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Fluorinated β-Diketonate Diglyme Lanthanide Complexes as New Second-Order Nonlinear Optical Chromophores: The Role of f Electrons in the Dipolar and Octupolar Contribution to Quadratic Hyperpolarizability

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Abstract: The second-order nonlinear optical (NLO) properties of [Ln(hfac)$_3$(diglyme)] (hfac = hexafluoroacetylacetonate; diglyme = bis(2-methoxyethyl)ether; Ln = La, Ce, Pr, Sm, Eu, Gd, Er, Lu) complexes have been investigated by a combination of electric-field second harmonic generation (EFISH) and harmonic light scattering (HLS) techniques, providing evidence for the relevant role of f electrons in tuning the second-order NLO response dominated by the octupolar contribution. These lanthanide NLO chromophores allow a clean valuation of the influence of f electrons on the quadratic hyperpolarizability and on its dipolar and octupolar contributions. Molecular quadratic hyperpolarizability values measured by the EFISH method, β_{EFISH}, initially increase rapidly with the number of f electrons, the value for the Gd complex being 11 times that of the La complex, whereas this increase is much lower for the last seven f electrons, the β_{EFISH} value of the Lu complex being only 1.2 times that of the Gd complex. The increase of $\langle\beta_{HLS}\rangle$, which is dominated by an octupolar contribution, is much lower along the Ln series. Remarkably, the good $\langle\beta_{HLS}\rangle$ values of these simple systems, well known for their luminescence properties, are reached at no cost of transparency.

Introduction

In the past two decades, coordination complexes have emerged as new and interesting second-order nonlinear optical (NLO) chromophores, due to the diversity of their tunable electronic properties by virtue of the metal center.[1] For instance, the second-order NLO response of various push−pull π-delocalized nitrogen donor ligands bearing a strong electron donor substituent increases significantly upon coordination to a metal center, mainly as the effect of the red shift of their intraligand charge-transfer (ILCT) transition induced by the Lewis acceptor properties of the metal center.[2] Whereas lanthanide (Ln) complexes have been intensively studied for their luminescent and magnetic properties as well as for some catalytic and biological applications,[3] there are only a few recent reports on their peculiar NLO properties.[4−9] In crystals of species such as Bi$_4$Ge$_3$O$_{12}$:Ln, the different lattice distortions caused by the

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different sizes of the various lanthanide ions have some effect on the efficiency of second harmonic generation (SHG).[5] Gatteschi et al.[6] showed that intermolecular π-stacking interactions lead to an enhancement of the solid-state second-order NLO properties of lanthanide-based single-chain magnets [Ln-(hfac)$_3$(4′-phenoxybenzyl-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide)] (hfac = hexafluoroacetylacetonate). Interestingly, at the molecular level, Le Bozec et al.[7,8] reported that dipolar [LLn(NO$_3$)$_3$] (L = dibutylaminophenyl-functionalized annelated terpyridine) complexes behave as second-order NLO chromophores, with a molecular quadratic hyperpolarizability $\langle\beta_{\mathrm{HLS}}\rangle$, measured by the harmonic light scattering (HLS) technique, that increases steadily along the Ln series. Such enhancement was reported to be linked to the increased number of f electrons but not to the effect of the increased Lewis acidity of the metal according to the decrease of the ionic radius along the Ln series.[7,8] In fact, the $\langle\beta_{\mathrm{HLS}}\rangle$ value of the related complex of Y is similar to those of the complex of La (no f electrons) and of the free ligand L (190×10^{-30} esu) but lower than that of the complex of Dy (f^9; 260×10^{-30} esu), despite their very similar ionic radii. In still another paper, Le Bozec et al.[9] reported that the increase of the relatively low $\langle\beta_{\mathrm{HLS}}\rangle$ values ($<2 \times 10^{-30}$ esu) of octupolar Na$_3$[Ln(pyridyl-2,6-dicarboxylate)$_3$] complexes along the Ln series could be attributed to the increased number of f electrons. This dependency of the quadratic hyperpolarizability on the number of f electrons has been theoretically explained by the polarization of the 4f electrons in these Ln complexes.[10] In all cases,[7−9] the Ln complexes investigated bore either a push−pull ligand[7,8] or a rather polarizable ligand.[9]

