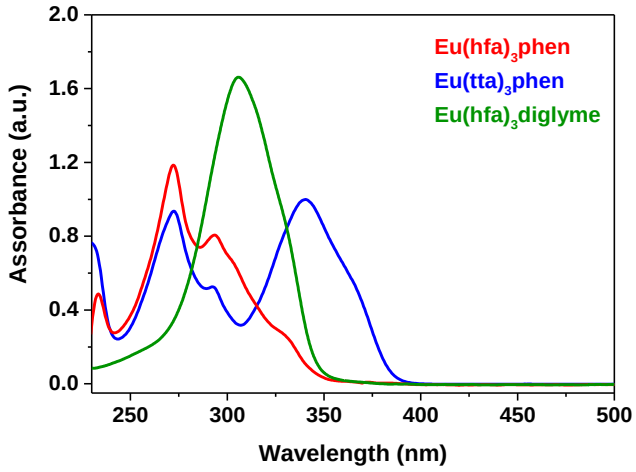


Figure 2. UV-vis spectra of [Eu(hfa)$_3$(phen)], [Eu(tta)$_3$(phen)] and [Eu(hfa)$_3$(diglyme)], complexes from 1×10^{-4} M solutions in CH_2Cl_2.

In particular, the [Eu(hfa)$_3$(diglyme)] adduct shows a strong band around 306 nm, whereas the [Eu(hfa)$_3$(phen)] presents bands centered at 233, 272 and 293 nm arising from the phen and hfa contributions. Notably, in both complexes, a shoulder around 325 nm can be assigned to the lowest spin-allowed π-π* transition of the β-diketonate hfa ligand [54,55]. Finally, the absorption spectrum of the [Eu(tta)$_3$(phen)] displays, together with the bands at 230 and 272 nm due to the 1,10-phenanthroline, a broad and intense signal at 341 nm arising from the tta ligand. For an easier comparison of the different contribution arising from each ligand, overlays of the UV-vis spectra of the complexes and the associated ligands are reported in Figure 3. Thus, the UV-vis spectra of **1** and **2** are due to the contribution of the relative β-diketonate, hfa and tta for **1** and **2**, respectively, and antenna ligand phen, while the UV spectrum of **3** is only due to the hfa contribution, the diglyme beeing inactive in the UV-vis region.

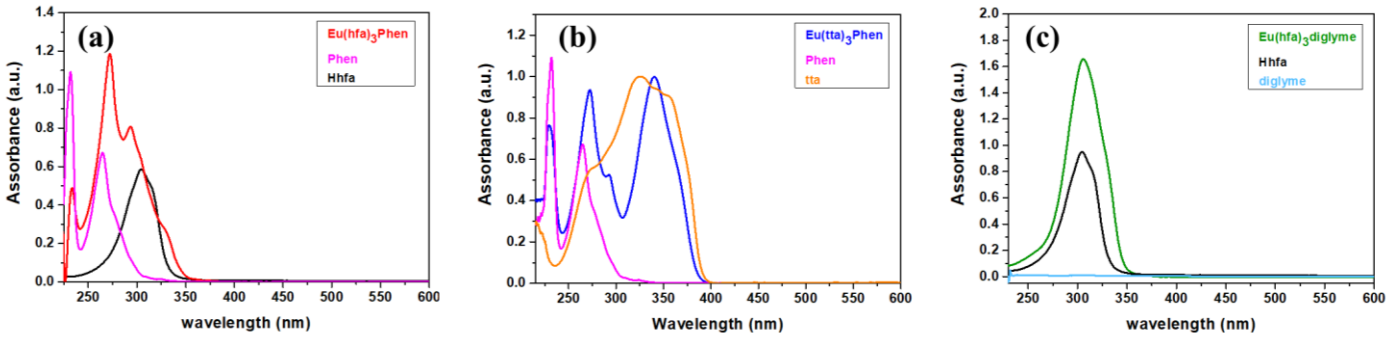


Figure 3. UV-vis spectra comparison of (**a**) [Eu(hfa)$_3$(phen)], (**b**) [Eu(tta)$_3$(phen)] and (**c**) [Eu(hfa)$_3$(diglyme)] complexes with the corresponding ligands (1×10^{-4} M CH_2Cl_2).