This latter observation prompted us to investigate the second-order NLO properties of some dipolar lanthanide complexes [Ln(hfac)$_3$(diglyme)] (diglyme = bis(2-methoxyethyl)ether; hfac = hexafluoroacetylacetonate; Ln = La, Ce, Pr, Sm, Eu, Gd, Er, Lu) and, for comparison, [Y(hfac)$_3$(diglyme)], where the ligands are not too polarizable, in order to provide evidence for the role of the Ln metal. A combination of HLS[11] and electric-field second harmonic generation (EFISH)[11,12] techniques was used to evaluate both the dipolar and octupolar contributions to the quadratic hyperpolarizability and therefore to more completely investigate the origin of the second-order NLO properties of these Ln complexes.

Experimental Section

General Comments. Commercial La$_2$O$_3$, Ce(NO$_3$)$_3\cdot$6H$_2$O, Eu$_2$O$_3$, Gd$_2$O$_3$, Er(NO$_3$)$_3\cdot$5H$_2$O, Lu(NO$_3$)$_3\cdot x$H$_2$O, Hhfac, and diglyme were purchased from Aldrich, whereas Pr(NO$_3$)$_3\cdot$6H$_2$O and Sm(NO$_3$)$_3\cdot$6H$_2$O were bought from Strem Chemicals; all these starting materials were used without any further purification. Products were characterized by elemental analysis and, when possible, by ^{1}H and ^{19}F NMR (Bruker DRX-400 spectrometers) and FAB mass spectrometry (Kratos MS 50 spectrometer). Electronic absorption spectra were obtained using a Jasco V-530 spectrophotometer, working in CHCl$_3$ in the concentration range 5×10^{-4}−5×10^{-6} M. Dipole moments, μ, were measured in CHCl$_3$ by using a WTW-DM01 dipolemeter (dielectric constant) coupled with a RX-5000 ATAGO digital refractometer (refractive index) according to the Guggenheim method.[13]

Synthesis. The known complexes [Ln(hfac)$_3$(diglyme)] (diglyme = bis(2-methoxyethyl)ether; Ln = La, Ce, Pr, Sm, Eu, Gd) and [Y(hfac)$_3$(diglyme)] were prepared as previously reported,[14] whereas the new complexes [Ln(hfac)$_3$(diglyme)] (Ln = Er, Lu) were prepared as described below.

Synthesis of [Er(hfac)$_3$diglyme]. Er(NO$_3$)$\cdot$5H$_2$O (2.566 g, 6.30 mmol) was first suspended in dichloromethane (200 mL). Diglyme (0.678 g, 5.50 mmol) and NaOH pellets (0.298 g, 7.45 mmol) were added to the suspension. Hhfac (3.155 g, 15.16 mmol) was then added under vigorous stirring after 10 min, and the mixture was refluxed for 1 h. The excess of erbium nitrate was filtered off. Light pink crystals were obtained after evaporation of the solvent. The crystals were crystallized from *n*-hexane, collected by filtration, and dried under vacuum (85% yield). The melting point of the product was 62−64 °C. ^{1}H NMR (400 MHz, CDCl$_3$, TMS): δ (ppm) −72.06 (br, 4H, 2CH$_2$ of diglyme), −31.49 (br, 4H, 2CH$_2$ of diglyme), 4.45 (br, 3H, 3CH of hfac ligands), 14.85 (br, 6H, 2CH$_3$ of diglyme). ^{19}F NMR (400 MHz, CDCl$_3$, TMS): δ (ppm) −94.56 (CF$_3$ of hfac ligands). Anal. Calcd (found) for ErC$_{21}$H$_{17}$F$_{18}$O$_9$: C, 27.32 (27.21); H, 1.86 (1.84). MS (dry FAB; *m*/*z* (fragment)): 714 [(M − hfac)$^+$, 100], 526 [(M − 2hfac + F)$^+$, 45], 338 [(M − 3hfac + 2F)$^+$, 45], 204 [(ErF$_2$)$^+$, 61]. The given *m*/*z* ratios are relative to the isotope ^{166}Er.