In addition, the luminescence spectra of the adducts, registered at room temperature, are reported in Figure 4. The spectra were obtained using an excitation wavelength of 348 nm for the [Eu(hfa)$_3$(phen)], [Eu(tta)$_3$(phen)] and [Eu(hfa)$_3$(diglyme)].

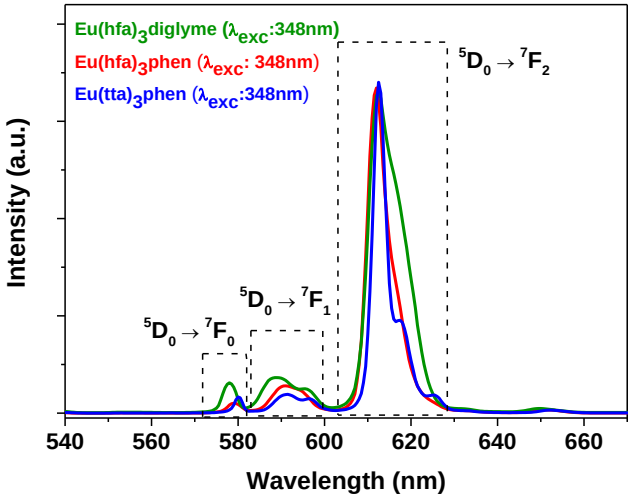


Figure 4. Luminescence spectra (λ_{exc} = 348 nm), of [Eu(hfa)$_3$(phen)], [Eu(tta)$_3$(phen)] and [Eu(hfa)$_3$(diglyme)], complexes in CH_2Cl_2.

The spectra, recorded as CH_2Cl_2 solutions, are reported normalized in intensity, but similar intensity values have been obtained with concentrations of 10^{-3} M, 10^{-5} M and 10^{-3} M for the complexes **1**, **2** and **3**, respectively. Therefore, the [Eu(tta)$_3$(phen)] has a much higher luminescence intensity. The emission peaks observed in Figure 4 consist of f—f emission transitions from the $^5D_0$ excited state to the ^7F_J multiplet of the Eu(III) ion. In particular, the peaks at 578, 590 and 612 nm are assigned to the Eu ion transitions $^5D_0 \rightarrow {}^7F_0$, $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$, respectively [56]. The presence of the band due to the $^5D_0$-$^7F_0$ transition in the 574–582 nm spectral region due to a singlet-to-singlet transition indicates that the Eu^{3+} ion occupies a low symmetry environment in all the three compounds [57]. This feature is also supported by the asymmetry ratio, i.e. the ratio between the $^5D_0 \rightarrow {}^7F_2$ and $^5D_0 \rightarrow {}^7F_1$ electronic transitions, which, with a value ranging from 9.05, to 11.89 and 17.6 for **3**, **1** and **2**, respectively, indicates a highly asymmetric environment [57].

3. Materials and Methods

All reagents and solvents were purchased from Sigma-Aldrich and were used without further purification.

[Eu(hfa)$_3$(1,10-phenanthroline)], (**1**). The adduct was synthetized through a one-step reaction from the Eu(III) acetate hydrate, Hhfa, 1,10-phenanthroline. Specifically, 1.5797 g (4.8 mmol) of $Eu(CH_3COO)_3 \cdot xH_2O$ was first suspended in dichloromethane (50 mL).

1,10-phenanthroline 0.8650 g (4.8 mmol) was added to the suspension. H-hfa 2.04 mL (14.4 mmol; d = 1.47 g/mL) was added under vigorous stirring after 10 min and the mixture was refluxed under stirring for 1 h. After solvent evaporation, the complex appears in form of very light orange crystals. The crystals were collected, washed several times with pentane in order to ensure a high degree of purity, and filtered. The yield was about 90%. Elemental analysis ($EuC_{27}H_{11}O_6N_2F_{18}$): Calc: C, 34.02; H, 1.16. Found: C, 33.69; H, 1.20.