Synthesis of [Lu(hfac)$_3$diglyme]. Prepared as described above for the erbium complex starting from 2.823 g (6.80 mmol) of Lu(NO$_3$)$\cdot x$H$_2$O, 0.717 g (17.94 mmol) of NaOH, 3.156 g (15.17 mmol) of Hhfac, and 0.678 g (5.50 mmol) of diglyme. The colorless crystals were collected, after crystallization from *n*-hexane, by filtration and dried under vacuum (81% yield). The melting point of the product was 65−67 °C. ^{1}H NMR (400 MHz, CDCl$_3$, TMS): δ (ppm) 6.17 (s, 3H, 3CH of hfac ligands), 3.95 (m, 4H, 2CH$_2$ of diglyme), 3.76 (m, 4H, 2CH$_2$ of diglyme), 3.49 (6H, 2CH$_3$ of diglyme). ^{19}F NMR (400 MHz, CDCl$_3$, TMS): δ (ppm) −77.0 (CF$_3$ of hfac). Anal. Calcd (found) for LuC$_{21}$H$_{17}$F$_{18}$O$_9$: C, 27.09 (26.98); H, 1.84 (1.85). MS (dry FAB; *m*/*z* (fragment)): 723 [(M − hfac)$^+$, 100], 535 [(M − 2hfac + F)$^+$, 46], 347 [(M − 3hfac + 2F)$^+$, 36], 213 [(LuF$_2$)$^+$, 56]. The given *m*/*z* ratios are relative to the isotope ^{175}Lu.

Determination of the Second-Order NLO Properties. EFISH Measurements. The molecular quadratic hyperpolarizabilities β of all the investigated complexes (Table 1) were measured by the solution-phase direct-current EFISH generation method,[12] which can provide direct information on the intrinsic molecular NLO properties through eq 1,

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

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}, which is usually negligible. β_λ is the projection along the dipole moment axis of the vectorial component of the tensor of the quadratic hyperpolarizability, working with an incident wavelength λ.

All EFISH measurements were carried out at the Dipartimento di Chimica Inorganica Metallorganica e Analitica “Lamberto Malatesta” of the Università degli Studi di Milano, in CHCl$_3$

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Table 1. Electronic Absorbtion Spectra, Dipole Moments (μ), β_{EFISH}, $\langle\beta_{\mathrm{HLS}}\rangle$, and Dipolar and Octupolar Contributions to the Quadratic Hyperpolarizability of [Y(hfac)$_3$(diglyme)] and [Ln(hfac)$_3$(diglyme)] Complexes, Measured in CHCl$_3$

Ln	no. of f electrons	λ_{max}[a] (nm)	$\mu\beta_{\mathrm{EFISH}}$ ($\times10^{-48}$ esu)	μ[b] (D)	β_{EFISH}[b] ($\times10^{-30}$ esu)	$\langle\beta_{\mathrm{HLS}}\rangle$[b] ($\times10^{-30}$ esu)	$\|\bar{\beta}^{J=1}\|$ ($\times10^{-30}$ esu)	$\|\bar{\beta}^{J=3}\|$[c] ($\times10^{-30}$ esu)	ϵ[d] ($\times10^{-30}$ esu)
Y	0	301	18	6.3	2.8				
La	0	307	17	6.8	2.5	202	1.9	654	452
Ce	1	308	58	5.8	10.0	189	7.7	612	423
Pr	2	307	94	6.6	14.2				
Sm	5	308	146	6.3	23.2				
Eu	6	303	161	6.1	26.4	214	20.4	693	479
Gd	7	306	170	6.1	27.9				
Er	11	302	185	6.0	30.8	236	23.8	764	528
Lu	14	305	210	6.3	33.3	265	25.8	858	593

[a] There is a shoulder at 325−327 nm. [b] The error on μ is ±1 D, whereas that of EFISH and HLS measurements is $\pm10\%$. [c] The total quadratic hyperpolarizability (from eq 2) is essentially equal to $\|\bar{\beta}^{J=3}\|$. [d] The difference between the total quadratic hyperpolarizability (from eq 2) and $\langle\beta_{\mathrm{HLS}}\rangle$.

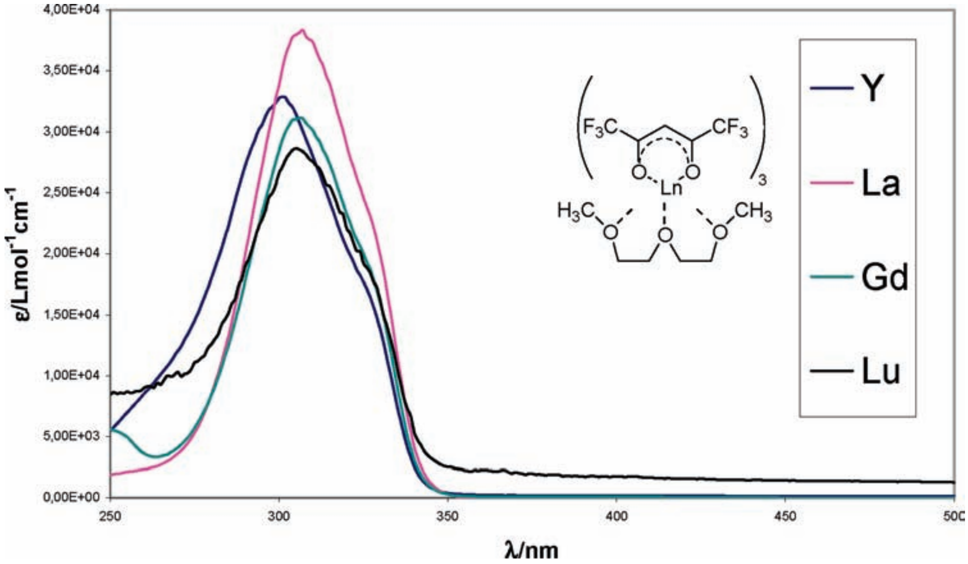

Figure 1. Electronic absorption spectra of some [Ln(hfac)$_3$diglyme] complexes and of [Y(hfac)$_3$diglyme] in CHCl$_3$ (for the other complexes, see Supporting Information).

solutions at a concentration of 1×10^{-3} M, working with a nonresonant 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 apparatus for the EFISH measurements was a prototype made by SOPRA (France). The $\mu\beta_{\mathrm{EFISH}}$ values reported are the mean of 16 successive measurements performed on the same sample.

HLS Measurements. The HLS technique[11] involves the detection of the incoherently scattered second harmonic generated by a solution of the molecule under irradiation with a laser of wavelength λ, leading to the measurement of the mean value of the $\beta \times \beta$ tensor product, $\langle\beta_{\mathrm{HLS}}\rangle$. All HLS measurements were carried out at the École Normale Supérieure de Cachan in CHCl$_3$ solutions at a concentration of 1×10^{-2} M, working with a low-energy nonresonant incident radiation of 1.907 μm, thereby avoiding any multiphoton fluorescence contribution to the HLS signal.

Results and Discussion

The known complexes [Ln(hfac)$_3$(diglyme)] (diglyme = bis(2-methoxyethyl)ether; Ln = La, Ce, Pr, Sm, Eu, Gd) and [Y(hfac)$_3$(diglyme)][14] and the new complexes [Ln(hfac)$_3$(diglyme)] (Ln = Er, Lu) were investigated in order to measure their quadratic hyperpolarizability in chloroform solution, working with an incident radiation of low energy (λ = 1.907 μm), by a combination of HLS and EFISH techniques in order to evaluate both the dipolar and octupolar contributions and therefore to get a better understanding of the origin of the second-order NLO properties of these Ln complexes.