[Eu(tta)$_3$(1,10-phenanthroline)], (**2**). The adduct was synthetized following a reaction similar to that of **1** from 1.5797 g (4.8 mmol) of the Eu(III) acetate hydrate suspended in ethanol (100 mL), 0.8650 g (4.8 mmol) of 1,10-phenanthroline, and 3.1993 g (14.4 mmol) of Htta. The adduct was collected after solvent evaporation, washed several times with pentane, and a yield of about 88% was obtained. Elemental analysis ($EuC_{36}H_{20}O_6N_2S_3F_9$): Calc: C, 43.43; H, 2.02. Found: C, 43.88; H, 1.97.

[Eu(hfa)$_3$(diglyme)], (**3**). The adduct was synthetized following a procedure similar to that of **1**, from 1.5797 g (4.8 mmol) of the Eu(III) acetate hydrate, 2.04 mL (14.4 mmol; d = 1.47 g/mL) Hhfa and 0.69 mL (4.8 mmol; d = 0.940 g/mL) of diglyme. A similar purification process was also executed for this product. The yield was about 92%. Elemental analysis ($EuC_{21}H_{17}O_9F_{18}$): Calc: C, 27.80; H, 1.89. Found: C, 27.35; H, 1.79.

Characterization. All EFISH measurements were carried out at the Dipartimento di Chimica of the Università degli Studi di Milano, in $CHCl_3$ solutions at a concentration of 1×10^{-3} M, working with a non-resonant incident wavelength of 1.907 μm, obtained by Raman shifting the fundamental 1.064 μm wavelength produced by a Q-switched, mode-locked Nd^{3+}: YAG laser manufactured by Atalaser. The spectrometer for the EFISH measurements was a prototype made by SOPRA (France). The reported $\mu\beta_{EFISH}$ values are the mean of 16 successive measurements performed on the same sample.

The UV-Vis spectra of the three adducts were collected using a JASCO V-650 UV − vis spectrophotometer, starting from 1×10^{-4} M solutions in CH_2Cl_2. Photoluminescence spectra were collected at room temperature using a JASCO FP-8300 spectrofluorimeter at a λ excitation of 348 nm for the [Eu(hfa)$_3$(diglyme)], [Eu(hfa)$_3$(phen)] and [Eu(tta)$_3$(phen)] complexes. Elemental microanalyses were carried out using a Carlo Erba 1106 elemental analyzer.

4. Conclusions

Lanthanide complexes have been intensively studied for their luminescent and magnetic properties, but recently, their NLO properties have also attracted great interest. Among them, the Eu non-centrosymmetric molecules, containing the 1,10-phenanthroline antenna ligand, have been the object of interest in the present study. This work has evidenced the unexpected huge second-order NLO response of luminescent β-diketonate europium complexes bearing a simple 1,10-phenanthroline, a result of particular relevance in the search of new multifunctional building blocks for photonic nanomaterials. Their $\mu\beta_{EFISH}$ values, higher than that of the benchmark Disperse Red One, open the way to the use of these Eu complexes in a wide range of technological fields such as photonic applications. Thus, the 1,10-phenanthroline ligand, a well-known antenna ligand for the photoluminescence of Eu(III), plays a crucial role in boosting the NLO response of these systems. In fact, the μβ value goes from 161($\times 10^{-48}$ esu) for the [Eu(hfa)$_3$(diglyme)] complex to 1061 ($\times 10^{-48}$ esu) for Eu(hfa)$_3$(1,10-phenanthroline), due to the substitution of diglyme by 1,10-phenanthroline. Because the two compounds have the same β-diketonate, the unique difference, and thus the factor responsible for the significant increase in the μβ value, is the phenanthroline. This observation is further supported by the μβ value of 920 ($\times 10^{-48}$ esu) found for [Eu(tta)$_3$(1,10-phenanthroline)]. Other important advantages of the present work are, on the one hand, the facile, one-pot, low-cost synthetic approach, and on the other hand, the non-hygroscopic, high-solubility and air stability features of the complexes, which represent added values and open a promising route for easily preparing multifunctional NLO-active lanthanide complexes.

Finally, the present results open the door to other intriguing EFISH investigations such as the study of the effect of donor substituents on the 1,10-phenanthroline coordinated to lanthanides.

Author Contributions: Conceptualization, G.M. and C.D., methodology, A.L.P. and A.C. and F.F.; investigation, A.L.P. and F.F.; writing—original draft preparation, A.L.P. and F.F.; writing—review and editing, A.L.P., G.M., F.F., A.C. and C.D.; supervision, G.M. and C.D.; funding acquisition, A.C., F.F. and G.M. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by Università degli Studi di Milano (Project PSR2020_DIP_005_PI_ACOLO "Synthesis and characterization of organic and coordination compounds for application in luminescent devices or in bioimaging").

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Data is contained within the article.

Acknowledgments: We deeply thank Stefania Righetto for EFISH measurements. F. Fagnani thanks MUR and Università degli Studi di Milano for a PhD fellowship. A. L. Pellegrino thanks the Ministero dell'Università e della Ricerca within the PON "Ricerca e Innovazione" 2014–2020 Azioni IV.4 program. Fondazione Cariplo and Regione Lombardia are acknowledged for the instrumentation bought during the *SmartMatLab Centre* project (2014).

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

Sample Availability: Samples of the compounds are not available.

References

1. Prasad, N.P.; Williams, D.J. *Introduction to Nonlinear Optical Effects in molecules and Polymers*; Wiley: New York, NY, USA, 1991.
2. Lupo, D. *Molecular Nonlinear Optics: Materials, Physics and Devices*; Academic Press: Boston, MA, USA, 1994.
3. Kanis, D.R.; Ratner, M.A.; Marks, T.J. Design and Construction of Molecular Assemblies with Large Second-Order Optical Nonlinearities. *Quantum Chemical Aspects. Chem. Rev.* **1994**, *94*, 195–242. [CrossRef]
4. Beverina, L.; Ruffo, R.; Patriarca, G.; De Angelis, F.; Roberto, D.; Righetto, S.; Ugo, R.; Pagani, G. 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]
5. Todescato, F.; Fortunati, I.; Carlotto, 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]
6. Marinotto, D.; Castagna, R.; Righetto, S.; Dragonetti, C.; Colombo, A.; Bertarelli, C.; Garbugli, M.; Lanzani, G. Photoswitching of the Second Harmonic Generation from Poled Phenyl-Substituted Dithienylethenes Thin Film and EFISH Measurements. *J. Phys. Chem. C* **2011**, *115*, 20425–20432. [CrossRef]
7. Powel, C.E.; Humphrey, M.G. Nonlinear otical properties of transition metal acetylides and their derivatives. *Coord. Chem. Rev.* **2004**, *248*, 725–756. [CrossRef]
8. Di Bella, S. Second-order nonlinear optical properties of transition metal complexes. *Chem. Soc. Rev.* **2001**, *30*, 355–366. [CrossRef]
9. 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.
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. Morrall, J.P.; Dalton, G.T.; Humphrey, M.G.; Samoc, M. Organotransition metal complexes for nonlinear optics. *Adv. Organomet. Chem.* **2007**, *55*, 61–136. [CrossRef]
13. Di Bella, S.; Dragonetti, C.; Pizzotti, M.; Roberto, D.; Tessore, F.; Ugo, R. Molecular Organometallic Materials for Optics. In *Topics in Organometallic Chemistry 28, Le Bozec, H., Guerchais, V., Eds.*; Springer: Berlin/Heidelberg, Germany, 2010.
14. Maury, O.; Le Bozec, H. Metal-based quadratic molecular materials. In *Molecular Materials*; Bruce, D.W., O'Hare, D., Walton, R.I., Eds.; Wiley: Chichester, UK, 2010.
15. Hannachi, D.; Fahim Haroun, M.; Khireddine, A.; Chermette, H. Optical and nonlinear optical properties of Ln(Tp)2, where Ln = La,...,Lu and Tp = tris(pyrazolyl)borate: A DFT+TD-DFT study. *New J Chem.* **2019**, *43*, 14377–14389. [CrossRef]