Values of β_{EFISH}, along with experimental dipole moments (μ) and electronic absorption spectra, are reported in Table 1.

The electronic absorption spectra (Figure 1) show a strong band around 301−308 nm and a shoulder around 325−330 nm, which could be assigned to the lowest spin-allowed $\pi-\pi^*$ transition of the β-diketonate ligand when coordinated to metal ions lacking energetically available d electrons, such as Tl(I), Pb(II), and Bi(III).[15] As for other NLO-active Ln complexes,[7−9] the spectra are basically insensitive to the nature of the lanthanide f core, due to the very low intensity of f−f transitions. Calculated electronic spectra (Supporting Information) for [Ln(hfac)$_3$(diglyme)] (La, Lu), including spin−orbit coupling, are in good agreement with the experimental ones, apart from a rigid red-shift of calculated data, which is corrected by using a hybrid functional. Inspection of the TDDFT eigenvectors confirms the β-diketonate ligand $\pi-\pi^*$ assignment of the main transitions (Supporting Information).

The relatively low value of β_{EFISH} ($2.5 \times 10^{-30}-33.3 \times 10^{-30}$ esu) increases along the Ln series, confirming an effect of the presence and number of f electrons on the value of β_{EFISH}, with a value close to zero for the Y and La complexes, both without f electrons. This latter observation is in support of the irrelevance

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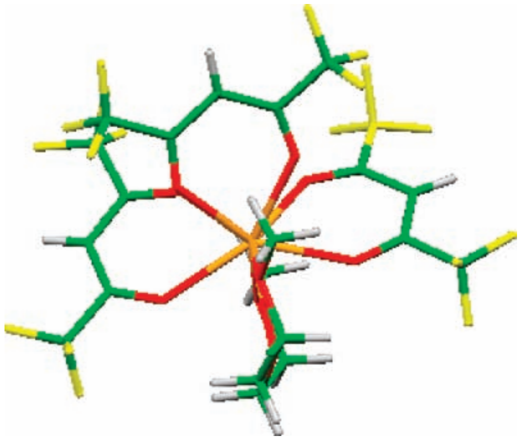

Figure 2. Structure of the Y(hfac)$_3$diglyme complex (space group $P2_1/c$).

on the β_{EFISH} value of transitions involving π electrons of the β-diketonate ligands (Table 1).

The structures of the known [Ln(hfac)$_3$(diglyme)] complexes are all similar along the Ln series. The structure of the [Y(hfac)$_3$(diglyme)] complex (space group $P2_1/c$) has been reported as a typical example of this type of compounds (Figure 2). In fact, all of them possess similar monoclinic structures; in particular, La, Ce, and Pr complexes belong to the $P2_1/c$ space group, while Sm, Eu, and Gd complexes belong to the $P2_1/n$ space group.

They consist of the metal ion with a nine coordination sphere with six oxygen donor atoms from three hfac ligands and three oxygen donor atoms from the diglyme ligand, producing a monocapped square antiprismatic coordination geometry. The mean Ln−O(diglyme) and Ln−O(hfac) distances decrease slightly along the lanthanide series, in agreement with the lanthanide contraction, with the distances for the Y complex being slightly lower than those of the related Gd complex.[14] However, these slight structural differences do not have any influence on dipole moments (oriented essentially along the direction connecting the hfac ligand *trans* to the diglyme ligand and the diglyme ligand itself; Supporting Information) or electronic spectra, as reported in other series of Ln derivatives.[7] In addition, they cannot be the origin of the increase of the β_{EFISH} value along the Ln series, since the Y complex has a β_{EFISH} value similar to that of the La complex and much lower than that of the Gd complex.