16. 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 nonlinear optical properties of cyclometallated platinum(II) complexes with tridentate NˆCˆN-binding ligands. *Chem. Eur. J.* **2013**, *19*, 9875–9883. [CrossRef] [PubMed]
17. Colombo, A.; Dragonetti, C.; Marinotto, D.; Righetto, S.; Roberto, D.; Tavazzi, S.; Escadeillas, M.; Guerchais, V.; Le Bozec, H.; Boucekkine, A.; et al. Cyclometalated 4-styryl-2-phenylpyridine Pt(II) acetylacetonate complexes as second-order NLO building blocks for SHG active polymeric films. *Organometalllics* **2013**, *32*, 3890–3894. [CrossRef]
18. Colombo, A.; Nisic, F.; Dragonetti, C.; Marinotto, D.; Oliveri, I.P.; Righetto, S.; Lobello, M.G.; De Angelis, F. Unexpectedly high second-order nonlinear optical properties of simple Ru and Pt alkynyl complexes as an analytical springboard for NLO-active polymer films. *Chem. Commun.* **2014**, *50*, 7986–7989. [CrossRef] [PubMed]
19. Prabu, S.; David, E.; Viswanathan, T.; Thirumoorthy, K.; Panda, T.; Dragonetti, C.; Colombo, A.; Marinotto, D.; Righetto, S.; Roberto, D.; et al. NLO-active Y-shaped ferrocene conjugated imidazole chromophores as precursors for SHG polymeric films. *Dalton Trans.* **2020**, *49*, 1854–1863. [CrossRef] [PubMed]
20. Colombo, A.; Dragonetti, C.; Guerchais, V.; Hierlinger, H.; Zysman-Colman, E.; Roberto, D. A trip in the nonlinear optical properties of iridium complexes. *Coord. Chem. Rev.* **2020**, *414*, 213293. [CrossRef]
21. David, E.; Colombo, A.; Dragonetti, C.; Palanisami, N. Novel Ferrocene-Appended β-Ketoimines and Related BF_2 Derivatives with Significant Aggregation-Induced Emission and Second-Order Nonlinear Optical Properties. *Eur. J. Chem.* **2021**, *27*, 7124–7137. [CrossRef]
22. Colombo, A.; Dragonetti, C.; Guerchais, V.; Roberto, D. An excursion in the second-order nonlinear optical properties of platinum complexes. *Coord. Chem. Rev.* **2021**, *446*, 214113. [CrossRef]
23. 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]
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_3, NO_2) on the emission properties and second-order NLO response of cationic Ir(III) organometallic chromophores. *Inorg. Chim. Acta* **2008**, *361*, 4070–4076. [CrossRef]
25. Dragonetti, C.; Righetto, S.; Roberto, D.; Ugo, R.; Valore, A.; Fantacci, A.; Sgamellotti, A.; De Angelis, F. Cyclometallated Iridium(III) complexes with substituted 1,10-phenanthrolines: A new class of highly active organometallic second order NLO-phores with excellent transparency with respect to second harmonic emission. *Chem. Commun.* **2007**, *40*, 4116–4118. [CrossRef]
26. Hierlinger, C.; Bradford Cordes, D.; Slawin, A.; Colombo, A.; Dragonetti, C.; Righetto, S.; Roberto, D.; Jacquemin, D.; Zysman-Colman, E.; Guerchais, V. An investigation on the second-order nonlinear optical response of cationic bipyridine or phenanthroline iridium(III) complexes bearing cyclometallated 2-phenylpyridines with a triphenylamine substituent. *Dalton Trans.* **2018**, *47*, 8292–8300. [CrossRef] [PubMed]
27. Marin, R.; Jaque, D. Doping Lanthanide Ions in Colloidal Semiconductor Nanocrystals for Brighter Photoluminescence. *Chem. Rev.* **2021**, *121*, 1425. [CrossRef] [PubMed]
28. Malandrino, G.; Bettinelli, M.; Speghini, A.; Fragalà, I.L. Europium "second generation" precursors for metal-organic chemical vapor deposition: Characterization and optical spectroscopy. *Eur. J. Inorg. Chem.* **2001**, *2001*, 1039–1044. [CrossRef]
29. Picot, A.; D'Aléo, A.; Baldeck, P.L.; Grichine, A.; Duperray, A.; Andraud, C.; Maury, O. Long-Lived Two-Photon Excited Luminescence of Water-Soluble Europium Complex: Applications in Biological Imaging Using Two-Photon Scanning Microscopy. *J. Am. Chem. Soc.* **2008**, *130*, 1532–1533. [CrossRef] [PubMed]
30. Walton, J.W.; Bourdolle, A.; Butler, S.J.; Soulie, M.; Delbianco, M.; McMahon, B.K.; Pal, R.; Puschmann, H.; Zwier, J.M.; Lamarque, L.; et al. Very bright europium complexes that stain cellular mitochondria. *Chem. Commun.* **2013**, *49*, 1600–1602. [CrossRef]
31. Hamon, N.; Galland, M.; Le Fur, M.; Roux, A.; Duperray, A.; Grichine, A.; Andraud, C.; Le Guennic, B.; Beyler, M.; Maury, O.; et al. Combining a pyclen framework with conjugated antenna for the design of europium and samarium luminescent bioprobes. *Chem. Commun.* **2018**, *54*, 6173–6176. [CrossRef]
32. Hamon, N.; Roux, A.; Beyler, M.; Mulatier, J.-C.; Andraud, C.; Nguyen, C.; Maynadier, M.; Bettache, N.; Duperray, A.; Grichine, A.; et al. Pyclen-Based Ln(III) Complexes as Highly Luminescent Bioprobes for In Vitro and In Vivo One- and Two-Photon Bioimaging Applications. *J. Am. Chem. Soc.* **2020**, *142*, 10184–10197. [CrossRef]
33. Galán, L.A.; Hamon, N.; Nguyen, C.; Molnár, E.; Kiss, J.; Mendy, J.; Hadj-Kaddour, K.; Onofre, M.; Trencsényi, G.; Monnereau, C.; et al. Design of polyazamacrocyclic Gd^{3+} theranostic agents combining magnetic resonance imaging and two-photon photodynamic therapy. *Inorg. Chem. Front.* **2021**, *8*, 2213–2224. [CrossRef]
34. Sénéchal, K.; Toupet, L.; Ledoux, I.; Zyss, J.; Le Bozec, H.; Maury, O. First lanthanide dipolar complexes for second-order nonlinear optics. *Chem. Commun.* **2004**, *19*, 2180–2181. [CrossRef]
35. Tancrez, N.; Feuvrie, C.; Ledoux, I.; Zyss, J.; Toupet, L.; Le Bozec, H.; Maury, O. Lanthanide Complexes for Second Order Nonlinear Optics: Evidence for the Direct Contribution of f Electrons to the Quadratic Hyperpolarizability. *J. Am. Chem. Soc.* **2005**, *127*, 13474–13475. [CrossRef]
36. Sénéchal-David, K.; Hemeryck, A.; Tancrez, N.; Toupet, L.; Williams, J.A.G.; Ledoux, I.; Zyss, J.; Boucekkine, A.; Guégan, J.-P.; Le Bozec, H.; et al. Synthesis, Structural Studies, Theoretical Calculations, and Linear and Nonlinear Optical Properties of Terpyridyl Lanthanide Complexes: New Evidence for the Contribution of f Electrons to the NLO Activity. *J. Am. Chem. Soc.* **2006**, *128*, 12243–12255. [CrossRef] [PubMed]