Structurally, these NLO chromophores cannot be considered in terms of classical push−pull systems since the potential donor part (the diglyme moiety) is connected to the potential acceptor part (the hfac moieties) not by a π-delocalized linker but by the f electrons of a Ln ion. Meanwhile, the negligible contribution of the π electrons of the hfac ligands to the EFISH quadratic hyperpolarizability would confirm a relevant role of f electrons. As shown in Table 1 and Figure 3, β_{EFISH} values initially increase rapidly with the number of f electrons, the value for the complex of Gd with seven f electrons being 11 times that of the complex of La without f electrons. The increase of β_{EFISH} is less marked upon addition of the other seven f electrons, the β_{EFISH} value of the complex of Lu (14 f electrons) being only 1.2 times that of the complex of Gd. The high enhancement of β_{EFISH} on going from La to Gd is reminiscent to the particular increase of the quadratic hyperpolarizabilities reported by Létard et al.[16] for metal transition complexes [ML$_2$(NCS)$_2$] (L = *N*-2′-pyridylmethylene-4-aminobiphenyl) upon increasing the number of unpaired d electrons: Zn (d^{10}, no unpaired d electron) < Ni (d^8, two unpaired d electrons) < Co (d^7, three unpaired d electrons) < Fe (d^6, four unpaired d electrons) < Mn (d^5, five unpaired d electrons). However, when the f orbitals are half-filled, an increase of f electrons leads to a further enhancement (although of lower intensity) of β_{EFISH} values, even though the number of unpaired f electrons decreases.

In order to evaluate the dipolar ($J = 1$) and octupolar ($J = 3$) contributions to the total quadratic hyperpolarizability (eq 2), we investigated some complexes by the HLS technique working with an incident wavelength of 1.907 μm (Table 1). In fact, for a molecule with a symmetry such as C_2 or $C_{\infty,v}$, the dipolar contribution $\|\bar{\beta}^{J=1}\|$ can be calculated from β_{EFISH} with eq 3. When the value of $\langle\beta_{\text{HLS}}\rangle$ is known, the octupolar contribution $\|\bar{\beta}^{J=3}\|$ can then be obtained by application of eq 4.[11d,17,18]

$$\|\bar{\beta}\|^2 = \|\bar{\beta}^{J=1}\|^2 + \|\bar{\beta}^{J=3}\|^2 \tag{2}$$

$$\|\beta^{J=1}\| = \sqrt{\frac{3}{5}}\beta_{\text{EFISH}} \tag{3}$$

$$\langle\beta^2_{\text{HLS}}\rangle = \langle|\beta_{XXX}|^2\rangle + \langle|\beta_{ZXX}|^2\rangle = \frac{2}{9}\|\bar{\beta}^{J=1}\|^2 + \frac{2}{21}\|\bar{\beta}^{J=3}\|^2 \tag{4}$$

Remarkably, the various complexes are characterized by a significant value of $\langle\beta_{\text{HLS}}\rangle$ ($189 \times 10^{-30}-265 \times 10^{-30}$ esu), which increases relatively slowly but steadily with the number of f electrons, the enhancement factor from La to Lu being 1.3. As shown in Table 1, these high values of $\langle\beta_{\text{HLS}}\rangle$ are due to a high octupolar $\|\bar{\beta}^{J=3}\|$ component, the dipolar component $\|\bar{\beta}^{J=1}\|$ being less than 3% of the octupolar one. Therefore, the total quadratic hyperpolarizability (calculated from eq 2) is essentially equal to $\|\bar{\beta}^{J=3}\|$. The difference between the total quadratic hyperpolarizability and $\langle\beta_{\text{HLS}}\rangle$, ϵ, is quite large ($452 \times 10^{-30}-593 \times 10^{-30}$ esu, Table 1) because $\langle\beta_{\text{HLS}}\rangle$ contains isotropic mean factors that decrease this parameter, as evidenced by the coefficients in eq 4. Interestingly, along the first half of the Ln series, the increase of $\|\bar{\beta}^{J=3}\|$ is much lower than that of $\|\bar{\beta}^{J=1}\|$, whereas a similar increase is observed in the second half (in both cases, enhancement by a factor of ca. 1.1 on going from Er to Lu; Table 1).