37. Andraud, C.; Maury, O. Lanthanide Complexes for Nonlinear Optics: From Fundamental Aspects to Applications. *Eur. J. Inorg. Chem.* **2009**, *2009*, 4357–4371. [CrossRef]
38. Valore, A.; Cariati, E.; Righetto, S.; Roberto, D.; Tessore, F.; Ugo, R.; Fragalà, I.L.; Fragalà, M.E.; Malandrino, G.; De Angelis, F.; et al. Fluorinated β-Diketonates Diglyme Lanthanide Complexes as New Second Order NLO Chromophores: The Role of f Electrons on the Dipolar and Octupolar Contribution to the Quadratic Hyperpolarizability. *J. Am. Chem. Soc.* **2010**, *132*, 4966–4970. [CrossRef]
39. Gulino, A.; Fragalà, I.L.; Lupo, F.; Malandrino, G.; Motta, A.; Colombo, A.; Dragonetti, C.; Righetto, S.; Roberto, D.; Ugo, R.; et al. Fascinating Role of the Number of f Electrons in Dipolar and Octupolar Contributions to Quadratic Hyperpolarizability of trinuclear lanthanides-biscopper Schiff base complexes. *Inorg. Chem.* **2013**, *52*, 7550–7556. [CrossRef] [PubMed]
40. Chakrabarty, R.; Dutta, A.; Roy, S.; Das, G.; Ledoux-Rak, I.; Mondal, P.; Prasad, S.K.; Rao, D.S.S.; Bhattacharjee, C.R. Multi-functional Lanthanide Complexes: Mesomorphism, Photoluminescence and Second Order NLO Property. *Chem. Sel.* **2018**, *3*, 8245–8251. [CrossRef]
41. Furet, E.; Costuas, K.; Rabiller, P.; Maury, O. On the Sensitivity of f Electrons to Their Chemical Environment. *J. Am. Chem. Soc.* **2008**, *130*, 2180–2183. [CrossRef]
42. Law, G.-L.; Wong, K.-L.; Lau, K.-K.; Lap, S.-T.; Tanner, P.A.; Kuo, F.; Wong, W.-T. Nonlinear optical activity in dipolar organic–lanthanide complexes. *J. Mater. Chem.* **2010**, *20*, 4074–4079. [CrossRef]
43. Walton, J.W.; Carr, R.; Evans, N.H.; Funk, A.M.; Kenwright, A.M.; Parker, D.; Yufit, D.S.; Botta, M.; De Pinto, S.; Wong, K.-L. Isostructural series of nine-coordinate chiral lanthanide complexes based on triazacyclononane. *Inorg. Chem.* **2012**, *51*, 8042–8056. [CrossRef]
44. Maker, P.D. Spectral broadening of elastic second-harmonic light scattering in liquids. *Phys. Rev. A* **1970**, *1*, 923–951. [CrossRef]
45. Clays, K.; Persoons, A. Hyper-Rayleigh scattering in solution. *Phys. Rev. Lett.* **1991**, *66*, 2980–2983. [CrossRef]
46. Zyss, J. Molecular engineering implications of rotational invariance in quadratic nonlinear optics: From dipolar to octupolar molecules and materials. *J. Chem. Phys.* **1993**, *98*, 6583–6600. [CrossRef]
47. Zyss, J.; Ledoux, I. Nonlinear optics in multipolar media: Theory and experiments, Chem. *Rev.* **1994**, *94*, 77–105. [CrossRef]
48. Ledoux, I.; Zyss, J. Influence of the molecular environment in solution measurements of the second-order optical susceptibility for urea and derivatives. *Chem. Phys.* **1982**, *73*, 203–213. [CrossRef]
49. Bunzli, J.-C.G.; Pecharsky, V.K. *Handbook on the Physics and Chemistry of Rare Earths: Including Actinides*; Elsevier: Amsterdam, The Netherlands, 2020.
50. 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]
51. Dirk, C.W.; Katz, H.E.; Schilling, M.L.; King, L.A. Use of thiazole rings to enhance molecular second-order nonlinear optical susceptibilities. *Chem. Mater.* **1990**, *2*, 700–705. [CrossRef]
52. 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]
53. Di Bella, S.; Colombo, A.; Dragonetti, C.; Righetto, S.; Roberto, D. Zinc(II) as a versatile template for efficient dipolar and octupolar second-order nonlinear optical molecular materials. *Inorganics* **2018**, *6*, 133. [CrossRef]
54. Strasser, A.; Vogler, A. Optical properties of thallium(I), lead(II) and bismuth(III) hexafluoroacetylacetonates. Intraligand phosphorescence under ambient conditions. *Inorg. Chem. Commun.* **2004**, *7*, 528–530. [CrossRef]
55. Strasser, A.; Vogler, A. Intraligand phosphorescence of lead(II) β-diketonates under ambient conditions. *J. Photobiochem. Photobiol. A Chem.* **2004**, *165*, 115–118. [CrossRef]
56. Shurygin, A.V.; Korochentsev, V.V.; Cherednichenko, A.I.; Mirochnik, A.G.; Kalinovskaya, I.V.; Vovna, V.I. Electronic structure and optical properties of Eu(III) tris-β-diketonate adducts with 1,10-phenanthroline. *J. Mol. Struct.* **2018**, *1155*, 133–142. [CrossRef]
57. Binnemans, K. Interpretation of europium(III) spectra. *Coord. Chem. Rev.* **2015**, *195*, 1–45. [CrossRef]