Conclusion

Our work represents a new step in the understanding of the second-order NLO properties of Ln complexes. Not only does it confirm that f electrons may tune the second-order NLO response of Ln complexes, but most importantly, it shows for the first time that this tuning can be 10 times higher for the dipolar contribution to the quadratic hyperpolarizability than for the octupolar contribution, although the major contribution to the total quadratic hyperpolarizability is controlled mainly by the octupolar part. In any case, the dipolar contribution and

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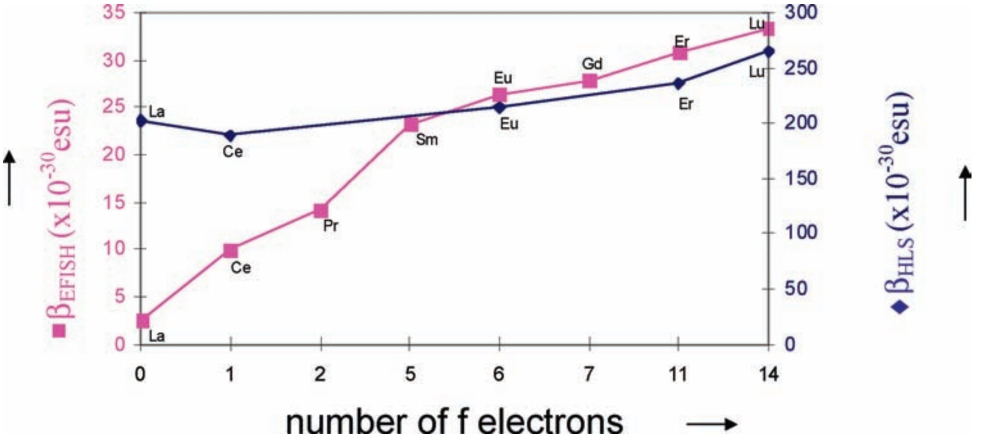

Figure 3. Dependence of β_{EFISH} and $\langle\beta_{HLS}\rangle$ ($\times 10^{-30}$ esu) upon the number of f electrons.

consequently the EFISH values are high enough to confirm the proposed and unexpected polarizable character of f electrons[10] as the origin of the behavior of an f electron tank as a weak transmitter system. Remarkably, our investigation suggests that this behavior is directly related to the number of unpaired f electrons and to the filling of the f orbitals. Interestingly, it appears that the increase of the dipolar component of the quadratic hyperpolarizability is higher than that of the octupolar component when the electron is added in an empty f orbital than in a half-filled orbital; this unexpected observation, which deserves more investigation, could be related to some buffering of the dipolar charge transfer between diglyme and hfac moieties through the Ln core when f orbitals are half-filled. Clearly, the significant second-order NLO activity of the dipolar Ln complexes investigated in this work, lacking ligands with intraligand charge transfer (ILCT) and therefore a classical push−pull structure, cannot be controlled by the well-known dipolar process. Moreover, the origin of the significant octupolar contribution cannot be explained by the classical two-level model[19] and merits further investigation. In any case, it is remarkable that the $\langle\beta_{HLS}\rangle$ values of such simple structures, well known for their luminescence properties,[14] are similar to those of [LLn(NO$_3$)$_3$] (L = dibutylaminophenyl-functionalized annelated terpyridine ligand)[7,8] but with a better transparency due to the absence of an ILCT.

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Supporting Information Available: Experimental electronic absorption spectra of the various [Ln(hfac)$_3$diglyme] complexes and calculation details of spectroscopic data of [Ln(hfac)$_3$diglyme] (Ln = La, Lu). This material is available free of charge via the Internet at http://pubs.acs.org.

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